Inclusion Changes during Reoxidation

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1. Abstract

This project studied the inclusion behavior before and after reoxidation. It focuses on the changes in inclusion size distributions and the mechanism by which reoxidation changes inclusion chemistries. This study examined the behavior of inclusions in laboratory heats after deoxidation with 0.1 wt% Al, Ca treatment, and reoxidation. MgO and Al₂O₃ crucibles were employed in the experiments to track the evolution of MgAlO₄ spinel inclusions and Al₂O₃ inclusions. For both crucibles, experiments with different Ca and S level and 100 ppm O additions were attempted. Samples were taken at various points after the different additions were made up to 20 minutes after reoxidation. Automated SEM/EDS microanalysis was used to analyze the inclusions detected on polished cross sections and inclusion compositions were studied over this time span. Size distributions were analyzed by calculating population density functions (PDF) of spinels, alumina and calcium aluminate formed at different time and compared to confirm the mechanism of inclusion formation. Electrolytic etching was performed on the sample surface and the morphology of inclusions was observed by manual SEM/EDS. After reoxidation new Al_2O_3 and/or spinel (MgAl_2O_4) inclusions formed. The inclusions that were present from deoxidation and Ca treatment became richer in Al₂O₃. The presence of excess CaS was found to decrease the amount of oxides that formed upon reoxidation. The shape of PDFs could be used to identify inclusions that formed due to reoxidation. Several suggested mechanisms for the inclusion chemistry and size distribution mechanisms are presented.

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2. Introduction

2.1 Production of Steel

Steel is a widely used alloy because of its high tensile strength and low cost. Steel is produced from iron ore or scrap. To make steel, facilities use one of two processes: the blast furnace (BF) following basic oxygen furnace (BOF), or the electric arc furnace (EAF).

In the blast furnace (BF), iron ore (mainly iron oxide) is chemically reduced and physically convert into iron. In basic oxygen furnace (BOF), by blowing oxygen through molten pig iron, the carbon content of the alloy is lowered and the carbon-rich molten pig iron is made into steel.

An alternative way of steelmaking is to produce steel from scrap. In an electric arc furnace (EAF), charged scrap metal is heated up by electric arc. Oxygen is blown into the scrap. Fluxes added will help to remove the impurities and protect the lining of the vessel. Slag will form and float at the surface of the molten steel.

After the steelmaking in BOF or EAF, refining of the crude steel is performed, usually in a ladle. The ladle metallurgy operations may modify inclusions to less harmful types and improve castability. The operations may include desulphurization, alloy addition, deoxidation, vacuum degassing, inclusion chemistry modification, inclusion removal, etc. High grades of steel require tight control of ladle metallurgy. After the ladle metallurgy, molten steel is solidified in the process called continuous casting for subsequent rolling. A schematic picture of ladle and tundish is shown below. This project focuses the reoxidation event that usually occurs in the ladle and the tundish.



Figure 2.1 – schematic of ladle and tundish^[1]

2.2 Deoxidation, Inclusion Modification, and Reoxidation

Research in steel cleanliness has been concerned with improving both castability and steel performance. For example, calcium additions to Al-killed steel have been established as an effective method to modify inclusions to less harmful types. The inclusion modification

process has been observed to proceed by formation of calcium sulfide (CaS) which then reacts with alumina (Al_2O_3) inclusions to form liquid calcium aluminates ^[2, 3].

Ensuring inclusions remain modified is also an important objective during steelmaking. There are several points after refining but prior to casting where liquid steel can become exposed to uncontrolled oxygen sources. This phenomenon is called reoxidation and it can significantly affect inclusion chemistry, size, and shape in steels. Reoxidation is a concern during any ladle-to-tundish transfer and is especially prevalent when ladles are tapped into empty tundishes during startup heats and after ladle exchanges ^[4, 5]. The most important source of oxygen is air, and other reoxidation sources are ferroalloys and SiO₂, FeO, MnO in the slags and lining refractories ^[6, 7]. Traditionally reoxidation is investigated by sampling liquid steel from ladle and tundish ^[8-10], and sometimes by examining the solidified final product ^[8, 9, 11]. Sasai et al. measured the increase of [O] in molten steel in a production scale tundish to be around 150 ppm during filling of the tundish, and 50 ppm at the stable stage (i.e. during casting) ^[12]. To inhibit reoxidation of molten steel during ladle change over and in tundish, effort has been devoted to inclusion control by ladle change strategy, modeling of tundish filling, as well as optimization of tundish and ladle slags ^[13-17]

This work focuses on Al-killed, Ca treated grades, and the reactive elements Al, Ca, Mg and Si all affect the inclusions after reoxidation. The following sections describe the current understanding of the effects of these elements on inclusion changes after reoxidation.

2.2.1 Role of Al and Ca

Aluminum is a key element when studying reoxidation. Aluminum is an effective deoxidizer which is used in many steelmaking operations, and alumina usually forms immediately upon reoxidation ^[18]. Al-killed steels can achieve total oxygen contents of only few ppm. Thus solid Al_2O_3 are commonly seen inclusions after deoxidation. However, solid Al_2O_3 inclusions reduce castability and are detrimental to mechanical performance of the steel. To mitigate these effects, Al-deoxidized steels are often Ca-treated to transform the alumina inclusions to calcium aluminate. An Al_2O_3 -CaO phase diagram generated by FactSage 6.4 (Figure 2.2) suggests calcium modified alumina inclusions can be liquid or partially liquid at ladle temperature with certain Al/Ca ratio.



Figure 2.2 - Calcium aluminate phase diagram generated by FactSage 6.4

Different initial S contents in the liquid steel will also affect the overall inclusion composition after Ca treatment ^[19]. Figure 2.3 shows the calculated trajectories of the overall inclusion composition with various S level.



Figure 2.3 - calculated trajectories of the overall inclusion composition during Ca modification of inclusion with various S level ^[19]

Several plant studies have detailed the evolution of inclusion chemistry after reoxidation. Maddalena observed increasing Al and decreasing S contents in inclusions when the molten steel was poured into an empty tundish ^[5]. This was attributed to the loss of CaS inclusions and formation of Al-rich inclusions.

Reoxidation can form new unmodified Al_2O_3 inclusions that can cause even more severe clogging at the caster. Zhang et al. reported that most of the large inclusions (>20 µm) in ingot are pure alumina that arise mainly from air reoxidation ^[20]. Story et al. has reported a very strong relationship between Al_2O_3 inclusion content in mold samples and addition of chill scrap with surface oxidation after deoxidation ^[21], indicating that reoxidation on an Al-killed non-Ca treated steel led to more Al_2O_3 inclusions. Therefore modifying solid Al_2O_3 inclusions to liquid or minimizing their formation is very necessary. The reoxidation on Al-killed, Ca treated heats was believed to create higher aluminum compounds ^[5, 9], e.g. Kaushik et al. reported that Al₂O₃ and CA₆/CA₁₂ were products of reoxidation ^[22]. Here CA₆ is used as shorthand notation for the compound (CaO) 6(Al₂O₃) or CaAl₁₂O₁₉. Maddalena has observed an inverse relationship between %Al and %S in inclusions at the start of a new heat ^[5], due to the loss of CaS inclusions and their replacement by calcium aluminates. CaS is an intermediate reaction product and with 500 ppm Al in steel, CaS is not stable in contact with liquid CaO-Al₂O₃ at CaAl₂O₄ saturation if the dissolved S content is less than around 100 ppm ^[2, 3]. It can be consumed to modify alumina, and the modification mechanism has been investigated ^[3]. But CaS could be a stable phase if the heat is over Ca treated, or in a S rich steel ^[23]. Plant data has shown that if there is remaining CaS in the inclusion after modification, it can act as a buffer to retard the formation of spinels during reoxidation and will disappear as the steel is exposed to oxygen ^[24].

2.2.2 Reoxidation of Mg

In facilities where steel is desulfurized in the ladle with basic slags containing low FeO and MnO, Al in the steel may reduce Mg and cause spinels (MgAl₂O₄) to appear after deoxidation which changes the inclusion compared to heats with only alumina inclusions. Several studies have shown MgO promoted liquid formation in the inclusions after calcium modification ^[9, 25] and MgO in the inclusions increase the range of compositions that are considered acceptably modified by promoting liquid inclusions after calcium modification ^[9, 25, 26]. Figure 2.4 demonstrates how a small amount of Mg will expand the boundary of liquid inclusion composition on the ternary phase diagram. It has been observed that Ca replaced Mg element in MgO-Al₂O₃ inclusions prior to Al ^[27]. Mg from the spinel dissolved in the steel upon Ca-treatment^[26]. Secondary spinels were observed

to form when Mg reappeared in the inclusions at the caster or when encountering high oxygen potential slag ^[28, 29]. Figure 2.5 and 2.6 demonstrate the change of Mg content in the inclusion after Ca treatment and after reoxidation.



Figure 2.4 - Partial AlO_{1.5} -MgO-CaO ternary phase diagram at 1550 $^{\circ}$ C. Dotted line represents the boundary where the amount of liquid phase inclusions is 50% of the total amount of inclusions ^[28]



Figure 2.5 – change in inclusion composition after Ca treatment. Spinel inclusions were modified to calcium aluminates ^[28].



Figure 2.6 – (a) inclusion composition of a lade depart sample, (b) inclusion composition of an early tundish sample $^{[29]}$

2.2.3 Reoxidation of Si

Inclusions in Al and Si-deoxidized steel have been studied and Al_2O_3 , SiO_2 and mullite $(Al_6Si_2O_{13})$ were found to form under different conditions:

 Effect of oxygen content: Wang et al. developed a model to calculate the reoxidation inclusion composition: in high-Al carbon steel (0.3%C, 0.35%Si, 0.8%Mn, 0.015%S, 0.15%Al) with 0.9 wt% oxygen absorbed, solid mullite, solid SiO₂, and liquid Mn₂SiO₄ were predicted to be the dominant inclusions at liquidus temperature ^[30]. A reoxidation study of different steel grades by Coletti et al. suggested that in Si and Al deoxidized steel, the amount of reoxidation of Si is higher than the reoxidation of Al during tapping of the converter and during ladle metallurgy ^[31]. Although the reoxidation of Si was more prominent than that of the Al at higher oxygen levels, Al₂O₃ inclusions were still the dominant type with lower oxygen absorbed ^[30]. 2) Effect of Al and Si content: Kwon et al. indicated the inclusion chemistry and morphology depended both on the Al and Si adding sequence and their amount ^[32]: with 0.03 wt% Al and 3 wt% Si addition, if Al was added 2 minutes before Si, Al₂O₃ inclusions tended to cluster and float to the surface before Si addition, therefore some mullite could form after Si addition. But if Si was added first, SiO₂ did not float out as readily as Al₂O₃ and Al₂O₃ as the stable phase would be the only type of inclusion after Al addition. ^[32] Figure 2.7 shows the stable phase at various Si and Al content with 240 ppm total oxygen. Recent research on nozzle clogging recommended no Al addition before ladle treatment and only SiMn addition at tap for deoxidation ^[33].



Figure 2.7 - Inclusion stability diagram in Fe-Si-Al-O melt^[32]

2.2.4 Summary

In the process of reoxidation, inclusions transform in their size, shape, location, and chemistry. Alumina usually forms immediately upon reoxidation and is subsequently changed depending on the steel chemistry. Secondary spinel formation due to reoxidation was observed both in laboratory heats 2 minutes after Fe_2O_3 addition ^[34] and in industrial early tundish samples, while inclusions from the sample departing from ladle metallurgy were mostly calcium aluminate ^[29]. The deoxidation by Si is slower than Al ^[32] and dissolved Si will not be oxidized until all the Al is consumed ^[30].

2.3 FactSage Simulation of Reoxidation on Ca Modified Inclusions

FactSage macros has been used to develop kinetic models to predict inclusion chemistry ^[35-41]. Ren et al. have developed a reaction model to simulate the inclusion evolution in the tundish based on FactSage macro processing and effect of Al, Mg and O concentration were investigated ^[42]. Thermodynamic equilibrium calculations have been used to provide insight into the effect of reoxidation on Ca modified Al₂O₃ and spinel inclusion chemistry ^[24]. Application of these calculations is qualitative since reoxidized heats are not likely in equilibrium. However, they can be a useful guide and qualitatively predict some observed phenomena. If equilibrium is assumed, the effect of increasing oxygen additions is shown in Figure 2.8. This simulation was made with FactSage 6.4 at 1550 °C for a steel with 310 ppm of Al, 5 ppm Mg, 39 ppm of Ca and 20 ppm of S. The simulation was performed by fixing the Al, Ca and S content while increasing O from 20 ppm to 120 ppm. The result shown in Figure 2.8 demonstrates composition changes from CaS and liquid slag to CA₂ and spinel (C=CaO, A=Al₂O₃).



Figure 2.8 - Calculated composition of inclusions at different oxygen content by FactSage, inputs: 310 ppm Al, 5 ppm Mg, 39 ppm Ca, 20 ppm S, 1550 ℃

However, inclusions compositions can depart from equilibrium in a non-equilibrium system. Solid Al_2O_3 inclusions form by reaction (1) before Ca modifies the inclusions by reaction (2); and reoxidation lead to formation of new Al_2O_3 again by reaction (1):

$$2\underline{Al} + 3\underline{O} = Al_2O_3(s) \tag{1}$$
$$3CaS(s) + Al_2O_3(s) = 3(CaO)_{inclusion} + 2\underline{Al} + 3\underline{S} \tag{2}$$

In modified inclusions, CaS can still be observed sometimes even it's not stable at equilibrium. Inclusions after reoxidation can be partially liquid as a non-equilibrium product.

To test the buffering effect of CaS, a revised simulation of reoxidation was performed by FactSage 6.4. All the inputs were same as the previous one, except for a lower Ca content of 20 ppm. The result is shown in Figure 2.9, which demonstrates a clear composition shift to lower oxygen level, indicating more solid inclusions forming at the same extent

of reoxidation with lower initial Ca content. Thus the simulation suggests the role of CaS as a buffer to reoxidation if equilibrium is achieved.



Figure 2.9 - Calculated composition of inclusions at different oxygen content by FactSage, inputs: 310 ppm Al, 5 ppm Mg, 20 ppm Ca, 20 ppm S, 1550 ℃

With Mg in the steel, Mg will affect reoxidation and inclusion after reoxidation will be composed of spinel and other Mg containing oxides.

The applicability of these FactSage calculations depends on a number of transient processes – inclusion chemistry changes, growth, agglomeration, and flotation. The time scales over which changes to inclusions occur are challenging to establish. In plant samples, studying the time evolution of inclusions after reoxidation in, for example, the tundish, is complicated by the continuous flow of steel from the ladle. One of the objectives of this study is to examine the time scales needed for changes to inclusions after reoxidation.

2.4 Inclusion Size Distribution

The size distribution of inclusions is an important factor to study in order to understand the mechanism of the formation and evolution of inclusions, control large and clustered inclusions and obtain clean steel. The most straight forward way to describe the inclusion size distribution is the histogram of inclusion frequency vs. inclusion size, as shown in Figure 2.10. However, the choice of bins may yield completely different histogram of particle size distribution ^[43]. Therefore, to eliminate the influence of the bin width, the population density function (PDF) is often used and it is defined as the frequency of inclusions in a bin $(n_v(L_{XY}))$, divided by the width of this bin $(L_Y - L_X)$ (equation (1)):

$$PDF = \frac{n_{\nu}(L_{XY})}{(L_Y - L_X)} \tag{1}$$



Figure 2.10 - (a), (b) and (c): different bin definitions will result in different histogram but similar PDF of a same group of particles. (d) The three PDFs curves superimposed ^[43]

Therefore, PDF eliminates the arbitrariness of the size and the number of the bins defined by the user and is more useful in comparing size distribution of different groups of inclusions. PDFs are often plotted with respect to particle size. The shape of the particle size distribution curve is often related to the mechanism of its formation and growth:



Figure 2.11 – particle number density versus radius if steady state nucleation and growth, Ostwald ripening, or coalescence is applied ^[44]. The slope of steady-state is related to constant growth rate G and the time scale available for growth τ ^[44]

Figure 2.11 shows some examples of size distribution and are distinguishing from the inclusion size distribution in steel deoxidation. Steady state in figure 2.11 refers to the assumption that the particle size don't change with time in the system. This assumption is just a mathematical convenience and was used in geological study. Figure 2.11 just gives examples of particle size distribution, but it may not apply to the steel inclusions.

