

Development of a Reliable Kinetic Model for Ladle Refining of Steel

Submitted in partial fulfillment of the requirements for
the degree of
Doctor of Philosophy
in
Materials Science and Engineering

Deepoo Kumar

B. Tech., Metallurgical Engineering and Materials Science, Indian Institute of Technology
Bombay

M. Tech. Metallurgical Engineering and Materials Science, Indian Institute of Technology
Bombay

M.S., Materials Science and Engineering, Carnegie Mellon University

Carnegie Mellon University
Pittsburgh, PA

May, 2018

© Deepoo Kumar, 2018

All Rights Reserved

Acknowledgments

I would like to thank my advisor Professor P. Chris Pistorius for his continuous guidance and encouragement to brainstorm the problems and test ideas. I would like to thank Professor Bryan Webler and Professor Richard Fruehan for their comments and discussions. I would also like to thank Dr. Pallava Kaushik for being in the committee and provide important comments and suggestions. I would also like to thank him and Kevin Ahlborg for their help in designing industrial trials. Very special thanks to Stephano Papadopoli Tonelli Piva and Mauro Ferreira for being awesome research companions. I would like to thank present and past graduate students/researchers at CISR, CMU for their help and support in and outside lab: Dai Tang, Megha Jampani, Alicia Gauffin, Yilmaz Kacar, Abhishek Bhansali, Jorge Gibson, Karina Assis, Pengcheng Yan, Ying Ren, Jia Tan, Yining He and Mary Story. I would also like to thank Ming Tang and Farzin Fatollahi-Fard for the discussion and help in experiments.

I would like to thank industry members of CISR members for the funding and suggestions. In particular, I would like to thank Dr. Eugene Pretorius, Dr. Scott Story and Dr. George Shannon for the discussion. I would also like to thank Dr. David Gildemeister from Arconic Technology Center for providing Al-10Mg alloy.

I also acknowledge the use of Materials Characterization Facility at Carnegie Mellon University supported by grant MCF-677785. The use of Advanced Photon Source supported by US Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract No. DE-AC02-06CH11357 is also acknowledged. I would like to thank Roxann Martin, Bill Pingitore, Brett Riale, Adam Wise and all CMU MSE staffs for their help during this project. I would like to thank Dr. Boopathy Kombaiah for his help in conducting Ga-FIB trial and Tom Nuhfer for help in

conducting PFIB experiment and SEM training. I would also like to thank Ross Cunningham for helping in X-ray microCT experiment. I would like to thank Professor Tzahi Cohen-Karni for his suggestion in understanding the formation mechanism of MgO whiskers.

In the end, I would like to thank my parents and extended family for always encouraging me to excel in the academics and in my life. This thesis is a tribute to the parents and uncle and aunt who could not graduate past primary school but dreamt and provided the best possible education to me.

Abstract

The advancement in computational thermodynamics can help researchers to test their hypotheses regarding complex steelmaking operations in a more quantified manner. The main aim of the current work was to use develop a kinetic model that can predict changes in steel, slag and inclusions during ladle refining and use this model as a tool to develop better understanding of the steelmaking process itself.

The important reactions during ladle refining are: steel-refractory reaction, slag-refractory reaction, flotation of inclusions to slag, steel-inclusion reaction, steel-slag reaction and inclusions originating from slag. The chemical reactions between two phases were considered to be mass transfer controlled. The macro-processing feature in FactSage was used to do multiple equilibrium calculations and calculate the change in steel, slag and inclusion composition. Targeted experiments and industrial trials were conducted to find model parameters. For laboratory experiments, the rate of magnesium-transfer to oxide inclusions in steel due to steel-crucible and steel-slag reaction was studied. It was concluded that the presence of spinel layer on MgO crucible at the steel-crucible reaction can help in significantly reduce the rate of Mg pick-up due to steel-crucible reaction. For industrial trials, a comparison between the rate of steel-slag reaction and inclusion flotation rate showed that the steel-slag reaction could be significantly slowed due to slag inhomogeneity. The kinetic model was also used to identify artifacts in steel and slag sampling during ladle refining. One of the main limitations of the kinetic model was the over-prediction of calcium pick-up in steel due to steel-slag reaction.

Induction furnace experiments were conducted using MgO, ZrO₂ and CaO crucible with different slag composition and silicon concentration to study the extent of calcium pick-up due to steel-slag

and steel-crucible reactions. The steel-CaO crucible equilibrium experiment was used to estimate Ca-O interaction parameter. The equilibrated steel was reoxidized with known amount of oxygen to allow all the dissolved calcium to precipitate as oxide inclusions. Inclusion analysis of sample taken after reoxidation was used to estimate dissolved calcium in steel. The measured dissolved calcium was used to estimate Ca-O interaction parameter. A private database for liquid steel was created in FactSage and used for kinetic modeling of laboratory scale steel-slag-crucible experiments. The use of private database for kinetic model helped in avoiding excess calcium pick-up in steel due to steel-slag reaction. However, the model and database should be tested for conditions where significant calcium pick-up is experimentally observed.

In the present work, the inclusion removal was assumed to be first order reaction with fixed rate constant. In practice, the inclusion removal is expected to be a more complicated process of agglomeration and flotation. Similarly, the steel-inclusion reactions were considered in equilibrium for each time step of calculation. Sometimes, the composition difference inside single inclusions was found. Some characterization tools were used that could be useful in future to study the agglomeration of inclusions and composition differences inside single inclusion. The agglomeration behavior of inclusions at the steel-argon interface inside confocal laser scanning microscope was compared to the agglomeration in bulk samples from laboratory and industrial steel samples. The size and morphology of inclusion clusters were studied using X-ray micro CT. The composition and morphology of single inclusion was studied using focused ion beam methods: Ga-FIB instrument and plasma-FIB instrument.

Contents

Contents	vii
List of Figures	xiii
List of Tables	xxix
1 Introduction and document organization	1
1.1 Document organization	2
2 Objectives and Hypotheses	3
2.1 Objectives.....	3
2.2 Hypotheses	5
3 Experimental and Characterization techniques.....	6
3.1 Experimental tools.....	6
3.1.1 Induction furnace experiments.....	6
3.1.2 Confocal Laser Scanning Microscope Experiments.....	9
3.2 Characterization	10
3.2.1 Bulk chemical analysis	10
3.3 Inclusion analysis	14
4 Development of a kinetic model: review and current approach	16
4.1 Background and previous studies.....	16
4.1.1 Overview of models.....	16

4.1.2	Summary of kinetic parameters of the model	19
4.2	Current Modeling Approach	26
4.2.1	Model implementation	30
5	Laboratory scale: experiments and kinetic modeling	37
5.1	Objective	37
5.2	Removal of inclusions	37
5.2.1	Experiments	38
5.2.2	Results and discussion	40
5.2.3	Conclusions	48
5.3	Rate of Mg transfer from MgO crucible to liquid steel.....	49
5.3.1	Introduction.....	49
5.3.2	Experimental	49
5.3.3	Kinetic modeling of magnesium pick-up from MgO crucible.....	50
5.3.4	Results and Discussion	54
5.3.5	Practical Implications.....	65
5.3.6	Conclusions.....	71
5.4	Steel-slag-crucible reactions	72
5.4.1	Experimental	72
5.4.2	Kinetic Modeling	74

5.4.3	Results and Discussion	75
5.4.4	Limitations of the model	86
6	Kinetic modeling of ladle refining.....	88
6.1	Objective	88
6.2	Trial description	88
6.2.1	Sampling method	88
6.2.2	Characterization	90
6.3	Model Description.....	91
6.4	Results	92
6.4.1	Steel and slag composition.....	92
6.4.2	Inclusion concentration and composition	95
6.5	Discussion	100
6.5.1	Model parameter and stirring power.....	100
6.5.2	Alloy dissolution and mixing time.....	108
6.5.3	Sampling issue: steel and slag.....	109
6.5.4	Inclusions originating from slag	113
6.6	Conclusions	115
7	Calcium transfer to oxide inclusions without calcium treatment.....	116
7.1	Objective	117

7.2	Effect of silicon on calcium transfer from slag	117
7.2.1	Experimental	117
7.2.2	Results.....	119
7.2.3	Using electronics grade silicon for silicon addition.....	123
7.2.4	Discussion	133
7.2.5	Liquid inclusion as a transient phase	135
7.2.6	Conclusion	140
7.3	Effect of crucible: MgO, ZrO ₂ and CaO	141
7.3.1	Experiments	141
7.3.2	On ASPEX analysis of ZrO ₂ containing inclusions.....	143
7.3.3	Results and discussion	144
7.4	Calcium transfer from CaS to oxide inclusions	161
7.4.1	Experimental	162
7.4.2	Results and Discussion	164
8	Estimating $\epsilon_{\text{Ca}}^{\text{O}}$ by measuring dissolved Ca in steel	166
8.1	Objective	166
8.2	Review and proposed experimental method	166
8.3	Experimental	169
8.4	Results and discussion.....	171

8.4.1	Reoxidation methods	171
8.4.2	Dissolved calcium calculation	174
8.5	Private database for liquid steel in FactSage.....	183
9	Evaporation of magnesium and calcium during steelmaking experiments	188
9.1	Objective	188
9.2	Evaporation of magnesium during CLSM experiments.....	189
9.2.1	Experiment details	189
9.2.2	Results and Discussion	192
9.2.3	Conclusions.....	201
9.3	Calcium evaporation from top of steel melt.....	201
9.3.1	Experiment details	201
9.3.2	Results and discussion	202
10	Agglomeration of inclusions.....	207
10.1	Literature Review	207
10.1.1	In-situ observation of inclusion agglomeration	209
10.2	Objective.....	212
10.3	Comparing inclusion agglomeration in CLSM to bulk	213
10.3.1	Experimental.....	213
10.3.2	Results and Discussi on	214

10.3.3	Conclusions.....	218
10.4	Using X-ray microCT to study inclusion agglomeration	219
10.4.1	Introduction.....	219
10.4.2	Experimental	220
10.4.3	μ XCT Results and Discussion	222
10.4.4	Statistical study of inclusion agglomeration	227
10.4.5	Conclusions.....	230
10.5	Morphological and chemical variation in a single inclusion.....	230
10.5.1	Focused Ion Beam (FIB) experiment: serial sectioning of an inclusion.....	230
11	Conclusions and suggestions	236
12	References.....	240
Appendix A	Challenges in induction furnace experiments	253
Appendix B	Developing private database for liquid steel	255
Appendix C	Assessing Fe-X-O using FactSage	258

List of Figures

Figure 1. Schematic of induction furnace setup.....	8
Figure 2. Image of new induction furnace setup with a stainless steel chamber	8
Figure 3. Confocal Laser Scanning Microscope setup	9
Figure 4. Comparing measured oxygen using LECO to that estimated from ASPEX-AFA analysis	12
Figure 5. Presentation of inclusion composition on ternary diagram	15
Figure 6. Schematic of phenomena occurring during ladle refining: 1) steel-refractory reaction, 2) slag-refractory reaction 3) flotation of inclusions to slag, 4) steel-inclusion reaction, 5) steel-slag reaction and 6) inclusions originating from slag.....	19
Figure 7 Concept of EERZ model for steel-slag reaction [7]	19
Figure 8. Schematic of the modeling scheme for mass-transfer controlled steel-slag reaction [36]	26
Figure 9. Magnesium concentration differences in large alumina inclusions 11 minutes after Al- addition [0.15 wt%] to the liquid steel in MgO crucible	29
Figure 10. Uniform inclusion composition in smaller inclusions just one minute after calcium- treatment	29
Figure 11. Tip of steel rod dipped in molten steel 1 minute after deoxidation (length scale in inches)	38
Figure 12. Al-Mg phase diagram (FactSage; BINS database).....	39

Figure 13. Phase and impurities in Al-10Mg alloy	39
Figure 14. Alumina inclusions on the surface of dipped steel rod for experiment-1.....	41
Figure 15. Initial changes in inclusion concentration during experiment-5.1	42
Figure 16. Inclusions on the surface of dipped steel rod in experiment-2	43
Figure 17. Inclusion composition and bound magnesium (in inclusions) in steel with time for experiment-5.2	44
Figure 18. Inclusion removal trend for experiment-5.2: fitting two rate constants	45
Figure 19. Formation of spinel whiskers on Al_2O_3 crucible wall due to Mg evaporation from liquid steel	45
Figure 20. Inclusion composition and magnesium concentration as inclusions with time for experiment-5.3	47
Figure 21. Inclusion removal behavior in experiment-5.3.....	48
Figure 22. Schematic of magnesium transfer from steel-crucible to steel-inclusion interface.....	50
Figure 23. Schematic of the model	54
Figure 24. $\text{Mg}/(\text{Mg}+\text{Al})$ molar ratio in inclusions with time in experiments-5.4 and 5.5, the horizontal broken line is stoichiometric MgAl_2O_4	55
Figure 25. Inner surface of crucible before and after experiment-5.4. Presence of a slag like layer can be seen in the microstructure after the experiment.....	57
Figure 26. Inner surface of MgO crucibles after experiment-5.5, showing a spinel coating.....	57

Figure 27. Measured and fitted amount of oxygen in inclusions for a) experiments 5.4, the arrow shows an increase in inclusion concentration possible due to reoxidation during sampling and b) 5.5.....	59
Figure 28. Population density function of inclusions for Samples 2-5 from exp. 5.4	60
Figure 29. Experimental and calculated inclusion composition for experiments 5.4 and 5.5	60
Figure 30. Measured and fitted amount of magnesium in inclusions for experiments 5.4 and 5.5.	61
Figure 31. Calculated dissolved magnesium with time for experiments 5.4 and 5.5	63
Figure 32. Role of slag/spinel layer on magnesium transfer from crucible to steel	64
Figure 33. Change in inclusion composition with time for total oxygen concentration=50 ppm, with (case-1) and without (case-2) reaction with refractory	68
Figure 34. Change in inclusion composition with time for total oxygen concentration=10 ppm, with participation of refractory (case-3) and without (case-4)	69
Figure 35. Change in inclusion composition and dissolved magnesium with time for case-1	70
Figure 36. Total magnesium pick-up in steel with time for four cases, with lower (cases 2 and 4, without steel-refractory reaction) and higher (cases 1 and 3 with steel-refractory reaction)	71
Figure 37. Experimental and calculated aluminum and silicon content in steel for experiment-5.6	77
Figure 38. Experimental and calculated aluminum and silicon content in steel for experiment-5.7	77
Figure 39. Crucible wall above melt surface after the experiment-5.7.....	78

Figure 40. Fitted bound oxygen to inclusion and predicted bound magnesium in inclusions for experiment-5.6	80
Figure 41. Fitted bound oxygen to inclusion and predicted bound magnesium in inclusions for experiment-5.7	80
Figure 42. Average size of inclusions observed in exp. 5.6 (no stirring) and exp. 5.7 (Ar stirring)	80
Figure 43. Calculated dissolved and total a) magnesium and b) calcium with time for experiment-5.6.....	82
Figure 44. Calculated dissolved and total a) magnesium and b) calcium with time for exp. 5.7.	83
Figure 45. Calculated slag composition for experiment-5.7	83
Figure 46. Calculated and measured $Mg/(Mg+Al)$ molar ratio in inclusions with time for (a) exp. 5.6 and (b) exp. 5.7	85
Figure 47. Calculated inclusion composition for (a) exp. 5.6 and (b) exp. 5.7	85
Figure 48. Composition of inclusions in sample taken at $t=50$ minutes during experiment-5.7 ..	86
Figure 49. Reported relationships between dissolved oxygen and dissolved calcium in liquid steel in equilibrium with CaO at 1873 K. Redrawn after reference [42]	86
Figure 50. Flow chart of calculations in kinetic model	92
Figure 51. Calculated and measured steel composition with time for heat-1	94
Figure 52. Calculated and measured FeO and Al_2O_3 concentration in slag with time for heat-1	95
Figure 53. Change in inclusion cluster with time for heat-1.....	96

Figure 54. Measured and fitted inclusion flotation for heat-1	97
Figure 55. Transformation of alumina inclusions to spinel inclusions with time for heat-1	98
Figure 56. Magnesium pick-up in deoxidation inclusions in ladle samples; LF7 (15.5 minute) and LF8 (18 minute). Magnesium and calcium pick-up in the tundish sample (T3)	99
Figure 57. Calculated inclusion composition with time for heat-1 (molar basis).....	100
Figure 58. Mass transfer coefficients with stirring power for all heats	103
Figure 59. Calculated interfacial oxygen concentration in steel for conditions in Table 29	105
Figure 60. Change in silicon and sulfur in steel during heat-1 for conditions in case-3 of Table 29	106
Figure 61. Difference in interfacial oxygen between case-1 and case-3 for heat-1.....	106
Figure 62. Stirring of steel bath for heat-1 and heat-2	107
Figure 63. Lime saturation in $\text{CaO}'\text{-SiO}_2'\text{-Al}_2\text{O}_3'$ system and desulfurization potential on l dependent on the lime-saturation index; reproduced from [61].....	108
Figure 64. Instantaneous addition of Fe-Mn in heat-1.....	109
Figure 65. Delayed addition of Fe-Mn in heat-2	109
Figure 66. Measured oxygen in inclusions for heat-3.....	110
Figure 67. Oxygen concentration in inclusions and total aluminum in steel: without and with reoxidation: (a) no reoxidation was considered in the model, (b) reoxidation at t=12 and t=17 minutes considered and Markers represent measured and solid line represents calculated values	111

Figure 68. Measured Al_2O_3 and FeO concentration in slag during heat-3	112
Figure 69. Inclusion concentration of pure alumina, slag like and total inclusions in heat-1	114
Figure 70. Average size of alumina and slag like inclusions with time	114
Figure 71. Inclusion composition 15 minutes after aluminum deoxidation during experiment-7.1 (MgO crucible).....	120
Figure 72. Inclusion composition 25 minutes after aluminum deoxidation during experiment-7.1 (MgO crucible).....	120
Figure 73. Inclusion composition 35 minutes after aluminum deoxidation during experiment-7.1	121
Figure 74. Inclusion composition 55 minutes after aluminum deoxidation during experiment-7.1	121
Figure 75. Al-Si-Ca phase present in ferrosilicon used for experiment-7.1	122
Figure 76. Transformation of spinel inclusion to MgO ; observed in a sample taken at 55th minute during experiment-7.1, note that the outer rim of the inclusion contains Mg and O, but not Al	122
Figure 77. MgO crucible wall coated with slag after experiment-7.2	124
Figure 78. Inclusion composition in steel 1 minute after aluminum addition during experiment-7.2 (no silicon)	125
Figure 79. Inclusion composition in steel 16 minutes after aluminum addition during experiment- 7.2 (no silicon)	125
Figure 80. Inclusion composition in steel 31 minutes after aluminum addition during experiment- 7.2 (no silicon)	126

Figure 81. Inclusion composition in steel 70 minutes (final sample) after aluminum addition during experiment-7.2 (no silicon)	126
Figure 82. MgO-CaS inclusion in sample taken at 70 th minute (final sample) from experiment-7.2 (no silicon)	127
Figure 83. Inclusion composition in steel 7 minutes after aluminum addition during experiment-7.3 (1% electronic grade silicon)	128
Figure 84. Inclusion composition in steel 20 minutes after aluminum addition during experiment-7.3 (1% electronic grade silicon)	128
Figure 85. Inclusion composition in steel 35 minutes after aluminum addition during experiment-7.3 (1% electronic grade silicon)	129
Figure 86. Inclusion composition in steel 50 minutes after aluminum addition during experiment-7.3 (1% electronic grade silicon)	129
Figure 87. Inclusion composition in steel 65 minutes after aluminum addition during experiment-7.3 (1% electronic grade silicon)	130
Figure 88. Inclusion composition in steel 75 minutes (final sample) after aluminum addition during experiment-7.3 (1% electronic grade silicon)	130
Figure 89. Change in average inclusion composition during experiment-7.3	132
Figure 90. Change in average inclusion size with time during experiment-7.3	133
Figure 91. Change in average size of inclusions with time from just before calcium treatment to after, reported by Ferreira et al. [66]	133

Figure 92. Equilibrium oxygen, magnesium and calcium activities for six cases described in Table 36.....	135
Figure 93. Calculated composition path of inclusions for experiment-7.2, path boundaries are for 1873 K.....	137
Figure 94. Calculated total and dissolved calcium in steel with time for experiment-7.2.....	137
Figure 95. Activities of species at the steel-slag and steel-inclusion interface with time for experiment-7.2: a) partial pressure of oxygen, b) activity of MgO (w.r.t. solid periclase), c) activity of alumina (w.r.t. corundum) and d) activity of CaO (w.r.t. lime)	138
Figure 96. Calculated inclusion evolution when steel-crucible reaction was not considered for conditions in experiment-7.2	139
Figure 97. Interfacial activities of species at the steel-slag and steel-inclusion interface with time for experiment-7.2 without steel-crucible reaction: a) partial pressure of oxygen, b) activity of MgO (w.r.t. solid periclase), c) activity of alumina (w.r.t. corundum) and d) activity of CaO (w.r.t. lime)	140
Figure 98. SEM-EDS analysis using ASPEX-Explorer for same inclusions at a) 20 kV and b) 10 kV	143
Figure 99. Detection of ZrO ₂ containing inclusions	144
Figure 100. Inclusion composition at 8 th minute during experiment-7.4.....	146
Figure 101. Inclusion composition at 31 st minute during experiment-7.4.....	146
Figure 102 Al-Mg-Zr-Ca-O inclusions observed in experiment-7.4 at 8 th minute	147
Figure 103 CaS-MgO inclusion observed in sample from experiment-7.4	147

Figure 104. Inclusions observed in sample taken at 24 th minute during experiment-7.5	148
Figure 105. Inclusions observed in sample taken at 92 nd minute during experiment-7.5.....	149
Figure 106. Type-1 inclusions: cluster of ZrO ₂ rich phase with Al ₂ O ₃ rich phase, experiment-7.5	149
Figure 107. Type-2 inclusions: Al ₂ O ₃ rich phase with some MgO, ZrO ₂ and CaO, experiment-7.5	149
Figure 108. CaO-ZrO ₂ -AlO _{1.5} phase diagram at 1873 K (1600°C) drawn using FactSage TM [44]	151
Figure 109 Si-Ca-Mg-Al-O fiber found on crucible after experiment-7.5	152
Figure 110. EDS spectrum of the fiber	152
Figure 111 Inclusion with ZrO ₂ in core, observed from the sample taken 90 minutes after Al- addition, similar inclusions were present in the sample taken at 20 and 50 minutes as well.	153
Figure 112 Formation of glaze on the inner wall of ZrO ₂ crucible, exp. 7.5.....	153
Figure 113 Slag attack on crucible wall, Spectrum 3 showed the composition of slag, exp. 7.5	153
Figure 114 MgO inclusion as a cluster found in a sample taken 18 minutes after Al-addition and 9 minutes after calcium treatment; the experiment was conducted in an induction furnace	154
Figure 115. Change in inclusion content and composition observed during experiment-7.6 (CaO crucible)	156
Figure 116. Calcium containing inclusion, observed in sample taken at 34 th minute during experiment-7.6	156
Figure 117. Slag penetration inside the CaO crucible at the end of experiment-7.6	157

Figure 118. Polished cross-section (near I. D.) of CaO-ZrO ₂ crucible, slag attack along grain boundary	158
Figure 119. Polished cross-section (near O. D.) of CaO-ZrO ₂ crucible	158
Figure 120. EDS map showing calcium on the polished cross-section of CaO-ZrO ₂ crucible, near I.D.	158
Figure 121. EDS map showing aluminum (hence slag) on the polished cross-section of CaO-ZrO ₂ crucible, near I.D.....	158
Figure 122. EDS at the grain boundary region of CaO-ZrO ₂ crucible, near O.D.....	159
Figure 123. Inclusion composition change during experiment-7.7 (CaO crucible, no slag)	160
Figure 124. Calcium containing inclusion observed in sample taken at 45 th minute from exp-7.7 (CaO crucible, no slag)	161
Figure 125. Al ₂ O ₃ -CaS inclusions used to study calcium transfer from CaS to oxide inclusions	162
Figure 126. CaS-Al ₂ O ₃ inclusions in steel sample used to study calcium transfer from CaS to Al ₂ O ₃ inclusions	163
Figure 127. Inclusion composition in S1 sample from experiment-7.8.....	164
Figure 128. Ca-Al-O inclusion found in S1 sample from experiment-7.8	165
Figure 129. Thickness of oxide layer after 12 minutes at 700°C.....	170
Figure 130. . Inclusion composition in samples taken after reoxidation during experiment-8 ..	172
Figure 131. Calcium containing inclusion observed in sample-2 (15 s after reoxidation) from experiment-8.1	172

Figure 132. Inclusion composition 30 s before reoxidation during experiment-8.2; presence of silicon in inclusions show possible contamination from sampling tube	173
Figure 133. Inclusion composition 60 s after reoxidation during experiment-8.2; presence of silicon in inclusions show possible contamination from sampling tube	173
Figure 134. Calcium containing inclusion observed in the sample taken at 138 th minute during experiment-8.3, just after reoxidation	174
Figure 135. Chemical composition of individual inclusions measured using manual SEM-EDS for sample just after reoxidation (S6) from experiment-8.3	175
Figure 136. Chemical composition of individual inclusions measured using manual SEM-EDS for sample just after reoxidation (S2) from experiment-8.4	176
Figure 137. Calcium aluminate layer on crucible wall at the end of experiment-8.3	178
Figure 138. CaS particle attached to the crucible wall at the end of experiment-8.3	178
Figure 139. (a) Reaction product layer of crucible and (b) variation in composition of crucible reactive layer for exp. 8.4	178
Figure 140. Comparing Fe-Ca-O thermodynamics: present results vs published results [42] ...	181
Figure 141. Effect of aluminum content on equilibrium dissolved calcium calculated, for zero Ca-O interaction and using the Ca-O interaction parameter from present work	182
Figure 142. Change in steel composition with time for conditions in experiment-5.6; comparing private database with FTmisc in FactSage-7.2	185
Figure 143. Calculated dissolved and total magnesium in steel from FTmisc and private database	186

Figure 144. Calculated dissolved and total calcium in steel from FTmisc and private database	186
Figure 145. Calculated inclusion composition (open circle) from FTmisc and private databases	187
Figure 146. Calculated dissolved oxygen in steel from two sources: FTmisc and private database	187
Figure 147. Powders used to prepare MgO-slag-C pellet (powders mounted on conductive carbon tape; secondary electron micrographs). a) MgO; b) carbon; c) slag	191
Figure 148. MgO whiskers observed on MgO crucible wall after CLSM experiment using steel and slag in an MgO crucible, held for 30 minutes at 1600°C. (a) Schematic of experimental configuration. (b), (c) and (d) are secondary electron micrographs of the whiskers at successively higher magnifications.	193
Figure 149. Calculated partial pressure of magnesium in equilibrium with different sources; "required p_{Mg} " is the magnesium pressure in equilibrium with pure MgO and oxygen ($P_{O_2}=10^{-20}$ atm).	194
Figure 150. Growth of plate like spinel on alumina crucible wall in the absence of liquid slag	195
Figure 151. EDS at the tip of whisker shows presence of slag phase	196
Figure 152. Typical features of MgO whisker growth on MgO crucible, from Mg vaporized from liquid steel. (a) Early growth stage; (b) out-of-plane growth; (c) whisker with visible facets; (d) growth of catalyzed by the presence of condensed iron phase (bright particle at whisker tip).	197
Figure 153. Proposed mechanism of growth of MgO whiskers from an MgO crucible through the VLS mechanism, catalyzed by slag	198

Figure 154. Presence of whiskers on top surface and at the MgO-C-slag pellet edge after heat treatment at 1650°C	199
Figure 155. EDS spectra of tip and body of whiskers shown in Figure 154(c).....	200
Figure 156. MgO whisker with flat tip observed at the fracture surface of pellet.....	201
Figure 157. Experimental setup to study calcium transfer from steel-crucible to steel-alumina rod interface.....	202
Figure 158. Flattening of tip of alumina rod during experiment-9.5, the scale is in mm	203
Figure 159. Formation of liquid oxide phase on top of the steel puck close to the tip of alumina rod	204
Figure 160. Presence of calcium on wall of the alumina rod after the experiment-9.5	205
Figure 161. Whisker present on alumina rod after experiment-9.5	205
Figure 162. Effect of stirring power on inclusion size distribution [86]	208
Figure 163 Non-clustering behavior of magnesium containing inclusions [91].....	210
Figure 164 Schematic diagram of capillary interaction between inclusion particles with different morphology [90]	211
Figure 165. Observation of inclusions at steel-argon interface using CLSM, the red arrow shows movement and collision of clusters that occur in the right side frame	213
Figure 166. Agglomeration of alumina inclusions: (a) observed on top of steel surface after CLSM experiment (b) observed on etched steel sample from induction furnace experiment and (c) observed on etched surface of sample taken during ladle refining	214

Figure 167. Transformation of alumina cluster into spinel cluster (samples provided by Mauro Elias Ferreira).....	215
Figure 168. Spinel and alumina clusters in first sample taken 2:45 minutes after Al-10Mg addition during experiment-5.3.....	216
Figure 169. Agglomeration of spinel inclusions: (a) observed on top of steel surface after CLSM experiment (b) observed on etched steel sample from induction furnace experiment and (c) observed on etched surface of sample taken during ladle refining.....	217
Figure 170. Agglomeration of solid $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ inclusions: (a) observed on top of steel surface after CLSM experiment (b) observed on etched steel sample from induction furnace experiment.....	217
Figure 171. Liquid $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ inclusions: (a) observed on top of steel surface after CLSM experiment (b) observed on etched steel sample from induction furnace experiment and (c) observed on etched surface of sample taken during ladle refining.....	218
Figure 172. Schematic of X-ray CT of a slice with two inclusions, adapted from http://www.cmu.edu/me/xctf/xrayct/index.html	221
Figure 173. Ring artefacts in a reconstructed CT slice.....	222
Figure 174. Post-processed micro-tomography (μXCT) image of inclusions in sample-1	223
Figure 175. Post-processed micro-tomography (μXCT) image of inclusions in sample-2	224
Figure 176. Comparing inclusion cluster in the first sample from μXCT (left) to electrolytically etched steel sample (right)	225

Figure 177. Comparing inclusion cluster in the second sample from μ XCT (left) to electrolytically etched steel sample (right)	225
Figure 178. Comparing population density of inclusions calculated using μ XCT data to SEM-AFA data.....	226
Figure 179. A section (darker region in the upper part of the figure) through a three-dimensional inclusion cluster (the cluster is that shown in Figure 177 (a)), indicating that a cluster tends to appear disconnected on a two-dimensional section.	229
Figure 180. Change with time in the degree of randomness of two-dimensional inclusion distribution (R) during ladle treatment of two industrial heats. The increase in randomness over time indicates that fewer large clusters are present, though the randomness drops in response to formation of new inclusions when alloys are added at the arrowed times.	229
Figure 181 Inclusion before (left) and after (right) FIB milling	232
Figure 182 Inclusion composition before FIB milling	232
Figure 183 Inclusion composition after FIB milling	233
Figure 184. Secondary electron image of an inclusion on a polished cross-section of the sample	234
Figure 185. Platinum coating of the inclusion to protect it from ion beam exposure.....	234
Figure 186. A U-shape trench around platinum coated inclusion	234
Figure 187. Section of the target inclusion revealed during the milling.....	234
Figure 188. Inside of inclusion and corresponding EDS maps.....	235
Figure 189. Aluminosilicate inclusion at the edge of sample	254

Figure 190 Structure of database	256
Figure 191 Writing Gibbs Energy Function for end members	256
Figure 192 Entering interaction parameter	257
Figure 193. Extracting standard activity coefficient from FactSage	259
Figure 194. Extracting first and second interaction parameters for Fe-X-O system	261

List of Tables

Table 1. Presentation of an experiment-an example	7
Table 2. Comparison of magnesium analysis from spectroscopy techniques to the expected from inclusion analysis	11
Table 3 Mass transfer coefficient for steel-slag reactions	20
Table 4 Mass transfer coefficients for refractory dissolution in slag.....	21
Table 5. Flotation behavior of inclusions	22
Table 6. Summary of mass transfer coefficient in steel phase for magnesium transfer	25
Table 7. Fe-Mg thermodynamic data with liquid Mg as reference.....	33
Table 8. Method of Fe-Mg-O equilibrium measurement.....	34
Table 9. Comparing Fe-Mg-O equilibrium data	36
Table 10. Addition and sampling details for experiment-5.1 (alumina crucible).....	38
Table 11. Addition and sampling details for experiment-5.2 (alumina crucible).....	39
Table 12. Addition and sampling details for experiment-5.3 (MgO crucible)	40
Table 13. Addition and sampling details for experiment-5.4 (MgO crucible)	50
Table 14. Addition and sampling details for experiment-5.5 (MgO crucible)	50
Table 15. Model parameter for industrial scale operation	66
Table 16. Simulation cases	66
Table 17. Composition of slags used for experiment-5.6 and 5.7	73

Table 18. Addition and sampling description for experiment-5.6 (MgO crucible).....	73
Table 19. Addition and sampling description for experiment-5.7 (MgO crucible).....	73
Table 20. Summary of fitted model parameters.....	81
Table 21. Steel and slag mass for all heats	89
Table 22. Steel and slag additions during heat-1	89
Table 23. Steel and slag sampling time for heat-1, time is in minutes	89
Table 24. Steel and slag additions during heat-2	90
Table 25. Steel and slag sampling times for heat-2, time is in minutes.....	90
Table 26. Additions in steel during heat-3.....	90
Table 27. Steel and slag sampling times for heat-3, time is in minutes.....	90
Table 28. Fitted model parameters for three industrial trials.....	101
Table 29. Four cases to study steel-slag interfacial reactions during heat-1	104
Table 30. Slag chemistry with time for heat-3.....	113
Table 31. The slag compositions used to test the effect of silicon on calcium transfer.....	118
Table 32. Addition and sampling description for experiment-7.1 (MgO crucible).....	118
Table 33. Addition and sampling description for experiment-7.2 (MgO crucible).....	119
Table 34. Addition and sampling description for experiment-7.3 (MgO crucible).....	119
Table 35. Inclusions in steel samples from experiment-7.3 (1% electronic grade silicon)	131
Table 36. Six cases considered to understand reduction of CaO and MgO from slag	135

Table 37. Composition of slag used to study the effect of crucible on calcium transfer	142
Table 38. Addition and sampling detail for experiment-7.4 (ZrO ₂ , type-1)	142
Table 39. Addition and sampling detail for experiment-7.5 (ZrO ₂ , type-2)	142
Table 40. Addition and sampling detail for experiment-7.6 (CaO crucible)	142
Table 41. Addition and sampling detail for experiment-7.7 (CaO crucible)	143
Table 42. Chemical composition of inclusion shown in Figure 98 after ignoring Fe peak and normalizing at 10 kV and 20 kV	144
Table 43 Characteristic of type-1 and type-2 inclusions	150
Table 44. Average inclusion composition with time for experiment-7.7	161
Table 45. Addition and sampling detail for experiment-7.8 (alumina crucible)	163
Table 46. Experimental and characterization method used by other researchers to study Fe-Ca and Fe-Ca-O thermodynamics	167
Table 47. Fe-Ca thermodynamic data from different sources (with respect to liquid calcium) .	169
Table 48. Addition and sampling details for experiment-8.1	171
Table 49. Addition and sampling details for experiment-8.2	171
Table 50. Addition and sampling details for experiment-8.3	171
Table 51. Addition and sampling details for experiment-8.4	171
Table 52. The average inclusion composition (mass%) in samples from experiment-8.2	173
Table 53. Estimated calcium and oxygen in inclusions in samples taken just after reoxidation during experiments-8.3 and 8.4	176

Table 54. Calculating Ca-O interaction parameter from exp. 8.3 and exp. 8.4	178
Table 55. Thermodynamic parameter for Fe-Ca-O from literature and present work.....	180
Table 56. Results of a thermodynamic calculation for experimental condition similar to experiments-8.3 and 8.4.....	183
Table 57. Summary of experiments	190
Table 58. Steel composition used for experiments	190
Table 59 . Standard activity coefficients of elements in liquid steel calculated using FactSage	258

1 Introduction and document organization

The aim of ladle metallurgical furnace (LMF) operations is to achieve the right chemistry and to obtain the desired level of steel cleanliness. The presence of solid inclusions like spinels or partially or over-modified alumina (to aluminates of Ca, Ti, Mg etc.) inclusions in liquid steel raise serious problems in steel processing and quality of final products. They often cause nozzle clogging in continuous casting or ingot casting. Due to their irregular shapes, even smaller inclusions act as crack initiation sites for applications sensitive to fracture toughness and fatigue properties. In their overview of steel cleanliness, Pretorius et al. [1] has concluded that “control of inclusions in the product and process requires an understanding of mechanism of formation and modification and preferably removal”. This project is a step to address this issue.

As reported by several authors [1], [2], solid alumina and spinel inclusions undergo a series of transformations into liquid inclusions in the presence of calcium in liquid steel. However, solid inclusions may remain partially modified, may get over-modified or even re-form due to reoxidation before final casting. Although calcium modification has been used for long time, the actual mechanism is not fully understood. Verma [3] experimentally determined the intermediate reaction products during modification of spinels and alumina inclusions. Pretorius et al. [1] also showed that the intermediate reaction products for modification of solid inclusions into liquid inclusions. Recent work by Mu [4] showed that alumina inclusions may change due to reduction of CaO and MgO (from slag) by aluminum in liquid steel. Another important contribution to change in inclusions may come from the interaction of steel and slag with refractories in ladle, tundish and submerged entry nozzles as discussed by Poirier [5]. For the experimental and plant trial based studies of these phenomena, sampling poses a significant challenge in addition to other experimental and characterization related difficulties. During sampling, gases in sampler may

reoxidize the sample and/or inclusions may float out. Inclusions can also change or form during sample solidification. Further experimental studies take time and are expensive. In order to alleviate these experimental difficulties, a model can be developed to understand kinetics of these transient inclusions for different chemistry of metal, slag and inclusions. A macro-based model for FactSageTM can consider different processing conditions including chemistry of steel and slag and alloying additions. Harada [6], Van Ende and Jung [7], Shin et al. [8] have proposed similar kinetic models.

The aim of this project is to develop such a model to understand important reactions responsible for observed kinetics. Some parameters of such models like solution thermodynamics of calcium in steel, the steel-crucible interaction and inclusion flotation behavior are not well known. Some targeted experiments were conducted in an induction furnace and a confocal laser scanning microscope to estimate these parameters. Modeling results were verified using kinetic experiments. Scalability of such models to plant scale operations was explored. Results from kinetic experiments were also used to better understand thermodynamics of Fe-Ca-O system.

1.1 Document organization

Chapter-2, 3 and 4 describe hypotheses, experimental and characterization aspects and literature review relevant to kinetic modeling respectively. Chapters 5-10 covers the results and discussion from present work. Relevant experiments and literature review (if needed) are described in each chapter. Every chapter also contains objective for that set of experiment/modeling.

2 Objectives and Hypotheses

2.1 Objectives

The thesis covers six topics in total. The objective of six topics are summarized below. The specific objectives are mentioned at the beginning of each chapter in the thesis.

Topic-1: Laboratory scale: experiments and kinetic modeling: The main aim of this topic was to develop a kinetic model for laboratory scale induction furnace experiments that can predict change in chemical composition of steel, slag and inclusions. Targeted experiments were conducted to determine rate of a) inclusion removal, b) steel-MgO crucible reaction and c) steel-slag reaction. The kinetic model was also used to understand the rate of magnesium transfer to the steel melt due to steel-crucible reaction.

Topic-2: Kinetic modeling of ladle refining: The aim of this topic was to test the applicability of the kinetic model under industrial conditions and identify challenges and limitations. The kinetic model was also used to develop a better understanding of a steelmaking practice that avoids Ca and Mg pick-up.

Topic-3: Calcium transfer to oxide inclusions without calcium treatment: The objective of this chapter was to test three strategies to improve calcium transfer to oxide inclusions without calcium treatment. 1) The effect of 1 wt% silicon addition on calcium transfer due to steel-slag reaction was tested. Two sources of silicon were tested: ferrosilicon (Fe-93% Si) and electronic grade silicon. 2) The steel-slag experiments (no silicon added) were also conducted in MgO, ZrO₂ and CaO crucibles to understand the effect of crucible on calcium transfer to liquid steel from slag or from crucible (for CaO crucible). 3) The calcium transfer from CaS inclusions to alumina inclusions was tested. A steel containing CaS inclusions was added to an aluminum killed steel

containing alumina inclusions and steel sample was taken to find the extent of calcium modification of alumina inclusions.

Topic-4: Estimating ϵ_{Ca^0} by measuring dissolved Ca in steel: The aim of this topic was to measure dissolved calcium in steel by reoxidizing steel that had equilibrated with a CaO crucible and measuring calcium content in inclusions in the sample taken just after reoxidation. The measured dissolved calcium was used to estimate the Ca-O interaction parameter in liquid steel. A private database for liquid steel was created in FactSage that could be used in the kinetic model.

Topic-5: Evaporation of magnesium and calcium during steelmaking experiments: The objective of this topic was to demonstrate the magnesium evaporation from liquid steel during confocal laser scanning microscopy experiments. The formation mechanism of MgO whiskers on the MgO crucible wall was explained and the idea of growing MgO whiskers using ladle slag as a catalyst was tested. The effect of calcium evaporation on the study of the rate of calcium transfer from CaO crucibles.

Topic-6: Agglomeration of inclusions: The aim of this topic was to clarify agglomeration behavior of spinel inclusions, compare agglomeration of inclusions observed on steel-argon interface in confocal laser scanning microscopy experiments to bulk steel samples and test X-ray micro CT and plasma focused ion beam method to understand inclusion agglomeration and chemical inhomogeneity within an inclusion.

2.2 Hypotheses

The hypotheses of the current work are as follows:

Hypothesis-1: For typical steelmaking conditions for aluminum killed steel, there may be calcium and magnesium pick-up in steel due to steel-slag reactions but the extent of calcium pick-up is much smaller compared to magnesium pick-up.

Hypothesis-2: The mass transfer coefficient in steel phase for steel-slag reaction can be much smaller than the inclusion flotation rate constant in the presence of a partially solid slag.

Hypothesis-3: The addition of 1 wt% silicon in steel can improve calcium transfer to liquid steel due to steel-slag reaction.

Hypothesis-4: At the steel-slag-inclusion equilibrium, the composition of the inclusions need not be same as the slag.

Hypothesis-5: The concentration of dissolved calcium can be estimated from the measured calcium contained in inclusions that formed by reoxidation of steel previously equilibrated with a CaO crucible.

Hypothesis-6: The magnesium evaporation from liquid steel can lead to formation of MgO whiskers at the MgO crucible wall through vapor-liquid-solid mechanism where liquid slag act as a catalyst.

Hypothesis-7: The agglomerated spinel inclusions appear less sintered compared to alumina inclusions.

3 Experimental and Characterization techniques

3.1 Experimental tools

3.1.1 Induction furnace experiments

A radio frequency induction furnace setup was used to conduct steel melting and deoxidation experiments. The schematic of experimental setup is shown in Figure 1. The current flowing in the water-cooled copper coil heats a graphite crucible inductively which in turn heats up an MgO/ZrO₂/CaO crucible and the electrolytic iron/slag kept inside the crucible. The outermost cover is a fused quartz tube; the inner wall of the fused quartz tube is covered by an insulating alumina paper to avoid radiation losses at higher temperature. The ends of the fused quartz tube are closed using water-cooled stainless steel caps with vacuum sealing. The bottom cap has an opening to flow ultra-high purity grade argon gas inside the chamber. The top cap has three openings: gas outlet, thermocouple sheath and a tube for sampling/additions. The heating rate is adjusted by controlling input power to the furnace. The setup is quite similar to a ladle furnace except that there is no argon stirring of the melt. One experiment was also conducted to understand the effect of stirring energy on the flotation of inclusions and steel-slag mass transfer coefficient for this setup. Liquid steel was stirred by flowing argon (~0.3 NL/min) into liquid steel from the top through an MgO tube. The experiments were conducted at 1600±10 °C; the temperature inside the furnace was measured by inserting a B-type thermocouple from top cap. An insulating alumina cap with openings for thermocouple sheath and sampling was used to cover the graphite crucible. This was essential for protecting the Viton gasket used for sealing top cap and avoid radiation loss from the top of the melt surface. In some trial experiments, the radiation loss, in the absence of insulating cap, was found to produce significant temperature differences resulting in wrong

temperature measurements. Samples were taken at a regular interval during the experiments for chemical analysis of steel and slag samples and inclusion analysis of steel samples. Samples were taken using fused quartz tubes (ID=4mm, OD=6mm) with the help of a small suction tube. In some experiments, samples were taken at very short intervals (<1 minute). The accuracy of sampling time was ensured by video recording the sampling practice.

At a later stage in the project, a new induction furnace was designed for better atmospheric control and ease of setup. A water cooled stainless steel chamber was designed and a setup similar to that described above was placed inside the chamber. A water cooled flange was placed at the center top of the chamber to accommodate a thermocouple and sampling/addition tube. The front view port of the chamber allowed visual observation of the setup/addition or sampling process. The stainless steel chamber and an image from the front view port are shown in Figure 2. The chamber was initially evacuated to ~0.13 atm pressure and then backfilled with ultra-high purity grade argon. The details of experiments are described in the respective sections of the thesis in the format shown in Table 1. The slag composition is also described in the respective sections. Experiments are named in the order of appearance along with chapter number: for example, first experiment of chapter 5 is named as 5.1. Sometimes a sample from the steel puck (metal remaining in crucible) was also analyzed for inclusions or used for bulk chemical analysis. These samples are named as SF (final sample). Some of the challenges related to conducting induction furnace experiments are discussed in Appendix A .

Table 1. Presentation of an experiment-an example

Time (minutes/seconds)	0	15	30	45	60
Events	Aluminum addition	Slag addition	Sample1	Reoxidation	Sample2

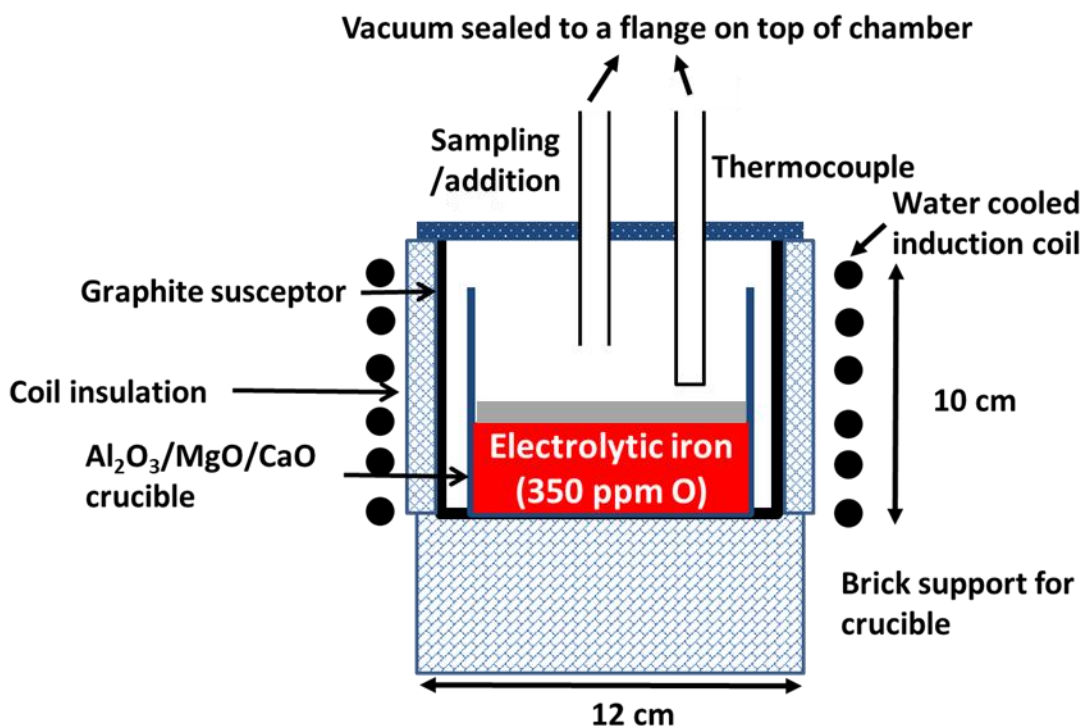


Figure 1. Schematic of induction furnace setup

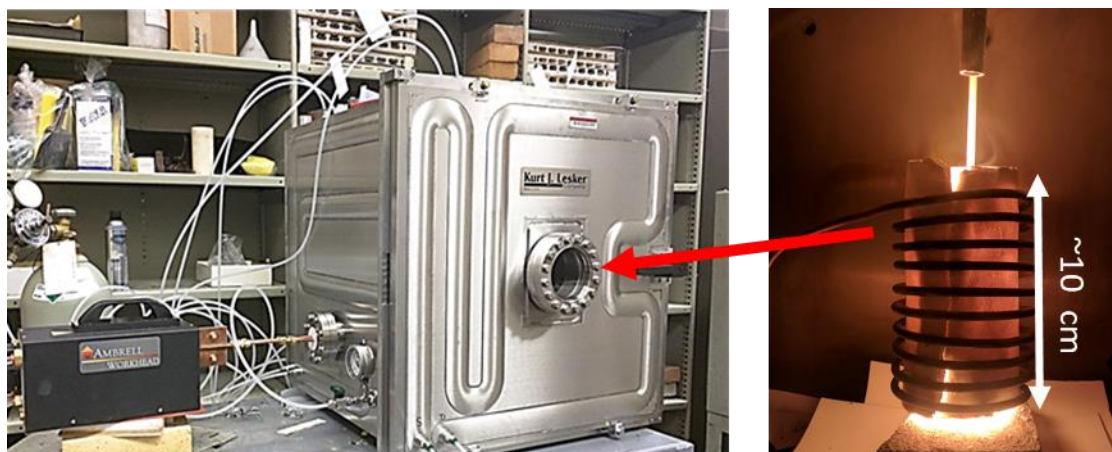


Figure 2. Image of new induction furnace setup with a stainless steel chamber

3.1.2 Confocal Laser Scanning Microscope Experiments

The confocal laser scanning microscope (CLSM) has an ellipsoidal gold plated chamber with a tungsten lamp (heat source) at one focal point and the sample holder at the second focal point. A low oxygen partial pressure was maintained by first evacuating chamber air and subsequently filling it with argon (0.250 litres/minutes) gettered by heated Cu and Mg chips. The partial pressure of oxygen was maintained at $10^{-21} - 10^{-20}$ atm during all experiments (as measured with an oxygen probe in the off-gas from the chamber). The schematic of the CLSM chamber is shown in Figure 3. The sample surface was observed on a computer screen using a laser microscope during the experiment. The video of this observation was recorded. The specifics of experiments are described in the respective sections of the thesis.

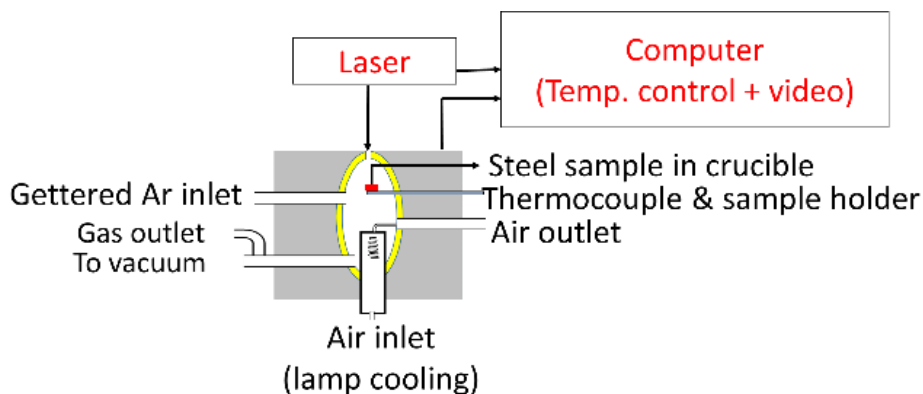


Figure 3. Confocal Laser Scanning Microscope setup

3.2 Characterization

3.2.1 Bulk chemical analysis

3.2.1.1 *Steel samples*

Steel samples from industrial trials were analyzed using Optical Emission Spectrometry at the plant. Samples from selected laboratory scale experiments were sent for chemical analysis to either of three external parties: WestPenn Testing Group, Clark Testing or Evans Analytical Group. Aluminum and silicon was analyzed using ICP-MS technique. Total oxygen and total sulfur were analyzed using LECO-CS or LECO-NS technique with a detection limit of 10 ppm. Total magnesium (dissolved + bound in inclusions) was analyzed using ICP-AA (atomic absorption), ICP-MS (mass spectroscopy) and ICP-GDMS (glow discharge mass spectroscopy). As shown in Table 2, the analyzed magnesium from all spectroscopy techniques from different companies were found lower than that estimated from inclusion analysis. Magnesium in inclusions was estimated from SEM-EDS and the measured area of 10^2 - 10^3 inclusions on polished cross-section of steel samples using SEM ASPEX-Explorer. The total expected magnesium was calculated as the sum of estimated magnesium from inclusion analysis and expected dissolved magnesium from kinetic modeling as described later.

Table 2. Comparison of magnesium analysis from spectroscopy techniques to the expected from inclusion analysis

Exp.#	Sample	Method	Company	Mg-analyzed	From ASPEX analysis	Exp. total (ASPEX + FactSage)
5.4	S1	ICP-AA	ClarkTesting	<10	16	17
5.4	S3	ICP-AA	ClarkTesting	10	45	60
5.4	S6	ICP-AA	ClarkTesting	20	38.5	56.5
5.6	SF	ICP-MS	WestPenn	<10	19.3	30
7.2	SF	ICP-GDMS	Evans	6.3	11	35
7.3	SF	ICP-GDMS	Evans	9.2	10	33

Figure 4 shows comparison between oxygen measured using LECO by different companies with the bound oxygen in inclusions estimated from ASPEX-AFA inclusion analysis. Since oxygen is a light element, the measured oxygen from EDS analysis is not expected to be reliable. Therefore, the mass fraction of bound oxygen in inclusions was estimated from the estimated mass fraction of cations using area fraction of inclusions. Since all steel samples are aluminum killed, the dissolved oxygen concentration was expected to be about 5 ppm. In most cases, the difference in oxygen measured using LECO was much more than 5 ppm indicating that there might additional oxygen in those samples. The samples taken using a fused quartz tube were immediately quenched in water. Sometimes pores in the samples could be seen in the center of cylindrical samples. During water quenching, samples may oxidize resulting in higher measured oxygen using LECO. Two samples (see red triangles) that shows very close agreement were analyzed from the final puck left in crucible after the experiment. Two samples on this plot also shows lower measured oxygen using LECO compared to that estimated from inclusion analysis. The over-estimation may be due to presence of large inclusion clusters in those samples. The number density of large clusters is

expected to be small but if a few such clusters are measured during automated feature analysis, the estimated area fraction of inclusions may be higher than actual.

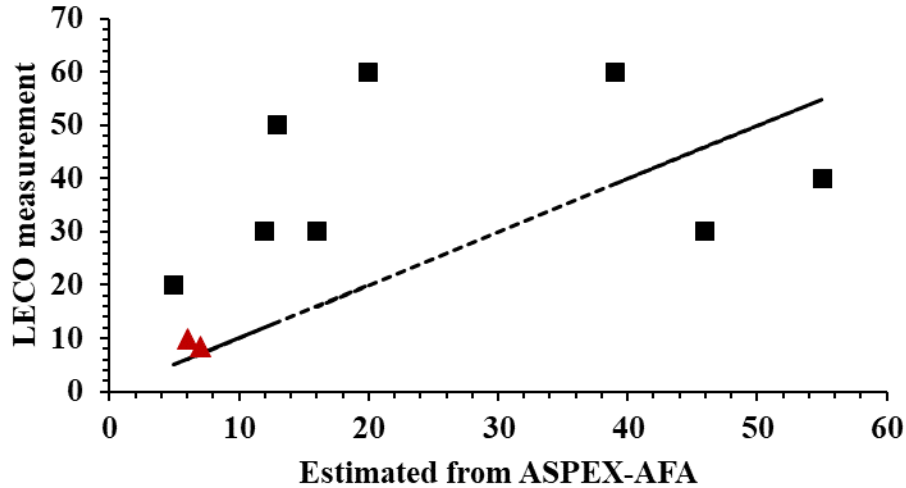


Figure 4. Comparing measured oxygen using LECO to that estimated from ASPEX-AFA analysis

3.2.1.2 Measuring bound Ca and Mg in inclusions in steel

The calcium content in steel is difficult to measure through usual spectroscopy techniques due to its very low concentration. It is possible to measure calcium present as inclusions through automated feature analysis in SEM-ASPEX with some limitations. It is difficult to measure inclusions smaller than 0.5 μm and the chemical analysis of smaller inclusions using EDS is affected by the steel matrix. Another idea to measure calcium content in steel is to get rid of the matrix effect by dissolving the steel matrix using electrolytic dissolution and filtering inclusions using filter paper having small (0.3 μm) pores. To test this, 3.14 g of steel was electrolytically dissolved in 180 ml solution of anhydrous methanol containing nearly 10 wt% each of acetylacetone and tetramethyammoniumchloride. The initial voltage and current for this dissolution were 11.5 V and 1.04 A. Details of the inclusion dissolution process can be found in [9]. The solution containing dissolved iron and inclusions was then filtered through nylon filters

(pore size = 0.3 μm); a second filter was used once filtration through first filter paper became extremely slow. These two filters were then sent to Clark Testing for chemical analysis. Filters containing inclusions were fused with lithium tetraborate and then dissolved in 50 ml aqueous solution; chemical analysis was performed using ICP. Blank filters, without any inclusions, were analyzed to measure initial Ca, Mg and Al contents of the filters. Actual Ca, Al and Mg concentrations were then obtained by subtracting blank from sample analyzed. Calcium, magnesium and aluminum content in inclusions analyzed from this method was found to be equal to 8.90, 7.0 and 17.0 ppm respectively. Inclusion analysis of a 25.48 mm² area of the same sample using SEM-ASPEX showed the calcium, magnesium and aluminum content in inclusion to be equal to 8.9 ppm, 5.7 ppm and 12.8 ppm. The result from two analyses are very close to each other, with the measured aluminum and magnesium from filters higher than that observed from ASPEX inclusion analysis. The higher measured content of Al and Mg from the analysis of filters also indicate that smaller inclusions were missed during ASPEX analysis of inclusions. It will be interesting to compare the size distribution of extracted inclusions and inclusions observed on the polished cross-section. It should also be pointed that the sample contained some CaS inclusions as well that are expected to dissolve during the dissolution/filtration process, therefore the actual Ca content is expected to be a little higher than reported here. In addition, the accuracy can be further improved by selecting a filter paper with smaller pores. Given the variation in magnesium measurement (and calcium measurement), this method may be useful in future for analyzing bound magnesium and calcium in steel sample.

3.2.1.3 Slag samples

The slag samples taken from an industrial trial was analyzed using the XRF-spectroscopy technique at the plant.

3.3 Inclusion analysis

The steel samples were cut and mounted using a graphite-based conducting powder and ground with 320 and 800 grit SiC paper followed by polishing up to 1 μm finish using diamond suspension. The accelerating voltage and spot size used for these analyses was 10 kV accelerating voltage and 40-45 % respectively. 10-30 mm^2 area was analyzed for each sample which corresponded to 10^2 - 10^3 inclusions generally. Inclusions were detected using backscattered electron imaging; analyzed EDS peak heights and the geometry of inclusions were recorded in a .csv file by the AFA software. The inclusions larger than 0.3 μm were analyzed. EDS quantification was obtained using the Merlet phi-rho-z algorithm [10], [11]. Polished unmounted samples of dimension 15 mm $\times$ 5 mm $\times$ 2 mm were electrolytically etched to reveal 3-D morphology of inclusions. Anhydrous methanol based solution containing 10 wt% of acetylacetone and 10 wt% of tetramethylammonium chloride was used to partially dissolve the steel matrix at a constant voltage of 10 V as described by Tan and Pistorius [9].

The inclusion analysis results are presented in the form of a ternary diagram, generally plotted on mole fraction basis and normalized for three elements shown in the diagram. An example of such ternary diagram is shown in Figure 5. The 50% liquid boundary is shown only in the case of Mg-Ca-Al ternary diagram.

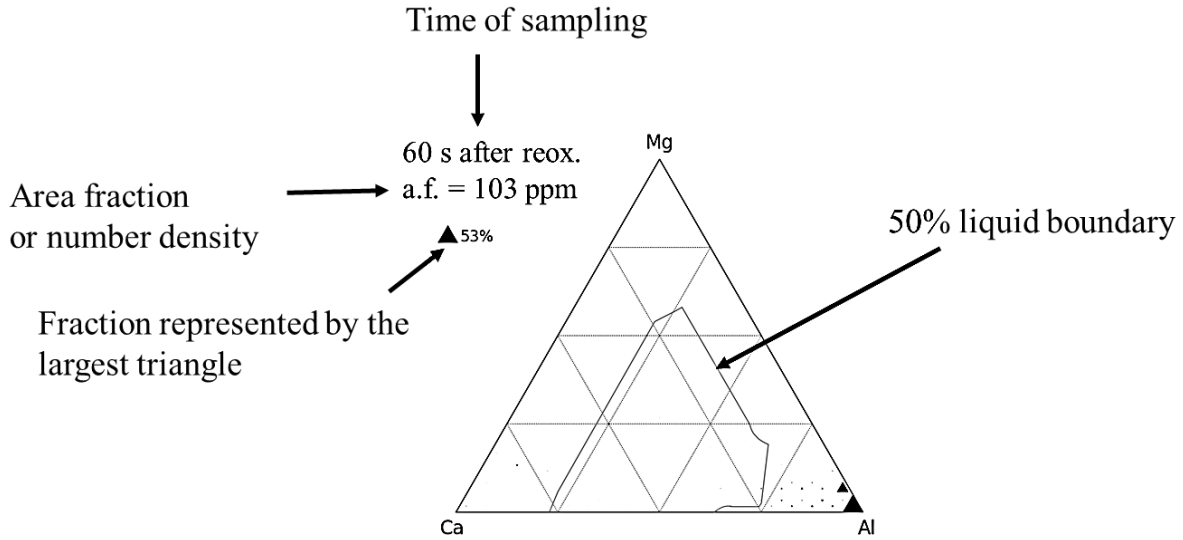


Figure 5. Presentation of inclusion composition on ternary diagram

The mass fraction of inclusions was estimated from the measured area fraction of inclusions. The volume fraction was taken equal to area fraction. The mass fraction of inclusion was calculated from volume fraction using density of steel and inclusions. The density of alumina inclusions was taken equal to 3980 kg/m^3 , density of spinel inclusion was equal to 3580 kg/m^3 and density of steel was equal taken equal to 7800 kg/m^3 . The density of complex oxide inclusions (Al-Mg-Zr-Ca-O) was calculated as the mass average density of oxides based on average chemical composition. The densities of MgO, CaO and ZrO_2 were taken equal to 3580, 3350 and 5680 kg/m^3 .

4 Development of a kinetic model: review and current approach

4.1 Background and previous studies

Kinetic modeling of steel-slag-inclusion reaction is helpful in understanding the effect of changes in operating conditions, like stirring energy, slag composition and ferroalloy additions, on the final chemistry and cleanliness of steel. It can also be used to develop a better understanding of the process itself. For example, predicted and observed changes in steel chemistry and cleanliness would help in understanding the reaction mechanism and effect of process parameters. In this section, previous works related to the kinetic modeling is summarized and model parameters reported by several researchers are compared.

4.1.1 Overview of models

The aim of ladle metallurgical furnace (LMF) operations is to achieve the right chemistry and to obtain the desired level of steel cleanliness. In the past, the focus has been the kinetics of steel-slag reactions to achieve the right level of dephosphorization [12] and desulfurization [13]–[18]. Since the composition and concentration of inclusion also change with time during and after ladle refining, the recent focus has been to include changes in inclusion composition in such kinetic models. One approach to develop the kinetic model is to obtain thermodynamic data from either published sources or using software like FactSage that stores all necessary thermodynamic data with reasonable accuracy. Several authors [16], [19]–[21] have used this approach in the past. An alternate approach is to link the kinetic model to FactSage [22] using ChemApp [6], [23], [24] or to use the macro-processing feature of FactSage [7] for thermodynamic calculations. These approaches either use the free energy minimizer within FactSageTM or free energy minimization is employed in the model. Järvinen et al. [25] used an approach based on the law of mass action

based approach to model mass transfer limited reactions in steelmaking. Instead of free energy minimization to achieve complete equilibrium, an approximate equilibrium was calculated with the help of a pre-defined residual. The use of pre-defined residual allowed the authors to solve a system of linear equations of flux with numerical stability. Such models are expected to be calculation friendly and can be used to develop computational fluid dynamics (CFD) based models.

A ladle refining system consists of following components: steel, slag, inclusions, refractory, ladle glaze and argon gas used for stirring. It can also include a heating mechanism; this was not considered in the present work. Although argon gas is chemically inert, it plays an important role by reducing ladle mixing time, enhancing steel-slag mass transfer and promoting the flotation of inclusions from liquid steel to slag. Chemical reactions occur between steel-slag, steel-refractory, steel-inclusion, slag-refractory and slag-inclusions. Yan et al. [26] reported that the dissolution of Al_2O_3 and MgO in slag can be considered to be controlled by mass transfer in slag phase and the effective diffusion coefficient for MgO and Al_2O_3 dissolution in slag can be in the range of 10^{-12} to $10^{-9} \text{ m}^2/\text{s}$. For this value, smaller inclusions ($< 10 \text{ }\mu\text{m}$) can be expected to dissolve in slag in less than 30 s provided saturation is not reached in slag. The other chemical reactions can be considered to be mass transfer controlled. Harada et al. [23] developed a kinetic model to predict compositions of steel, slag and inclusions using a coupled reaction model proposed by Ohguchi et al. [27]. In the coupled reaction model, mass transferred controlled reactions between two phases are modeled using local equilibrium at the reaction interface. The amount of individual species transported to the interface is calculated using individual mass transfer coefficients of species in the particular phase. Mass transfer coefficients for steel-slag and slag-refractory reactions were experimentally determined in their work [12], [28]. The kinetic model also considered inclusions originating from

slag, agglomeration of inclusions originating from slag with deoxidation inclusions and the flotation of inclusions to the slag. Figure 6 shows a schematic of all phenomena occurring in ladle refining and considered in their model. Inclusions originating from slag implies inclusions generated due to entrapment of fine slag droplets into liquid steel as shown in the 6th reaction in Figure 6. Some examples of such inclusions will be shown later in the document. A sensitivity analysis was carried out to find appropriate parameters for inclusion agglomeration and flotation to fit the model for a plant operation. Experiments were conducted with different stirring conditions to validate the model and further refine flotation behavior of inclusions. Relative flotation behavior of inclusions was associated with the Stokes velocity based on the densities of alumina (β), spinel (1.1β) and inclusions originating from slag (1.3β). Flotation of alumina clusters were taken as 100β , where β is the flotation rate constant in mass %/s [24]. Van Ende and Jung [7] and Shin et al. [8] used an effective equilibrium reaction zone (EERZ) to develop a similar model. The concept of EERZ is illustrated in Figure 7 for mass transfer controlled reaction between steel and slag. V2 and V3 represent reaction zone volumes for steel and slag respectively. The equilibrium occurs between V2 and V3 followed by steel and slag homogenization. Steel homogenization is essentially mixing of equilibrated V2 with V1 in the steel phase and V3 and V4 for the slag [7]. The volume V2 and V3 are calculated using mass transfer coefficients in steel and slag phase. In this work, EERZ based modeling approach was used for all chemical reactions. Van Ende and Jung also used an energy balance considering chemical reactions, arcing and heat loss to predict temperature change during ladle refining process.

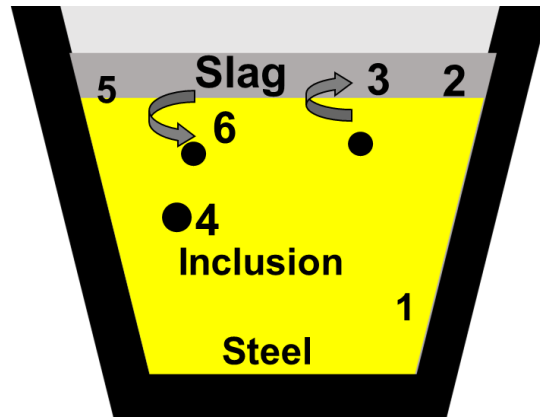


Figure 6. Schematic of phenomena occurring during ladle refining: 1) steel-refractory reaction, 2) slag-refractory reaction 3) flotation of inclusions to slag, 4) steel-inclusion reaction, 5) steel-slag reaction and 6) inclusions originating from slag

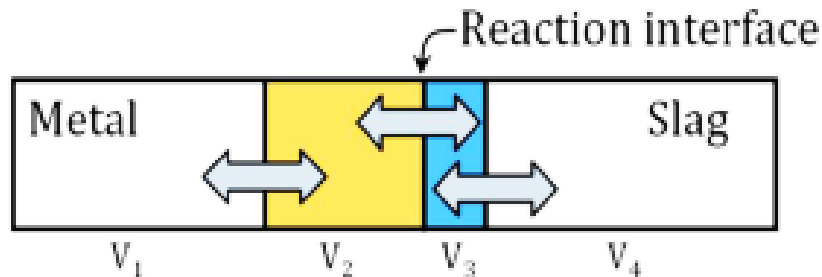


Figure 7 Concept of EERZ model for steel-slag reaction [7]

4.1.2 Summary of kinetic parameters of the model

4.1.2.1 Steel-slag reaction

Mass transfer coefficients greatly depend on the rate of argon stirring and ladle geometry. Few combinations of stirring energy and ladle geometry have been used to calculate mass transfer coefficients in the steel phase. Since the diffusivity in slag is around 100-times smaller than that in steel phase and mass-transfer coefficient is proportional to $\sqrt{D}$, slag phase mass transfer coefficients are generally considered smaller and calculated as 5-20 times smaller than steel phase. Relevant expressions/values for mass transfer coefficients are summarized in Table 3. The laboratory scale experiments and industrial work are marked as crucible and ladle in the first column of the table.

Table 3 Mass transfer coefficient for steel-slag reactions

Reference	In steel phase (k_m)	In slag phase (k_s)
Peter et al. [19], ladle	$\frac{0.08}{m} \sqrt{14.23 \left(\frac{QT_l A_{top}}{N^{\frac{1}{4}}} \right) \log \left(1 + \frac{h_0}{1.5P_0} \right)} \text{ min}^{-1}$	$k_s = \frac{k_m}{20}$
Harada et al. [23], crucible	$\log k_m \text{ (m/s)} = 1.98$ $+ 0.5 \log \left\{ (\dot{\epsilon} \text{ (in } W/t) \times 1000) \left(\frac{h_v^2}{d_v} \right) \right\}$ $- \frac{125000}{2.3RT_l}$ $\dot{\epsilon} = \frac{6.18QT_l}{m} \left\{ \ln \left(1 + \frac{h_0}{1.46 \times 10^{-5} P_0} \right) + \eta \left(1 - \frac{T_g}{T_l} \right) \right\}$	$k_s = \frac{k_m}{10}$ k_{MO_n} $= k_s \times \sqrt{\frac{D_{MO_n}}{D_{CaO}}}$
Graham & Irons [16], ladle	$(0.006 \pm 0.002) \dot{\epsilon}^{1.4 \pm 0.09} \text{ in s}^{-1}$ $\dot{\epsilon} \text{ (W/t)} = \left(\frac{\dot{n}RT_l}{m} \right) \ln \left(\frac{P_t}{P_o} \right)$	
Van Ende & Jung [7], ladle	$\frac{0.08}{m} \sqrt{14.23 \left(\frac{QT_l A_{top}}{N^{\frac{1}{4}}} \right) \log \left(1 + \frac{h_0}{1.5P_0} \right)} \text{ min}^{-1}$	$\frac{k_s}{k_m} = 0.05 - 0.1$
Shin et al. [8], crucible	$1 \times 10^{-4} \text{ m/s}$	$k_s = 0.035 k_m$
Cicutti et al. [20], ladle	$\dot{A} \times 10^{-5} \epsilon^{0.5} \text{ m/s}$ $\dot{A} = 5 \text{ (for [Ca])}, 10 \text{ (for [Mg]) and } 50 \text{ (for [s])}$	$\dot{A} = 1$
Okuyama et al. [21], crucible	$2 \times 10^{-4} \text{ m}^3/\text{s}$	$k_s = \frac{k_m}{20}$ $k_{SiO_2} = \frac{k_m}{100}$
Roy et al. [14], [15], crucible	$1 \times 10^{-4} \text{ m/s}$	$k_{slag} = \frac{k_m}{10}$
Iwamasa & Fruehan [17], crucible	$3 \times 10^{-5} \text{ m/s}$	

Where, m : steel mass, Q : argon flow rate, T_l : temperature, A_{top} : area of the top of liquid steel, h_0 : injection depth of argon, P_o : pressure over steel-bath, N : number of porous plugs, h_v : bath depth, T_g : gas temperature, d_v : bath diameter, $\dot{\epsilon}$: stirring energy, R : gas constant, k_{MO_n} and D_{MO_n} are mass transfer coefficient and diffusion coefficient of MO_n in slag phase, $\dot{n}$ is the molar flow rate of argon and P_t is the total gas pressure at the base of the ladle.

4.1.2.2 Slag-refractory reaction

Harada et al. [23], Shin et al. [22] and Cicutti et al. [20] also considered dissolution of MgO refractory into slag. The mass transfer coefficients used to model slag dissolution in refractory are summarized in Table 4.

Table 4 Mass transfer coefficients for refractory dissolution in slag

Harada [23]	Shin [8]	Cicutti [20]
$0.0791u^{0.7}D^{-0.644}d^{-0.3}v^{-0.344} \text{ m/s}$	$5 \times 10^{-6} \text{ m/s}$	$3 \times 10^{-4} \text{ m/s}$

Where, u and d are characteristic velocity and length, D : diffusivity and v : dynamic viscosity

4.1.2.3 Inclusion removal from liquid steel

The flotation of inclusions is expected to depend on the size, clustering and flow conditions in the ladle. In practice, as larger inclusion clusters float to the top slag, the size of cluster and inclusion cluster is expected to reduce with time unless there is a reoxidation or an additional source of inclusions. Schwerdtfeger [29] showed that the inclusion removal can be modeled assuming it to be a first reaction. The flotation rate constants are summarized in Table 5. Except for work by Harada et al. [24], tabulated flotation rate constants are for industrial ladle refining conditions. The concentration of inclusion was considered to reduce by $C_i \times \beta$ per second, where C_i is the current

concentration and β is the flotation rate constant. It can be seen that the values reported by Van Ende and Jung [7] and Graham and Irons [16] are same. Cicutti et al. [20] did not provide melt depth for 180 ton ladle but if we assume the melt depth to be approximately equal to 2 m, the flotation rate constant is about 5%/minute which is very close to that reported by others. Harada et al. [28] used two rate constants to model inclusion flotation. The rate constant for clusters was considered to be 100-times flotation of smaller inclusions which is much higher than other values shown in the table. The value of β is however close to other rate constants.