Lognormal shaped size distributions are associated with nucleation of new, small inclusions as well as growth of existing inclusions ^[43]: upon deoxidation, inclusions nucleate and grow. This process is controlled by diffusion and Ostwald ripening. Ostwald ripening is known to cause shrinkage of smaller inclusion and growth of larger ones ^[45]. Inclusions that are smaller than this critical size will dissolve and redeposit on inclusions larger than the critical size.

Linear power-law type PDFs are associated with chemical equilibrium between inclusions and melt ^[46] after the rapid nucleation and diffusion controlled growth of the inclusions, collision becomes most important in further growth of the inclusions^[47].

Predictions of Al₂O₃ inclusions size distribution overtime had been made by J. Zhang et al. ^[48] and L. Zhang et al. ^[49] based on static models which include nucleation, Ostwald ripening and various types of collision:



Figure 2.12 – Numerical modeling of Al_2O_3 inclusions size distribution as a function of time after deoxidation by (a) J. Zhang and H. Lee ^[48] and (b) L. Zhang and W. Pluschkell ^[49]

2.5 2D to 3D Conversion

The analysis of inclusion is usually performed on a two-dimensional cross section. And the results need to be converted to three-dimensional data. The stereology used to perform this conversion is summarized by Cashman ^[50]. The simplest case is a random plane intersecting many randomly distributed uniform spheres. This case was discussed by Kellerhals et al ^[51]. Radom cuts through spherical particles has been studied in many works. ^[52-55] Measured on a 2D cross section, the spheres are missassigned into smaller size classes and the expected value of apparent diameter d' is 0.785D', where D' is the true diameter of the sphere. ^[51]



Figure 2.13 – Density function f(d '), and probability function F(d '), of random cuts through spherical particles.^[51]

Higgins has studied more complicated situations where different size and shape of particles need to be considered ^[56]. He used the degree of roundness and three aspect ratios to describe the shape of particles, and the three-dimensional size distribution can be calculated based on the diameters of all particles measured on two-dimensional plane.



Figure 2.14 – Higgins uses short, intermediate and long aspect ratio to characterize a particle ^[56]

3. Objectives

Most existing reoxidation studies have been performed on industrial samples from the tundish, but since there is continuous flow through the tundish, a full understanding of the evolution of inclusions with time has not yet been obtained. From this work there will be much insight gained on the behavior of inclusions after reoxidation.

The main objectives are as follows:

- Investigate the behavior of inclusions after reoxidation in Al deoxidized, Ca treated steel: use controlled reoxidation additions in laboratory scale heats to measure changes to inclusion chemistry and size distributions.
- 2) Understand the mechanism of reoxidation by analyzing inclusions chemistry evolution, calculating population density function (PDF) of inclusions at various times, and studying the morphology of inclusions. Use experimental results to identify the sequence of events that occurs after reoxidation and the kinetics of the reactions that occur.
- Understand the effect of Ca-treatment on reoxidized inclusions by varying amounts of Ca and S additions. Investigate how different degree of inclusion modification will affect the subsequent reoxidation.

4. Hypotheses

- 1) In Al-killed steel, upon reoxidation a transient population of alumina inclusions form that react with the melt and other inclusions to change the overall chemistry distribution. If the initial inclusions after deoxidation are spinels, then Ca treatment will cause Mg to return into the melt and secondary spinels will reform upon reoxidation; If the initial inclusions after deoxidation are alumina, then Ca treatment will cause some Al to return into the melt and alumina will reform upon reoxidation
- 2) Ca treatment is achieved by the formation CaS as an intermediate product, which will modify solid inclusions into liquid. If there is excess CaS which is discrete and not associated with other inclusions before reoxidation, it will collide and react with oxide inclusions when reoxidation happens.
- 3) The population density function of inclusions will show a clear change after reoxidation. Reoxidation changes the PDF from that characterizing a steady state to one consistent with generating new inclusions. The PDF can be used to identify new inclusions formed after reoxidation.

5. Methodology

5.1 Induction Furnace Experiment Setup

The laboratory heats were prepared by melting 500 g electrolytic iron pieces in an induction furnace at 1550 °C. Melting occurred in a dense MgO crucible or a dense Al_2O_3 crucible nested into a graphite crucible. No slags were used in any experiment. Argon gas was flushed through the furnace throughout the experiment to minimize oxidation from the atmosphere. Ten configurations of additions to deoxidize, Ca treat, and reoxidize the melt were investigated. Experiments using MgO crucible are summarized in Table 1 and experiments using Al_2O_3 crucible are summarized in Table 2.

	Al [wt%]	Ca [ppm]	S [ppm]	Reoxidation O
Experiment	(as pure Al	(as CalSil	(as FeS	[ppm]
	shot)	powder)	powder)	(as Fe ₂ O ₃ powder)
А	0.1	0	0	0
В	0.1	667	0	0
С	0.1	0	0	100
D	0.1	667	0	100
Е	0.1	1333	0	100
F	0.1	667	50	100
G	0.1	1333	50	100

Table 1: Designed additions made to deoxidize, Ca-treat, and reoxidize the liquid Fe melt in MgO crucible.

	Al [wt%]	Ca [ppm]	S [ppm]	Reoxidation O	
Experiment	(as pure Al	(as CalSil	(as FeS	[ppm]	
	shot)	powder)	powder)	(as Fe ₂ O ₃ powder)	
Н	0.1	0	0	100	
Ι	0.1	667	0	100	
J	0.1	2000	50	100	

Table 2: Designed additions made to deoxidize, Ca-treat, and reoxidize the liquid Fe melt in Al_2O_3 crucible.

All additions except for CalSil powder were made by placing powder or shot in a Fe foil capsule and dropping the capsule in the melt. Ca retention in the melt was expected to be a challenge due to its low boiling point relative to the experimental temperature. The CalSil powder was also wrapped in an Fe capsule, but for this addition the capsule was attached to an Al_2O_3 rod with Fe wire and the rod was used to push it to the bottom of the melt. This method was employed to maximize the amount of Ca that could react with the inclusions. The Ca addition in Experiments E and G was made by two sequential additions of CalSil powder; Considering the reaction between Ca and Al_2O_3 crucible, the Ca addition in Experiments J was made by three sequential additions of CalSil powder to achieve a better inclusion modification.



Figure 5.1 – Schematic of induction furnace experimental setup

The timing of additions made and samples taken for these ten experiments is summarized in Figure 5.2.



Figure 5.2 - Time/temperature profiles with details on additions and sampling. See Table 3 and 4 for addition detail on sampling.

Sampling was conducted by suction of liquid metal into a quartz tube (diameter 4 mm) inserted in the melt. It should be noted that the sampling plans are differ slightly for the ten experiments. Sampling time in all ten experiments is summarized Table 3 and 4.

	Expt. A	Expt. B	Expt. C	Expt. D	Expt. E	Expt. F	Expt. G
Time Taken	No Calino	1 0 n 0		Single	Double	Single	Double
Time Taken	NO Ca, 110	No reox. x.	No Ca	Single	Ca-treated	Ca-treated,	Ca-treated,
	reox.			Ca-treated		50 ppm S	50 ppm S
5 min after deox.	A1		C1				
10 min after							
deox., right before	A2	B1					
Ca							
Right after Ca		B2					G1
15 min after deox.	A3		C2				
	A4 (25 min	B3 (15 min	C3	D1	E1	E 1	
right before reox.	after deox.)	after Ca)				FI	62
right after reox.			C4	D2	E2	F2	G3
5 minutes after		B4 (20 min	C 5	D2	E2	F 2	C 4
reox.		after Ca)	CS	D3	E3	F3	64
10 minutes after	A5 (35 min	B5 (25 min	06	D4	E4	E4	05
reox.	after deox.)	after Ca)	Co	D4	E 4	F4	63
20 minutes after	A6 (45 min	B6 (35 min	C7		D 5	E5	Cé
reox.	after deox.)	after Ca)	C/	כע	EJ	ГJ	00

Table 3: Identification scheme for samples taken in experiments using MgO crucible

	Expt. H Expt. I		Expt. J	
Timo Tokon	No Ca	Cinala	Triple	
Time Taken		Single	Ca-treated,	
		Ca-treated	50 ppm S	
right after deox.	H1			
5 min after deox.,		τ1		
right before Ca		11		
right before reox.	H2	I2	J1	
right after reox.	H3	13	J2	
5 minutes after reox.	H4	I4	J3	
10 minutes after	Н5	I5	J4	
reox.				
20 minutes after			15	
reox.				

Table 4: Identification scheme for samples taken in experiments using Al₂O₃ crucible

5.2 Material

12 mm diameter high purity (99.97%) electrolytic iron pieces were used for conducting experiments. Aluminum shot (99.99%) was used for deoxidation. Gettered argon gas (oxygen pressure approximately 10^{-20} atm) was flushed through the furnace at the flow rate of 350 mL/min to minimize the oxidation of heats. The iron foil to make the capsule is 0.025 mm in thickness. The capsule of Al shot is usually 2-3 wraps and about 0.4×1 cm in size. The capsule of CaSi₂ powder is usually 4-5 wraps and about 1×5 cm in size. The capsule of Fe₂O₃ powder is usually 3-4 wraps and about 0.5×1.5 cm in size. The mass of the capsule for all additions are lower than 1

gram and will not affect the total mass of steel. CalSil powder (Calcium disilicide - CaSi₂) was used for Ca treatment after deoxidation of the melt. XRD analysis of the CalSil powder is shown in Figure 5.3. The powder contains CaSi₂, Si and small amount of SiO₂.



Figure 5.3 - XRD analysis of the CalSil powder

High purity (99.9%) dense MgO crucibles and dense Al_2O_3 crucibles were employed to melt iron. The outer diameter of the crucibles is 64 mm, inner diameter is 60 mm, and the height of the crucibles is 137 mm. An insulating alumina fiber lining was wrapped around the crucible to minimize the heat losses. SiO₂ sampling tubes were used.

5.3 Electrolytic Etching of the Samples

The morphology of inclusions can be observed in two dimensional or three dimensional

view after several commonly used sample preparation method^[57]:

1) The polished surface of steel sample will give a two dimension view of the inclusion shape

2) Inclusions can also be extracted by dissolving the steel matrix and recovered by filtering the solution. This method will provide a three dimensional view of inclusion morphology but will not preserve the spatial relationship between inclusions.

3) By etching the steel sample, inclusions will be exposed on the sample surface and the spatial association of inclusions can be preserved. Surface etching can be performed chemically using bromine-methanol solution or electrolytically. In both cases, the steel matrix is dissolved by oxidation. When using bromine-methanol, bromine acts as a strong oxidizer, dissolving the steel as iron(II) bromide or iron(III) bromide, both of which are highly soluble in alcohol^[58]. During electrolytic dissolution, the steel matrix is oxidized by connecting the steel sample as the anode in an electrochemical cell, passing current through the sample using an external power supply. Since current is passed through the solution, the solution must be sufficiently conductive. Methanol itself has low conductivity, and a salt (supporting electrolyte) needs to be added. Two supporting electrolytes (for electrolytic extraction) were commonly used in this method: sodium perchlorate (NaClO₄, which has high solubility in methanol), and tetramethylammonium chloride [(CH₃)₄NCl]. Finally, the iron oxidation product must be soluble. In the bromine-methanol method, iron bromide dissolves readily. In the electrolytic approach, in general a chelant must be added to dissolve the iron. In this work, acetylacetone was used as chelant.

In general, the steel matrix dissolved preferentially around the inclusions (forming trenches or cavities at the steel-inclusion interface). This is useful, since the enchanced local dissolution helped to expose the morphology and spatial relationships of these inclusions. Unlike bromine-methanol dissolution, the electrolytic dissolution method used here does not dissolve all sulfides. However, CaS decomposes upon contact with water. And CaS may not have survived the electrolytic etching process because the $(CH_3)_4NCl$ used as supporting electrolyte in sample etching is hygroscopic which may introduce small amount of water into the methanol solution.

In this project, method 1) and 3) were employed to study the morphology of inclusions. The surface of the steel samples was etched electrolytically with a 10% acetylacetone-5wt% tetramethylammonium chloride-methanol solution, similar to the approach used in previous work ^[59]. The voltage was 10 V and electric current were varied from 0.2 A to 0.5 A, depending on the surface area of the sample. The current density at the steel sample surface was around 0.16 A/cm². The etching time was 20 minutes. Manual SEM/EDS was performed on the etched samples and the polished cross-sections.

5.4 Characterization

Samples were mounted and prepared using standard metallographic preparation methods without exposure to water. SiC papers were used for grinding and alcohol based diamond suspension was used for polishing. The final polish was performed with 1 μ m diamond suspension. During polishing, suspension containing alumina or silica was never employed to avoid their contamination.
5.4.1 Automated Feature Analysis

Samples were examined by scanning electron microscopy with energy dispersive x-ray analysis (SEM/EDS) and inclusions in the samples were analyzed by AFA (Automated Feature Analysis) software. AFA is highly efficient and can collect data of hundreds of inclusions in an hour. The most commonly used AFA systems are INCA ^[60], ASPEX ^[61] and ASCAT ^[4, 21, 62, and 63]. These softwares all detect features automatically based on the Back Scattered Electron (BSE) image. This method of characterizing features is especially practicable in this research, because inclusions studied in this project are mostly CaO-MgO-Al₂O₃ and non Ti or Mn containing, therefore contrast (determined by the difference of atomic number) between these inclusions and steel matrix is strong.

For samples from experiment D, F and G, the SEM used was Phillips XL-30 equipped with a field emission gun (FEG) source. The acceleration voltage used was 10 kV. Although lower acceleration voltage would require longer analysis time, 10 kV largely avoids distorting effect of the steel matrix and is recommended for analysis of CaO-Al₂O₃-MgO inclusions ^[64-66]. A silicon drift detector (SDD) was used to collect X-rays for EDS analysis. Inclusions were examined with automated feature analysis software INCA Gun Shot Residue (GSR). The brightness of the Fe is set to be 170 and Al tape was set to be 40. Features with brightness lower than 100 were counted as inclusions. Inclusions smaller than 0.28 μ m were ignored. This minimum detectable size is determined by the magnification and threshold settings. The advantage of INCA is that any analyzed inclusions can be located and examined automatically after the AFA process, allowing further manual analysis to be performed on the inclusions of interest to have detailed information on their elemental mapping and morphology.

For samples from experiment A, B, C and E, the SEM used was FEI/Aspex Explorer. 10

kV acceleration voltage and the same brightness settings was adopted in Aspex as in software INCA. Aspex works on a similar principle as INCA GSR: the selected sample area to be analyzed by Aspex is equally divided into many small fields. A backscattered electron image of each field is captured and inclusions in them are recognized when its brightness fall into a certain range. Operating conditions for automated inclusion analysis are summarized in Table 5:

	INCA	Aspex
Working distance	10 mm	16-17 mm
Accelerating Voltage	10 kV	10 kV
Spot size	5	40%
magnification	1200	1200
Image resolution	1024×846	1024×1024
Search grid dimensions	0.1 μm	0.17 μm
Inclusion size	0.28-50 μm	0.2-50 μm

 Table 5: Operating conditions for automated inclusion analysis

The raw counts of an element in SEM/EDS analysis can be converted into the mass percentage by INCA and Aspex: the mass of the material penetrated by the incident electrons is about constant regardless of composition, therefore the mass concentration of the element concerned is approximately proportional to the it raw counts, or relative intensity. An "apparent concentration" (C') can be derived from the following equation:

$$C' = \left(\frac{I_{measured}}{I_{standard}}\right) C_{standard} \tag{2}$$

where $I_{measured}$ is the intensity measured for sample, $I_{standard}$ is standard intensity, and $C_{standard}$ is the concentration of the element in the standard. To obtain the true concentration, certain corrections like background correction and matrix correction are required.

Various ways of demonstrating inclusion compositions on ternary plot have been used in inclusion studies, like scatter plot, contour plot and proportional symbol plot. Among them proportional symbol plots was observed to give the best representation of composition distribution because it is able to display multiple inclusions of same composition by varying the size of each small triangular symbol rather than overlapping data points.

The measured inclusion compositions are plotted as proportional symbol maps projected on the Mg-Al-Ca or S-Al-Ca ternary diagrams in mole fractions. The area of each triangular symbol is proportional to the area of inclusions of which the compositions lie in that area of the diagram. For each projection, the total of the relevant three elements was normalized to 100%. The dashed line represents the region where at least approximately 50% of the inclusions are liquid ^[28].