Table 5. Flotation behavior of inclusions

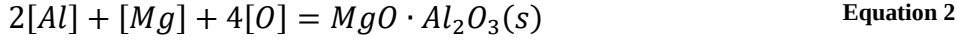
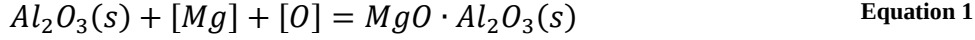
Reference	Rate constant(β)
Van Ende & Jung [7]	6%/minutes
Cicutti et al. [20]	$1.5 \times 10^{-3} m/s$
Grahan & Irons [16]	0.1%/s, varies with stirring rate as follows: $\beta = (0.57 \pm 0.15)\epsilon^{0.28 \pm 0.08}$
Harada et al. [24]	$\beta_1 = 0.05 \text{ mass\%/s}$ (For Ar flow rate = 5 NL/min) $\beta_2 = 0.1 \text{ mass\%/s}$ (For Ar flow rate = 20 NL/min) alumina: β , alumina cluster: 100β , spinel: 1.1β , inclusion originating from slag: 1.3β

4.1.2.4 Steel-refractory reaction

Aluminum killed steel may react with MgO-C refractory during industrial production or MgO crucible during laboratory scale experiment resulting into transformation of alumina inclusions to magnesium aluminate spinel $((MgO)_x \cdot Al_2O_3)$, referred to as spinel from now on) inclusions. Spinel inclusions are undesirable due to nozzle clogging and severely affecting mechanical properties of final products. Several researchers have used a phase stability diagram to understand the stability of spinel inclusions in liquid steel. Deng and Zhu [30] reported a phase stability diagram, based

on available thermodynamic data, to verify the stability of spinel inclusions. Yang et al. [31] also used available thermodynamic data to calculate phase stability diagrams under different conditions. These stability diagrams showed that alumina and spinel becomes more stable than MgO inclusions at lower operating temperature and the stability window is also affected by dissolved oxygen concentration. They also pointed out that the stability region of spinel is affected by the activities of oxides used for calculation: lower oxide activities yield a narrower spinel stability window. Zhu and Sichen [32] found that at lower oxygen activity ($=1$ ppm, maintained by flowing CO gas), magnesium transfer from MgO refractory to steel would transform alumina inclusions into spinel but this would not occur at a higher oxygen activity ($=456$ ppm, maintained by CO+4% CO₂ mixture). Liu et al. [33] reported that both MgO-C refractory and MgO bearing slag can be source of magnesium responsible for the transformation of alumina inclusions to spinel inclusions. Tan and Webler [34] showed that magnesium transfer from an MgO crucible can result in formation of spinel inclusions after deoxidation. They also reported that a reoxidation event after calcium modification of these inclusions may result in a re-appearance of spinel inclusions. However, Okuyama et al. [21] reported that alumina inclusion did not transform to spinel inclusion when experiment was conducted using an MgO crucible. Verma et al. [35] showed that there was very limited magnesium transformation from MgO crucible due to formation of anchored spinel patch/agglomerates on the crucible wall. Deng et al. [32] showed that reaction between liquid steel and MgO refractory can also provide sufficient [Mg] to transform alumina into spinel inclusions. The difference in reported magnesium transfer may be due to different types of MgO crucibles used in these studies. Yang et al. [31] noted other sources of magnesium responsible for spinel inclusions during steelmaking and continuous casting as deoxidants, tundish slag and tundish lining.

There are two reactions of interest to researchers regarding the mechanism of formation of spinel inclusions as shown by Equation 1 and Equation 2.



Deng et al. [32] showed that spinel inclusions can form on an alumina rod from pure liquid iron when the reaction was conducted in an MgO crucible indicating that dissolved aluminum was not necessary for the formation of spinel inclusions. Liu et al. [33] experimentally concluded that although spinel inclusions can be generated from both Equation 1 and Equation 2, Equation 1 is favored as the formation of spinel can occur through heterogeneous nucleation whereas Equation 2 requires homogeneous nucleation of spinel inclusions.

Several researchers ([21], [28], [33]) used magnesium pick-up in inclusions to study the kinetics of transformation of alumina to spinel inclusions. The extent of transformation is measured by %(MgO) in inclusions. Liu et al. [33] considered magnesium transfer in the steel melt to be the rate limiting step for the transformation of alumina inclusions to spinel inclusions due to reaction between steel and MgO-C. Okuyama et al. [21] concluded that magnesium transfer in the steel-slag boundary layer was the rate limiting step and the diffusion within inclusions was fast (6 μm size can completely transform to spinel within 20 s). Harada et al. [28] studied the transformation of alumina inclusions to spinel inclusions due to steel-refractory and steel-slag reactions. In that study, mass transfer coefficient in steel was determined for steel-refractory reaction for different rotation speeds of refractory inside liquid steel. It was also found that magnesium transfer is more prominent in case of steel-slag reaction compared to steel-refractory reaction. The mass transfer coefficient or magnesium transfer rate in steel phase reported from these laboratory scale studies

are summarized in Table 6. The order of magnitude of mass transfer in these studies is close i.e. $1-5 \times 10^{-4}$ m/s.

Table 6. Summary of mass transfer coefficient in steel phase for magnesium transfer

Reference	K_{steel} (m/s)
Liu et al. [33]	5×10^{-4}
Harada et al. [28]	$k \left(\frac{L}{D} \right) = 1.3 Re^{\frac{1}{2}} Sc^{\frac{1}{3}}$ k is mass transfer coefficient (m/s), L is characteristic length (m), D is diffusivity (m^2/s), Re is Reynolds number and Sc is Schmidt number. Range: $k = 0.7 - 1.5 \times 10^{-4} \text{ m/s}$
Okuyama et al. [21]	2×10^{-4}

As part of the development of a kinetic model in the present work, aluminum killed steel was equilibrated with an MgO crucible to find the mass transfer coefficient in the steel phase for steel-crucible reaction. Two experiments were conducted for the sake of reproducibility. However, the results revealed a rapid and limited magnesium transfer in two cases. The rate of magnesium transfer to steel was quantified using statistical analysis of inclusion area fraction and MgO concentration with the help of the kinetic model. The practical implication of this observation for industrial operation is discussed as well (see section 5.3.5)

4.2 Current Modeling Approach

The important reactions to consider during steel refining on an industrial scale ladle or in a crucible in the laboratory scale set-up are: 1) steel-refractory reaction, 2) slag-refractory reaction, 3) inclusion removal, 4) steel-inclusion reaction, and 5) steel-slag reaction.

Except for the flotation of inclusions, the other four reactions involve reaction between two phases, which can be modeled by assuming mass transfer control. The mass transfer controlled reactions were modeled using effective equilibrium reaction zone (EERZ) method as described by Van Ende and Jung [7]. In a given time-step of length Δt , a fraction of each phase reaches the interface and the products mix back into the bulk phases, as shown in Figure 8. This reacting fraction can be calculated using Equation 3.

$$f_{phase} = \frac{k_p A_i \rho_p \Delta t}{W_p} \quad \text{Equation 3}$$

Where k_p is the mass transfer coefficient in the phase, A_i is the interfacial area, ρ_p is the density, W_p is the total mass of the phase and Δt is the time step length.

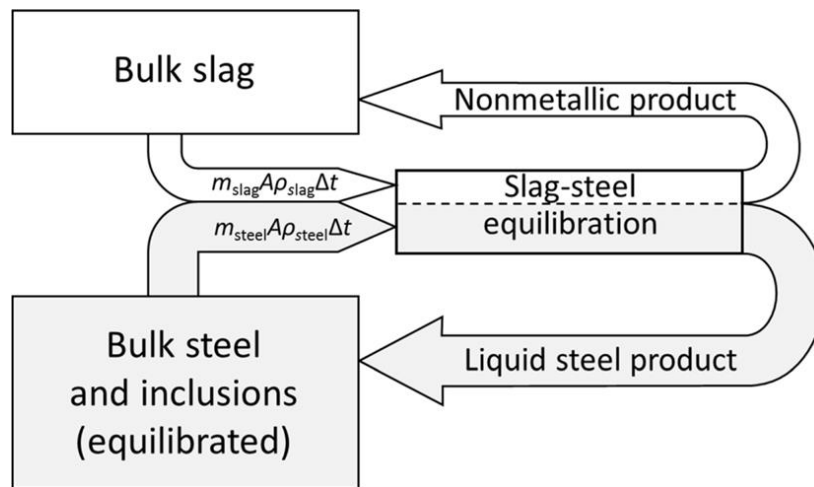


Figure 8. Schematic of the modeling scheme for mass-transfer controlled steel-slag reaction [36]

According to Higbie's penetration theory [37] of mass transfer between two phases the mass transfer coefficient (k) is proportional to $\sqrt{D}$ (where D is diffusivity in a phase), according to Equation 4. Here, v and L represent fluid velocity and the boundary layer thickness.

$$k = 2 \left(\frac{D}{\pi t_e} \right)^{1/2} = 2 \left(\frac{Dv}{\pi L} \right)^{1/2} \quad \text{Equation 4}$$

The mass transfer coefficient in the slag-phase was taken 10-times smaller than that in liquid steel phase as diffusivity of each component in the slag phase is expected to be 10-100 times smaller than that in steel phase [12]. The mass transfer coefficients used by other researchers are described in Table 3. Since there was no argon stirring in the laboratory scale induction furnace setup, it was not possible to use empirical equations used by other researchers to estimate the mass transfer coefficients. In this work, the mass transfer coefficient in steel phase for steel-slag reaction and steel-crucible reaction was obtained using targeted experiments described in a later section. For industrial heats, argon flow rate measurements are generally unreliable. Therefore, the mass transfer coefficient was calculated by fitting observed changes in chemical composition of steel and slag. The results would be compared to those of other researchers in chapter 6.

Other than the reaction layers, the steel and slag bath were assumed to be homogeneous. This was implemented by equilibrating the entire steel bath and slag bath separately in each time step of calculation.

The Sherwood number for the mass transfer coefficient in steel phase for steel-inclusion reaction is equal to 2 due to very small Reynolds number. This is equivalent to:

$$k_{steel} = \frac{D_{steel}}{R} \quad (5)$$

Assuming $D_{steel} = 10^{-9} m^2/s$ [24], $R = 3 \mu m$ and inclusion concentration to be 50 ppm by mass, the fraction of steel reacting with inclusions per unit time is $\sim 8/\text{minute}$. The typical time step in this work was 0.5 minute. Therefore, it is natural to assume that entire mass of steel reacted to inclusions in each time step. Mass transfer inside inclusions is also expected to be fast for smaller inclusions, say less than $5 \mu m$. This is in line with experimental observations regarding composition gradients inside inclusions. Figure 9 and Figure 10 show larger and smaller inclusions present in the samples taken 11 minutes after the aluminum deoxidation and one minute after calcium addition in a laboratory scale trial. Magnesium pickup in these inclusions is due to steel-crucible reactions. It can be seen that even after 11 minutes, the core of larger inclusion remained as alumina, however the smaller inclusion had a uniform calcium content within a minute of calcium treatment. Therefore, it can be assumed that steel and inclusions attain full equilibrium in each calculation step.

The removal of inclusions under laboratory scale experimental conditions is expected to be different than that for industrial operation due to two reasons: 1) the melt depth in the laboratory scale experiments was about two orders of magnitude smaller than industrial heats ($\sim 4 \text{ cm}$ vs $\sim 2 \text{ m}$) and 2) the steel-refractory and steel-slag area to volume ratio is about 100 times larger than industrial operation. The calculations were done for 600 g steel in 5 cm diameter crucible and 200 metric tonnes of steel in 2 m cylindrical ladle. A significant number of inclusions generated after reoxidation may collide with and stick to the crucible wall during laboratory scale experiments. Alumina inclusions forms large clusters ($\sim 100 \mu m$) just after aluminum deoxidation. These large clusters are also expected to float at a higher rate than smaller inclusions; the effect is expected to be much stronger for laboratory scale experiments due to reasons described above. Harada et al. [24] used different flotation rates for alumina, alumina cluster, spinel and liquid inclusions. In this

work, inclusion removal was modeled using two inclusion removal rate constants: β_1 and β_2 for laboratory scale experiments. The removal of inclusions slag was considered to be a first order reaction, which was implemented as described in Equation 6.

$$\frac{dC}{dt} = -\beta C$$

$$\Delta C = -\beta C \Delta t$$

Equation 6

Where ΔC is the change in inclusion concentration, β is the inclusion removal rate constant and Δt is the size of time step in seconds. The floated inclusion mass was added to the slag mass in each time step. Some deoxidation experiments will be discussed in the following section to justify the use of two inclusion removal rate constants. For modeling industrial scale operation, a single inclusion removal rate constant was used as suggested by Schwerdtfeger [29].

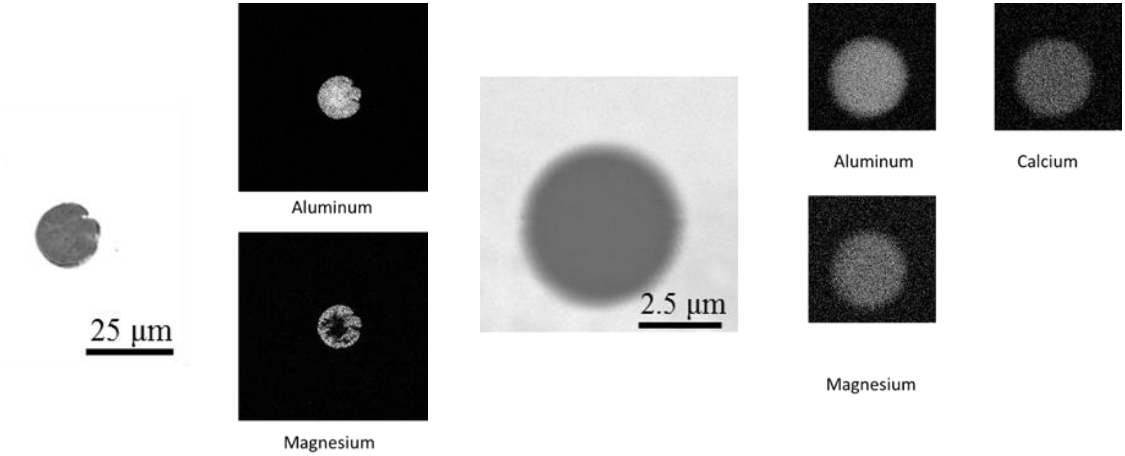


Figure 9. Magnesium concentration differences in large alumina inclusions 11 minutes after Al-addition [0.15 wt%] to the liquid steel in MgO crucible

Figure 10. Uniform inclusion composition in smaller inclusions just one minute after calcium-treatment

4.2.1 Model implementation

The modeling of these reactions thus involves multiple thermodynamic equilibrium calculations, which were performed using the macro-processing feature available in FactSage 6.4 or FactSage 7.0. The FTmisc database was used for liquid steel and FToxid for slag. The FToxid and the FactPS databases were used for inclusions. The inputs of this model include relevant mass transfer coefficients, flotation rate constants, initial composition of steel and slag, details of additions (time, amount and chemistry) and geometry of crucible/ladle. The output of the model was the composition and amounts of steel, slag and inclusions with time. The input and output were communicated between MS-Excel/.txt file and FactSageTM by implementing the model algorithm in a .mac (macro) file.

4.2.1.1 *Liquid steel solution database in FactSage*

4.2.1.1.1 Associate solution model

FactSage uses an associate solution model for the liquid steel solution instead of uniform interaction parameter model using Wagner formalism. The associate solution model is well described by Jung et al. [38]. A brief description of the model is presented here. It uses fewer temperature dependent parameters and can be easily extrapolated over the range of temperature and composition. A deoxidizer can be assumed to be present in liquid steel as the dissolved element and as associates like M^*O and M_2^*O , instead of just in elemental dissolved form as considered in Wagner formalism. For a strong deoxidizer having large interaction parameter with oxygen, most of the dissolved element will be present in the liquid steel solution as associates. The total dissolved amount is then defined as the sum of the amount as dissolved element and that present

as associates. The associate solution model can be used to determine the total dissolved deoxidizer and total oxygen as follows:

Standard free energy for M_aO_b :



Dissolution of deoxidizer M in liquid steel:



Dissolution of oxygen in liquid steel:



Deoxidation reaction with dissolved M and O as reference states:



Formation of associate M^*O :



Formation of associate M_2^*O :



For equation (10):

$$K = \frac{1}{(f_{[M]}X_M)^a (f_{[O]}X_{[O]})^b} \quad (13)$$

For a given X_M , $f_{[M]}$ can be calculated as follows:

$$\ln f_{[M]} = \epsilon_M^M X_{[M]} \quad (14)$$

ϵ_M^M can be calculated using Fe-M binary system. In this case $f_{[O]}$ is taken equal to 1 as interaction of oxygen with the deoxidizer M is considered using $\Delta g_{[M^*O]}^0$ and $\Delta g_{[M_2^*O]}^0$. For $f_{[O]}=1$, $X_{[O]}$ can be calculated using equation (13). Since X_M and X_O are known, $X_{[M^*O]}$ and $X_{[M_2^*O]}$ can be calculated using $\Delta g_{[M^*O]}^0$ (equation (11)) and $\Delta g_{[M_2^*O]}^0$ (equation (12)) as $f_{[M^*O]}$ and $f_{[M_2^*O]}$ are taken equal to 1. The unknowns of this model (ϵ_M^M , $\Delta g_{[M^*O]}^0$ and $\Delta g_{[M_2^*O]}^0$) are calculated by evaluation/optimization of available thermodynamic data. These parameters were summarized by Jung et al. [38].

4.2.1.1.2 On the accuracy of FTmisc database

Several researchers have pointed out the inconsistency in Fe-Ca-O and Fe-Mg-O thermodynamics [39]–[42]. The kinetic modeling of the present work showed that the use of FTmisc database could accurately predict the rate of transformation of alumina inclusion to spinel inclusions due to the reaction of steel with an MgO crucible or MgO bearing slag. However, the extent of calcium pick-up from such reactions was over-predicted. In this section, the Fe-Mg-O thermodynamics is reviewed.

Zhang et al. [43] measured the activity coefficient of magnesium in Fe-Mg system by conducting iron-magnesium vapor equilibrium experiment. They used a TiN crucible for liquid iron and an

iron crucible for liquid magnesium. Electrolytic iron was first deoxidized to below 70 ppm using calcium deoxidation. The magnesium concentration was measured using atomic absorption method and the equilibrium was established by conducting reaction for four hours. Gran and Sichen [41] used partitioning of magnesium between iron and silver where iron was equilibrated with an Ag-Mg alloy. The iron and Ag-Mg alloy were reacted for six hours to ensure equilibrium. The chemical composition of iron and Ag-Mg alloy was measured using ICP-AES (inductively coupled plasma atomic emission spectroscopy) method. The results from these two researches are summarized in Table 7 along with the value obtained from FactSage-7.1, FTmisc database [44]. It can be seen that the reported Fe-Mg thermodynamics is fairly consistent. The magnesium-magnesium interaction is not expected to play an important role in steelmaking conditions where magnesium solubility is expected to be in ppm level (note that this is interaction parameter for Raoultian standard state).

Table 7. Fe-Mg thermodynamic data with liquid Mg as reference

Reference	Zhang et al. [43]	Gran and Sichen [41]	FactSage 7.1 [44]
γ^0	91	57	76.7
ϵ_{Mg}^{Mg}	0	-495	0

Fe-Mg-O equilibrium have been studied by several researchers. Table 8 summarizes common methods used for this purpose.

Table 8. Method of Fe-Mg-O equilibrium measurement

Reference	Method	Characterization
Itoh et al. [45]	Crucible: MgO Ar-H ₂ deoxidized till 20 ppm at 1873 K followed by Mg addition Reaction time: 4 hours	Chemical analysis: infrared absorbable for dissolved oxygen, ICP for magnesium, aluminum and calcium
Seo et al. 2003, [46]	200 g electrolytic iron, MgO or Al ₂ O ₃ crucible, Ni-10%Mg for deoxidation Time: 30 minutes, no acid-insoluble inclusions, confirmed with fusion method.	Analysis: ICP for Mg and Al. Mg analysis accuracy: 0.1 ± 0.02 ppm Oxygen using LECO: ± 1 ppm accuracy
Ohta and Suito, [47]	Steel slag equilibrium experiment using CaO and MgO crucibles. Reaction time: 1-3 hours	Mg-measurement: ICP-ES, 1 ± 0.02 ppm [48], and O-measurement: LECO, 1 ± 0.7 ppm [49]
Nadif and Gatellier [50]	MgO crucible, Ni-15%Mg for magnesium addition, C and Al-deoxidation	Oxygen measured using electrochemical sensor

Table 9 shows a comparison of reported interaction parameters and equilibrium constants. The logarithm of the equilibrium constant (K , for $(\text{MgO})_s = [\text{Mg}]_{\text{wt}\%} + [\text{O}]_{\text{wt}\%}$) varies between -7.86 and 5.70. The value reported by Nadif and Gatellier [50] appears to be more than an order higher than all other values presented here. The larger value of Mg-O interaction parameter or non-unity activity of oxides could not explain the deviation between the measured equilibrium constant from that study and other studies and thermodynamically calculated values. A similar point applies to the deviation between the experimentally measured equilibrium constant of CaO reported by those authors as discussed later in section 8.2. Some issues that may have affected these studies are mentioned here. As presented in Table 8, the study reported in [50] used an electrochemical probe to measure oxygen activity in the melt. Turkdogan [51] proposed that the dissolved magnesium

and calcium in steel are likely to affect oxygen measurement in such setup. Moreover, the change in magnesium concentration with time was used to calculate the equilibrium constant. The decrease in magnesium concentration may also be due to flotation of spinel or MgO inclusions. The equilibrium constant and interaction parameter from different sources was also used to calculate the concentration of dissolved magnesium corresponding to 6 ppm dissolved oxygen. An iterative calculation was done using Goal Seek option in MS-Excel. It shows that the values calculated by FS7.1 database [44] is very close to that by Seo et al. [46]. The equilibrium data of Ohta and Suito [47] and of Itoh et al. [45] predicts lower dissolved magnesium. As expected, the equilibrium data of Nadif and Gatellier [50] predicts a much higher dissolved magnesium concentration. As shown later, the magnesium solubility predicted by FactSage did match the observed rate of Mg transfer to inclusions.

Table 9. Comparing Fe-Mg-O equilibrium data¹

Ref.	e_O^{Mg}	r_O^{Mg}	$r_O^{O,Mg}$	e_{Mg}^O	r_{Mg}^O	$r_{Mg}^{Mg,O}$	e_O^O	logK	Mg- ppm
[45]	-280	-2×10^4	4.62×10^5	-430	3.5×10^5	-61000	-0.17	-6.80	3.8
[46]	-266	-4×10^4	-6.96×10^5	-404	5.27×10^5	-1.2×10^5	0	-7.24	13.5
[47]	-300	1.6×10^4	4.8×10^5	-460	3.7×10^4	48000	0	-7.86	0.41
[50]								-5.70	33
[44]								-7.69	9

¹ For [O] = 6 ppm and unit MgO activity, K is the equilibrium constant for (MgO) = [Mg]+[O]

5 Laboratory scale: experiments and kinetic modeling

5.1 Objective

The objectives of laboratory experiments were as follows:

- a) To experimentally determine the inclusion removal rate constant(s) for laboratory scale aluminum deoxidation of steel
- b) To determine the effective rate and mechanism of magnesium transfer in steel due to steel-crucible reaction with the help of induction furnace aluminum deoxidation experiment and a kinetic model.
- c) To develop a kinetic model for laboratory scale induction furnace experiments that can predict changes in steel, slag and inclusions during steelmaking and to test its usability and limitations

5.2 Removal of inclusions

As described earlier, significant differences can be expected in inclusion removal behavior under laboratory conditions compared with industrial operation. Harada et al. [28] used two inclusion flotation parameters to model some of their laboratory experiments, the parameters were much larger than the laboratory experiments in this work. However, there has not been any study, to the best of my knowledge, to experimentally study the kinetics of inclusion removal just after aluminum deoxidation. Experiments were designed to track early inclusion removal by taking samples at very small time intervals after aluminum deoxidation. The formation and removal of spinel inclusions was also studied by deoxidizing a steel melt with Al-10% Mg alloy.

5.2.1 Experiments

5.2.1.1 Formation and removal of alumina inclusions

250 g of electrolytic iron was placed in an Al_2O_3 crucible supplied by Almath (dimension: O. D. = 47 mm, I. D. = 42 mm and h = 49 mm). Expected oxygen concentration in the electrolytic iron was about 360 ppm. Molten electrolytic iron was deoxidized by dropping aluminum shot (0.15 wt% of steel mass to have access of aluminum in the melt to account for higher oxygen in electrolytic iron and/or from any reoxidation) on the melt surface using the addition/sampling port; the time of aluminum addition was considered as time=0. The sampling details are described in Table 10. A steel rod of 0.25" diameter was dipped in the steel bath 15 s after deoxidant addition to sample inclusions floating on the steel surface. The dipped section of the rod was subsequently cut longitudinally (see Figure 11) and analyzed by SEM.

Table 10. Addition and sampling details for experiment-5.1 (alumina crucible)

Time (minutes)	0:00	0:15	0:45	1:40	3:25	4:25	5:35
Event	Al-addition	Steel-rod dipped	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5



Figure 11. Tip of steel rod dipped in molten steel 1 minute after deoxidation (length scale in inches)

5.2.1.2 Formation and removal of spinel inclusions

Al-10% Mg alloy was used for deoxidation to form spinel inclusions just after reoxidation instead of alumina inclusions upon deoxidation. As expected from the Al-Mg phase diagram (see Figure 12), the alloy had pure aluminum (matrix) and β -phases (see Figure 13). The alloy also contained some spinel inclusion clusters as shown in Figure 13.

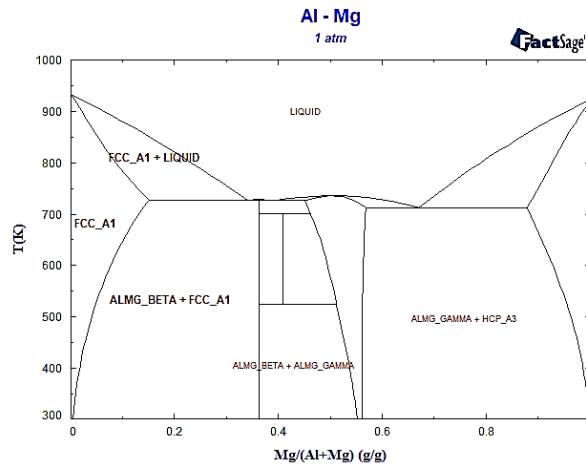


Figure 12. Al-Mg phase diagram (FactSage; BINS database)

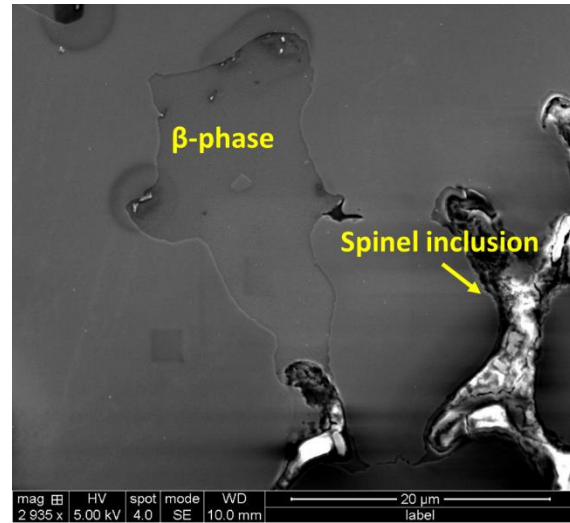


Figure 13. Phase and impurities in Al-10Mg alloy

Experiment-5.2 was similar to experiment-5.1 except that Al-10Mg alloy wrapped in iron foil (0.15 wt% of steel mass) was added for deoxidation to avoid loss of magnesium due to vaporization during the addition. The sampling details for this experiment are described in Table 11.

Table 11. Addition and sampling details for experiment-5.2 (alumina crucible)

Time (min.)	0:00	1:00	2:00	4:12	7:00	9:30	12:00	14:36
Event	Al-10% Mg addition	Steel-rod dipped	S1	S2	S3	S4	S5	S6

Although initial inclusions formed in experiment-5.2 were spinel (with molar Mg:Al < 0.5), these reverted to pure alumina inclusions possibly due to magnesium evaporation from the melt surface (see Figure 17). Therefore, experiment-5.3 was conducted in an MgO crucible ($\varnothing=61$ mm, supplied by Tateho Ozark Technical Ceramics Inc.) to maintain MgO concentration in inclusions throughout the experiment. The Al-10Mg alloy wrapped in iron foil (0.15% of steel mass) was added at t=0 minute in 600 g of electrolytic iron at 1873 K. The addition and sampling details are provided in Table 12.

Table 12. Addition and sampling details for experiment-5.3 (MgO crucible)

Time (minutes)	0:00	1:00	2:45	6:15	10:45	12:45
Event	Al-10Mg addition	Steel-rod dipped	Sample 1	Sample 2	Sample 3	Sample 4

5.2.2 Results and discussion

5.2.2.1 Removal of alumina inclusions

Figure 14 shows the presence of large alumina clusters on the surface of the steel rod dipped 15 seconds after aluminum deoxidation. High magnification micrographs revealed that though the clusters are readily sintered, individual micron and submicron sized alumina particles were still present. The large concentration of inclusions on this surface also shows that a significant proportion of inclusions immediately float to top surface of steel bath resulting in a sharp decrease in inclusion concentration at the beginning of experiment. It should be noted that the aluminum shots were dropped on the melt surface. The drop distances for the previous induction furnace setup and new setup were 0.3 m and 0.5 m respectively and the corresponding impingement velocities are 2.4 m/s and 3.1 m/s respectively. The distance traveled by falling aluminum shot

inside steel melt was calculated considering drag force $\left(\frac{1}{2} A \rho v^2 C_D\right)$, buoyancy and gravity. It was found that the aluminum shot was expected to reach to the bottom of the steel melt in both cases but was expected to be in the melt for a brief time (0.1 second) before bouncing back to the top of liquid steel.

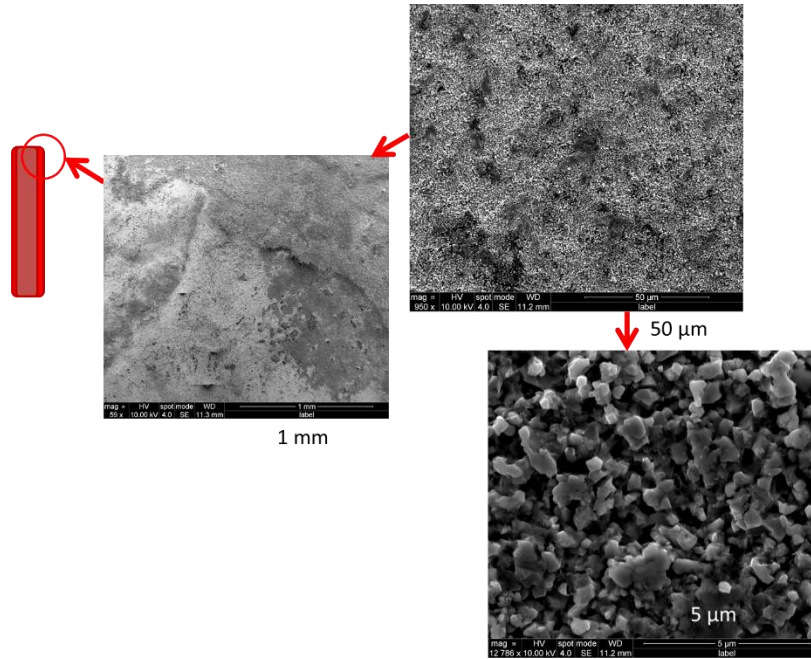


Figure 14. Alumina inclusions on the surface of dipped steel rod for experiment-1

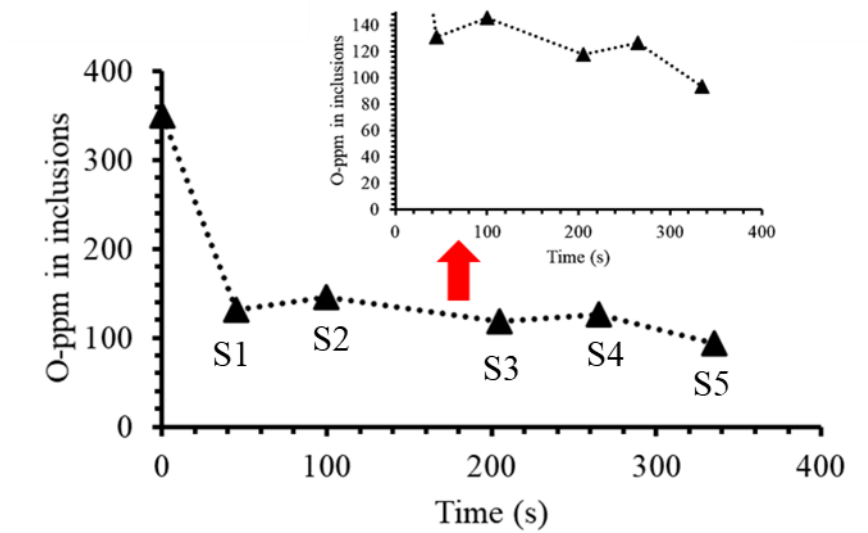


Figure 15. Initial changes in inclusion concentration during experiment-5.1

The inclusion concentration (plotted as bound oxygen in inclusions) for experiment-5.1 is shown in Figure 15. The expected dissolved oxygen in steel was about 5 ppm for ~0.3 wt% aluminum and the initial oxygen in molten electrolytic iron was expected to be ~360 ppm based on measured oxygen using LECO from one such experiment. Therefore, initial bound oxygen was taken to be 350 ppm for the plot in Figure 15 and other similar plots shown later. The initial drop in inclusion concentration is expected due to rapid flotation of inclusions just after aluminum addition as observed on dipped steel rod surface. When aluminum piece is dropped in the melt, it is expected to hit the bottom of the crucible and bounce back to the top surface within 0.1 second. As aluminum touches the melt surface, a solid layer of steel is expected to develop due to quenching which may not melt within 0.1 s and effective deoxidation may occur from top surface of the melt resulting in faster removal of deoxidation product from the bulk of the melt to the top. The samples taken after 100s show a much slower decrease in inclusion concentration as shown in inset. The difference in initial inclusion removal behavior between laboratory experiment and industrial operation (as

shown later in Figure 54) may also be attributed to a smaller flotation distance (2.5 cm compared to 2.5 m) and differences in Al addition practice.

5.2.2.2 Removal of spinel inclusions (in alumina crucible)

Al-10Mg was used to deoxidize electrolytic iron melt in experiment-5.2 to form spinel inclusions after deoxidation. The surface of steel rod dipped 1 minute after deoxidation showed the formation of spinel inclusions just after deoxidation; see Figure 16.

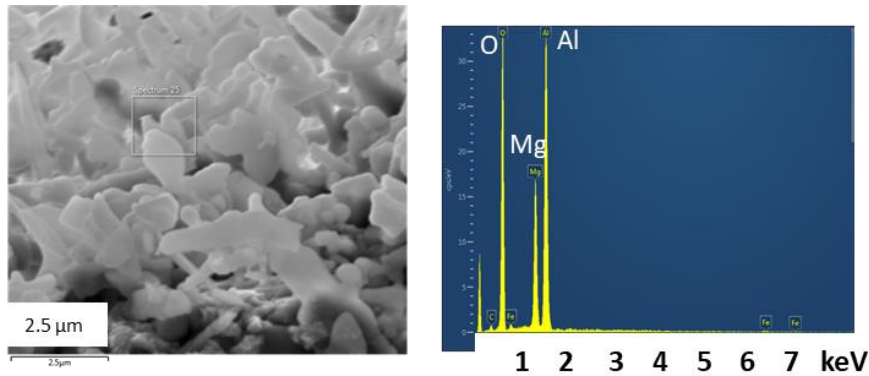


Figure 16. Inclusions on the surface of dipped steel rod in experiment-2

Figure 17 (a-c) show the composition of inclusions at $t=2$, 9.5 and 14.6 minutes. The MgO concentration in inclusion was found to reduce significantly until 10 minutes after deoxidation indicating magnesium evaporation from the melt. The loss of magnesium from inclusions was quantified based on inclusion composition and concentration and plotted in Figure 17(d). The net magnesium loss in inclusions was expected to be the sum of loss due to inclusion flotation and change in equilibrium MgO concentration in inclusions due to magnesium vapor loss from the melt. The initial sharp decrease can be attributed to faster inclusion removal commensurate to reduction in bound oxygen in inclusions as shown in Figure 18. Magnesium loss due to evaporation was also shown by the formation of MgO and spinel whiskers on the crucible wall

above steel melt surface as shown in Figure 19. The evaporation of magnesium from steel melt will be discussed later in section 9.2.

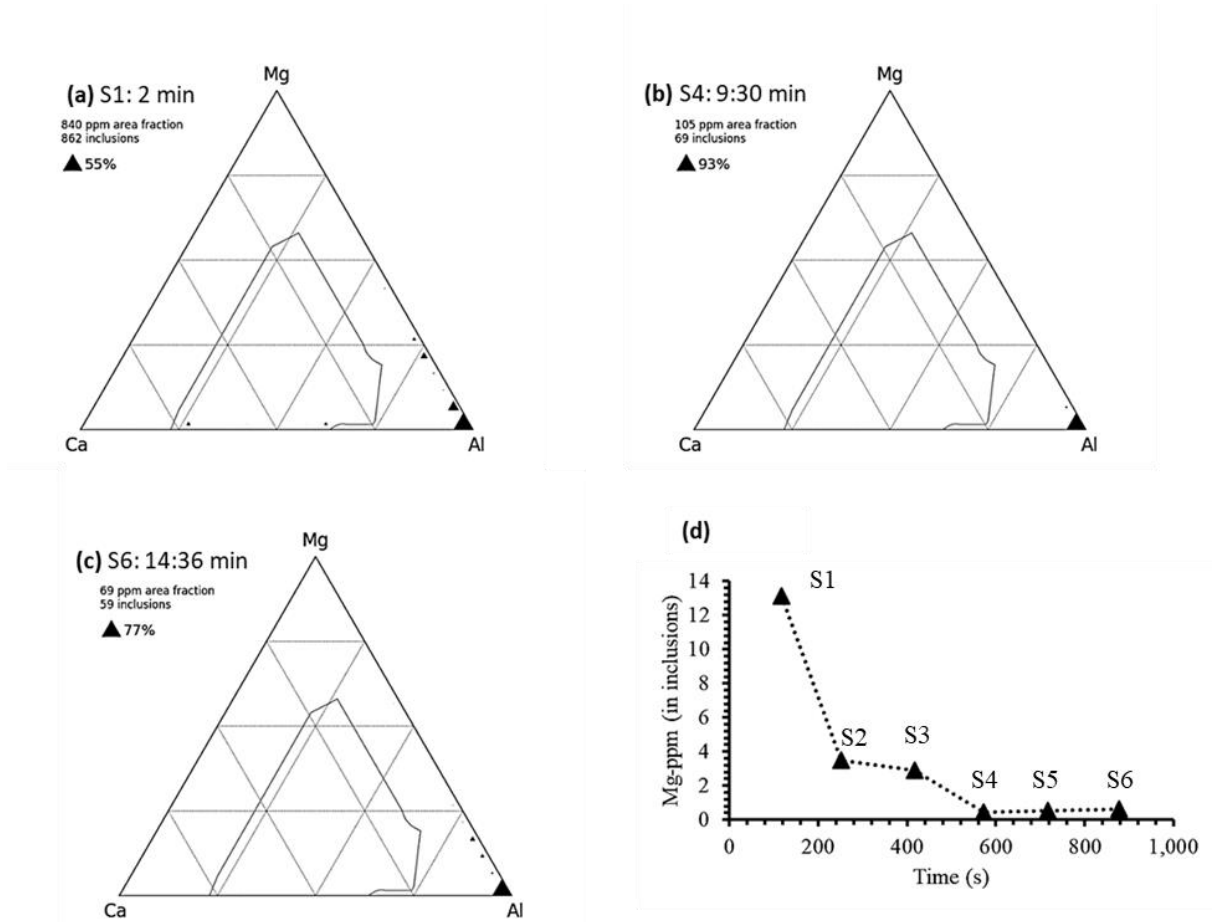


Figure 17. Inclusion composition and bound magnesium (in inclusions) in steel with time for experiment-5.2

A continuous decrease in inclusion concentration was observed during experiment-5.2 as shown in Figure 18. Two regimes of inclusion removal can be seen in this plot as fitted by two first order rate constants namely β_1 and β_2 . The first regime corresponds to the removal of large inclusions/large clusters formed upon deoxidation, and the other to flotation of generally smaller inclusions. The first order rate constants were fitted using experimentally measured inclusion concentration represented in terms of bound oxygen to inclusions. The bound oxygen was calculated from the concentration of aluminum and magnesium cations estimated from area

fraction of inclusions. The fitted values of β_1 was 0.55%/s and the value of β_2 was 0.35%/s. The time for the change in inclusion flotation rate was taken equal to three minutes based on observation of this and several other experiments as shown later.

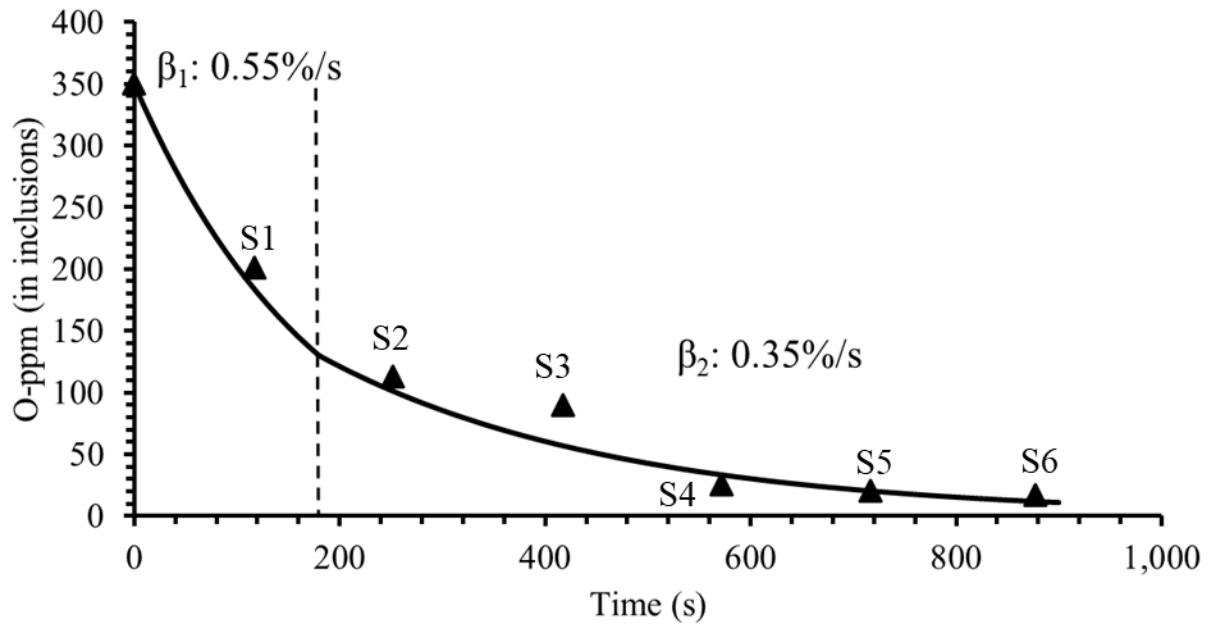


Figure 18. Inclusion removal trend for experiment-5.2: fitting two rate constants

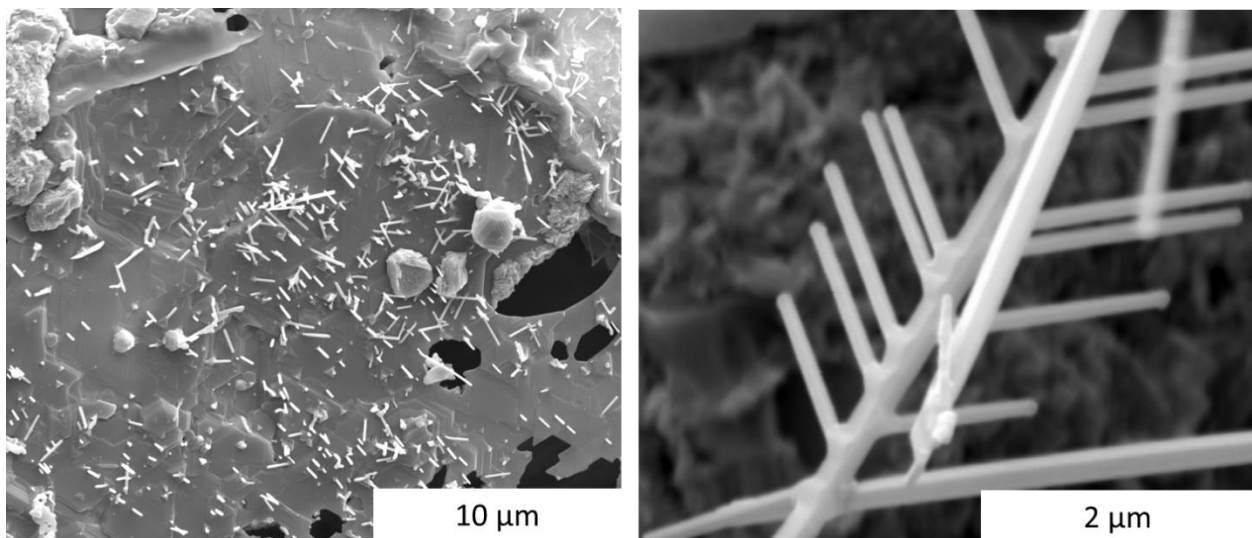


Figure 19. Formation of spinel whiskers on Al_2O_3 crucible wall due to Mg evaporation from liquid steel

5.2.2.3 *Removal of spinel inclusions (in MgO crucible)*

The MgO concentration in inclusions reduced significantly after Al-10Mg addition during experiment-5.2 (alumina crucible). As an MgO crucible is known to transform alumina inclusions to spinel inclusions by supplying magnesium to steel through steel-crucible reactions [52], experiment-5.3 was conducted in an MgO crucible to compensate magnesium loss from liquid steel due to evaporation. The inclusion analysis results (see Figure 20 (a-c)) showed that the MgO crucible helped in compensating for magnesium loss by evaporation and the MgO concentration in inclusions initially remained almost constant and increased towards the end. In the S4 sample (taken at t=12:45 minutes), the MgO concentration in inclusions was at a maximum. Figure 20 (d) shows the magnesium content in inclusions over time with changes due to inclusion removal, magnesium evaporation from melt and magnesium pick-up in melt due to steel-crucible reaction. The net magnesium pick-up from MgO crucible is discussed in more detail for different MgO crucibles in the next section.

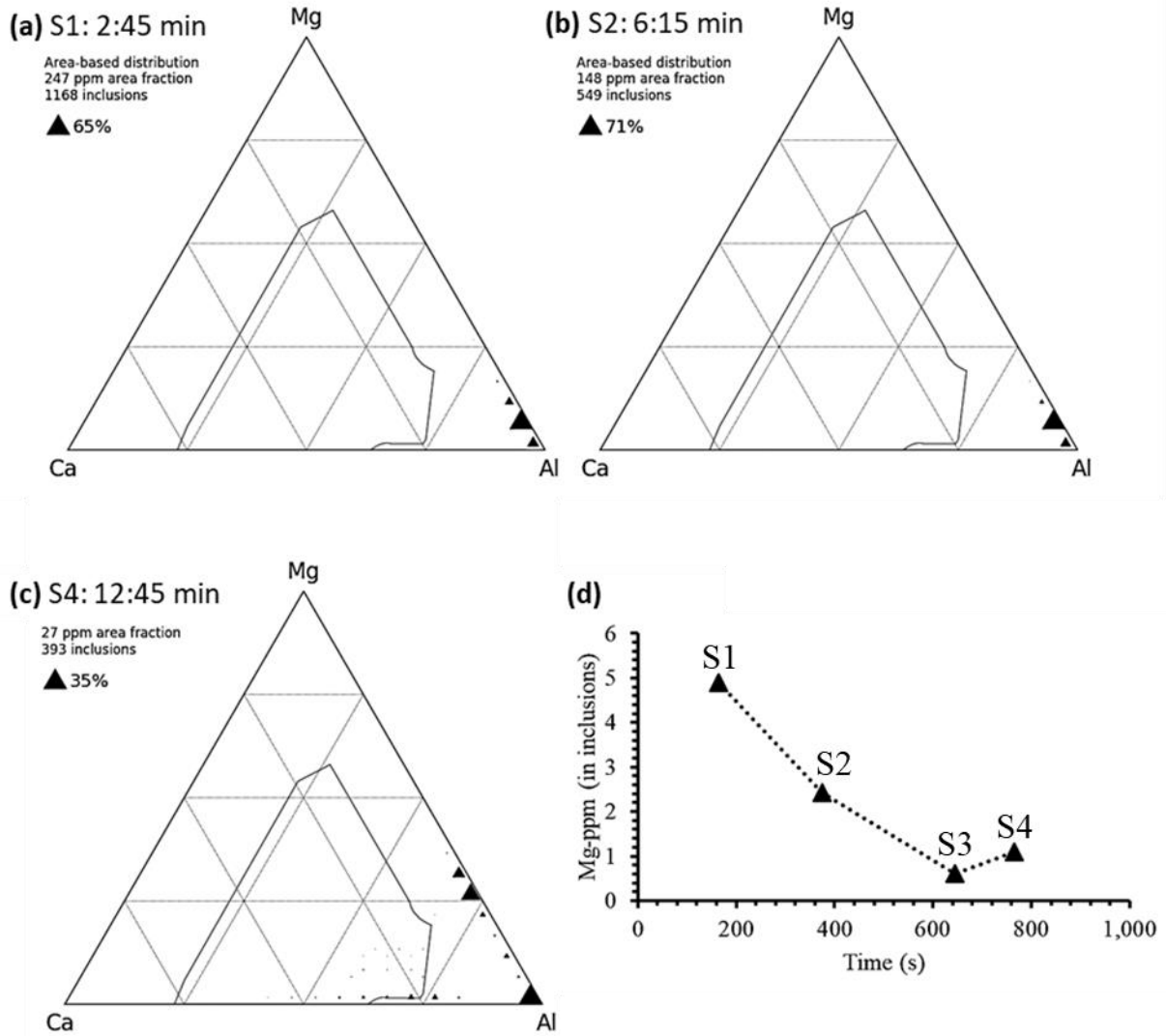


Figure 20. Inclusion composition and magnesium concentration as inclusions with time for experiment-5.3

Similar to experiment-5.2, the inclusion removal in experiment-5.3 also had a transition in behavior. The fitted inclusion removal rate constants for two inclusion removal regimes were: $\beta_1 = 1.1\%/s$ and $\beta_2 = 0.35\%/s$. The initial inclusion removal rate was much faster in experiment-5.3 compared to experiment-5.2. Since the initial inclusions in both experiments had similar composition, the difference in inclusion removal rate might be due to crucible dimensions. The diameter of MgO and Al₂O₃ crucible was 61 mm and 42 mm respectively and the melt depths in

two cases were 2.6 and 3.0 cm respectively. The top area to volume ratio for experiment 5.2 and 5.3 were 7 cm² and 12 cm². For experiment-5.3, larger surface area on top of the steel melt may improve the inclusion removal rate as a larger space is available to cover for the floated inclusion on top of the liquid steel.

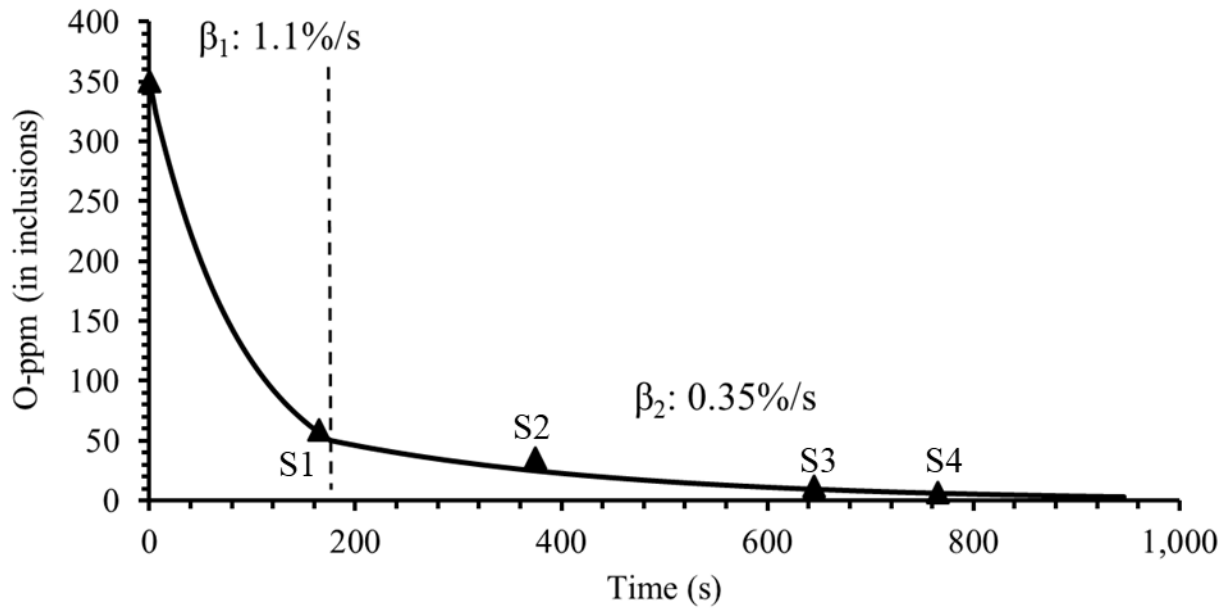


Figure 21. Inclusion removal behavior in experiment-5.3

5.2.3 Conclusions

It can be concluded that the inclusion removal behavior under laboratory condition changes with time and it needs two first order rate constants to model. The initial rate constant was higher for an MgO crucible, with a larger diameter, compared with smaller diameter alumina crucible. As shown later, the inclusion removal during ladle refining in the plant could be modeled using one rate constant. The difference in inclusion behavior is likely due to smaller flotation distance for inclusions under laboratory condition. Also, the liquid steel was partially killed during tapping, the flotation of those inclusions were not studied in the current work. Initial dissolved oxygen at the

beginning of ladle refining was in 100-180 ppm; much lower than that expected at tap (~1000 ppm).

5.3 Rate of Mg transfer from MgO crucible to liquid steel

5.3.1 Introduction

A literature review regarding transformation of alumina inclusions to spinel inclusions due to magnesium pick-up was presented in section 4.1.2.4. There appears to be a difference in observations regarding whether MgO crucible or refractory can supply enough Mg for spinel formation. Induction furnace experiments were conducted to find the rate of magnesium transfer with the help of a kinetic model and inclusion analysis (size and composition) using automated SEM ASPEX. The steel-crucible interface was also analyzed after the experiment to understand the mechanism of magnesium transfer.

5.3.2 Experimental

The induction furnace setup and steel sampling method were described in section 3.1.1. 600g of electrolytic iron containing 7 ppm of sulfur and approximately 350 ppm of oxygen was melted and then deoxidized by adding aluminum at 1873 ± 10 K. An MgO crucible of 61 mm diameter crucible was used inside a graphite crucible susceptor. The time of aluminum addition was assigned as time = 0 for experiment-5.4 and 5.5. It should be noted that the MgO crucible used for experiment-5.4 and 5.5 were from the same supplier but from different batches. The MgO crucibles used for experiment-5.4 and experiment-5.5 were marked as type-1 and type-2. Experiment-5.4 was conducted in the vacuum sealed quartz tube chamber and experiment-5.5 was conducted inside a stainless steel chamber. The addition and sampling details for these experiments are described in Table 13 and Table 14.

Table 13. Addition and sampling details for experiment-5.4 (MgO crucible)

Time (minutes)	0:00	3:00	7:00	12:00	17:00	25:00	40:00
Event	0.3% Al addition	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6

Table 14. Addition and sampling details for experiment-5.5 (MgO crucible)

Time (minutes)	0:00	1:00	6:00	11:00	15:00	30:00	46:00
Event	0.16% Al addition	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6

5.3.3 Kinetic modeling of magnesium pick-up from MgO crucible

Magnesium transfer from MgO crucible was modeled using the approach described in section 4.2. The change in inclusion composition and concentration due to steel-crucible interaction can be modeled by considering 1) inclusion removal due to flotation 2) the reaction between steel and MgO crucible, 3) the loss of magnesium from liquid steel due to evaporation and 4) the steel-inclusion reaction as shown in Figure 22.

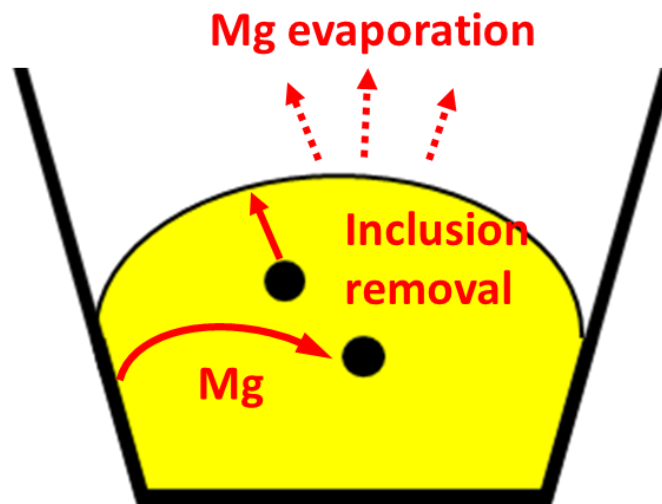


Figure 22. Schematic of magnesium transfer from steel-crucible to steel-inclusion interface

Inclusion removal was modeled using two removal rate constants β_1 and β_2 as described earlier. The reaction between steel and crucible was considered a mass-transfer controlled reaction with mass transfer in steel as the rate controlling step. To model the mass transfer controlled reaction, a fixed fraction of steel was assumed to reach the steel-crucible interface in each time step and equilibrate with the crucible. The fraction of steel reacting to crucible in each time step was calculated using Equation 3.

As magnesium has a relatively high vapor pressure over the liquid steel melt, some magnesium loss may occur from the melt. There are two possible interfaces for this under the conditions of experiment-5.4 and experiment-5.5: magnesium evaporation from top of steel melt (there was no slag) and diffusion of magnesium vapor through pores in MgO crucible. Mitsutaka et al. [53] studied evaporation of zinc from liquid iron and its kinetics. Magnesium evaporation from top of the liquid steel surface was studied in a similar fashion in this work. It can be described as a three step process: magnesium transport from bulk of liquid steel to the steel-argon interface, evaporation of magnesium at liquid steel-argon interface and transport of magnesium in the gas phase. Since the magnesium vapor pressure under the current experimental condition was very high ($=0.025$ atm for Fe-0.26%Al-7.7 ppm O and $a_{\text{MgO}} = 1$), the Langmuir evaporation rate at the steel-argon interface was expected to be very fast compared to other two and was not expected a rate determining step. Mass transfer coefficient in bulk steel was fitted to the MgO concentration in inclusions and was equal to $4.5 \times 10^{-5} \text{ m/s}$ as shown later in Figure 30. Gas phase mass transfer coefficient was calculated using Equation 15 for natural convection [54]. The binary diffusivity for magnesium vapor in argon at 1873 K was calculated using the method suggested by Poling et al. [55] and was equal to $5.8 \times 10^{-4} \text{ m}^2/\text{s}$. The calculated gas phase mass transfer coefficient (using $k = \text{Sh} \cdot L / D_{\text{AB}}$) for conditions in experiment-5.4 was equal to 0.12 m/s which

was much higher than the mass transfer coefficient in liquid steel. This results in very large value of $k\Delta C$ for gas phase mass transfer compared to liquid phase mass transfer ($\Delta C_{\text{gas phase}} = 0.16$ and $\Delta C_{\text{liquid steel}} = 1.1 \times 10^{-4}$ moles). Therefore, mass transfer in the liquid steel was considered to be the rate controlling step for magnesium evaporation from liquid steel. Assuming mass transfer in steel to be the rate limiting, magnesium loss rate (in mass fraction/s) was calculated using Equation 16.

$$Sh = 0.54Ra^{\frac{1}{4}} \quad \text{Equation 15}$$

Where Sh is Sherwood number and Ra is Rayleigh number

$$\dot{M}_{g_{loss}} = \frac{k_s A_c \rho_s C_{Mg}}{W_{steel}} \quad \text{Equation 16}$$

k_s : steel mass transfer coefficient, A_c : steel-crucible interfacial area, W_s : mass of steel, ρ_{steel} : density of liquid steel and C_{Mg} : concentration of dissolved magnesium in steel at that instant of time in calculation.

Magnesium loss through crucible pore was calculated using an estimated effective diffusivity of magnesium vapor through pores in MgO crucible. The effective diffusivity was calculated from total diffusivity and porosity and tortuosity of crucible using Equation 17 ($D_{eff} = 3.1 \times 10^{-8} \text{ m}^2/\text{s}$, for crucible porosity of 1% as reported by the supplier). The magnesium loss rate was estimated using Fick's first law of diffusion, see Equation 18. The magnesium loss was approximately 10^{-6} ppm/s and dissolved magnesium=10 ppm. Thus the magnesium loss through crucible pores can be considered insignificant.

$$D_{eff} = (\text{porosity})^2 D_{total} \quad \text{Equation 17}$$

Where: $D_{total} = \frac{D_{Ar-Mg} \times D_{Knudsen}}{D_{Ar-Mg} + D_{Knudsen}}$

$$J = -D_{eff} \left(\frac{\Delta C}{\Delta x} \right)$$

Equation 18

Where J is the magnesium flux through crucible wall, ΔC is the concentration gradient across the wall (concentration outside crucible was considered zero) and Δx is the crucible thickness.

The steel-inclusion reaction was considered to be at equilibrium due to the very large interfacial area of inclusions compared to their volume and rapid mass transfer as discussed in previous work [52]. The MgO concentration in alumina inclusions increase due to steel-inclusion reaction resulting into a net Mg transfer from crucible to inclusions during the experiment.

Figure 23 shows a flow chart illustrating the sequence of calculations in the model. The model was implemented using the macro processing feature in FactSage which can take input from MS-Excel and calculate required chemical equilibrium. The output was also written back to another sheet in MS-Excel. For the equilibrium calculation, the FTmisc solution database was used for the steel phase and FToxid and Fact-PS (pure substance) databases were used for inclusions.

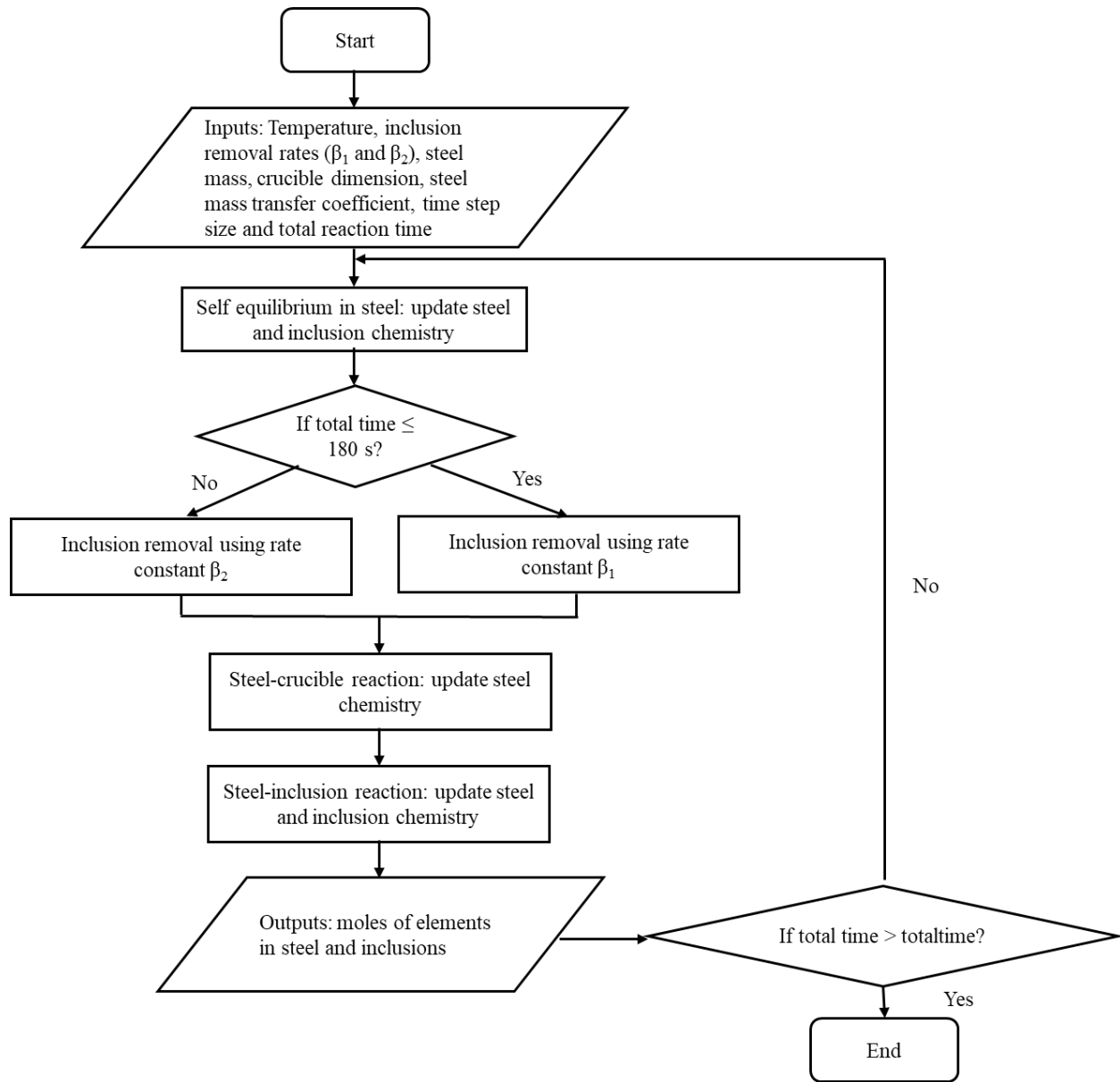


Figure 23. Schematic of the model

5.3.4 Results and Discussion

5.3.4.1 Experimental results

Six steel samples were taken per experiments for experiments 5.4 and 5.5. The steel samples were analyzed for inclusion chemistry and geometry using automated feature analysis in SEM ASPEX-Explorer. The rate of transformation of alumina inclusions to spinel inclusions was quantified by

calculating area based average Mg:Al molar ratio in inclusions using Equation 19.. The change in Mg/(Mg+Al) molar ratio with time during experiments -5.4 and 5.5 is shown in Figure 24.

$$(Mg:Al)_{average} = \frac{\sum x_i A_i}{\sum A_i} \quad \text{Equation 19}$$

Where x_i and A_i are Mg:Al molar ratio and area of individual inclusions in a sample.

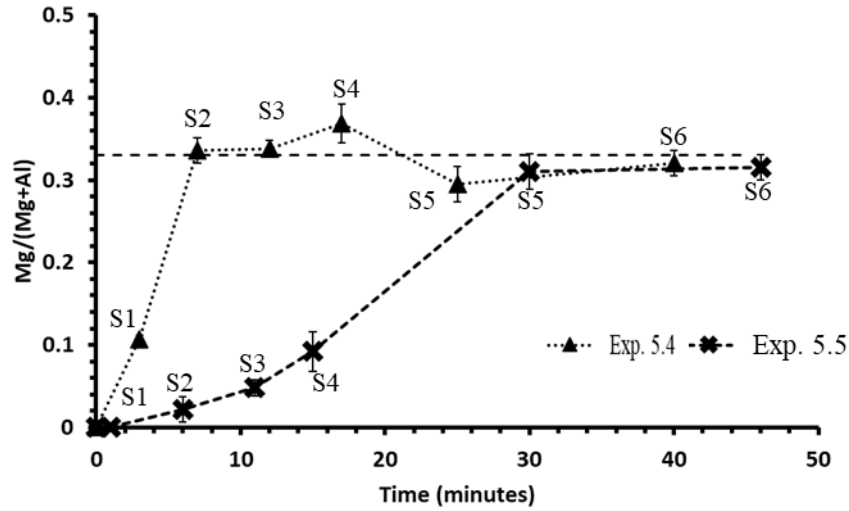


Figure 24. Mg/(Mg+Al) molar ratio in inclusions with time in experiments-5.4 and 5.5, the horizontal broken line is stoichiometric $MgAl_2O_4$

As shown in Figure 24, alumina inclusions transformed to spinel inclusions during both experiments. The decrease in Mg/(Mg+Al) molar ratio in the sample taken at the 25th minute during experiment-5.4 was most likely due to reoxidation of liquid steel during sampling. Reoxidation of liquid steel is expected to generate fresh alumina inclusions which can bring down the average magnesium oxide concentration in inclusions. The effect of reoxidation on inclusion concentration and composition will be discussed in detail later. It can also be seen from Figure 24 that the rate of transformation was much lower during experiment-5.5 (type-2 crucible) : all

inclusions were transformed to spinel within 6 minutes for experiment-5.4 but it took more than 20 minutes during experiment-5.5. The different magnesium transfer rate in these two experiments was likely due to different impurities levels in the crucibles. According to the crucible supplier, the allowed maximum impurities are: 0.6% CaO, 0.2% SiO₂, 0.4% Al₂O₃, 0.1% Fe₂O₃ and 0.01% B₂O₃. Figure 25 shows part of a cross-section of the crucible wall before the experiment and the inner surface of the crucible after experiment-5.4. It can be seen that the crucible contained CaO-Y₂O₃ impurity which helped in the formation of a liquid slag like layer during the experiment. In addition to CaO-Y₂O₃, CaO-Al₂O₃-SiO₂ impurities were also found in the crucible. A detailed EDS analysis of crucible before and after experiment revealed that the average Ca²⁺/Al³⁺ ratio reduced from 1.5 to 0.5 in the slag layer during the experiment-5.4. An increase in Al₂O₃ concentration in the slag layer was expected due to reduction of MgO from the slag like layer by dissolved aluminum in liquid steel. However, the inner surface of type-2 crucible was coated with a spinel (*MgO · Al₂O₃*) layer after the experiment as shows in Figure 26. This observation was similar to that by Verma et al. [35] where a much lower rate of the transformation of alumina inclusions to spinel inclusions was observed when inner surface of the MgO crucible was found to be coated with a spinel layer after the experiment. It was likely that the impurities in type-2 crucible were not enough to form a slag like layer on the crucible wall. This effect was considered in the model by equilibrating the liquid steel with MgO saturated slag (52% CaO, 35% Al₂O₃ and 13% MgO) for experiment-5.4 and with spinel for experiment-5.5, for the steel-crucible reaction.

Previous studies have shown that the FTmisc database of FactSage tends to over-predict calcium concentration in steel [52], [56]. In order to avoid this discrepancy, the calcium transfer from slag layer to steel was ignored by deleting Ca and Ca*O (Ca-O associate) end members from the Fe-

LQ phase in the FTmisc database. No calcium containing inclusions were observed in either of the experiments.

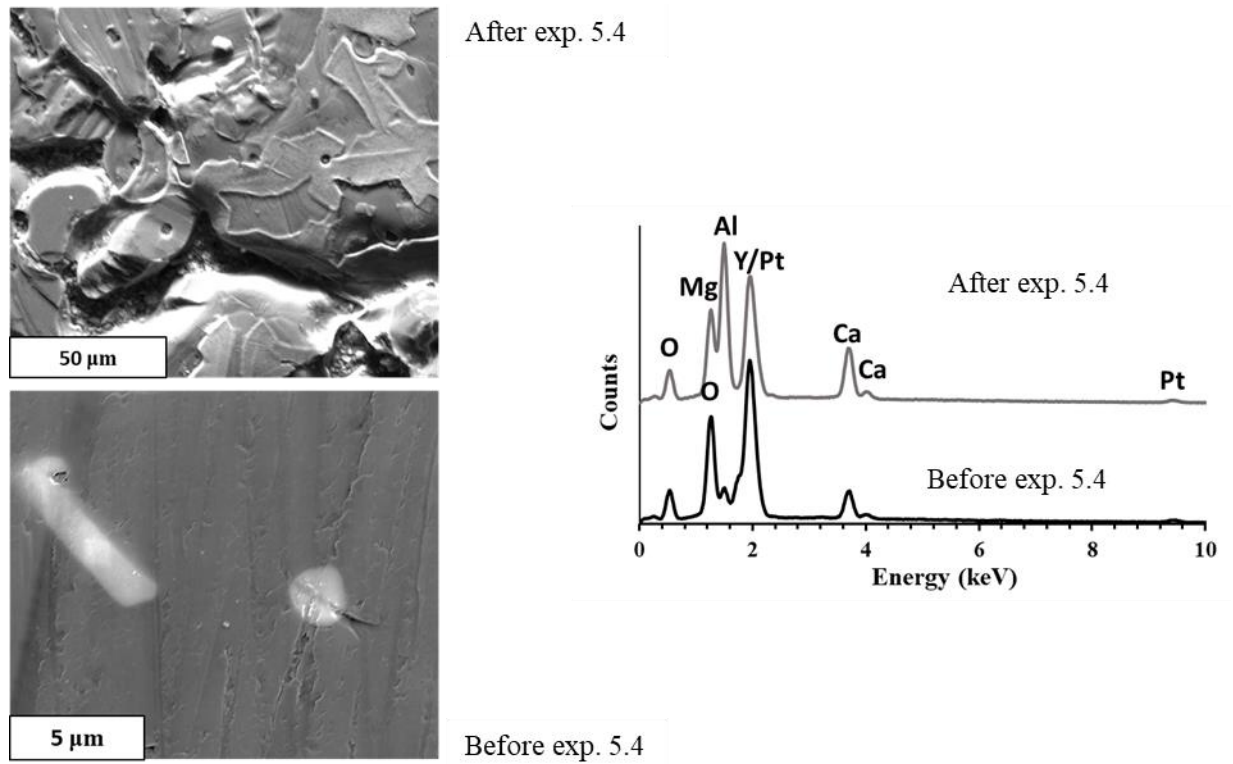


Figure 25. Inner surface of crucible before and after experiment-5.4. Presence of a slag like layer can be seen in the microstructure after the experiment.

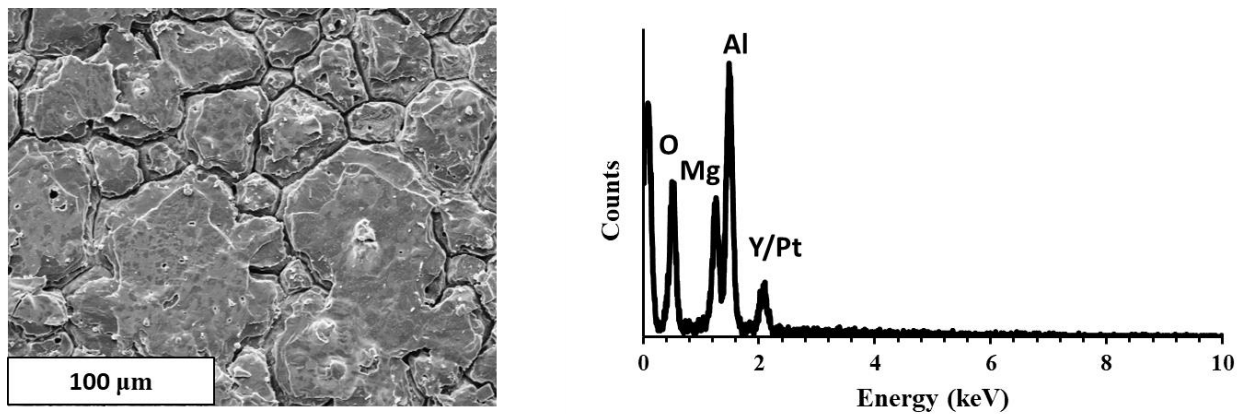


Figure 26. Inner surface of MgO crucibles after experiment-5.5, showing a spinel coating

5.3.4.2 Modeling results

As described earlier, there were three unknowns for the kinetic model: two flotation rate constants (β_1 and β_2) and the mass transfer coefficient in steel phase. All three parameters were found using the measured area and composition of inclusions from SEM ASPEX-Explorer. The volume fraction of inclusions was considered same as area fraction. The mass fraction of inclusion was then calculated using Equation 20.

$$\text{Mass fraction} = (\text{volume fraction}) * \frac{\rho_i}{\rho_s} \quad \text{Equation 20}$$

Where ρ_i is the density of inclusions ($\rho_{Al_2O_3} = 3980 \text{ kg/m}^3$, $\rho_{MgAl_2O_4} = 3580 \text{ kg/m}^3$ [44]) and density of steel (ρ_s) = 7800 kg/m^3 .

An area based average inclusion composition (as Mg:Al molar ratio) was used to calculate the total oxygen and magnesium in inclusions as described in Equation 19. The bound oxygen in inclusions was used to fit inclusion removal rate constants β_1 and β_2 for two inclusion flotation regimes as shown in Figure 27. The calculated values agree well for experiment-5.5 but the fitting is not that good for experiment-5.4. The likely reason is the reoxidation during sampling, for sample 2 and sample 4, as shown by arrows in Figure 27 (a). The inset of Figure 27 (b) illustrates fitting of second rate constant (β_2). The fitted β_1 and β_2 rate constants for experiment-5.4 were 0.45%/s and 0.09%/s and the values for experiment-5.5 were 0.91%/s and 0.13%/s. The smaller values of β_1 and β_2 in for experiment-5.4 could be attributed to reoxidation during experiment-5.4. It should also be noted that the flotation rate constants for experiment 5.5 are smaller than those for experiment-5.3 as shown in Figure 21 ($\beta_1 = 1.1\%/s$ $\beta_2 = 0.35\%/s$). The higher flotation rate constant for experiment-5.3 can be attributed to initial evaporation of magnesium assisted by

expected vigorous stirring by magnesium vapor during Al-10%Mg addition. Van Ende et al. [57] showed that inclusions generated from reoxidation are expected to have a log-normal size distribution as their sizes are controlled by nucleation and growth. According to [57], the inclusion sizes are expected to follow a power law distribution if the growth is controlled only by collision and breaking of inclusions. The population density function was calculated for samples 2-5 from experiment-5.4 using Equation 21 [57].

$$PDF = \frac{n_v(L_{XY})}{L_Y - L_X} \quad \text{Equation 21}$$

Where $n_v(L_{XY})$ is the volume density of inclusions (number/m³) and $(L_Y - L_X)$ is the width of the size interval. For this calculation, volume density of inclusions was calculated from area density of inclusions using $n_v = n_A/\bar{D}$ where $\bar{D}$ is the average diameter of inclusions in a sample.

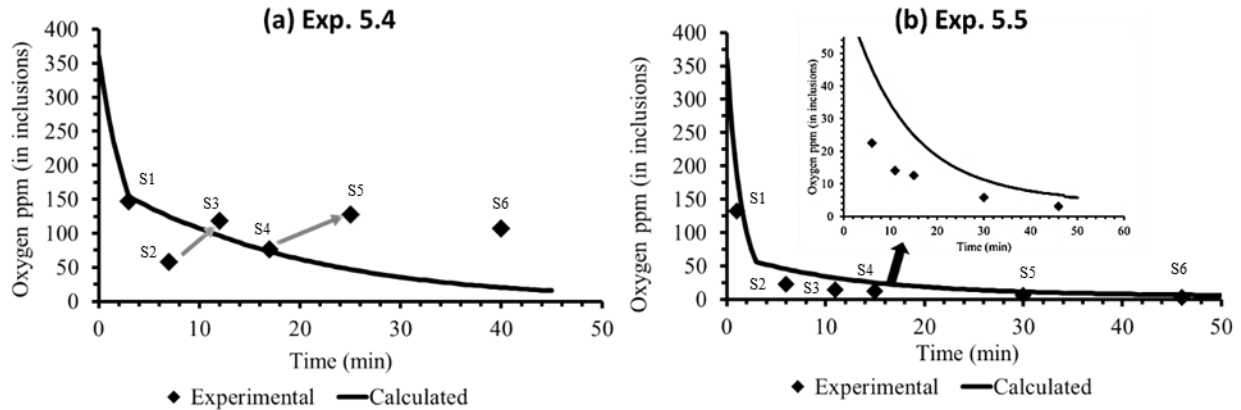


Figure 27. Measured and fitted amount of oxygen in inclusions for a) experiments 5.4, the arrow shows an increase in inclusion concentration possible due to reoxidation during sampling and b) 5.5.

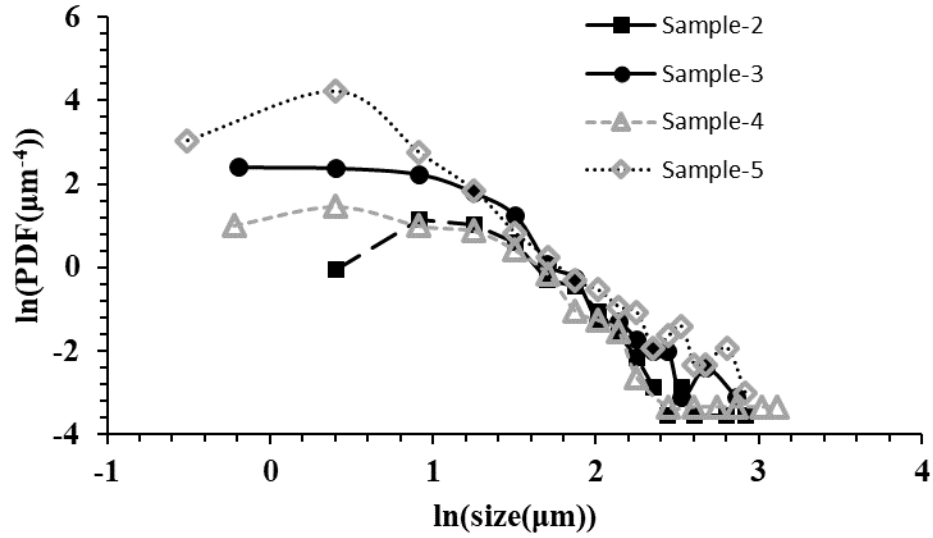


Figure 28. Population density function of inclusions for Samples 2-5 from exp. 5.4

It can be seen from Figure 28 that the number density of smaller inclusions is much higher for samples-3 and 5 compared to samples-2 and 4 indicating the formation of fresh alumina inclusions due to reoxidation. The inclusion size distribution appears to be between log normal and power law distributions indicating that the size distribution was never completely controlled by collision/breaking of inclusions, also indicating a role of reoxidation.

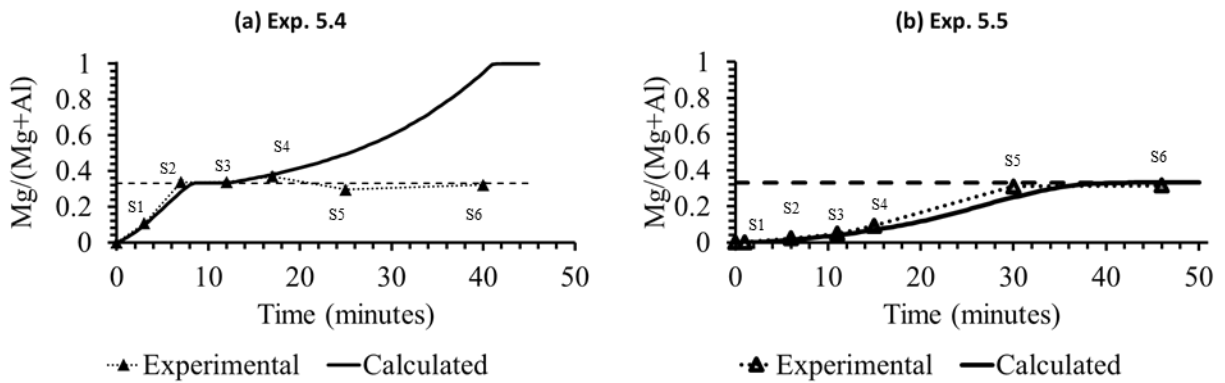


Figure 29. Experimental and calculated inclusion composition for experiments 5.4 and 5.5

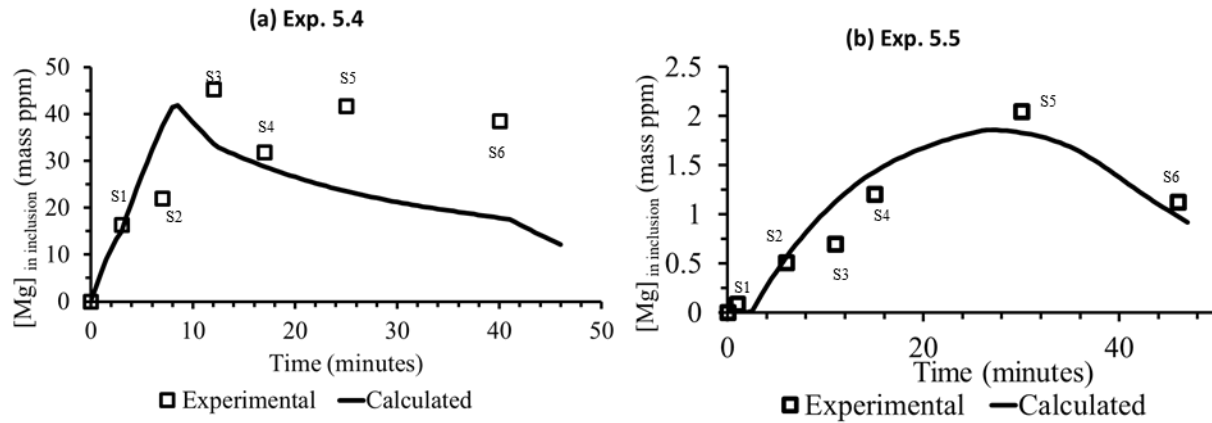


Figure 30. Measured and fitted amount of magnesium in inclusions for experiments 5.4 and 5.5.

Figure 29 shows the experimental and calculated average inclusion experiment-5.4 and 5.5. The calculated inclusion composition is the same as experimental for experiment-5.5: both show the transformation of alumina inclusions to spinel inclusions. For experiment-5.4, the calculated inclusion composition shows that the MgO pick-up in inclusions should have continued beyond the transformation to spinel inclusions if there was no reoxidation. The average inclusion composition in sample taken at $t=17$ minutes, Figure 29, can be seen to be more than stoichiometric spinel composition. In later samples from experiment-5.4, a few pure MgO inclusions were also observed. The bound magnesium in inclusions in steel was used to fit the mass transfer coefficient in steel for steel-crucible reaction and for magnesium evaporation as shown in Figure 30. The calculated magnesium content in inclusions agrees well with the experimental values except for the later data points from experiment-5.4. As shown in Figure 30 (a), the calculated bound magnesium concentration increased during the transformation of alumina to spinel inclusions followed by a decrease during transformation of spinel to MgO inclusions. The mismatch in fitting for magnesium concentration for experiment-5.4 for later samples can also be attributed to the formation of fresh alumina inclusions due to reoxidation. The presence of pure alumina inclusions in steel was expected to be driving force for magnesium pick-up from the steel-crucible interface

as MgO activities at the interface between newly formed inclusions and steel would be much smaller than that at the steel-crucible interface. The net magnesium-transfer to inclusions would result in an increase in magnesium content in inclusions after reoxidation as seen in the measurements. For experiment-5.5, the total bound magnesium in inclusions increased during transformation of alumina to spinel inclusions but decreased in later samples.

The change in the bound magnesium content in inclusions is expected to depend on three factors: the rate of pick-up of magnesium at the steel-crucible interface, the removal of MgO containing inclusions due to flotation/collision with crucible wall and the loss of magnesium due to evaporation from liquid steel. In the beginning, the MgO concentration in inclusions was very low and their removal did not significantly affect magnesium content in inclusions in steel. As shown in Figure 31, the dissolved magnesium at earlier times was expected to be very low indicating magnesium evaporation was not significant at those times. Therefore, a constant and steep increase in magnesium content in inclusions was observed for early times. However, at later times, significant magnesium loss occurred by flotation of MgO containing inclusions and by magnesium evaporation, as seen in Figure 30 (a) and (b).

Figure 31 shows change in calculated dissolved magnesium for experiments-5.4. And 5.5. The dissolved magnesium in steel remained very low (<1 ppm) during inclusion transformation from alumina to alumina saturated spinel phase (Mg/Al=0.2) in both cases. As inclusion transformation continued to MgO saturated spinel and beyond (for experiment-5.4), the MgO activity at the steel-inclusion interface increased along with increased dissolved magnesium concentration. The net magnesium transfer from steel-crucible to steel-inclusion interface can be described using Equation 22. The reaction can go forward till MgO activity in inclusions become equal to that at the crucible: for experiment-5.4, $a_{MgO} = 1$ and for experiment-5.5, $a_{MgO} = 4.6 \times 10^{-2}$.

$$(MgO)_{crucible} + \frac{1}{3}(Al_2O_3)_{inclusion} = (MgO)_{inclusion} + \frac{1}{3}(Al_2O_3)_{crucible} \quad \text{Equation 22}$$

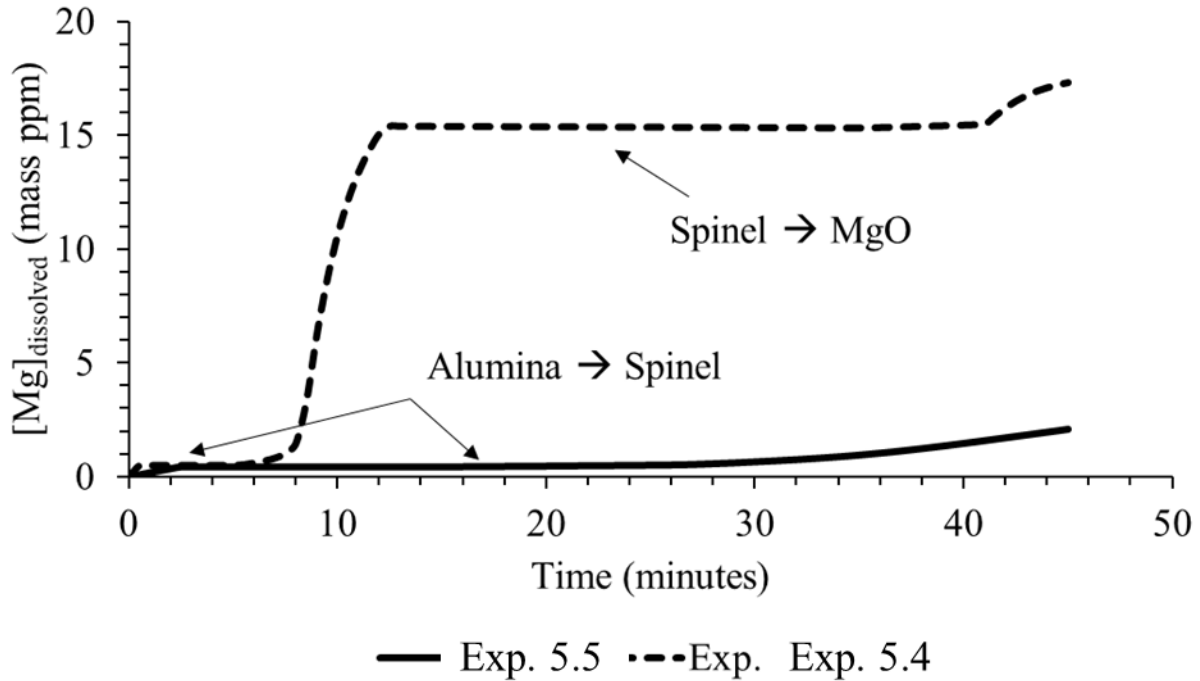
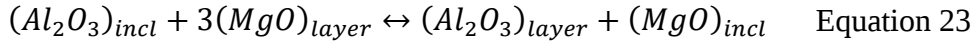


Figure 31. Calculated dissolved magnesium with time for experiments 5.4 and 5.5

5.3.4.2.1 Mechanism of magnesium transfer and mass transfer coefficients

As shown in the experimental results section, the inner surface of MgO crucible may either be coated with a slag like layer or a spinel layer for the experimental conditions described here. Based on this observation, there can be two possible magnesium transfer mechanism from MgO crucible to liquid steel: 1) the MgO from the crucible dissolves in the slag film and steel equilibrates with the MgO saturated slag film and 2) MgO diffuses through a solid spinel layer and steel equilibrates with spinel. The roles of slag/spinel layer on magnesium transfer is schematically shown in Figure 32. The net reaction for inclusion transformation can be summarized as Equation 23. The activity of alumina in case of slag layer (52% CaO, 35%Al₂O₃ and 13%MgO) and MgO saturated spinel

layer are 0.0063 and 0.0593 respectively (with solid alumina as reference state). The lower alumina activity in the slag layer was expected to favor forward reaction in Equation 23.



Whether the crucible inner surface is coated with a spinel layer or slag film is expected to depend on the impurity level in the MgO raw material used to manufacture crucibles. In present work, the maximum impurities in the MgO crucibles were: 0.6% CaO, 0.2% SiO₂, 0.4% Al₂O₃, 0.1% Fe₂O₃ and 0.01% B₂O₃. The large difference in the rate of transformation of alumina inclusions to spinel inclusions in two experiments show that the magnesium transfer rate is very sensitive to impurity concentration in MgO crucibles.

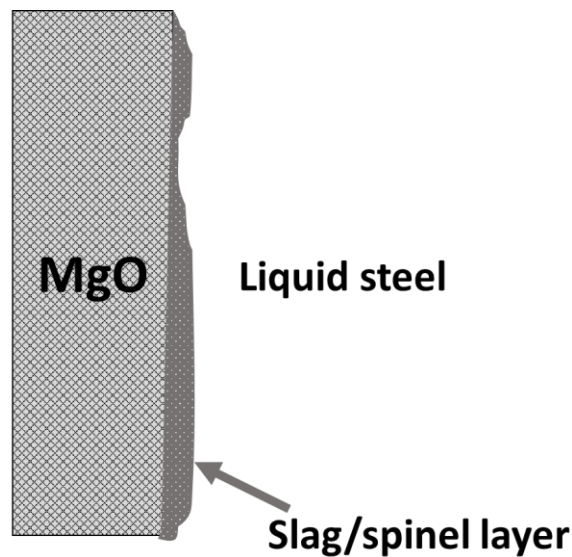


Figure 32. Role of slag/spinel layer on magnesium transfer from crucible to steel

The effect of the presence of an intermediate layer was thermodynamically considered in the present model by equilibrating steel with MgO saturated slag layer for experiment-5.4 and with spinel for experiment-5.5. The presence of liquid slag or a solid spinel layer was also expected to affect the kinetics of steel-crucible reaction as MgO diffusion is expected to be slower in the spinel

layer compared to a slag like layer. This was implicitly considered by fitting calculated magnesium transfer to inclusions to the observed values as shown in Figure 30. The fitted mass transfer coefficient in steel phase for steel-crucible reaction for experiments 5.4 and 5.5 were $5.5 \times 10^{-5} \text{ m/s}$ and $3.2 \times 10^{-6} \text{ m/s}$. It should be noted here that the mass transfer coefficient in steel phase for experiment-5.4 was close to that for steel-slag reaction ($k_{steel} = 4.5 \times 10^{-5} \text{ m/s}$) under similar experimental conditions (will be shown in next section) which indicates that the MgO transfer through slag layer was not expected to be the rate limiting for magnesium transfer to steel.

5.3.5 Practical Implications

5.3.5.1 *Relative contributions of slag and refractory*

In the industrial ladle refining process of aluminum killed steel, alumina inclusions may transform into spinel inclusions and beyond due to steel-slag and/or steel-refractory reaction. The rate of MgO pick-up in inclusions may be simulated using the kinetic model developed in this work. The model parameters are listed in Table 15. The mass transfer coefficient in steel phase was considered to be the same for steel-slag and steel-refractory reactions. The mass transfer coefficient in the slag phase was considered to be 10 times smaller than in the steel phase as described elsewhere [58]. The mass transfer coefficient in steel phase was taken equal to 0.002 m/s based on previous work [59]. The MgO-C refractory (in contact with steel and slag) was expected to have a ladle glaze with composition similar to the slag layer found in laboratory experiments as described before: 52% CaO, 35% Al₂O₃ and 13% MgO. The liquid steel was considered aluminum killed with 0.05% Al. The total oxygen concentration in steel was fixed to 50 ppm and 10 ppm. The slag composition was considered to be 51.2% CaO, 41.6% Al₂O₃ and 7.2% MgO which is very close to the saturation of CaO ($a_{CaO} = 0.96$ [44]) and MgO ($a_{MgO} = 0.99$ [44]). Four conditions were simulated to illustrate the effect of total oxygen concentration (and

hence the initial alumina inclusion concentration) and the relative contribution of refractory and slag to the inclusion transformation. These conditions are described in Table 16.

Table 15. Model parameter for industrial scale operation

Steel mass	250 metric tonnes
Slag mass	2000 kg
Temperature	1873 K
Steel mass transfer coefficient	0.002 m/s
Slag mass transfer coefficient	0.0002 m/s
Steel density	7000 kg/m ³
Slag density	3000 kg/m ³
Steel-slag projected interface area	12.5 m ²
Steel-refractory interface area	43.6 m ²

Table 16. Simulation cases

Cases	Total oxygen concentration	Steel-refractory reaction	Steel-slag reaction
1.	50 ppm	Yes	Yes
2.	50 ppm	No	Yes
3.	10 ppm	Yes	Yes
4.	10 ppm	No	Yes

The kinetic model used to simulate these conditions was similar to the one for simulating laboratory scale experiments described earlier in this chapter with few changes. In this case, total oxygen concentration (and inclusion concentration) was kept constant by ignoring inclusion flotation and steel-slag reaction was also considered in addition to the steel-refractory reaction. The kinetic calculations were made using macro processing feature available in FactSage7.1 [44]. The FTmisc database was used for the liquid steel solution and the slag and the inclusions were simulated using the FToxid and FACTPS databases. As reported before, the FTmisc database over-predicts calcium solubility in steel [52], [59], [60]. In order to avoid this anomaly, Ca and Ca*O (Ca-O associate) end members were removed from Fe-LQ phase in the FTmisc database.

Figure 33 shows the increase in calculated Mg^{2+} cation fraction in inclusions with time for case-1 and case-2. It should be noted that the change in $\text{Mg}/(\text{Mg}+\text{Al})$ from 0 to 0.33 shows the transformation from alumina to spinel inclusions and from 0.33 to 1 shows the transformation of spinel to MgO inclusions. At complete equilibrium, the activities of MgO in inclusions should be equal to that in slag and refractory. Since, the refractory was considered to have an MgO saturated glaze ($a_{\text{MgO}}=1$) and the activity of MgO in the slag was equal to 0.99, the equilibrium inclusion composition was expected to be pure MgO. The activity of alumina in inclusions should also become equal to that in slag at equilibrium. The alumina activities in slag and in MgO saturated spinel were 6.3×10^{-3} and 0.0593. For 50 ppm total oxygen, the inclusions were found to transform from alumina to spinel for both cases. In case-1, when steel reacted with both slag and refractory, the transformation continued beyond spinel and approached towards MgO but in the absence of steel-refractory reaction the transformation of alumina to stoichiometric spinel was barely completed in 1800 s. At $t=1800$ s, $\text{Mg}/(\text{Mg}+\text{Al})$ in inclusions was 0.27 for case-2. For case-1, the same inclusion composition was achieved in 400 s which was about 4.5 times faster than

that for case-2. The ratio is very close to the ratio of steel-(slag+refractory) area ($=56 \text{ m}^2$) and steel-slag area ($=12.5 \text{ m}^2$). Figure 34 shows the similar effect for much lower total oxygen concentration ($=10 \text{ ppm}$). For a given steel chemistry, the lower inclusion concentration can be achieved by prolonged ladle treatment allowing smaller inclusions to float. In this case, the rate of transformation is much faster, the inclusion completely transformed to MgO for case-3 and to stoichiometric spinel for case-4. It clearly demonstrates that the rate of MgO pick-up in inclusions would be much faster for a lower inclusion concentration in steel. From this calculation, it can be shown that the refractory can be a significant source of magnesium while considering transformation of alumina inclusions to spinel inclusions and the use of alumina refractory in contact with steel is expected to help in avoiding spinel formation.

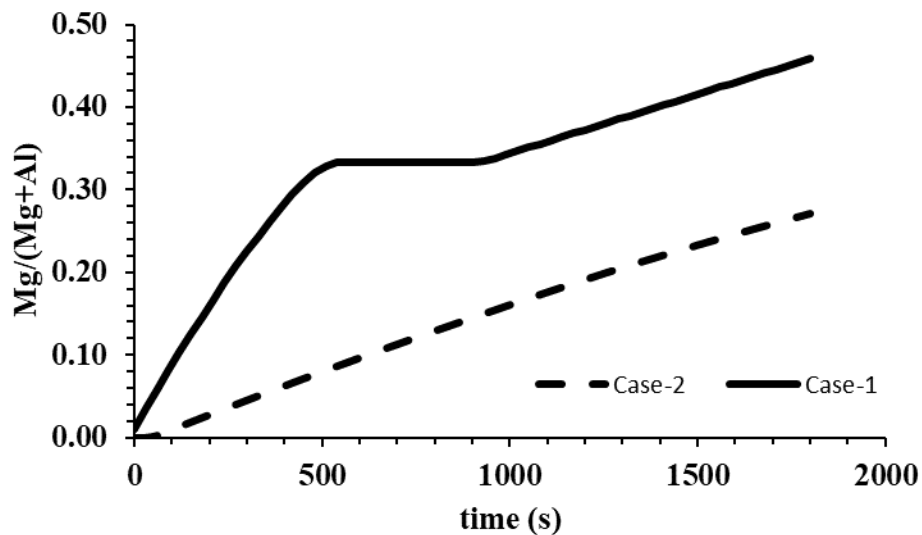


Figure 33. Change in inclusion composition with time for total oxygen concentration= 50 ppm , with (case-1) and without (case-2) reaction with refractory

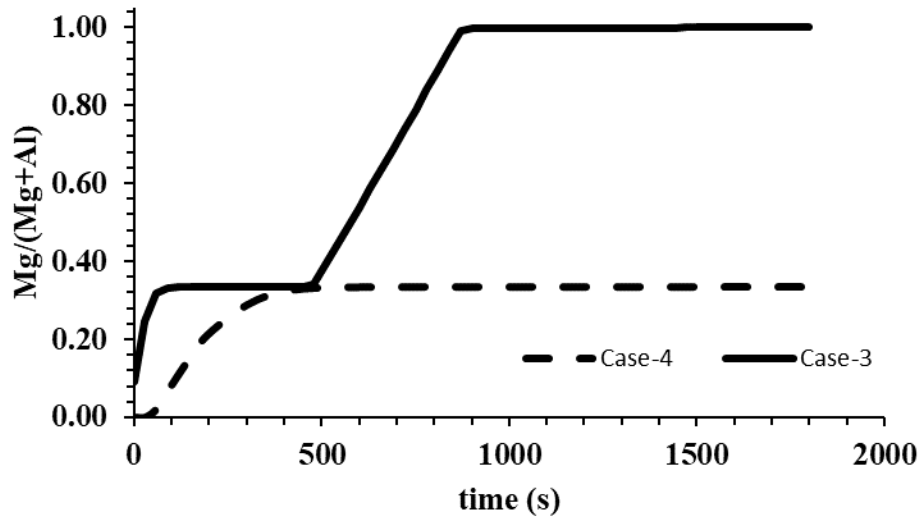


Figure 34. Change in inclusion composition with time for total oxygen concentration=10 ppm, with participation of refractory (case-3) and without (case-4)

It is interesting to note a plateau once inclusion composition reached to stoichiometric spinel ($\text{Mg}/(\text{Mg}+\text{Al}) = 0.33$) for cases 1, 3 and 4. As shown in Figure 35 (for case-1), the dissolved magnesium concentration remains very low during transformation of alumina inclusions to spinel inclusions. As discussed earlier, due to a large difference in the activity of MgO in inclusions compared with that in the slag and in the refractory, inclusions act as a sink for magnesium transferred to the liquid steel. As the inclusion composition approaches spinel, the dissolved magnesium concentration increases to achieve the equilibrium magnesium concentration in steel with spinel inclusions. It can also be seen that the dissolved magnesium remains almost constant while inclusions transform from spinel to MgO. The small decrease was due to a change in equilibrium dissolved oxygen concentration in steel during this transformation.

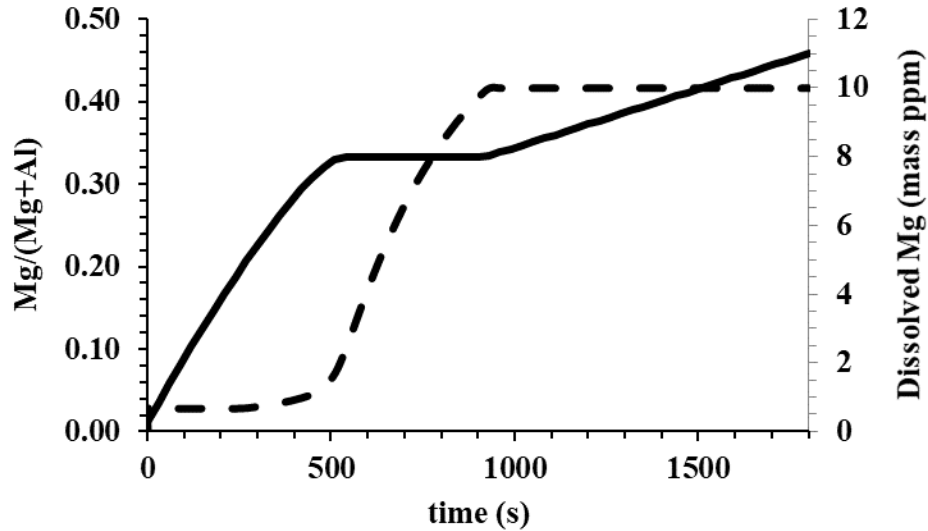


Figure 35. Change in inclusion composition and dissolved magnesium with time for case-1

Figure 36 shows total magnesium (dissolved + inclusions) pick-up in steel with time for all four cases. It can be seen that both the total oxygen concentration and the extent of transformation affects the amount of total magnesium pickup in steel. The magnesium pick-up was maximum when inclusion concentration was higher and the inclusion transformation continued to MgO (Case-1). The total magnesium pick-up was higher in case-3 compared to case-2. This is expected as inclusions in case-2 could not complete transformation to spinel and the dissolved magnesium was very small, as shown in Figure 35. However, for case-3, inclusions transformed to MgO which corresponds to the maximum possible dissolved magnesium as well as maximum possible magnesium in inclusions. The analysis also shows a very interesting possible consequence regarding calcium treatment of spinel inclusions. As noted by Verma et al.[35], the calcium modification of spinel inclusions occurred via reduction of MgO from spinel inclusions resulting in an increase in dissolved magnesium concentration. Tan and Webler [34] reported that a reoxidation event followed by the calcium modification of spinel inclusions was likely to result in the re-appearance of spinel inclusions. From present work, it is noted that if inclusions are not

completely transformed to spinel, the dissolved magnesium concentration (and hence total magnesium concentration in steel) is expected to be much smaller. The calcium modification of this partially transformed spinel inclusions is expected to result in much smaller increase in dissolved magnesium concentration. A reoxidation event followed by such modification may not find enough magnesium to form spinel inclusions. This strategy may help in avoiding the re-appearance of spinel due to any reoxidation event post calcium treatment.

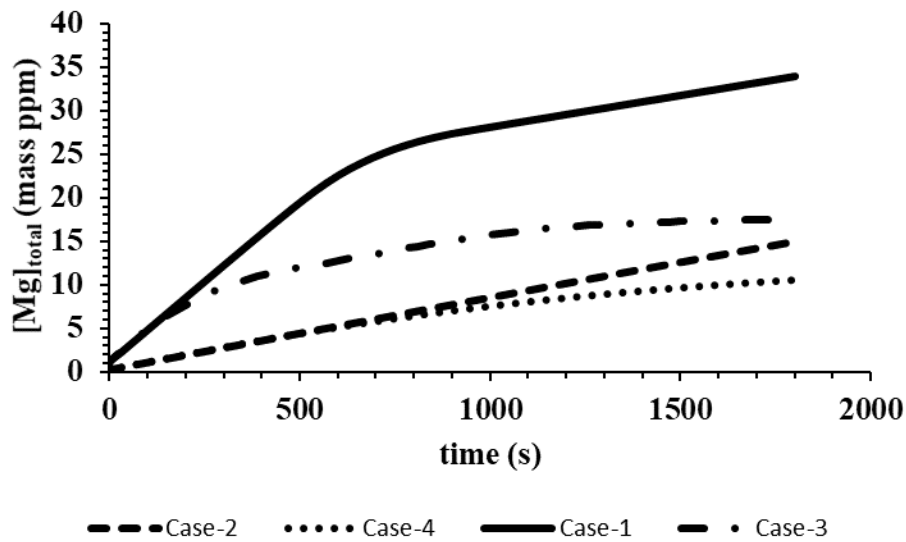


Figure 36. Total magnesium pick-up in steel with time for four cases, with lower (cases 2 and 4, without steel-refractory reaction) and higher (cases 1 and 3 with steel-refractory reaction)

5.3.6 Conclusions

Aluminum deoxidation experiments were conducted in MgO crucibles using an induction furnace setup. The transformation of alumina inclusions to spinel inclusions was experimentally quantified by measuring increase in the bound magnesium in inclusions. A kinetic model was developed that can predict changes in steel and inclusion composition considering steel-crucible reaction, inclusion removal and magnesium evaporation from liquid steel. It was concluded that a liquid slag like layer can form on the crucible wall due to impurities in the refractory. This slag like layer

could enhance the rate of increase in the bound magnesium in inclusions leading to the transformation of alumina inclusions to spinel or even MgO inclusions. The effective magnesium transfer rate for this case was $6 \times 10^{-5} \text{ m/s}$ which was about 20 times higher than the case when inner surface of the crucible was found coated with a spinel layer.

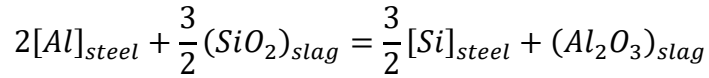
Some practical implication of the kinetic model was also discussed. The MgO pickup in alumina inclusions was simulated for different total oxygen concentrations along with the effect of steel-refractory reactions. Following conclusions can be made from this set of simulations:

- a) For lower total oxygen concentration, the transformation of alumina to spinel and beyond was much quicker.
- b) When steel picks up magnesium due to both steel-slag and steel-refractory reactions, inclusions may transform to MgO for both high and low inclusion concentrations.
- c) The dissolved magnesium concentration in steel was much lower until alumina inclusions completely transformed to alumina saturated spinel inclusions indicating the calcium modification of partially transformed spinel inclusions may be beneficial in avoiding the re-appearance of spinel inclusions upon a reoxidation event at a later stage.

5.4 Steel-slag-crucible reactions

5.4.1 Experimental

Two induction furnace experiments (5.6 and 5.7) were conducted to use the kinetic model for steel-slag-crucible reactions. These experiments were conducted in an MgO crucible ($\varnothing = 61 \text{ mm}$). Electrolytic iron containing 350 ppm was deoxidized by adding 0.3 wt% aluminum followed by slag addition. Dissolved aluminum in the liquid steel was expected to reduce silica from slag resulting in silicon pick-up in steel. The expected reaction at the steel-slag interface was as follows:



In experiment-5.7, the liquid steel was stirred by flowing argon ($3 \times 10^{-4} \text{ Nm}^3/\text{min}$) through an MgO tube inserted in the melt through the top cap of the induction furnace chamber shown in Figure 1. The slag composition used for these two experiments is given in Table 17. Higher MgO concentration was used in experiment-5.7 to avoid the corrosion of MgO crucible under Ar-stirring.

Table 17. Composition of slags used for experiment-5.6 and 5.7

Slag#	CaO (wt%)	Al ₂ O ₃ (wt%)	SiO ₂ (wt%)	MgO (wt%)
5.1	47.5	36.5	9	7
5.2	40	38	10	12

Table 18. Addition and sampling description for experiment-5.6 (MgO crucible)

Time (minutes)	0	3	11	20	25	30	35
Events	0.3 % Al	S1	180 g slag-5.1	S2	S3	S4	S5

Table 19. Addition and sampling description for experiment-5.7 (MgO crucible)

Time (minutes)	0	4	8	18	24	34	49
Events	0.3% Al	S1	150 g slag-5.2	S2	S3	S4	S5

5.4.2 Kinetic Modeling

The steel-slag-crucible reaction was modeled in a similar way to the modeling of steel-crucible reaction with an additional step of steel-slag reaction. The mass transfer coefficient in slag was taken as 10-times smaller than that in steel. It should be noted that the order of events matters while modeling such experiments with multiple reactions. For example: the removal of inclusion was considered with two inclusion removal rate constants which were separate from the steel-slag reaction. Therefore, steel transported to slag should not contain any inclusions at self-equilibrium. This was considered by equilibrating steel with inclusions and updating inclusion concentration and composition before steel was transported to the slag in each step. Two important factors were considered essential to calculate steel, slag and inclusion composition close to observed values. These are described in the following:

- a) Reoxidation during slag addition: as shown in Table 18 and Table 19, slag was added after the deoxidation of liquid steel. The addition port (shown in Figure 1) was opened to add slag and the slag may also contain some air. The mass balance of aluminum and change in inclusion composition indicated that there should be about 150 ppm oxygen addition along with slag addition. This was included in the model by adding 150 ppm of oxygen along with slag and assuming a higher inclusion floatation rate constant (β_1) in the time step following slag addition.
- b) Magnesium evaporation: evaporation of magnesium during steel-crucible reaction was described in the previous section. Magnesium evaporation from the top surface was not considered after slag addition. For experiment-5.7, the magnesium loss through argon bubbles during argon stirring can be expected to be significant. The mass transfer coefficient of steel to argon bubbles can be calculated using Higbie's model of mass transfer described by Javed

[37] where velocity (v_b) and diameter of bubble (d_b) were estimated calculated using the expression by Bannenberg [61].

$$k_{steel} = 2 \sqrt{\frac{D_{steel} v_b}{\pi d_b}}$$

$$v_b = Q_h / A_{bath}$$

$$d_b = 0.9(v_b(in\ cm/s))^{0.44}$$

Where Q_h is the argon flow rate in the bottom of crucible (T=1873 K and ferrostatic pressure).

The calculated mass transfer coefficient in steel to argon bubbles was 1.2×10^{-4} m/s. The fraction of steel reaching to argon bubbles per second was equal to 0.80. Therefore, for a 30 s calculation step size, argon bubbles were assumed to be saturated with magnesium and the magnesium loss was calculated by multiplying the argon flow rate (moles/second) with the equilibrium partial pressure of magnesium. The average partial pressure of magnesium during one such simulation was about 0.004 atm (for average $[Mg]_{dissolved} = 7.6$ ppm) which corresponds to loss of 0.03 ppm (by mass) of per second.

5.4.3 Results and Discussion

5.4.3.1 Fitting model parameters

The mass transfer coefficient in steel was calculated by finding the best fit for measured aluminum and silicon concentrations in steel with time as shown in Figure 37 and Figure 38. Calculated and measured aluminum indicate total aluminum (dissolved + aluminum in inclusions) in steel. Since the steel-slag interface is not flat as noted by Kim and Fruehan [13], the kinetic model was used to find $k_{steel}^{steel-slag} \times A_{interface}$. The fitted value for $k_{steel}^{steel-slag} \times A_{interface}$ was equal to 1.30×10^{-7}

m^3/s for experiment-5.6 and $1.70 \times 10^{-7} \text{ m}^3/\text{s}$ for experiment-5.7. The root mean squared error (RMSE) for the fitting was calculated using Equation 24. The model could fit to the experimental aluminum concentration with an error of 0.008 for experiment-5.6. The error for experiment-5.7 was much higher ($=0.039$) indicating there was additional aluminum loss that was not accounted even after considering magnesium evaporation. The current estimated value of kA (under non-stirred condition) is close to that found by Roy et al. [15] ($1.2 \times 10^{-7} \text{ m}^3/\text{s}$) for a similar setup. In the present work, the value of kA was found to increase by 30% when the melt was stirred by flowing argon $3 \times 10^{-4} \text{ Nm}^3/\text{min}$. Argon stirring is expected to increase the steel-slag interface area as noted by Kim and Fruehan [13]. Figure 39 shows the inner surface of the crucible after experiment-5.7. Steel droplets can be seen attached to the crucible wall indicating vigorous stirring and the presence of eye opening, which may have reduced steel-slag contact area and reduce the effect of stirring on mass transfer. The formation of eye may also result in the formation of FeO at the steel eye due to oxygen in argon bubbles if there was a small leak in the chamber. There was not any unexpected large increase in bound oxygen in inclusions after slag addition as shown in Figure 41 indicating that there was no reoxidation of bulk steel.

$$RMSE = \sqrt{\frac{\sum \Delta[\%Al]}{N}}$$

Equation 24

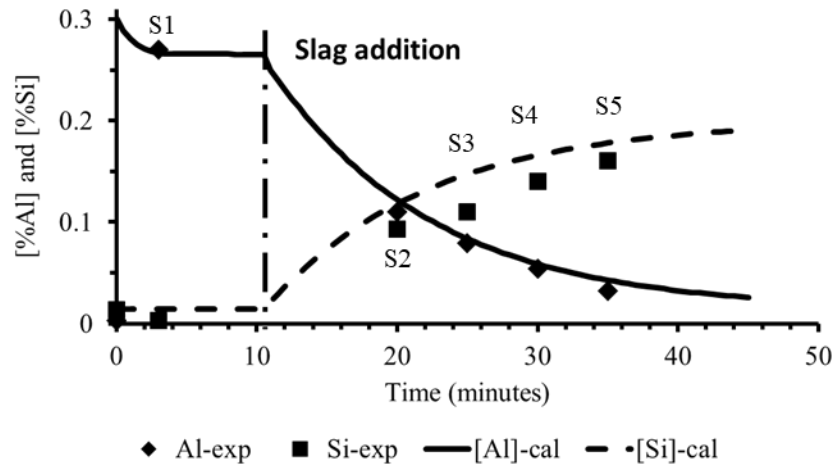


Figure 37. Experimental and calculated aluminum and silicon content in steel for experiment-5.6

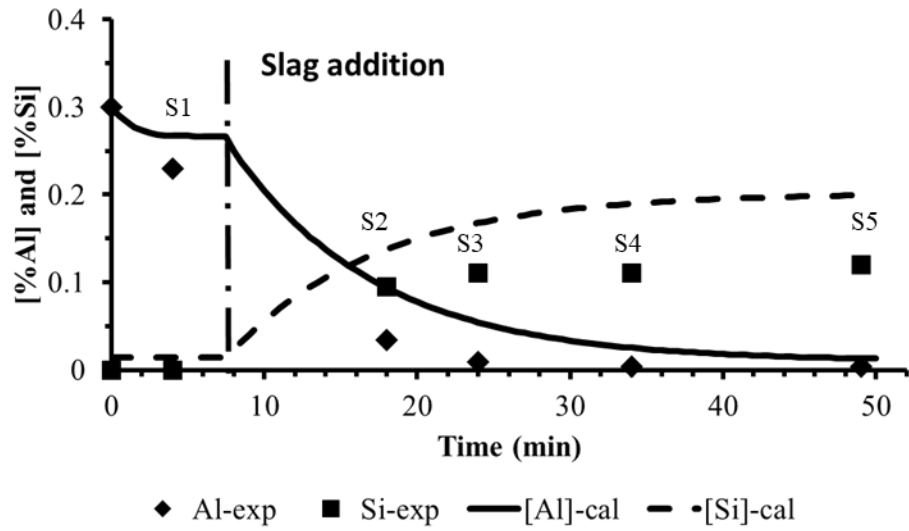


Figure 38. Experimental and calculated aluminum and silicon content in steel for experiment-5.7

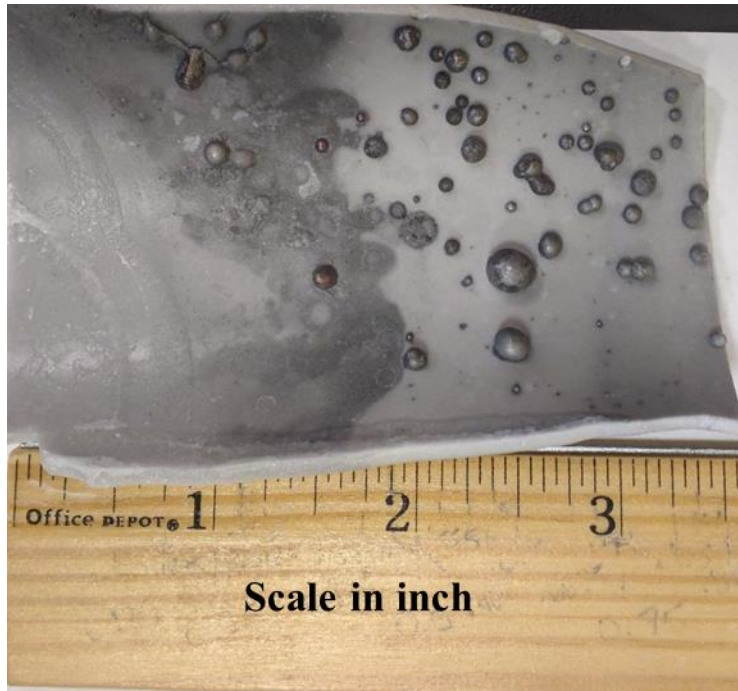


Figure 39. Crucible wall above melt surface after the experiment-5.7

The bound oxygen and magnesium in inclusions was calculated from inclusion analysis of steel sample using SEM-ASPEX as described in section 5.3.4. The bound oxygen from experiment-5.6 and 5.7 were used to find the inclusion removal rate constants as shown in Figure 40(a) and Figure 41(a) respectively. The fitted flotation rate constants for experiment-5.6 were 1%/s and 0.08%/s and those for experiment-5.7 were 0.2%/s and 0.86%/s. The root mean squared error for these fittings were 16.5 ppm (exp. 5.6) and 7.2 ppm (exp.5.7). The poorer fit for experiment-5.6 can be attributed to possible reoxidation from sample-2 to sample-3 as shown by a red arrow in Figure 40 (a). As described earlier, in the model, an addition of 150 ppm oxygen was made during slag addition as expected from the comparison between bound oxygen in inclusions analysis for samples before and after slag addition. The flotation rate constant for later times (β_2) during exp.-5.7 was 2.5 times larger than that for exp. 5.6, 5.5 and 5.4. As noted by Miki and Thomas [62], the flotation of inclusions in an argon stirred system is expected to occur by the attachment of

inclusions to argon bubbles in addition to Stokes flotation. The change in the average size of inclusions with time for two experiments are shown in Figure 42. It can be seen that the average size of inclusions remains around 3-4 μm for experiment-5.6 until 35 minutes of experiment time but it steadily decreases to 1.5 μm (at $t=35$ minutes) for experiment-5.7. Figure 40(b) and Figure 41(b) show calculated and measured change in bound magnesium concentration with time. The bound magnesium in inclusions is expected to be result of the magnesium pick-up in steel due to steel-crucible and steel-slag reactions and magnesium loss due to removal of MgO containing inclusions and due to evaporation from top surface (before slag addition) and through argon bubbles (for experiment-5.7). Fresh alumina inclusions formed due to expected reoxidation during slag addition are expected to act as a sink for magnesium as they transformed from alumina to spinel. The increase in calculated bound magnesium just after slag addition show such an increase. The decrease in magnesium concentration at later time interval was due to inclusion removal and also significant magnesium evaporation in case of experiment-5.7 (see Figure 41(b)). The current set of fitted parameters can be seen to closely predict change in bound magnesium with time for later samples. The slag takes up to five minutes to completely melt, no sample could be taken just after slag addition. Therefore, the calculated peak in magnesium concentration at those times could not be experimentally verified.

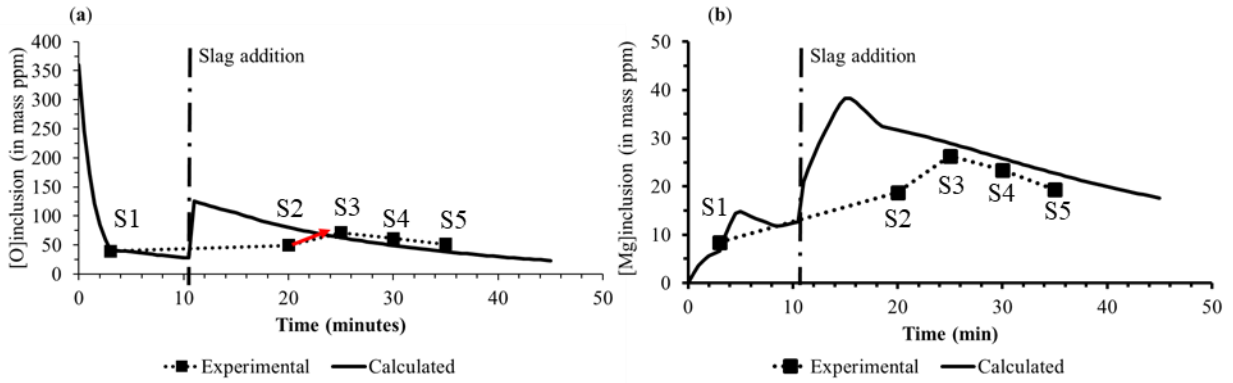


Figure 40. Fitted bound oxygen to inclusion and predicted bound magnesium in inclusions for experiment-5.6

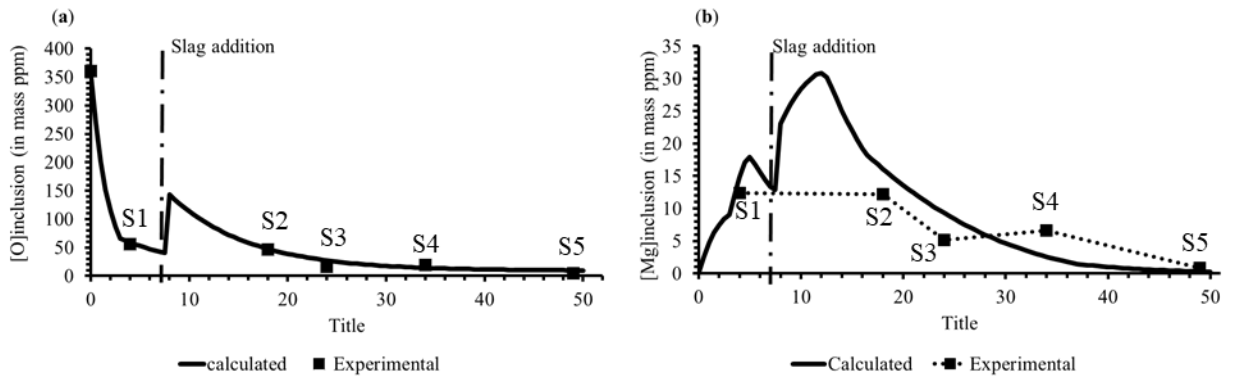


Figure 41. Fitted bound oxygen to inclusion and predicted bound magnesium in inclusions for experiment-5.7

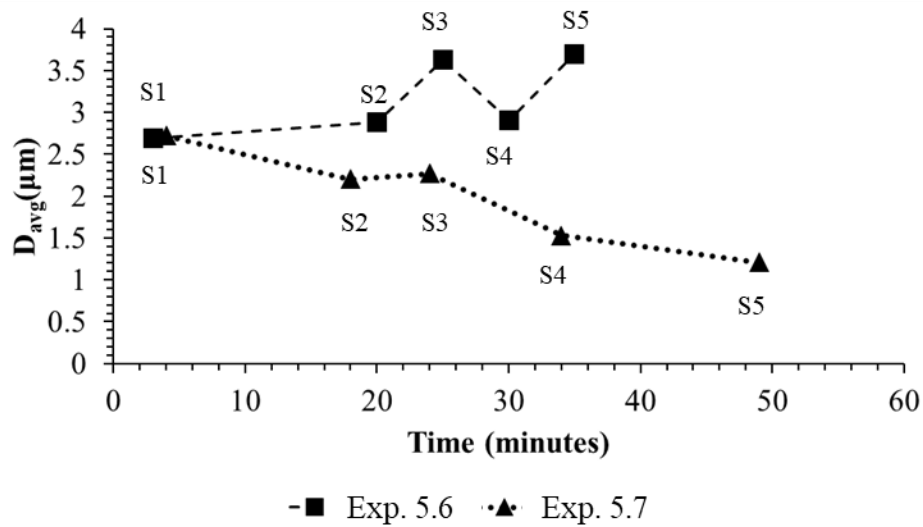


Figure 42. Average size of inclusions observed in exp. 5.6 (no stirring) and exp. 5.7 (Ar stirring)

The fitted model parameters are summarized in Table 20. The fitted mass transfer coefficient in steel for steel-crucible reaction was kept constant for steel-crucible and steel-slag-crucible experiments except for experiment-5.5 where a spinel layer present on the crucible wall was found to reduce rate of magnesium transfer to steel and to the oxide inclusions. The large difference in fitted flotation rate constants can be due to difference in experimental setup, expected reoxidation during the experiment or difference in initial oxygen concentration in liquid electrolytic iron.

Table 20. Summary of fitted model parameters

Exp.#	Description	$k_{steel}^{steel-refractory}$ (m/s)	$k_{steel}^{steel-slag} \times A$ (m ³ /s)	β_1 (%/s)	β_2 (%/s)
5.2	Al ₂ O ₃ crucible: Al-10Mg deoxidation	No reaction	No slag	0.55	0.35
5.3	MgO-crucible; Al-10Mg deoxidation	Not calculated		1.1	0.35
5.4	Steel-MgO crucible (type-1)	5.5×10^{-5}		0.45	0.09
5.5	Steel-MgO crucible (type-2)	3.2×10^{-6}		0.91	0.13
5.6	Steel-slag	4.5×10^{-5}	1.3×10^{-7}	1.0	0.08
5.7	Steel-slag with Ar stirring	4.5×10^{-5}	1.7×10^{-7}	0.86	0.2

5.4.3.2 Calculated steel and slag composition

As noted above, aluminum fade and silicon pick-up in steel were used to find the mass transfer parameter for steel-slag reaction for experiments conducted in the induction furnace with and without forced stirring. The model can be further used to predict changes in calcium, magnesium

concentrations in steel during the process. Figure 43 and Figure 44 show calculated dissolved and total calcium and magnesium content in steel for experiment-5.6 and experiment-5.7 respectively. Since an excess oxygen (150 ppm) was added in the calculation at the instant of slag addition, the dissolved magnesium concentration was immediately reduced to zero at that instant for both experiments: all magnesium precipitated as inclusions. At the end of reaction time for experiment-5.6, the predicted dissolved calcium and magnesium concentrations are 3 ppm and 9 ppm and the predicted total calcium and magnesium (dissolved in iron + in inclusions) was 6.6 ppm and 31 ppm. Calculated dissolved calcium (2.7 ppm) and magnesium (7.7 ppm) concentrations in steel for experiment-5.7 were similar to that for experiment-5.6. However, the predicted total magnesium and calcium concentration in steel was much lower in experiment-5.7 compared to experiment-5.6 due to lower inclusion concentration (the calculated bound oxygen in inclusion was 1.30 ppm at the end of experiment-5.7).

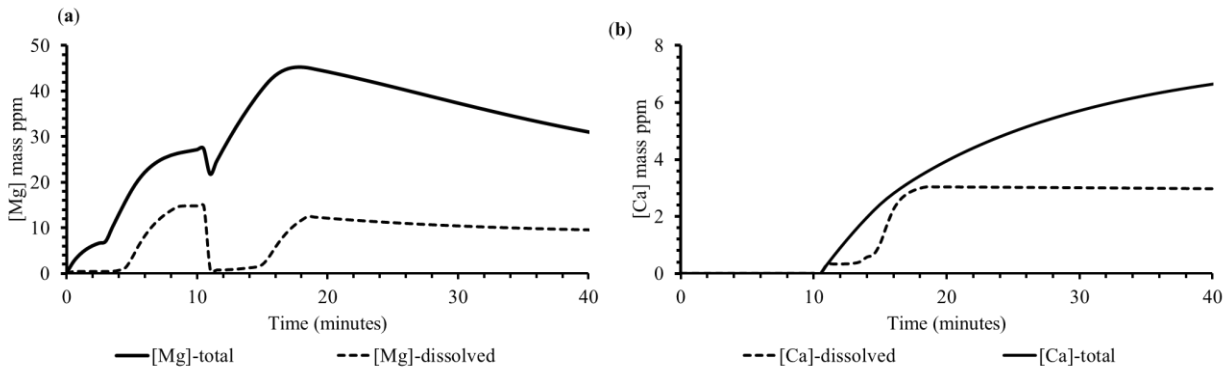


Figure 43. Calculated dissolved and total a) magnesium and b) calcium with time for experiment-5.6

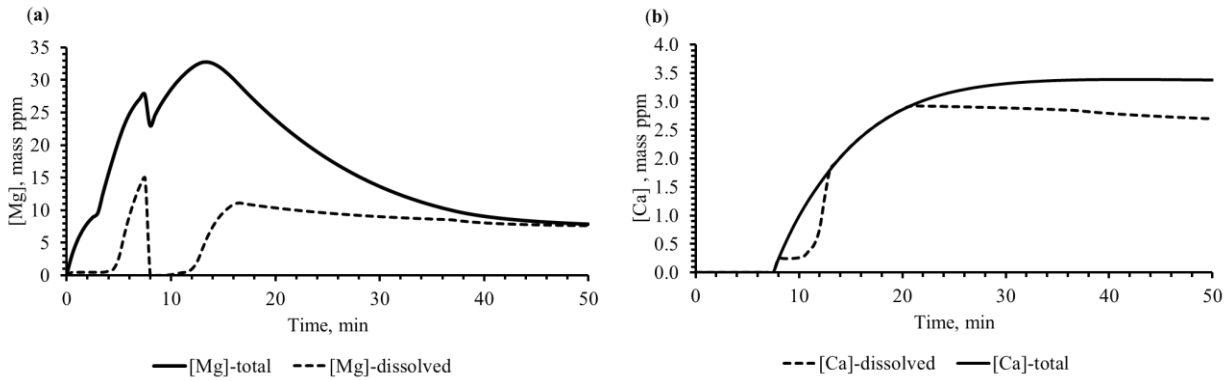


Figure 44. Calculated dissolved and total a) magnesium and b) calcium with time for exp. 5.7

Figure 45 shows the calculated slag composition for experiment-5.7. Since slag was added at the 8th minute, the slag composition before that time represents floated inclusions. There is not any substantial change in slag composition after 8th minute except for the decrease in silica and increase in alumina concentrations that is due to reduction of silica from slag by aluminum in steel.

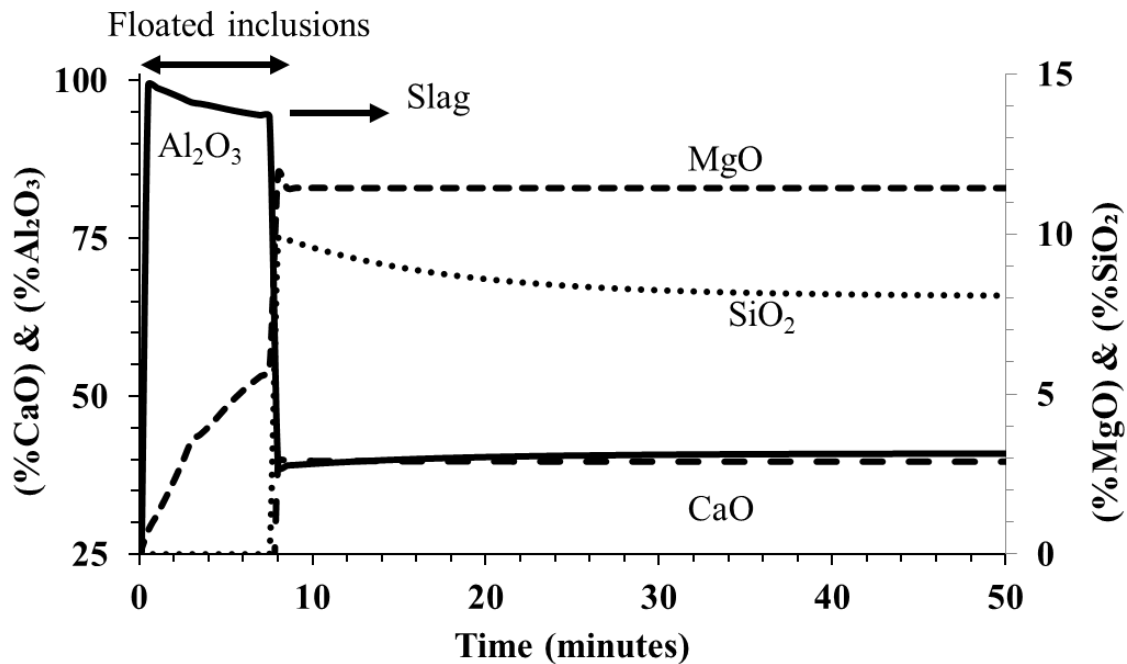


Figure 45. Calculated slag composition for experiment-5.7

5.4.3.3 Inclusion composition

Figure 46 shows the $\text{Mg}/(\text{Mg}+\text{Al})$ ratio in inclusions observed in experiment-5.6. Magnesium pick-up in inclusions was likely due to both steel-crucible reaction and steel-slag reaction; the presence of magnesium in inclusions before slag addition clearly indicates magnesium pick-up from crucible. As described earlier, the magnesium pick-up in inclusions depend on several factors during such experiments. It is interesting to see that the kinetic model can predict the limited Mg^{2+} fraction in inclusions during experiment-5.7 which is expected to depend on the rate of steel-crucible reaction, steel-slag reaction, inclusion removal and magnesium loss through argon bubbles. The overall calculated inclusion compositions for experiment-5.6 and 5.7 are shown in Figure 47. The predicted inclusion composition shows calcium pick-up along with magnesium pick-up for both experiments: for experiment 5.6 the predicted Ca^{2+} molar cation fraction was about 4% at $t=35$ minutes and about 6% at $t=35$ minutes for exp.-5.7. The final Ca^{2+} molar cation fraction (at $t=50$ minutes) was about 30%. However, there was no calcium found in the measured inclusion composition from experiment 5.6 in any samples. The inclusion composition for sample taken at $t=50$ minutes during experiment-5.7 is shown in Figure 48. It shows only limited calcium pick-up in inclusions with average Ca^{2+} molar cation fraction equal to 2%. In these diagrams, the area of each triangle is scaled proportional to the relative number of inclusions with that particular composition. The line inside ternary diagram represent 50% liquid phase boundary. The left side ternary diagram shows inclusion number density and right side shows the area fraction of inclusions. It can be seen that there were large numbers of small inclusions that showed some calcium pick-up.

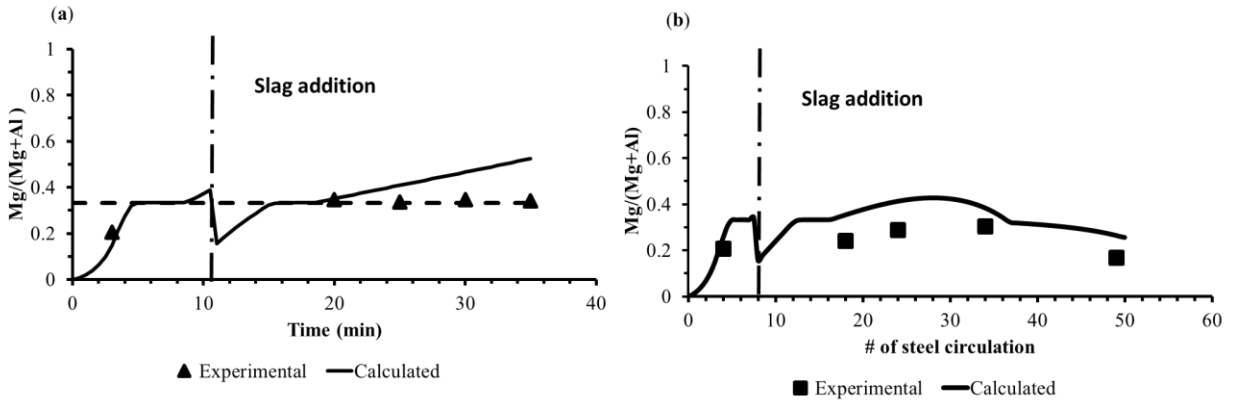


Figure 46. Calculated and measured Mg/(Mg+Al) molar ratio in inclusions with time for (a) exp. 5.6 and (b) exp. 5.7

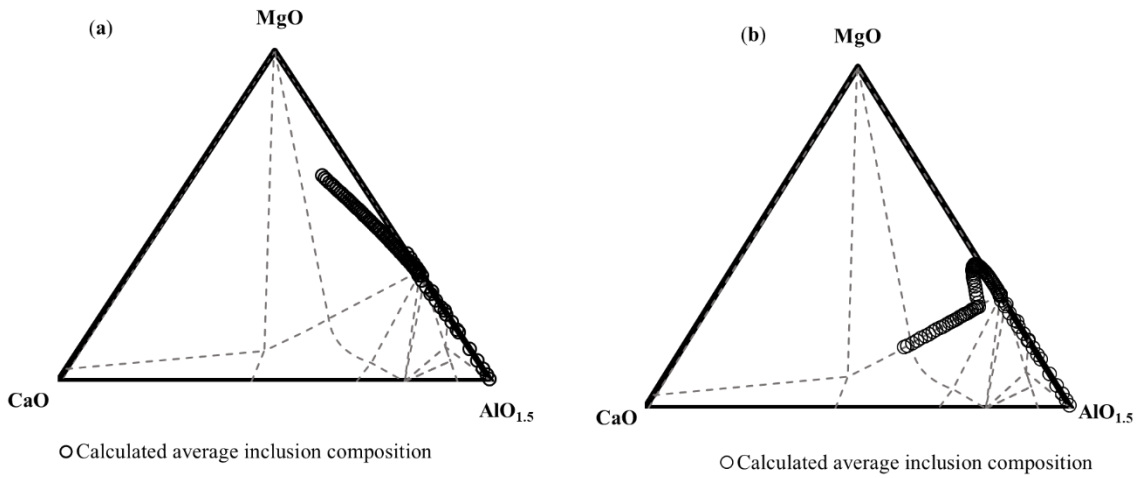
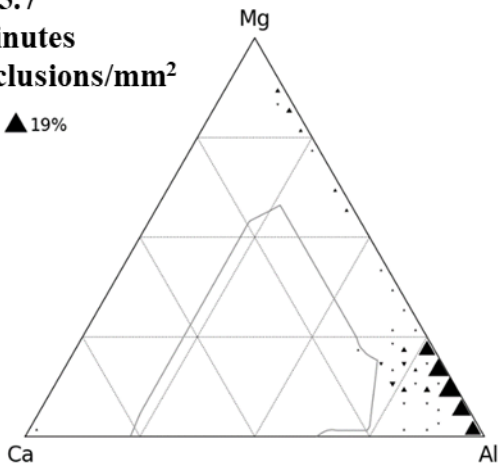


Figure 47. Calculated inclusion composition for (a) exp. 5.6 and (b) exp. 5.7

Exp. 5.7
50 minutes
15 inclusions/mm²
▲ 19%



Exp. 5.7
50 minutes
15 ppm a.f.
▲ 50%

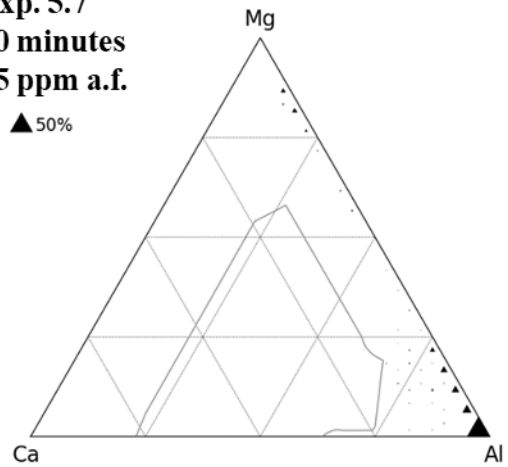


Figure 48. Composition of inclusions in sample taken at t=50 minutes during experiment-5.7

5.4.4 Limitations of the model

The kinetic model described in the previous section can predict steel, slag and inclusion composition changes with time. There was a good agreement for the kinetics of changes in steel composition and transformation of alumina to spinel inclusions. However, the predicted calcium content in inclusions is much higher than observed. It appears that the available solution database overestimates calcium solubility, which would cause the rate of calcium pick-up to be overestimated. Figure 49 shows the uncertainty in calcium solubility data available in literature.

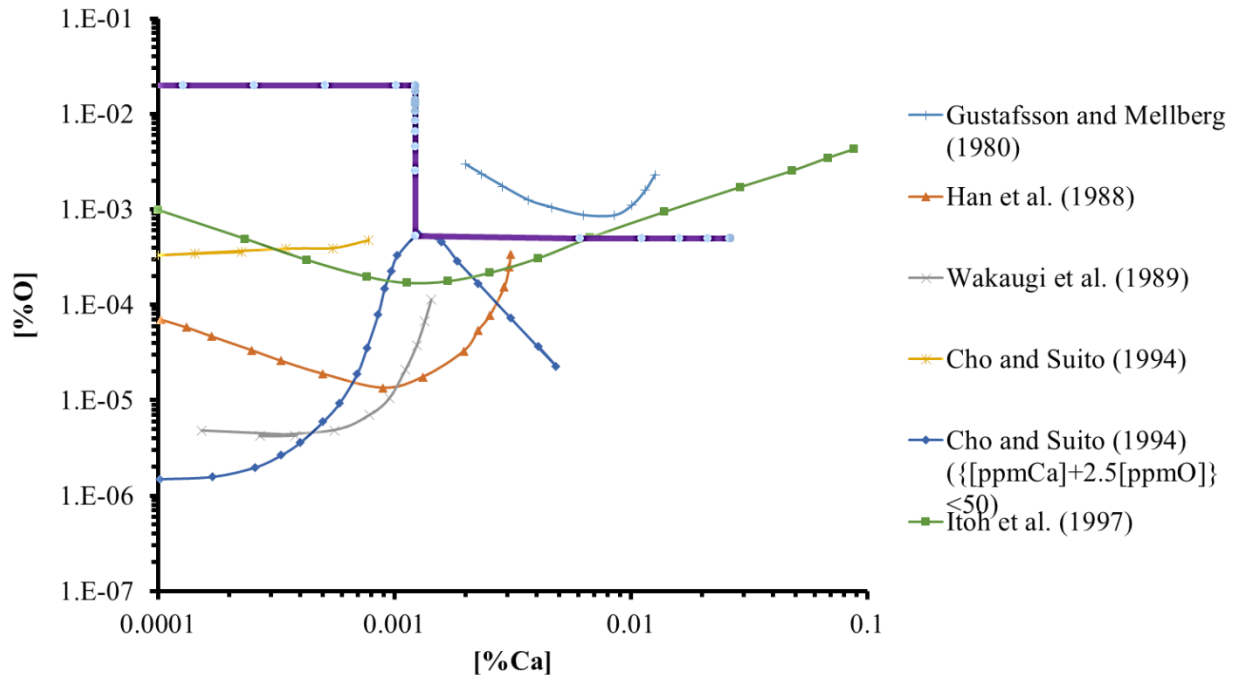


Figure 49. Reported relationships between dissolved oxygen and dissolved calcium in liquid steel in equilibrium with CaO at 1873 K. Redrawn after reference [42]

It can be seen that the FactSage FTmisc database predicts much higher calcium solubility over the range of oxygen concentration expected in typical aluminum killed steel (few ppm). According to experimental observation (no CaO precipitation on inclusion), the calcium solubility in steel is

expected to be very low under current experimental conditions. It is interesting to note that quantifying calcium pick-up in steel due to steel-slag reaction can be a more practical approach to measure calcium solubility in steel as compared to the usual approach involving equilibration of steel melt with calcium vapor. Calcium pick-up by steel at steel-slag or steel-crucible interface is expected to modify alumina inclusions in similar way as magnesium. This change in inclusion composition can be utilized to estimate the calcium content of steel avoiding usual difficulty of measuring calcium in steel. These aspects will be discussed in the later part of this document.

6 Kinetic modeling of ladle refining

6.1 Objective

The objective of applying the model to industrial conditions were as follows:

- a) To develop a kinetic model for industrial operation that can predict the change in steel, slag and inclusion compositions during ladle refining
- b) To use the kinetic model to develop a better understanding of the steelmaking practice that avoids Ca and Mg pick-up
- c) To describe the challenges and limitation of such a kinetic model

6.2 Trial description

6.2.1 Sampling method

Steel and slag samples were taken from three ladle furnace heats from the same plant. The samples were taken after tapping from BOF, and throughout ladle refining. Table 20 shows steel and slag mass for each of three heats. Slag mass was calculated based on an aluminum mass balance: the fade in aluminum concentration in steel was balanced with the increase in alumina concentration in slag. The aluminum mass balance was preferred over phosphorus and silicon mass balance due to smaller concentration of silicon and phosphorus and possibilities of silicon and phosphorus as contaminants from aluminum and ferrosilicon additions. Typical steel chemistry was: 0.20% C, 0.40% Mn and 0.050% Al. Table 22, Table 24 and Table 26 show additions in steel and slag during the ladle refining process for each of three trials. In the modeling approach, alloying elements were assumed to be added in steel and oxides were added to slag. The majority of aluminum was added

in wire form but sometimes aluminum was added with CaO as slag conditioner. Carbon was added as carbon wire or as carbon in ferromanganese. Wire additions are mentioned in the table. The time of steel and slag sampling for each heat is mentioned in Table 23, Table 25 and Table 27. The starting of aluminum wire addition was taken as t=0 minutes. The negative time for few slag samples indicate that those samples were taken after tapping from BOF and before the beginning of aluminum wire addition. Steel samples were also taken from the tundish to note any changes in steel or inclusion composition from ladle to tundish. Intermittent arcing was performed to maintain temperature of the melt, see Table 21.