Samples containing MgO-Al₂O₃ type of inclusions or CaO-Al₂O₃ type of inclusions have been analyzed by both INCA and Aspex with similar settings and these two AFA softwares yielded almost identical results on inclusion chemistry and population (see Figure 5.4). Therefore the results of inclusion analyses from the two instruments in this research should be consistent.



Figure 5.4 – comparison of INCA and Aspex analysis on same sample (Inclusion area fraction: 176 ppm by INCA, 192 ppm by ASPEX)

Both INCA and Aspex will provide information on chemistry, area, and longest and shortest dimension of each detected inclusion in the analyzed area. Inclusion chemistries were plotted on ternary diagrams. The program R^[67] was used for plotting inclusion chemistry from the lab samples. R is a free software environment for statistical computing and graphics. One of R's strengths is the ease with which well-designed publication-quality plots can be produced, including mathematical symbols and formulae where needed. For each sample, at least 150 inclusions were analyzed.

PDF calculations were performed by the CSDCorrections v1.51 software ^[56]. This software was used to convert the size distribution of particles detected on a 2D plane into 3D data. Four parameters are needed along with the length of every inclusions measured on 2D plane and the total area analyzed, then the conversion will be completed by this software. The parameters needed in software CSDCorrections are:

- 1. Degree of roundness: it can any value between 0 (block) and 1 (ellipsoid). We use 1 in our calculation because many inclusions are spherical or near spherical.
- 2. Short aspect ratio: always assumed to be 1.
- 3. Intermediate aspect ratio: we use the average aspect ratio of the inclusions measured on 2D plane. This value can be obtained directly from the AFA data.
- 4. Long aspect ratio: since many inclusions are near equant shapes rather than foliated or lineated, the long aspect ratio is expected to be close to the intermediate aspect ratio. Therefore in this report, long aspect ratio took same value as intermediate aspect ratio.

Higgins suggested using 4 to 5 size intervals (bins) per decade ^[56], but in this study inclusions were sometimes distributed in a narrow range, so 6 to 10 bins per decade were usually used in the PDF calculations. More bins requires larger amount of data to have enough inclusions in each bin.

It should be noted that the minimum and maximum detectable particle size when using automated feature analysis software like ASPEX or ASCAT will affect the shape of PDF curve, especially when inclusions start to nucleate and grow, or when inclusions agglomerate to large clusters. Analysis on industrial samples usually has a 1 μ m cutoff because smaller inclusions are not as detrimental as large ones. But for this lab study, the detectable size in ASPEX is 0.28 to 50 μ m (INCA) or 0.2 to 50 μ m (Aspex) to track the initial growth of inclusions.

5.4.2 Manual SEM/EDS

Automated feature analysis of inclusions will not give any indication of three-dimensional morphology or the homogeneity of the inclusions. For this purpose, manual SEM/EDS analysis was also performed on etched steel surface and selected inclusions using microscope XL-30 (acceleration voltage: 10 kV, working distance: 10 mm, spot size: 3). Analyzing individual inclusion manually will give an clear view of the inclusion two dimensional shape on polished surface or three dimensional morphology on etched surface, not only the longest and shortest dimension from automated analysis. In addition, many inclusions are multi-phased and elemental mapping of them will help obtain more detailed compositional information.

5.4.3 Bulk Chemical Analysis

Bulk chemical analyses have been performed on electrolytic iron pieces and various steel samples to measure the concentrations of element O, S, Mg, Al and Ca in them. Analyses of all samples were performed by the West Penn Testing Group Facility located in New Kensington, PA.

The total O content was measured by the instrument LECO NO using inert gas fusion (IG) method. The sample is accurately weighed and placed in a high purity graphite crucible in a fusion furnace under an inert gas atmosphere. The crucible is heated, resulting in the sample fusing to a molten state. The oxygen released from the sample then reacts with the carbon from the graphite crucible to produce CO or CO_2 . Oxygen is then analyzed through CO or CO_2 gases.

The total sulfur content in the samples was analyzed by the instrument LECO CS. The sample is combusted in pure oxygen atmosphere, and the sulfur from the sample then reacts with the oxygen to form SO_2 . Sulfur content is then quantified by measure the SO_2 gas through infrared detection.

Chemical analyses of metal elements Mg, Al and Ca were conducted using Inductively Coupled Plasma (ICP) spectroscopy. An ICP is a type of plasma source in which the energy is supplied by electric currents which are produced by electromagnetic induction, that is, by time-varying magnetic fields. This technique first dissolve solid samples in a liquid (typically acid), then sprayed the solution into the core of an inductively coupled argon plasma, which can reach temperatures of approximately $8000 \,$ °C. All analyte elements are atomized, ionized and thermally excited at such high temperature, and they can then be detected and quantified with a spectrometer. By measuring the intensity of the light emitted, the concentration of the analyzed element can be calculated.

Chemical analyses have been performed on electrolytic iron pieces and various steel samples: the O content of the iron pieces was measured to be 20-140 ppm. The O content of in steel sample taken right before deoxidation was measured to be 370 ppm. Positive error of the O content measurement can be caused by iron oxide rust on the sample surface. The negative error of the O content measurement can be caused by incomplete release of O from the inclusion during the inert gas fusion process: the graphite crucible is usually heated up to 2000~3000 °C. The melting point of Al_2O_3 and spinel is 2072 °C and 2135 °C respectively. Therefore some O bond in the oxide inclusions may not be all counted.

6. Results and Discussion: Inclusions with Mg

In these experiments, select additions were made to examine the effect of O and S additions on changes to inclusion chemistry distribution upon reoxidation. Inclusions in experiments A to G contained Mg, even though none was intentionally added. However, the metal was contained in an MgO crucible and the Al added for deoxidation reduced Mg into the melt. As a result, spinel inclusions were initially produced prior to Ca treatment.

This chapter presents the evolution of inclusion chemistry for all experiments using MgO crucible, followed by discussion and interpretation. The experiments performed are listed below. Experiments A and B were baseline experiments that involved no reoxidation. Experiments C-G were performed to examine the effect of reoxidation on various initial inclusion distributions.

	Al [wt%]	Ca [ppm]	S [ppm]	Reoxidation O
Experiment	(as pure Al	(as CalSil	(as FeS	[ppm]
	shot)	powder)	powder)	(as Fe ₂ O ₃ powder)
А	0.1	0	0	0
В	0.1	667	0	0
С	0.1	0	0	100
D	0.1	667	0	100
Е	0.1	1333	0	100
F	0.1	667	50	100
G	0.1	1333	50	100

Table 1: Designed additions made to deoxidize, Ca-treat, and reoxidize the liquid Fe melt in MgO crucible.

6.1 No reoxidation baseline experiments A and B

6.1.1 Inclusion Chemistry

The evolution of inclusion chemistry with time is given in Figure 6.1. A few minutes after deoxidation (Expt. A) and deoxidation + Ca treatment (Expt. B), inclusion chemistries did not change significantly with time. The area and number density of inclusions is given in Table 6. The macro inclusions that formed immediately on deoxidation were likely to float out immediately on Al addition and were not examined.



Figure 6.1 – Composition distribution of inclusions from experiment A (no Ca addition, no oxygen addition) and experiment B (no oxygen addition) plotted on Mg-Al-Ca ternary diagram

		•		-		
	A1	A2	A3	A4	A5	A6
Inclusion area fraction (ppm)	171	150	115	77.6	74.8	33.3
Inclusion number density (/mm ²)	42.0	35.7	27.5	21.5	17.4	8.64
	B1	B2	B3	B4	B5	B6
inclusion area fraction (ppm)	142	125	79.8	63.0	59.2	52.0
Inclusion number density (/mm ²)	45.8	31.4	25.5	23.0	11.1	8.4

Table 6: Area fraction and number density of inclusions in experiment A and B

6.1.2 Inclusion Morphology

Baseline experiment A (Al deoxidation, no Ca treatment, no reoxidation) is a good example to study the inclusion morphology after deoxidation. Sample A1 taken 5 min after deoxidation shows large number of Al_2O_3 inclusions either gather together of scatter randomly (Figure 6.2). The growth of these Al_2O_3 inclusions was dominated by diffusion of O and Al to the surface of the inclusion, which is not directional and thus led to a spherical morphology ^[49]. The cluster of Al_2O_3 formed by collision of small spherical Al_2O_3 inclusions. Due to their small size which is often below the threshold of AFA detection, the area fraction of Al_2O_3 inclusions could be underestimated on the ternary composition map (Figure 6.1). Small spinel particles were also observed among many Al_2O_3 inclusions and they are more angular in morphology. 10 minutes after reoxidation, number of Al_2O_3 inclusions dropped sharply and spinel inclusions grew larger. Spinels formed from deoxidation are more angular at this time, sometimes even show a perfect octahedral shape. Figure 6.3 demonstrates two examples of such spinel taken 10 minutes after deoxidation.



Figure 6.2 – 5 minutes after deoxidation in experiment A: (a) Al_2O_3 cluster, (b) and (c) scattered Al_2O_3 inclusions and (d) a small angular spinel inclusion



Figure 6.3 – 10 minutes after deoxidation in experiment A: two examples of polygonal spinel inclusion

There was some evidence of CaS in Experiment B (Al deoxidation, Ca treatment, no reoxidation), even though no S was intentionally added.

Figure 6.4 show the elemental mapping of a CaS containing inclusion. It gives a clear view of typical CaS morphology on inclusion surface. When the content of CaS in inclusion is not very high, it often attaches to the surface of an inclusion. The CaS on the inclusion shown below is only partially dissolved. Contacting with water during electrolytic etching may completely dissolve CaS and leave some holes or pits on the inclusion surface. This was frequently observed in the morphology study in this research and will be demonstrated the images shown later. Although water was avoided as much as possible, the $(CH_3)_4NCl$ used as supporting electrolyte in sample etching is hygroscopic which may introduce small amount of water into the methanol solution. Water is suggested to be strictly avoided by using dry $(CH_3)_4NCl$ in the future morphology study.



Figure 6.4 – An example of CaS containing inclusion and the elemental mapping of it. CaS is partially dissolved and distinct from other part of the inclusion.

CaS was known as an intermediate product to modified Al₂O₃ and spinel inclusions after

Ca addition. This was observed in inclusion morphology study. The elemental mapping of a spherical inclusion 5 minutes after Ca addition in Experiment B shows CaS takes half of the sphere (Figure 6.5). And the amount of CaS in inclusions dropped during the modification process: 15 minutes after Ca addition in experiment B, inclusions were still liquid but there was only tiny amount of CaS attached to the surface of these spherical inclusions as some small round patches (Figure 6.6). The partially dissolved CaS in Figure 6.4 shows a similar morphology as on this inclusion surface. Regardless of the inclusion size, each CaS area on the surface is always around 200 nm in diameter.



Figure $6.5 - an Al_2O_3$ -CaO-CaS inclusion and its elemental mapping in the sample taken 5 minutes after Ca addition in experiment B



Figure $6.6 - a MgO-Al_2O_3$ -CaO inclusion in the sample taken 15 minutes after Ca addition in experiment B. Pits were probably where the CaS was before dissolution in the electrolytic etchant.

6.2 Reoxidation Experiments C-G

6.2.1 Inclusion chemistry

The experiments C-G were performed to examine the effect of reoxidation with several different initial inclusion distributions. There are five relevant variables - Mg, Al, Ca, S, and time. Data representation was therefore a challenge. Highlights of results are presented below and complete sets of ternary diagrams (Mg-Al-Ca and Ca-Al-S) for each time point can be found in the Appendix. Figure 6.7 shows the Mg-Al-Ca diagrams for inclusions just before and just after reoxidation for all experiments. Spinel inclusions reappeared after reoxidation in all experiments with the lowest amount reforming in Experiment G.

Some amount of S was found in all inclusions just before reoxidation. Diagrams of Ca-Al-S are shown in Figure 6.8 for Experiments D and G just before and after

reoxidation (all Ca-Al-S ternary diagrams in the Appendix). After reoxidation in Expt. D the S content in the liquid inclusions decreases to low levels. Only experiment G contained discrete CaS inclusions. In Expt. F with 50 ppm S addition the Ca retention was insufficient to cause CaS formation.



Figure 6.7 - Composition distribution of inclusions from experiment C (no Ca treatment), D (single Ca), E (double Ca), F (single Ca, 50 ppm S) and G (double Ca, 50 ppm S) plotted on Mg-Al-Ca ternary diagram

	Just before reox.	Just after reox.
Experiment C	18.1	39.3
Experiment D	117	331
Experiment G	165	235

Table 7: Area fraction and number density of inclusions in experiment C, D and G



Figure 6.8 - Composition distribution of inclusions from experiment D (single Ca), and G (double Ca, no S) plotted on S-Al-Ca ternary diagram

6.2.2 Inclusion Morphology

The backscattered electron image of inclusions on polished sample surface is a simple way to distinct different phases in inclusions. Figure 6.9 demonstrate the evolution of modified liquid inclusion to a partially liquid inclusion right after reoxidation, and finally to an angular, spinel inclusion 20 minutes after reoxidation in experiment D. The size of the inclusion also grew significantly after reoxidation.



Figure 6.9 - Backscattered electron images of inclusions from experiment D: (a) a successfully modified inclusion in 15 minutes after Ca addition, (b) a partially liquid inclusion immediately after reoxidation, and (c) a spinel inclusion with a little calcium aluminate on the edge 20 min after reoxidation

Figure 6.10 demonstrates the transformation of inclusion phase and shape in experiment F.



Figure 6.10 Backscattered electron images of inclusions from Experiment F: (a) a CMA inclusion with a CaS ring 15 minutes after Ca addition, (b) an calcium aluminate-spinel inclusion 5 minutes after reoxidation, and (c) a spinel inclusion with a little calcium aluminate on the edge 20 min after reoxidation

On the other hand, observation of inclusions on etched steel sample was able to reveal inclusions of very small size and the spatial relationship of inclusions. Right after reoxidation, great amount of tiny spherical Al₂O₃ inclusions appeared (Figure 6.15 (a)) which could not be observed by BSE discussed above. The size of the alumina was a consequence of the oxygen addition method. When the capsule containing Fe₂O₃ is dropped onto the surface of the melt, oxygen will be consumed by Al at the top of the melt. Oxygen is transported into the melt but its concentration is much lower and consequently smaller Al₂O₃ form ^[68]. Spinels were found to be angular and their size varies from as small as Al₂O₃ inclusion to up to a few microns (Figure 6.11 (a) and (b)). Calcium aluminates which transformed from the existing liquid inclusions were the largest type among all inclusions: it can be 2 or 3 μ m in diameter. Calcium aluminates were no longer liquid but they somehow keep the morphology of the liquid inclusions: they are usually near spherical but have a rough surface (Figure 6.11 (b)).



Figure 6.11 – upon reoxidation in experiment D: (a) a spinel inclusion among Al_2O_3 cluster, (b) comparison of size and morphology of the three types of inclusion

Figure 6.12 to 6.14 show some examples of inclusions 5 minutes to 20 minutes after reoxidation. Small spherical Al_2O_3 inclusions were still observed later after reoxidation, but spinel inclusions had grown larger in size. The chemistry of calcium aluminate inclusions gradually transformed towards a spinel composition, but there were differences in size and morphology between the two types of inclusions that formed after reoxidation: the calcium-containing spinels that evolved from calcium aluminates usually have round holes or pits on the surface, which is the evidence of CaS; the non-calcium containing spinels which formed after reoxidation, were smaller, more angular and always had a smooth surface.



Figure 6.12 – 5 minutes after reoxidation in experiment D: (a) Al_2O_3 cluster, (b) an angular spinel inclusion, (c) a spherical MgO-Al₂O₃-CaO inclusion containing only 1.2 at%

Mg and (d) a more angular MgO-Al₂O₃-CaO inclusion containing 11.4 at% Mg



Figure 6.13 – Two MgO-Al₂O₃-CaO inclusions 10 minutes after reoxidation in experiment D



Figure 6.14 – 20 minutes after reoxidation in experiment D: (a) a spinel inclusion, (b) a $MgO-Al_2O_3$ -CaO inclusion

The double Ca addition plus S in experiment G successfully increased the Ca content in the inclusions before reoxidation. 15 minutes after Ca addition, large amount of CaS was preserved. Figure 6.15 shows two examples of such inclusions in which CaS is a major component.



Figure 6.15 – Two modified inclusions containing CaS 15 minutes after Ca addition in experiment G. CaS was partially dissolved.