Table 21. Steel and slag mass for all heats

	Heat-1	Heat-2	Heat-3
Steel mass (metric tonne)	241.3	247.3	244.9
Slag mass	12 kg/tonne	4 kg/tonne	4 kg/tonne
Dissolved oxygen (arriving at the LMFs)	173 ppm	100 ppm	130 ppm
Arc power	13.2 kWh/ton	7.2 kWh/ton	7.4 kWh/ton

Table 22. Steel and slag additions during heat-1

Time (min)	0-5	4	13	14	22	23
Addition (wt% or ppm)	0.08% Al wire	0.27% Mn 0.022% C	0.021% Al 3.7 % CaO in slag 0.028% C-wire	0.06% Mn 45 ppm C	56 ppm Al-wire	55 ppm C-wire

Table 23. Steel and slag sampling time for heat-1, time is in minutes

Time	-4	0	3.5	7	8.5	11	13	15.5	18	22.5
Steel			LF3	LF4	LF5		LF6	LF7	LF8	
Slag	LF1	LF2	LF3	LF4		LF5				LF6

Table 24. Steel and slag additions during heat-2

Time (minutes)	0-6	20	21	35
Addition	0.08% Al	0.02% Al 10% CaO in slag	0.31% Mn 0.025 % C	0.08% Mn 65 ppm C

Table 25. Steel and slag sampling times for heat-2, time is in minutes

Time	0	4	7.5	11	13	14.5	17	19	24.5	30.5	37.5
Steel	LF1	LF2	LF3	LF4	LF5	LF6	LF7	LF8	LF9	LF10	LF11
Slag	LF1	LF2	LF3	LF4	LF5	LF6	LF7	LF8	LF9		LF10

Table 26. Additions in steel during heat-3

Time	0-6 min	21 min	30 min	31 min
Additions	0.082% Al-wire	0.33% Mn 0.026% C	54 ppm Al-wire	38 ppm C-wire

Table 27. Steel and slag sampling times for heat-3, time is in minutes

Time	0	4	7	12.5	14.5	16.5	25			
Steel	LF1	LF2	LF3	LF4	LF5	LF6	LF7			
Time	-1.5	3	6.5	12.5	24	28.50	30	32	33	
Slag	LF1	LF2	LF3	LF4	LF5	LF6	LF7	LF8	LF9	

6.2.2 Characterization

Lollipop steel samples were grounded and chemical analysis was done using spark optical emission spectroscopy technique and the slag samples were analyzed using X-ray Fluorescence (XRF) Spectroscopy. The area fraction and chemistry of inclusions in each steel sample were measured using automated feature analysis (AFA) available in the SEM-ASPEX Explorer instrument.

6.3 Model Description

The chemical composition of steel, slag and inclusions can change during ladle refining due to following six factors (see also Figure 6): 1) steel-refractory reaction, 2) slag-refractory reaction, 3) inclusion flotation to the slag, 4) steel-inclusion reaction, 5) steel-slag reaction and 6) inclusions origination from slag. In this set of trials, the refractory lining was designed to minimize the reactions of refractory with steel slag. The refractory lining in contact with steel and slag was alumina and MgO-C. Hence, reactions 1) and 2) were not considered in the model. The inclusion removal was considered a first order reaction as described before. One inclusion removal rate constant (β) was found sufficient to model plant scale ladle refining operation. The steel-inclusion reaction was considered to be at equilibrium: inclusion composition was equilibrated with the changing steel composition (due to steel-slag reaction) in every step of calculation.

Steel-slag reactions were considered to be mass transfer controlled using the effective equilibrium reaction zone (EERZ) approach as shown earlier, Figure 8. A single mass transfer coefficient was used for all species in the steel and slag phases. Generally, the mass transfer coefficient in the slag phase was considered to be 10 times smaller as the mass transfer coefficient varies with $\sqrt{D}$ [37] and diffusivity in the slag phase is typically 100 times smaller than in liquid steel. Since the slag was partly solid in this case (containing up to 40 wt% solids according to FactSage), the mass transfer coefficient in slag was considered to be 15 times smaller than in the steel phase. Sometimes, inclusions with composition similar to slag were also observed in inclusion analysis; this phenomenon was not considered in the model. The addition of alloying elements (aluminum, manganese and carbon) in liquid steel and CaO in slag were also considered in the model in addition to inclusion flotation to slag, steel-inclusion reaction and steel-slag reactions. The model was implemented using the FactSage macro-processing feature and MS-Excel was used for

reading input and writing output of the model. The FTmisc database was used for liquid steel and FToxid and FACTPS databases were used for slag and inclusions. Figure 50 shows a flow chart describing the steps for the calculation.

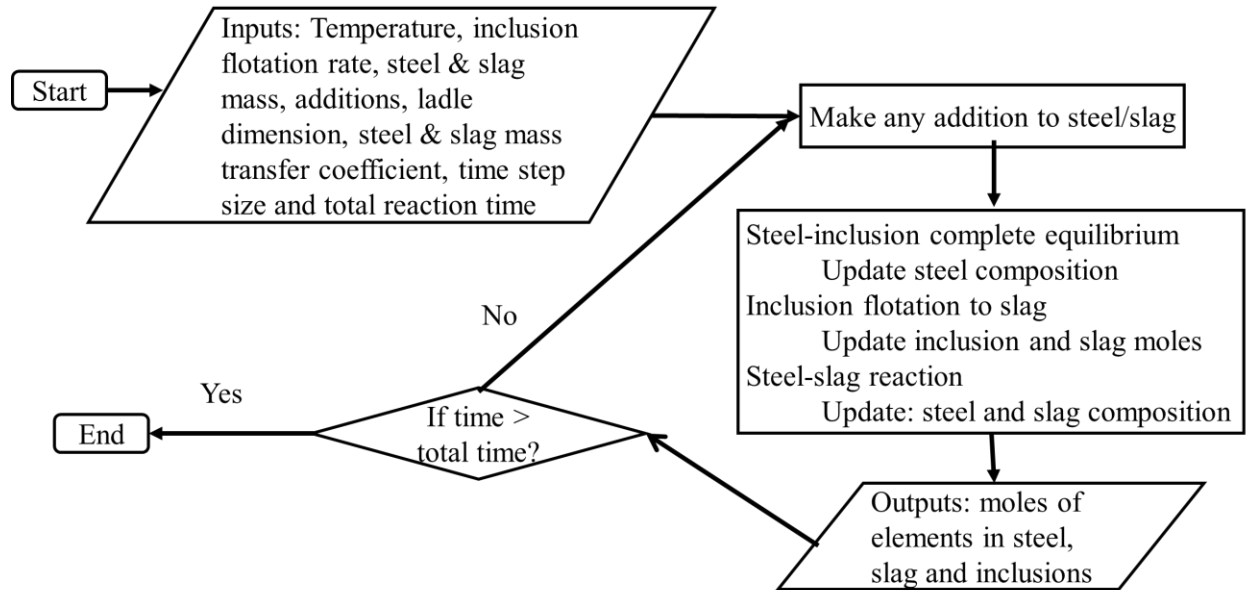


Figure 50. Flow chart of calculations in kinetic model

6.4 Results

6.4.1 Steel and slag composition

The mass transfer coefficient in steel and the flotation rate constant of inclusions were two unknown kinetic parameters for the kinetic model. These parameters were found by fitting the model results of the changes in chemical compositions of steel and slag and concentration inclusions in steel samples with time for individual heats. The parameters were fitted to find qualitatively the best fit to all measured changes in steel and slag composition. Some deviations in the steel and slag chemistry can be due to impurities from alloying additions or reoxidation during alloying. Due to this reason, a qualitative fitting procedure was used instead of quantitative.

Figure 51 (a-e) show calculated lines and measured (markers) changes in aluminum, chromium, sulfur, manganese and carbon concentration in steel with time for heat-1. The aluminum concentration (total=dissolved + inclusions) in steel increases at the times of aluminum addition but decreases otherwise due to 1) flotation of alumina inclusions and 2) reaction between steel and slag. The FeO concentration in slag decreases (see Figure 52 (a)) with time due to its reaction with aluminum in steel. The chromium concentration in steel increases with time due to reduction of Cr_2O_3 from slag by aluminum; the calculated chromium concentration fits well to measured values. The net increase in Al_2O_3 concentration due to reduction of FeO and Cr_2O_3 and inclusion flotation is shown in Figure 52 (b). As shown in Table 22, a mixture of CaO (3.7% of slag) and Al (0.021% of steel) was added to the slag at time 13 minutes. The corresponding increase in aluminum concentration in steel was about 0.01% and hence the alumina concentration in slag was expected to increase. Since the slag was partially solid (as shown in Figure 62), the local increase in alumina concentration may be much higher. Therefore, the higher measured alumina concentration in LF6 slag sample shows the sampling difficulty associated with an inhomogeneous slag. The measured sulfur concentration in steel did not change significantly and the calculated values also did not predict any significant change. Manganese and carbon concentrations in steel increased only when these were added as ferroalloys or carbon wire. In the kinetic model, ferromanganese addition was assumed to be instantaneous; however, the measured values clearly indicate that there was a dissolution and mixing time for these alloying elements. This effect will be discussed further later in this section. The fitted mass transfer coefficient in steel for heat-1 was equal to 2×10^{-3} m/s that fit to measured changes in steel and slag composition. A similar fitting procedure was adopted for heat-2 and heat-3 as well; those values are in Table 28.

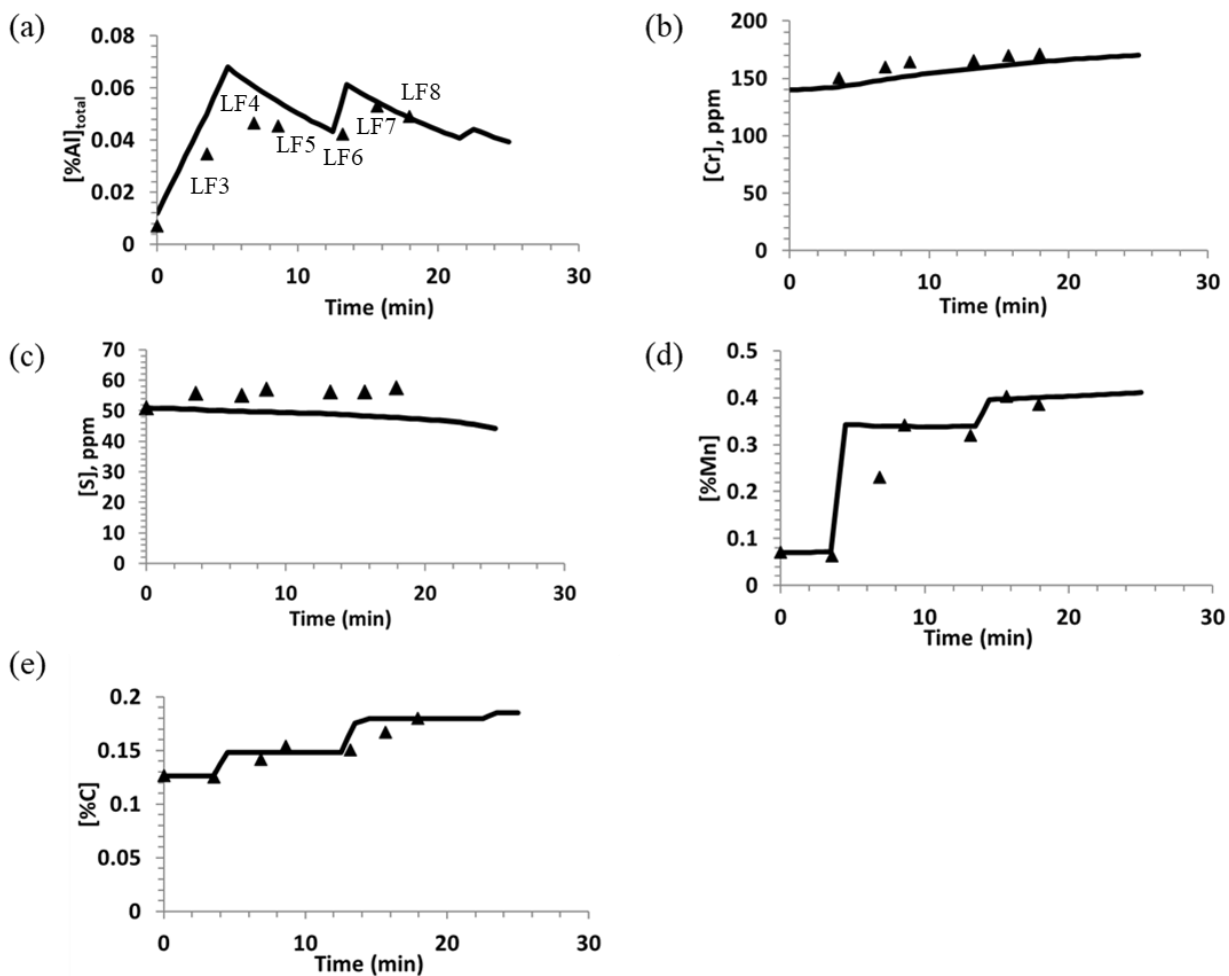


Figure 51. Calculated and measured steel composition with time for heat-1

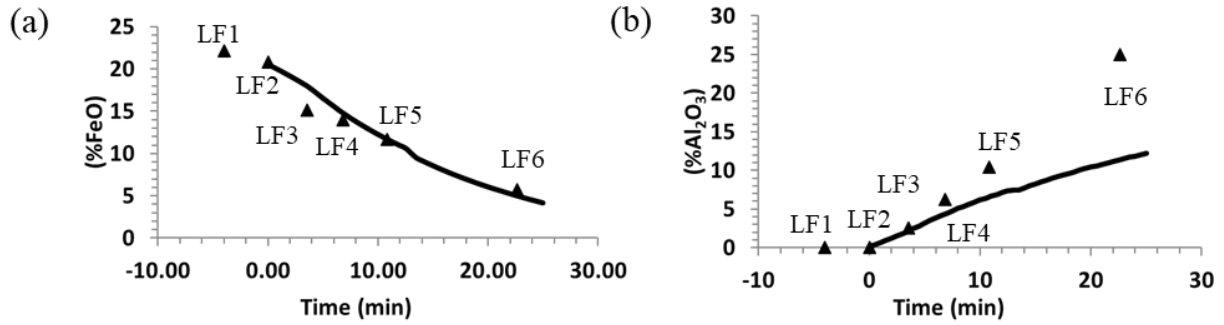


Figure 52. Calculated and measured FeO and Al₂O₃ concentration in slag with time for heat-1

6.4.2 Inclusion concentration and composition

The flotation of inclusions is known to be enhanced by argon stirring of the steel bath: stirring promotes the collision of inclusions leading to formation of large clusters and the clusters are subsequently floated with argon bubbles to slag. The agglomeration of alumina inclusions was revealed using an electrolytic etching technique: the steel matrix was etched to reveal the 3D morphology of inclusion clusters. Figure 53 shows change in cluster size with time for samples taken from heat-1 (The smaller spherical particles surrounding the large inclusion in sample LF8, t=18 min, are remnant of electrolytic solution on the steel surface and not inclusions.). The cluster size changed from around 200 μm (t=4 min) to 5 μm (t=18 min) during ladle refining process.

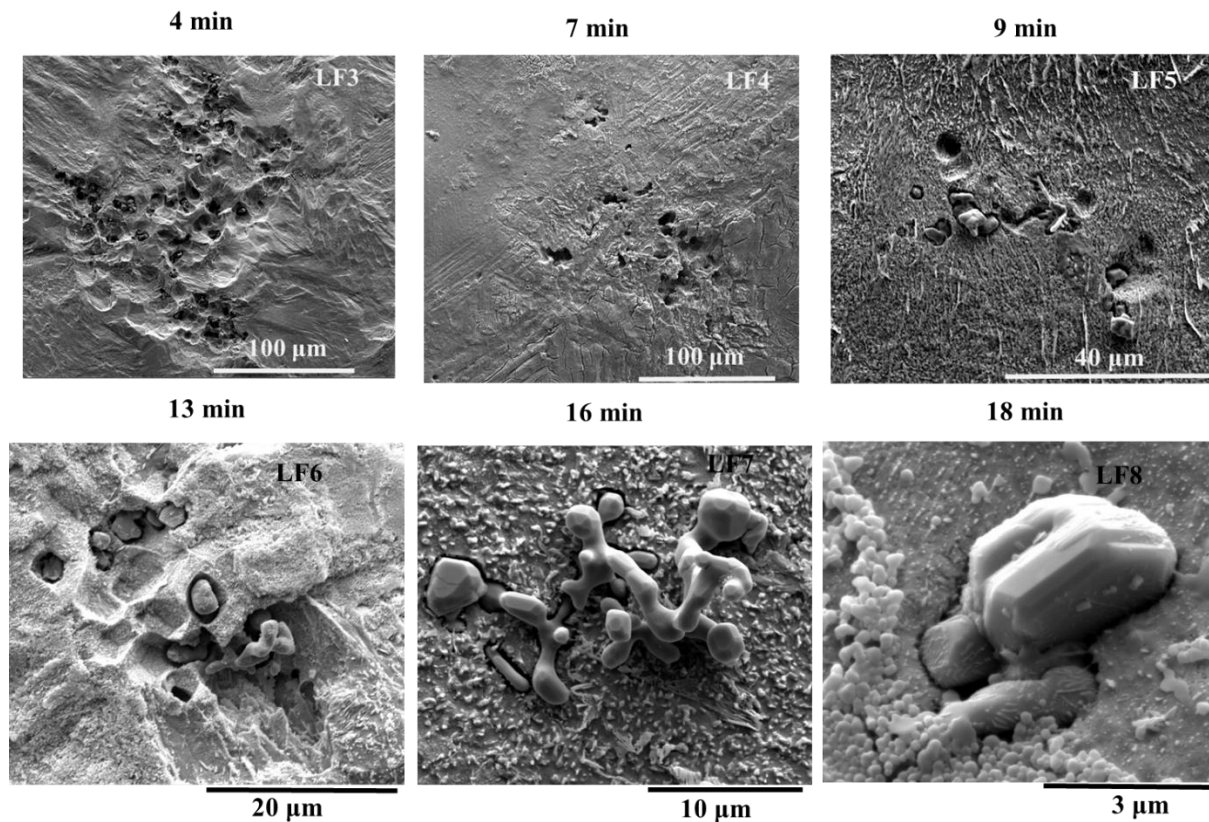


Figure 53. Change in inclusion cluster with time for heat-1

The change in inclusion concentration with time was measured as bound oxygen in inclusions. The area fraction of inclusions as measured using SEM ASPEX-Explorer was converted into the mass fraction of inclusions assuming area fraction = volume fraction. The bound oxygen in inclusions was then calculated using the measured average composition of inclusions. The measured inclusion concentration was then fitted to find the flotation rate constant assuming inclusion flotation to be first-order as discussed earlier. Figure 54 shows the fitting of calculated inclusion concentration to the measured for heat-1. The fitted flotation rate constant was equal to 0.26%/s which is the fraction of the inclusions that is removed to the slag per second. It should be noted that sometimes inclusions chemical analysis showed the presence of CaO and SiO₂, suggested that those inclusions might originate due to intermixing of slag. Such inclusions were not considered

while calculating the flotation rate constant. The fitted flotation rate constants for all heats are in Table 28.

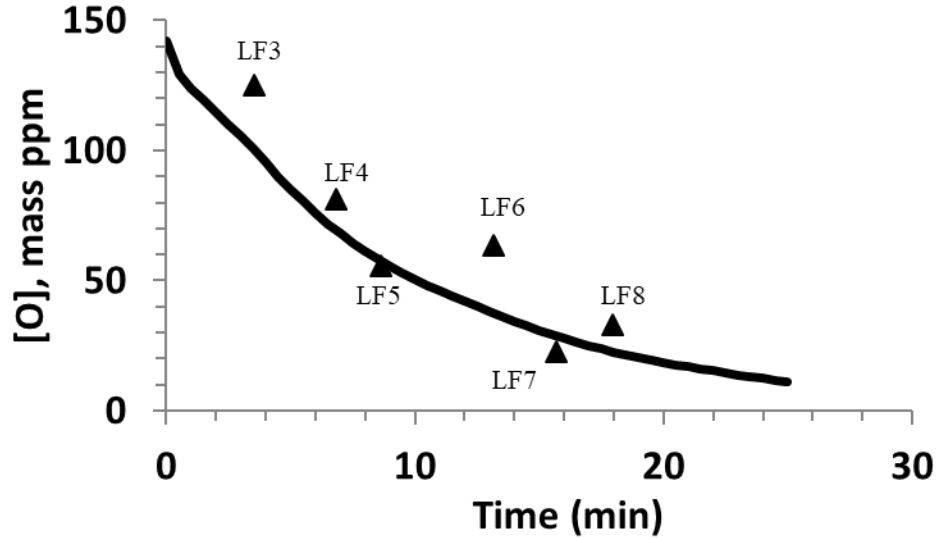
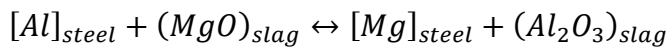


Figure 54. Measured and fitted inclusion flotation for heat-1

The composition of deoxidation inclusions changed from alumina to non-stoichiometric spinel with time. Figure 55 shows the rate of transformation as the increase in molar MgO concentration with time. The samples taken at 15.5 minutes and 18 minutes in ladle clearly showed small increase in MgO concentration in inclusions and the sample taken from tundish showed significant MgO pick-up in inclusions. It should be noted that the inclusion concentration changes with time and the sample from tundish had just 7 ppm of bound oxygen in inclusions. Lower concentration in inclusions was expected to show significant transformation of alumina inclusions to spinel inclusions for the fixed rate of magnesium pick-up in steel due to steel-slag reaction. The change in composition was expected due to reduction of MgO from slag by aluminum in steel as shown in Equation 25 and Equation 26.



Equation 25

$$x[Mg]_{steel} + <Al_2O_3>_{inclusion} \leftrightarrow$$

Equation 26

$$<(MgO)_x \cdot (Al_2O_3)_{1-\frac{x}{3}}>_{inclusion} + \frac{2x}{3}[Al]_{steel}$$

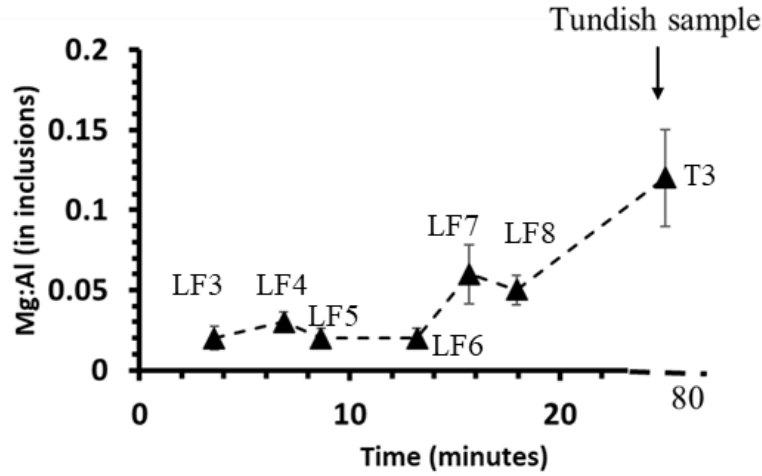


Figure 55. Transformation of alumina inclusions to spinel inclusions with time for heat-1

Figure 56 shows magnesium pick-up in inclusions from ladle (15.5 minute and 18 minute after the beginning of aluminum wire addition) and tundish sample. These steel samples were electrolytically etched before SEM analysis. SEM-EDS analysis of inclusions from tundish samples also showed barely detectable calcium pick-up in inclusions.

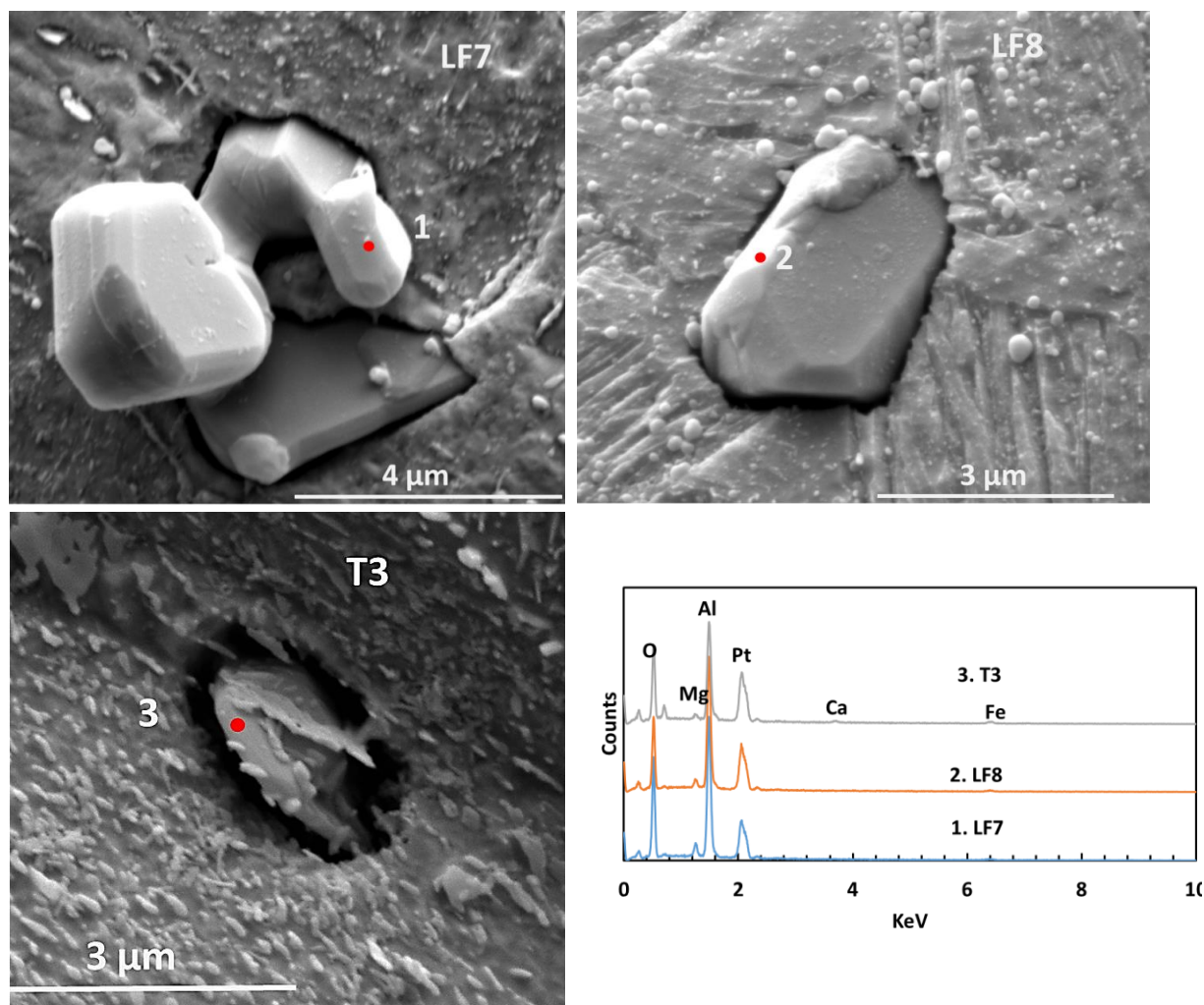


Figure 56. Magnesium pick-up in deoxidation inclusions in ladle samples; LF7 (15.5 minute) and LF8 (18 minute). Magnesium and calcium pick-up in the tundish sample (T3)

The calculated composition of inclusions for heat-1 is shown in Figure 57. The MgO pick-up in inclusions were predicted by the model calculation as well. However, the predicted CaO pick-up in inclusions was not observed in the samples taken from ladle samples. This observation is consistent with previous results from kinetic model developed for laboratory scale induction furnace aluminum deoxidation experiments discussed in section 5.4. The likely reason is the over-prediction of calcium solubility in the FTmisc database for liquid steel.

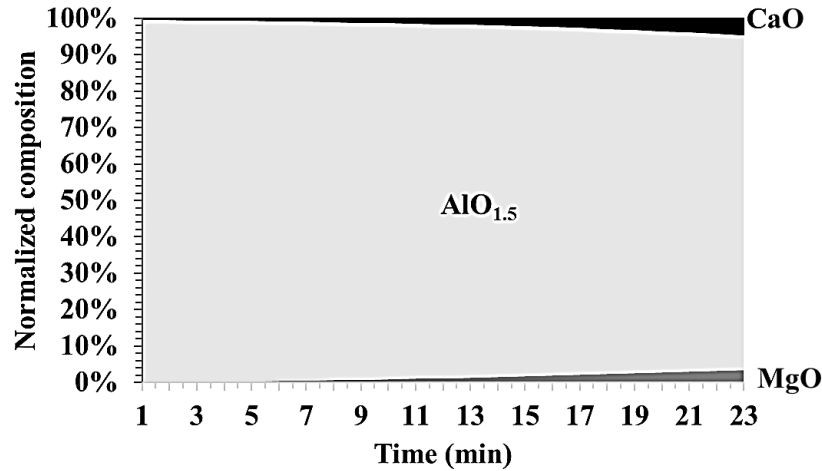


Figure 57. Calculated inclusion composition with time for heat-1 (molar basis)

6.5 Discussion

The kinetic model can be a useful tool for steelmakers to predict changes in steel, slag and inclusion composition with time during ladle refining process under similar process conditions. As shown in the previous section, the effect of argon stirring on the mass transfer coefficient and flotation rate constant can be considered using empirical equations or by fitting the model to a set of stirring conditions. It was also shown that the FTmisc database tends to over-predict calcium transfer to steel by steel-slag reaction. There is a need for more reliable thermodynamic data regarding calcium solubility under steelmaking conditions. The chemical analysis of steel and slag samples and inclusion analysis of steel samples from three heats helped in identifying some other issues that need to be considered while using such a kinetic model. These are discussed in this section.

6.5.1 Model parameter and stirring power

Table 28 summarizes the fitted steel mass transfer coefficient and inclusion flotation rate constants for all three heats. It can be seen that the mass transfer coefficient and flotation rate constant increases with increase in measured argon flow rates. There are several correlations available to

calculate mass transfer coefficients in steel based on stirring energy [16], [19], [23]. The stirring energy due to argon injection can be calculated as the sum of isobaric expansion at the injection point (due to increase in temperature) and isothermal expansion (due to change in pressure as argon bubbles move upwards). Sundberg [63] considered these two effects to calculate total mechanical stirring power for argon injection (see Equation 27). Abel et al. used Equation 28 to calculate stirring energy.

$$\epsilon = 371 \left(\frac{QT}{M} \right) \left[\left(1 - \frac{T_0}{T} \right) + \ln \left(\frac{P_1}{P_0} \right) \right] \quad \text{Equation 27}$$

$$\epsilon = 371 \left(\frac{QT}{M} \right) \ln \left(\frac{P_1}{P_0} \right) \quad \text{Equation 28}$$

Where ϵ : stirring energy in W/ton, Q: argon flow rate at STP in m³/s, M: steel mass in tonne, P₀: atmospheric pressure and P₁: pressure in the bottom of the ladle. The calculated stirring energy for three heats (using Equation 27) are mentioned in Table 28.

Table 28. Fitted model parameters for three industrial trials

Parameter	Heat-1	Heat-2	Heat-3
Steel mass transfer coeff (m_{steel})	2×10^{-3} m/s	6×10^{-4} m/s	7.5×10^{-4} m/s
Slag mass transfer coeff. (m_{slag})	1.3×10^{-4} m/s	4.0×10^{-5} m/s	5×10^{-5} m/s
Flotation rate constant (k)	0.26%/s	0.18%/s	0.2%/s
Argon flow rate (measured)	0.45 Nm ³ /s	0.02 Nm ³ /s	0.03 Nm ³ /s
Stirring energy (W/tonne)	1599	79	116

Several researchers have shown that there is an exponential relationship between mass transfer coefficient and stirring energy of the form shown in Equation 29 [16], [19], [20]. As shown in

Equation 30, the slope and intercept of $\ln(m_{steel})$ vs $\ln(\epsilon)$ plot are equal to n and $\ln A$ respectively. Figure 58 shows this type of plot for current work along with that from Peter et al. [19], Graham & Irons [16] and Abel et al. [64]. The stirring power for heat-1 is lot higher than the range used by Graham & Irons [16] and Peter et al. [19]. The graph in Figure 58 shows the plots only in the stirring power range in which those correlations were developed. Abel et al. used Equation 31 to calculate the product of mass transfer coefficient and area. The effective mass transfer coefficient was deduced using planar steel-slag interface area. The values of n and A were 0.39 and 0.0024. Peter et al. [19] found that n and A were 0.47 and 0.0181 and Graham & Iron found $n=1.4$ and $A=0.0036$. It should be noted that the mass transfer coefficients was converted to min^{-1} unit from m/s using the depth of steel in order to compare the expression reported by Peter et al [19]. Although the value of n from current work is close to the one reported by Peter et al. [19], the mass transfer coefficient in steel found in this work was much smaller than that calculated from other expressions in the literature. Although the results from Graham & Irons [16] was not extended to the stirring power relevant to current work, it can be seen that even at lower stirring powers, the mass transfer coefficient calculated from their work was higher than those found from current work. Schwerdtfeger [29] proposed that the inclusion flotation rate constant was expected to be similar to mass transfer coefficient in steel phase as both inclusion removal and steel-slag reaction are controlled by transfer across the steel-slag boundary layer. Flotation rate constants calculated for three heats from the current work is also plotted in Figure 58. The observed relationship between flotation rate constant and stirring energy from current work is: $k = 0.18\epsilon^{0.11}$, which shows a weak correlation with stirring energy. However, the absolute values of the flotation rate constants are very close to the mass transfer coefficients calculated with the expressions of Peter et al. [19] and Abel et al. [64].

$$m_{steel} = A\epsilon^n \quad \text{Equation 29}$$

$$\ln m_{steel} = \ln A + n \ln \epsilon \quad \text{Equation 30}$$

$$m_{L-L}A = 76.2 \left(\frac{\epsilon^{1.07} \rho_L^{1.06} V_u^{0.63} H_L^{0.30} D}{Q_{g,T,P}^{0.19} \Delta \rho_{L-U}^{0.8} \sigma_{L-L}^{1.32} d_b^{1.95} (1-\alpha)^{0.05}} \right) \quad \text{Equation 31}$$

Where ρ_L : steel density, ρ_U : slag density, V_U : slag volume, H_L : depth of steel, D : diffusivity in liquid steel, $Q_{g,T,P}$: argon flow rate at steelmaking temperature and pressure, σ_{L-L} : surface tension at the steel-slag interface ($=0.8 \text{ kg/s}^2$), d_b : diameter, α : volume fraction of bubbles

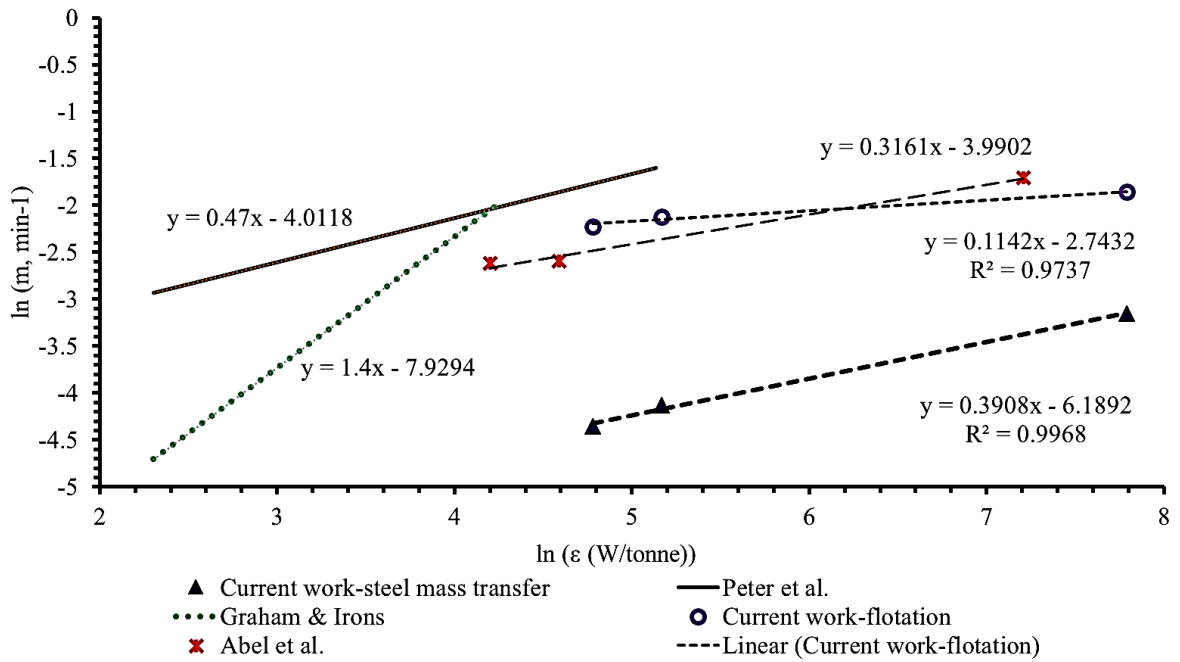


Figure 58. Mass transfer coefficients with stirring power for all heats

The inclusion flotation to slag is expected to be only limited by mass transfer in liquid steel (the slag was not alumina saturated) but the rate of steel-slag reaction could be affected by the mass transfer coefficient in slag. Therefore, it is important to understand what could be happening at the

steel-slag interface. To understand this, four combinations of steel and slag mass transfer coefficients were considered for simulating heat-1, as shown in Table 29. The first case has the same steel and slag mass transfer coefficient as fitted earlier, with the steel to slag mass transfer coefficient ratio=15. For the other three cases, the steel mass transfer coefficient was calculated by multiplying the flotation rate constant for heat-1 with the depth of the steel bath. For case-2, the slag mass transfer coefficient was the same as case-1, and for case-3 the ratio of steel to slag mass transfer coefficient was equal to 15. Okuyama et al. [21] reported that the mass transfer coefficient of SiO_2 in slag can be as low as 100-times smaller than in steel. In case-4, the mass transfer coefficient in slag was considered 100-times than in steel. Figure 59 shows the resulting calculated dissolved oxygen concentration in steel at the steel-slag interface. The oxygen concentration at the interface was found to be dependent on both steel and slag mass transfer coefficients, with relatively reducing conditions in steel and oxidizing conditions in slag. All three additional cases (2-4) were found to be reducing enough to allow silicon pick-up in steel and desulfurization of liquid steel neither of these were evident in measured silicon and sulfur concentrations (some silicon pick-up at the early stage is expected from silicon in aluminum wire and ferromanganese). This means that the only way in which the mass transfer coefficient in steel could be the same as for inclusion flotation if there was an additional source of oxygen at the steel-slag interface.

Table 29. Four cases to study steel-slag interfacial reactions during heat-1

Case#	m_{steel}	m_{slag}	Ratio
1	0.002	0.000133	15
2	0.00728	0.000133	54.75
3	0.00728	0.000485	15
4	0.00728	0.0000728	100

The most likely combination of mass transfer coefficient is that described in case-3: steel mass transfer coefficient same as inclusion flotation and slag mass transfer coefficient 15 times smaller than in steel. For this case, the additional oxygen can be estimated using the sum of difference in oxygen concentration for case-1 and case-3. The difference in oxygen concentration at the interface is shown in Figure 61. The total oxygen required was equivalent to 107.2 ppm of bulk steel. Such oxygen pickup may be possible at the steel-slag interface due to oxygen ingress through ladle eye as shown in Figure 62. However, the measured aluminum concentration did not show any such fade (of about 0.01 wt%), see Figure 51.

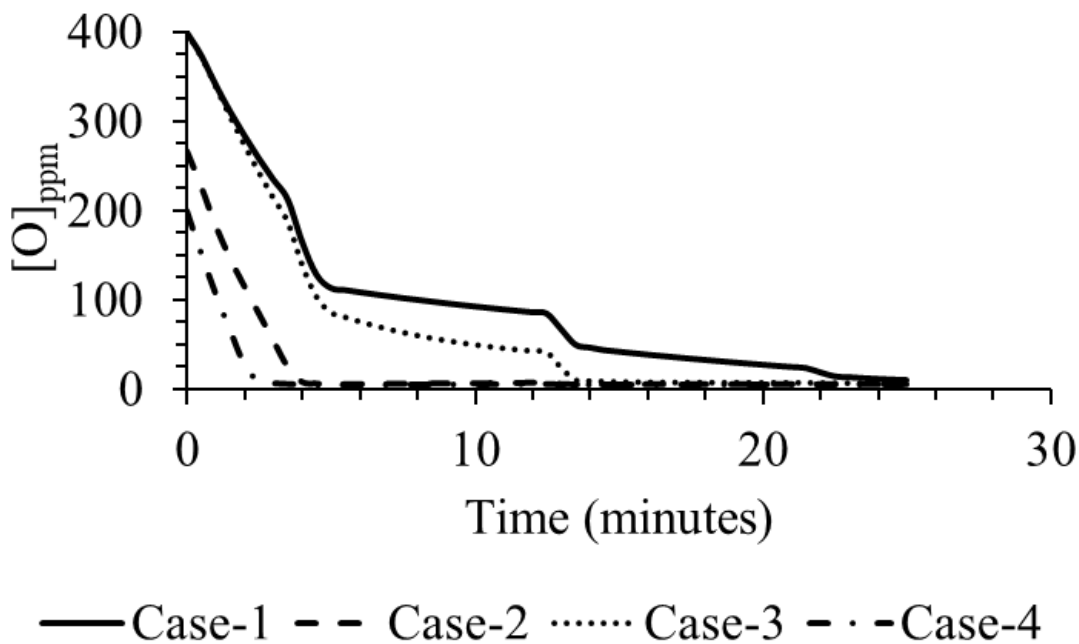


Figure 59. Calculated interfacial oxygen concentration in steel for conditions in Table 29

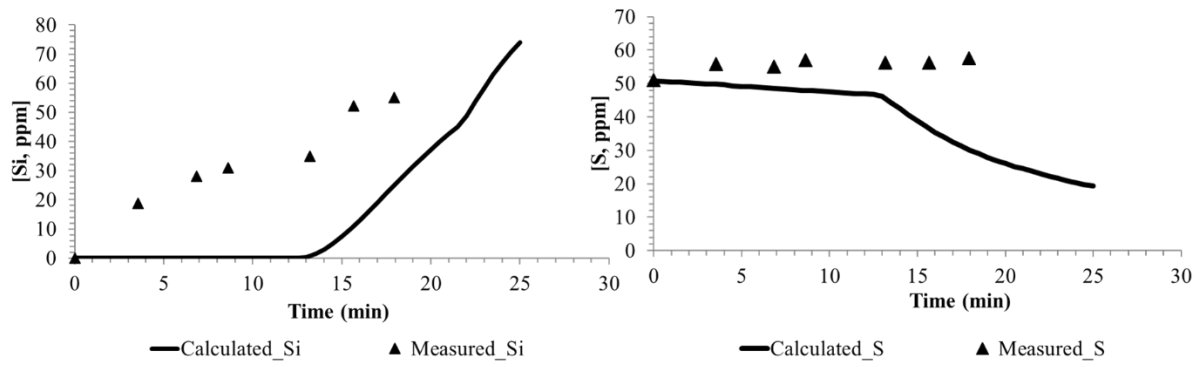


Figure 60. Change in silicon and sulfur in steel during heat-1 for conditions in case-3 of Table 29

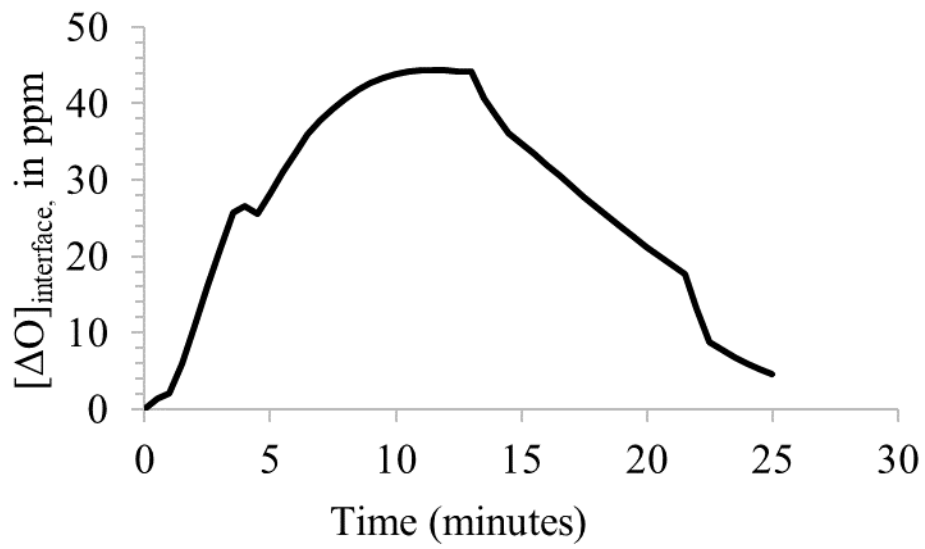


Figure 61. Difference in interfacial oxygen between case-1 and case-3 for heat-1

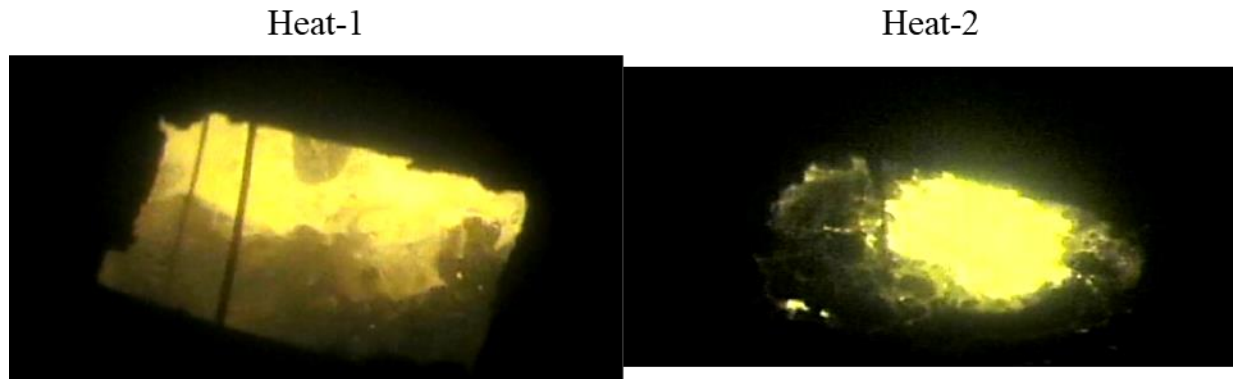


Figure 62. Stirring of steel bath for heat-1 and heat-2

The likely explanation for the reduced reaction rate between steel and slag can be the reduced reaction rate due to presence of solid in slag (see Figure 62). As shown by Bannenberg et al. [61], the heterogeneity in the slag (lime saturation index > 1) due to lime super-saturation can adversely affect the desulfurization rate, see Figure 63. It shows that even if the situation is thermodynamically favorable, the kinetics of steel-slag reaction can be adversely affected by the presence of solid phase in slag. It should be noted that, the flotation of alumina inclusion can be seen as independent from steel-slag reaction responsible for silicon pick-up and desulfurization in the present work. Since slag was not saturated in alumina, all alumina inclusion transported with liquid steel to the steel-slag interface could be expected to be absorbed by the slag phase. The mass transfer coefficient correlations developed by other researchers [16], [19] did not explicitly describe the effect of partially solid slag on the kinetics of steel-slag reaction. The slag composition reported by Graham & Irons was close to fully liquid; initial slag composition was approximately 50% CaO, 32% Al_2O_3 , 5.5% SiO_2 , 1.5% FeO, and 8% MgO. A closer look at the slag composition reported by Peter et al. [19] reveal that for aluminum killed steel (LMF 1) the slag was supersaturated with CaO (CaO saturation index=1.07); slag composition (at $t=5$ minutes) was

approximately 58% CaO, 30% Al₂O₃, 4% FeO, 2% SiO₂, 5% MgO and 0.7% S. Only 10% of the slag was liquid in this case (at 1610°C) which may or may not be enough to affect mass transfer.

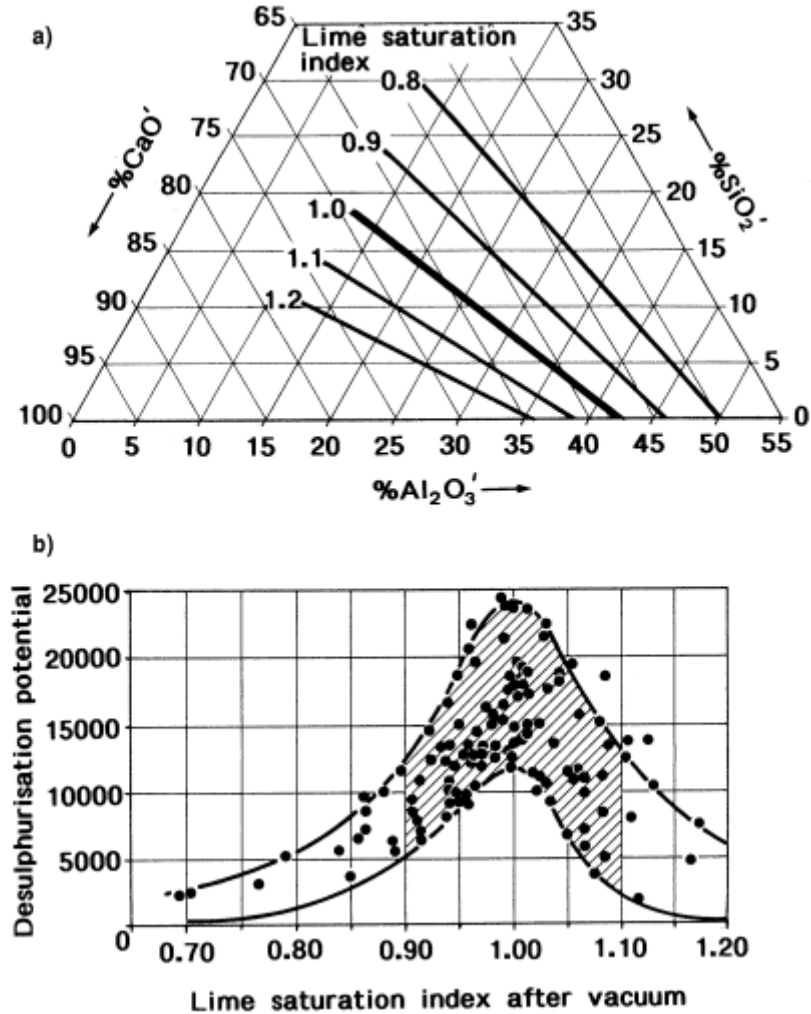


Figure 63. Lime saturation in CaO'-SiO₂'-Al₂O₃' system and desulfurization potential on l dependent on the lime-saturation index; reproduced from [61]

6.5.2 Alloy dissolution and mixing time

Initial modeling results suggested that there was a significant melting and homogenization time associated with the addition of ferromanganese. As shown in Figure 64, when 0.27 wt% of manganese was added (as ferromanganese) to the steel at $t=4$ minutes in the model, the calculated manganese composition was much higher than measured for the next six minutes. Figure 65 shows

a better agreement to measured manganese concentration when 0.31 wt% of total manganese addition (as ferromanganese) was distributed over 15 minutes under mild stirring condition compared to heat-1. The approach to add ferromanganese over an extended period was used to approximate melting and mixing of the ferroalloy; the dissolution time was chosen to approximate the observed concentration change.

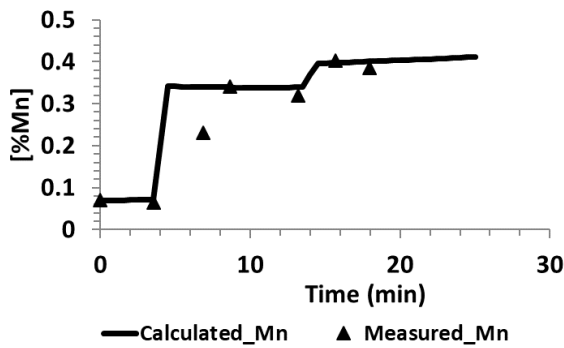


Figure 64. Instantaneous addition of Fe-Mn in heat-1

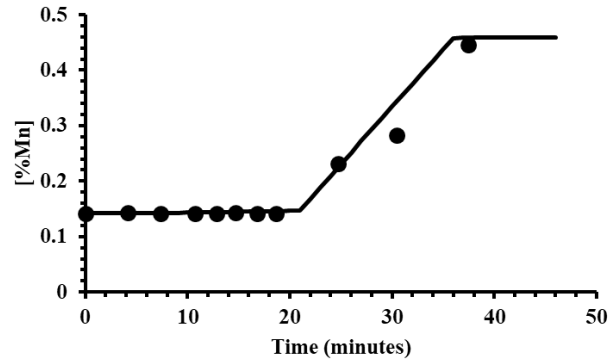


Figure 65. Delayed addition of Fe-Mn in heat-2

6.5.3 Sampling issue: steel and slag

6.5.3.1 Steel sample reoxidation

Steel samples were taken using a lollipop sampler which used argon flushing followed by vacuum to avoid any reoxidation during sampling. Despite these measures; the inclusion analysis of samples from heat-3 showed several outlier points on inclusion concentration with time plot as shown in Figure 66. The higher inclusion concentration in samples taken at $t=12$ minutes and 17 minutes indicates possible reoxidation either during sampling or due to actual reoxidation of steel bath. To test these possibilities, reoxidation events were simulated in the model by adding 150 ppm and 350 ppm oxygen to the bulk steel at 12th and 17th minutes respectively.

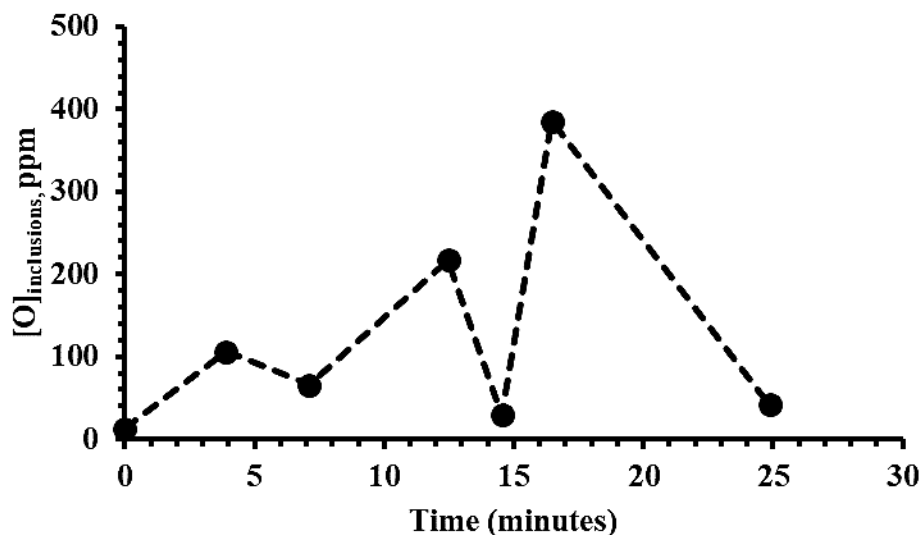


Figure 66. Measured oxygen in inclusions for heat-3

Figure 67 compares calculated and measured oxygen (in inclusions) and aluminum concentration in steel samples for two cases: (a) no reoxidation and (b) both reoxidation. The measured aluminum concentration in the tundish sample is shown as the last data point. As expected, the calculated oxygen concentration for case (a) does not show reoxidation at $t=12$ and 17 minutes but the calculated aluminum concentration agrees well with the measured value. For case (b), the calculated oxygen concentration in inclusion was forced to approximate both reoxidation events but the calculated bound oxygen was higher than measured for $t=15$ and 25 minutes. Also, the calculated aluminum concentration was much lower than measured for times after simulated reoxidation, including in the tundish sample. The large decrease in calculated aluminum concentration is due to two oxygen additions in the melt of which the major contribution was the second reoxidation event (350 ppm O addition). From this analysis, it can be concluded that the observed increase in inclusion concentration was due to reoxidation of the sample and there was no bulk reoxidation of the melt. These two samples were ignored when fitting the calculated inclusion concentration to the measured for heat-3. The fitted flotation rate constant was 0.2%/s

(see Table 28). The measured inclusion concentration at $t=25$ minutes was also higher than the calculated values by about 30 ppm. The likely source of this oxygen was the addition of 0.33% Mn (as ferromanganese) at $t=20$ minute. An increase of 20-30 ppm in oxygen concentration in inclusions was always observed after ferromanganese additions in the other heats studied in this work.

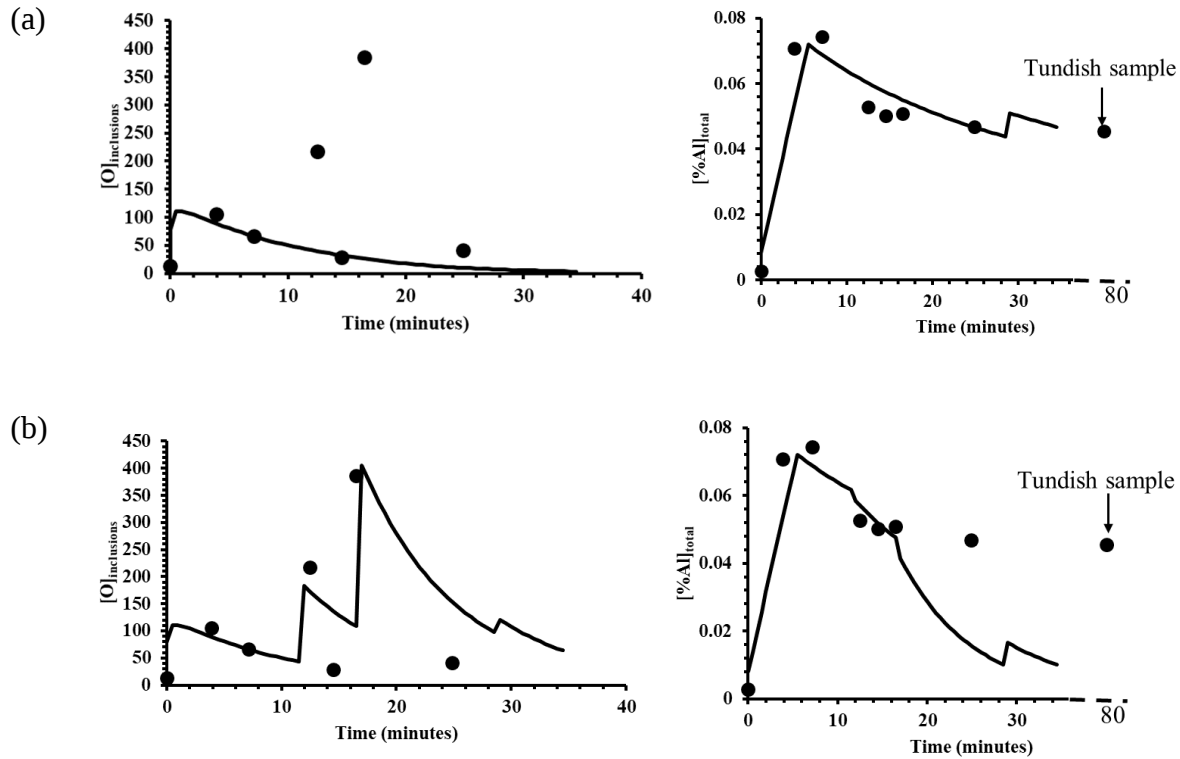


Figure 67. Oxygen concentration in inclusions and total aluminum in steel: without and with reoxidation: (a) no reoxidation was considered in the model, (b) reoxidation at $t=12$ and $t=17$ minutes considered and Markers represent measured and solid line represents calculated values

6.5.3.2 Slag sampling issue

The slag sampling and analyses were generally consistent with the expected weak desulfurization trend and magnesium pick-up in inclusions as seen from the comparison between measured and calculated results. In heat-3, there was an issue related to slag sampling. As shown in Figure 68, the measured alumina concentration in slag is much less than expected in most samples even

though the alumina concentration in slag was expected to increase with time due to flotation of alumina (deoxidation product). There are two possible slag sampling issues that may result into such errors: 1) presence of metallic iron in slag may result into a higher measured FeO concentration in slag and 2) the slag was inhomogeneous (partially molten (see Figure 62)) which poses risk of sampling only liquid slag. The measured slag chemistry with time is shown in Table 30. The presence of metallic iron cannot explain the measured lower alumina concentration as the CaO and MgO concentrations are also expected to be lower if there was any FeO dilution effect in samples with lower alumina.

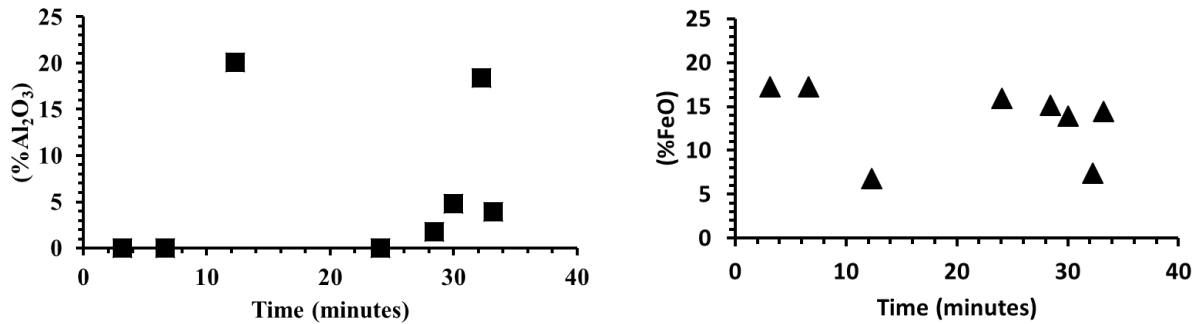


Figure 68. Measured Al_2O_3 and FeO concentration in slag during heat-3

Table 30. Slag chemistry with time for heat-3.

Time (min)	P ₂ O ₅	Cr ₂ O ₃	FeO	Al ₂ O ₃	MgO	CaO	SiO ₂
-1.47	0.3	0.3	19.5	0.0	18.7	49.6	6.4
3.17	0.3	0.3	17.3	0.0	17.4	52.9	6.0
6.60	0.3	0.4	17.2	0.0	20.5	50.1	6.0
12.30	0.1	0.1	6.8	20.0	14.9	43.4	5.5
24.07	0.3	0.3	15.9	0.0	19.0	52.2	6.4
28.43	0.2	0.3	15.1	1.7	18.7	51.9	6.0
30	0.1	0.3	13.9	4.8	17.6	51.4	5.9
32.2	0.1	0.1	7.4	18.4	15.2	44.2	5.6
33.2	0.2	0.3	14.4	3.9	17.5	51.5	6.2

6.5.4 Inclusions originating from slag

There were inclusions with high CaO, SiO₂ and MgO concentrations (along with Al₂O₃) in steel samples taken during heat-1. Figure 69 shows the concentration of such slag-like inclusions along with alumina inclusions and total inclusions. The concentration of slag-like inclusions also decreased with time due to flotation. There was an increase in both alumina and slag like inclusions after slag conditioner addition at t=13 minutes. The increase in alumina inclusions was expected due to reoxidation during addition and the increase in slag-like inclusion concentration was expected due to entrapment during additions. It should be noted that the slag-like inclusions were rarely observed in heat-2 and heat-3 in which stirring conditions were relatively mild. Figure 70 shows the average size of alumina and slag like inclusions with time. It can be seen that the slag like inclusions were larger than alumina inclusions but were in the same size range, indicating the entrapment of very fine slag droplets in liquid steel. The slag-like inclusions may be generated due to surface instabilities caused by the fluid flow turbulence at the steel-slag interface or extreme

changes in interfacial tension during steel-slag reactions. Consideration of these effects are beyond the scope of this model. However, slag-like inclusions can be manually added to the model considering expected fluid flow conditions as discussed by Harada et al. [24].

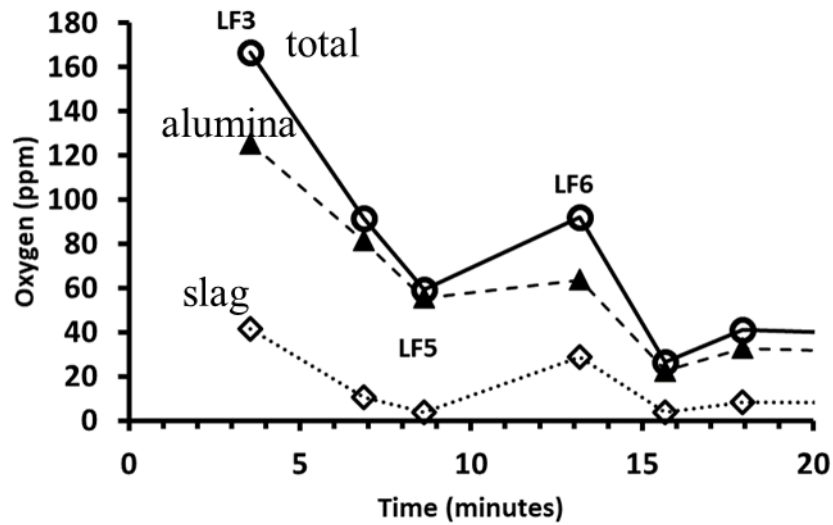


Figure 69. Inclusion concentration of pure alumina, slag like and total inclusions in heat-1

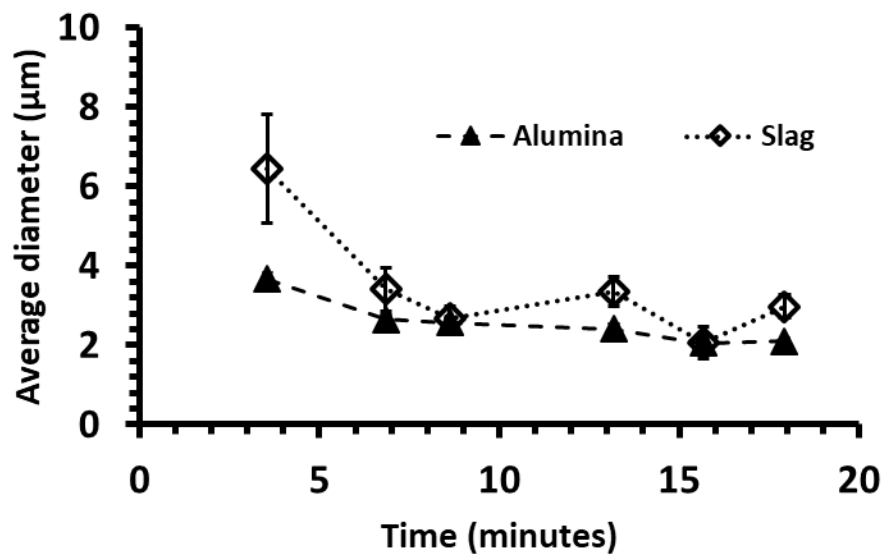


Figure 70. Average size of alumina and slag like inclusions with time

6.6 Conclusions

A two-parameter based kinetic model was developed to simulate the changes in steel, slag and inclusion composition changes during ladle refining operation. The model parameters were fitted to measured steel and slag chemistry and inclusion chemistry and concentration measured using SEM ASPEX-Explorer. The fitted inclusion flotation parameter shows close agreement to published correlations for mass transfer coefficient.

Some important considerations and limitations are highlighted as well. The ferroalloy dissolution and mixing was found important and dependent on stirring conditions. The use of the kinetic model to diagnose artifacts due to steel and slag sampling practices was also discussed. The formation of slag-like inclusions could not be considered in the model due to fluid flow complexity involved. The model used databases from FactSage software to do multiple equilibrium calculations using its macroprocessing feature. It was found that the FTmisc. database used to model liquid steel over-predicts calcium pick-up by steel due to steel-slag reactions.

7 Calcium transfer to oxide inclusions without calcium treatment

The effect of reaction of aluminum killed steel with MgO crucible and CaO-Al₂O₃-SiO₂-MgO slag on the transformation of alumina was reported in chapter- 5. The alumina inclusions transformed to spinel in experiment-5.6 (without argon stirring) but there was no observed calcium transfer in inclusions in any sample taken upto 35 minutes after aluminum addition. In experiment-5.7, the steel melt was stirred by flowing argon: the alumina inclusions transformed to spinel with limited calcium transfer observed in sample taken at 49th minute after aluminum addition. Pretorius et al. [1], [65] reported the presence of calcium transfer to alumina/spinel inclusions without calcium treatment. Deng and Zhu [30] also reported transformation of alumina inclusions into spinel inclusions followed by calcium modification due to calcium pick-up in steel from slag during ladle refining of Al-killed alloyed steel. However, in chapter 6 of present work, it was shown that there was no calcium containing inclusions at the end of ladle refining and barely detectable calcium containing inclusions were found in tundish samples, see Figure 56. It can be argued that the higher oxidation potential at the steel-slag interface could have successfully avoided calcium pick-up and limited magnesium pick-up under these conditions. However, there were slag-like micro-inclusions observed in steel samples which raises question of how much calcium transfer observed during ladle refining are due to steel-slag chemical reaction and how much due to slag entrapment. In this section we try to address this issue by using different strategies to improve calcium transfer under laboratory conditions.

7.1 Objective

The objectives of this chapter are:

- a) To understand the effect of silicon concentration (1%) on calcium transfer to inclusions in steel due to steel-slag reaction using
 - I. Ferrosilicon (Fe-93% Si)
 - II. Electronic grade silicon wafer
- b) To study the effect of the crucible on calcium transfer: a steel-slag-crucible experiment was conducted using a ZrO_2 crucible to test the limiting effect (if any) of the MgO crucible on calcium transfer to inclusions. Similar experiments were also conducted using $\text{CaO-3\%ZrO}_2$ crucibles with and without slag.
- c) To study calcium-transfer from CaS to oxide inclusions: steel containing known concentration of CaS inclusions was prepared and added to a melt containing alumina inclusion in a subsequent experiment.

7.2 Effect of silicon on calcium transfer from slag

7.2.1 Experimental

All three experiments in this section were conducted using 600 g of low sulfur (7-8 ppm) electrolytic iron in MgO crucibles supplied by Tateho Ozark Technical Ceramics. Experiment-7.1 was conducted to test the effect of silicon addition on calcium transfer to inclusions due to steel-slag reaction. Table 32 describes the addition and sampling for experiment-7.1. The electrolytic iron melt was deoxidized by adding 0.3 wt% Al at $t=0$ minute followed by 1 wt% equivalent of silicon addition using ferrosilicon (93% silicon) at $t=3$ minutes. 180 g of slag-7.1 was added at $t=7$

minutes. The compositions of slag 7.1 and slag 7.2 are given in Table 32. Slag-7.2 was used for experiment-7.2 and 7.3.

Table 31. The slag compositions used to test the effect of silicon on calcium transfer

	%CaO	%Al ₂ O ₃	%MgO	%SiO ₂
Slag-7.1	47.5	36.5	7	9
Slag-7.2	51	42	7	0

Table 32. Addition and sampling description for experiment-7.1 (MgO crucible)

Time (minutes)	0	3	7	15	25	35	55
Event	0.3% Al	1% Si (Fe-93Si)	180 g of slag-7.1	S1	S2	S3	S4

As described later in detail, samples from experiment-7.1 had calcium containing inclusions. As ferrosilicon may contain some calcium contamination, additional experiments were needed to confirm if the silicon addition can affect calcium transfer to inclusions. Experiment-7.2 and 7.3 were carefully designed to study this effect. Electrolytic iron was kept with CaO-Al₂O₃-MgO slag (slag-7.2) at the beginning of experiment, and 0.3 wt% aluminum wrapped in a clean iron foil was added to molten liquid iron at t=0 minute. The capsule containing aluminum was hung in an alumina rod which was dipped in the melt to make sure aluminum reached the molten electrolytic iron. For experiment-7.3, 1% silicon was added as electronics grade Si at t=5 minutes. The addition and sampling details for experiment-7.2 and 7.3 are described in Table 33 and Table 34. It should also be noted that the slag-7.2 does not contain any silica. In the absence of silica in slag, negligible aluminum fade from liquid steel was expected compared to experiments-5.6 and 5.7.

Table 33. Addition and sampling description for experiment-7.2 (MgO crucible)

Time	0.00	1 min	16 min	31 min	70 min
Event	0.3% Al addition	S1	S2	S3	SF

Table 34. Addition and sampling description for experiment-7.3 (MgO crucible)

Time	0.00	5 min	7 min	20 min	35 min	50 min	65 min	75 min
Event	0.3% Al	1% Si	S1	S2	S3	S4	S5	SF

7.2.2 Results

7.2.2.1 Ferrosilicon as a source of silicon

Figure 71 through Figure 74 show changes in inclusion composition and content during the experiment. The left side ternary diagram show number density and right side shows area density of inclusions. Calcium and magnesium content in inclusions increased with time; the rate and the extent of magnesium pick-up was more than calcium pick-up. Calcium containing inclusions were present as oxides and sulfides. The inclusion composition in the calcium corner of the ternary diagram represents CaS inclusions. The sample taken at the 35th minute contained four types of inclusions: alumina, spinel, calcium modified alumina/spinel and CaS. Alumina inclusions must have formed due to re-oxidation (most likely during sampling), which is evident from their relatively larger numbers and smaller area. CaS inclusions were also relatively small in size but large in number. Spinel inclusions were the largest. The final sample (taken at 55th minute, Figure 74) contained MgO or MgO rich Mg-Al-Ca-O inclusions. The oxygen content in this sample due to detected inclusions was only 12 ppm. The average size of inclusions observed in the final sample

was around 1.50 μm , much smaller than in steel-slag-crucible experiment-5.6 and slightly larger than the steel-slag-crucible experiment-5.7 (with argon stirring).

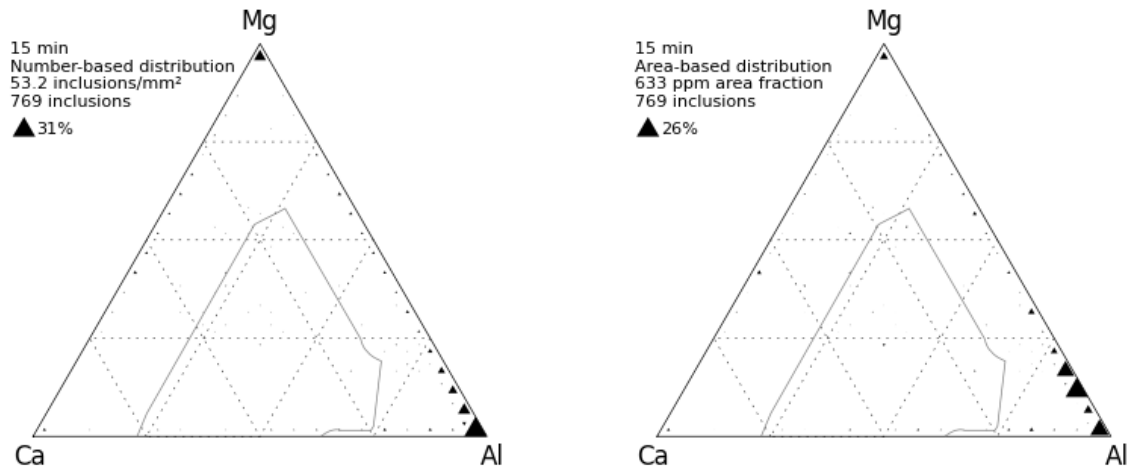


Figure 71. Inclusion composition 15 minutes after aluminum deoxidation during experiment-7.1 (MgO crucible)

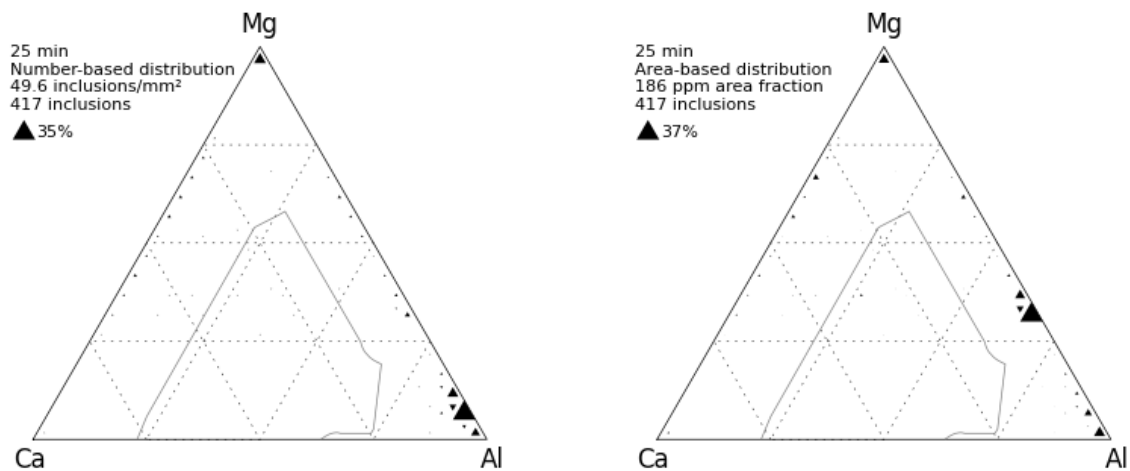


Figure 72. Inclusion composition 25 minutes after aluminum deoxidation during experiment-7.1 (MgO crucible)

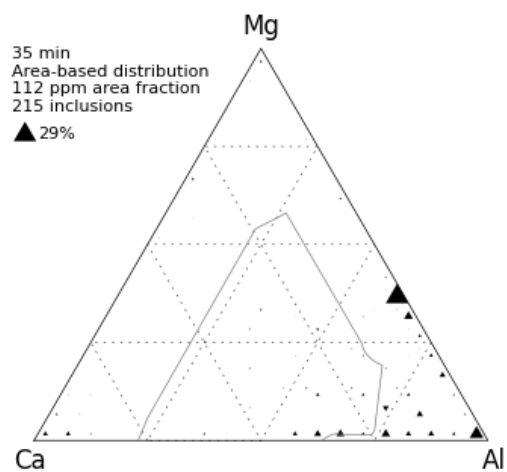
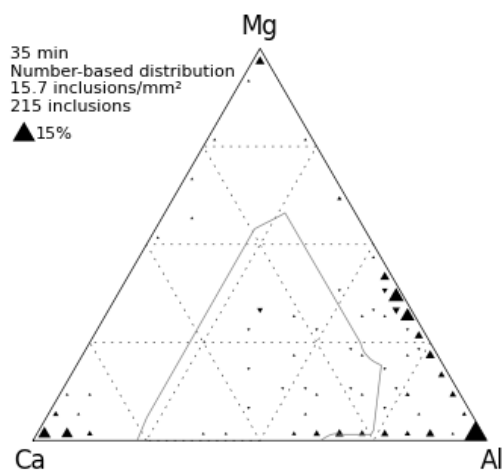


Figure 73. Inclusion composition 35 minutes after aluminum deoxidation during experiment-7.1

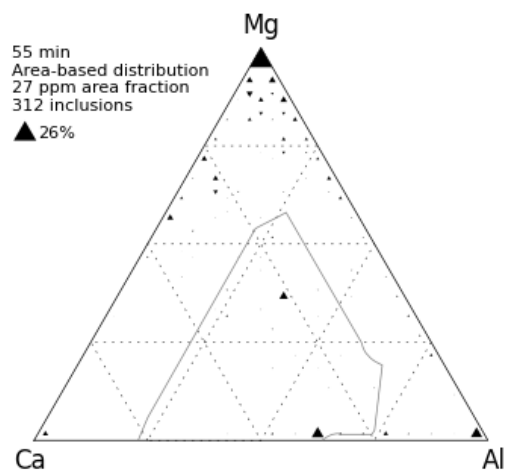
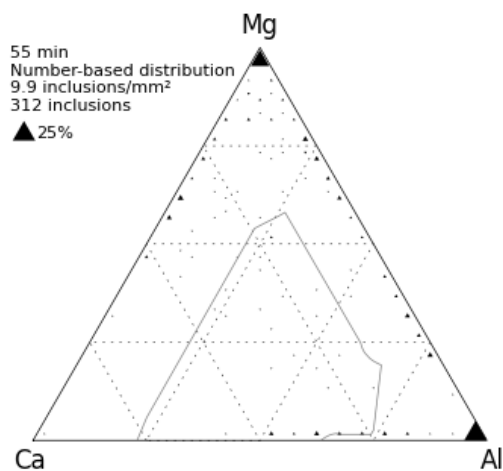


Figure 74. Inclusion composition 55 minutes after aluminum deoxidation during experiment-7.1

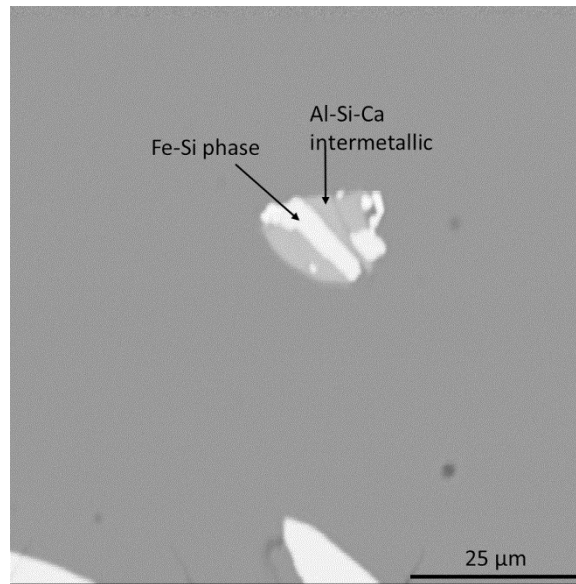


Figure 75. Al-Si-Ca phase present in ferrosilicon used for experiment-7.1

The possible sources of calcium in liquid steel (and inclusions) can be calcium transfer from slag and/or calcium contamination from ferrosilicon used for silicon addition. Figure 75 shows the presence of a calcium containing phase in the ferrosilicon used for experiment-7.1. In the experiments reported in the next section, electronics grade silicon was used to distinguish the source of calcium in such experiments. Similar to experiments-5.6 and 5.7, magnesium pick-up in steel was observed (as MgO-containing inclusions) in all samples. Pure MgO inclusions were also present in the sample taken at the 55th minute. (see Figure 74). A spinel inclusion transforming into an MgO inclusion was observed in the final sample from experiment-7.1 (see Figure 76).

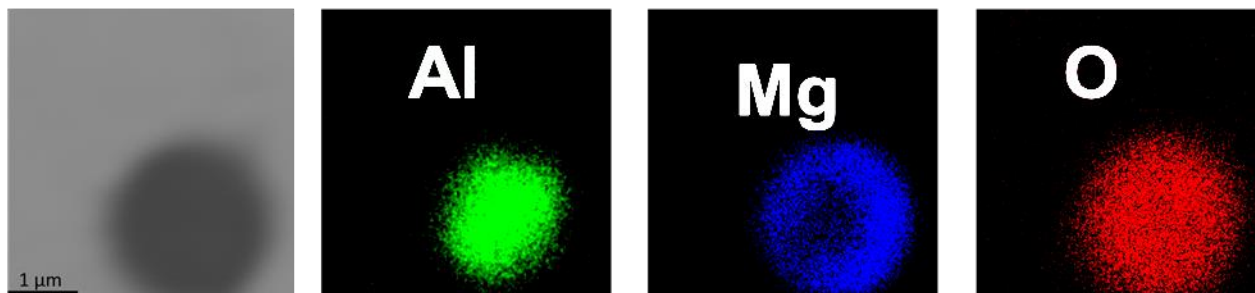
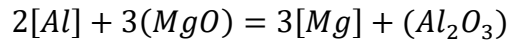


Figure 76. Transformation of spinel inclusion to MgO; observed in a sample taken at 55th minute during experiment-7.1, note that the outer rim of the inclusion contains Mg and O, but not Al

In conclusion, calcium containing inclusions were clearly observed in this experiment. The addition of 1 wt% silicon was found to enhance calcium pick-up in liquid steel from slag. Although ferrosilicon contained limited amount of calcium, the increase in calcium pick-up with time indicates that calcium pick-up was more likely due to steel-slag reaction than calcium contamination from ferrosilicon. The formation mechanism of MgO inclusions in the later sample was found to occur due to continuous supply of magnesium from the crucible.

7.2.3 Using electronics grade silicon for silicon addition

The evolution of inclusion composition during experiment-7.2 (steel-slag experiment without silicon addition) is shown in Figure 78 through Figure 81. It can be seen that the inclusions completely transformed to MgO by $t=16$ minutes. Under these conditions, aluminum in steel is expected to react with MgO in slag and in crucible. The rate of transformation of alumina inclusions to spinel to MgO appears faster than previous steel-slag experiments (5.6 and 5.7) in MgO crucible. It should be noted that the initial added aluminum in all experiments was 0.3 wt%. Since slag in experiments-5.6 and 5.7 contained silica, the concentration of aluminum was expected to decrease with time as aluminum in steel would reduce silica in slag (as shown in section 5.4). In the absence of silica in slag, aluminum concentration in steel was expected to remain constant leading to faster magnesium pick-up in steel as expected from reaction shown in Equation 32. As described before, slag was added at the beginning with solid electrolytic iron. It was expected that the slag would melt and wet crucible wall before electrolytic iron melts. Figure 77 shows the crucible wall in contact with steel after experiment-7.2. A slag layer ($\text{CaO-Al}_2\text{O}_3\text{-MgO}$) was commonly present which was expected to improve magnesium transfer at the steel-crucible interface.



Equation 32

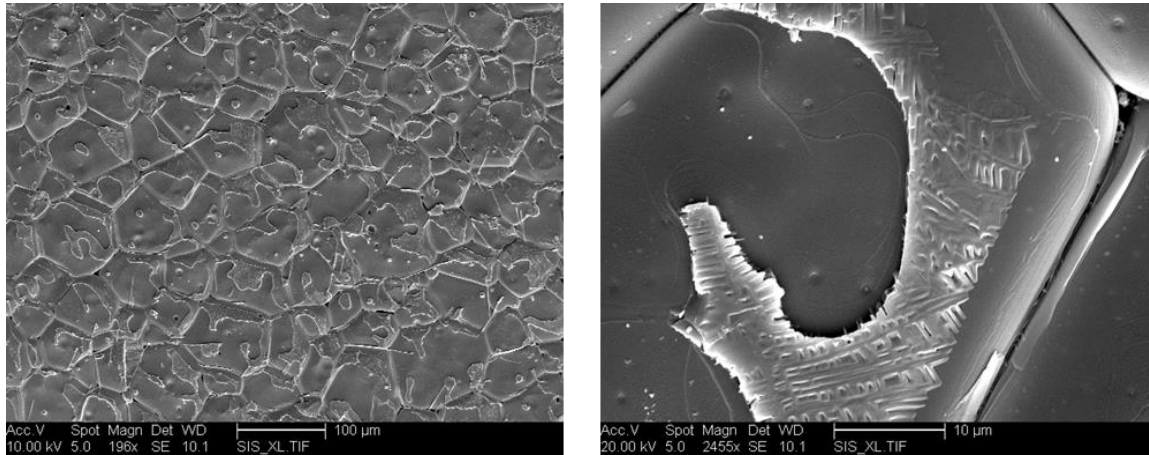


Figure 77. MgO crucible wall coated with slag after experiment-7.2

The increase of alumina in inclusions from sample-2 (t=16 minutes) to sample-3 (t=31 minutes) may be due to minor reoxidation of the melt which may generate fresh Al-Mg-O inclusions. Final sample (t=70 minutes) had mainly MgO inclusions along with small calcium concentration. Figure 82 shows one such calcium containing inclusions: the inclusion was mainly MgO with small amount of calcium sulfide. In conclusion, very limited calcium transfer was found only in the final sample of experiment-7.2.

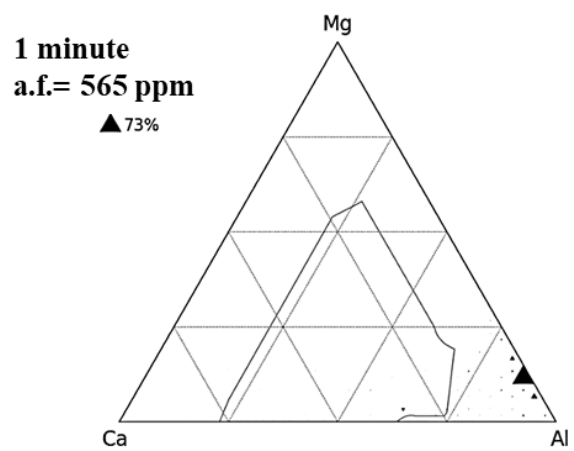
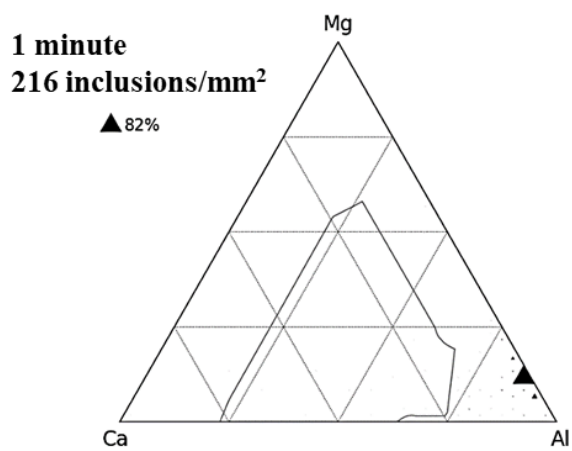


Figure 78. Inclusion composition in steel 1 minute after aluminum addition during experiment-7.2 (no silicon)

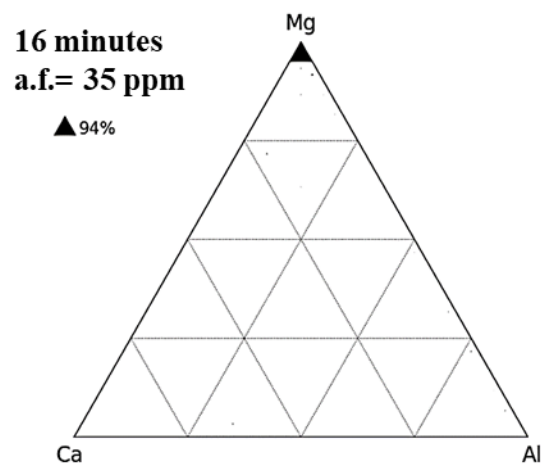
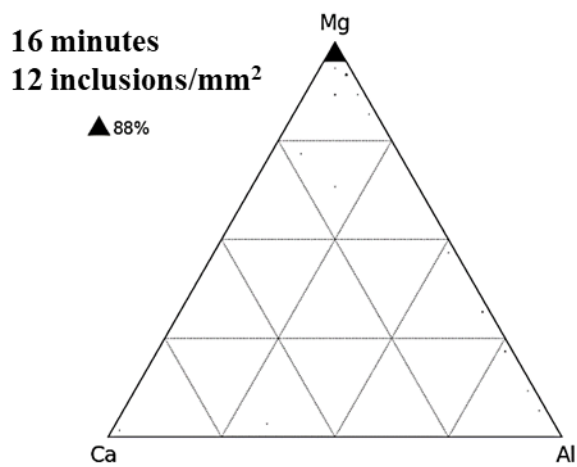
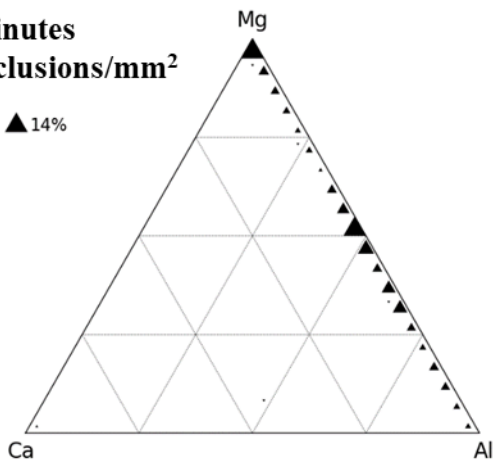


Figure 79. Inclusion composition in steel 16 minutes after aluminum addition during experiment-7.2 (no silicon)

31 minutes
16 inclusions/mm²

▲ 14%



31 minutes
a.f.= 41 ppm

▲ 25%

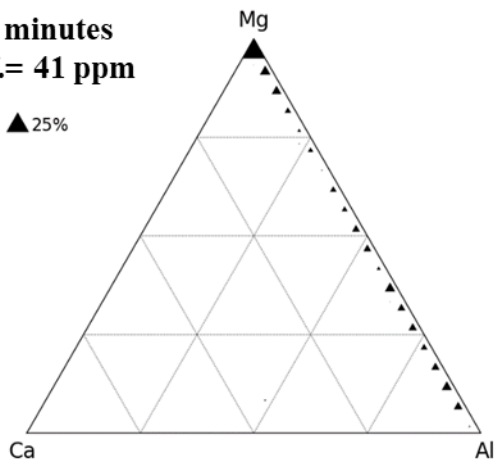
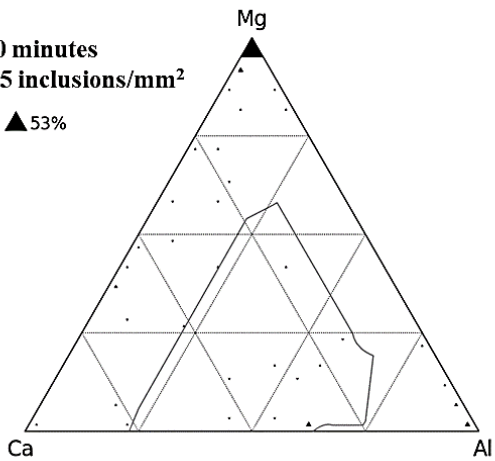


Figure 80. Inclusion composition in steel 31 minutes after aluminum addition during experiment-7.2 (no silicon)

70 minutes
4.5 inclusions/mm²

▲ 53%



70 minutes
a.f.= 19 ppm

▲ 77%

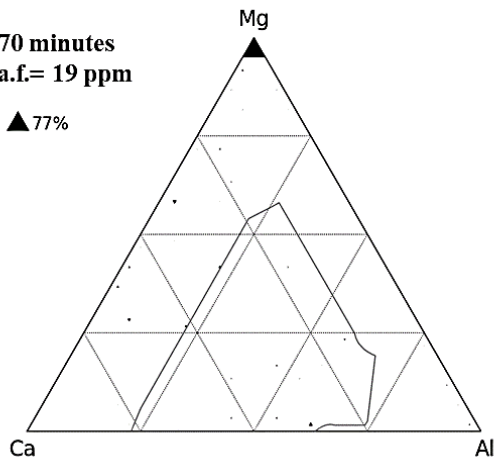


Figure 81. Inclusion composition in steel 70 minutes (final sample) after aluminum addition during experiment-7.2 (no silicon)

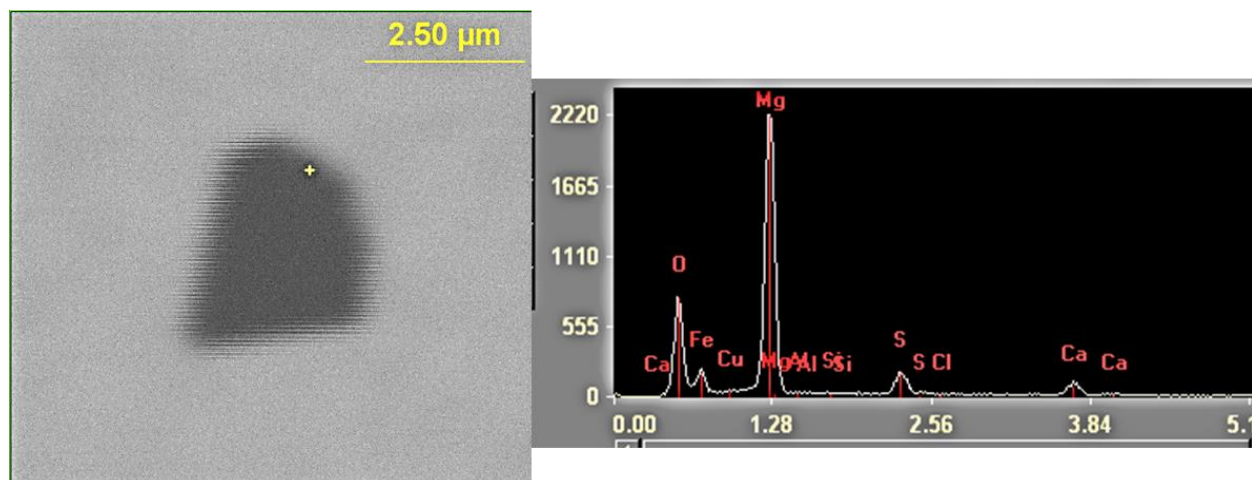


Figure 82. MgO-CaS inclusion in sample taken at 70th minute (final sample) from experiment-7.2 (no silicon)

The inclusion evolution during experiment-7.3 (with added 1% Si) is shown in Figure 83 through Figure 88. The inclusions in sample-1 were a mixture of spinel and spinel transforming to MgO. Some calcium containing inclusions were also observed. In sample-2, inclusions contained more calcium than sample-1. Some inclusions can be seen in the calcium corner of the ternary diagram representing CaS inclusions (see Figure 84). Some MgO-CaS type inclusions were also found. The inclusion composition in sample-3 (see Figure 85) demonstrates continued pick-up of calcium and reduction in magnesium concentration in inclusions indicating that calcium from steel-slag reaction could have reduced MgO at the steel-inclusion interface as described by Yang et al. [31]. The inclusion in this sample was mixture of liquid CaO-Al₂O₃-MgO inclusions and MgO rich MgO.Al₂O₃ inclusions. Figure 86 indicates that the total magnesium concentration in steel kept increasing due to the reaction of steel with MgO crucible (assisted by slag layer) and with MgO containing slag. The inclusions in the final sample (Figure 88) were a mixture of MgO rich inclusions with CaO-Al₂O₃-MgO inclusions with occasional MgO-CaS inclusions. The evolution of inclusion composition was verified by doing manual inclusion analysis using the FEI/SEM, Philips XL-30 showing a similar trend to that observed from SEM ASPEX-Explorer area analysis.

Micrographs of inclusions from this analysis are shown in Table 35. The area-based average composition of inclusions (from ASPEX-Explorer) for all samples are shown on Mg-Al-Ca ternary in Figure 89, illustrating the evolution of inclusion composition.

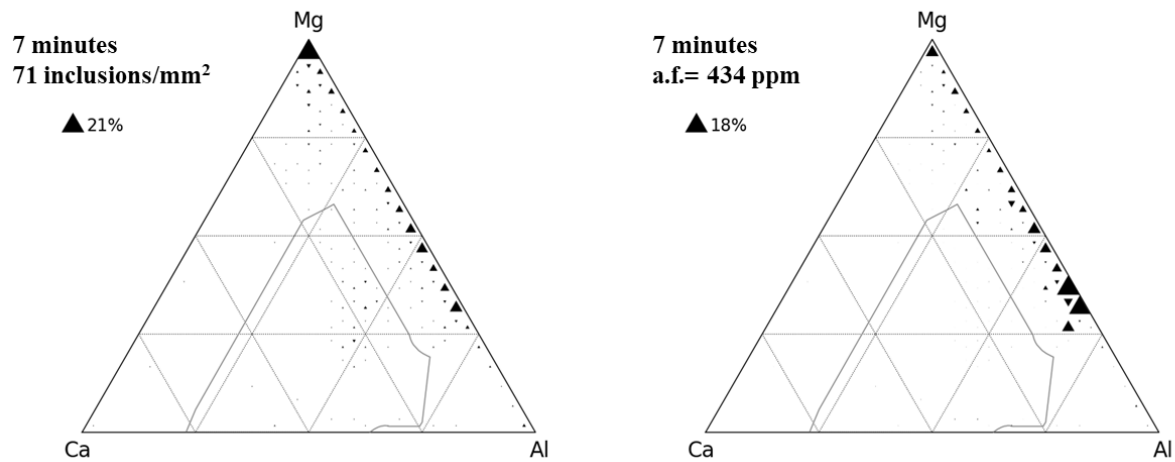


Figure 83. Inclusion composition in steel 7 minutes after aluminum addition during experiment-7.3 (1% electronic grade silicon)

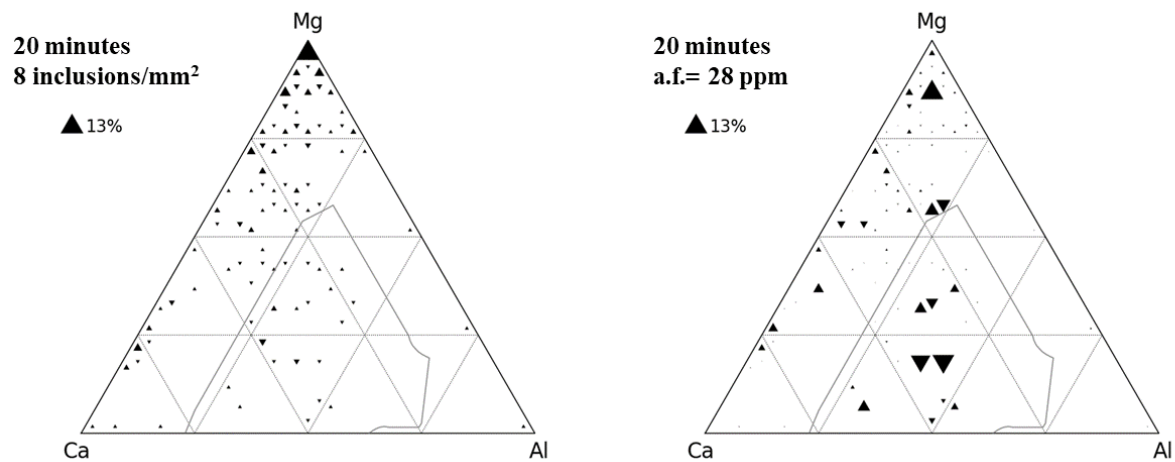


Figure 84. Inclusion composition in steel 20 minutes after aluminum addition during experiment-7.3 (1% electronic grade silicon)

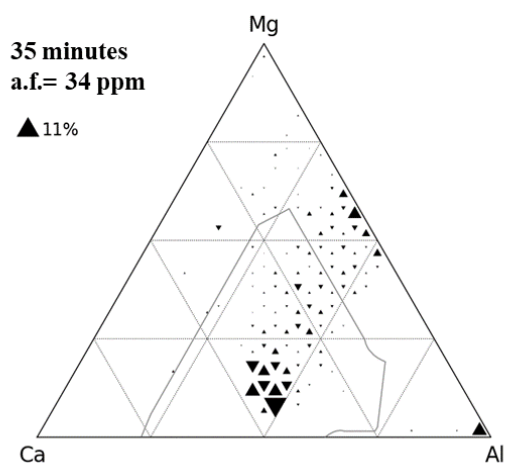
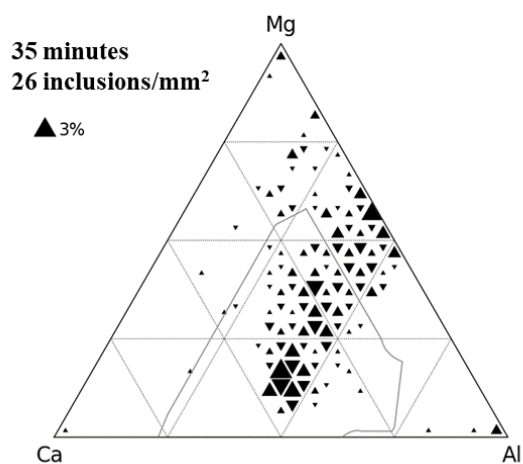


Figure 85. Inclusion composition in steel 35 minutes after aluminum addition during experiment-7.3 (1% electronic grade silicon)

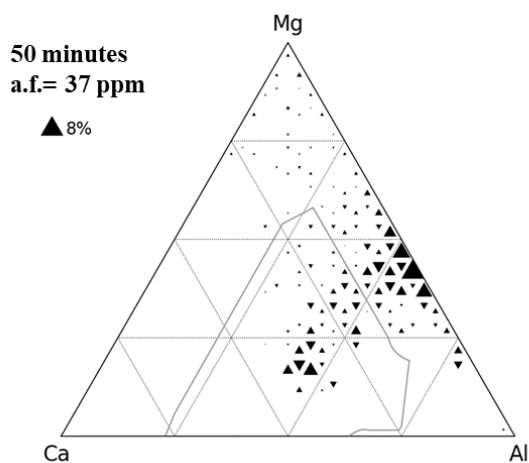
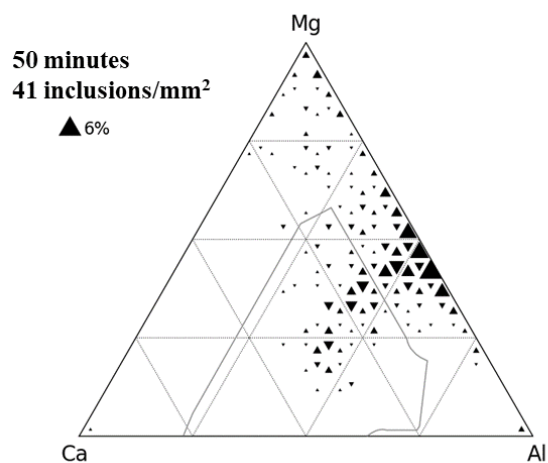


Figure 86. Inclusion composition in steel 50 minutes after aluminum addition during experiment-7.3 (1% electronic grade silicon)

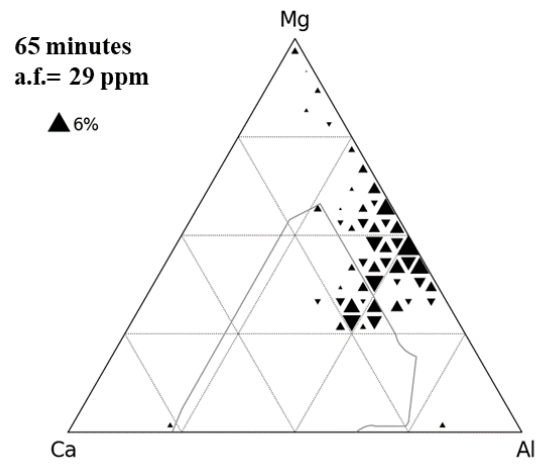
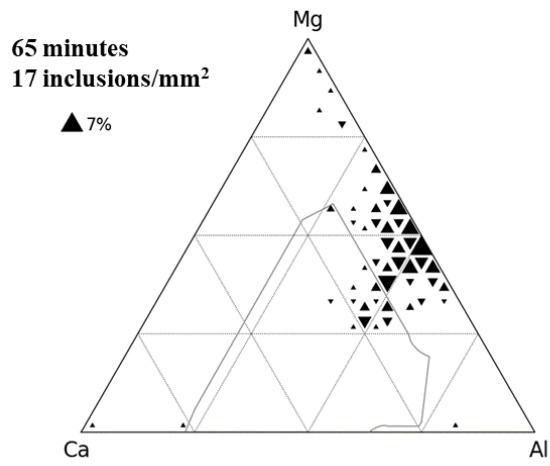


Figure 87. Inclusion composition in steel 65 minutes after aluminum addition during experiment-7.3 (1% electronic grade silicon)

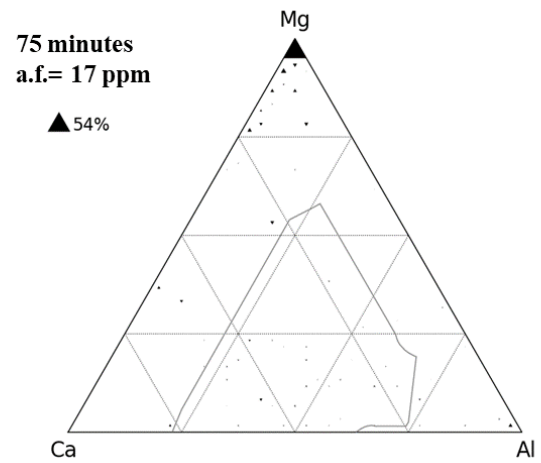
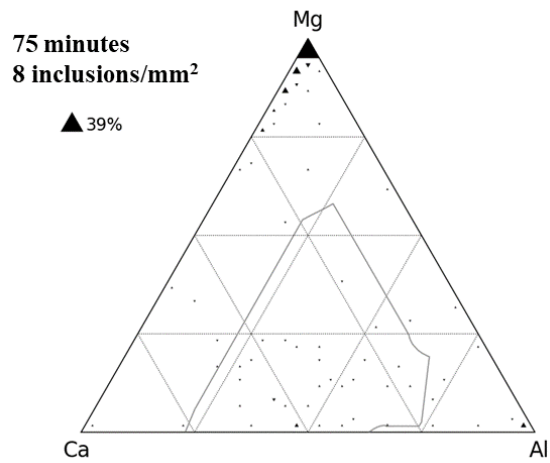
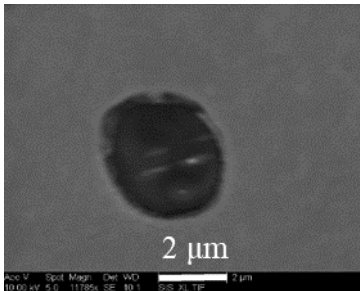
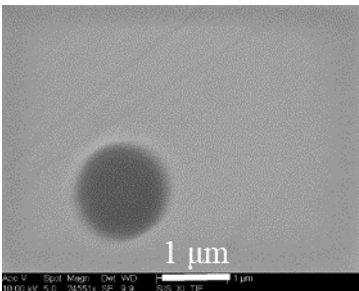
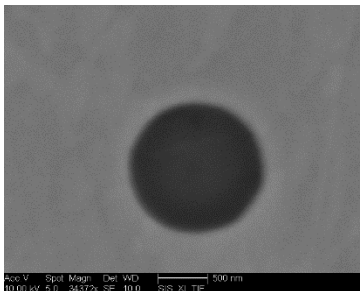
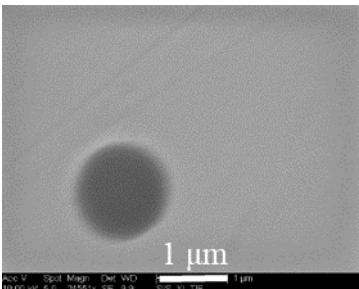
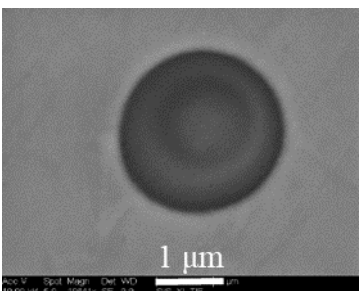
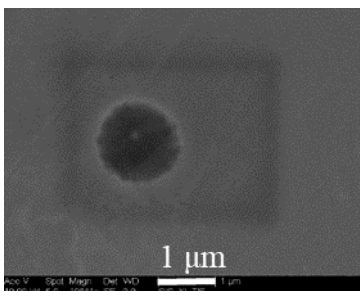
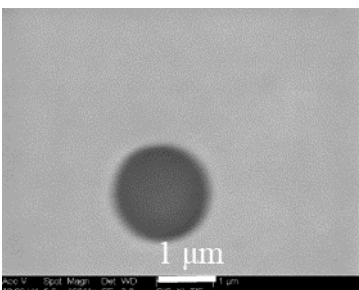
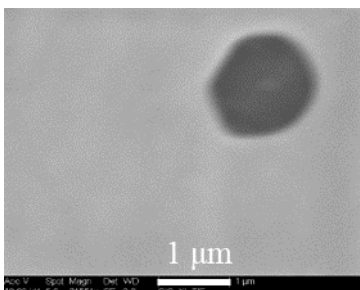


Figure 88. Inclusion composition in steel 75 minutes (final sample) after aluminum addition during experiment-7.3 (1% electronic grade silicon)

Table 35. Inclusions in steel samples from experiment-7.3 (1% electronic grade silicon)

Sample	Calcium rich	MgO rich
S1		
S2		
S3		
S4		
S5		

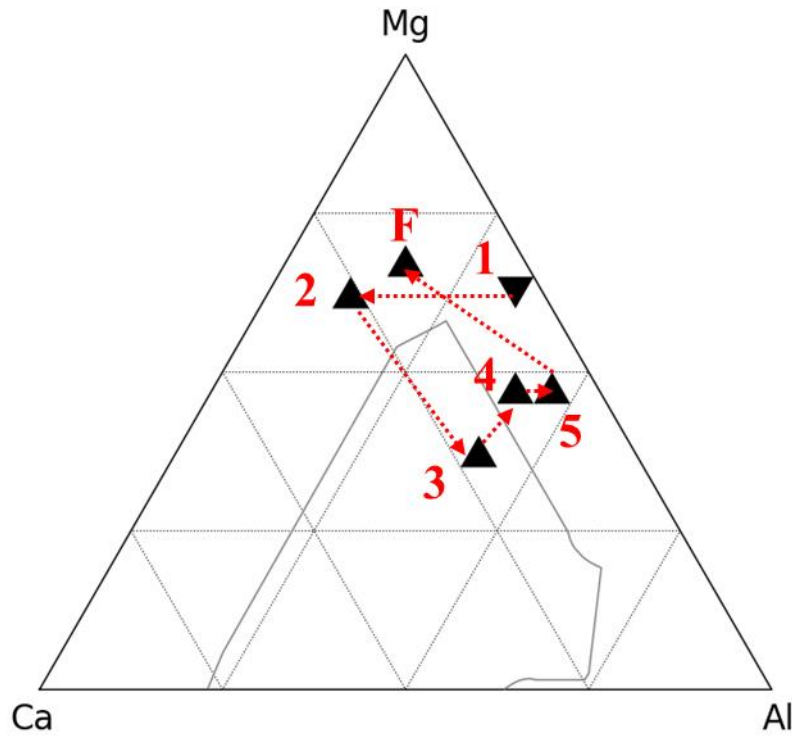


Figure 89. Change in average inclusion composition during experiment-7.3

The left side ternary for all samples (Figure 83 through Figure 88) show number density of inclusions and right side show area fraction of inclusions. It can be seen that from sample-2 ($t=20$ minutes) to sample-3 ($t=35$ minutes), the number density of inclusions increased from 8 inclusions/ mm^2 to 26 inclusions/ mm^2 whereas the area fraction of inclusions remained almost constant. The change in average size of inclusions is shown in Figure 90. A decrease in average size of inclusions can be observed from sample-2 to sample-3. The average size of inclusions increased from sample3-5 and area fraction of inclusions almost remained same. The change in average size looks very similar to the one showed by Ferreira et al. [66] in case of calcium treatment of spinel inclusions. In their case, a sudden drop in average size was observed due to instantaneous increase in calcium concentration; in present work calcium pick-up was gradual due to steel-slag reaction.

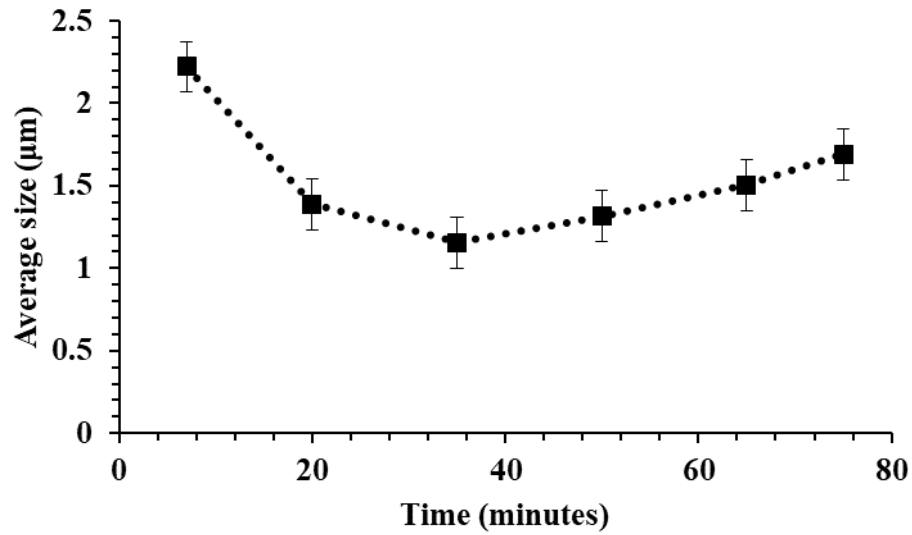


Figure 90. Change in average inclusion size with time during experiment-7.3

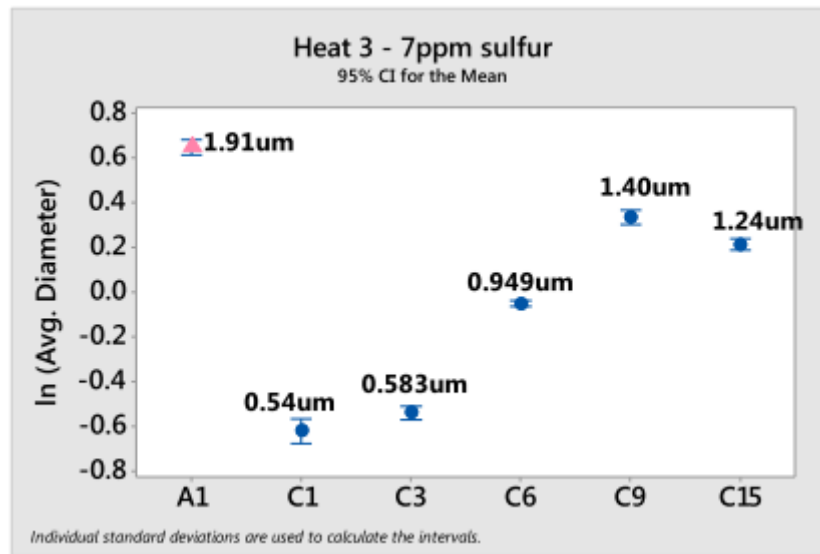


Figure 91. Change in average size of inclusions with time from just before calcium treatment to after, reported by Ferreira et al. [66]

7.2.4 Discussion

Comparison of inclusion analysis from experiments-5.6 to 7.2 show that in the absence of silica in slag, calcium and magnesium transfer to inclusions is faster. A similar conclusion can be made by

comparing inclusion analysis from experiment-7.1 to 7.3. The comparison of experiment-5.6 to 7.1 and 7.2 to 7.3 show that the calcium-transfer to inclusions could be improved for same slag composition but higher silicon concentration in steel. Dissolved aluminum and silicon (if any) in steel can react with CaO and MgO from slag. In order to understand the effect of silicon in steel and silica in slag on the abovementioned reaction, the equilibrium chemical composition and activities were considered for six cases described in Table 36. Initial total aluminum and oxygen concentration in steel in each case was 0.3% Al and 360 ppm O. The steel to slag mass ratio was 4 for all cases (except cases 1a and 1b). The additional conditions related to silicon and slag addition are described in bold. Considering these conditions as initial conditions, steel-slag equilibria (in cases of 1a and 1b, only steel) was calculated using FactSage-7.2 using FTmisc, FToxid and FactPS databases. The calculated partial pressures of oxygen, calcium and magnesium in equilibrium with liquid steel and slag are shown in Figure 92. The slag used for experiments-7.2 and 7.3 (cases 3a and 3b) is expected to result in a lower oxygen activity compared to conditions without slag and with silica containing slag. Therefore, the improved calcium and magnesium pick-up in experiments-7.2 and 7.3 compared to experiments-5.6 and 5.7 respectively can be explained based on the reduced oxygen partial pressure. The addition of silicon (for the same slag composition) was also found to reduce equilibrium oxygen partial pressure for both types of slag. The partial pressure of calcium and magnesium was found to increase as conditions became more reducing which explains the effect of silicon addition on calcium transfer to inclusions. The most effective calcium and magnesium transfer observed in experiment-7.3 was due to combined effect of slag with low Al_2O_3 and SiO_2 activities and presence of silicon in steel.

Table 36. Six cases considered to understand reduction of CaO and MgO from slag

Cases	Description
1a	Steel: 0.3% Al, 360 ppm O
1b	Steel: 0.3% Al, 360 ppm O, 1%Si
2a	Steel: 0.3% Al, 360 ppm O, slag for experiment 5.6 and 7.1 (47.5% CaO, 36.5% Al ₂ O ₃ , 9% SiO ₂ , 7% MgO)
2b	Steel: 0.3% Al, 360 ppm O, slag for experiment 5.6 and 7.1, 1%Si
3a	Steel: 0.3% Al, 360 ppm O, slag for experiment-7.2 and 7.3 , (51% CaO, 42% Al ₂ O ₃ , 7% MgO)
3b	Steel: 0.3% Al, 360 ppm O, slag for experiment-7.2 and 7.3, 1% Si

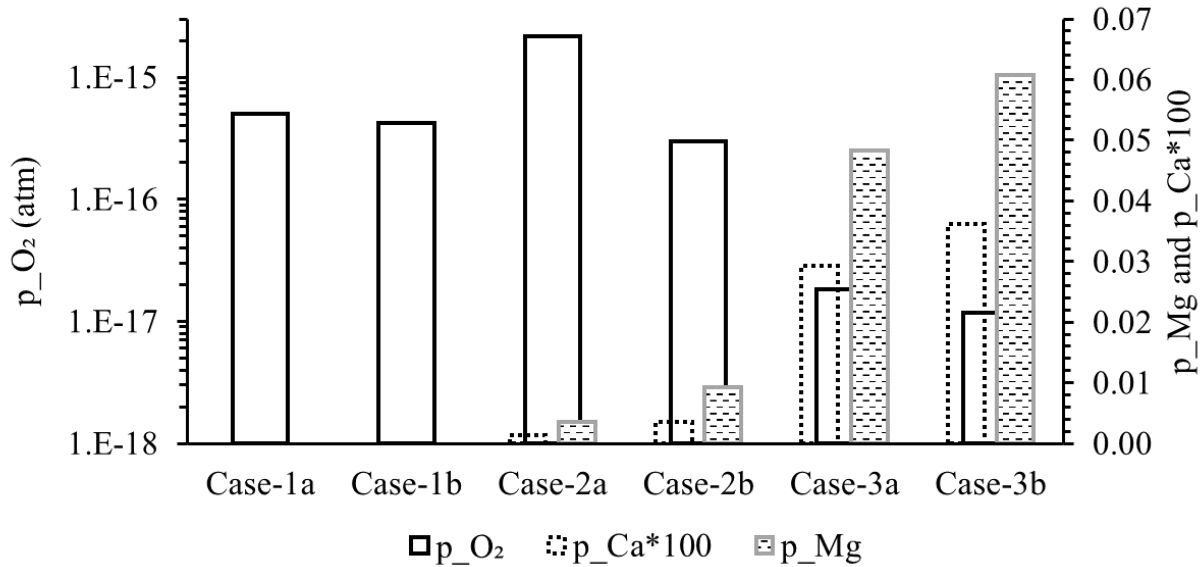


Figure 92. Equilibrium oxygen, magnesium and calcium activities for six cases described in Table 36

7.2.5 Liquid inclusion as a transient phase

Inclusion analysis of steel samples from experiment-7.3 showed a very interesting trend: the presence of liquid CaO-Al₂O₃-MgO inclusions as a transient phase almost all of which finally transformed to solid MgO inclusions. It raises some interesting questions: 1) what happens to CaO

in liquid inclusions and why does this transformation not stop at the double saturation of CaO and MgO in inclusions? 2) Why the final composition of inclusions is not similar to the slag?

The model developed for experiment-5.6 (steel-slag-crucible reaction) was used for experimental conditions of exp. 7.2 (without silicon) to understand the change in composition of inclusions with time. As noted earlier, the model predicts higher than observed calcium pick-up at the steel-slag interface resulting in formation of calcium containing inclusions. Nevertheless, it could predict the formation of liquid inclusions as a transient phase and MgO as the final phase. It should be noted here that there was no strong effect of 1% silicon addition on the evolution of inclusions (there was small increase in CaO and faster transformation to MgO due to reduced oxygen activity). Figure 93 shows the calculated evolution of inclusions compositions. It can be seen that the kinetic model calculated the formation of transient liquid phase (in these phase fields: L+M, L+M+S). The reduction of bound calcium in inclusions by magnesium picked up from steel-crucible interface can be seen in Figure 94. Figure 95 shows changes in the interfacial oxygen activity and activities of oxides at the steel-inclusion interface and at the steel-slag interface. It can be seen that the oxygen activity and oxide activities at the steel-slag interface remains almost constant but change considerably at the steel-inclusion interfaces, eventually becoming the same as at the steel-slag interface. It shows that although CaO concentration in inclusions was close to zero towards the end, the CaO activity at both steel-slag and steel-inclusion interface was same (≈ 1). The three phase CaO + MgO + liquid region in Figure 93 show that the same activities can be obtained with very different overall compositions. Hence, there is no need for inclusion composition to be same as slag composition.

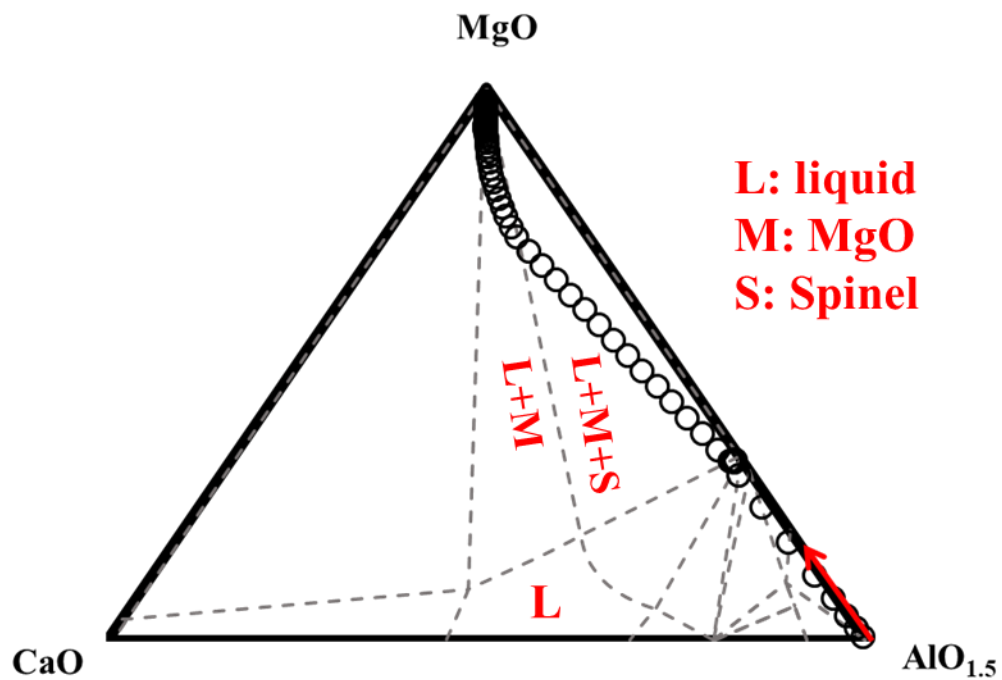


Figure 93. Calculated composition path of inclusions for experiment-7.2, path boundaries are for 1873 K

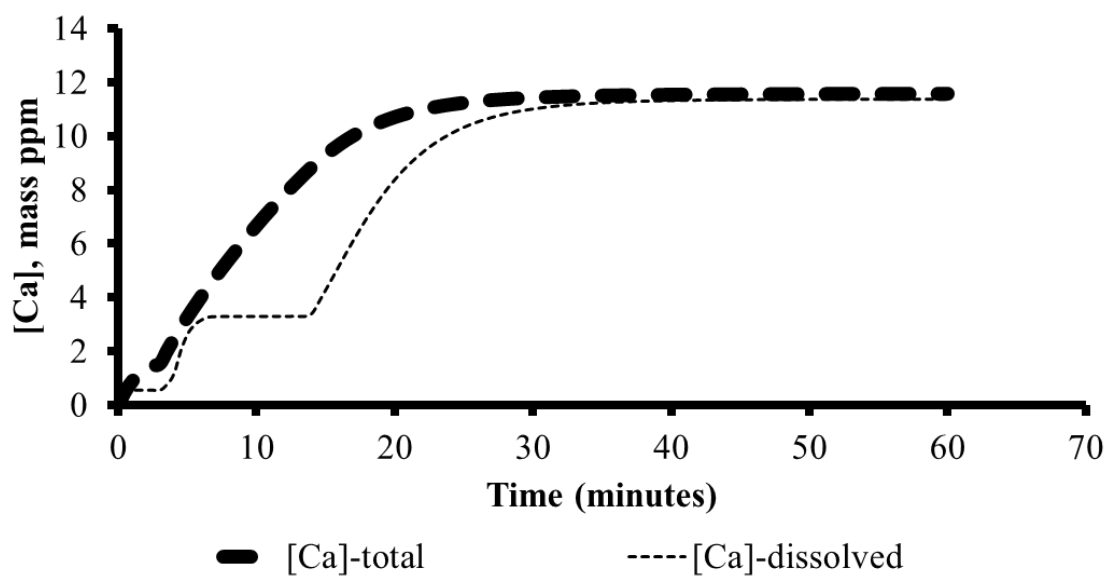


Figure 94. Calculated total and dissolved calcium in steel with time for experiment-7.2

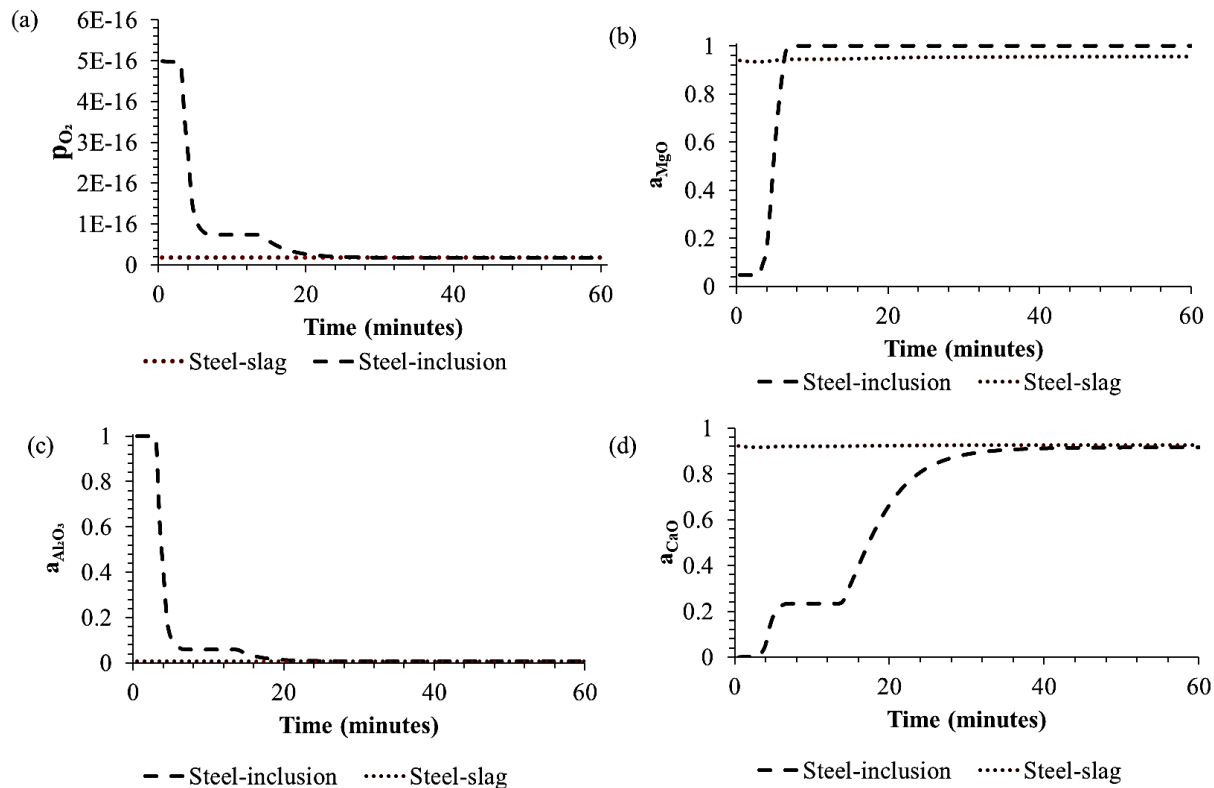


Figure 95. Activities of species at the steel-slag and steel-inclusion interface with time for experiment-7.2: a) partial pressure of oxygen, b) activity of MgO (w.r.t. solid periclase), c) activity of alumina (w.r.t. corundum) and d) activity of CaO (w.r.t. lime)

The conditions in experiment-7.2 were also simulated without considering steel-crucible reaction. The evolution of inclusions in the absence of steel-crucible reaction is shown in Figure 96, more calcium transfer to inclusions was expected. Since this was calculated using FTmisc database in FactSage, the actual extent of calcium transfer would be less but a similar trend could be expected while comparing the cases with and without steel-crucible reactions. The interfacial oxygen and oxide activities are shown in Figure 97. The reduction in oxygen partial pressure at the steel-inclusion interface was found to be slower than that found in the case with steel-crucible reaction. Moreover, the activity of MgO at the steel-inclusion interface was found to fluctuate around MgO activity at the steel-slag interface. Similar to the previous case, the activity of CaO in inclusions takes the longest to approach equilibrium with slag. The inclusion composition towards the end

approached to CaO, MgO double saturation point in the phase diagram for (activities of both CaO and MgO close to 1). This comparison emphasizes that many inclusion compositions can equilibrate with slag, including close to pure MgO (the previous case) and at the double saturation point of liquid oxide (shown in Figure 96). At equilibrium, the composition of inclusions need not to be the same as slag. Theoretically, if the rate of Mg pick-up in steel is controlled such that the CaO activity at the steel-inclusions interface does not become equal to that at the steel-slag interface before MgO activity then one should expect the inclusion composition to pass through pure liquid region. In other experiments, attempts were made to achieve such conditions by conducting experiments in ZrO_2 and CaO-ZrO_2 crucibles.

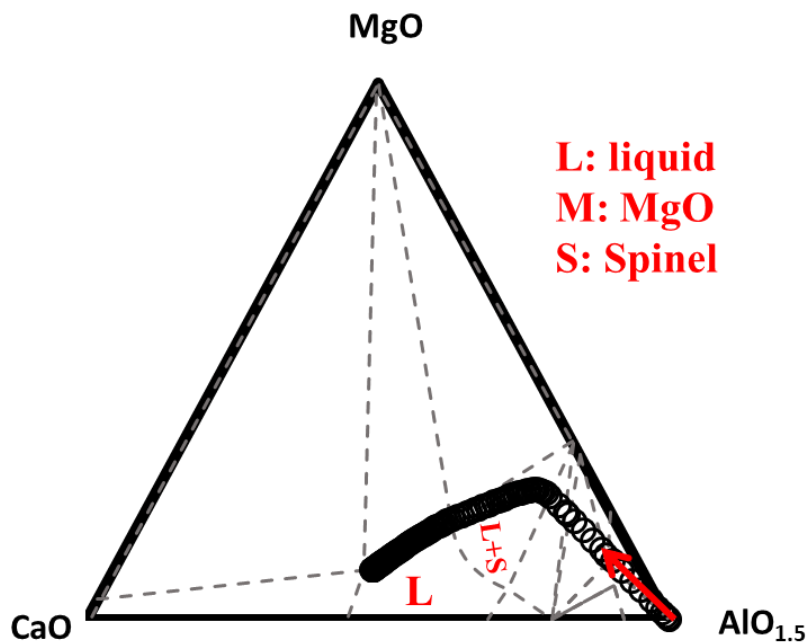


Figure 96. Calculated inclusion evolution when steel-crucible reaction was not considered for conditions in experiment-7.2

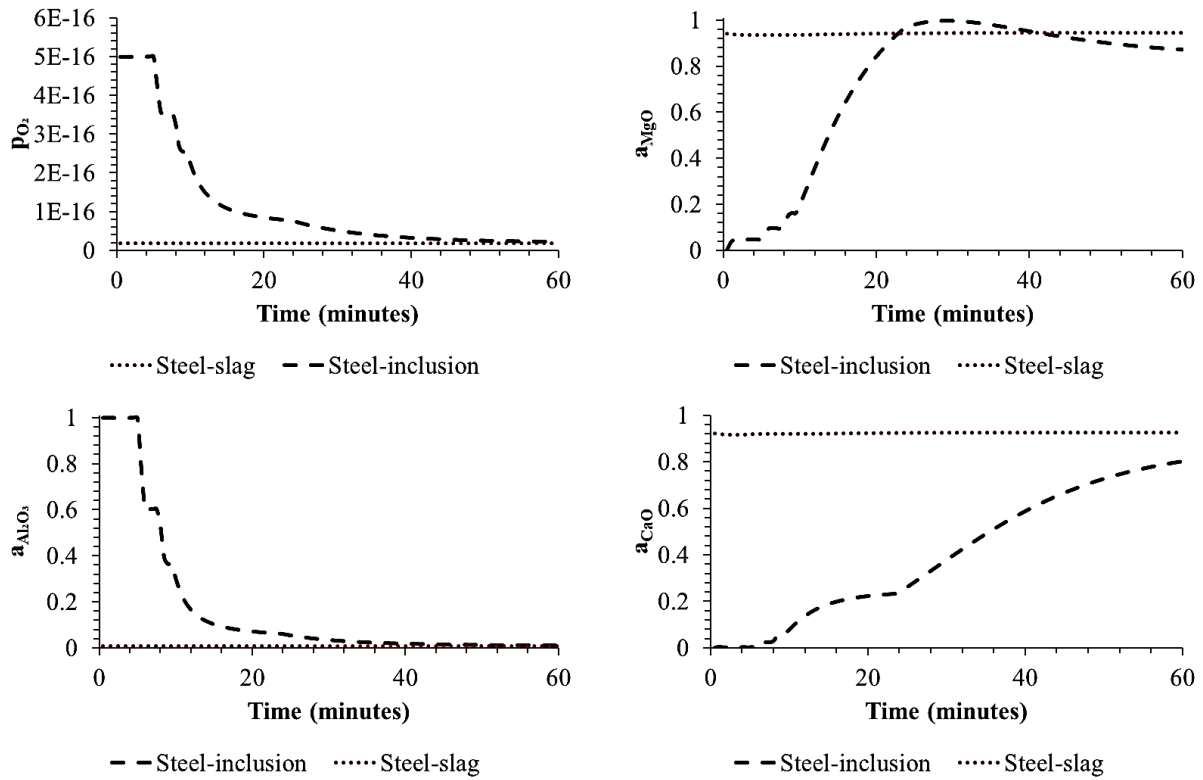


Figure 97. Interfacial activities of species at the steel-slag and steel-inclusion interface with time for experiment-7.2 without steel-crucible reaction: a) partial pressure of oxygen, b) activity of MgO (w.r.t. solid periclase), c) activity of alumina (w.r.t. corundum) and d) activity of CaO (w.r.t. lime)

7.2.6 Conclusion

Induction furnace experiments were carefully designed to clarify the effect of silicon addition on the calcium modification of spinel inclusions due to steel-slag reaction. The use of electronic grade silicon clarified that the source of calcium can be steel-slag reaction in addition to calcium impurities in ferrosilicon. The rate of calcium transfer, while low in all cases, was higher in experiment-7.3 compared to 7.1 due to zero initial silica in slag.

7.3 Effect of crucible: MgO, ZrO₂ and CaO

The inclusion analysis results from steel-slag-crucible experiments conducted using MgO crucibles were discussed in section 5.4 and 7.2. In all of those experiments, there was significant magnesium transfer to inclusions along with calcium transfer, if any. In order to understand the effect of magnesium transfer on calcium transfer, experiments were conducted in ZrO₂ crucibles and CaO crucibles. In section 5.3.5, it was shown that a lower concentration of alumina inclusions would transform faster to spinel/MgO compared with a higher inclusion concentration. These experiments (in ZrO₂ and CaO crucible) were conducted in smaller crucibles (30-40 mm diameter) with a smaller mass of steel (100-250 g) to allow faster flotation of inclusions so that calcium transfer to inclusions could be detected.

7.3.1 Experiments

Experiments-7.4 and 7.5 were conducted using type-1 and type-2 ZrO₂ crucibles of 31 mm and 39 mm inner diameters respectively. In experiment-7.4, 100g of solid electrolytic iron (7 ppm S), 0.15% Al and 15 g of slag 7.3 were added in a ZrO₂ crucible before the experiment due to smaller diameter of the crucible (that is, additions after melting were not feasible). Time zero was defined as the time temperature reached ~1600°C during the experiment. The time of sampling is shown in Table 38. The compositions of slags used in this section are described in Table 37. In experiment-7.5, the larger crucible diameter allowed aluminum and slag addition during the experiment as described in Table 39. The mass and type of electrolytic iron used for this experiment was same as experiment-7.4. 2% ZrO₂ was added in the slag to control the corrosion of crucible during a longer experiment. A larger slag mass was added to make sure that the slag completely covered top of liquid steel for larger ZrO₂ crucible.

Table 37. Composition of slag used to study the effect of crucible on calcium transfer

	%CaO	%Al ₂ O ₃	%MgO	%ZrO ₂
Slag-7.3	50.30	42.30	7.40	0
Slag-7.4	56	42	0	2
Slag-7.5	57	43	0	0

Table 38. Addition and sampling detail for experiment-7.4 (ZrO₂, type-1)

Time	Beginning	8	23	31
Event	0.15 % Al, 15 g slag-7.3	S1	S2	SF

Table 39. Addition and sampling detail for experiment-7.5 (ZrO₂, type-2)

Time	0	6	24	52	68	92
Event	0.15% Al	30 g slag-7.4	S1	S2	S3	SF

Two experiments were conducted using 40 mm diameter CaO-3% ZrO₂ crucible supplied by Zhengzhou Mission Ceramic Products Co, Ltd, Zhengzhou, China. Experiment-7.6 was conducted using 250 g of electrolytic iron containing 40 ppm of sulfur and approximately 360 ppm of oxygen. The addition and sampling detail for this experiment is described in Table 40. Experiment-7.7 was conducted using 200 g of low sulfur electrolytic iron (8 ppm) without any slag addition. The addition and sampling details are described in Table 41.

Table 40. Addition and sampling detail for experiment-7.6 (CaO crucible)

Time	0	6	13	19	24	34	43	54
Event	0.16% Al	50 g slag-7.5	S3	S4	S5	S6	S7	S8

Table 41. Addition and sampling detail for experiment-7.7 (CaO crucible)

Time	0	4	15	30	45
Events	0.15% Al	S2	S3	S4	S5

7.3.2 On ASPEX analysis of ZrO₂ containing inclusions

The steel samples contained some ZrO₂ containing inclusions when experiments were conducted using ZrO₂ crucibles and CaO-ZrO₂ crucibles. Figure 98 show counts (on y-axis) from SEM-EDS analysis for a micrometer sized Al-Mg-Zr-O inclusion. As expected, the SEM-EDS analysis at 20 kV show larger interference from steel matrix. However, the normalized chemical composition without iron for these two analyses show that the chemical composition of inclusions analyzed at 10 kV and 20 kV can be expected to be very close as shown in Table 42. For 10 kV, the counts were converted into chemical composition using Merlet's phi-rho-z algorithm [10], [11].

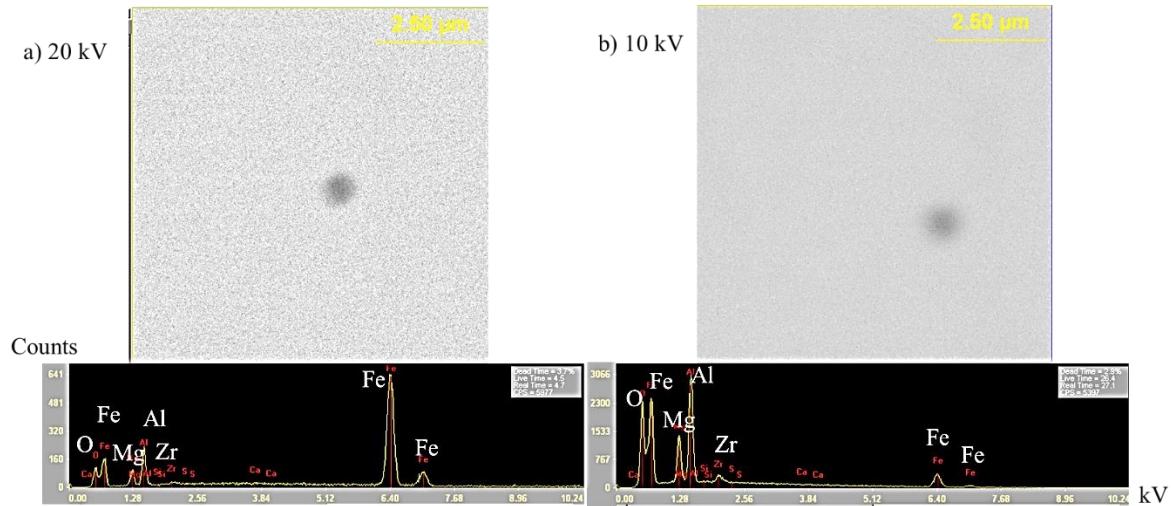


Figure 98. SEM-EDS analysis using ASPEX-Explorer for same inclusions at a) 20 kV and b) 10 kV

Table 42. Chemical composition of inclusion shown in Figure 98 after ignoring Fe peak and normalizing at 10 kV and 20 kV

	%MgO	%Al ₂ O ₃	%ZrO ₂
10 kV	19.4	66.2	14.4
20 kV	20.1	67.0	12.9

In this work, inclusion analysis was conducted at 10 kV using ASPEX-Explorer for better resolution. Figure 99 shows that ZrO₂ containing inclusion like the one shown in Figure 98 could be detected with usual ASPEX-AFA setting; the brightness of steel matrix =170 and that of aluminum tape was 110.

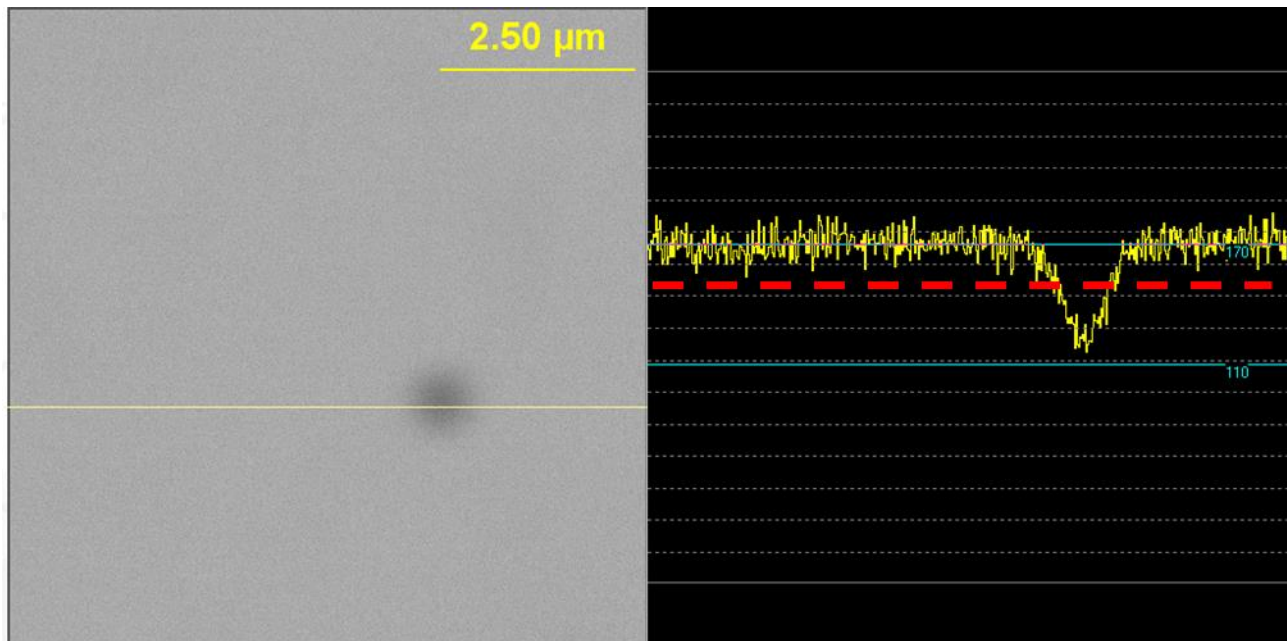


Figure 99. Detection of ZrO₂ containing inclusions

7.3.3 Results and discussion

7.3.3.1 ZrO₂ crucible experiment

The result of inclusion analysis of samples S1 (t=8min) and SF (t=31 min) from experiment-7.4 are shown in Figure 100 and Figure 101 respectively. The sample taken 8 minutes after steel was molten contained three types of inclusions: Al-Mg-O (Mg:Al = 0.5 by mass), Al-Mg-Zr-O, and

Al-Mg-Zr-Ca-O as shown in Figure 100. As the inclusion contained Al, Mg, Zr and Ca, ternaries of Mg-Al-Ca and Mg-Al-Zr were plotted to show the compositions of inclusions. The molar amounts of three elements of a ternary diagram were normalized before plotting. The average composition (wt %) of Al-Mg-Zr-O inclusions was 65% Al_2O_3 , 13% MgO , and 22% ZrO_2 ; there was significant transfer of magnesium from slag and zirconium from crucible. A typical calcium containing inclusion is shown in Figure 102. These inclusions were rich in Al, Mg and Zr but lean in Ca. A larger extent of magnesium transfer from slag to steel in comparison to calcium was likely due to the low equilibrium concentration of calcium in steel as compared to magnesium. The sample taken at the 31st minute contained mainly MgO and CaS inclusions with small amount of alumina and magnesium spinel inclusion as shown in Figure 101 but slightly larger area fraction. An example of an inclusion containing MgO and CaS is shown in Figure 103. The magnesium-transfer to inclusions show that the MgO bearing slag can be an effective source of magnesium responsible for the transformation of alumina inclusions to spinel and to MgO similar to MgO crucibles as shown in chapter 5. The steel produced in this experiment (7.4) was very clean as the bound oxygen concentration in steel from analyzed inclusions was always less than 10 ppm. It may be due to two reasons: there was just 100 g of steel (in the smaller zirconia crucible) which means that the flotation distance for inclusions to reach to slag was less than 2 cm compared to ~4.5 cm in steel-slag experiments conducted in MgO crucibles. The average size of inclusions was 1-2 μm due to flotation of larger inclusions. Secondly, addition of slag (and aluminum) at the beginning of experiment resulted into liquid slag and liquid aluminum covering solid iron pieces before melting of the iron (as slag and aluminum melts at a lower temperature than steel); such good mixing likely promoted inclusion removal.