As can be seen on the ternary composition plot (Figure 6.7 and 6.8), amount of spinel inclusions was much lower in inclusions after reoxidation in experiment G than that in experiment D with single Ca addition. Figure 6.16 demonstrates inclusions composed of different phases at various time: CaS was detected in the sample taken 15 minutes after Ca addition (Figure 6.16 (a)) and still remained 20 minutes after reoxidation (Figure 6.16 (c)).



Figure 6.16 - Backscattered electron images of inclusions from experiment G: (a) a half Al_2O_3 -MgO half CaS inclusion in sample right before reoxidation, (b) an calcium aluminate-spinel inclusion 5 minutes after reoxidation, and (c) a spinel inclusion with a

little calcium aluminate on the edge 20 min after reoxidation

Observed three dimensionally on the electrolytically etched steel sample, many inclusions after reoxidation appeared to be near spherical and have some CaS attached on the surface (Figure 6.17). As Mg content increased, some inclusions grew more angular in morphology, as shown in Figure 6.18.



Figure 6.17 – right after reoxidation in experiment G: (a) a spherical MgO-Al₂O₃-CaO inclusion with low Mg content, (b) a spherical Al₂O₃-CaS inclusion with the CaS dissolved



Figure 6.18 - 20 minutes after reoxidation in experiment G: (a) Two Al₂O₃-CaO-CaS inclusions, the hole on the left inclusion is probably where the CaS used to be, (b) an angular MgO-Al₂O₃-CaO

It should be noted that the size and morphology of reoxidation inclusions could depend on local supersaturation. For example, the Al_2O_3 inclusion has a spherical shape under high oxygen and aluminum supersaturation conditions, and a polygonal shape under low supersaturation conditions ^[69]. Therefore in-situ observation of inclusions is suggested for the future work.

6.3 Discussion

expt	additions	Right before	Right after	20 minutes after
		reoxidation	reoxidation	reoxidation
А	deox	Al ₂ O ₃ gradually transformed to spinel after deox		
В	deox, 1×Ca	Spinels modified to liquid and composition kept unchanged over time		
С	deox, reox	spinels	Al ₂ O ₃ formed and obtaining Mg from existing spinels	Composition returned to spinel
D	Deox, 1×Ca, reox	Modified to liquid	Al ₂ O ₃ and spinels formed, Mg content dropped in liquid inclusion	Spinels grew larger, liquid inclusions obtaining Mg from crucible and losing Ca
Е	Deox, 2×Ca, reox	Same as D	Same as D	Same as D
F	Deox, 1×Ca, 50 ppm S, reox	Same as D	Same as D	Same as D
G	Deox, 2×Ca, 50 ppm S, reox	Spinel, calcium aluminate and CaS	Number of CaS inclusion dropped sharply	CaS kept decreasing as Mg content slowly increased

Table 8: Summary of inclusion chemistry change in experiment A to G

In this section, spinel formation prior to reoxidation was examined first, then the re-formation of spinels after reoxidation was instigated, and finally the role of CaS was studied.

Baseline experiment A showed that the aluminum added to deoxidize the electrolytic Fe reacted with the MgO crucible by the following reaction:

$$\underline{Al} + MgO(s) = Al_2 O_3(s) + Mg \tag{3}$$

The dissolved Mg reacted with the alumina inclusions to form spinels. In all of the experiments using MgO crucible discussed in this report, the inclusions after deoxidation were spinels.

The baseline experiment A was conducted to study the spinels formed from deoxidation in the same time span as other experiments with Ca treatment and reoxidation. Sample A1 taken 5 min after deoxidation shows the immediate formation of Al_2O_3 inclusions and their gradual transformation into spinels (Figure 6.1). Al_2O_3 inclusions short time after deoxidation were tiny spheres which tend to cluster together and are generally smaller half micron. The inclusion morphology was discussed in section 6.1.2. Just 10 minutes after deoxidation, almost all the Al_2O_3 inclusions had been transformed to spinels and the inclusion composition stayed unchanged up to 45 minutes after reoxidation.

After Al deoxidation, the possible sequence of reactions by which the spinels formed are proposed as follows (note that underlined species are in a metallic solution and those in parentheses are in an oxide solution). Immediately upon deoxidation, alumina inclusions formed:

$$2\underline{Al} + 3\underline{O} = Al_2O_3(s) \tag{1}$$

Less than 1 min after deoxidation, dissolved Al reduced Mg from MgO crucible by

reaction (3) and spinels formed by reaction (4):

$$2\underline{Al} + 3MgO(s, crucible) = (Al_2O_3)(crucible) + 3\underline{Mg}$$
(3)
$$3Mg + 4Al_2O_3(s, inclusion) = 3MgAl_2O_4(s, inclusion) + 2\underline{Al}$$
(4)

The Al addition made in this series of experiments was 1000 ppm, which was much higher than the initial oxygen content of the electrolytic iron pieces used and the amount of O added for reoxidation. The dissolved Al reduced Mg from the crucible and caused spinels to form. While this was not originally intended, the focus of the current results will be on Mg-containing inclusions. These results will be relevant to EAF-produced steels that are desulfurized in the ladle, conditions under which spinel formation is promoted. To eliminate or reduce the influence of Mg, induction furnace experiments using Al_2O_3 crucible were also attempted and will be discussed in Chapter 7.

Experiments A and C were used to examine the kinetics of spinel formation after deoxidation. These experiments should have been similar for the first 25 minutes. Spinel inclusions form in five steps:

- 1) Dissolved Al reduces Mg from the MgO crucible (reaction (3))
- 2) Mass transfer of dissolved Mg from steel-crucible interface to liquid steel
- 3) Mixing of dissolved Mg in liquid steel;
- 4) Mass transfer of dissolved Mg from liquid steel to steel-inclusion interface
- 5) Reaction (4) at steel-inclusion interface

Reactions in step 1) and 5) are fast due to the high temperature. And mass transfer in step 3) is also supposed to be fast. Therefore, the mass transfer of dissolved Mg from

steel-crucible interface to liquid steel and from liquid steel to steel-inclusion interface are likely to be the rate-controlling step.

Mass transfer of Mg from steel-crucible interface to liquid steel is given by equation (3):

$$\frac{d[Mg\%]}{dt} = -\frac{k_{steel}\rho_{steel}A}{W_{steel}} \left([Mg^{int}\%] - [Mg^{bulk}\%] \right)$$
(3)

where k_{steel} is the mass transfer coefficient of Mg in steel, ρ_{steel} is steel density and W_{steel} is the total weight of steel. A is the area for mass transfer, that is the area of crucible that is in contact with steel melt. The term ([Mg^{int}%]-[Mg^{bulk}%]) represents the concentration difference of element Mg from steel-crucible or steel-inclusion interface to bulk steel, which is the driving force of the mass transfer of Mg in steel.

[Mg^{bulk}%] was 0 upon Al addition, and increased as MgO was reduced from the crucible by dissolved Al. [Mg%] in liquid steel at equilibrium can be taken as [Mg^{int}%] if we assume the thin layer at the steel-crucible interface to achieve local equilibrium. The dissolved Mg content [Mg] in equilibrium with 1000 ppm Al, 0-400 ppm O and MgO crucible was calculated by FactSage:



Figure 6.19 – Dissolved Mg in liquid steel as a function of O content calculated by FactSage.

Assume the total O before reoxidation was 370 ppm, then the $[Mg^{int}\%]$ was around 2.1 ppm. The term ($[Mg^{int}\%]$ - $[Mg^{bulk}\%]$), which is the driving force of mass transfer of Mg from crucible wall to liquid steel, is a small value and decreases as $[Mg^{bulk}\%]$ increases with time.

Derived from equation (3), the change of Mg content is liquid steel is shown in equation (4):

$$[Mg\%] = [Mg^{int}\%] + ([Mg^{initial}\%] - [Mg^{int}\%])e^{(-\frac{kA}{v}t)}$$
(4)

The mass transfer coefficient of Mg from the crucible to the melt was estimated to be $k=6\times10^{-6}$ m/s ^[70]. The inner diameter of the MgO crucible is 6 cm, the total weight of the

steel is W_{steel} =500 g. Therefore the contact area of liquid steel and crucible is 76.03 cm². The volume of the liquid steel is 71.63 cm³. [Mg^{initial}%] is 0; [Mg^{int}%] is calculated to be 0.0192 by FactSage.

In experiment A and C, The Mg pickup in inclusions can be calculated from the inclusions chemistry and are plotted in dashed lines in Figure 6.20. The mass transfer of Mg calculated from equation (4) is plotted in solid line.



Figure 6.20 – Calculated [Mg] content from equation (4), compared with the Mg pickup in inclusions in experiment A and C

In Figure 6.20, The inclusion Mg/(Mg+Al) curve of experiment A and C was not identical. Calculations suggested that the temperature and initial O content did not affect the shape of the curve. It could possibly be other experiment conditions like different

fluid flow that affect the mass transfer rate of Mg, or the slightly different flotation velocity of alumina inclusions due to their different size distribution in experiment A and C.

The calculated mass transfer rate of Mg from the crucible to liquid steel approximately agrees with the Mg pickup in the inclusions. This indicated that the mass transfer of Mg from the crucible to liquid steel is the rate controlling step of the initial spinel formation.

The baseline experiment B simulated the inclusion evolution after Ca treatment when no reoxidation happened. This experiment was also designed to test the extent of reoxidation from sources other than the intentional addition. Before Ca treatment, the inclusions were spinel inclusions formed from deoxidation and reduction of MgO. Modification of these spinel inclusions by Ca took place immediately upon Ca addition (Figure 6.1). In this and all other ternary plots, CaS was not subtracted. Right after Ca addition, among all the 108 inclusions at the Ca corner, 4 are CaS and 104 are CaO.

The inclusion Mg content decreased to low levels 15 minutes after Ca treatment, and increased slightly afterwards. This was attributed to continued Mg supply to the melt from the crucible walls. Al content also increased slightly due to some reoxidation on sampling or from the atmosphere. However, sampling each time would not have any significant influence on the overall experimental results and inclusion compositions were well within the 50% liquid boundary. As will be shown below, the extent of the changes was much lower than those that occurred from the intentional oxygen addition. The results of experiment B showed that the sampling and furnace setup could be sufficiently controlled to minimize unintended changes to inclusions.

Spinel re-formation after reoxidation:

Experiment C explores how inclusions will evolve after reoxidation without Ca treatment. As in baseline experiment A, the inclusion composition before reoxidation was $MgO-Al_2O_3$ with Mg to Al molar ratio about 1:3.

Upon reoxidation, Al_2O_3 inclusions formed first. From the inclusion composition on the ternary diagrams (Figure 6.7) it can be observed that the newly formed Al_2O_3 inclusions were transforming into spinels: The Mg content in the MgO-Al_2O_3 inclusions kept decreasing until 5 minutes after reoxidation and the area fraction of Al_2O_3 inclusions also dropped.

In the meantime more Mg was reduced from the MgO crucible and in 10 minutes after reoxidation, Mg content in the inclusions rose to level reached before reoxidation. The inclusion composition was about the same right before reoxidation and 20 minutes after reoxidation. Secondary spinels formed after reoxidation by reaction (1) and (4), and Mg was further reduced from the crucible by reaction (3):

$$2\underline{Al} + 3\underline{O} = Al_2O_3(s) \qquad (1)$$

$$3\underline{Mg} + 4Al_2O_3(s, inclusion) = 3MgAl_2O_4(s, inclusion) + +2\underline{Al} \qquad (4)$$

$$2\underline{Al} + 3MgO(s) = Al_2O_3(s) + 3\underline{Mg} \qquad (3)$$

The addition of Fe_2O_3 led to higher level of dissolved <u>O</u> and formation of more Al_2O_3 inclusions as shown in reaction (1). Therefore more spinel inclusions appeared by reaction (4), consuming the dissolved <u>Mg</u> and resulting a lower dissolved <u>Mg</u> content in liquid steel. Therefore Mg was reduced from the crucible (Reaction (3)) after reoxidation

until the equilibrium was reached between the liquid steel and MgO crucible wall. In this way the same Mg content in the inclusion was maintained as before reoxidation

In experiment C, the difference of primary spinels that formed from deoxidation and secondary spinels that formed from reoxidation is the sequence of reactions. Right after deoxidation, dissolved <u>Mg</u> was not contained in the melt and reaction (3) took place prior to reaction (4) to reduce Mg from the crucible which then reacted with the Al_2O_3 from deoxidation to form spinels. After reoxidation, dissolved <u>Mg</u> was contained in the liquid steel which reacted with newly formed Al_2O_3 inclusions right away.

Experiment D studied reoxidation of 100 ppm O on the Ca treated heat. Inclusions were modified to liquid Mg containing calcium aluminate before reoxidation according to the ternary diagram Figure 6.7. Upon reoxidation with 100 ppm O, two groups of inclusions formed: spinels and solid calcium aluminates. Manual SEM/EDS on the etched sample demonstrated a large number of tiny Al_2O_3 inclusions which scatter randomly or cluster and form colonies (discussed in section 6.2.2). These Al_2O_3 inclusions are not shown on the composition diagrams in Figure 6.7 because most of them are below the detectable size threshold in AFA. Over time, Mg reappeared in the calcium aluminate and its content kept increasing until 20 minutes after reoxidation. These two types of inclusions: spinel and Ca containing spinel seem to have close composition but are actually two distinct groups. This has been discussed in section 6.2.2.

The spinel formation reactions took place right upon reoxidation in experiment D. This was attributed to the Ca treatment, after which some Mg is returned to the melt. This has been proposed to occur by Deng^[27] an Pretorius^[29]:

$$[Ca] + (MgO \cdot Al_2O_3) = (CaO \cdot Al_2O_3) + [Mg]$$

A comparison of Experiments C and D is consistent with this reaction. In samples taken just after reoxidation, Al_2O_3 inclusions were observed in Experiment C (no Ca treatment) while only spinels were observed in Experiment D (Ca treatment). This would suggest there was higher [Mg] due to Ca treatment.

This process is similar to the spinel formation after reoxidation in experiment C. Immediately upon reoxidation:

$$2\underline{Al} + 3\underline{O} = Al_2 O_3(s) \qquad (1)$$
$$Mg + Al_2 O_3(s) + \underline{O} = MgAl_2O_4(s) \qquad (4)$$

Mg was continuously picked up from the MgO crucible:

$$2Al + 3MgO(s) = Al_2 O_3(s) + 3Mg$$
(3)

The behavior of inclusions after reoxidation in experiment D was consistent with industrial observations that spinel inclusions can be transformed to liquid by Ca treatment and then reformed by reoxidation^[29]. This work shows there is transient behavior with formation of a new spinel population immediately upon reoxidation and then subsequent transformation of the inclusions formed after Ca treatment towards spinel.

The S-Al-Ca ternary composition maps shown in Figure 6.8 demonstrated the S content change is experiment D. Although no intentional S additions were made, some was originally contained in the electrolytic iron pieces, which was confirmed by bulk

chemical analysis discussed in section 6.4. S was detected in inclusions in sample D1 right before reoxidation, but decreased sharply to near zero upon reoxidation (Figure 6.8). S content in inclusions was low but non zero until 20 minutes after reoxidation. Evidence of CaS could still be observed on inclusions surface, discussed in section 6.2.2.

Experiment E were designed to confirm the role of CaS in inclusion modification: Experiment E investigated whether Ca additions alone could substantially affect the modification of inclusions and subsequently the evolution after reoxidation, and experiment F studied the effect of S. The evolution of inclusion chemistry after reoxidation in experiment E and F turned out to be very similar to that in experiment D, thus the ternary diagrams are not shown here and can be found in appendix.

Comparing experiment E and F with experiment D: the inclusions 15 minutes after Ca addition were mostly well within the 50% liquid boundary, indicative of successful modification. In experiment F with 50 ppm S addition, some inclusions are out of the 50% liquid boundary 15 minutes after reoxidation, these are inclusions not fully modified to liquid. This amount of S will not change the inclusion composition at higher oxygen level, as discussed in FactSage simulation in section 6.5, but will have negative effect on inclusion modification at lower oxygen level like 20 ppm.

Another way to qualify the effectiveness of Ca modification is the Ca/Al ratio, and it's also necessary to exclude the amount of Ca in CaS^[2, 62]. Story et al. suggested following equation to estimate Ca/Al ratio in modified inclusions^[62]:

$$\left(\frac{Ca}{Al}\right)_{mod} = \frac{pct\ Ca - pct\ S+2}{pct\ Al} \tag{5}$$
The percentages used in this equation are molar-based. Mg was also involved in this set of induction furnace experiments, but we didn't include it into the calculation because the role of Mg is more complicated: the Mg containing spinels are detrimental and certainly need to be modified, but Mg in the calcium aluminate inclusions is known to promote the liquid formation of inclusions. The average Ca/Al ratio of inclusions can be calculated directly from the automated feature analysis data. 15 minutes after Ca treatment, the average modified Ca/Al ratio of inclusions in experiment D is 0.343, in experiment E is 0.804, and in experiment F is 0.117. These Ca/Al ratios indicated that highest degree of inclusion modification is achieved in experiment E. The degree of inclusion modification is low in experiment F, which can be observed on the Mg-Al-Ca and S-Al-Ca ternary diagrams as well: some Mg containing calcium aluminate inclusions are out of the 50% liquid boundary (sample F1); And sample F1 taken right before reoxidation demonstrates a higher S content in the modified inclusions than the S content in experiment D and E.

In summary, compared to experiment D, the double Ca addition in experiment E slightly improved the Ca retention. However, the initial S content in the electrolytic iron pieces is low and there was no CaS remained before reoxidation. The inclusions in experiment E were modified to approximately same extent as those in experiment D before reoxidation, and the evolution of inclusions after reoxidation follow the same path as the single Ca addition experiment D.

Experiments F and G were conducted to examine the effect of intentional S additions on Ca-treated heats. Due the low Ca retention, addition of 50 ppm S in experiment F didn't lead to extra CaS formation. Addition of 50 ppm S in experiment F resulted in a less effective inclusion modification after Ca treatment as some spinel inclusions were not fully modified to liquid 15 minutes after Ca addition. The extra S addition did result in a

slightly higher S content in modified inclusions after Ca addition, but after reoxidation the S content of the inclusions was approximately zero, similar to experiment D and E. Subsequent changes in experiment F were similar to experiment D and E.

Experiment G was designed to study inclusion evolution after a higher degree of Ca modification and investigate reoxidation when excess CaS is present. Here two separate Ca additions were made which successfully increased the Ca content, according to the bulk chemical analysis result in section 6.4. The distribution of inclusion chemistries just before reoxidation is much more diffuse than in other experiments, but the oxide inclusions were generally Mg-containing calcium aluminates as in other experiments. There was also a large amount of CaS inclusions (see Figure 6.8). Upon reoxidation, the distribution shifted to calcium aluminate inclusions and the content of CaS decreased. With time the inclusion Mg content increased, but the amount of spinels was smaller than in other experiments and no spinels appeared immediately upon reoxidation. Proposed by Verma, Al_2O_3 inclusions that form after deoxidation will be modified to calcium aluminates by the following reaction ^[2, 3]:

$$3CaS(s) + Al_2O_3(s) = 3(CaO)_{inclusion} + 2\underline{Al} + 3\underline{S}$$

$$\tag{2}$$

The possible mechanism of sulfide reaction could be solid state reaction on the CaS and oxide interface, or dissolved Ca modifying inclusions through liquid steel. The solid state reaction on the interface between two particles is expected to be slow. Neerav et al. observed that it took several minutes for Ca to modify inclusions when CaS was a non-equilibrium phase ^[3], and this is consistent with the observation in my study. He suggested that in high S steel, inclusion modification via dissolved Ca rejecting Al and S to the molten steel is the possible mechanism ^[3].

The CaS inclusions disappeared very quickly upon reoxidation (figure 6.8). Considering modification of newly formed oxides by CaS could be relatively slow, it is possible that the decrease of CaS was caused by direct reaction between CaS and dissolved O.

Thermodynamic calculations ^[24] suggested CaS could serve as a Ca reservoir that would modify spinels formed after reoxidation. This was observed experimentally: the amount of spinel inclusions was much lower in experiment G for the time period sampled compared to experiment D (no CaS). While excess CaS can be detrimental to castability, its presence appeared to delay the reformation of solid spinels associated with reoxidation.

Modification of Inclusions by CaS:

In hypothesis 2), it is assumed that if there is excess CaS which is discrete and not associated with other inclusions before reoxidation, it will collide and react with oxide inclusions when reoxidation happens.

S is known to capture Ca upon calcium injection to modify solid inclusions. CaS in the inclusions could be a stable, equilibrium product due to high Ca or S level, a transient product, or form during solidification of the steel. CaS that precipitate on the inclusions during solidification often form a shell around calcium aluminate. In experiment G, CaS didn't appear to be a shell on the surface but was usually a major part of a spherical inclusion (Figure 6.15). Clearly, the CaS in this experiment formed during Ca treatment rather than during solidification.

The morphology of CaS containing inclusions in experiment G suggests that the inclusion

modification was likely to be achieved by collision of CaS inclusions and other inclusions. Especially Figure 6.15 (b) which could possibly be two oxide inclusions colliding into a CaS particle from opposite direction, and Figure 6.16 (b) which could possibly be two CaS particles colliding into an oxide.

To quantitatively test of the feasibility of solid-solid reactions as opposed to reaction of dissolved Ca, the collision frequency of inclusions needs to be calculated. Brownian collision, turbulent collision and Stokes collision are investigated in this calculation. The assumptions we made in this calculation are: there are only two types of inclusion, CaS particle i and oxide (spinel or Al_2O_3) particle j; The inclusions are solid, spherical, and uniformly distributed in the melt; Inclusions of the same type have same density and radius.

The rate constant of Brownian collision caused by Brownian movement between two particles i and j is given in equation (6): ^[71]

$$\beta_{ij}^{B} = \frac{2kT}{3\mu} \left(\frac{1}{r_i} + \frac{1}{r_j} \right) (r_i + r_j) \tag{6}$$

The rate constant of turbulent collision between two particles i and j is given in equation (7): ^[72]

$$\beta_{ij}^{T} = 1.3\pi^{\frac{1}{2}}(r_{i} + r_{j})^{3}(\varepsilon/\nu)^{\frac{1}{2}}$$
(7)

The different floatation velocity of CaS and oxide inclusions will cause Stokes collision and its rate constant can be derived as follow ^[73]:

$$\beta_{ij}^{S} = \frac{2\pi\Delta\rho g}{9\mu} |r_i^2 - r_j^2| (r_i + r_j)^2 \tag{8}$$

Considering Brownian collision, turbulent collision and Stokes collision, the total number of collisions per unit volume and per unit time between CaS and oxide inclusions is:

$$N_{ij} = (\beta_{ij}^B + \beta_{ij}^T + \beta_{ij}^S)n_in_j \tag{9}$$

The parameters in equation (6) to (9) are summarized in Table 9:

-	
parameter	value
Boltzmann constant k	$1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$
Temperature T	1823.15 K
Liquid steel dynamic viscosity µ	7×10 ⁻³ Pa•s ^[74]
Radius of CaS inclusion r _i	0.31 µm (right after Ca addition)
	0.64 µm (right before reoxidation)
Radius of oxide inclusion r _j	0.35 µm (right after Ca addition)
	0.58 µm (right after reoxidation)
Turbulent energy dissipation rate ε	$0 \text{ m}^2 \text{ s}^{-3}$ (no stirring in lab experiment)
Liquid steel kinetic viscosity v	$1 \times 10^{6} \text{ m}^{2}/\text{s}^{[73]}$
Difference between the density of molten	4.1 (3
steel and inclusions $\Delta \rho$	4.1 g/cm ⁻
Gravitational acceleration g	9.8 m/s ²
Number density of CaS inclusions n _i	$5.65 \times 10^{14} \mathrm{m}^{-3}$ (right after Ca addition)
	$1.61 \times 10^{14} \mathrm{m}^{-3}$ (right before reoxidation)
Number density of oxide inclusions n _j	$2.36 \times 10^{14} \text{ m}^{-3}$ (right after Ca addition)

From the volume fraction and the average radius of inclusions, the number density of CaS right after Ca injection is estimated to be $5.65 \times 10^{14} \text{ m}^{-3}$, and the number density of oxide inclusions right after Ca injection is estimated to be $2.36 \times 10^{14} \text{ m}^{-3}$. Therefore, the number of collisions between CaS and oxide inclusions is calculated to be $3.3 \times 10^{12} \text{ m}^{-3} \text{s}^{-1}$ from equation (9). After Ca treatment, to have all the oxide inclusions collide with CaS inclusions, it will take about 71 seconds. However, once an oxide collides with CaS and reacts immediately with it, it may contain a CaS phase as well, as those shown in Figure 6.15. This will increase the number density of CaS containing inclusions and accelerate the frequency of oxides being collided. The change in inclusion size over time will also affect the collision frequency. Therefore, the actual time for all the inclusions modified by collision is likely shorter than the calculated 71 seconds. It needs to be noted that this time was calculated based on the assumption that the modification reaction take place upon the collision of two inclusions.

Right after Ca addition (Figure 6.7), the modification of oxide inclusions had started, and large number of Al_2O_3 had been modified to calcium aluminates. Therefore collision plays an important role in inclusion modification after Ca addition.

Considering the modification of newly formed oxides after reoxidation, all the existing CaS containing inclusions could collide and react with them. The number density of CaS containing inclusions right before reoxidation is estimated to be 1.61×10^{14} m⁻³. From equation (6) to (9), the time for all the oxide inclusions (newly formed and existing unmodified) to be collide with CaS inclusions is calculated to be 40 seconds. This is consistent with what we observed in the inclusion chemistry change (Figure 6.8): area fraction of CaS inclusions dropped sharply upon reoxidation, which is the result of solid-solid reactions between CaS and newly formed Al₂O₃. The further decrease of CaS

could be a result of slow transport of Mg from crucible-steel interface to inclusions (discussed in section 6.2.3) and modification of these spinels. Collisions between CaS containing inclusions and oxide inclusions also played an important role in inclusion modification after reoxidation.

6.4 Chemical Compositions of Steel Samples

S content in the electrolytic iron pieces was measured to be lower than 10 ppm, which is basically consistent with the 60 ppm S level in the S addition experiment F.

Al content in experiment D before reoxidation was measured to be 1000 ppm, which is exactly the amount added. But its content dropped to 920 ppm and 780 ppm 20 minutes after reoxidation in experiment D and F, probably due to flotation. Mg and Ca content were both measured to be about 10 ppm before and after reoxidation.

The chemical information of some samples is summarized in Table 10.

0	S	Mg	Al	Ca
10				
10				
50	<10	10	1000	10
50		<10	920	10
20				
10				
30	60			
30		10	780	10
	O 10 10 10 50 50 20 10 30 30	O S 10 10 50 <10	O S Mg 10 10 50 <10	OSMgAl101050<10

Table 10: chemical composition of samples from experiment D and F, all in ppm

6.5 FactSage Simulation

FactSage ^[75] is one of the largest integrated database computing systems in chemical thermodynamics. It is a powerful software which is able to calculate changes in thermodynamic properties for chemical reactions, to calculate the concentrations of chemical species when system reach a state of chemical equilibrium, and to plot various types of phase diagram. In this research, FactSage 6.4 was used to simulate inclusion compositions at 1550 $\$ to study the equilibrium phases before and after reoxidation and compare them with the experimental results.

FactSage simulation of inclusion composition before and after reoxidation in experiment D through G was made based on the bulk chemical analysis result. The O content of in steel sample taken right before deoxidation was measured to be 370 ppm. However, most of the deoxidation inclusions have floated out and total oxygen in the steel are supposed to be much lower. Therefore the O level was roughly assumed to be 20 ppm according to the chemical

analysis in table 10. The Fe_2O_3 powder for reoxidation was drop on the surface of the melt and some oxides would form at the top and immediately float out. According to the mass balance calculation in section 7.1, 70 ppm of O was estimated to reoxidize the heat after O addition.

S level was 10 ppm in the non S added experiment D and E, and 60 ppm in experiment F and G with S addition. Mg was assumed to be 10 ppm, Al was 1000 ppm. Ca was 10 ppm in the single Ca addition experiment D and F, and 20 ppm in the double Ca addition experiment E and G. Equilibrium phases predicted by FactSage, especially those before reoxidation, are found to be quite temperature sensitive. Therefore calculations at 1550 $^{\circ}$ C were made and summarized in Table 11.

Ca	0	S	experiment	CaS	liquid	spinel	CA ₂	CM ₂ A ₈
10	20	10	Expt. D before reox.		35.2	5.0		
10	90	10	Expt. D after reox.			4.5	16.8	173
20	20	10	Expt. E before reox.		44.5			
20	90	10	Expt. E after reox.			50.1	121	28.5
10	20	60	Expt. F before reox.	14.9	2.3	36.0		
10	90	60	Expt. F after reox.			4.5	16.8	173
20	20	60	Expt. G before reox.	29.1	10.3	28.6		
20	90	60	Expt. G after reox.			50.1	121	28.5

Table 11: FactSage predictions of inclusion chemistry at 1550 °C and amounts in ppm before and after reoxidation in experiment D to G

It should be noted that CM_2A_8 phase is compounds between spinel and CA_6 , but these could not be distinguished from spinel because many inclusions are multi-phased.

Before reoxidation, inclusions are predicted to be modified mostly into liquid in experiment D and E at 1550 °C. The 50 ppm S addition in experiment F did not promote Ca modification, but led to formation of CaS and more unmodified spinels. In experiment G, inclusions composition was predicted to be liquid, spinel and CaS at 1550 °C, this is consistent with the experimental result (Figure 6.7 and 6.8). Overall the FactSage simulations of inclusion composition before reoxidation match well with the experimental results.

After reoxidation, the amount of solid inclusions was much higher and inclusions were richer in Al_2O_3 . Experiment D and F have same inclusions types and amounts. This indicates that 50 ppm S addition to the heat in experiment F did not cause any change in

inclusion chemistry after reoxidation. This similarity between experiments D and F were also observed in induction furnace experiments. FactSage simulations predicted same inclusion composition after reoxidation in experiment E and G, which is obviously not the case in the experiment because Ca retention in experiment E is supposed to be low without extra S addition.

In general, the inclusions in all experiments evolve to higher Al composition after reoxidation, and more MgAlO₄ (as spinel or as CM_2A_8) was also predicted by FactSage. This is consistent with the lab results.

7. Results and Discussion: Inclusions without Mg

To eliminate the influence of Mg, Al₂O₃ crucible was employed in experiment H, I and J instead of MgO crucible. Additions made in these experiments are summarized in Table 2.

Table 2: Designed additions made to deoxidize, Ca-treat, and reoxidize the liquid Fe melt in Al_2O_3 crucible.

	Al [wt%]	Ca [ppm]	S [ppm]	Reoxidation O
Experiment	(as pure Al	(as CalSil	(as FeS	[ppm]
	shot)	powder)	powder)	(as Fe ₂ O ₃ powder)
Н	0.1	0	0	100
Ι	0.1	667	0	100
J	0.1	2000	50	100

7.1 Experiment $H(Al_2O_3 \text{ crucible, no } Ca)$

Since inclusions from the Al-killed, non-Ca treated experiment H were all Al_2O_3 before and after reoxidation, the composition maps are not necessary here. The area fraction and number density of inclusions are summarized in Table 12.

	Right	Right	Right	5 min	10 min
	after deox	before reox	after reox	after reox	after reox
Inclusion area fraction (ppm)	176	28.2	322	300	133
Inclusion number density (/mm ²)	163	18.5	298.5	206	15.7

Table 12: Area fraction and number density of inclusions in experiment H

Experiment H is a good example to verify whether the added oxygen did form inclusions as expected, because the inclusion chemistry didn't change over time and there was no influence of Mg or Ca. In this experiment, 100 ppm of oxygen (0.5 g) was added as Fe_2O_3 for reoxidation, 212.4 ppm Al_2O_3 should form. Considering the density of Al_2O_3 and iron is 3.95 g/cm³ and 7.874 g/cm³, the inclusion area fraction should increase by 423 ppm after reoxidation. Measured by Aspex, the area fraction of Al_2O_3 inclusions increased by 293.8 ppm right after reoxidation and increased by 271.8 ppm 5 minutes after reoxidation. These are both lower than the expected value because 1) Some oxides formed at the melt surface and floated out; large number of tiny Al_2O_3 inclusions nucleated upon reoxidation and they are smaller than the minimum size that Aspex can analyze. These inclusions were not counted in the total area fraction in the sample taken right after reoxidation. 2) 5 minutes after reoxidation, Al_2O_3 inclusions tended to cluster and float to the surface of the melt. These inclusions were missed during sampling.