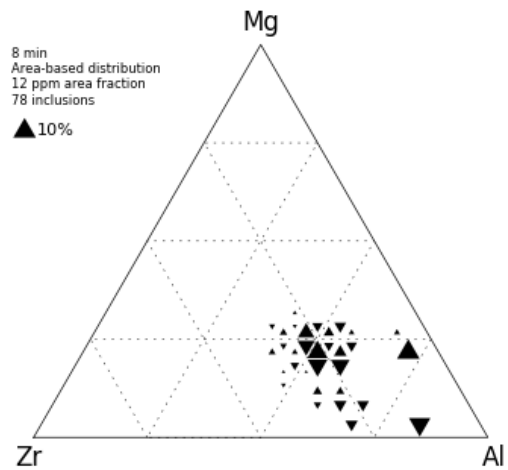
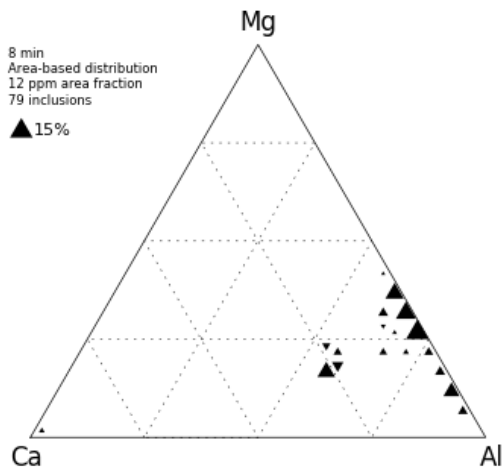


Figure 100. Inclusion composition at 8th minute during experiment-7.4

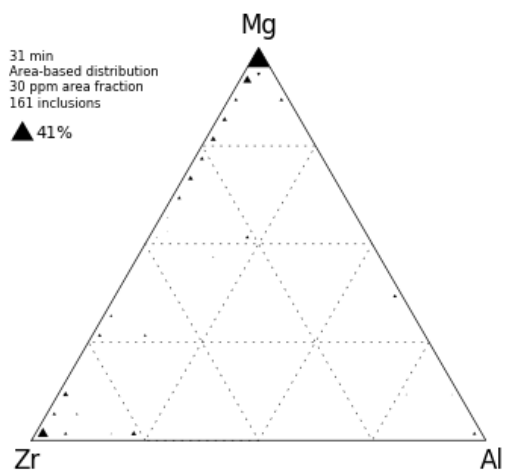
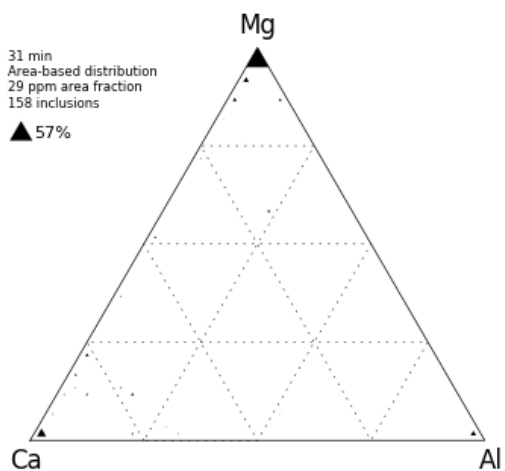


Figure 101. Inclusion composition at 31st minute during experiment-7.4

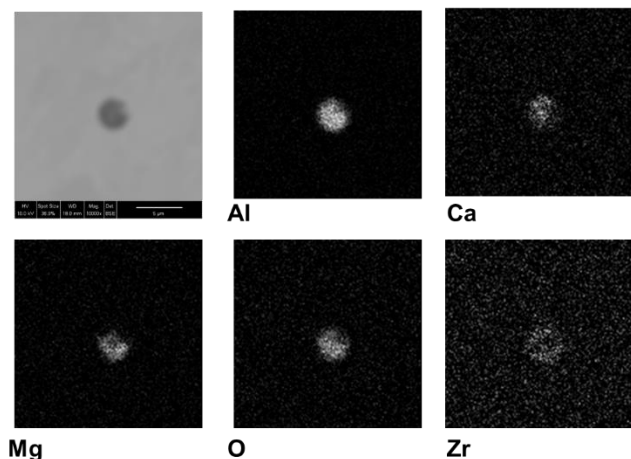


Figure 102 Al-Mg-Zr-Ca-O inclusions observed in experiment-7.4 at 8th minute

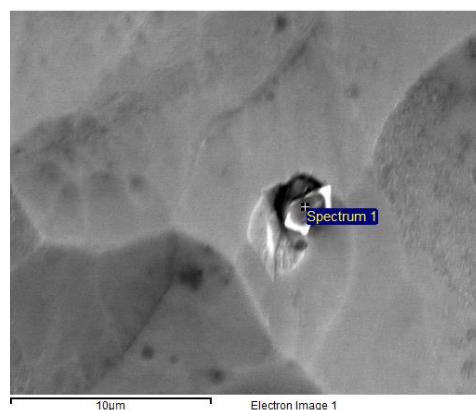


Figure 103 CaS-MgO inclusion observed in sample from experiment-7.4

In experiment-7.4, the measured calcium pick-up in inclusions might be due to slag entrainment in the melt rather than due to steel-slag reaction at the interface. Experiment-7.5 was conducted to test this effect using a larger ZrO₂ crucible (diameter = 39 mm) where aluminum and slag were added after electrolytic iron was molten in the crucible (see Table 39). The slag was also kept MgO free to test the effect of competition between Mg and Ca pickup in steel at the steel-slag interface. The inclusion analysis of S2 (52 minutes) and SF (90 minutes) samples are shown in Figure 104 and Figure 105. Two types of inclusions were found in these samples: ZrO₂ rich inclusions and Al₂O₃ rich inclusions. Figure 106 shows type-1 inclusions as a cluster of ZrO₂ rich inclusions with Al₂O₃ rich inclusions and Figure 107 shows type-2 inclusions with only Al₂O₃ rich phase. All images are backscattered electron images taken using FEI Quanta-600, the brighter phase in Figure 106 is ZrO₂ and the darker phase is an Al₂O₃ rich phase. Table 43 presents characteristics of type-1 and type-2 inclusions. The chemistry of inclusions measured during automated feature analysis of these inclusions are affected by the presence of the brighter ZrO₂ phase. The backscattered electron yield of the ZrO₂ rich phase was higher than the alumina rich phase as atomic number of Zr (Z=40) is greater than Al (Z=13). Typically, inclusions are identified by the darker phase during

automated feature analysis (AFA) as the atomic number of elements (Al, Mg, Ca, and Si) present in the inclusions is lower than that of iron. It was likely that significant number of ZrO_2 rich inclusions were missed during automated feature analysis of these samples. Therefore, the measured ZrO_2 content (as seen in Figure 104 and Figure 105) in inclusions from AFA analysis was expected to be lower than the actual.

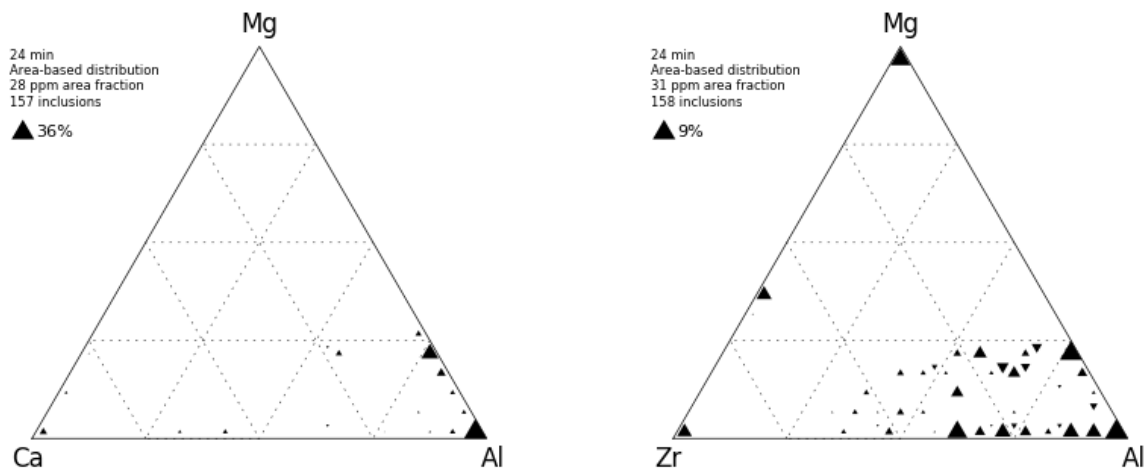


Figure 104. Inclusions observed in sample taken at 24th minute during experiment-7.5

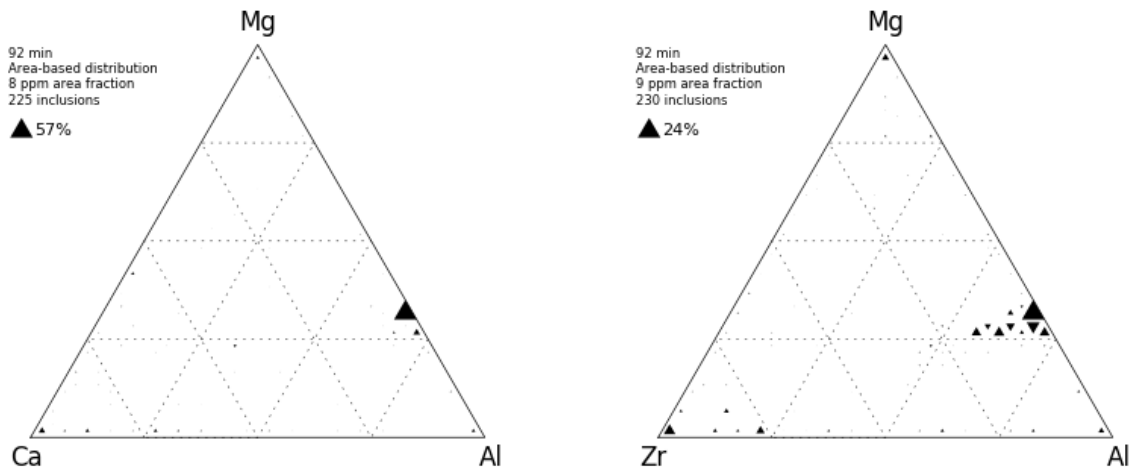


Figure 105. Inclusions observed in sample taken at 92nd minute during experiment-7.5

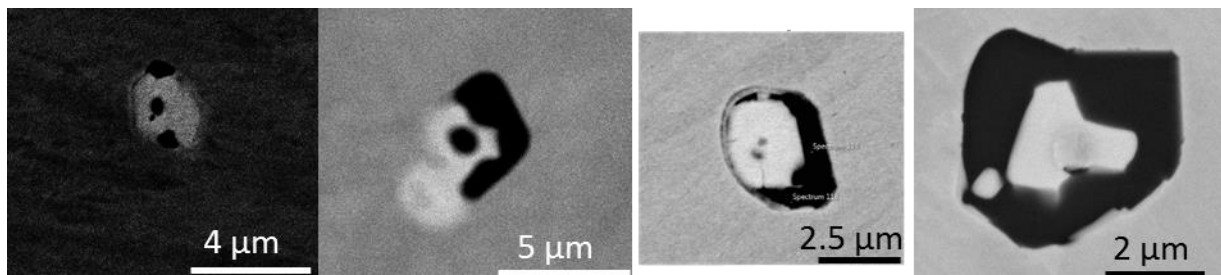


Figure 106. Type-1 inclusions: cluster of ZrO₂ rich phase with Al₂O₃ rich phase, experiment-7.5

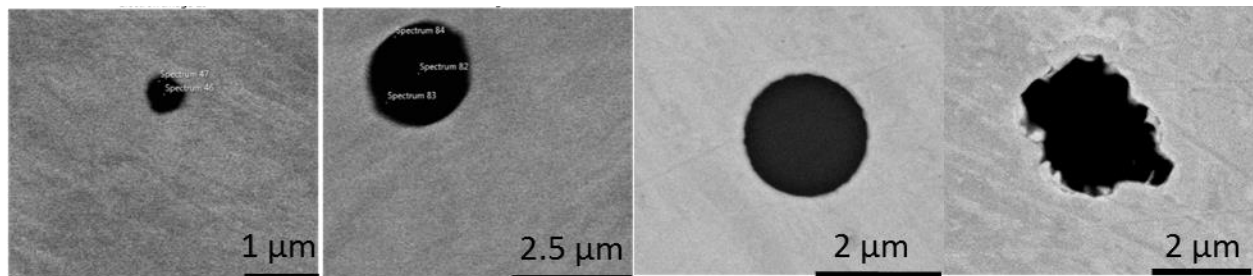


Figure 107. Type-2 inclusions: Al₂O₃ rich phase with some MgO, ZrO₂ and CaO, experiment-7.5

Table 43 Characteristic of type-1 and type-2 inclusions

Type-1 inclusions	Type-2 inclusions
• ZrO₂ rich phase: This is almost pure ZrO₂, containing less than 2 wt% each of Al₂O₃ and MgO. CaO content (wt%) in this phase increase as follows: 0 in S1, <1 in S2, <2 in S3 and <5 in S4. • Al₂O₃ rich phase: MgO content in this phase is up to 17 wt%, ZrO₂ content is generally low (<5 wt%), sometimes higher ZrO₂ (up to 40 wt%) content was also found. For later samples, traces of CaO (<1 wt%) was also found	• Most of these inclusions have higher ZrO₂ content than Al₂O₃ rich phase of type-1 inclusions (>15 wt%) • MgO content is very low as compared to the Al₂O₃ rich phase in type-1 inclusions except for the final sample (S4) where MgO content was around 25 wt% • Inclusions in S1 and S2 did not have any trace of CaO; S3 and S4 had trace amount of CaO (<1.5 wt%)

The higher calcium content in the ZrO₂ phase of type-1 inclusions may be due to the formation of a calcium zirconate layer at the slag-crucible interface that might have eroded into the steel melt at a later stage during the experiment. It is highly unlikely to form due to diffusion of calcium from spinel phase to zirconia phase since aluminum would then also have diffused as CaO, Al₂O₃ and ZrO₂ have mutual solubility as can be seen in CaO-ZrO₂-AlO_{1.5} phase diagram in Figure 108. In experiment-7.4 when Al and slag was kept with electrolytic iron in a ZrO₂ crucible from the beginning of experiment, type-1 inclusions were not found and only type-2 inclusions were present. In the samples taken after 20 minutes, inclusions containing ~5 wt% CaO (Al₂O₃: 62%, ZrO₂: 22%, MgO: 10% and CaO: 5.5%) were found; these had a much higher CaO content than

that of type-2 inclusions in this case. It can be concluded that Ca-transfer is limited when slag was added to molten steel and Ca mass-transfer is limited by steel-slag reactions.

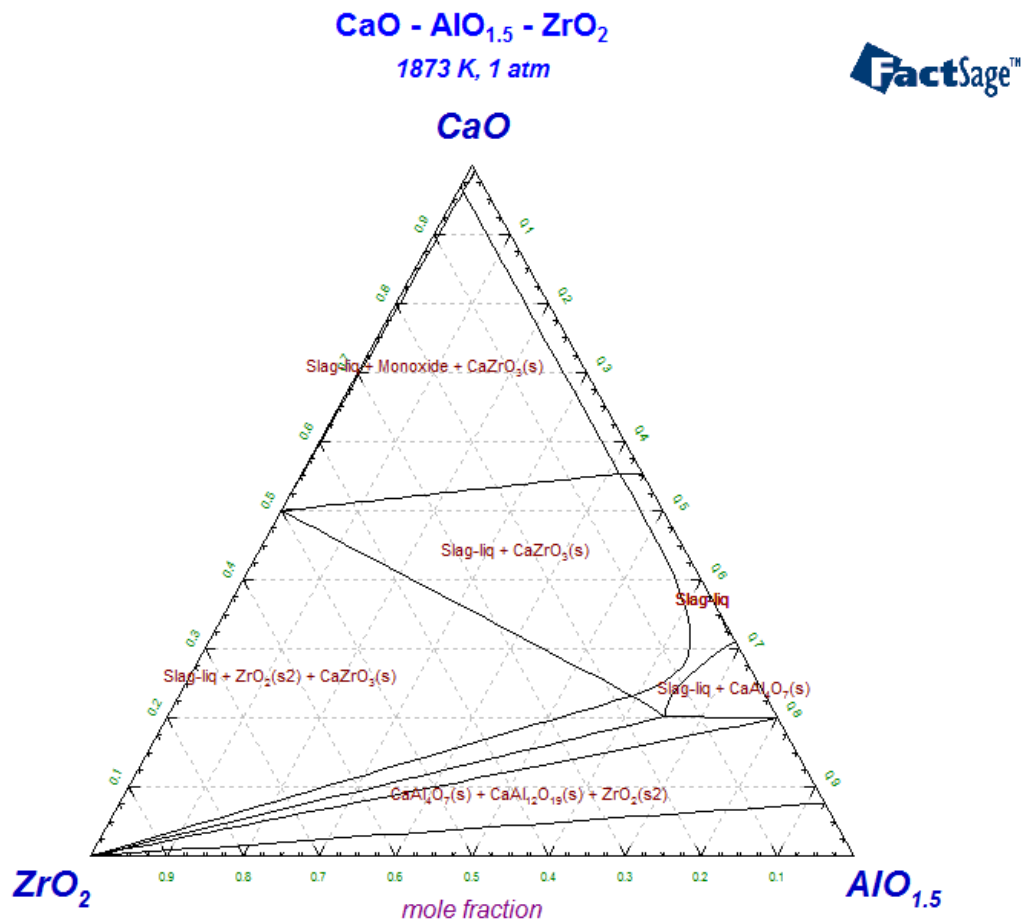


Figure 108. CaO-ZrO₂-AlO_{1.5} phase diagram at 1873 K (1600°C) drawn using FactSage™ [44]

Even though the slag and crucible did not contain any MgO, the MgO content in these inclusions was surprisingly high, although lower than that observed in experiment-7.4 (see Figure 101). Analysis of the crucible before and after the experiment did not show much evidence of MgO except a strand of Si-Ca-Mg-Al-O fiber on the crucible wall after the experiment as shown in Figure 109 and Figure 110. The most likely source of such fibers is paper used in wrapping these crucibles or used during experimental setup. In total the steel contained only ~0.1 ppm of MgO

which is equivalent to 10 micrograms of MgO. This level of contamination could be due to contamination from the fiber in paper. MgO is used in the chemical pulping during paper manufacturing process [67].

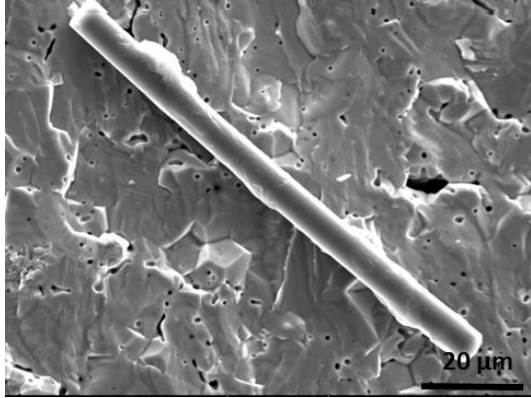


Figure 109 Si-Ca-Mg-Al-O fiber found on crucible after experiment-7.5

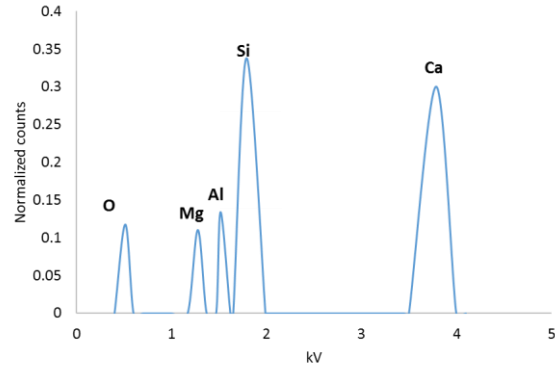


Figure 110. EDS spectrum of the fiber

7.3.3.2 ZrO_2 and MgO Crucible as source of inclusions

The type-2 ZrO_2 crucible used for experiment-7.5 was found to disintegrate during the experiment and directly contributed to inclusions in steel. Several inclusions containing ZrO_2 at the center were observed in the samples taken 24, 52, 68 and 92 minutes after aluminum addition, similar to the one shown in Figure 106 and Figure 111. The formation of ZrO_2 from dissolved zirconium in liquid steel would have resulted in the precipitation of ZrO_2 on already existing alumina rich inclusions, as the steel was aluminum-killed. Therefore, such inclusions are likely to form if crucible fines of around a micrometer in size were picked up by the melt and remained there. SEM analysis of crucible wall clearly showed slag attack on the crucible; Figure 113.

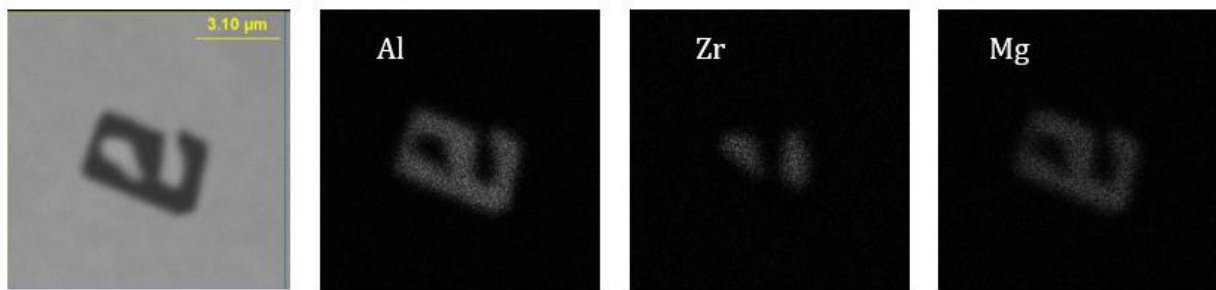


Figure 111 Inclusion with ZrO_2 in core, observed from the sample taken 90 minutes after Al-addition, similar inclusions were present in the sample taken at 20 and 50 minutes as well.

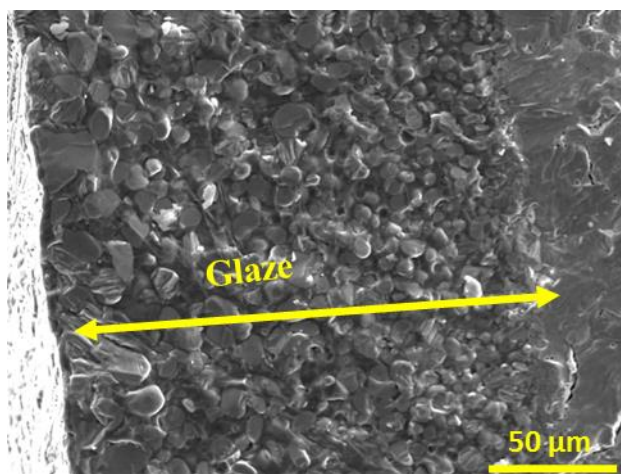


Figure 112 Formation of glaze on the inner wall of ZrO_2 crucible, exp. 7.5

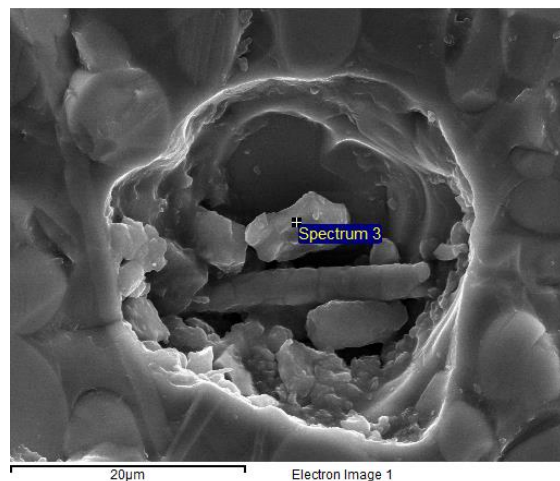


Figure 113 Slag attack on crucible wall, Spectrum 3 showed the composition of slag, exp. 7.5

Similar results were found for experiments conducted in an MgO crucible, for a sample taken 18 minutes after aluminum addition and 9 minutes after Ca-addition. Pure MgO phase attached to a calcium aluminate inclusion can be seen see Figure 114. As the size of MgO phase is more than one μm , it was unlikely to have formed during solidification. The source of MgO part could be the transfer of crucible fines into the liquid steel melt during the experiment.

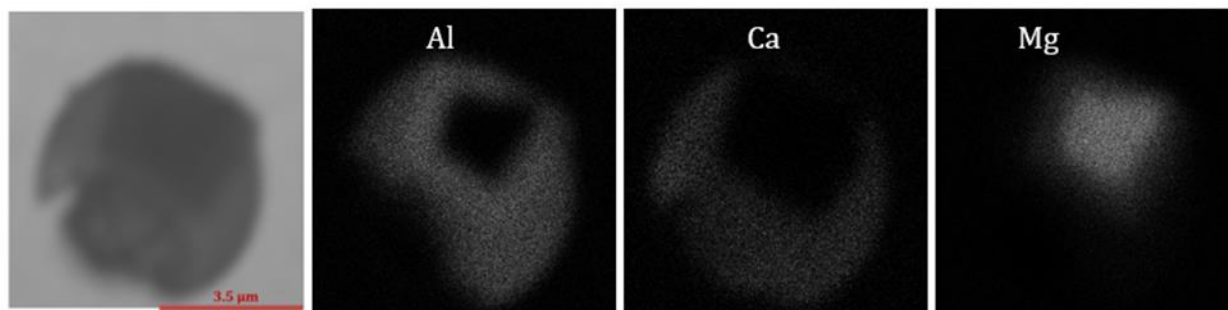


Figure 114 MgO inclusion as a cluster found in a sample taken 18 minutes after Al-addition and 9 minutes after calcium treatment; the experiment was conducted in an induction furnace

These two examples show that the crucible can be a significant source of inclusions during induction furnace experiments. In chapter 5, the steel-crucible reaction was considered when modeling steel-crucible and steel-slag crucible reactions. However, quantification of crucible fines as a source of inclusions is not possible and could not be accounted for in such kinetic models. The effect of steel-crucible reaction on the evolution of inclusion composition was discussed in detail in section 7.2.5.

7.3.3.3 *CaO crucible experiments*

The experiments conducted in MgO and ZrO₂ crucibles resulted in significant transfer of magnesium and zirconium to liquid steel as observed from magnesium and zirconium pick-up in inclusions. The calcium transfer in those inclusions were somewhat limited (<5wt% CaO). Experiments-7.6 (with slag) and 7.7 (without slag) were conducted in CaO-ZrO₂ crucibles (Table 40 and Table 41).

Figure 115 shows the change in inclusion composition from 34th to 54th minutes during experiment-7.6. The initial inclusions were alumina + spinel with limited calcium and zirconium content. It can be seen that the extent of magnesium pick-up in these inclusions was less than those from previous experiments conducted using MgO and ZrO₂ crucibles. The calcium and zirconium

content in inclusions was found to increase slightly with time. The average molar cation fraction of calcium (calculated by normalizing molar composition with respect to Ca, Mg, Al, Si and Zr) increased from 0.90% to 3.8%. Figure 116 shows a calcium containing inclusion observed in the sample taken at 34th minute. The area fraction of inclusions decreased from 102 ppm to 28 ppm due to inclusion flotation. The average size of inclusion in the sample taken at the 54th minute was 1.1 μm . Zirconium pick-up in these inclusions were apparently by the reduction of zirconia from the crucible by aluminum from steel.

There was no slag observed on top of the solidified steel. The observation of crucible revealed that the slag penetrated into the crucible (see Figure 117), most likely during the experiment. Therefore, the rate of calcium transfer from slag to steel for such experiments is expected to be higher than that observed in inclusion compositions in the samples from experiment-7 as shown in Figure 115.

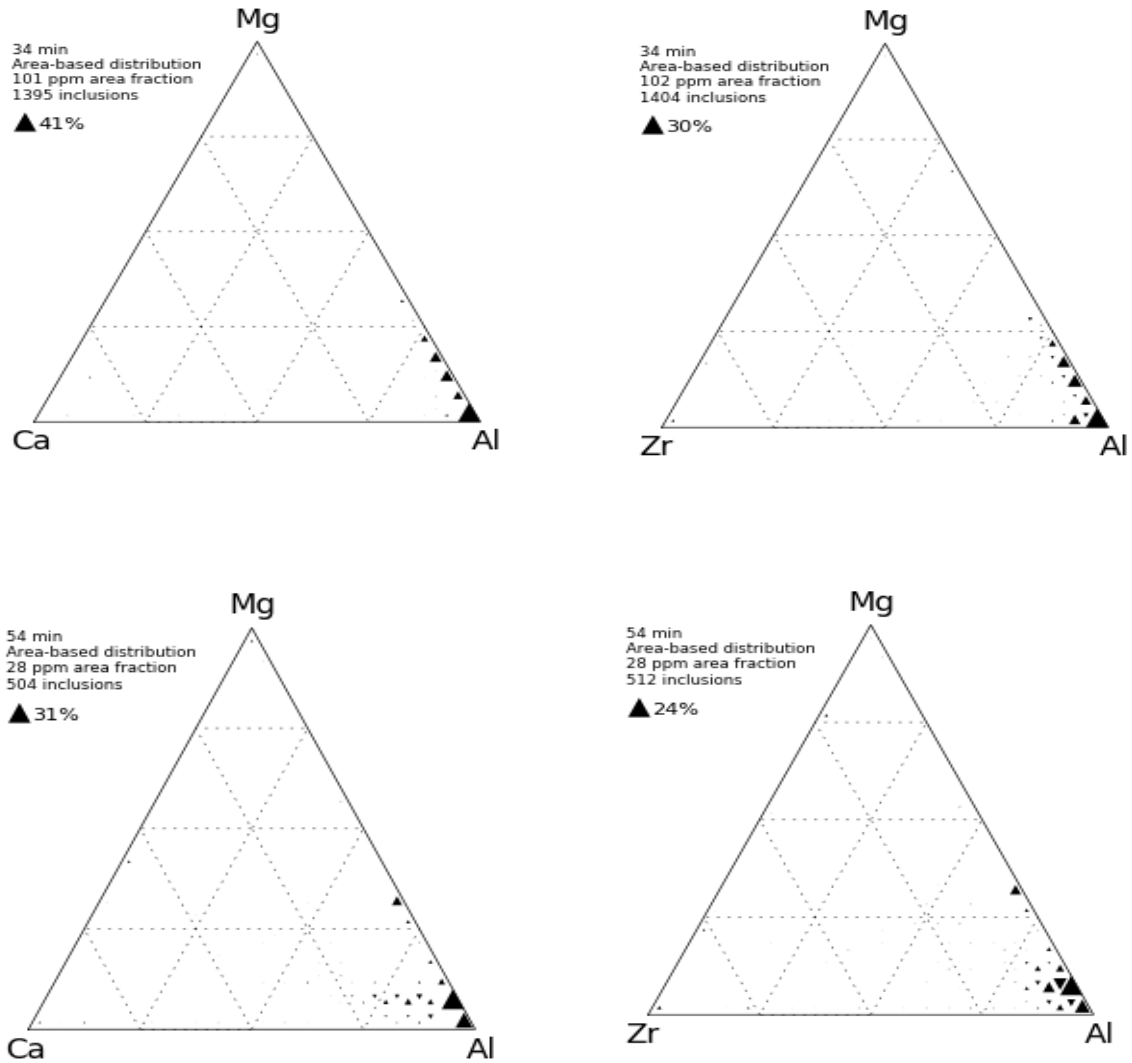


Figure 115. Change in inclusion content and composition observed during experiment-7.6 (CaO crucible)

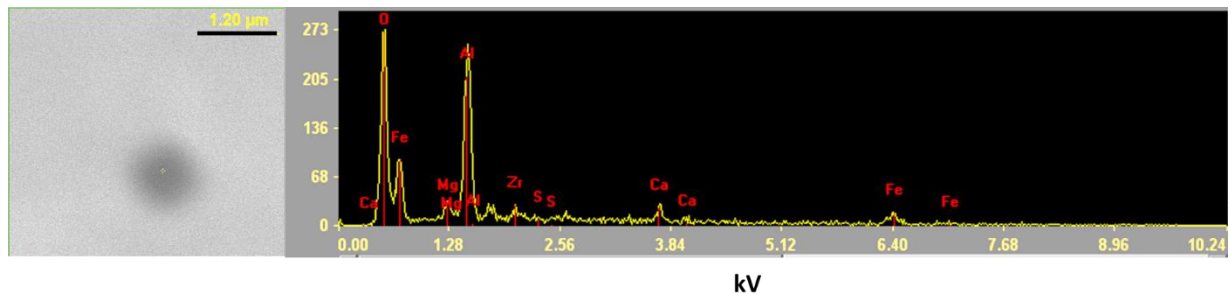


Figure 116. Calcium containing inclusion, observed in sample taken at 34th minute during experiment-7.6

A cross-section of the CaO-ZrO₂ crucible after the experiment was polished and observed in a SEM to identify the likely reason for the slag penetration. Acetone was used at all stages for cleaning during polishing to avoid attack of the crucible by water. Figure 118 and Figure 119 show backscattered electron images of the polished cross-section of the crucible near inside and outside of the crucible wall respectively. The slag attack can be seen along the grain boundaries of the crucible near inside edge of the crucible; the brightest spots in this image is ZrO₂. The presence of aluminum in the elemental map verified the slag attack along the grain boundary as shown in Figure 120 and Figure 121.

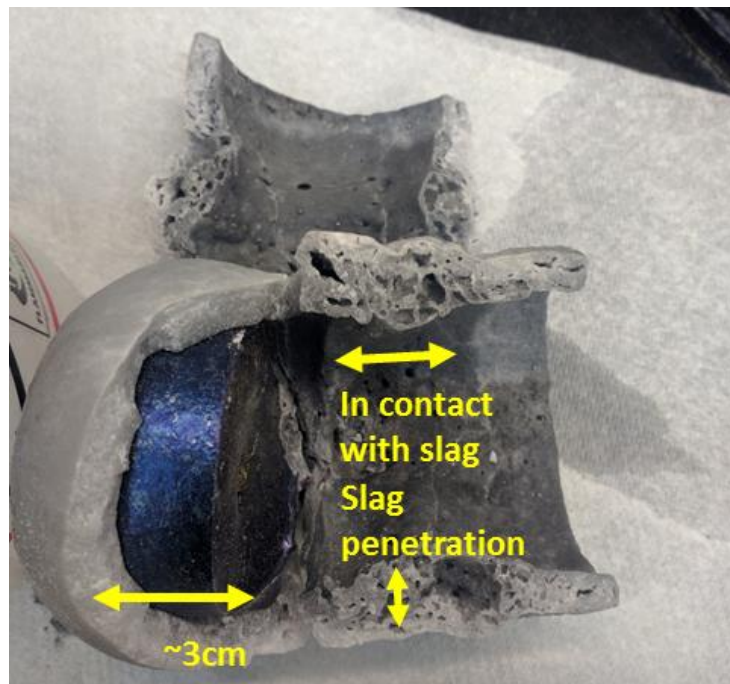


Figure 117. Slag penetration inside the CaO crucible at the end of experiment-7.6

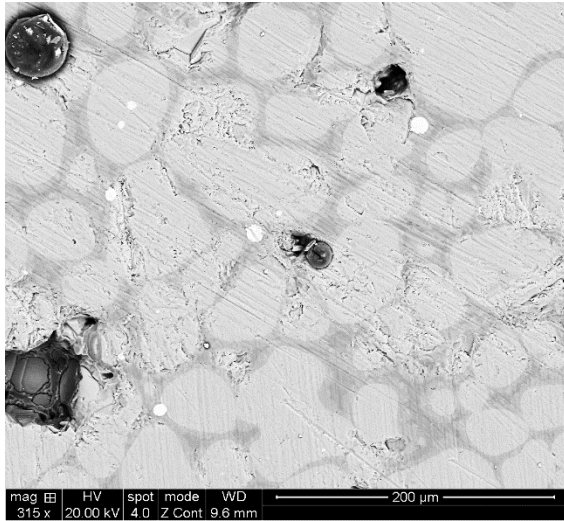


Figure 118. Polished cross-section (near I. D.) of CaO-ZrO₂ crucible, slag attack along grain boundary

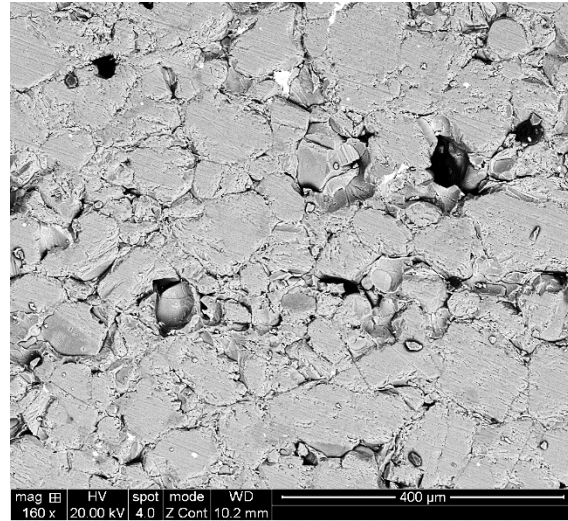


Figure 119. Polished cross-section (near O. D.) of CaO-ZrO₂ crucible

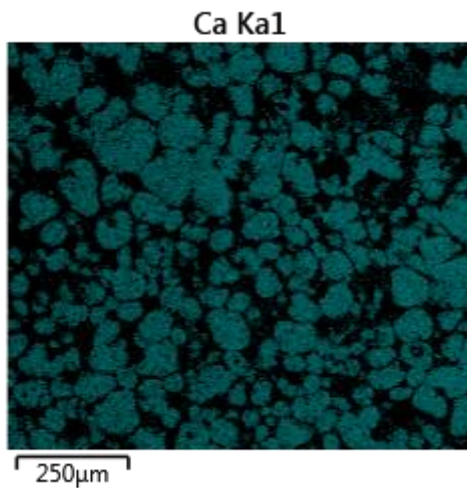


Figure 120. EDS map showing calcium on the polished cross-section of CaO-ZrO₂ crucible, near I.D.

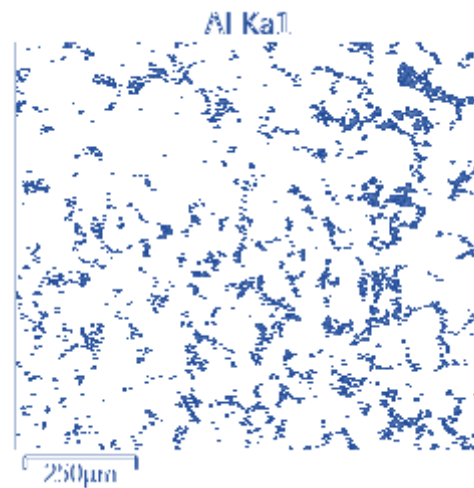


Figure 121. EDS map showing aluminum (hence slag) on the polished cross-section of CaO-ZrO₂ crucible, near I.D.

SEM-EDS analysis of the grain boundary region of the crucible showed the presence of silicon and magnesium as shown in Figure 122. There was no SiO₂ and MgO used in the slag. It indicated that the crucible could have been the source of magnesium observed in the inclusions (Figure 115).

The possible dissolution of SiO_2 and MgO in $\text{CaO-Al}_2\text{O}_3$ slag can be the reason for the extensive penetration of slag into the crucible.

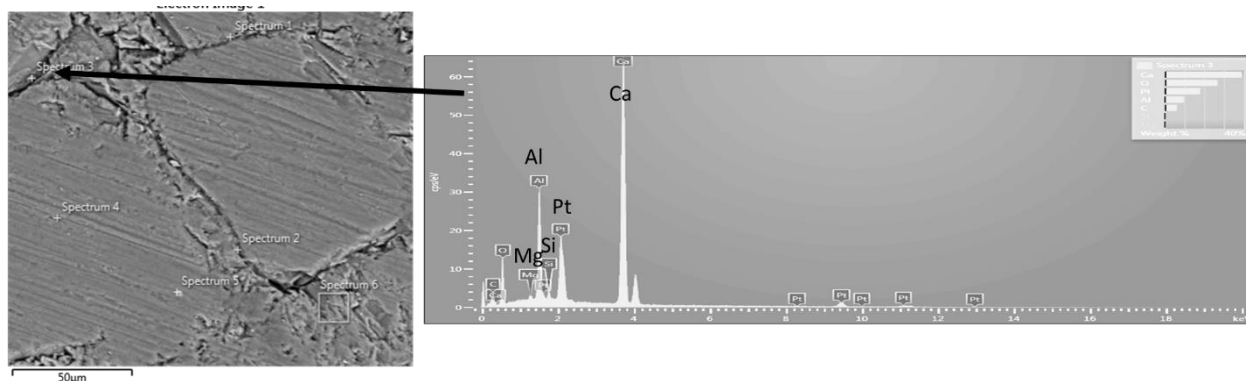


Figure 122. EDS at the grain boundary region of CaO-ZrO_2 crucible, near O.D.

Experiment-7.7 was conducted in a similar CaO-ZrO_2 crucible using 200 g of low sulfur (8 ppm) electrolytic iron but without slag addition. Figure 123 shows the change in inclusion composition in the samples taken at the 15th, 30th and 45th minutes. The inclusion composition in a sample taken at 15th minute was alumina + spinel with limited calcium and zirconium content. Magnesium, calcium and zirconium were expected to dissolve in steel at the steel-crucible interface and reduce alumina at the steel-inclusion interface. The calcium and zirconium content in inclusions increased with time; partial calcium modification of spinel inclusions can be observed in the final sample. Figure 124 shows a calcium containing inclusion observed in the sample taken at 45th minute. The sample taken at the 30th minute showed an increase in the area fraction of inclusions (from 13 ppm to 95 ppm) and inclusions were alumina rich, indicating reoxidation during the sampling. The change in average inclusion composition in three samples are shown in Table 44. For sample taken at $t=30$ minute, the increase in silicon concentration indicates that the silica contamination/reoxidation could have occurred due to silica from quartz sampler tube used for

sampling. %CaO in inclusions in the final sample was significant and it indicated continued calcium pick-up due to steel-crucible reaction.

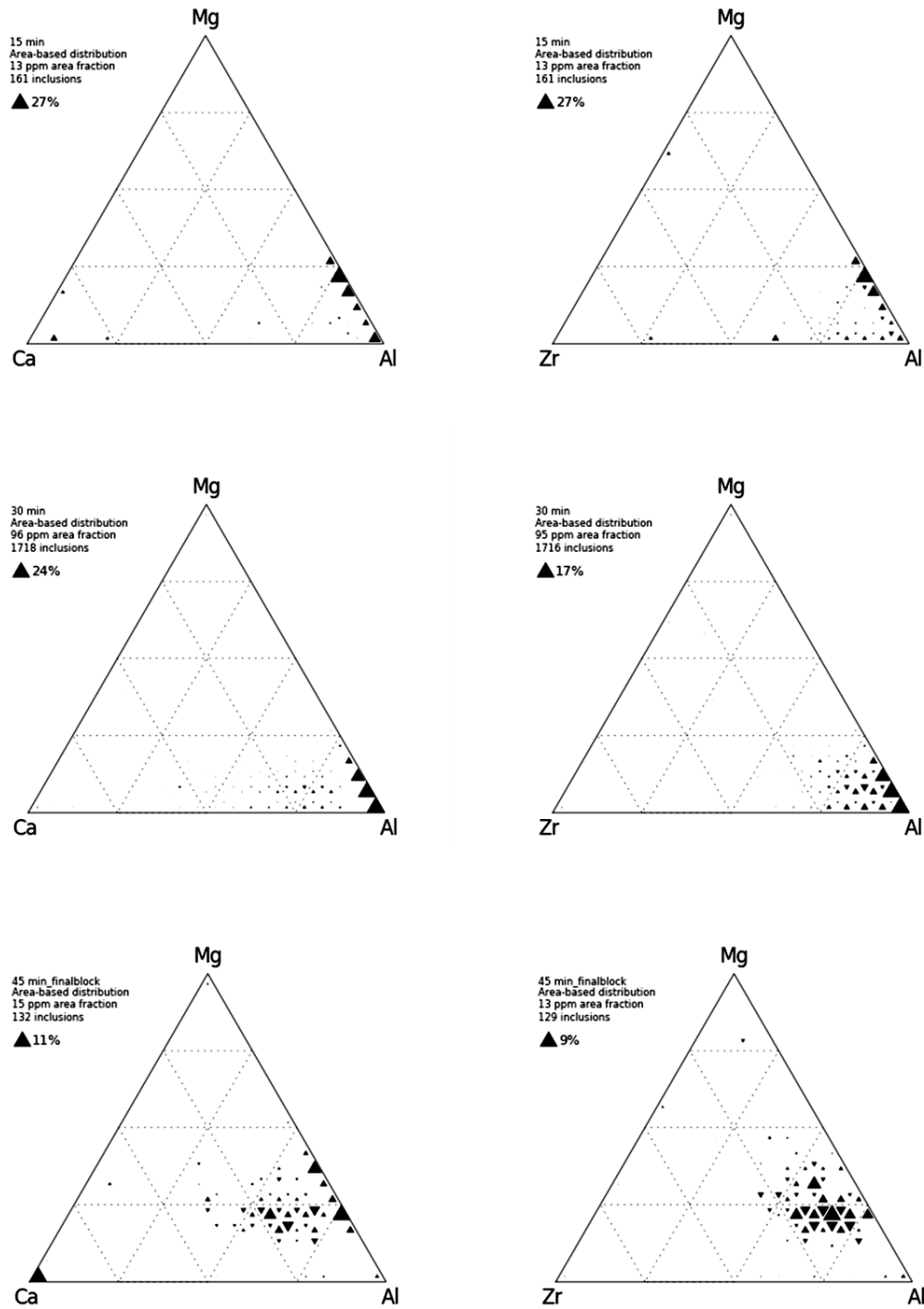


Figure 123. Inclusion composition change during experiment-7.7 (CaO crucible, no slag)

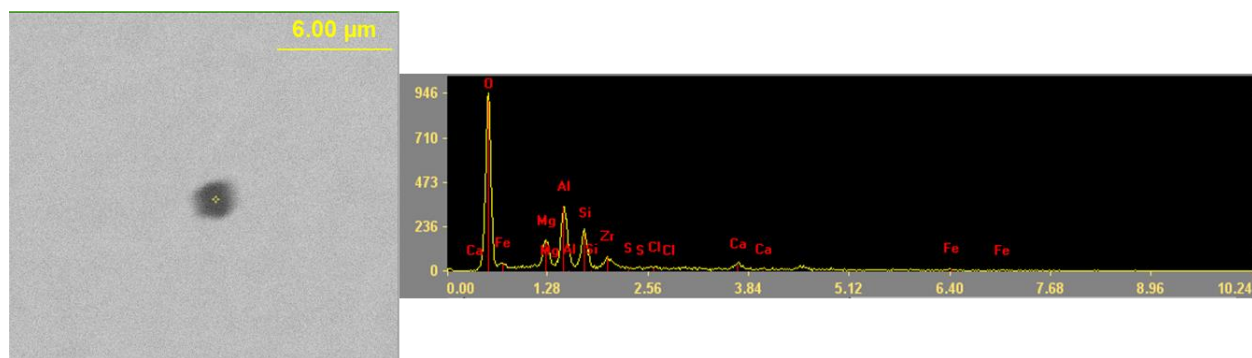


Figure 124. Calcium containing inclusion observed in sample taken at 45th minute from exp-7.7 (CaO crucible, no slag)

Table 44. Average inclusion composition with time for experiment-7.7

Time	Mg	Al	Si	Ca	Zr
15	5.4	71.8	0.0	3.8	19.1
30	2.9	42.0	43.6	4.4	7.1
45	12.0	40.3	14.4	11.8	21.6

7.4 Calcium transfer from CaS to oxide inclusions

Calcium treatment is the common way to supply calcium to oxide inclusions (alumina and spinel) in liquid steel. Verma et al. [68] showed that CaS could be a transient phase during modification of alumina inclusions containing more than 40 ppm S. Therefore, the addition of CaS particles in steel melt containing alumina inclusions should be able to modify alumina inclusions. An efficient way to add CaS in steel melt could be to create a steel containing known higher concentration of CaS inclusions. This would ensure that CaS particles are added inside melt and have known size range. In this section a similar experiment is described. The main idea of the experiment was to use the kinetics of calcium transfer to estimate dissolved calcium in liquid steel.

7.4.1 Experimental

The steel sample containing CaS inclusions were prepared by adding FeS (250 ppm equivalent S) and CaSi₂ (6 wt%) at 44 and 45 minute after 0.15% aluminum addition (see experiment-5.1). Final calcium and sulfur concentrations in steel were 17 ppm (estimated from inclusion analysis) and 50 ppm (measured using LECO). The inclusion composition in the sample is shown in Figure 125. The average inclusion composition in this sample was 72.5% Al₂O₃, 17.3% CaS and 10.2% CaO. Figure 126 shows the growth of CaS inclusions on Al₂O₃ inclusions in this sample. The mass fraction of inclusions in this sample was 100 ppm (estimated from area fraction)

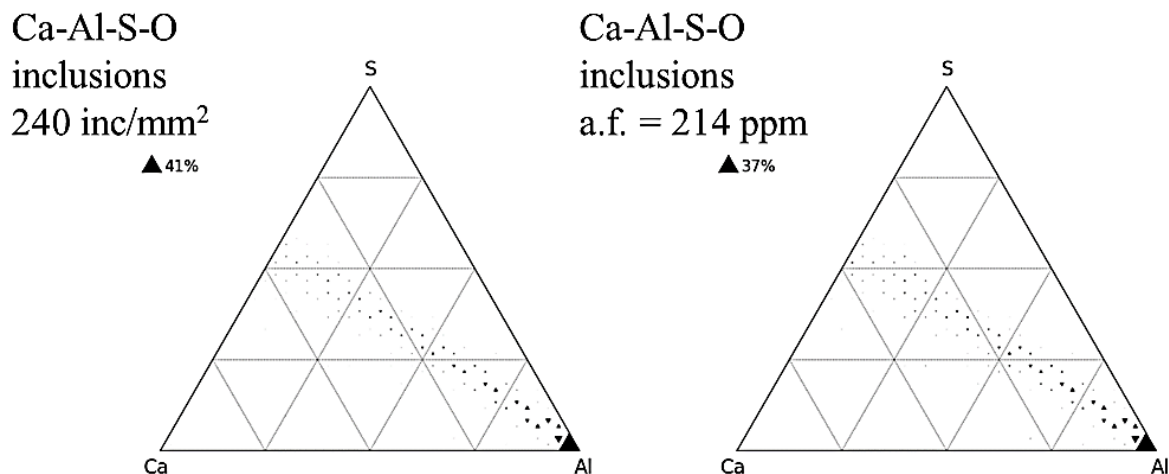


Figure 125. Al₂O₃-CaS inclusions used to study calcium transfer from CaS to oxide inclusions

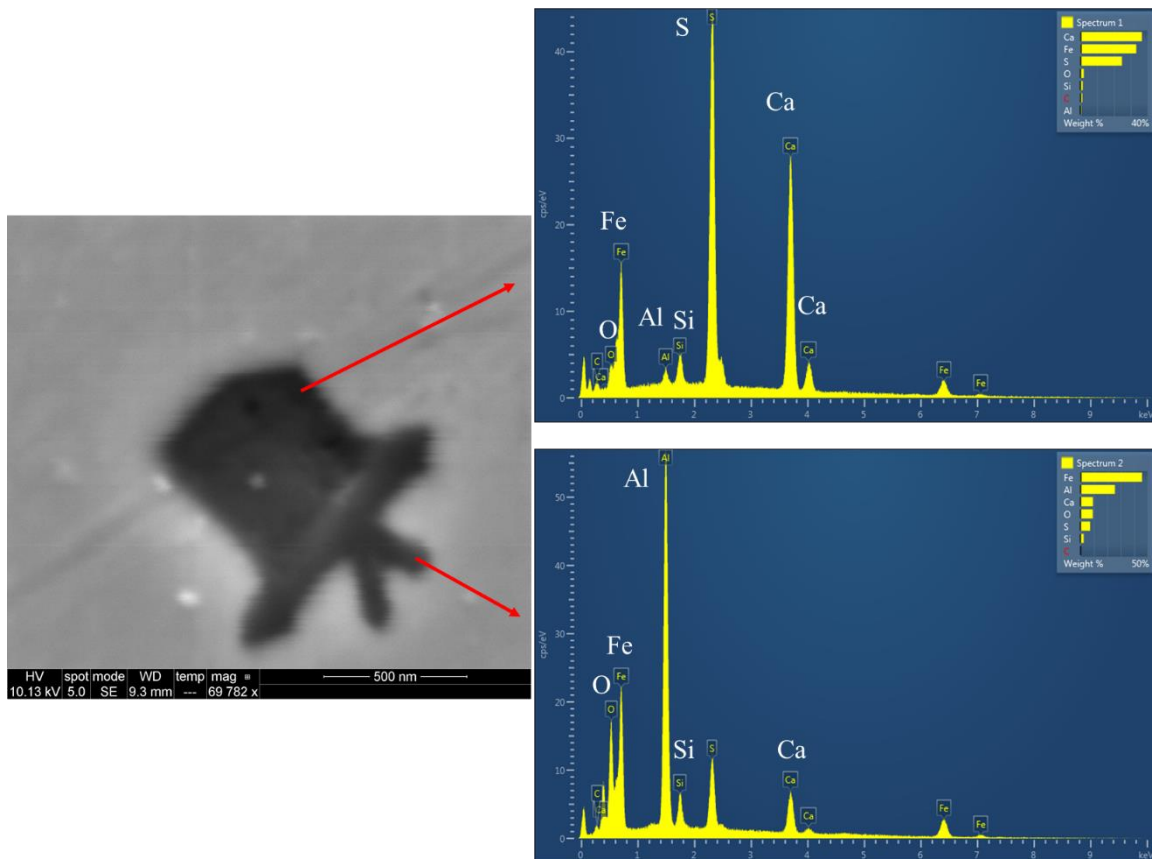


Figure 126. CaS-Al₂O₃ inclusions in steel sample used to study calcium transfer from CaS to Al₂O₃ inclusions

Experiment-7.8 was conducted in an alumina crucible; 200 g of electrolytic iron was deoxidized by adding 0.15% Al at t=0 minute. 22 g of steel containing Al₂O₃-CaS-CaO inclusions, described above, was added to steel melt at t=16 minutes. This addition was equivalent to adding 1.9 ppm calcium for experiment-7.8. A sample was taken 2:30 minutes after the addition as described in Table 45.

Table 45. Addition and sampling detail for experiment-7.8 (alumina crucible)

Time (minutes)	0	16	18:30
Event	0.15% Al addition	CaS containing steel added	S1

7.4.2 Results and Discussion

Figure 127 shows inclusion composition in sample taken 2:30 minutes after the addition of steel sample containing CaS inclusions to the melt. The inclusion composition is shown on a Ca-Al-S ternary. It can be seen that the CaS inclusions disappeared within 2.5 minutes and existing alumina inclusions was transformed to calcium aluminate. The inclusion composition was 80% Al_2O_3 and 20% CaO. Figure 128 show an inclusion in S1 sample from experiment-7.8 showing that CaS phase from inclusions disappeared and the calcium transfer occurred from CaS to alumina inclusions. The mass fraction of inclusions in this sample was about 10 ppm and estimated bound calcium in inclusions was 1.50 ppm which is very close to amount of calcium added (1.9 ppm) in the form of Al-Ca-S-O inclusion.

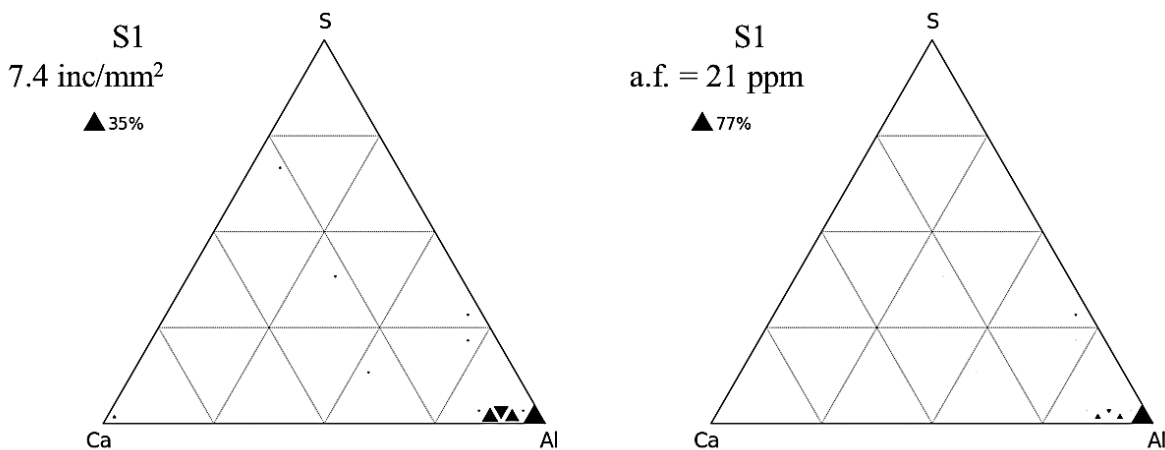


Figure 127. Inclusion composition in S1 sample from experiment-7.8

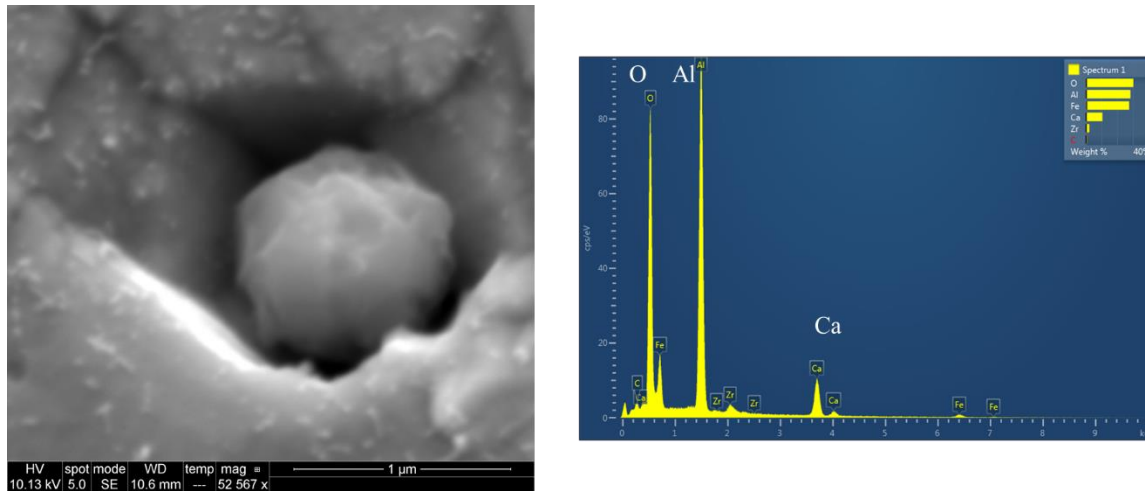


Figure 128. Ca-Al-O inclusion found in S1 sample from experiment-7.8

Since there was no CaS inclusions in the sample taken at 2.5 minutes. It can be concluded that the calcium-transfer from CaS to oxide inclusions completed in less than 2.5 minutes. Therefore, in order to study the rate of calcium transfer, the samples must be taken at very short interval.

8 Estimating $\varepsilon_{\text{Ca}}^{\text{O}}$ by measuring dissolved Ca in steel

The inclusion analysis results from previous chapter (chapter-7) confirm that it is possible to consistently transfer calcium to oxide inclusions in steel without calcium treatment. In this chapter, results of experiments are presented to estimate dissolved calcium in steel using calcium transfer to oxide inclusions using CaO-3%ZrO₂ crucibles.

8.1 Objective

The objectives of current chapter are:

- a) To design and conduct experiments to measure dissolved calcium in steel
- b) To use measured dissolved calcium in steel and estimate activities of Al, Al₂O₃ and CaO to estimate the Ca-O interaction parameter in steel
- c) To develop a private database in FactSage-7.2 for liquid steel consistent with other thermodynamic databases

8.2 Review and proposed experimental method

Fe-Ca and Fe-Ca-O equilibrium experiments were conducted by several researchers in the past. The experimental methods used by these researchers are summarized in Table 46 along with the calcium and oxygen measurement techniques. The range of calcium measurement from these studies are shown in bold in the right column of the table. It should be noted that Sponseller and Flinn [69], Song and Han [70] and Berg et al. [40] conducted study for measuring calcium solubility and Raoultian activity coefficient. In pure iron, the calcium solubility was consistently expected to be higher. The measured Raoultian activity coefficients from these studies are summarized in Table 47 along with value from FTmisc. database in FactSage-7.1. Some of the

measured activity coefficients were reported with respect to vapor phase; those were converted using free energy of formation of calcium vapor from liquid calcium at 1873 K ($=-8123$ J/mol) using FactPS database in FactSage-7.1. The value of activity coefficient for Song and Han [70] had to be re-calculated using their experimental data due to an error in free energy value in the original paper. The measured interaction parameters from other studies will be summarized later and will be compared with present study.

Table 46. Experimental and characterization method used by other researchers to study Fe-Ca and Fe-Ca-O thermodynamics

Reference	Method	Characterization
Sponseller and Flinn, 1964 [69]	Crucible: TiN, two layer (Fe and Ca in same crucible) Temperature: 1880.3 K Standard state: liquid calcium Pressure: 1.4×10^6 Pa Argon Time: 3 min	Wet chemistry for Ca measurement accuracy of $\pm 0.002\%$ at 0.05% [Ca]: 0.02-0.2 wt%
Han et al., 1988 [71]	Crucible: mixture of CaO and CaS Electrolytic iron: <30 ppm iron (deoxidized beforehand using Mg vapor) Mo crucible containing Ca in low temperature zone, 1200-1400°C, Atmosphere: Argon Temperature: 1600°C Standard state: calcium vapor Time: 3.5-5 hrs	Chemical analysis: atomic absorption for Ca and chemical methods for P [Ca]: 30-50 ppm
Kimura and Suito, 1994 [49]	Crucible: CaO, Al ₂ O ₃ Electrolytic iron equilibrated with 4% Ca enclosed in Fe capsule Without slag: equilibrium not achieved	Ca-measurement: ICP-ES, 1 ± 0.03 ppm O-measurement: inert gas fusion-infrared absorptiometry, 1 ± 0.7 ppm, standard steel sample contained 3.4 ppm O

Reference	Method	Characterization
	With slag: equilibrated in less than 60 minutes for Al but O not in equilibrium Exp. time: 90-100, 180 min	[Ca] _{total} : 0.3-14.4 ppm
Ohta and Suito, 1997 [47]	EI and slag (CSAM, CSM) equilibrium experiment Time: 1-3 hrs	Same as above [Ca]: <0.05-3.6 ppm
Nadif and Gatellier, 1986 [50]	CaO crucible, deoxidized by carbon 0.24 wt% Ca added, argon atmosphere	O measured using electrochemical probe and later analyzed Ca and Mg measurement method not mentioned [Ca]: ~10-220 ppm
Song and Han, 1998 [70]	CaO crucible Two temperature zone, vapor liquid equilibration sealed in a Mo chamber. Reaction time: 4 hrs Deoxidized by Ba, achieved 10 ppm O.	Ca measured using ICP method [Ca]: 24-110 ppm
Berg et al., 2017, [40]	Equilibrated with Ca vapor in Mo chamber Ca vapor pressure varied with temperature by moving Ca container	Ca measurement: ICP-SFMS [Ca]: 83-376 ppm

Table 47. Fe-Ca thermodynamic data from different sources (with respect to liquid calcium)

Reference	$\gamma_{Ca,l}^0$
Sponseller and Flinn [69]	2270
Han et al. [71]	77
Song and Han [70]	1528
Berg et al. [40]	1551
FactSage-7.1 (FTmisc)	1687

In the present work, Al-killed liquid steel was equilibrated with CaO-3%ZrO₂ crucibles for 100-136 minutes. The liquid steel was reoxidized afterwards to allow dissolved calcium to precipitate as inclusions. The calcium transfer to reoxidation inclusions was quantified from inclusion analysis and considered as dissolved calcium. The activities of aluminum, Al₂O₃ and CaO at equilibrium were estimated from inclusion analysis of sample taken just before deoxidation and SEM-EDS analysis of crucible wall in contact with steel.

8.3 Experimental

Four reoxidation experiments were conducted as described in Table 48 through Table 51. Experiments-8.1, 8.2 and 8.4 were conducted using electrolytic iron containing 8 ppm S. Experiment-8.3 was conducted using electrolytic iron containing 40 ppm sulfur. The sulfur level was further increased to 107 ppm by adding FeS. However, sulfur analysis, using LECO, of the first sample taken 15 minutes later (see Table 50) showed the sulfur concentration to be less than 10 ppm indicating rapid desulfurization at the steel-crucible interface; this is discussed later. The initial mass of electrolytic iron used for experiment-8.2, 8.3 and 8.4 were 200 g and that for

experiment-8.1 was 250 g (to account for the mass of sample taken before aluminum addition). Three methods of reoxidation were used to allow precipitation of dissolved calcium after steel-crucible equilibrium: 1) use of Fe_2O_3 2) addition of electrolytic iron (EI) containing ~360 ppm of oxygen and 3) addition of oxidized electrolytic iron. For the third method, electrolytic iron was oxidized at 700°C for 12 minutes. The thickness of the oxide layer was approximately 20 μm as shown in Figure 129. Another piece from same batch of reoxidation was used for experiment-8.4. For experiment-8.2, the oxygen in oxidized electrolytic iron was estimated from measured mass gain of electrolytic iron, after oxidizing at 700°C. The reoxidation methods used for individual experiments are mentioned in the respective tables. The inclusion analysis of samples from experiment-8.3 showed that after 105 minutes of steel-crucible reaction, the area fraction of inclusions (measured using SEM ASPEX-AFA) was almost zero (<1 ppm). The experimental and modeling results of steel-MgO crucible reaction in chapter-5 showed that steel-crucible equilibrium was achieved in about 40 minutes (see Figure 29). Therefore, liquid steel was reoxidized at $t=105$ minutes during experiment-8.4.

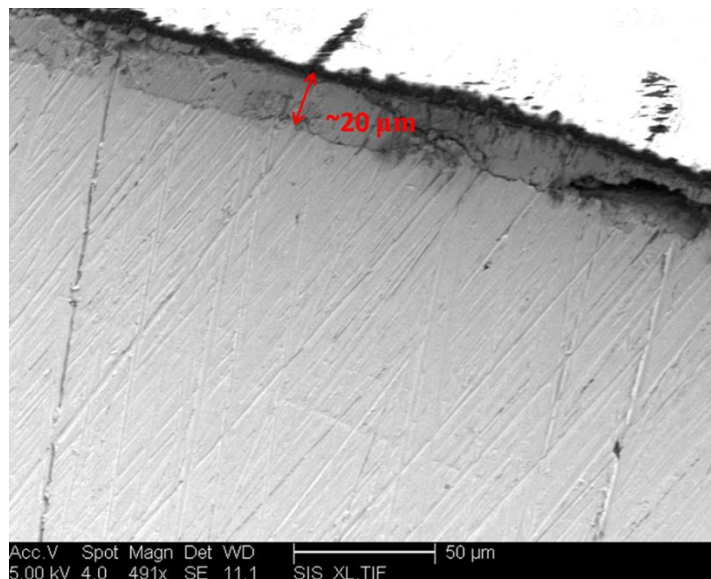


Figure 129. Thickness of oxide layer after 12 minutes at 700°C

Table 48. Addition and sampling details for experiment-8.1

Time	0	173	173:15	174:30
Events	0.29% Al	25 ppm O using Fe ₂ O ₃	S2	S3

Table 49. Addition and sampling details for experiment-8.2

Time	0	120	120:30	121:30
Events	0.16% Al	S1	12.5 ppm O, oxidized EI	S2

Table 50. Addition and sampling details for experiment-8.3

Time	0	15	45	75	105	135	136	138	158	171
Events	0.28% Al	S1	S2	S3	S4	S5	~15 ppm O using EI	S6	S7	SF

Table 51. Addition and sampling details for experiment-8.4

Time	0	104	105	105:20	108:30	112:30
Event	0.3% Al	S1	10 ppm O, oxidized EI	S2	S3	S4

8.4 Results and discussion

8.4.1 Reoxidation methods

Figure 130 shows the composition of inclusions in S2 and S3 samples taken 15 and 90s after reoxidation using Fe₂O₃ during experiment-8.1. On the Mg-Ca-Al ternary, most inclusions were in alumina corner showing that there was almost no calcium containing inclusions in these samples. These inclusions also contained ZrO₂ (not shown on the ternary). The area fractions of inclusions were about 150 ppm in both samples (~40 ppm oxygen equivalent) which was more than oxygen added using Fe₂O₃; additional oxygen may come from the iron foil used for making the Fe₂O₃ capsule. Manual analysis of inclusions showed that there were very few calcium containing inclusions in these samples indicating that had some calcium transfer (see Figure 131).

Such rarity of calcium containing inclusions indicate that the calcium concentration must have been very small compared to inclusion concentration. This confirms the very small solubility of calcium. Due to this reason, subsequent reoxidation was done using a smaller oxygen addition.

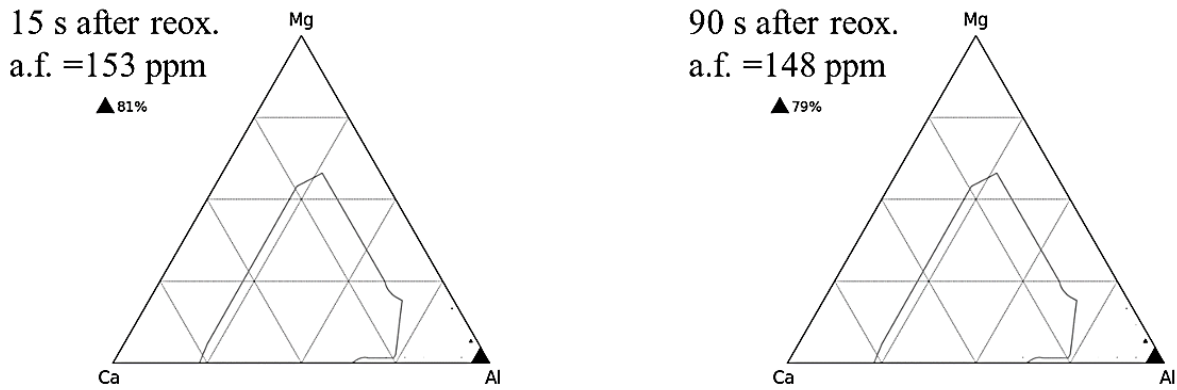


Figure 130. . Inclusion composition in samples taken after reoxidation during experiment-8

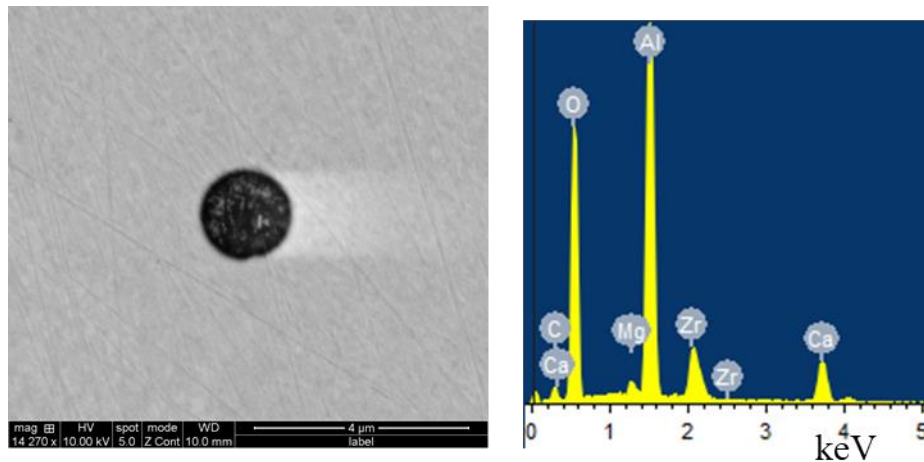


Figure 131. Calcium containing inclusion observed in sample-2 (15 s after reoxidation) from experiment-8.1

Figure 132 and Figure 133 show inclusion composition in sample S1 (30 s before reoxidation) and S2 (60 s after reoxidation) during experiment-8.2. The higher inclusion concentration (49 ppm area fraction) in sample taken 30 s before reoxidation was most likely due to contamination from quartz tube used for sampling steel. As shown in the right most ternary diagrams of Figure 132

and Figure 133, inclusions contained significant concentration of SiO_2 . The average inclusion composition for S1 and S2 is shown in Table 52. Assuming all calcium to be present as oxides, the calculated calcium contained in inclusions in samples S1 and S2 were 0.24 and 0.41 ppm respectively.