The oxygen addition method could influence reoxidation. In this study, Fe_2O_3 capsule was dropped onto the surface of the melt and the biggest inclusions would have formed at the top of the melt and floated out.^[47]

7.2 Experiment I (Al₂O₃ crucible, single Ca)

In experiment B, D and F when MgO crucibles were employed, 667 ppm Ca addition was proved to successfully modify the spinel inclusions into liquid. However, a large part of Ca added in this experiment reacted with Al₂O₃ crucible, so the Al₂O₃ inclusions were not fully modified to liquid. Changes in inclusion chemistry (S, Al, and Ca) are demonstrated in the following partial composition maps. The region inside the dot-dash line in these composition maps represents the region where at least approximately 50% of the inclusions are liquid. Full ternary diagrams can be found in appendix.



Figure 7.1 - Composition of inclusion chemistry from experiment I (667 ppm Ca addition). Chemistry values are plotted as mole fraction S-Al-Ca and the symbol size is proportional to the area fraction of inclusions in that sample.

		-		-	
	I1	I2	I3	I4	I5
Inclusion area fraction (ppm)	215	104	505	785	318
Inclusion number density (/mm ²)	37.7	15.1	177	126	79.9

Table 13: Area fraction and number density of inclusions in experiment I

The possible sequence of reactions in this experiment is as follows. After deoxidation:

$$2\underline{Al} + 3\underline{O} = Al_2O_3 \tag{1}$$

Ca treatment:

$$3\underline{Ca} + Al_2O_3(s) = 3(CaO)_{inclusion} + 2\underline{Al}$$
(5)

After reoxidation:

$$2\underline{Al} + 3\underline{O} = Al_2O_3 \qquad (1)$$

$$(CaO)_{inclusion} = \underline{Ca} + \underline{O} \qquad (6)$$

$$3\underline{Ca} + Al_2O_3(s) = 3(CaO)_{inclusion} + 2\underline{Al} \qquad (5)$$

7.3 Experiment J (Al₂O₃ crucible, triple Ca, 50 ppm S)

Although not all inclusions were modified to liquid, the excess Ca and S addition significantly raised he Ca/Al ratio and some CaS was preserved before reoxidation. Changes in inclusion chemistry are demonstrated in the partial composition maps in Figure 7.2. Full ternary diagrams can be found in appendix.



Figure 7.2 - Composition of inclusion chemistry from experiment J (2000 ppm Ca and 50 ppm S addition). Chemistry values are plotted as mole fraction S-Al-Ca and the symbol size is proportional to the area fraction of inclusions in that sample.

	J1	J2	J3	J4	J5
Inclusion area fraction (ppm)	261	326	305	308	207
Inclusion number density (/mm ²)	91.9	109	96.3	71.9	40.0

Table 14: Area fraction and number density of inclusions in experiment J

 Al_2O_3 appeared right after reoxidation in this experiment were much fewer than the existing Ca containing inclusions, and also much fewer than the Al_2O_3 that appeared right

after reoxidation in experiment H and I, even with same amount of O addition. This was likely due to the buffering effect of CaS, as demonstrated above for spinel inclusions and from industrial studies ^[24]. Because the CaS is available to modify the reoxidation inclusions, formation of solid Al_2O_3 is delayed. In this experiment, the number density of Al_2O_3 was highest 5 minutes after reoxidation. This could be explained by the immediate modification of Al_2O_3 by existing CaS upon reoxidation: the liquid inclusions tended to lose Ca and S faster and this helped to modify newly formed Al_2O_3 right away. After this initial modification, the Ca and S in the solid inclusions gradually diffused into the melt to further react with the Al_2O_3 formed after reoxidation.

The possible reactions in experiment J are:

After deoxidation:

$$2\underline{Al} + 3\underline{O} = Al_2O_3 \tag{1}$$

Ca treatment:

$$\underline{Ca} + \underline{S} = CaS(s) \tag{7}$$

$$3CaS(s) + Al_2O_3(s) = 3(CaO)_{inclusion} + 2\underline{Al} + 3\underline{S} \tag{2}$$

After reoxidation:

$$2\underline{Al} + 3\underline{0} = Al_2O_3 \qquad (1)$$

$$3CaS(s) + Al_2O_3(s) = 3(CaO)_{inclusion} + 2\underline{Al} + 3\underline{S} \qquad (2)$$

8. Results and Discussion: PDF of Inclusions

Population Density Function (PDF) is a useful way to describe inclusion distribution. However, automated feature analysis is performed in two dimensional cross sections and only yields 2D inclusions parameters like length, width and area of each inclusion. In this research, the 2D data is converted to 3D by the software CSDCorrections.

With higher spatial resolution of SEM, the automated analysis of inclusions will have a finer search grid. The search grid dimensions for INCA and Aspex are 0.1µm and 0.17 µm respectively, which should be smaller than the minimum inclusion size targeted to detected. A higher spatial resolution will ensure that the small inclusions could be found, and will enable the AFA software to accurately recorded shape of the inclusions. Therefore, automated inclusion analysis using SEM with low spatial resolution may miss small inclusions, and leads to inaccurate size distribution of inclusions, especially at small diameter.

The uncertainty in the size distributions was accessed by multiple measurements on different area of a same sample. Measurement 1 contains 327 inclusions and measurement 2 contains 471 inclusions. The PDFs of the two measurements could be found in Figure 8.1. The PDFs generated from two measurements of the sample are almost identical. Therefore the single measurement of inclusions was applied on samples discussed in this chapter.



Figure 8.1 – Comparison of PDF plotted from two measurements.

8.1 experiment A (MgO crucible, no Ca, no reoxidation)

Figure 8.2 shows the spinel size distribution evolution of experiment A. In this experiment, all spinels were formed from deoxidation. The population density of spinel inclusions at different time decreased slightly over time due to floatation, but the shape of the functions and its position relative to inclusions diameter stayed about the same. Overall, like the inclusion composition (Figure 6.1), the inclusion PDFs didn't change much either over time (Figure 8.2).



Figure 8.2 – PDFs of spinel inclusions in experiment A

The inclusion population density function (PDF) plotted in log(PDF) versus log(inclusion size) diagram in many publications ^[43, 46, 76-78] showed either a upward convex curve (corresponding to a lognormal size distribution), a linear decrease (corresponding to a power law distribution), or combination of both.

These PDFs can be modeled by straight lines. Take the PDF of spinels formed 25 minutes after deoxidation as an example: its PDF can be modeled by the function

y=-3.6509x-8.3286. This suggests that the system almost reach equilibrium and there's not many new spinels forming or old spinel growing since 5 minutes after deoxidation.

- 8.2 Experiment D (MgO crucible, single Ca), E (MgO crucible, double Ca) and F (MgO crucible, single Ca, 50 ppm S)
- 8.2.1 Spinel inclusions

PDFs of spinel inclusions in experiment D, E and F are shown in Figure 8.3-8.5.



Figure 8.3 – PDFs of spinel inclusions in experiment D



Figure 8.4 – PDFs of spinel inclusions in experiment E



Figure 8.5 – PDFs of spinel inclusions in experiment F

The average inclusion diameters were are summarized in Table 15 and plotted in Figure 8.6. These average inclusion diameters are equivalent spherical diameters which were obtained directly from the automated inclusion analysis data: the average length of all inclusions measured on the sample surface by AFA was timed by the average aspect ratio of inclusions.

	Expt. A	Expt. D	Expt. E	Expt. F
Time Taken	no Ca, no reox.	Single Ca-treated	Double Ca-treated	Single Ca-treated, 50 ppm S
5 min after deox.	4.39	3.69		
10 min after deox.	5.21			
15 min after deox.	5.28			
right before reox.	5.47 (25 min after deox.)			
right after reox.		1.90	2.68	2.01
5 minutes after reox.		2.29	3.34	3.25
10 minutes after reox.	5.39 (35 min after deox.)	2.91	4.37	4.56
20 minutes after reox.	5.15 (45 min after deox.)	3.23	5.16	5.02

Table 15: Average spinel diameter (μm) at various times in experiment A, D, E and F



Figure 8.6 – Average spinel diameter formed from deoxidation or reoxidation in experiment A, D, E and F

Bindeman suggested that the power law distributed inclusions are scale invariant because they are generated from the scale-invariant process ^[79]. Zinngrebe et al. also observed this power law distribution within 10 minutes after deoxidation or reoxidation, and they suggested breakup/coalescence control this type of size distribution ^[62]. In experiment D, E and F (Figure 8.3-8.5), spinel size distributions were most curved right upon reoxidation, then became more linear at longer times. The change from lognormal to power law distribution in experiment D, E and F indicates that many new spinel inclusions emerged upon reoxidation, and the formation of new spinels slowed down as time increased. The PDFs at different times in all three experiments were curved at smaller inclusion diameter, and became more linear at larger inclusion size. This suggests that above a certain size, inclusion growth is no longer controlled by diffusion, but by collision and coalescence. While at smaller size, new inclusions nucleate and grow by diffusion. The newly formed spinels are smaller compared with the existing spinels.

The size distribution of spinel inclusions was consistent with the observations that a new spinel population appeared after reoxidation. In experiment A, the average size of spinel inclusions, which all formed from deoxidation, were generally larger than the spinels formed form reoxidation in experiment D, E and F (see Table 16 for the average spinel diameter). In experiment D (Figure 8.3), the secondary spinels formed upon reoxidation were much smaller than the primary spinels formed 5 minutes after deoxidation. The reoxidation inclusions grew until 20 minutes after reoxidation. In experiment E and F (Figure 8.4 and 8.5), the size of spinel inclusions showed a similar trend after reoxidation. The static model of Zhang et al. predicted that, with increasing time, the size distribution range of inclusions became larger ^[48]. This broader size distribution was observed in later stage of reoxidation in experiment D, E and F.

8.2.2 Calcium Aluminate inclusions

It has been discussed in section 6.2 that in this experiment D, two groups of inclusions formed after reoxidation: newly formed spinel and alumina inclusions, and calcium aluminates which transform from the existing modified inclusions and evolve into Mg containing calcium aluminates later on (Figure 6.7). In this section, the size distribution of the second type, calcium aluminate inclusions, will be discussed. PDF of calcium aluminate inclusions in experiment D is shown in Figure 8.8



Figure 8.7 – partial Mg-Al-Ca ternary composition map showing how modified Mg containing calcium aluminate inclusions (red symbols) transform after reoxidation in experiment D.



Figure 8.8 - PDFs of calcium aluminate inclusions in experiment D

	experiment D				
Time taken	Right	Right after	5 min after	10 min after	20 min after
	before reox.	reox.	reox.	reox.	reox.
diameter	1.96	2.35	2.74	2.86	2.89

Table 16: Average diameter (μm) of calcium aluminate inclusions at various times in

Figure 8.8 shows the PDFs of calcium aluminate or Mg containing calcium aluminate inclusions in experiment D. The reason why both these two PDFs show a minimum at around 1.125 μ m inclusion diameter (Ln (inclusion diameter = 0.118) is not clear yet, but the very similar shape of PDF right before reoxidation and right after reoxidation is another evidence that the calcium aluminate inclusions right after reoxidation evolved from the existing modified inclusions.

The size of the calcium aluminate inclusions in experiment D kept growing after reoxidation as Mg reappeared in the inclusions (Table 16). Diffusion of metal Al and Mg still played a role this stage of inclusion growth, as PDFs of calcium aluminates 5 to 20 minutes after reoxidation are still quite curved (Figure 8.8). Comparing Figure 8.3 and Figure 8.8 of the population density change of spinel inclusions and calcium aluminate inclusions, it seems that the nucleation of new spinel inclusions happened immediately after reoxidation with their size grew rapidly by diffusion, and then entered the stage of collision controlled growth. Since the calcium aluminate inclusions gradually evolve into Mg containing calcium aluminates and Mg continued to diffuse into the inclusion to take place of Ca, the growth of this group of inclusions were controlled by diffusion until the last sample taken.

8.3 experiment $H(Al_2O_3 \text{ crucible, no } Ca)$

Inclusions from the Al-killed, non-Ca treated experiment H were all Al_2O_3 before and after reoxidation. The inclusion PDFs from this experiment are shown in Figure 8.9.



Figure 8.9 – PDF of Al_2O_3 inclusions in sample 1 (right after deoxidation), 2 (20 minutes after deoxidation, right before reoxidation), 3 (right after reoxidation), and 4 (5 minutes after reoxidation)

 Al_2O_3 right before reoxidation (20 minutes after deoxidation) has a narrower size range compared to those right after deoxidation, for the reason that small inclusions grew rapidly and large Al_2O_3 agglomerations tended to floated out over time. Reoxidation immediately brought tiny Al_2O_3 again and caused a sharp rise in inclusion number density, as can be observed in the curved PDF right after reoxidation. Predictions of Al₂O₃ inclusions size distribution overtime had been made by J. Zhang et al. ^[48] and L. Zhang et al. ^[49] based on static models which include nucleation, Ostwald ripening and various types of collision. These models both predicted a significant growth in inclusions size just a few seconds after deoxidation. But removal of inclusions due to flotation was not considered in these two models, and that results in the different density of large inclusions longer after deoxidation in lab results (Figure 8.9 right before reoxidation) and numerical predictions (Figure 8.10).

It is believe that lognormal shaped size distributions are associated with nucleation of new, small inclusions as well as growth of existing inclusions ^[43]: upon deoxidation, inclusions nucleate and grow. This process is controlled by diffusion and Ostwald ripening; While linear power-law type PDFs are associated with chemical equilibrium between inclusions and melt ^[46] after the rapid nucleation and diffusion controlled growth of the inclusions, collision becomes most important in further growth of the inclusions^[47].



Figure 8.10 – Numerical modeling of Al_2O_3 inclusions size distribution as a function of time after deoxidation by (a) J. Zhang and H. Lee ^[46] and (b) L. Zhang and W. Pluschkell ^[47]

8.4 Experiment I (Al₂O₃ crucible, single Ca)

The PDFs of Al_2O_3 inclusions are plotted in Figure 8.11. Note that the Ca containing inclusions are not included.



Figure 8.11 - PDFs of Al_2O_3 inclusions in experiment I (667 ppm Ca). The Ca containing inclusions are not included in this plot

With (Figure 8.11) or without Ca treatment (Figure 8.9), Al_2O_3 inclusions right before reoxidation were medium in size: the smallest Al_2O_3 have grown rapidly after deoxidation and the largest agglomerations have been removed by floatation. Right after reoxidation, a significant number of tiny Al_2O_3 inclusions reappeared: at large inclusions diameter, the PDF right after reoxidation almost overlaps with the PDF right before reoxidation, but the high PDF curve at smaller inclusion diameter is a clear sign of reoxidation. The modified Ca containing inclusions gradually lost Ca to modify the newly formed Al_2O_3 inclusions and the overall Ca content dropped until at least 5 minutes after reoxidation (Figure 7.1).

8.5 *Experiment J* (*Al*₂*O*₃ *crucible, triple Ca, 50 ppm S*)

The PDFs of Al_2O_3 inclusions and calcium aluminate inclusions are plotted in Figure 8.12.



Figure 8.12 - PDFs of Ca containing inclusions as dotted lines and Al_2O_3 inclusions as solid lines. All inclusions were Ca containing right before reoxidation and 20 minutes after reoxidation.

This size distribution of Ca containing inclusions almost kept unchanged after reoxidation. The Al_2O_3 inclusions formed right after reoxidation are low in population density, and if we add its PDF to the PDF of CA right after reoxidation, it will not cause great difference from the PDF of all inclusions before reoxidation. This is quite different from the significant change of PDF in experiment H and I. 5 minutes after reoxidation,

unmodified Al_2O_3 inclusions began to agglomerate, as can be seen in the segmented PDF.

9. Results and Discussion: Study of Industrial Heats

Reoxidation is a transient phenomenon and is a concern during any ladle-to-tundish transfer and is especially prevalent when ladles are tapped into empty tundishes during startup heats and after ladle exchanges ³,⁴. There are several oxygen sources in the tundish³:

1. Air	4. Ladle slag
2. Tundish lining	5. Tundish slag
3. Ladle sand	6. Shroud cleaning residue

In this chapter, a Ca treated grade and a non-Ca treated grade will be discussed. Chemistry and size distribution of inclusions taken at various time in the ladle or at the caster will be studied to understand the reoxidation phenomenon in industrial heats.

9.1 Al-killed, Ca treated heats

9.1.1 Heat 1

Heat 1 is a startup heat. Sample L8 was taken after Ca treatment at the LMF. Samples T1, T2, T3, T4 and T5 were samples taken successively at the tundish throughout the startup heat 1. Mg-Al-Ca ternary plots in Figure 9.1 and S-Al-Ca ternary plots in Figure 9.2 demonstrate the inclusion composition of sample L8 and T1 to T5 in heat 1. The scan area was the same for each sample. Note that the ternary diagrams in this chapter are different from those in lab results. In these scatter plot, points with different color represents inclusions of different size.



Figure 9.1 - Composition distribution of inclusions from a startup heat (Ca treated) plotted as mass fractions on Mg-Al-Ca ternary diagram. Each point represents an inclusion. Average mass percent of elements in the inclusions are shown in the table.


Figure 9.2 - Composition distribution of inclusions from a startup heat (Ca treated) plotted as mass fractions on S-Al-Ca ternary diagram. Each point represents an inclusion.

	L8	T1	T2	Т3	T4	T5
Number of inclusions	1434	569	389	276	238	198
% solid	44.42	76.98	61.95	30.80	26.47	8.08
% liquid	55.30	21.62	37.02	65.94	69.33	88.89
Average diameter (µm)	2.76	2.76	3.10	3.45	3.81	3.64
Average area (µm ²)	5.77	7.48	8.27	13.22	19.27	12.57
Total area (µm ²)	8274.18	4256.52	3218.00	3648.98	4585.36	2488.44

Table 17 – summary of inclusions in all samples from heat 1

In this Al-killed, Ca treated heat, inclusions were successfully modified after Ca treatment and some CaS was preserved in the ladle depart sample L8. As a startup heat, reoxidation can be observed: lots of new spinel inclusions appeared in early tundish samples T1 and T2. Then it almost recovers to the LMF depart condition when sample T4 and T5 was taken, but CaS was consumed to react with the secondary spinels.

PDFs of inclusions in the ladle depart sample L8 and the early tundish sample T1 are shown in Figure 9.3 (a). Inclusions in these samples are mostly spinel and calcium aluminate. Great amount of small spinels appeared in this early tundish sample, as shown in the red curve. And this caused the rise of the overall PDF plotted in blue curve, especially at small inclusion diameter.

PDFs of inclusions from tundish sample T1-T5 are shown in Figure 9.3 (b). The darker lines are early tundish samples and the lighter lines are samples taken when the tundish was filled up. The most significant reoxidation of this heat happened during the initial tundish filling when the molten steel was poured into an empty tundish and sample T1

was taken. The left side of the PDF curve shows some characteristic changes when reoxidation occurs. The other tail doesn't look to be as affected



Figure 9.3 – PDFs of (a) all inclusions in ladle depart sample L8 and tundish sample T1 from startup heat 1; (b) all inclusions in tundish sample T1-T5 from startup heat 1; (c) spinel inclusions in tundish sample T1-T3

Same as the lab experiments, Reoxidation event in industrial heat, especially if large

amount of new inclusions form after reoxidation, can be diagnosed from the change of inclusions PDFs. However, the change of these PDFs is not as evident as that in lab results, for the reason that analysis on these industrial samples has a 1 μ m cutoff while for the lab study, the size threshold is 0.2 μ m. Inclusions formed upon reoxidation are usually small at the beginning and a high cutoff size in PDF will lose track of some tiny inclusions upon reoxidation.

9.2.2 Heat 2

Heat 2 is the follow-up heat after the startup heat 1. The L8 sample was taken after Ca at the LMF and the T1 to T3 samples were taken successively at the caster for this sequence heat. Figure 9.4 and 9.5 demonstrates the inclusion composition of sample L8 and T1 to T3 in heat 2.



Figure 9.4 - Composition distribution of inclusions from heat 2 (Ca treated) plotted as mass fractions on Mg-Al-Ca ternary diagram. Each point represents an inclusion. Average mass percent of elements in the inclusions are shown in the table.



Figure 9.5 - Composition distribution of inclusions from heat 2 (Ca treated) plotted as mass fractions on S-Al-Ca ternary diagram. Each point represents an inclusion.

	L8	T1	T2	T3
Number of	178	676	1367	989
inclusions				
% solid	16.29	22.04	1.24	1.32
% liquid	82.02	77.51	98.68	98.58
Average diameter	2.54	2.61	1.77	2.57
(µm)				
Average area (μm^2)	6.54	5.10	2.39	4.48
Total area (µm ²)	1164.87	3445.88	3263.01	4427.31

Table 18 – summary of inclusions in all samples from heat 12

Compared to heat 1, reoxidation in this heat was less significant and inclusions almost recovers to the LMF depart condition when sample T2 was taken. In general, reoxidation is most prevalent when ladles are tapped into empty tundishes during startup heats.

PDFs of inclusions in the ladle depart sample L8 and the early tundish sample T1 are shown in Figure 9.6 (a). Some small spinels appeared in this early tundish sample, as shown in the red curve. And this caused the rise of the overall PDF plotted in blue curve, especially at small inclusion diameter.

PDFs of inclusions from tundish sample T1-T5 are shown in Figure 9.6 (b). PDFs in this heat didn't show a clear trend as in the startup heat 1 and reoxidation event could not be told from the change of PDF.



Figure 9.6 – PDFs of inclusions in (a) ladle depart sample L8 and tundish sample T1 from startup heat 2; (b) Tundish sample T1-T5 from heat 2

9.2 All-killed, Non-Ca treated heats

Ti-stabilized ultra-low carbon grade heats were also studied. These are Al-killed and non-Ca treated heats. The chemistries of these steel heats are shown in Table 19.

	С	Mn	Р	S	Si	Ni	Cr	Al	Ν	Ti	Ca
Heat 1	0.002	0.109	0.007	0.008	0.004	0.01	0.04	0.034	0.002	0.061	0.0001
Heat 2	0.002	0.139	0.01	0.009	0.004	0.01	0.04	0.035	0.003	0.056	0.0001
Heat 3	0.002	0.121	0.007	0.006	0.003	0.01	0.04	0.037	0.005	0.064	0.0001
Heat 4	0.001	0.11	0.007	0.007	0.002	0.01	0.04	0.032	0.003	0.058	0.0001

Table 19: chemistry of Ti-stabilized ultra-low carbon grade heats

Mold samples were collected during initial filling of the tundish and then through the ladle exchange on the next heat. These samples were taken in relatively rapid succession

from the mold and the samples were taken as a function of cast feet. In general, 500-1000 inclusions were analyzed for each sample. Inclusions are Al_2O_3 -TiO₂ and their chemistry did not change significantly as a function of cast length (Figure 9.7 gives an example). Therefore, study of inclusion size distribution is necessary to learn reoxidation.



Figure 9.7 - Composition of inclusion chemistry from heat 1 at cast length of 5 feet and 164 feet. Chemistry values are plotted as mole fraction Ti-Al-O and the symbol size is proportional to the area fraction of inclusions in that sample.

PDFs of inclusions from heat 1, 2 and 4 are shown in Figure 9.8 (a). PDF of inclusions at shortest cast length are in blue curve and inclusions at longest cast length in red. The major difference is the population density of smaller inclusions. Ladle exchanges caused reoxidation as we can clearly see that the in all three heats, more reoxidation happened at shortest cast length. Figure 9.8 (b) demonstrates the inclusion PDF from short cast length to long cast length in heat 4 in detail. Inclusion population density gradually drops as cast length increases, especially at smaller inclusion diameter.

PDFs of inclusions in heat 3 didn't follow the same trend as in other three heats and its PDFs are plotted in figure 9.8 (c). There might be some errors in the measurement or a

reoxidation event occurred near the end of the heat.



Figure 9.8 - (a) PDFs of inclusions at shortest cast length and at longest cast length from heat 1, 2 and 4. (b) Details of how inclusion PDFs evolve as a function of cast length in heat 4. (3) PDFs of inclusions as a function of cast length in heat 3.

In summary, both initial filling of the tundish (comparing heat 1, 5 ft and heat 1, 164 ft)

and ladle exchanges (see heat 2, 6 ft and heat 4, 4 ft) caused reoxidation.

10. Conclusions

This study documents inclusion evolution after controlled O additions made to simulate reoxidation in an industrial ladle or tundish. Al_2O_3 were produced upon deoxidation and gradually transformed into spinels when MgO crucible was employed. The equilibrium after deoxidation was established rapidly.

Hypothesis 1): In Al-killed steel, upon reoxidation a transient population of alumina inclusions form that react with the melt and other inclusions to change the overall chemistry distribution. If the initial inclusions after deoxidation are spinels, then Ca treatment will cause Mg to return into the melt and secondary spinels will reform upon reoxidation. If the initial inclusions after deoxidation are alumina, then Ca treatment will cause some Al to return into the melt and alumina will reform upon reoxidation. This was supported by the results. After Ca treatment and 100 ppm O addition to the melt, Al_2O_3 inclusions formed right away in both experiments using MgO crucible or Al_2O_3 crucible and reacted with the melt, as well as the existing inclusions. In experiments with MgO crucible, inclusions were divided into two groups: 1) newly formed Al_2O_3 and spinels transformed from Al_2O_3 upon reoxidation, and 2) Al_2O_3 -CaO evolved from the pre-existing Ca modified inclusions. The After 20 minutes spinels which formed after reoxidation grew larger, and Al_2O_3 -CaO gradually transformed into MgO-Al_2O_3-CaO.

Hypothesis 2) part 1: Ca treatment is achieved by the formation CaS as an intermediate product, which will modify solid inclusions into liquid. In experiment G, the excess CaS remained in the inclusion before reoxidation work as a Ca reservoir and help to modify the inclusions formed after reoxidation. As a result, the inclusions after reoxidation were lower in Mg and Al content. The double Ca treatment in experiment E and extra S

addition in experiment F didn't lead to a better modification, for the reason that they didn't produce more CaS. Therefore the role of CaS in Ca modification is confirmed.

Hypothesis 2) part 2: If there is excess CaS which is discrete and not associated with other inclusions before reoxidation, it will collide and react with oxide inclusions when reoxidation happens. This was also supported by the results. In experiment G, both after Ca addition and after reoxidation, large chunk of CaS was found attached to the oxide inclusions rather than form a shell. The morphology of these multi-phased inclusions suggested the collision and reaction between inclusions. The collision frequency between CaS containing inclusions and oxide inclusions was also calculated in section 6.3. It suggested that when there was excess CaS, oxide inclusion were modified by collisions with CaS containing inclusions both after Ca addition and after reoxidation.

Hypothesis 3): The population density function of inclusions will show a clear change after reoxidation. Reoxidation changes the PDF from that characterizing a steady state to one consistent with generating new inclusions. The PDF can be used to identify new inclusions formed after reoxidation. This was partially supported by the results. The change of PDF can be used to diagnose the reoxidation event, especially if large number of new inclusions forms after reoxidation. However, the change of the PDF curve in its shape is related to the amount of inclusions associated with reoxidation. That means if CaS is present before reoxidation and reduces the formation of oxides after reoxidation by modifying them, there will not be PDF change as significant as in low Ca inclusions, and reoxidation event can only be told by the chemistry change.

11. Suggestions for Future Work

This projected has investigated the evolution of inclusions after reoxidation in lab heats. The limitations of understanding the reoxidation event largely arise from the lack of chemical information of steel samples and thermodynamic data in relevant process. The following improvements in the future induction furnace experiments will be helpful:

- A better chemistry control: The CalSil powder injected for Ca treatment has decomposed and contains Si and SiO₂. The iron pieces used for melting need to be consistent in O and S content over experiment.
- 2. A better sampling method and chemical analysis: samples need to be taken quickly and carefully to avoid interior pores and rough surface because they will cause rust and affect the O measurement of the steel sample. Chemical analysis of the steel requires at least several grams of sample for measurement of metallic elements using ICP spectroscopy. But frequent and heavy sampling may reduce the amount of remaining steel melt and affect the result of subsequent additions. More accurate chemical analysis of samples over time would be helpful.
- 3. Crucibles which do not react with the liquid steel or the inclusions could be attempted.

Following properties need to be obtained to better understand the inclusion evolution:

- 1. Mass transfer coefficient of Mg, Al, and Ca in the liquid steel
- 2. Concentration of Ca on the inclusion-melt interface in various conditions

3. Fluid flow velocity distribution in the steel melt

Future work in this subject could involve several aspects:

- Reoxidation from other O source: Slag is an important source of reoxidation in industrial heats. The effect of different slag composition on reoxidation could be investigated in the future.
- Reoxidation with different amount of O, especially with larger amount of O addition is also industrial relevant: 500 ppm to 1000 ppm of O addition may result in the formation of silica or aluminum silicate in Al-killed steel.
- 3. Comparing experiments with Al₂O₃ as primary inclusions and experiments with spinel as primary inclusions, it seems that Al₂O₃ inclusions were more difficult to modify than spinels but less vulnerable than spinels during reoxidation. Generating spinel inclusions in a Al₂O₃ crucible is a possible method to test this.
- 4. Study of industrial samples: More industrial samples that have undergone reoxidation could be analyzed for inclusions study. In addition, industrial samples could be reoxidized in the lab using confocal scanning electron microscope for in-situ observation and further analysis.
- 5. Stirring in liquid steel would enhance the inclusion collision and affect the inclusion evolution after reoxidation. This could be investigated in the future.
- 6. Similar to the inclusion growth after deoxidation, models could be established for the size distribution of inclusions after reoxidation.

12. Appendix

expt	additions	Right before	Right after	20 minutes after				
Слрг	additions	reoxidation	reoxidation	reoxidation				
А	deox	Al ₂ O ₃ gradua	Al ₂ O ₃ gradually transformed to spinel after deox					
В	deox, 1×Ca	Spinels modified to liqu	pinels modified to liquid and composition kept unchanged over time					
С	deox, reox	spinels	Al ₂ O ₃ formed and obtaining Mg from existing spinels	Composition returned to spinel				
D	Deox, 1×Ca, reox	Modified to liquid	Al ₂ O ₃ and spinels formed, Mg content dropped in liquid inclusion	Spinels grew larger, liquid inclusions obtaining Mg from crucible and losing Ca				
Е	Deox, 2×Ca, reox	Same as D	Same as D	Same as D				
F	Deox, 1×Ca, 50 ppm S, reox	Same as D	Same as D	Same as D				
G	Deox, 2×Ca, 50 ppm S, reox	Spinel, calcium aluminate and CaS	Number of CaS inclusion dropped sharply	CaS kept decreasing as Mg content slowly increased				

Change of inclusion chemistry in experiment A to G with MgO crucible

ovet	additiona	Right before	Right after	longer after
cxpt additions		reoxidation	reoxidation	reoxidation
Н	deox, reox	Al ₂ O ₃	Large number of small Al ₂ O ₃ formed	Some Al ₂ O ₃ clustered and floated out
Ι	Deox, 1×Ca, reox	Solid calcium aluminates with low Ca content	Large number of small Al ₂ O ₃ formed	Newly formed Al ₂ O ₃ gradually modified by existing Ca containing inclusions
J	Deox, 3×Ca, 50 ppm S, reox	Partially liquid calcium aluminates with some CaS	Some Al ₂ O ₃ formed and were immediately modified to calcium aluminate	Modification of new Al ₂ O ₃ continued, S content inclusion close to 0

Change of inclusion chemistry in experiment H to I with Al_2O_3 crucible

















Composition distribution of inclusions from experiment F (single Ca addition, 50 ppm S addition, 100 ppm reoxidation) plotted on Mg-Al-Ca ternary diagram



Composition distribution of inclusions from experiment F (single Ca addition, 50 ppm S addition, 100 ppm reoxidation) plotted on S-Al-Ca ternary diagram









Steps to generate 3D size distribution by CSDCorrections Software

The CSDCorrections software was originally designed for estimating size distribution of rocks, but it can also be used for steel inclusions. More details can be found in two of Higgins' papers: "Measurement of crystal size distributions" (American Mineralogist, Volume 85, pages 1105–1116, 2000) and "Closure in crystal size distributions (CSD), verification of CSD calculations, and the significance of CSD fans" (American Mineralogist, Volume 87, pages 171–175, 2002).

Parameters needed are listed below:

- Measurement: for inclusions measured by AFA software such as INCA or ASPEX, select "maximum length" for measurement.
- 2. Fabric: select "massive" for fabric.
- 3. Shape: The short aspect ratio is always 1; The average aspect ratio measured on 2D plane by AFA can be used as intermediate aspect ratio and same value can be taken as long aspect ratio if inclusions are near-spherical rather than foliated or lineated; The roundness of inclusions can be set to 1 when most inclusions are ellipsoid.
- 4. Size scales: Log 10 is usually used. The number of bins per decade used will depend on the amount of inclusions analyzed and the range of their size distribution. 5 to 10 bins per decade is suitable for most cases of inclusion analysis.
- 5. The measured area is the area of sample surface scanned in AFA.
- 6. The length of each inclusion measured on 2D plane is needed. It can be obtained from the AFA raw data. For example, in ASPEX raw data, the length of inclusions is the "DMAX" column in the spreadsheet.