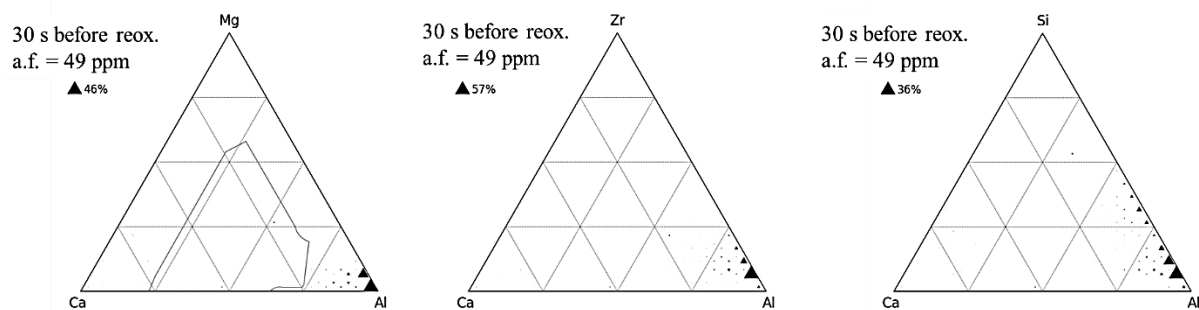


Figure 132. Inclusion composition 30 s before reoxidation during experiment-8.2; presence of silicon in inclusions show possible contamination from sampling tube

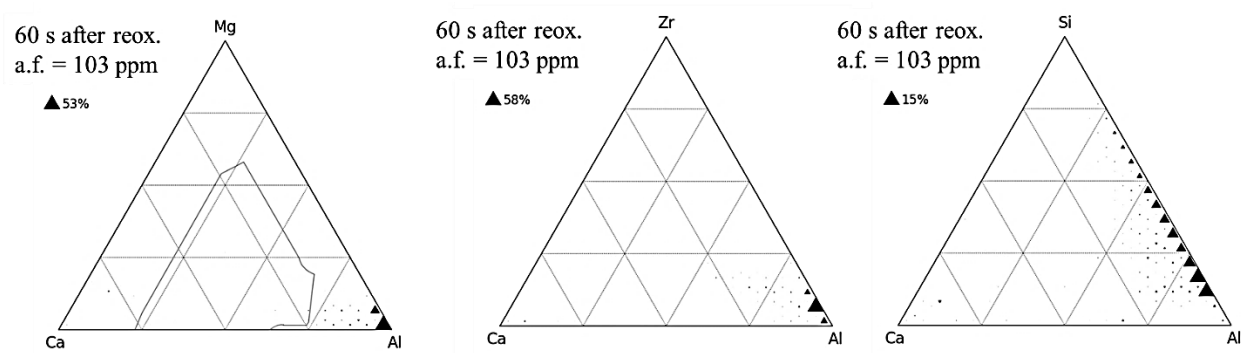


Figure 133. Inclusion composition 60 s after reoxidation during experiment-8.2; presence of silicon in inclusions show possible contamination from sampling tube

Table 52. The average inclusion composition (mass%) in samples from experiment-8.2

Time	MgO	Al_2O_3	SiO_2	CaO	ZrO_2
S1	2.4	61.9	17.1	1.4	17.3
S2	1.8	56.2	29.6	1.2	11.3

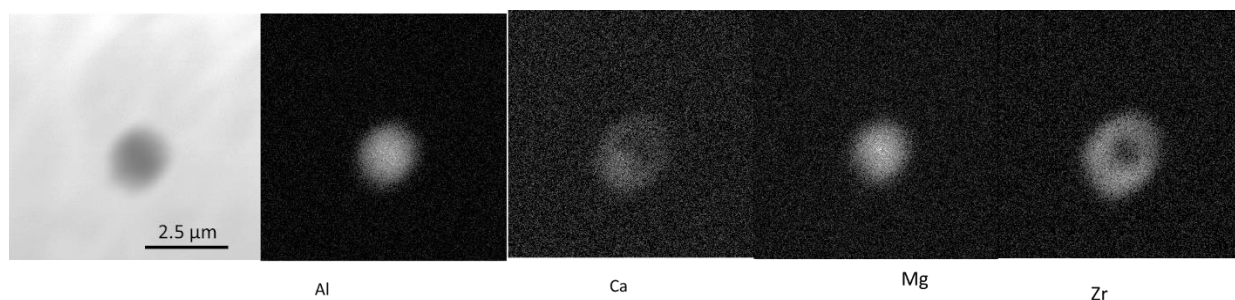


Figure 134. Calcium containing inclusion observed in the sample taken at 138th minute during experiment-8.3, just after reoxidation

8.4.2 Dissolved calcium calculation

The inclusion analysis of samples from experiments-8.1 and 8.2 showed that the calcium transfer to inclusions can be detected only if the oxygen addition is small (<15 ppm). For such a small concentration of inclusions, there was a need to make sure inclusion analyses were correct with respect to area fraction and chemical composition. The samples after reoxidation from experiments-8.3 and 8.4 were also analyzed using automated feature analysis with INCA software coupled with FEI-SEM-Quanta-600 for better spatial resolution; inclusions larger than 0.2 μm were analyzed. For small inclusions formed just after reoxidation (average inclusion size $\sim 0.5 \mu\text{m}$), the SEM-EDS analysis was expected to be affected by the steel matrix effect during automated feature analysis. In addition, it was difficult to filter calcium containing inclusions from automated inclusion analysis; even a single wrong filtering would have significantly affected measured dissolved calcium. Therefore, the composition of inclusions was manually measured for multiple inclusions in both samples: 33 inclusions were measured for sample from experiment-8.3 and 9 inclusions were measured for the sample from experiment-8.4. The chemical compositions of inclusions in the S6 sample from experiment-8.3 and S2 sample from experiment-8.4 are shown in Figure 135 and Figure 136 respectively. The bound calcium and oxygen in these samples were estimated from the average inclusions composition (manual analysis) and measured area fraction

of inclusions (from Quanta-600 AFA). The mass fraction of inclusions was estimated from measured area fraction (=volume fraction) and average mass density of inclusions based on the average composition. The results are summarized in Table 53. It is interesting to note that the estimated bound oxygen from S2 sample of experiment-8.4 was equal to 9 ppm which is very close to 10 ppm O added for reoxidation. The lower estimated bound oxygen for S6 sample from experiment-8.3 may be attributed to variation in oxygen concentration in solid chips of electrolytic iron used for reoxidation.

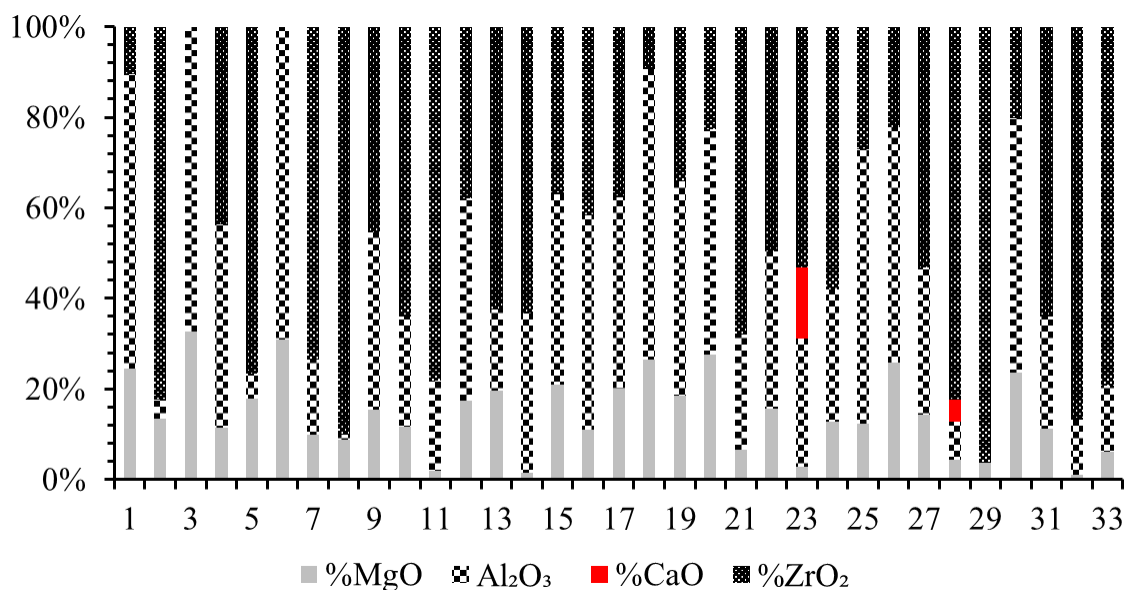


Figure 135. Chemical composition of individual inclusions measured using manual SEM-EDS for sample just after reoxidation (S6) from experiment-8.3

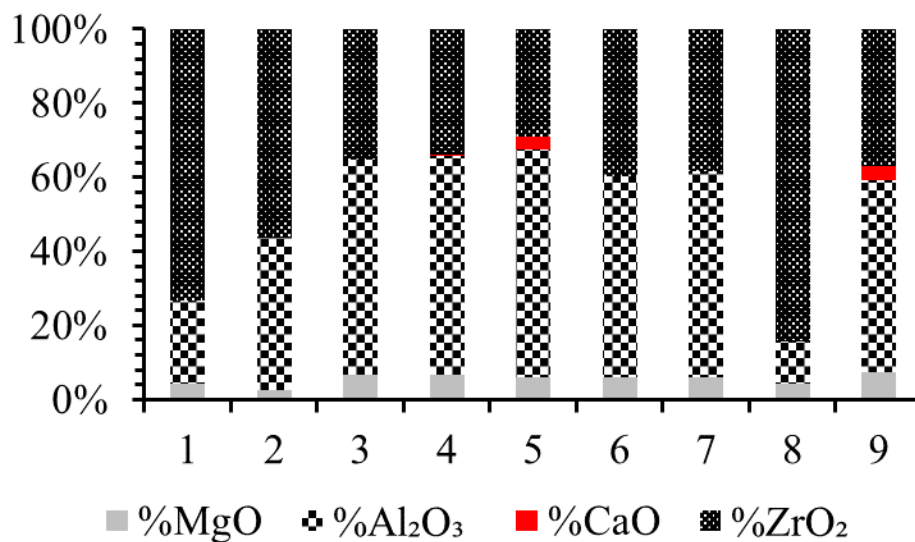
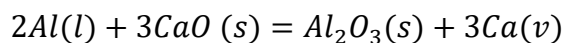


Figure 136. Chemical composition of individual inclusions measured using manual SEM-EDS for sample just after reoxidation (S2) from experiment-8.4

Table 53. Estimated calcium and oxygen in inclusions in samples taken just after reoxidation during experiments-8.3 and 8.4

Exp.#	Area fraction (ppm)	Average composition	Bound calcium, ppm	Bound oxygen, ppm
8.3	26.4	13.4% MgO, 32% Al ₂ O ₃ , 0.6% CaO, and 54% ZrO ₂	0.073	5.70
8.4	50.9	5.5% MgO, 44.3% Al ₂ O ₃ , 0.9% CaO, and 49.3% ZrO ₂	0.16	9.0

The experimentally measured dissolved calcium can be used to estimate Ca-O interaction parameter using the method described here. The activity of dissolved calcium was found from the activities of Al, Al₂O₃ and CaO using Equation 33. Ca-O interaction parameter was then estimated using Equation 34 from measured dissolved calcium and estimated calcium activity.



$$K = \frac{a_{Ca}^3 \cdot a_{Al_2O_3}}{a_{Al}^2 \cdot a_{CaO}^3}$$

Equation 33

$$\ln(\gamma_{Ca}) = \ln\left(\frac{a_{Ca}}{X_{Ca}}\right) = \ln \gamma_{Ca}^0 + \epsilon_{Ca}^O X_O + \epsilon_{Ca}^{Al} X_{Al}$$

$$\epsilon_{Ca}^O = (\ln \gamma_{Ca} - \ln \gamma_{Ca}^0 - \epsilon_{Ca}^{Al} X_{Al})/X_O \quad \text{Equation 34}$$

Where a_i : activity of species i , K represents equilibrium constant, γ_{Ca}^0 : standard activity coefficient and γ_{Ca} : activity coefficient and ϵ_{Ca}^O us the first order Ca-O interaction parameter.

The values of K (2.49×10^{-6}) was calculated using FactPS databases in FactSage-7.1. The reference state of calcium for this calculation was calcium vapor. The activities of CaO and Al_2O_3 were calculated based on the analysis of crucible wall for each experiment. For experiment-8.3, the crucible wall was coated with a calcium aluminate layer as shown in Figure 137. The composition of calcium aluminate layer was 58% CaO and 42% Al_2O_3 . The presence of CaS particles attached to crucible wall shown in Figure 138 shows that the desulfurization occurred at the steel-crucible interface during experiment-8.3. The presence of a reaction product layer in case of experiment-8.4 is shown in Figure 139(a). The composition of the layer on the crucible at different spots varied a lot as shown in Figure 139. The activity of CaO and MgO was calculated based on the average composition of layer: 3.8% MgO, 17.4% Al_2O_3 , 6.7% SiO_2 , 68.6% CaO and 3.1 % ZrO_2 . The activities of CaO and Al_2O_3 was calculated using FactSage-7.1 as was the activity of aluminum. The mole fraction of oxygen was calculated for alumina activity at the inner surface of the crucible as shown in Table 54. The calculated Ca-O interaction parameter from these two experiments are shown in Table 54. The large difference in interaction parameter for small variation in $\ln \gamma_{Ca}$ was due to small oxygen concentration in steel (see Equation 34). The average first order Ca-O interaction parameter is -6.5×10^4 as an average of two estimates. The values of $\ln(\gamma_{Ca}^0)$ and ϵ_{Ca}^{Al} were assessed using FactSage-7.2 FTmisc. database and were equal to 7.95 and -6.98 respectively.

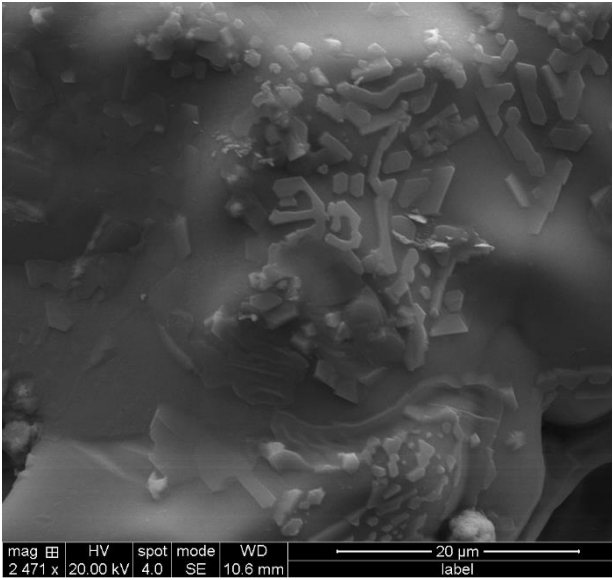


Figure 137. Calcium aluminate layer on crucible wall at the end of experiment-8.3

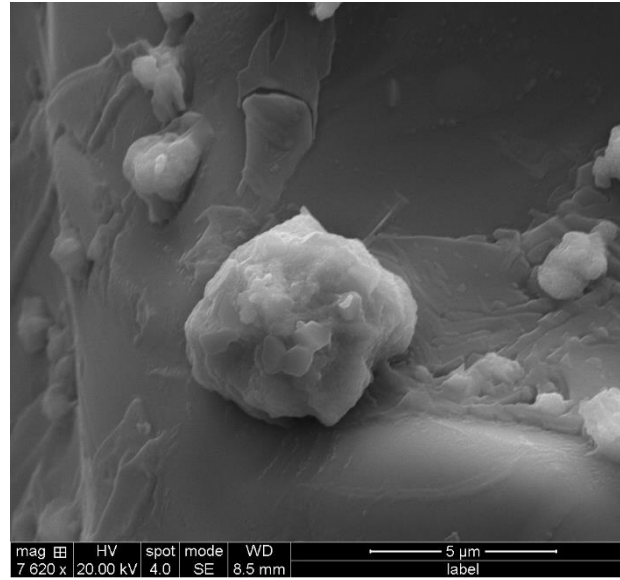


Figure 138. CaS particle attached to the crucible wall at the end of experiment-8.3

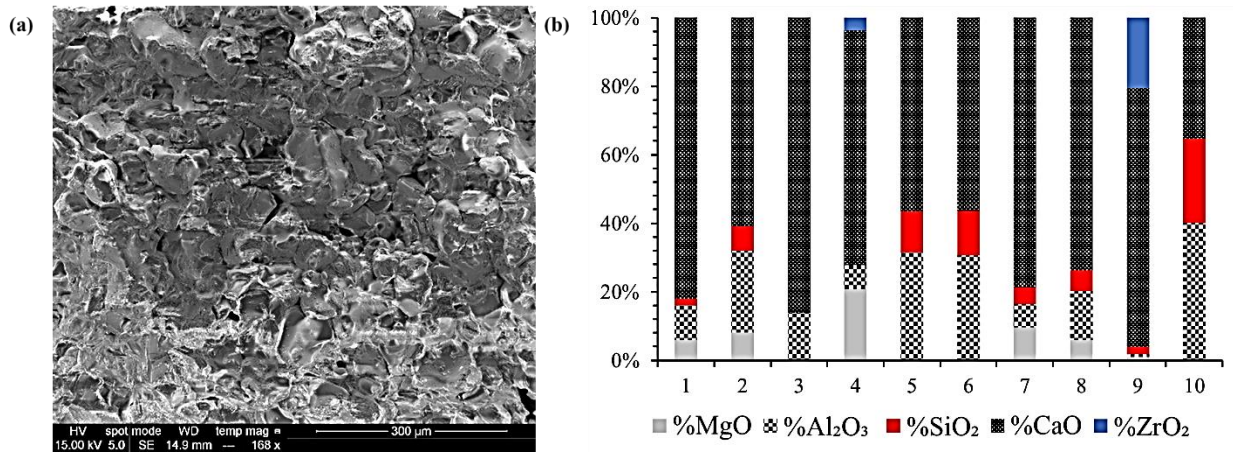


Figure 139. (a) Reaction product layer of crucible and (b) variation in composition of crucible reactive layer for exp. 8.4

Table 54. Calculating Ca-O interaction parameter from exp. 8.3 and exp. 8.4

Exp. #	a_{CaO}	$a_{Al_2O_3}$	a_{Al}	a_{Ca}	X_{Ca} (ppm)	X_O (ppm)	$\ln(\gamma_{Ca})$	ε_{Ca}^O
8.3	1	0.00889	3.0×10^{-4}	2.9×10^{-4}	0.1	4.3	7.97	1.3×10^4
8.4	0.95	0.0044	3.0×10^{-4}	3.6×10^{-4}	0.224	3.8	7.37	$-1. \times 10^5$

The interaction parameter estimated from current experimental work is compared to the published values in Table 55. Equation 35 was used to estimate e_i^j from ϵ_i^j as recommended by Sigworth and Elliot [72].

$$\epsilon_i^j = 230 \left(\frac{M_i}{M_1} \right) e_i^j + \frac{M_1 - M_j}{M_1} \quad \text{Equation 35}$$

The value of equilibrium constants ((CaO) = [Ca]_{1 wt%}+ [O]_{1 wt%}) from literature are also shown in Table 55; the values vary from -10.3 to -6.05. It is interesting to noted that Kimura and Suito [49] indicate different equilibria for different concentration of dissolved calcium and oxygen ([Ca]+2.51[O], in mass ppm) in liquid steel. For the present work, the equilibrium constant (for CaO=[Ca]+[O]) was calculated from FactSage. The dissolved calcium was calculated from all sources for 5 ppm dissolved oxygen and unit activity of CaO. The present work estimates minimum value of dissolved calcium (=7 ppb, in mass) and the work by Nadif and Gatellier [50] estimates the maximum value, about an order of magnitude higher than any other work. . It should be noted that Ca-O interaction was neglected in that work, hence activities were considered equal to mass%. The deviation between experimentally measured equilibrium constant from their work with other studies or thermodynamically calculated values are discussed earlier in section 4.2.1.1.2. The estimated dissolved calcium (for 5 ppm O) for other correlations were in the range of 0.5-12 ppm. As noted from current experimental results and modeling work discussed earlier, the value reported by FactSage over-predicted the calcium concentration in liquid steel.

Table 55. Thermodynamic parameter for Fe-Ca-O from literature and present work

Reference	e_O^{Ca}	ρ_O^{Ca}	$\rho_O^{Ca,O}$	e_{Ca}^O	ρ_{Ca}^O	$\rho_{Ca}^{Ca,O}$	logK	[Ca]*
[71]	-475			-1187.51			-8.26	0.45
[49] ($\alpha < 8$)**	-5000			-12500			-10.3	
[49]($\alpha: 8-30$)**	-600			-1500			-7.6	7.8
[73]	-3600	5.7×10^5	2.9×10^6	-9000	3.6×10^6	2.9×10^6	-10.22	5.5
[47]							-10.22	8.7
[50]							-6.05	90
FS7.1 (FTmisc.)							-9.94	12.3
Present work	-398			-994			-9.94	0.007

*for [O] = 5 ppm, ** $\alpha = [Ca]_{ppm} + 2.51[O]_{ppm}$

Figure 140 shows calculated relationship between dissolved [%Ca] and dissolved [%O] using interaction parameters estimated from present work along with other values as shows in Figure 49. The value calculated using present work predicts much smaller Ca-O interaction parameters than other published results. The current interaction parameters were estimated for ~1 ppm dissolved

oxygen and 0.1 ppm dissolved calcium in steel. There are not many published experimental results in this range of calcium and oxygen concentration.

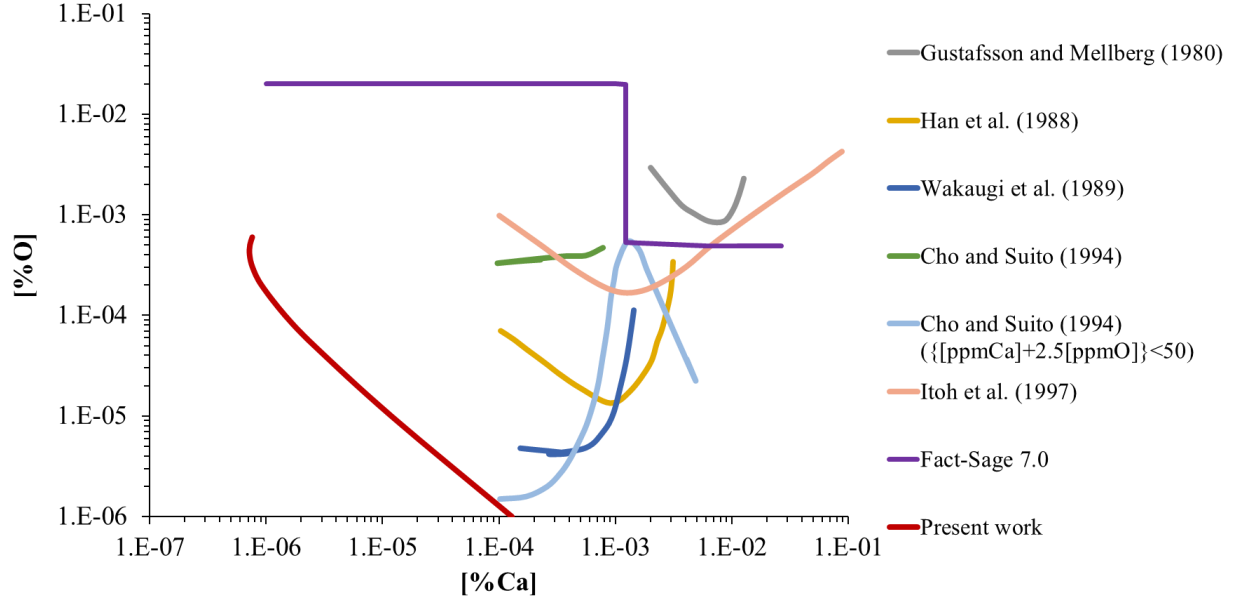


Figure 140. Comparing Fe-Ca-O thermodynamics: present results vs published results [42]

A more practical result should include aluminum concentration in steel while calculating relationship between [%O] and [%Ca]. Figure 141 shows the relationship between dissolved [%O] and [%Ca] in the presence of 0, 0.05% and 0.26% Al. 0.05% aluminum is the typical concentration in aluminum killed steel and 0.26% Al corresponds to the experimental condition of the current work which was used to estimate the Ca-O interaction parameter. For typical steelmaking condition of aluminum killed steel (0.05% Al and few ppm dissolved oxygen), the estimated calcium is about 7 ppb. The straight line in Figure 141 shows the calculated relationship between [%O] and [%Ca] without considering any interaction between Ca and O ($\ln \gamma_{Ca}^o = -7.95$, $e_{Ca}^{Al} = -0.07$). There is small difference between calculated dissolved calcium from the two methods for dissolved oxygen < 2 ppm for all aluminum concentration. Considering the variations in published results and some uncertainty involved in the current calculation, one can argue that the Ca-O

interaction can be completely ignored under typical aluminum-killed steelmaking conditions (0.05% Al).

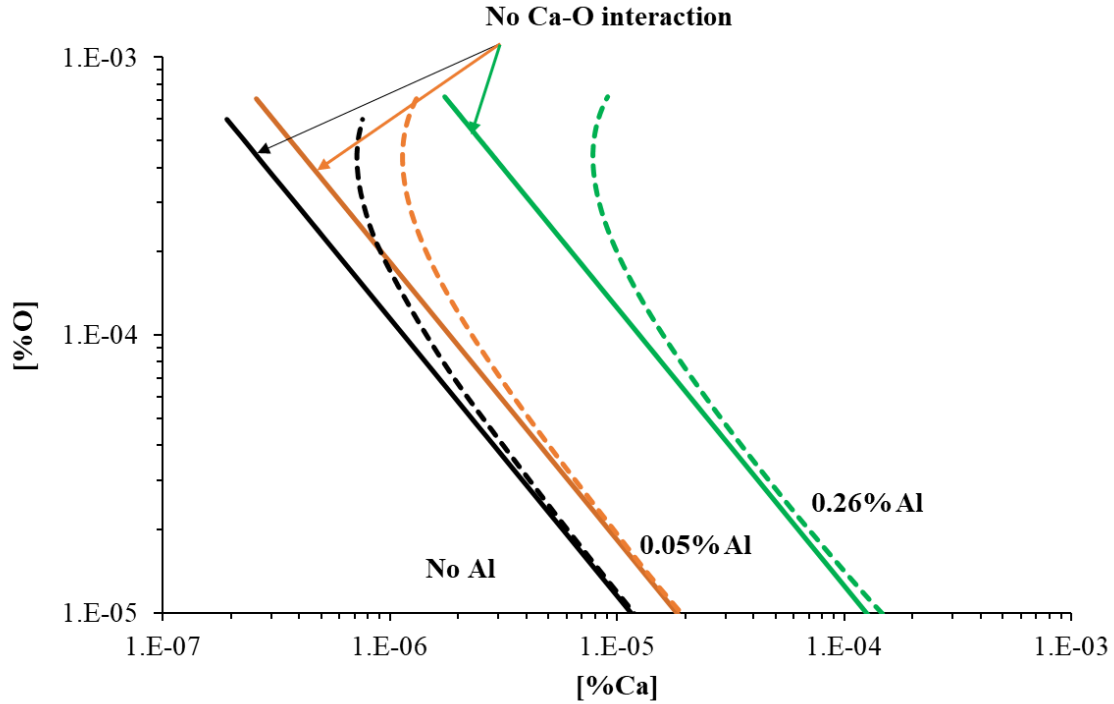


Figure 141. Effect of aluminum content on equilibrium dissolved calcium calculated, for zero Ca-O interaction and using the Ca-O interaction parameter from present work

In conclusion, the inclusion analysis of samples taken after reoxidation of steel equilibrated with CaO crucible was used to estimate the Ca-O interaction parameter in liquid steel at 1873 K. For typical steelmaking condition of aluminum killed steel (0.05% Al), the relationship obtained from current interaction parameter is very close to the case with interaction parameter = 0. As discussed earlier, the value of interaction parameter from two experiments differed significantly. The difference can be due to uncertainty in oxygen concentration in the single piece of electrolytic iron added in experiment-8.3 for reoxidation. The other source of uncertainty is the inclusion analysis, although care was taken to accurately determine average inclusion composition using manual SEM-EDS of individual inclusions. There were very few CaO containing inclusions in the sample.

As the crucible contained 3% ZrO₂ and other impurities (see Figure 122), the reaction layer at the crucible wall did not have a uniform chemical composition as shown in Figure 139. This was also reflected in the inclusion composition. Therefore, use of a higher-purity CaO crucible is expected to improve the accuracy and consistency of such experiments.

8.5 Private database for liquid steel in FactSage

In order to use Ca-O interaction parameter found in this work or even from other sources for the kinetic model, one needs to update liquid steel database. This can be best done by creating a private database in a computational thermodynamics package like FactSage. The “Solution” module allow users to create a uniform interaction parameter based model for liquid steel in private database. Appendix B describes the method to create such a database. Appendix C describes the method to use FTmisc and FactPS databases from FactSage to back-calculate interaction parameters. A thermodynamic calculation for experimental condition (initial condition: 0.3% Al, 0.035% O and 2% CaO) similar to experiments-8.3 and 8.4 was performed using this database. The result of thermodynamic calculation is given in Table 56.

Table 56. Results of a thermodynamic calculation for experimental condition similar to experiments-8.3 and 8.4

a_{Al}	$a_{Al_2O_3}$	a_{CaO}	a_{Ca}	[Al]	[O]	[Ca]
3×10^{-4}	0.0089	0.99	3×10^{-4}	0.26%	4 ppm	0.2 ppm

The kinetic model developed for experiment-5.6 (steel-slag equilibrium experiment in MgO crucible without Ar stirring) was updated to use the private database for liquid steel (other databases remained the same). The calculated results from the two sources are compared in Figure 142 through Figure 146. In the legend of these plots, ‘FS’ denotes results from the native databases used in FactSage (FTmisc for liquid steel) and ‘Pvt’ denotes results from using the private database

for liquid steel. As shown in Figure 142, the calculated change in aluminum and silicon concentration in steel with time was almost same. Total magnesium (dissolved + inclusions) was also same for two cases but the dissolved magnesium was lower in the private database, more prominently in the presence of slag (see Figure 143). As expected, the biggest difference was in the calculated dissolved and total calcium from two sources as shown in Figure 144. The calculated dissolved and total calcium from the private database was about 1000-times smaller than that calculated from FTmisc. Figure 145 shows calculated inclusion compositions. As expected, there was almost zero calcium in inclusions at any point of time as calculated from private database. However, the FTmisc database based kinetic model calculated about 8% cation molar fraction equivalent of Ca at $t=45$ minutes. It should be noted that there was no calcium containing inclusions observed in this experiment.

The apparent decrease in dissolved calcium and dissolved magnesium at later time of calculation in these plots indicate potential problem associated with converting the associate solution based model to a unified interaction parameter description. This problem is further illustrated with help of dissolved oxygen plot in Figure 146. For practical reasons, higher order interaction parameters could not be calculated. As discussed in Appendix C, it was not possible to fit to aluminum activity for large range of variation in aluminum concentration. The values used in the current database were for [Al] in 0.13 wt%-0.30 wt% range. As aluminum concentration reduced (from 0.3 wt%) with time during the kinetic model calculation, the chosen interaction parameters were not expected to match the activities from FTmisc. This resulted in smaller dissolved oxygen concentrations for calculation from private database as shown in Figure 146. Although such a difference in oxygen concentration did not affect the kinetics of reaction between aluminum in steel and silica in slag but the dissolved magnesium and calcium were certainly affected. When

creating a private database, such limitations must be noted. One may use interaction parameters from other sources, but must be careful about any difference in free energy values in the pure substance database (FactPS) compared with the source of the interaction parameter.

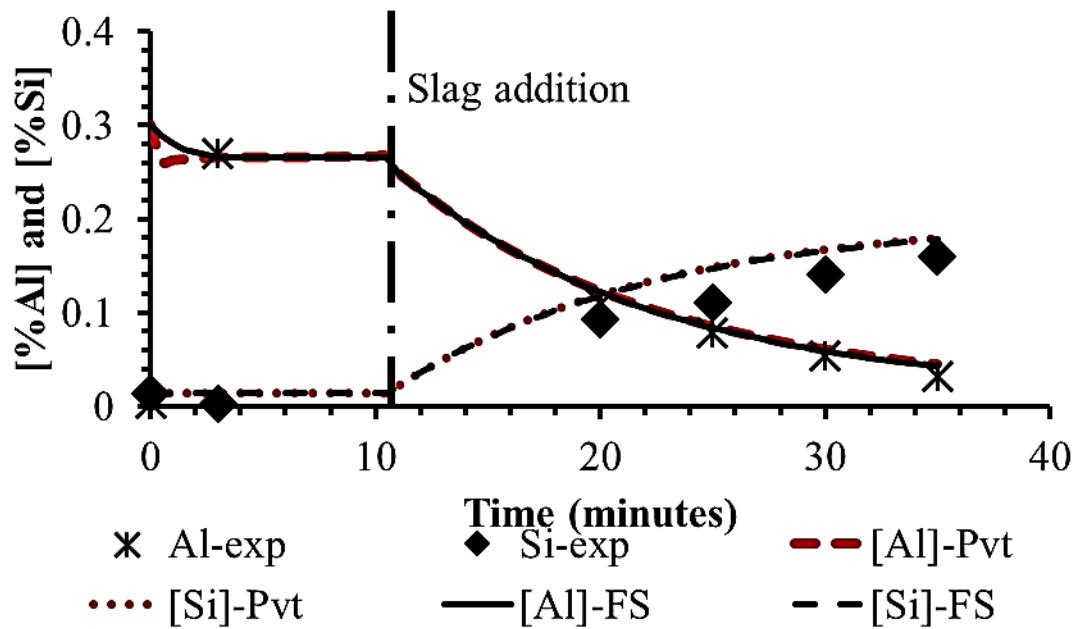


Figure 142. Change in steel composition with time for conditions in experiment-5.6; comparing private database with FTmisc in FactSage-7.2

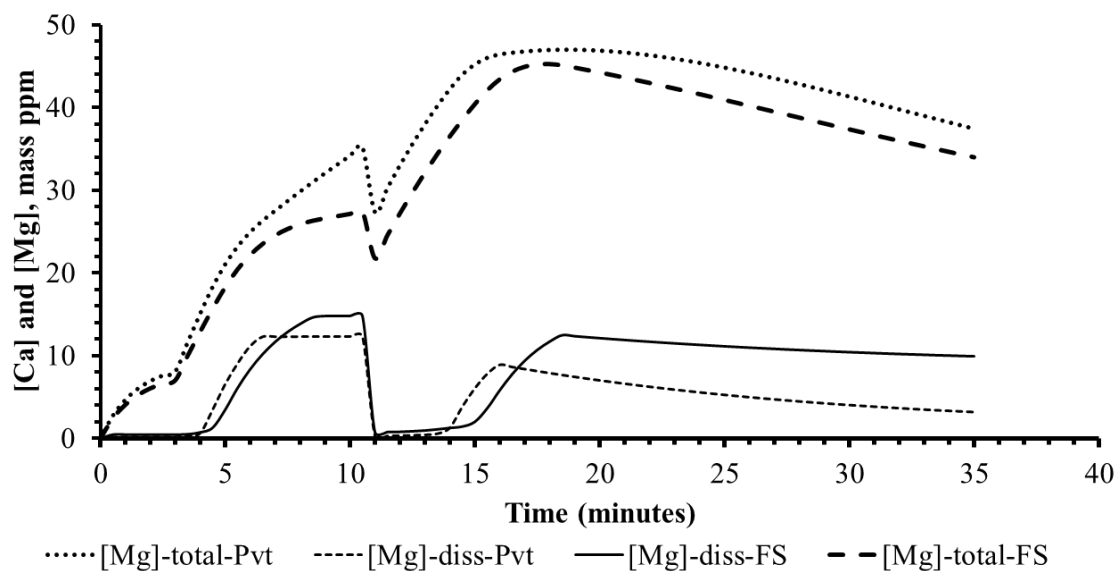


Figure 143. Calculated dissolved and total magnesium in steel from FTmisc and private database

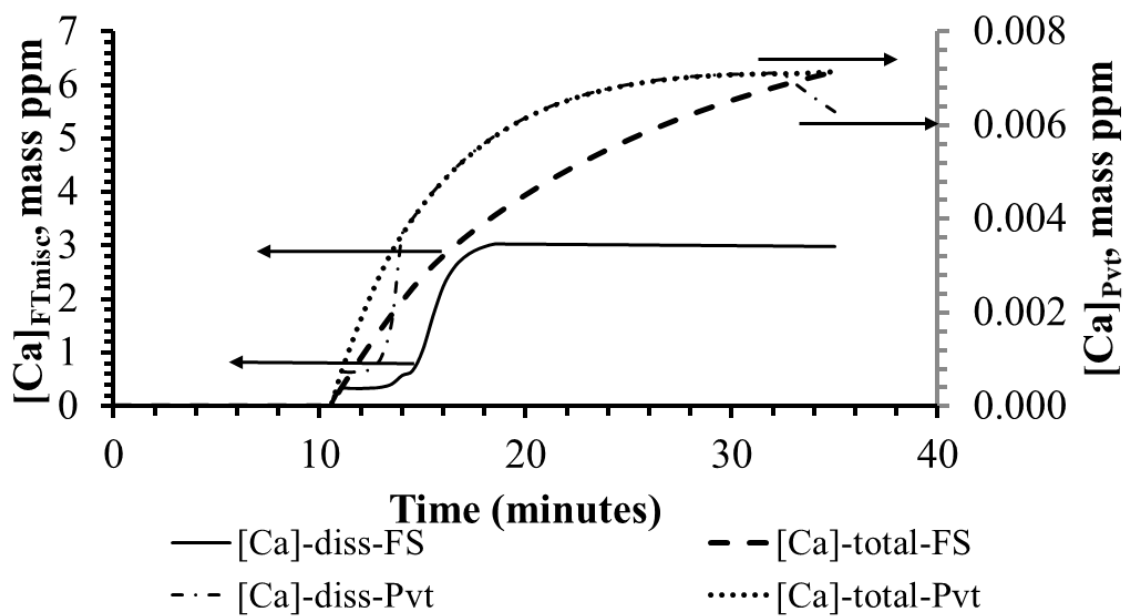


Figure 144. Calculated dissolved and total calcium in steel from FTmisc and private database

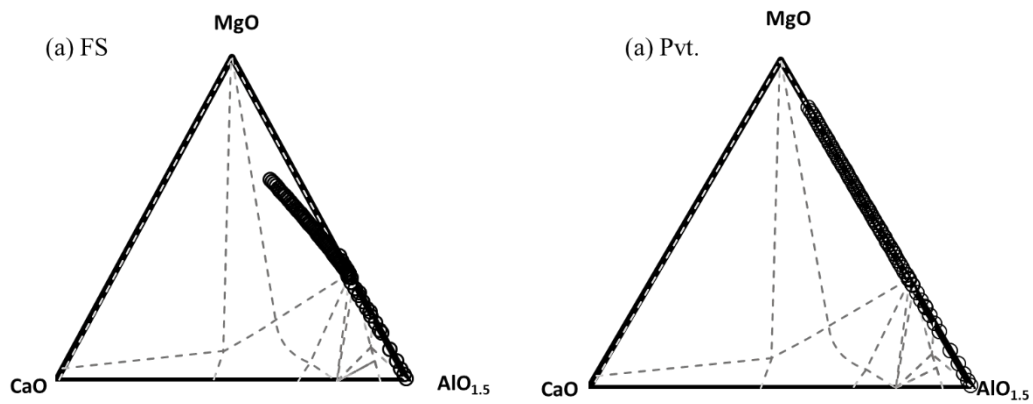


Figure 145. Calculated inclusion composition (open circle) from FTmisc and private databases

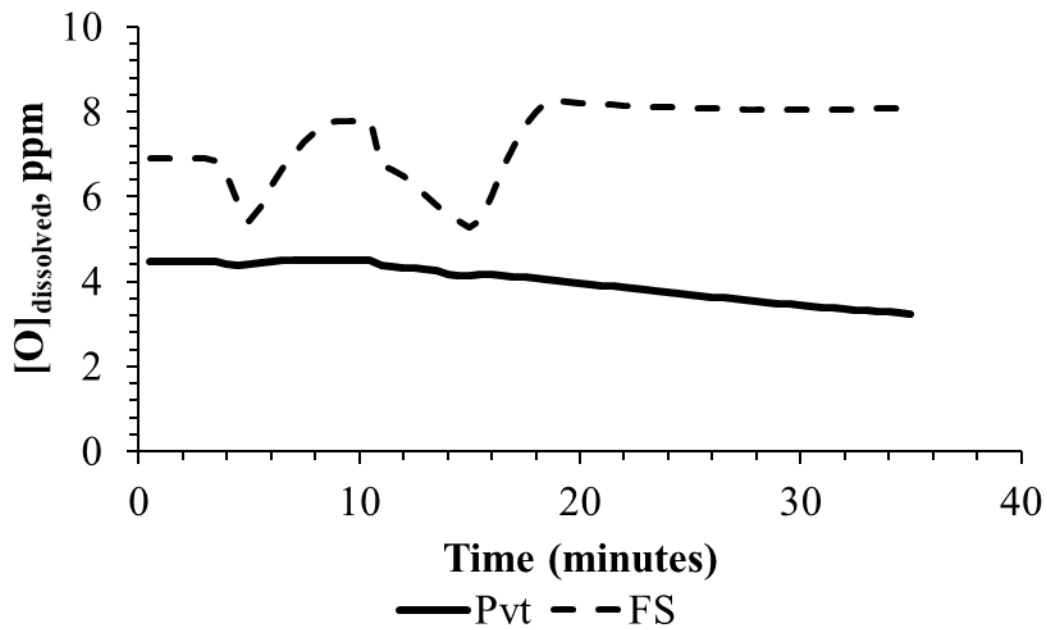


Figure 146. Calculated dissolved oxygen in steel from two sources: FTmisc and private database

9 Evaporation of magnesium and calcium during steelmaking experiments

The evaporation of magnesium during an Al-Mg deoxidation experiment using an alumina crucible in the induction furnace setup was described in section 5.2.2. In that experiment, the initial spinel inclusions transformed back to alumina. Magnesium loss was also expected to occur during the steel-slag experiment with argon stirring, conducted in an MgO crucible. In this section, the magnesium vaporization is demonstrated in a much smaller setup: steel-slag experiments using the confocal laser scanning microscope.

The evaporation of calcium was also studied for experiment conducted using CaO-3%ZrO₂ crucible using induction furnace setup. The aluminum killed liquid steel was expected to pick calcium due to steel-crucible reaction and evaporation was observed from precipitation on the oxide surfaces above the steel melt. The experimental setup and results from this experiment are described later.

9.1 Objective

The objectives of current chapter are:

- a) To demonstrate evaporation of magnesium from liquid steel during confocal laser scanning microscopy
- b) To find the growth mechanism of MgO whiskers
- c) To test the idea of growing MgO whiskers using ladle slag as a catalyst
- d) To show the effect of calcium evaporation on the study of rate of calcium transfer from CaO crucibles

9.2 Evaporation of magnesium during CLSM experiments

9.2.1 Experiment details

The confocal laser scanning microscope (CLSM) setup was described in section 3.1.2. Different experiments were conducted in this work to first understand the mechanism of formation of whiskers (and confirm magnesium evaporation) and further test the usability of these whiskers in the manufacturing of whisker reinforced MgO-C refractory. The experimental conditions for the four experiments are summarized in Table 57. For experiments 1 and 3, 0.1 g of steel and 0.05 g slag were kept in an MgO crucible and placed on the sample holder of CLSM, as shown in Figure 3. The compositions of steel samples used for experiments 9.1-9.3 are shown in Table 58. These samples were obtained from the samples taken during induction furnace experiments and were not at complete steel-slag equilibrium. Total oxygen (aluminum and magnesium) represent the sum of dissolved species and present in the form of inclusions. The sulfur content in all steel samples was 7 ppm. The slag used in experiments 9.1, 9.2 and 9.4 contained CaO (48%), Al₂O₃ (36%), SiO₂ (9%) and MgO (7%) with melting point at ~1450°C as calculated from FactSage 7.0 [44].

For experiment-9.4, a MgO-C-slag pellet of 12.70 mm diameter was made by cold pressing a mixture of 1 g MgO powder, 0.1 g C and 0.05 g slag at 350 MPa pressure. MgO powder used in the experiment contained particle agglomerates of several microns but individual particles appeared to be submicron size (Figure 147 a). Carbon black particles were also agglomerated to several microns size but the individual carbon particles appeared to be much smaller (Figure 147 b). Slag was prepared by pre-melting the oxide mixture (using pure oxides) in a graphite crucible using induction heating (under argon) followed by crushing and decarburization. The crushed and decarburized slag powder had a size distribution of tens of micrometers to sub-micron (Figure 147

c). There was no need to use a crucible for experiment-9.4 and the pellet sample was placed directly on the sample holder.

For all the experiments, samples were heated to the maximum temperature in approximately 10 minutes. Temperature measurement was by means of a Type R thermocouple placed on the sample holder.

Table 57. Summary of experiments

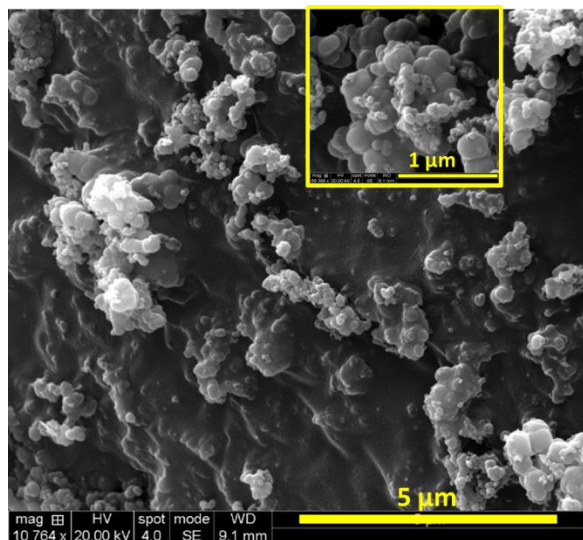
Exp. #	Crucible	Sample	Temperature	Time at temperature (minutes)
9.1	MgO	Steel-slag	1600°C	30
9.2	Al ₂ O ₃	Steel (0.1 g)	1600°C	18
9.3	MgO	Steel-slag	1600°C	5
9.4	-NA-	MgO-C-slag pellet	1650°C	5

Table 58. Steel composition used for experiments

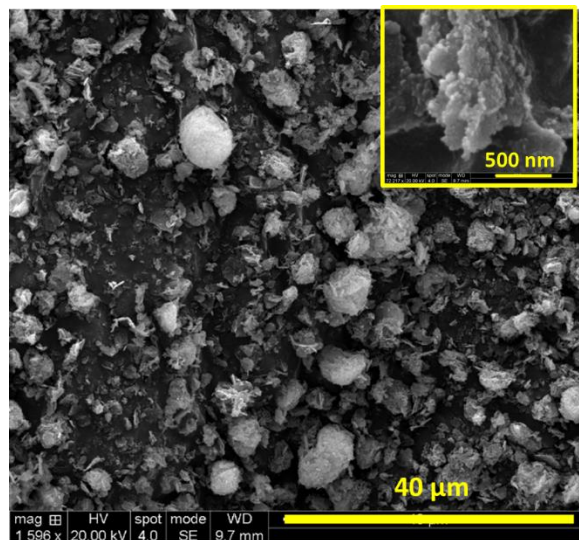
Exp. #	Al _{total} (ppm)	O _{total} (ppm)	Mg _{total} (ppm)	Si _{total} (wt%)
9.1	100	30	12	0.13
9.2	600	65	30	0
9.3	160	30	15	1

After the CLSM experiments, samples were analyzed using an FEI Quanta-600 scanning electron microscope (SEM), with microanalysis by energy-dispersive spectroscopy (EDS).

(a)



(b)



(c)

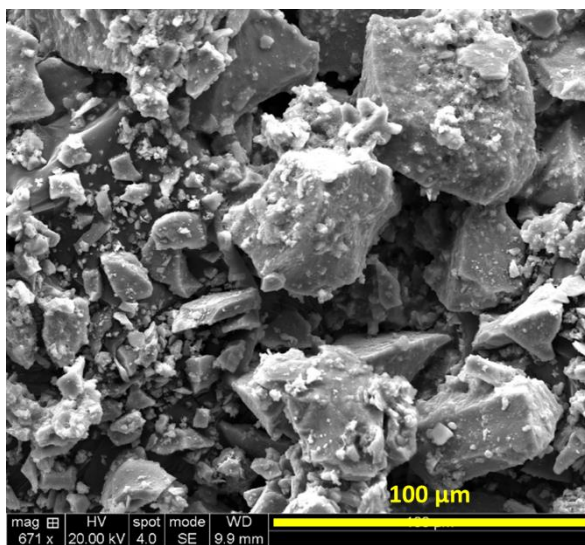


Figure 147. Powders used to prepare MgO-slag-C pellet (powders mounted on conductive carbon tape; secondary electron micrographs). a) MgO; b) carbon; c) slag

9.2.2 Results and Discussion

At the end of experiment-9.1 (steel and slag in an MgO crucible), a fibrous structure was observed on top of the MgO crucible wall; see Figure 148. SEM and EDS analysis of the fibrous structure revealed that it consisted of MgO whiskers (diameter: less than a micrometer; length: several micrometers). Such whiskers must have precipitated from the vapor phase. Magnesium vapor can form due to the evaporation of magnesium from liquid steel, slag or MgO crucible. The required magnesium partial pressure to form MgO whiskers (for fixed oxygen partial pressure = 10^{-20} atm) along with the partial pressure of magnesium that can be provided by the three sources is shown in Figure 149, as functions of temperature (calculated using the ‘Reaction’ and ‘Equilib’ modules of FactSage 7.0 [44]). Evidently liquid steel (containing dissolved Al as reductant) would have provided the highest partial pressure of magnesium vapor in this experiment (that is, in the absence of carbon). The minimum required partial pressure of magnesium to sustain whisker growth was calculated from the following reaction: $\text{Mg (g)} + \frac{1}{2} \text{O}_2(\text{g}) = \text{MgO (s)}$

$$K = \frac{a_{\text{MgO}}}{p_{\text{Mg}} * \sqrt{p_{\text{O}_2}}} \quad \text{Equation 36}$$

Where $K, a_{\text{MgO}}, p_{\text{Mg}}, p_{\text{O}_2}$ are the equilibrium constant, activity of MgO, and partial pressures of magnesium and oxygen.

Taking the activity of MgO to be 1, and a constant oxygen partial pressure in the chamber (10^{-20} atm), the minimum required partial pressure of magnesium for whisker growth was calculated using Equation 37.

$$p_{Mg} = \frac{1}{K * \sqrt{p_{O_2}}}$$

Equation 37

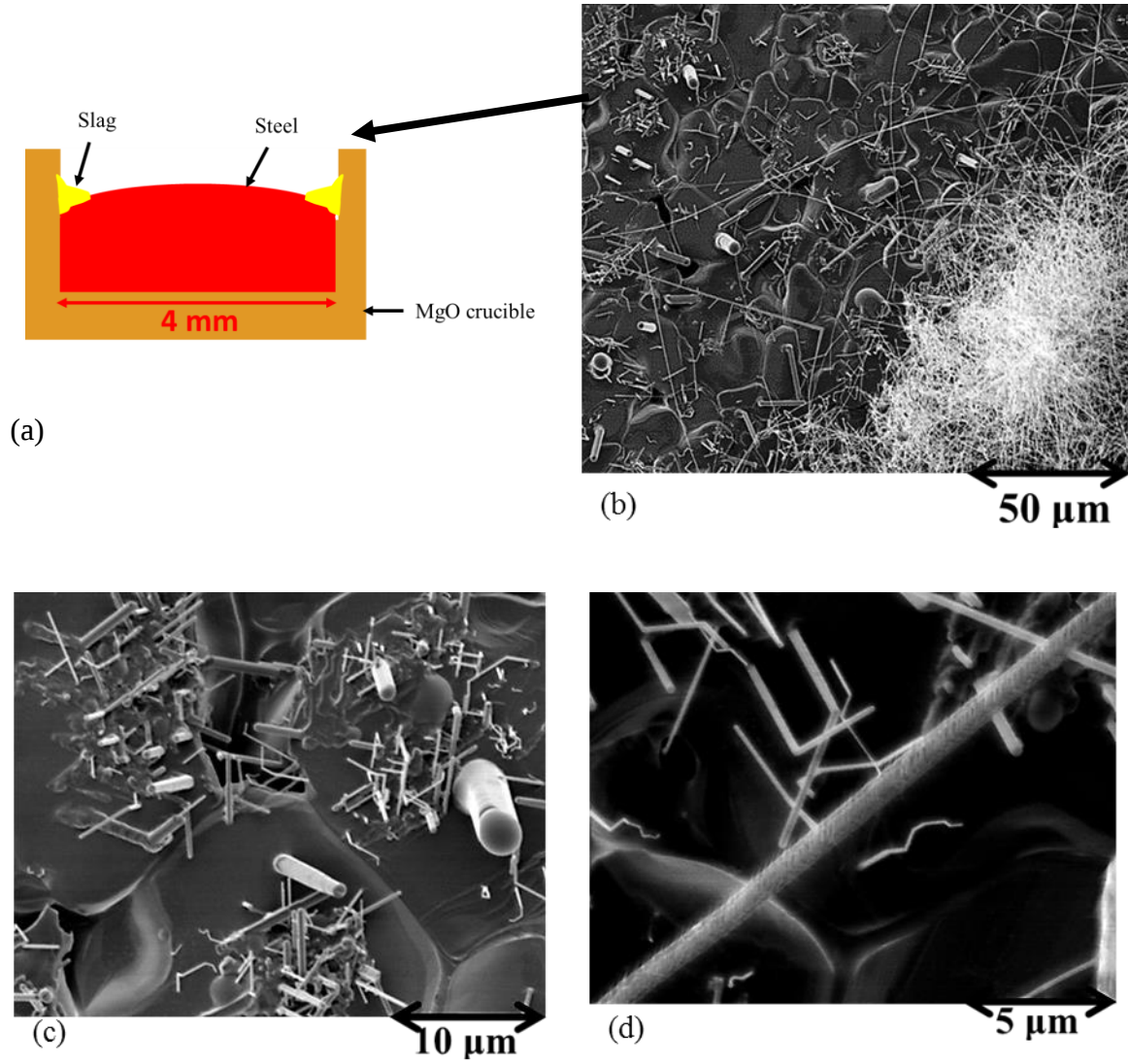


Figure 148. MgO whiskers observed on MgO crucible wall after CLSM experiment using steel and slag in an MgO crucible, held for 30 minutes at 1600°C. (a) Schematic of experimental configuration. (b), (c) and (d) are secondary electron micrographs of the whiskers at successively higher magnifications.

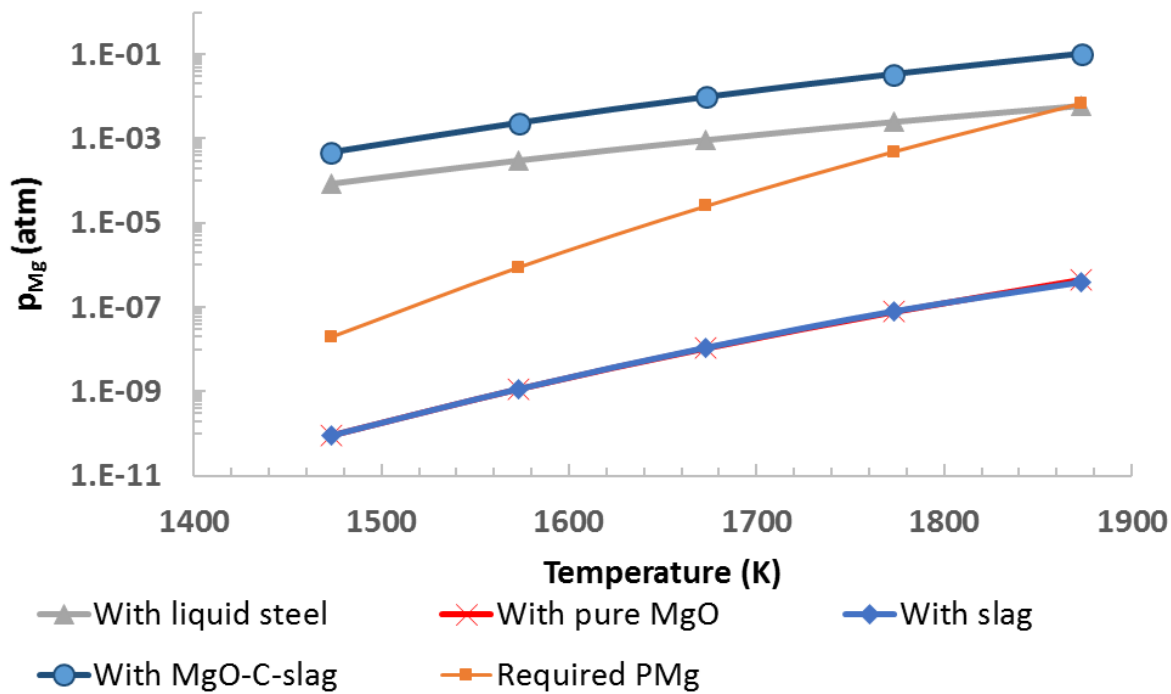


Figure 149. Calculated partial pressure of magnesium in equilibrium with different sources; "required p_{Mg} " is the magnesium pressure in equilibrium with pure MgO and oxygen ($P_{O_2}=10^{-20}$ atm)

To clarify that evaporation of magnesium from the steel is a feasible source, experiment-9.2 was conducted in an alumina crucible, with no slag. SEM analysis of the top of the crucible wall after the experiment showed the presence of a plate-like structure (similar location as shown in Figure 148) after 18 minutes at 1600°C, as shown in Figure 150. SEM-EDS analysis of this sample revealed that the deposits were magnesium spinel (approximate composition $MgAl_2O_4$). Since the crucible was alumina and no slag was used in this experiment, the only source of magnesium in this case was evaporation from the liquid steel. Evaporated magnesium may have reacted directly with alumina crucible to form spinel, or magnesium and oxygen gas may have reacted at the alumina crucible wall to form MgO as intermediate product before transformation into spinel. In either case, the reaction must have occurred via vapor-solid (VS) reaction mechanism since no slag was present. The absence of whisker-shaped spinel in experiment-9.2 also indicates a possible catalytic role of slag in whisker growth such as was observed in experiment-9.1.

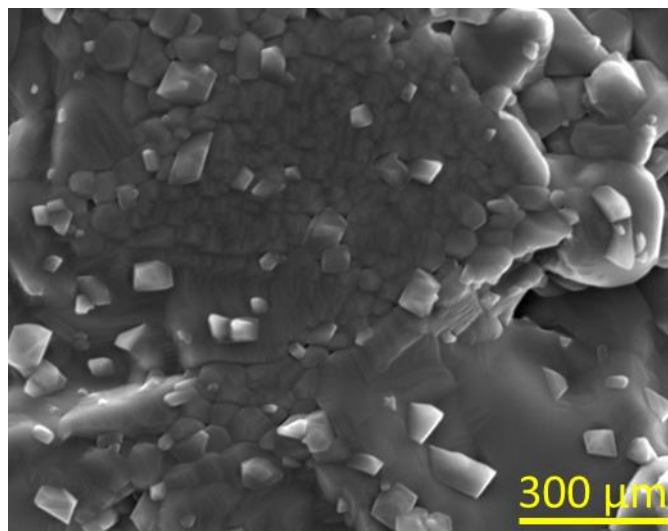


Figure 150. Growth of plate like spinel on alumina crucible wall in the absence of liquid slag

The MgO whiskers formed in experiment-1 had a characteristic round tip indicating VLS growth. The composition of the whisker tip was similar to the composition of slag used for this experiment; Ca, Al, Mg and Si peaks can be seen in the EDS spectrum shown in Figure 151 (exact quantification of the composition is not possible, because of the small size of the whisker tip relative to the electron interaction volume).

For clarification of early stages of whisker growth, experiment-9.3 was conducted with the same setup (steel + slag in an MgO crucible), but stopped after 5 minutes at 1600°C. The SEM images in Figure 152 show early stages of whisker growth: in Figure 152a, the hexagonal whisker profile surface indicates growth in the $\langle 111 \rangle$ direction (MgO has a FCC NaCl type crystal structure [74]); similar growth is seen in Figure 152c, with visible facets. In Figure 152b, the whisker cross-section appears square indicating $\langle 100 \rangle$ growth. The tips of the whiskers in Figure 152a-c have slag as a liquid phase catalyzing the growth of whiskers; however, in rare cases (Figure 152d is an example) whiskers were tipped by iron indicating that iron (condensed from the vapor phase) may also catalyze growth of MgO whiskers.

Since slag has solubility for MgO and iron has solubility for Mg, whisker growth at the whisker-catalyst interface seems to occur due to super saturation of MgO/Mg in the catalyst.

Metallic droplets on the tip of MgO whiskers have been reported by several authors before [75]–[83], in particular Zhu et al [83] demonstrated the use of nickel as a catalyst to form MgO whiskers in an MgO-C matrix. In experiment-3, while a few whiskers with iron tips were observed, these were not common, likely because the experimental temperature was not that high - close to the melting temperature of iron (limiting the vaporization rate of iron). Zhu [84] reported that CaO-SiO₂-Al₂O₃ impurities in MgO can catalyze the growth of MgO rich hollow spinel whiskers in experimental MgO-C pellets. The results from the current set of experiments show that intentional addition of slag can catalyze the whisker growth as well. The proposed growth mechanism of MgO whiskers through VLS mechanism with slag as catalyst is summarized in Figure 153.

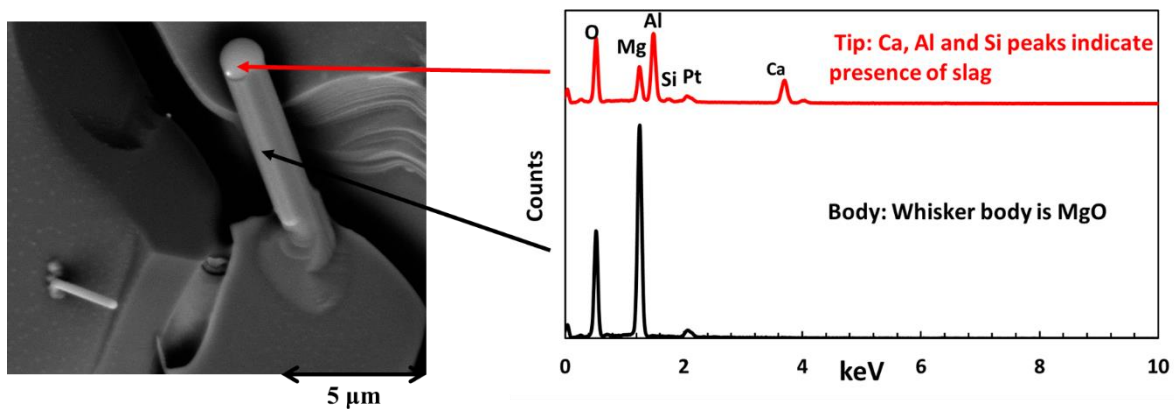
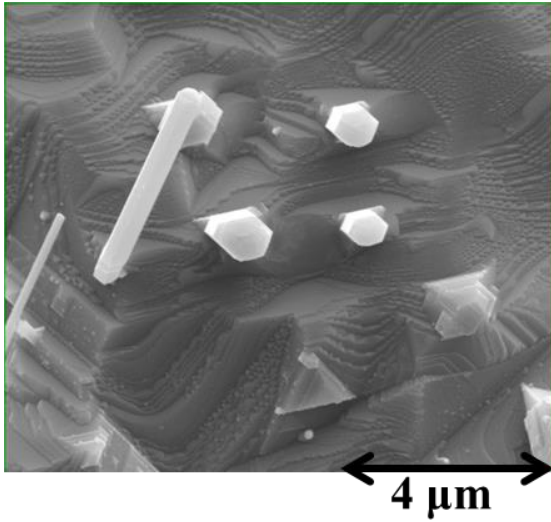
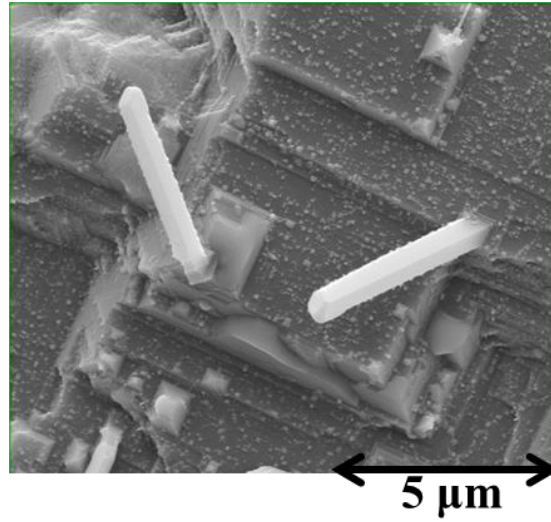


Figure 151. EDS at the tip of whisker shows presence of slag phase

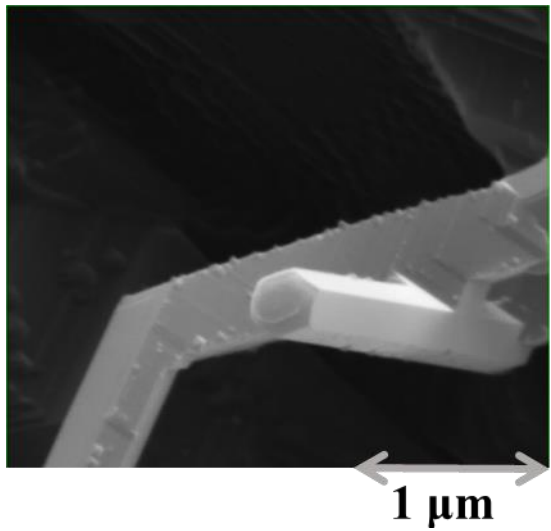
(a)



(b)



(c)



(d)

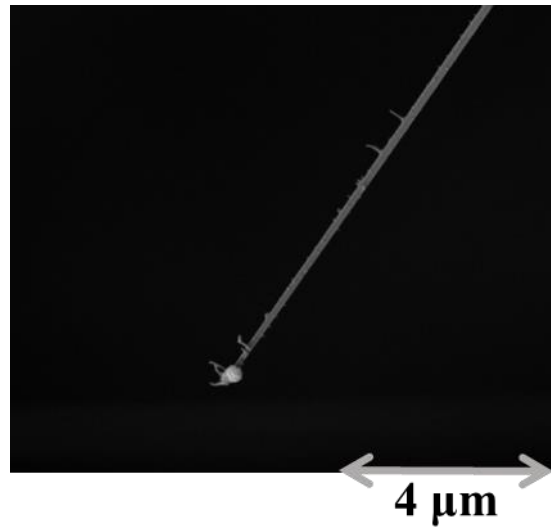


Figure 152. Typical features of MgO whisker growth on MgO crucible, from Mg vaporized from liquid steel. (a) Early growth stage; (b) out-of-plane growth; (c) whisker with visible facets; (d) growth of catalyzed by the presence of condensed iron phase (bright particle at whisker tip).

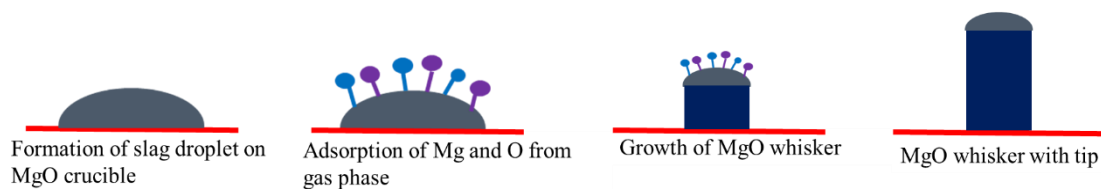


Figure 153. Proposed mechanism of growth of MgO whiskers from an MgO crucible through the VLS mechanism, catalyzed by slag

Experiment-9.4 was conducted to test the catalytic behavior of slag for in-situ formation of MgO whiskers in MgO-C pellets. The MgO pellet containing 10% C and 5% slag (mass percentages) was heated in the CLSM, holding for 5 minutes at 1650 °C; in this case, there was no need to use any crucible. The top surface and pellet interior were examined using an FEI Quanta-600 SEM. As shown in Figure 154(b), the top surface of the pellet was uniformly covered with newly formed MgO whiskers. Higher-magnification images of the whiskers, see Figure 154(c), revealed the characteristic round tip similar to that observed for experiment-9.1 (see Figure 148). EDS analysis of the tip and the body of whiskers (Figure 155) showed the peaks of calcium, aluminum and silicon along with magnesium and oxygen (the tip volume was too small for quantitative analysis; the Mg peak is the highest because the electron interaction volume included the slag droplet and MgO whisker). This confirmed the catalytic behavior of slag for the in-situ formation of MgO whiskers through VLS mechanism: slag was present at the growth tips of the whiskers.

The pellet had several cracks as shown schematically in Figure 154 (a). The pellet was broken open along one such crack to examine the formation of MgO whiskers inside. As shown schematically in Figure 154(d), MgO whiskers were observed only ~1 mm from outside of the pellet. As revealed in Figure 154(e), the density of whiskers was high on this fracture surface compared with the exposed top surface of the pellet. The higher density of whiskers can be related to higher magnesium vapor pressure resulting from MgO-C-slag equilibrium as shown in Figure

149. The local partial pressure of magnesium in this region is expected to be more than top surface of the pellet as CLSM chamber is continuously purged by Ar (0.250 litre/min). The formation of MgO whiskers near the outside diameter of the pellet likely reflect the gradients of temperature (lower near the outside radius) and oxygen pressure (higher near the outside pressure). The temperature gradient arises from the focused heating in the ellipsoidal CLSM chamber, with a heat spot diameter of approximately 3.5 mm in the center of the pellet as shown in Figure 154(a). The lower temperature near the outer diameter of the pellet would have driven the reaction $\text{Mg}_{(v)} + \frac{1}{2} \text{O}_2 = \text{MgO}_{\text{whisker}}$ in the forward direction.

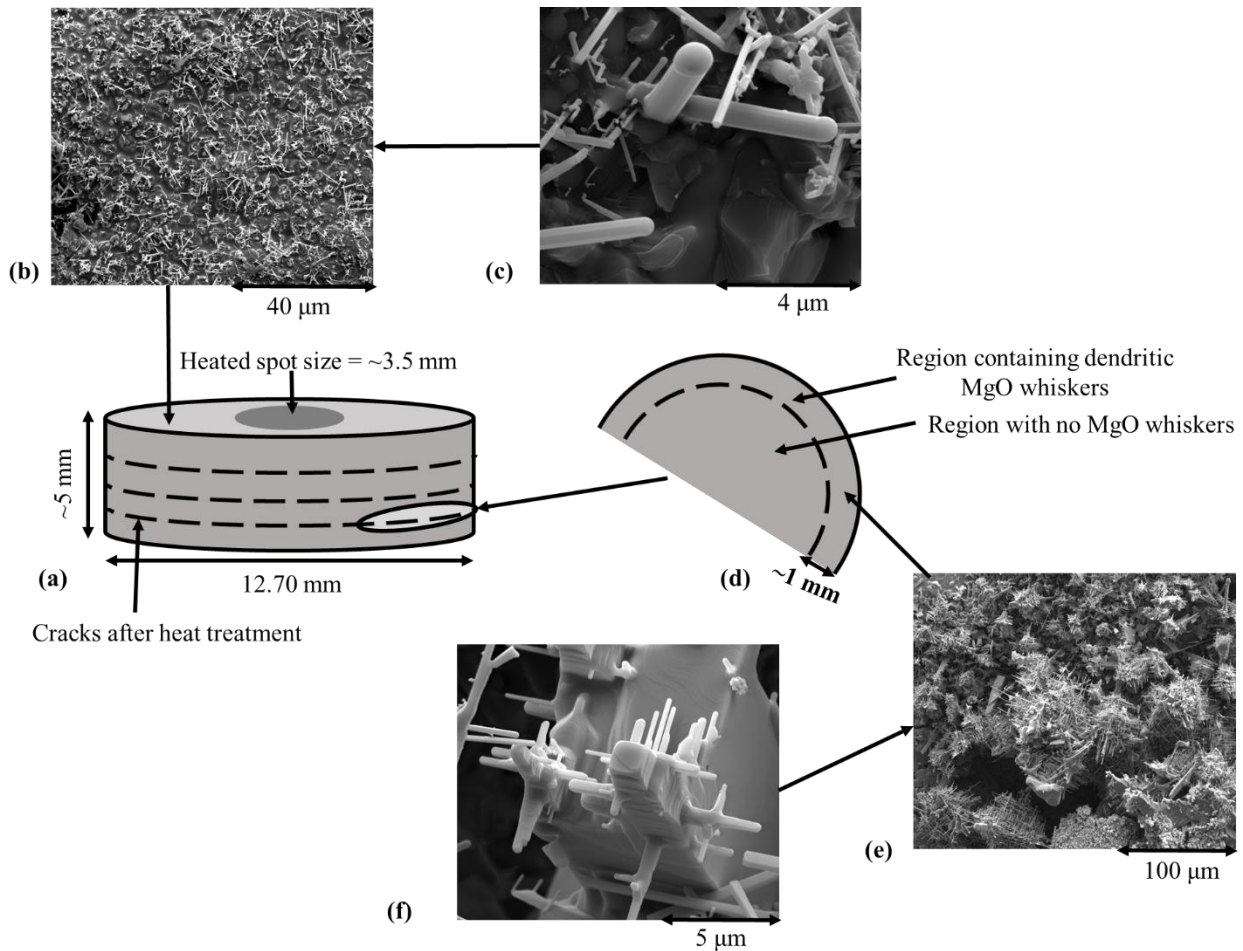


Figure 154. Presence of whiskers on top surface and at the MgO-C-slag pellet edge after heat treatment at 1650°C

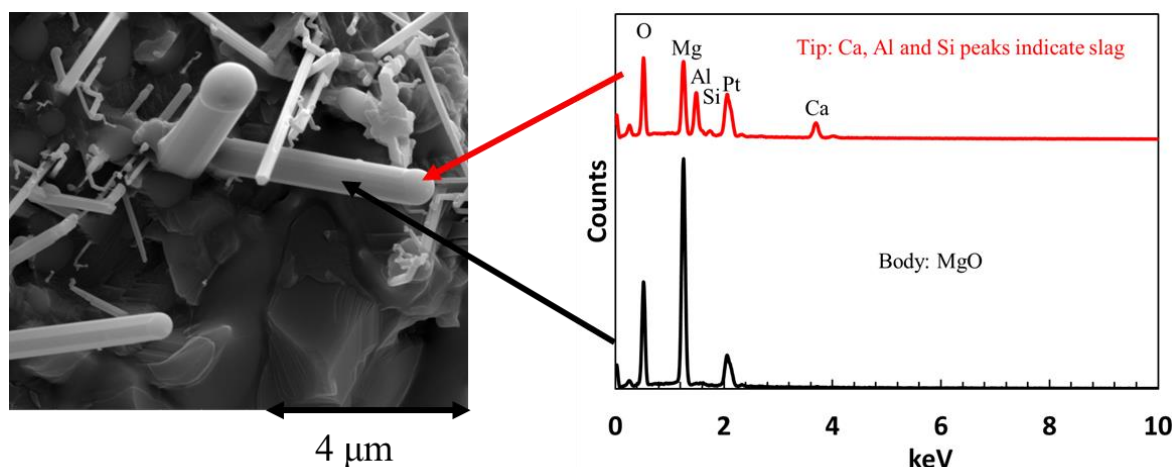


Figure 155. EDS spectra of tip and body of whiskers shown in Figure 154(c)

Higher-magnification images revealed the dendritic nature of MgO whiskers in this region; see Figure 154(f). The secondary whiskers can be seen growing at 90° angles to the main whiskers. The cross-section of these whiskers were square indicating $\langle 100 \rangle$ growth. Analysis of whisker body in these dendrites also revealed the presence of the elements from slag (see Figure 156); indicating that a slag layer on the whisker body also catalyzed the growth of dendrites arms. The tips of these whiskers were flat, rather than hemispherical on the whiskers present on top surface of the pellet (see Figure 154(f)). Yanagida et al. [80] reported that if the ambient pressure near growing MgO whiskers is low, the gold catalyst (used in that work) may migrate from the tip to the body of whiskers resulting in a flat tip even if the growth occurred through VLS mechanism. In the present work, the ambient pressure in the bulk of the pellet is expected to be same as that on the top of the pellet. The flat tip of the whisker and the presence of slag on the tip and the body of dendritic whiskers can be due to a larger concentration of liquid slag in the lower part of pellet as compared to top of the pellet. The larger concentration of slag would tend to wet the newly grown whiskers resulting into a flat tip and whiskers covered with slag. The presence of slag on primary whiskers would also catalyze of the secondary MgO whiskers resulting in a dendritic structure.