Data input Size Results Shape results Orientation results Distribution	ition re	sults	Please refere	ence the use o	f this prograr	n: See help	file
Measurement 3 Essential data in yellow boxes	Raw [Data - Main_set	Raw Data s	et 2 Freque	ncv data		
Maximum length Shape		5	ture but o	7200000	10) uutu) mainta	
Short 1.0 Roundness	†	♦ Weat	sured Area T	7320000		points	
Inter 1.416		Length Wid	dth Area	Angle	X-centre	Y-centre	Notes
2 Long 1.416 Block Ellipsoid	1	1.3820191					
Fabric	2	1.5273100					
Massive	3	3.0902800					
	4	2.811/699					
	5	2.1380898					
OFoliated	7	4.4431500					
Correct for vesicles / voids	8	2.4067699					
Correct to phase abundance	9	3 4854900					
Vesicles 0	10	5.0947799					
	11	3.5234699					
4 Size Scale	12	2.7978100					
Log 10 Log 2 Linear Custom	13	1.9057999					
Log Z Lincul Oustonn	14	2.5024399					
	15	1.8473999					
Logarithmic base 10 size scale.	16	3.0902800					
Number of bins per decade	17	3.3690099					
	18	5.8820600					
	19	0.8073701					
Notes on this sample	20	2 7327098					
	22	1 5677700					
	23	2.8532199					
	24	2.8805201					
	25	3.3033099					
	26	1.7382500					
	27	6833399					
	28	2.7978/00					

7. Click the "Calculate button on the top to generate the 3D size distribution. Size result on the "Classic CSD" tab is often used. The size distribution can also be replotted by taking the logarithm of size ("Mid Inter" column) as well.



13. Reference

[1] <u>http://www.dantecdynamics.com/flow-in-metallurgical-reactors</u>, last visited July 2016
[2] N. Verma et al., Transient Inclusion Evolution During Modification of Alumina

Inclusions by Calcium in Liquid Steel: Part I. Background, Experimental Techniques and Analysis Methods, *Metallurgy and Transaction B* (2011), volume 42B, pp 711-719

[3] N. Verma, et al., Transient Inclusion Evolution During Modification of Alumina Inclusions by Calcium in Liquid Steel: Part II. Results and Discussion, *Metallurgical & Material Transactions B*, vol. 42B, pp. 711-719, August 2011

[4] S. Story et al., A Study of Casting Issues using Rapid Inclusion Identification and Analysis, *AISTech Proceedings*, Volume 1, pp. 879, 2006

[5] R. Maddalena et al., Advanced SEM Methodology for Tracking Reoxidation in the Tundish, *AISTech Proceedings*, pp 2113-2121, 2013

[6] L. Zhang et al., Inclusions in Continuous Casting of Steel, *National Steelmaking Symposium*, 26-28, pp. 138-183, Nov 2003

[7] L. Zhang et al., Evaluation and Control of Steel Cleanliness—Review, 85th Steelmaking Conference Proceedings, pp. 431-452, 2002

[8] G. Yang et al., Influence of Reoxidation in Tundish on Inclusion for Ca-Treated Al-Killed Steel, *Steel Research International*, Volume 85, Issue 5, pp. 784–792, May 2014

[9] R. Rampersadh et al., Reoxidation and Castability of Aluminum-killed Steels, *the Journal of the South African Institute of Mining and Metallurgy*, Volume 106, pp. 265-268, 2011

[10] D. Yang et al., Effect of Reoxidation on Cleanliness of Molten Steel in Tundish for Low Carbon Aluminum Killed Steel, *Iron and Steel*, Vol. 48, pp. 37-41, 2013

[11] P. Thomas, Variations in Steel Cleanness during Transient Continuous Casting Practices, Materials Science and Technology, Vol. 25, No. 30, pp. 334-338, 2005 [12] K. Sasai et al., Reoxidation Behavior of Molten Steel in Tundish, *ISIJ International* (2000), Vol. 40, No. 1, pp. 40-17

[13] M. Burty et al., Definition of a Ladle Change Strategy to Avoid Slag Entrapment and to Control Inclusion Population, *European Commission Technical Steel Research*, 2006

[14] H. Watkinson et al., A study on Tundish Powders and Their Influence on Tundish Slag Chemistry and Steel Cleanness for Carbon and Stainless steels, *European Commission Technical Steel Research*, 1997

[15] C. Treadgold et al., Enhanced Steel Product Quality and Yield by Applying the Results of Improved Modelling of Transient Conditions in the Tundish, *European Commission Technical Steel Research*, 2001

[16] N. Banerjee et al., Tundish Metallurgical Practices for Slab Production in Bokaro Steel, *Metal 2003*, 20. -22, 5

[17] J. Nakashima et al., Improvement of Continuously Cast Slabs by Decreasing Nonmetallic Inclusions, Nippon steel technical report No. 104, August 2013

[18] T. Kawawa and M. Ohkubo, A Kinetics on Deoxidation of Steel, *Transactions of The Iron and Steel Institute of Japan*, vol. 8, pp. 203-219, 1968

[19] I. H. Jung et al., Computer Applications of Thermodynamic Databases to Inclusion Engineering, *ISIJ International*, Vol. 44 (2004), No. 3, pp. 527–536

[20] L. Zhang, Large Inclusions in Plain-carbon Steel Ingots Cast by Bottom Teeming, *ISIJ International*, Vol. 46, No. 5, pp. 670-679, 2006

[21] S. Story et al., Application of Rapid Inclusion Identification and Analysis, *Iron and Steel Technology* (September 2005), pp. 41-49

[22] P. Kaushik et al., State of the Art in Control of Inclusions, Their Characterization, and Future Requirements, *Metallurgical and Materials Transactions B* (2012), Volume 43B, pp. 710-725

[23] P. C. Pistorius et al., Examples of How Fundamental Knowledge can Improve

Steelmaking: Desulphurisation Kinetics Calcium and Modification, *Trans Indian Inst Met* (October–December 2013) 66(5–6):519–523

[24] E. Pretorius et al., An Overview of Steel Cleanliness From an Industry Perspective, *AISTech Proceedings* (2013), pp. 993-1026

[25] P. C. Pistorius et al., Magnesium: Origin and Role in Calcium-treated Inclusions, Sohn International Symposium - Advanced Processing of Metals and Materials (2006), Vol. 2

[26] S. Yang et al., Modification of MgO Al₂O₃ Spinel Inclusions in Al-killed Steel by Ca-treatment, *International Journal of Minerals, Metallurgy, and Materials* (2011), Volume 18, Issue 1, pp. 18-23

[27] Z. Deng et al., Evolution Mechanism of Non-metallic Inclusions in Al-Killed Alloyed Steel during Secondary Refining Process, *ISIJ International* (2013), Vol. 53, No. 3, pp. 450–458

[28] N. Verma et al., Calcium Modification of Spinel Inclusions in Aluminum-Killed Steel: Reaction Steps, *Metallurgical and Materials Transactions B* (2012), Volume 43B, pp. 830-840

[29] E. Pretorius et al., The Effective Modification of Spinel Inclusions by Ca-treatment in LCAK Steel, *AISTech Proceedings* (2009), Volume I, pp. 1035-1049

[30] L. Wang et al., Prediction of Reoxidation Inclusion Composition, *Metallurgical and Materials Transactions B* (2006), Vol. 37B, pp. 571-588

[31] B. Coletti et al., Reoxidation during Ladle Treatment, *Ironmaking and Steelmaking* (2003), Vol. 30 No. 2, pp. 101-105

[32] Y. Kwon et al., the Morphology and Chemistry Evolution of Inclusions in Fe-Si-Al-O Melts, *Metallurgical and Materials Transactions B* (2011), Vol. 42B, pp. 814-824

[33] K. Chattopadhyay et al., Thermodynamic Evaluation of Inclusion Formation and
Nozzle Clogging During Slab Casting, (Oct 2014), pp. 100-106

[34] N. Verma et al., Decrease in MgO Content of Spinel Inclusions During Calcium Modification, *AISTech Proceedings* (2011), Volume II, pp. 607-615

[35] A. Harada et al., A Kinetic Model to Predict the Compositions of Metal, Slag and Inclusions during Ladle Refining: Part 1. Basic Concept and Application, *ISIJ International*, Vol. 53 (2013), No. 12, pp. 2110–2117

[36] P. R. Scheller et al., Inclusion Development in Steel during Ladle Metallurgical
Treatment - A Process Simulation Model – Part: Industrial Validation, *steel research int*.
85 (2014) No. 8

[37] M. A. Van Ende et al., A Kinetic Ladle Furnace Process Simulation Model: Effective Equilibrium Reaction Zone Model Using FactSage Macro Processing, *Metallurgical and Materials Transactions B* (2017), Volume 48B, pp. 28-36

[38] S. Piva et at., Modeling Manganese Silicate Inclusion Composition Changes during Ladle Treatment Using FactSage Macros, *Metallurgical and Materials Transactions B* (2017), Volume 48B, pp. 37-45

[39] J.H. Shin et al., Refractory–Slag–Metal–Inclusion Multiphase Reactions Modeling Using Computational Thermodynamics: Kinetic Model for Prediction of Inclusion Evolution in Molten Steel, *Metallurgical and Materials Transactions B* (2017), Volume 48B, pp. 46-59

[40] J. Peter et al., Introduction of a Novel, Scrap-Based, Fully Continuous Steelmaking Process, *AISTech 2005 Iron and Steel Conference Proceedings*

[41] Ying Ren, Ying Zhang, Lifeng Zhang, Wen Fang, A Kinetic Model for Ca Treatment of Al-killed Steels Using FactSage Macro Processing, *Ironmaking and Steelmaking*, 2016, 1-8.

[42] Y. Ren et al., A Reaction Model for Prediction of Inclusion Evolution During Reoxidation of Ca-Treated Al-Killed Steels in Tundish, *Metallurgical and Materials* Transactions B (2017), Volume 48B, pp. 1433-1438

[43] M. Van Ende et al., Evolution of Non-metallic Inclusions in Secondary Steelmaking:Learning from Inclusion Size Distributions, *ISIJ International* (2013), Vol. 53, No. 11, pp. 1974–1982

[44] J. Blower et al., The evolution of bubble size distributions in volcanic eruptions, *Journal of Volcanology and Geothermal Research*, vol. 120, pp. 1-23, 2003

[45] C. Wagner, Theorie der Alterung von Niederschlägen durch Umlösen (Ostwald-Reifung) (Theory of the aging of precipitates by dissolution-reprecipitation (Ostwald ripening)), Zeitschrift für Elektrochemie, vol.65 (7), pp. 581–591, 1961

[46] E. Zinngrebe et al., Inclusion Population Evolution in Ti-alloyed Al-killed Steel during Secondary Steelmaking Process, *ISIJ International*, Vol. 52, No. 1, pp. 52-61, 2012

[47] U. Lindborg and K. Torssell, A Collision Model for the Growth and Separation of Deoxidation Products, Transactions of the Metallurgical Society, vol. 242, pp. 94-102, 1968

[48] J. Zhang et al., Numerical Modeling of Nucleation and Growth of Inclusions in Molten Steel Based on Mean Processing Parameters, *ISIJ International*, Vol. 44 (2004), No. 10, pp. 1629–1638

[49] L. Zhang et al., Nucleation and Growth Kinetics of Inclusions during Liquid Steel Deoxidation, Iron and Steelmaking, vol. 30, no. 2, pp. 106-110, 2003

[50] K. Cashman et al., Crystal Size Distribution (CSD) in Rocks and the Kinetics and Dynamics of Crystallization II: Makaopuhi lava lake, *Contributions to Mineralogy and Petrology* (1988), pp. 292-305

[51] R. Kellerhals et al., On Grain Size from Thin Sections, *The Journal of Geology* (1975), Vol. 83, No. 1, pp. 79-96

[52] T. H. Hangerman, 1924

[53] S. D. Wicksell, The Corpuscle Problem: a Mathematical Study of Biometric Problem, *Biometrika*, 1925, vol. 17, pp. 84-99

[54] E. Scheil, 1935

[55] W. C. Krumbein, Thin Section Mechanical Analysis of Indurated sediments, *Jour. Geology*, vol. 43, pp. 482-496

[56] M. Higgins, Measurement of Crystal Size Distributions, American Mineralogist(2000), Vol. 85, pp. 1105–1116

[57] J. Tan et al., Comparison of Three Approaches to Study Inclusions in Al-Si Deoxidized Steel and Al-killed Steel, *AISTech Proceedings*, 2013

[58] A.M. Stolzenberg, Iron compounds, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, 2004

[59] Y. Kanbe et al., Application of Extreme Value Analysis for Two- and Three-Dimensional Determinations of the Largest Inclusion in Metal Samples, *ISIJ International* (2011), Vol. 51, No. 14, pp. 593-602

[60] INCA Feature

https://www.oxford-instruments.com/products/microanalysis/energy-dispersive-x-ray-sys tems-eds-edx/eds-for-sem/particle-analysis, last visited June 10, 2017

[61] F. Schamber, Introduction to Automated Particle Analysis by Focused Electron Beam, *Aspex Corporation*

[62] S. Story et al., Inclusion Analysis to Predict Casting Behavior, *Iron and Steel Technology*, vol. 9, pp. 163-169, 2004

[63] K. Ahlborg et al., Inclusions in Aluminum-Killed Steel with varying Calcium Additions, *ISSTech 2003 Conference Proceedings*, pp. 177-194

[64] P. C. Pistorius et al., Matrix Effects in the Energy Dispersive X-Ray Analysis of CaO-Al₂O₃-MgO Inclusions in Steel, *Microscopy and Microanalysis*, 17, pp. 963–971, 2011

[65] P. C. Pistorius et al., the Steel Matrix Affects Microanalysis of CaO-Al₂O₃-CaS Inclusions, 8th International Conference on Clean Steel, 2012

[66] P. C. Pistorius et al., Correction of Matrix Effects on Microanalysis of Calcium Aluminate Inclusions, *AISTech Proceedings*, 2013

[67] https://www.r-project.org/, last visted June 2017

[68] M. Van Ende et al., Laboratory Study on the Formation of Al_2O_3 Inclusions at the On-set of Deoxidation and Reoxidation, *Frontiers of Materials Science*, Vol. 5, is. 1, pp. 69-76.

[69] R. Dekkers: Non-Metallic Inclusions in Liquid Steel, Katholieke Universiteit Leuven, Leuven, Belgium, 2002, pp. 25 - 34, 107 - 12.

[70] H. Mu, Reduction of CaO and MgO by Al in Steel and Inclusion Modification, *Thesis for the Degree of Doctor of Philosophy*, 2016

[71] S. Taniguchi et al., Tetsu-to-Hagane, 1992, vol. 78 (4), pp. (m2)527-35

[72] P.G. Saffman and J.S. Turner: J. Fluid Mechanics, 1956, No. 1, pp. 16-30.

[73] L. Zhang et al., Fluid Flow and Inclusion Removal in Continuous Casting Tundish, *Metallurgical and Materials Transactions B*, Volume 31B, April 2000-253

[74] M. Korolczuk-Hejnak et al., Determination of the Liquid Steel Viscosity Curves Using a High Temperature Rheometer, *1st International Conference on Rheology and Modeling of Materials*, 2015

[75] C. W. Bale et al., FactSage Thermochemical Software and Databases,2010–2016, *Calphad*, 54 (2016) 35–53

[76] M. Van Ende et al., Morphology and Growth of Alumina Inclusions in Fe–Al Alloys at Low Oxygen Partial Pressure, *Ironmaking and Steelmaking*, Vol. 36, No. 3, pp.201-208, 2009

[77] A. Karasev et al., Analysis of Size Distributions of Primary Oxide Inclusions in Fe-10 Mass Pct Ni-M (M 5 Si, Ti, Al, Zr, and Ce) Alloy, *Metallurgical and Materials*

Transactions B, Vol. 30B, pp. 259-270, 1999

[78] Y. Miki et al., Modeling of Inclusion Removal in a Tundish, *Metallurgical and Materials Transactions B*, Vol. 30B, pp. 639-654, 1999

[79] I. Bindeman, Fragmentation Phenomena in Populations of Magmatic Crystals, *American Mineralogist*, Vo. 90, pp. 1801-1815, 2005