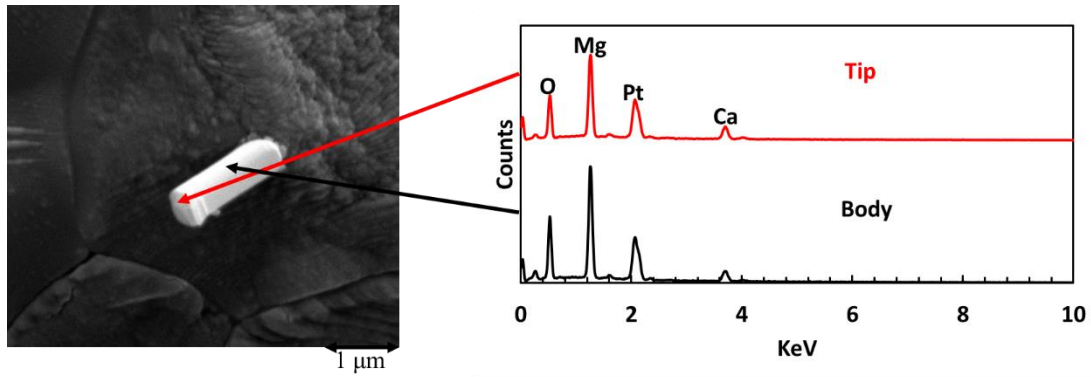


Figure 156. MgO whisker with flat tip observed at the fracture surface of pellet

9.2.3 Conclusions

The catalytic effect of ladle slag on in-situ growth of MgO whiskers by VLS was investigated. The following conclusions can be drawn from this work:

- (1) CaO-Al₂O₃-SiO₂-MgO (slag) droplets can act as a catalyst, allowing Mg and O to precipitate from vapor phase, and facilitating the growth of MgO whiskers on an MgO substrate.
- (2) Chemical reaction between MgO and C in MgO-C-slag pellet can be an effective source of Mg-vapor leading formation of MgO whiskers near the outer surface of the pellet.
- (3) MgO whiskers can be grown inside an MgO-C pellet. This may impart increased toughness to MgO-C refractory used by the steel industry.

9.3 Calcium evaporation from top of steel melt

9.3.1 Experiment details

Experiment-9.5 was conducted in a CaO-ZrO₂ crucible. A steel puck from a previous experiment conducted in CaO-ZrO₂ crucible with aluminum deoxidation (by adding 0.15 wt%) and kept at 1600°C for several hours was used as the starting material for this experiment. The puck was ground and cleaned to ensure there was no surface oxidation remaining. A hole was drilled on top

of the puck to insert an alumina rod (3.2 mm diameter). Figure 157 show experimental setup along with expected reaction at the steel-crucible and steel-alumina rod interface. A growth of calcium aluminate layer was expected with time on the alumina rod with time. The experiment was conducted at 1600°C for two hours.

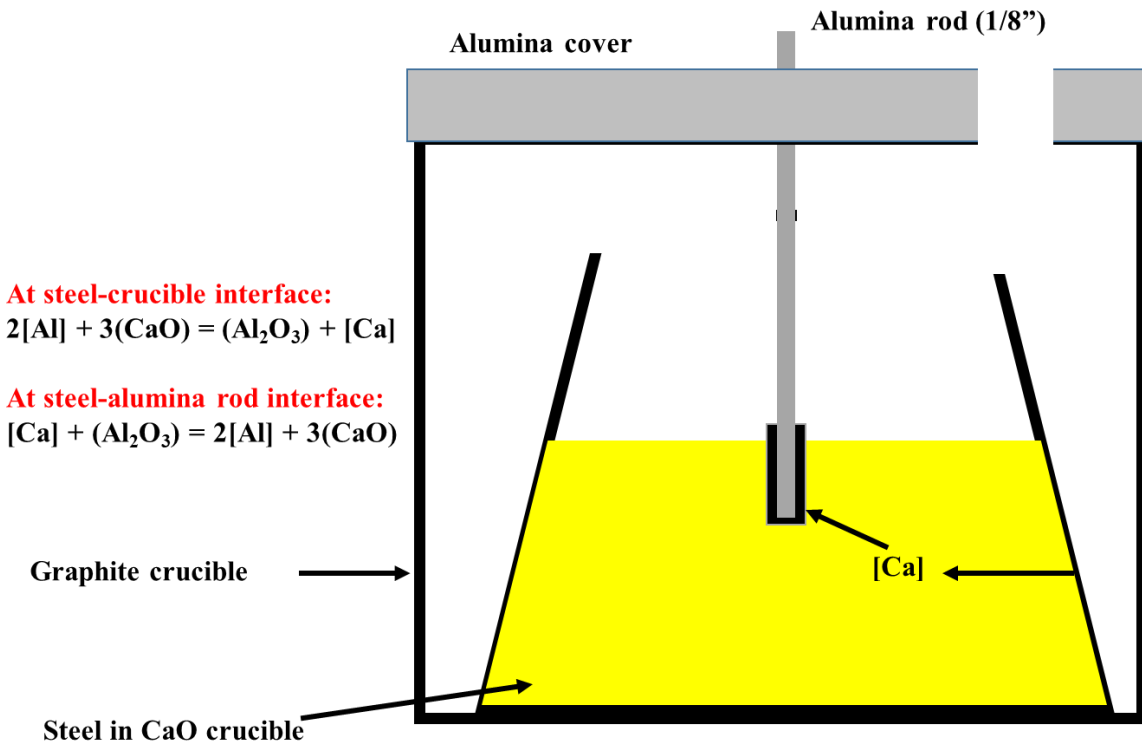


Figure 157. Experimental setup to study calcium transfer from steel-crucible to steel-alumina rod interface

9.3.2 Results and discussion

After the experiment, the shape of the tip of the alumina rod turned to a disc from a cylinder as shown in Figure 158. Figure 159 shows the imprint of disc shape tip of alumina rod on top of the steel puck. As shown in the right side micrograph, liquid oxide phase (Al-Ca-Zr-O) was present which could have transformed the shape of the tip from cylindrical to the disc. The possible reason for the formation of liquid phase is the calcium modification of alumina due to its reaction with steel or due to the presence of crucible fines (CaO -3% ZrO_2) on top of the steel melt. Another

interesting observation from this experiment was the presence of glaze like structure on the wall of cylindrical alumina rod as shown in Figure 158.

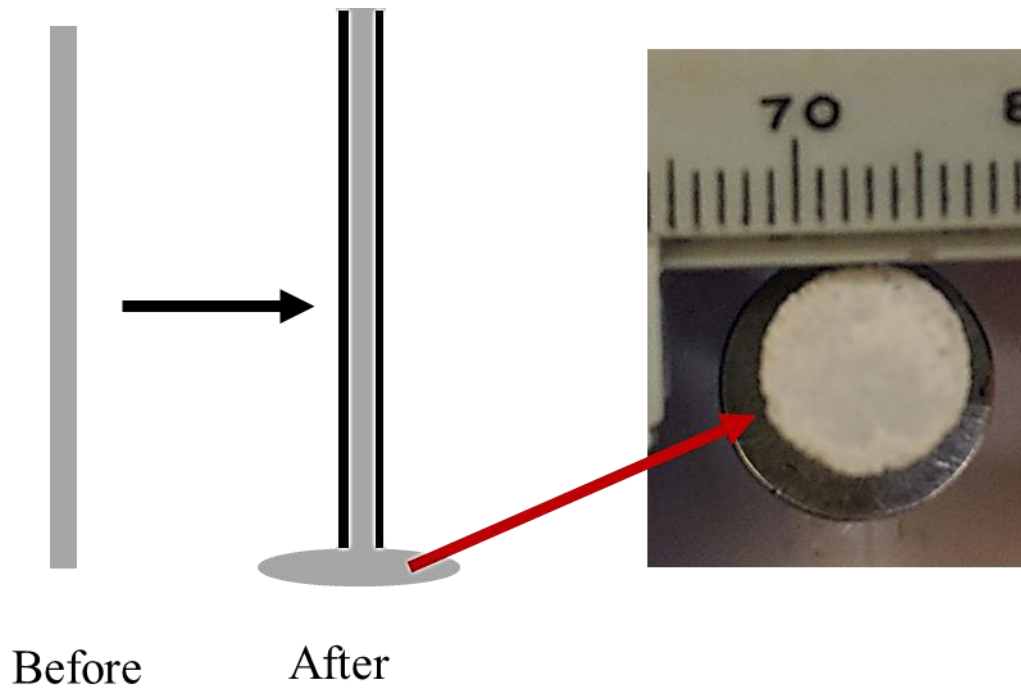


Figure 158. Flattening of tip of alumina rod during experiment-9.5, the scale is in mm

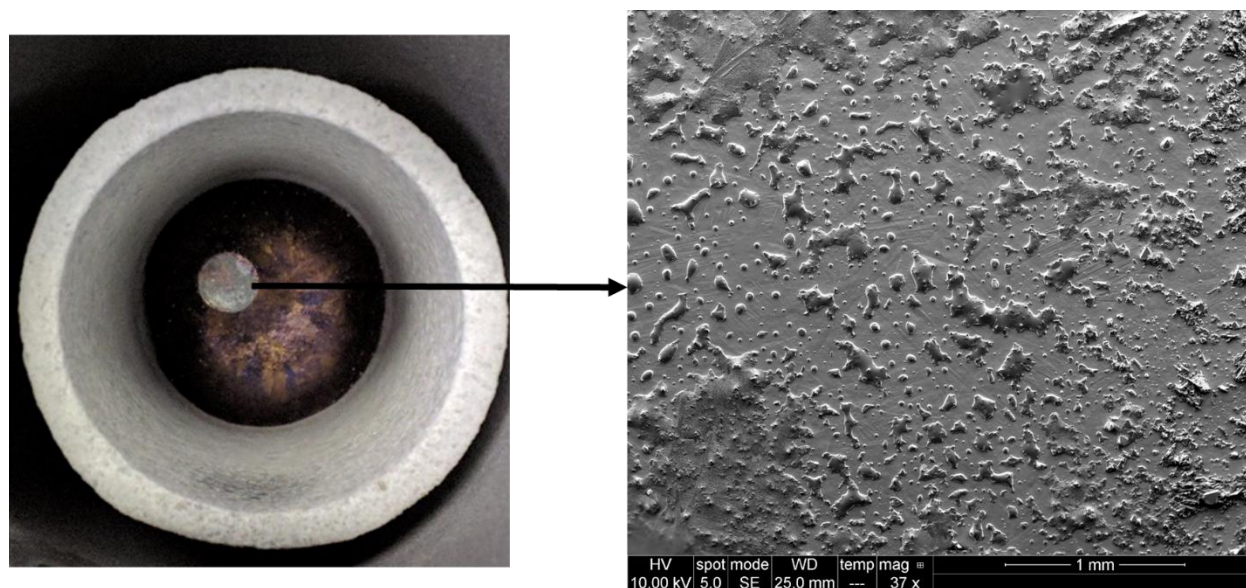


Figure 159. Formation of liquid oxide phase on top of the steel puck close to the tip of alumina rod

Figure 160 show the SEM micrograph and its EDS of the wall of the alumina rod few centimeters above melt surface after the experiment. The presence of calcium on the wall of alumina rod indicated possible evaporation of calcium from top of the liquid steel. Careful observation of the rod surface revealed the presence of some whisker like structure which appears similar to MgO whiskers shown in previous section. The SEM-EDS analysis of whiskers showed calcium, aluminum and oxygen peaks. It is not sure if aluminum peaks are from the whisker or from the surface of rod in the background. The tip of the whisker is flat instead of hemispherical tip observed for the formation of MgO whisker. MgO whiskers were found to form due to vapor-liquid-solid mechanism with liquid slag acting as a catalyst; the hemispherical tip was a signature of this growth mechanism. In the present case, the growth mechanism appears to be vapor-solid. The presence of whiskers shows that there was calcium evaporation from liquid steel. Based on this observation, the transformation of alumina rod tip to disc shape can be expected to form through following mechanism: the calcium evaporation resulted in precipitation of CaO on the alumina rod which can lead to formation of a liquid calcium aluminate layer. Liquid calcium aluminate may travel

downwards due to gravity and accumulate on the tip of the rod. The accumulation of liquid phase for an extended period of time on the tip of the alumina rod may change its shape from cylinder to a disc.

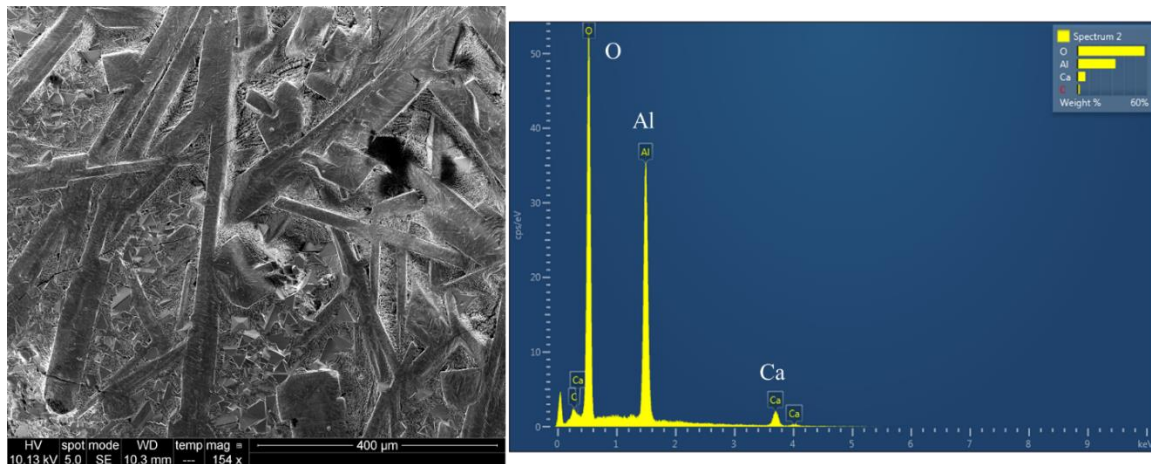


Figure 160. Presence of calcium on wall of the alumina rod after the experiment-9.5

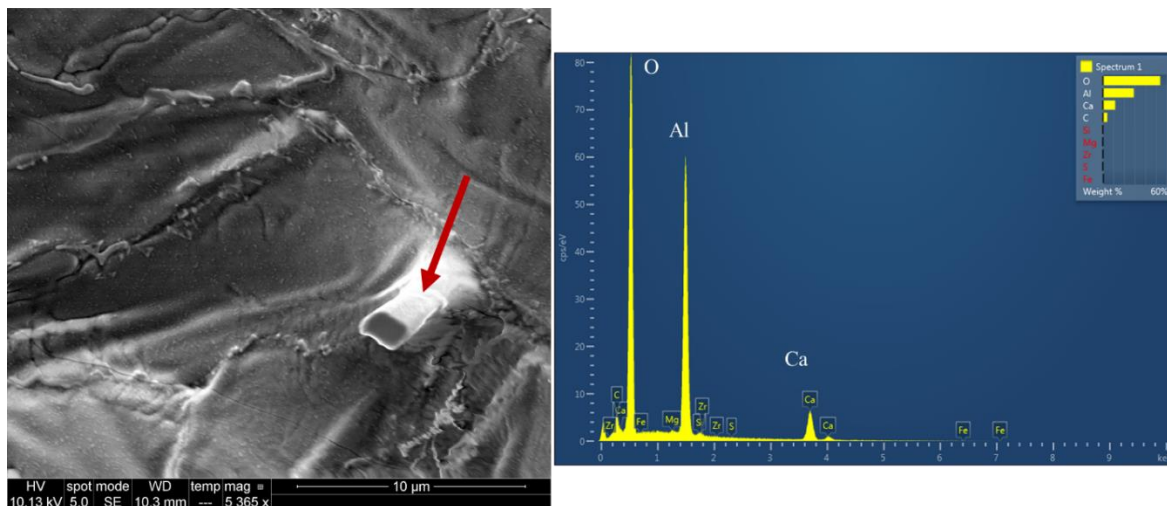


Figure 161. Whisker present on alumina rod after experiment-9.5

In conclusion, the calcium evaporation from top of the liquid steel was confirmed. It may be the likely reason for the shape transformation of the tip of alumina rod. Current observation also indicates that the calcium evaporation should be accounted while modeling steel-CaO crucible

experiments in a similar way the magnesium evaporation was considered for modeling steel-MgO crucible reaction.

10 Agglomeration of inclusions

In the kinetic model developed in the present work, the flotation of inclusions was modeled as be a first-order process: two rate constants were needed to model laboratory scale experiments and one first order rate constant was needed to model plant scale operations. Physically, the flotation is expected to be governed by collision and flotation of inclusions. The collision of inclusions may or may not lead to agglomeration. In this section, the agglomeration behavior of different types of inclusions in aluminum-killed and calcium treated samples is discussed. A brief literature review is also included regarding methods to study.

In the kinetic model, the reaction between steel-inclusions was assumed to be at equilibrium implicitly assuming that the inclusions had uniform composition. As discussed earlier, the assumption appears to be true for smaller inclusions ($<3\text{ }\mu\text{m}$, see Figure 9 and Figure 10). However, there was always some composition distribution among inclusions as shown by numerous ternary diagrams. In this section, the development of a plasma focused ion beam method for looking inside a single inclusion is also discussed in order to closely look at the variation in composition and morphology of single inclusion.

The results from the current section are of exploratory nature and intended to address some of the issues related to kinetic modeling. Specifically, agglomeration and flotation of inclusions, quantification of volume fraction of inclusions in a sample containing large inclusion clusters and understanding variation of morphology and chemistry within a single inclusion.

10.1 Literature Review

Alumina, spinel and calcium aluminate inclusions are common types of inclusion in aluminum-killed steels. Solid inclusions are known to deposit on nozzle walls resulting in reduced

productivity and increased risk of quality rejection of products. Singh [85] studied the process of agglomeration and sintering of alumina inclusions at the nozzle wall resulting in nozzle clogging during continuous casting of aluminum killed steel. As noted by Zhang and Thomas [86], in the bulk of liquid steel, inclusions agglomeration is controlled by Brownian, turbulent and Stokes' collisions. The controlling collision mechanism varies with the size of inclusions. Brownian collision is independent of fluid flow and occurs for inclusions smaller than 1 μm . As Brownian collision is independent of direction, smaller inclusions tend to be spherical. Turbulent collisions are more prominent in inclusions that are larger than 2 μm . These inclusions form dendrite like structure upon collision but retain spherical features from early nucleation and growth in the Brownian regime. Figure 162 shows the calculated growth of inclusion size with increasing stirring power. Increase in stirring power increases the effective size of inclusions, which is harmful unless there is sufficient time for inclusions to float to slag after vigorous stirring.

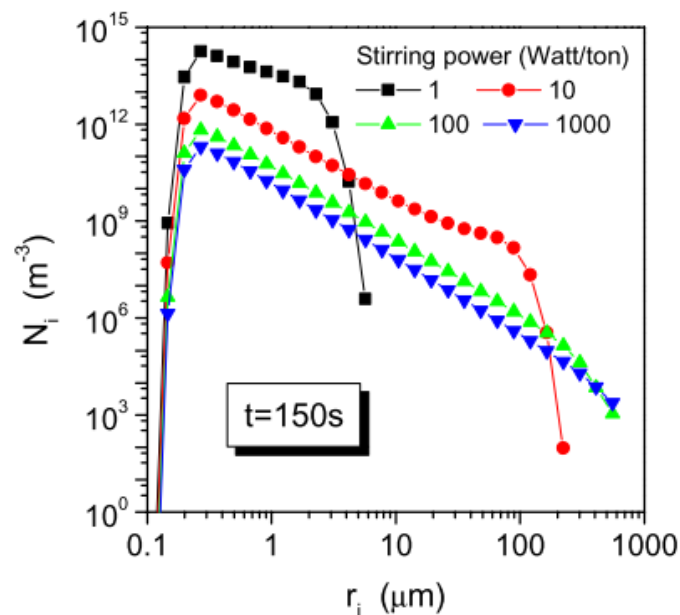


Figure 162. Effect of stirring power on inclusion size distribution [86]

10.1.1 In-situ observation of inclusion agglomeration

In-situ agglomeration behavior of inclusions on steel-gas interface has been studied by several authors using confocal laser scanning microscopy (CLSM). Initial studies by Yin *et al.* [87], [88] showed an attractive force between solid inclusions at the steel-gas interface, and the absence of attraction between liquid inclusions. There are two prominent mechanisms of inclusion cluster formation at the liquid steel-argon interface during remelting of a steel sample containing inclusions in a confocal laser scanning microscope (CLSM): an attractive force between inclusions and/or random collision between inclusions. Previous studies have shown that solid inclusions experience attractive force even if they are apart by 100 μm but such a force is missing for liquid inclusions or between liquid and solid inclusions. Liquid-liquid or liquid-solid agglomeration is found to occur only due to random collisions caused by the circulation of liquid steel. Previous studies have shown that the magnitude of this force of attraction is 10^{-14} to 10^{-16} N which is most likely caused by capillary force [89], [90]. This force of attraction can be calculated using Equation 38.

$$F = 0.5g(\rho_L - \rho_G)w\Delta h^2 \quad \text{Equation 38}$$

$$\text{Where } \Delta h = \frac{2\gamma\cos\theta}{g(\rho_L - \rho_G)R}$$

Where, g : gravity acceleration, w : horizontal diameter of the particle, and ρ_L and ρ_G are the densities of the liquid and gas. Δh stands for equilibrium height difference between the surfaces inside and outside of the particles; γ , θ , and R are the surface tension of the liquid, the contact angle of the particles on the liquid and the distance between the two particles, respectively.

It can be seen that the capillary force of attraction is strongly dependent on the height difference Δh , which is also dependent on particle morphology. Yin et al. [88] presented a schematic that qualitatively shows the extent of the capillary force of attraction, see Figure 164. While comparing forces for solid inclusions, contact angle and surface tension plays important role. The contact angle and surface tension reportedly decreases with increase in oxygen content steel. Kimura et al. attributed high oxygen content as the reason for reduced attraction force for the observed non-agglomeration behavior of magnesium containing inclusions [91].

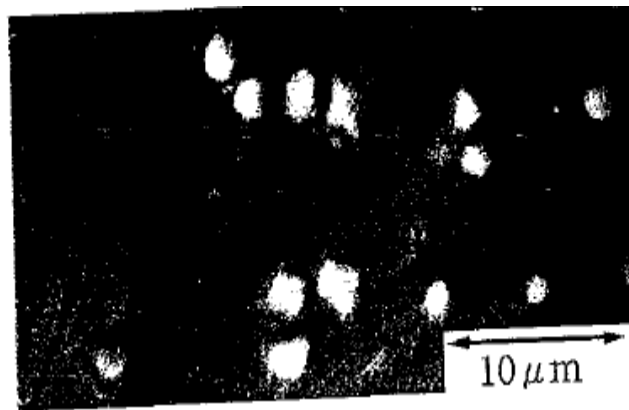


Figure 163 Non-clustering behavior of magnesium containing inclusions [91]

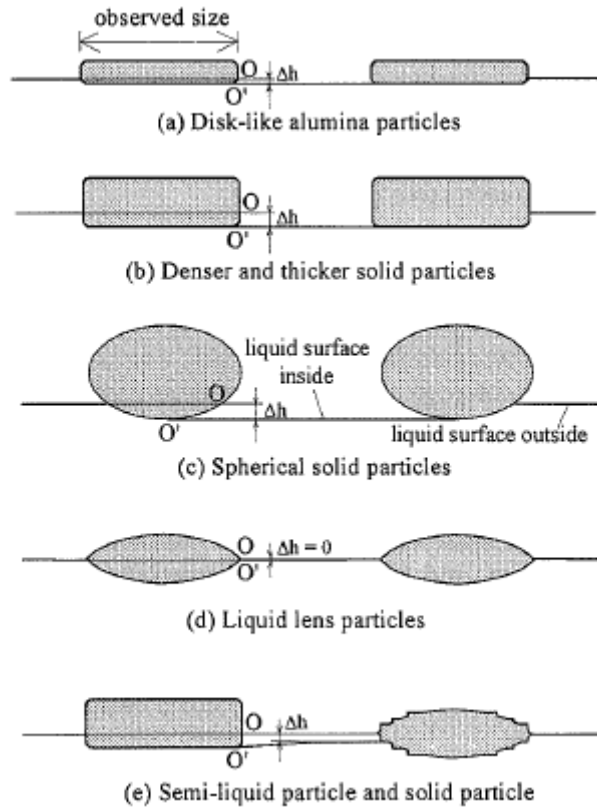


Figure 164 Schematic diagram of capillary interaction between inclusion particles with different morphology [90]

Shibata *et al.* [90] also concluded that the capillary forces could explain the difference in interaction behavior. The absence of long-range interaction between liquid inclusions was ascribed to the lack of a depression of the steel melt surface between two approaching liquid particles. Kang *et al.* [89] observed that alumina inclusions readily agglomerate at the steel-gas interface but did not observe attraction between any other type of inclusions like spinel, solid calcium aluminate and liquid calcium aluminate. They also concluded that capillary force can explain the long-range interaction between inclusions, yet the observed difference in interaction between inclusions could not be explained using capillary forces, according to their calculations. They also noted that capillary force can be used to explain inclusion interaction only at the steel-gas or steel-slag

interface (and not within liquid steel) and hence it is necessary to compare CLSM observations with industrial data. In their recent work, Mu *et al.*[92] used a revised Kralchevsky-Paunov model to quantitatively compare the attractive capillary forces for different types of inclusions at the steel-argon interface. Their main conclusion was that the inclusion composition is the least important to inclusion collisions; rather, inclusion number density followed by the size of inclusions drive the collision of inclusions. In the work presented here, inclusion agglomeration observed at the steel-argon interface in CLSM is compared to that from laboratory scale induction furnace experiments and industrial samples. The agglomeration of spinel inclusions in bulk steel is also discussed.

10.2 Objective

The objectives of the current chapter are:

- a) To clarify the agglomeration of spinel inclusions in bulk steel samples from laboratory scale induction furnace experiments
- b) To compare inclusion agglomeration behavior observed at the steel-argon interface in confocal laser scanning microscope (CLSM) to bulk steel samples from laboratory and the plant
- c) To use X-ray micro CT techniques to 3D image alumina clusters in early samples from ladle refining
- d) To use a statistical technique to find the extent of inclusion agglomeration in steel samples based on ASPEX-AFA data
- e) To develop a method to use the focused ion beam based technique to study chemical and morphological variations inside a single inclusion

10.3 Comparing inclusion agglomeration in CLSM to bulk

10.3.1 Experimental

The experiments to study inclusion agglomeration were done using a confocal laser scanning microscope; the setup is described in section 3.1.2. The steel samples (~0.2 g) taken from induction furnace aluminum deoxidation and calcium treatment experiments were kept in an MgO or Al₂O₃ crucible and laser imaging was done to observe the behavior at the steel-argon interface. Figure 165 shows collision and agglomeration of inclusion clusters that occurred in 5 s.



Figure 165. Observation of inclusions at steel-argon interface using CLSM, the red arrow shows movement and collision of clusters that occur in the right side frame

Industry aluminum-killed steel samples containing these inclusions were obtained from industry members of the Center of Iron and Steelmaking Research (CISR). Bulk steel samples were electrolytically etched, using the method described by Tan and Pistorius [9], to reveal inclusion agglomeration behavior in 3D. The upper surface of the steel samples after CLSM experiments (type A), and etched bulk samples from induction furnace experiments (type B) and industrial samples (type C) were observed using an FEI Quanta 600 scanning electron microscope (using secondary electron imaging).

10.3.2 Results and Discussion

10.3.2.1 Agglomeration of alumina inclusions

The results of agglomeration of alumina inclusions in the three types of samples are shown in Figure 166. Alumina inclusions were found to readily agglomerate in all cases. CLSM showed a large network of alumina inclusions that floated from the bulk of the steel sample. This observation is consistent with previous studies [87], [88], [89]. Alumina inclusions in the bulk of steel samples from laboratory and industrial heats appear similar. It is interesting to note that the network structure appears sintered in all three cases. Singh noted that such sintering of alumina inclusions was an important step in nozzle clogging during continuous casting.[85]

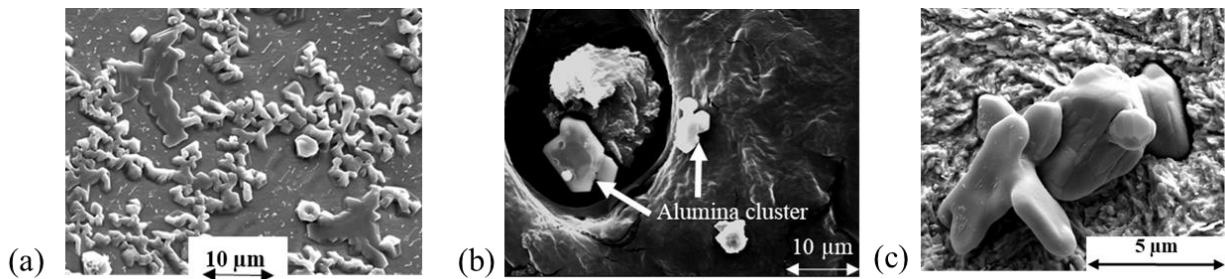


Figure 166. Agglomeration of alumina inclusions: (a) observed on top of steel surface after CLSM experiment (b) observed on etched steel sample from induction furnace experiment and (c) observed on etched surface of sample taken during ladle refining

10.3.2.2 Agglomeration of spinel inclusions

Two ways to form spinel inclusions in liquid steel was discussed in section 5.2.2: transformation of alumina inclusions (using aluminum as the deoxidant) to spinel inclusions due to magnesium pick-up in liquid steel from MgO crucible and/or slag and the formation of spinel inclusions upon deoxidation using Al-10Mg (see section 5.2.2.3). The electrolytic etching of steel samples was used to see the difference in agglomeration behavior of spinel inclusions formed from two mechanisms.

Figure 167 shows the increase in MgO concentration with time in three steel samples taken at 5, 10 and 15 minutes after aluminum deoxidation (0.15% Al addition at $t=0$), for an experiment conducted in an MgO crucible using the induction furnace setup. In all three cases inclusions can be seen to be present as cluster indicating that an alumina cluster may transform into a spinel cluster as it picks up MgO due to magnesium dissolved into the steel at the steel-crucible interface. Figure 168 (a) shows the morphology of a spinel cluster present in the sample taken 2:45 minutes after Al-10Mg addition during experiment-5.3 (0.15% Al-10Mg deoxidation in MgO crucible at $t=0$). Thus, it can be concluded that the spinel inclusions may collide and form spinel agglomerates. The spinel inclusion clusters in steel may form due to transformation of alumina clusters to spinel clusters or simply due to collision of spinel inclusions.

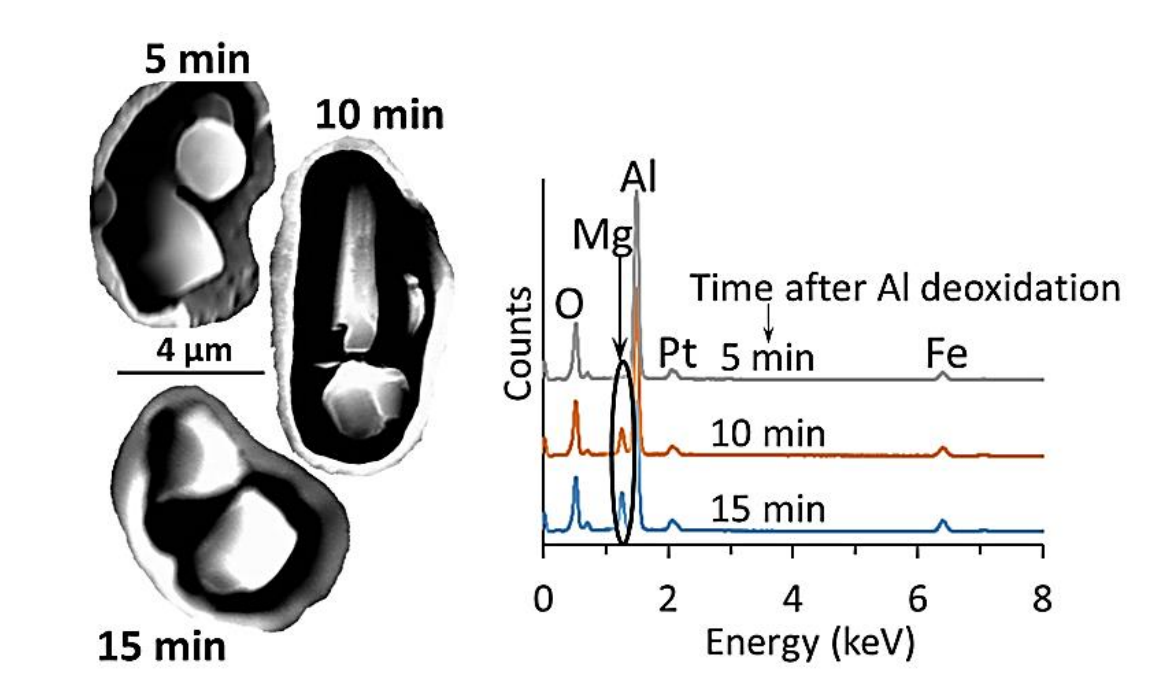
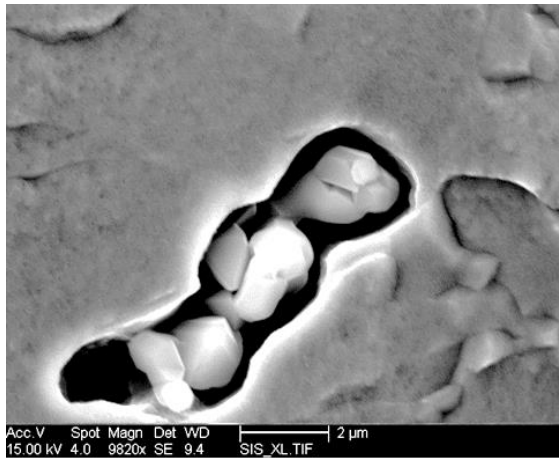
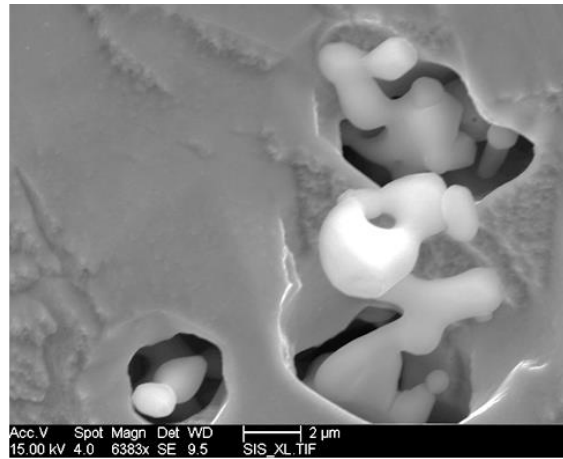


Figure 167. Transformation of alumina cluster into spinel cluster (samples provided by Mauro Elias Ferreira)



a) Spinel cluster



b) Alumina cluster

Figure 168. Spinel and alumina clusters in first sample taken 2:45 minutes after Al-10Mg addition during experiment-5.3

Figure 169 show the presence of spinel clusters from three type of samples: from CLSM, from induction furnace and from the ladle. This observation is in contrast to that by previous researchers who found no agglomeration of spinel inclusions[89]–[91], [93]. Recent work by Mu *et al.* [92] concluded that the most important contributor to inclusion agglomeration is the inclusion number density. The relatively high inclusion density in the sample used in this CLSM experiment (~ 90 mass ppm) may be the reason for the difference in behavior. Comparing the agglomeration of spinel inclusions (Figure 169) to alumina inclusions (Figure 166) reveals that spinel inclusions did not sinter as readily as alumina inclusions, which can be attributed to the lower sintering temperature of alumina. This can be also seen in Figure 168 (a) and (b) which compares morphological difference between a spinel cluster and an alumina cluster present in same sample. Similar transformation was also found in the industrial sample; Figure 169 (c) shows transformation of an alumina cluster to a spinel cluster at the location marked by an arrow.

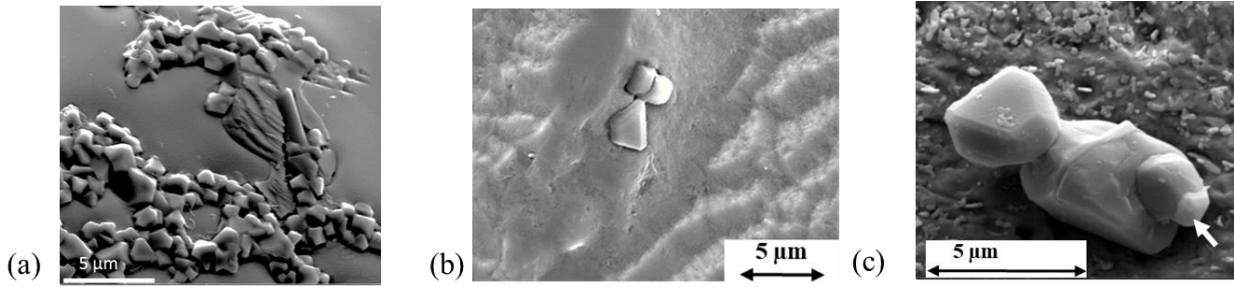


Figure 169. Agglomeration of spinel inclusions: (a) observed on top of steel surface after CLSM experiment (b) observed on etched steel sample from induction furnace experiment and (c) observed on etched surface of sample taken during ladle refining

10.3.2.3 Agglomeration of solid $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ inclusions

Solid $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ inclusions were found to readily agglomerate and sinter during CLSM experiments and in bulk samples from an induction furnace experiment as shown in Figure 170 (a) and (b). The formation of solid inclusions in industrial calcium treatment is avoided and hence there was no industrial sample available for comparison.

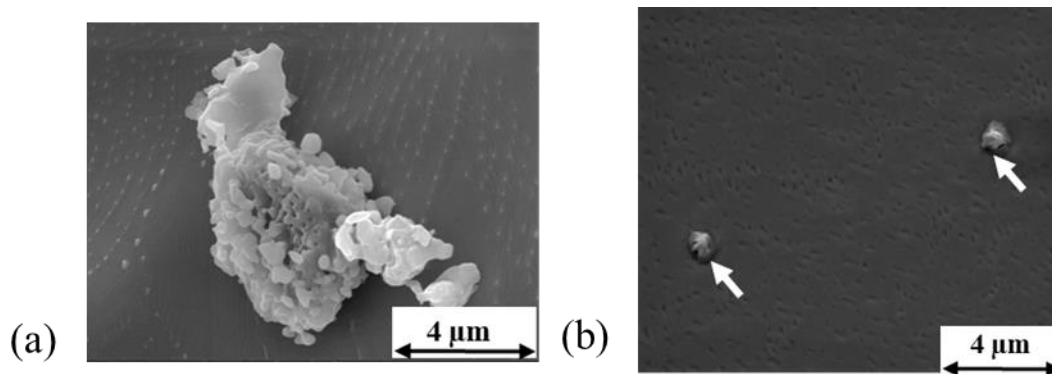


Figure 170. Agglomeration of solid $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ inclusions: (a) observed on top of steel surface after CLSM experiment (b) observed on etched steel sample from induction furnace experiment

10.3.2.4 Agglomeration of liquid $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ inclusions

Figure 171 (a-c) shows liquid $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ inclusions observed in the three types of samples. During CLSM experiments, liquid inclusions did not attract each other on the melt surface. However, solid inclusions collided with liquid inclusions. In contrast, Ferreira *et al.* [66] found

that the average size of even fully liquid inclusions increased with time in *bulk* steel, indicating agglomeration in bulk samples.

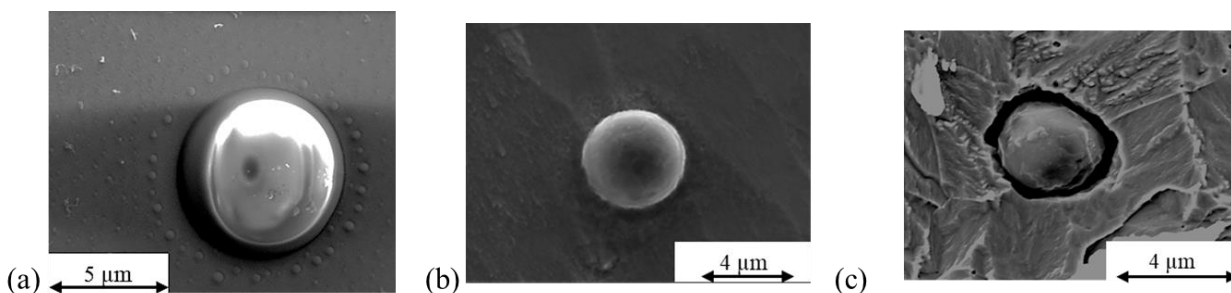


Figure 171. Liquid $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ inclusions: (a) observed on top of steel surface after CLSM experiment (b) observed on etched steel sample from induction furnace experiment and (c) observed on etched surface of sample taken during ladle refining

10.3.3 Conclusions

The agglomeration behavior of inclusions in aluminum-killed and calcium-treated steels observed on the steel surface after CLSM experiments was compared with bulk samples from laboratory scale induction furnace experiments and industrial samples. Similar agglomeration behavior of solid inclusions was observed for all three types of samples. Alumina, solid $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ and spinel inclusions agglomerated in all three types of samples with significant sintering of the former two types of inclusions; spinel formed a loosely connected network. Agglomeration of fully liquid inclusions was not observed in CLSM experiments but it occurred in bulk samples. The current set of results can be used to develop better model for inclusion flotation and removal. Spring et al. [94] developed a numerical model for the nucleation, growth and removal of inclusions. From the current study, the agglomeration behavior of inclusions based on its chemistry can be included in such a model.

10.4 Using X-ray microCT to study inclusion agglomeration

10.4.1 Introduction

Tozawa et al. [95] used fractal theory to calculate the density of alumina clusters and found that the flotation of clusters was expected to be much slower than assuming a uniform density of clusters. Guo et al. [96] used a water model and the fractal dimension analysis of agglomerates to show that both density and the number of primary inclusion particles in the cluster are expected to play important roles in the flotation velocity. There are not many studies regarding statistics of inclusion clusters in a solid steel sample. Li et al. [97], [98] recently reported the use of an X-ray based microtomography technique for the three-dimensional analysis of TiB₂ and SiC clusters in aluminum. In this section, the use of synchrotron-based X-ray microtomography (μ XCT) to find the number, shape and size of alumina clusters in steel samples taken during ladle refining of steel is discussed.

In recent years, the backscattered electron imaging based contrast in scanning electron microscope has become a common tool to automatically detect the size and chemical composition of inclusions [99]–[101]. The inclusion analysis data can also be used to study the evolution of size distribution of inclusions. Based on a similar study, Ferreira et al. [66] concluded that the calcium treated liquid inclusions agglomerate during laboratory scale experiments. The use of such two-dimensional inclusion analysis to study the agglomeration of solid alumina or spinel inclusions is challenging as a section of cluster may appear disconnected on a polished section of steel sample even though the cluster is connected in three dimensions (see Figure 179). Data from automated feature analysis (of 2D sections) has apparently not yet been used to quantitatively study the clustering of solid

inclusions. In this section, a first nearest neighbor distance based method is proposed to quantitatively determine agglomeration of solid inclusions.

10.4.2 Experimental

Lollipop samples of liquid steel (sample-1 and sample-2) were taken at 4th and 7th minute during ladle refining of 241.3 tonne heat of steel (heat-1, see section 6.2). The beginning of aluminum wire addition at the ladle station was considered as $t=0$. The sampling procedure and process details are described in chapter- 6. The lollipop samples from another 247.7 tonne heat of steel (heat-2, see section 6.2) was used for statistical analysis of inclusion agglomeration. The nominal chemistry of steel at the end of process was 0.05% Al, 0.4% Mn and 0.2% C for both heats.

For μ XCT, the samples were machined to 1 mm $\times$ 1 mm $\times$ 3 mm dimension. These samples were analyzed using synchrotron μ XCT at the 2-BM beamline at the Advanced Photon Source at Argonne National Lab which was operated in the white beam mode. In this analysis, the projection of inclusions was obtained by passing an X-ray beam through the sample and measuring the attenuated X-ray. The attenuation depends on the atomic number and density of materials; inclusions having lower atomic number and density would create a contrast. Figure 172 shows a schematic of X-ray CT operation of a slice of the steel sample. The projections obtained from different angles were used to reconstruct the slices with inclusions. A total of 1500 projections were taken over 180° with a 100 ms exposure time at a resolution of 0.65 μ m per pixel. The contrast between steel matrix and alumina inclusions was obtained due to difference in mass attenuation coefficient between the steel matrix and alumina inclusions. TomoPy 0.0.3, developed by Gürsoy et al. [102], was used for filtering the obtained radiographs and reconstruction. Avizo 9.1.1 was used for the segmentation and analysis. The presence of ring artefacts (with darker contrast) in the

radiographs presented a challenge to obtain the right contrast between steel matrix and inclusions (see Figure 173 for an example). These are the result of marks on the detector or scintillator screen that do not move as the sample rotates, and introduce noise into the reconstructed image. The tophat tool (with size 8 spherical shape) in Avizo 9.1.1 was found to be useful in selecting inclusions with minimum ring artefacts as shown later. A minimum of 12 face-connected voxels were used as the minimum feature size, establishing a minimum feature size of approximately $1.8\text{ }\mu\text{m}$.

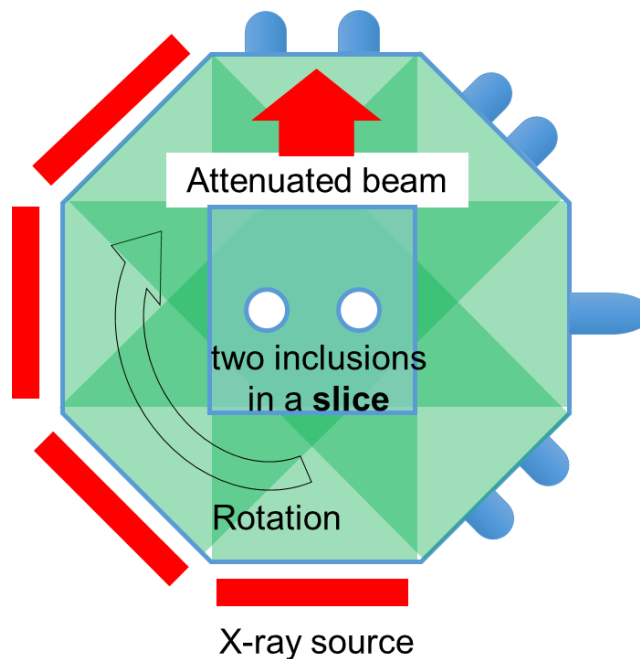


Figure 172. Schematic of X-ray CT of a slice with two inclusions, adapted from <http://www.cmu.edu/me/xctf/xrayct/index.html>

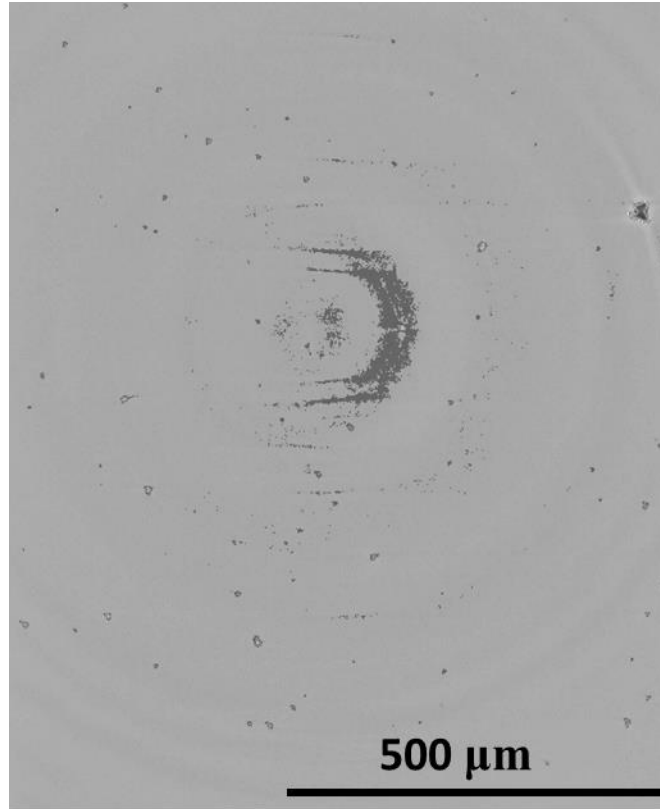
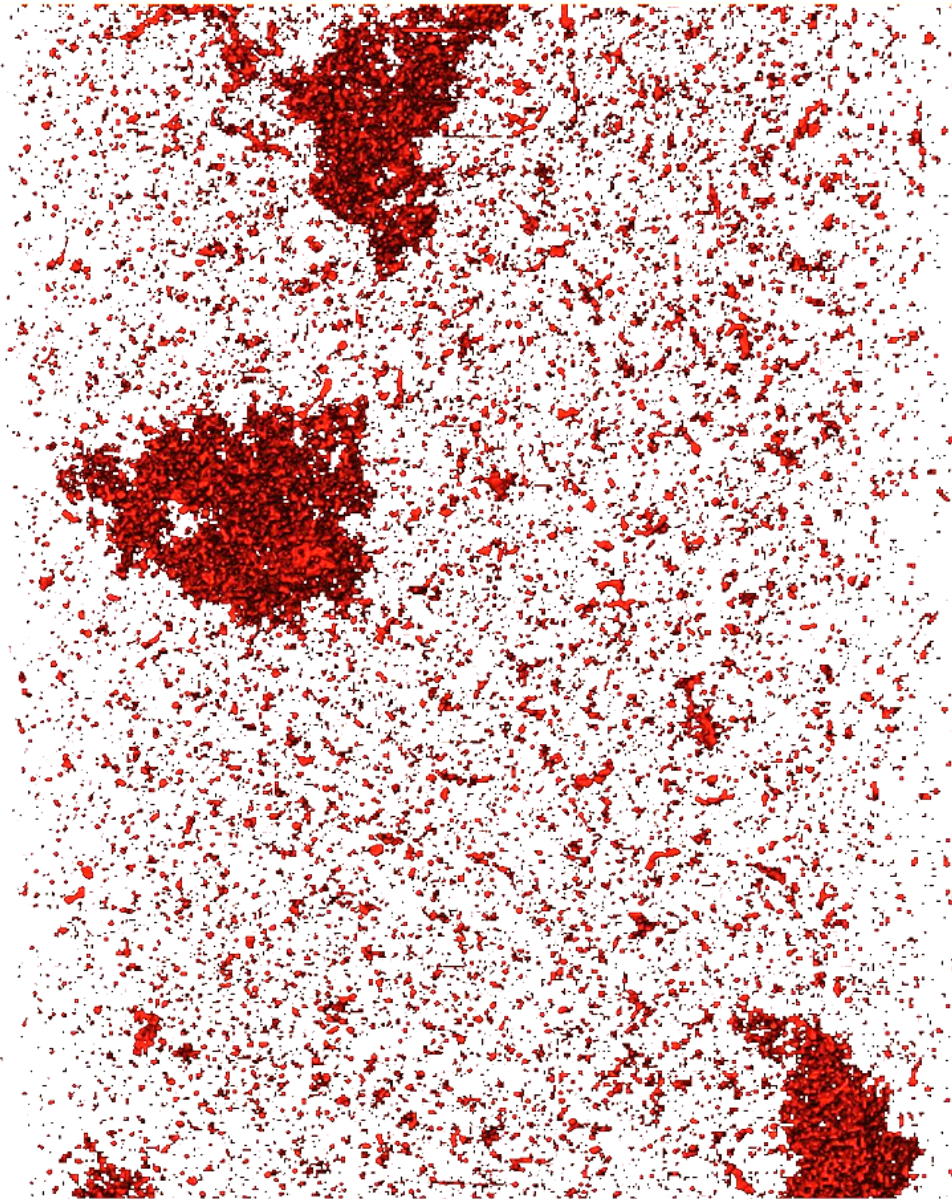


Figure 173. Ring artefacts in a reconstructed CT slice

10.4.3 μ XCT Results and Discussion

The post-processed μ XCT images of sample-1 and sample-2 are shown in Figure 174 and Figure 175 respectively. There were three large clusters ($>100\ \mu\text{m}$) in sample-1 and only one large cluster in sample-2. It should be noted that these images were reconstructed from more than 2000 slices. Given how rare large clusters are, the probability of finding a representative large cluster on a polished cross-section would be very small. Figure 176 (a) and Figure 177 (a) show the largest clusters present in samples-1 and 2; these were larger than $500\ \mu\text{m}$ and $200\ \mu\text{m}$. The longest dimension of these clusters appears larger than those found on the etched steel surface as shown in Figure 176 (b) and Figure 177 (b).



500 μm

Figure 174. Post-processed micro-tomography (μXCT) image of inclusions in sample-1

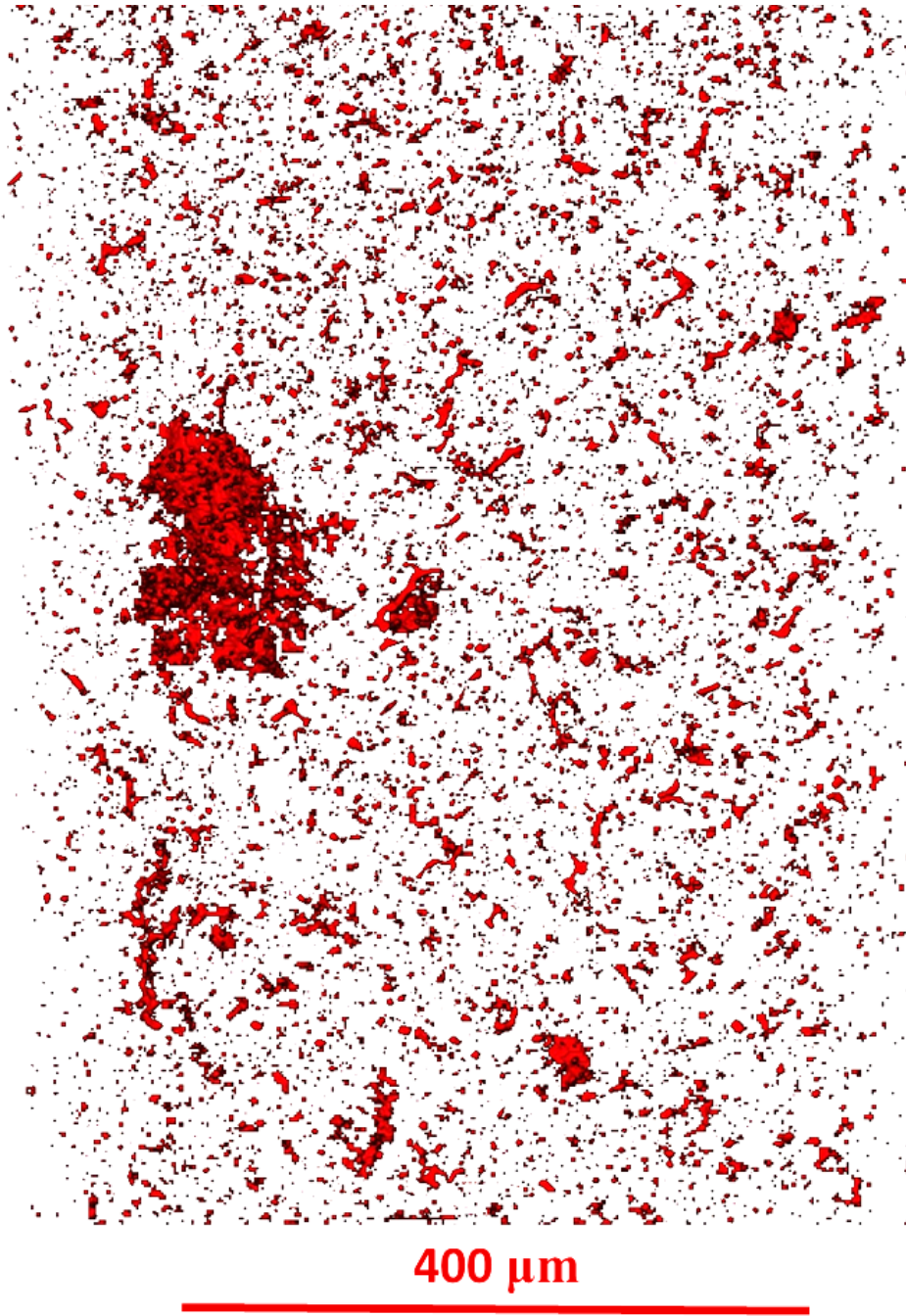


Figure 175. Post-processed micro-tomography (μXCT) image of inclusions in sample-2

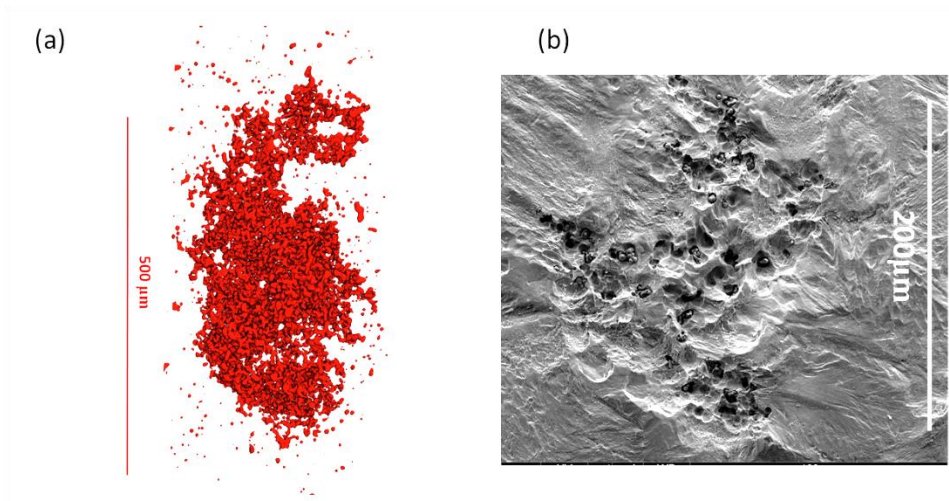


Figure 176. Comparing inclusion cluster in the first sample from μ XCT (left) to electrolytically etched steel sample (right)

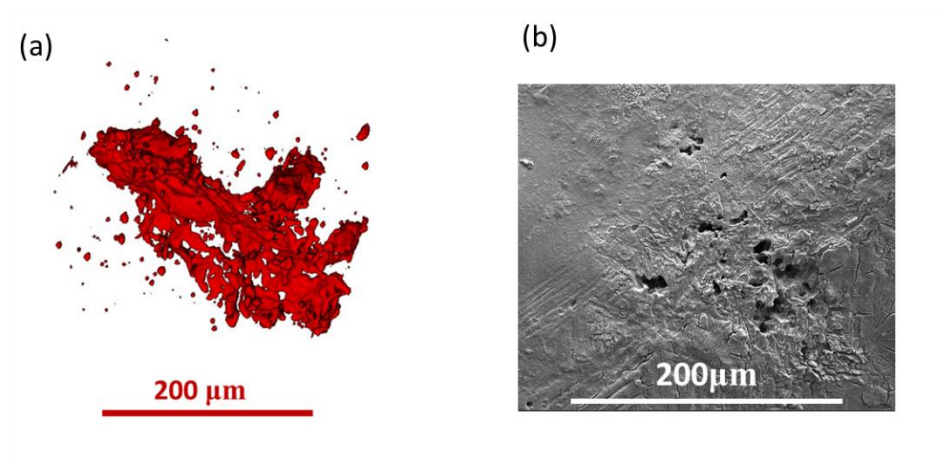


Figure 177. Comparing inclusion cluster in the second sample from μ XCT (left) to electrolytically etched steel sample (right)

The position coordinates and volume of inclusions in each sample were also found using Avizo 9.1.1 software. The volume fraction for sample-1 and sample-2 was 2040 and 913 ppm which corresponds to approximately 470 and 210 ppm mass fraction of oxygen in liquid steel. These are clearly overestimates: the initial dissolved oxygen concentration in the liquid steel before final aluminum killing was 170 ppm (measured using an electrochemical probe) at the beginning of ladle refining. In contrast, from automated inclusion analysis the estimated concentration of bound

oxygen in inclusions for sample-1 and sample-2 were more realistic at 125 and 80 ppm respectively. The estimated higher oxygen concentrations using μ XCT may be due to porosity in the sample (porosity would tend to be counted as oxide inclusions) or the presence of some ring artefacts. Wei et al. [103] proposed a method (based on polar FFT) to eliminate ring artefacts, which may be useful for improvement of the volume fraction estimates. The presence of inclusion clusters may also skew the volume fraction as the frequency of these clusters are expected to be small and random. It should be noted that porosity was filtered from 2D automated inclusion analysis (using SEM ASPEX Explorer), based on EDAX analyses. Figure 178 shows a comparison of the natural logarithm of the population density function of inclusion size distribution obtained from μ XCT to 2D analysis for both samples on a log-log plot. The nature of population density functions plot from μ XCT are similar to those from SEM-AFA analysis. The μ XCT shows the presence of larger cluster which are expected to influence volume fraction estimates. As the resolution of SEM-AFA was better than μ XCT, large number of smaller inclusions were detected in that case. The population density function was defined using Equation 21, as described in detail by Van Ende et al. [57].

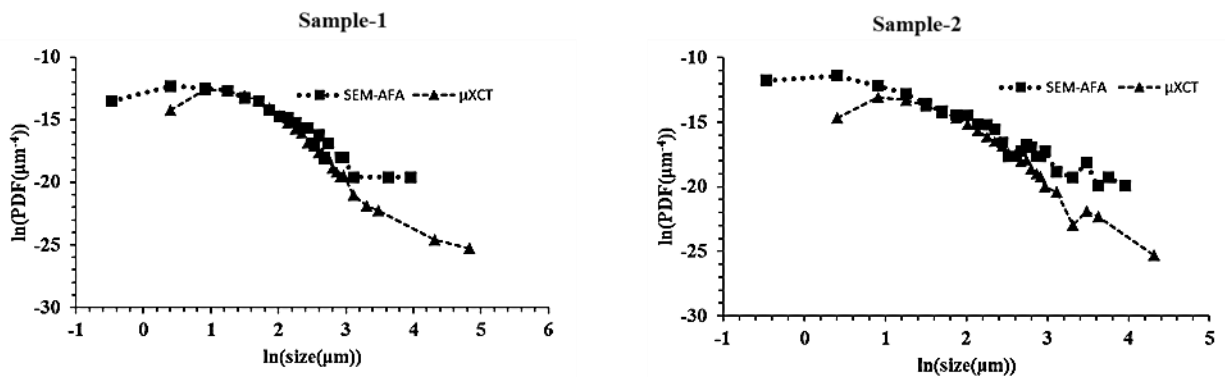


Figure 178. Comparing population density of inclusions calculated using μ XCT data to SEM-AFA data

As shown in Figure 178, large regions of the PDF plots are linear indicating a power-law distribution rather than a log-normal distribution. As noted by Van Ende et al. [57] such an inclusion distribution is expected to be caused by collision/agglomeration and break up of inclusions, rather than nucleation and growth of inclusions. This is expected, as inclusions present in these samples were in the form of clusters as shown in a previous publication [59].

10.4.4 Statistical study of inclusion agglomeration

Clark and Evans [104] described the application of nearest-neighbor analysis to study the distribution of spacing in a population of objects. They described a parameter, R , that measures the degree of departure from a random spacing of objects. R is defined as the ratio of mean nearest neighbor distance in the sample ($\bar{r}_A$) to the mean nearest neighbor distance of a random distribution of the same number density ($\bar{r}_E$) as described in Equation 39 - Equation 41.

$$\bar{r}_A = \frac{\sum r}{N} \quad \text{Equation 39}$$

$$\bar{r}_E = \frac{1}{2\sqrt{\rho}} \quad \text{Equation 40}$$

$$R = \frac{\bar{r}_A}{\bar{r}_E} \quad \text{Equation 41}$$

Where r is an individual nearest neighbor distance, N is the total number of objects and ρ is the number density (m^{-2}) of the object.

This appears to be a useful and readily calculated parameter to quantify the agglomeration of inclusions studied, based on the results of inclusion analysis by automated feature analysis. A section of a cluster may appear as a disconnected set of inclusions on a polished steel sample (see Figure 179). When a sample has many such clusters, one can expect a negative departure from random distribution of inclusions for the fixed number density of inclusions. Figure 180 shows two examples of change in ‘R’ with time during ladle refining of two heats. Figure 180 (a) corresponds to samples from the same heat to the samples used for μ XCT with the first two samples being used there. It can be seen that the mean nearest neighbor distance approaches a random distribution with time. As shown previously [59], the cluster size of inclusions decreases with time during ladle refining, and the mean nearest neighbor distance was expected to approach a random distribution with time. The final samples were taken from tundish. By that time samples rarely had any large inclusion clusters left. The significance test was done by calculating the standard variate using Equation 42.

$$c = \frac{\bar{r}_A - \bar{r}_E}{\sigma_{\bar{r}_E}}$$

Equation 42

Where $\sigma_{\bar{r}_E} = 0.26136/\sqrt{N\rho}$

Since automated feature analysis measures 10^2 - 10^3 of inclusions, the chance of errors was almost always less than 1% in the current analysis.



Figure 179. A section (darker region in the upper part of the figure) through a three-dimensional inclusion cluster (the cluster is that shown in Figure 177 (a)), indicating that a cluster tends to appear disconnected on a two-dimensional section.

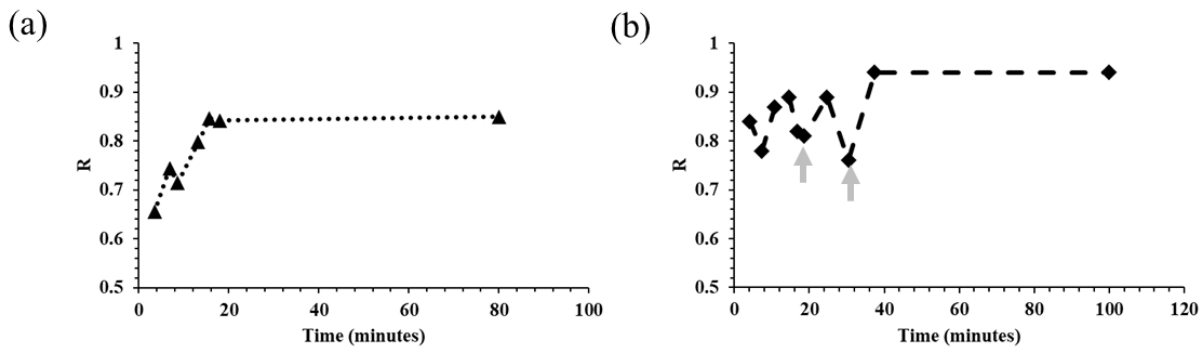


Figure 180. Change with time in the degree of randomness of two-dimensional inclusion distribution (R) during ladle treatment of two industrial heats. The increase in randomness over time indicates that fewer large clusters are present, though the randomness drops in response to formation of new inclusions when alloys are added at the arrowed times.

It is interesting to note the fluctuation in the R vs time plot at $t = 19$ and 31 minutes during heat-2 as shown in Figure 180 (b) as some reoxidation was expected at these moments due to ferromanganese addition in the melt. The reoxidation was expected to generated fresh alumina inclusions that may collide with existing inclusions resulting into the formation of newer inclusion clusters. This demonstrates that the value of “ R ” can be used to diagnose the steel making process and quantitatively study the 3-dimensional agglomeration of solid inclusions from two-dimensional statistical inclusion analysis.

10.4.5 Conclusions

Micro-CT (μ XCT) was successfully used to qualitatively study alumina inclusion clusters that formed in liquid steel at the early stage of ladle refining. The qualitative study illustrated the difficulties associated with finding a representative sample to analyze samples with large clusters. The estimated inclusion volume fractions from μ XCT were much larger than expected, likely due to porosity in the samples and ring artefacts in the X-ray images. The shape of the population density function plot from μ XCT data was similar that from automated inclusion analysis (using SEM ASPEX-Explorer) and indicated collision and agglomeration to be the cluster formation mechanism.

The measured mean nearest distance between inclusions on 2D sections through a steel sample was compared with that for a random distribution of inclusions with the same number density. The ratio of two mean separations was proposed as an indicator of the extent of inclusion clustering in sample. The method was applied to two industrial heats and found to have a good correlation with observed clustering behavior of inclusions: the clustering decreased with time as large clusters floated to the slag.

10.5 Morphological and chemical variation in a single inclusion

10.5.1 Focused Ion Beam (FIB) experiment: serial sectioning of an inclusion

Several examples of composition differences within inclusions have been shown earlier in the document, for example, see Figure 9. A technique like focused ion beam (FIB) can be used to mill through any inclusion and make SEM and EDS observations to allow more complete quantification of the internal composition differences. In such an analysis, one can find an inclusion and mill through the inclusion using an ion beam. Two types of FIB milling equipment are available in the

Materials Science and Engineering department of Carnegie Mellon University: Gallium FIB and Plasma FIB which uses Xenon as ion source.

10.5.1.1 Milling of inclusion using Ga-FIB

A sample taken after 45 minutes of deoxidation from experiment-7.1 (deoxidized by 0.3 wt% Al followed by the addition of 1% Si and slag) was taken for this analysis. A 3 mm × 3 mm section was polished and mounted on a stub with carbon tape, an inclusion was located and analyzed in a SEM equipped with EDS (FEI Quanta-600) and then the sample was inserted in a chamber equipped with secondary electron detector and Ga ion based FIB. Once located, around 10 nm of inclusion thickness was milled and inclusion composition at various locations on inclusions was measured again in a separate SEM equipped with EDS. Figure 181 shows the inclusion before and after FIB milling. Steel mills much faster than the inclusion and hence thickness of steel milled appears more than the milling of thickness of inclusion. Figure 182 shows the inclusion composition map before FIB milling: the inclusion is mostly MgO with small aluminum content at one edge (spectrum-9) and Ca peak on another edge (spectrum-11). A stronger aluminum peak is observed (spectrum-30) after milling near the same edge where the smaller Al-peak was seen before milling; a small aluminum peak can be seen at the other locations in the inclusion as well (spectrum-28) and a calcium peak seems to be present at most of the locations in the inclusion indicating calcium pickup in inclusion. Instead of spinel transforming into MgO inclusions, this condition may also arise due to formation of an MgO-spinel agglomerated inclusion due to a collision between them. Such MgO inclusions can be generated from crucible grains moving into the melt due to crucible degradation (erosion) or due to transformation of alumina inclusion beyond spinel when steel is equilibrated with MgO saturated slag and MgO crucible.

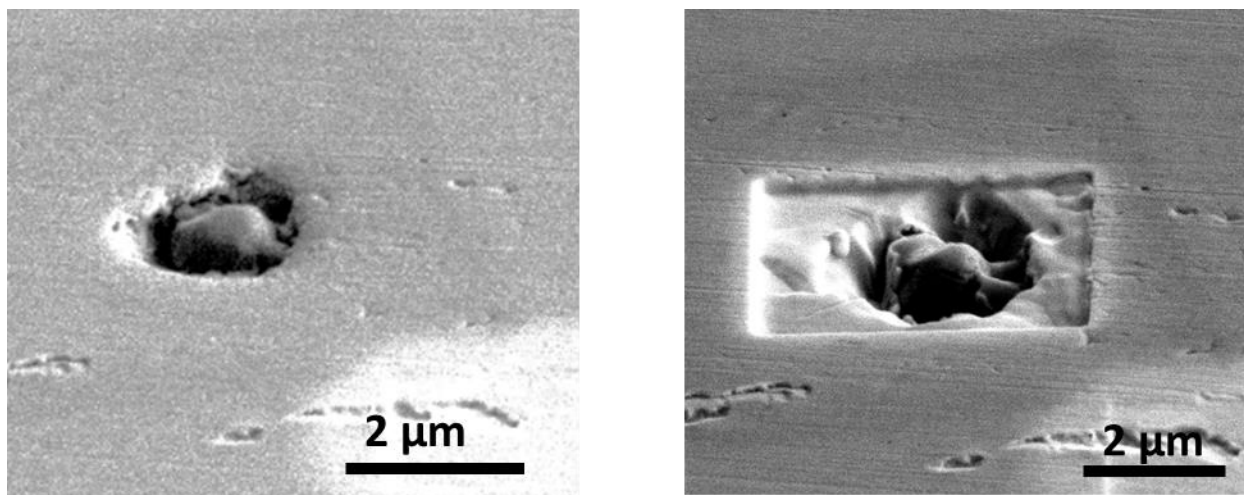


Figure 181 Inclusion before (left) and after (right) FIB milling

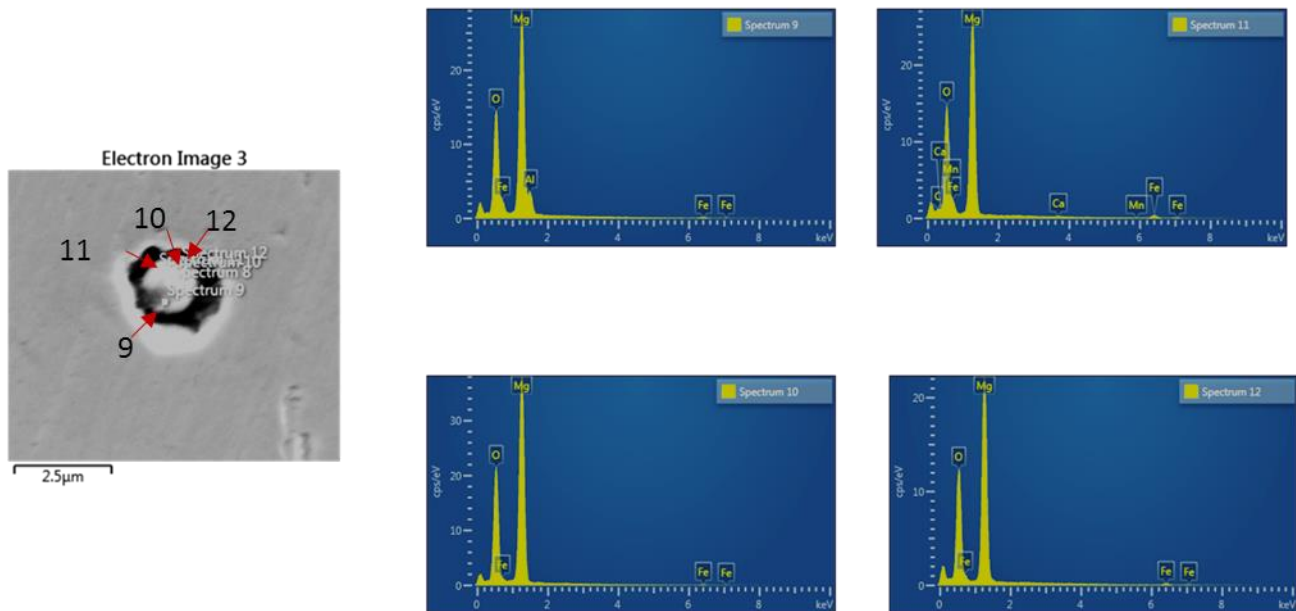


Figure 182 Inclusion composition before FIB milling

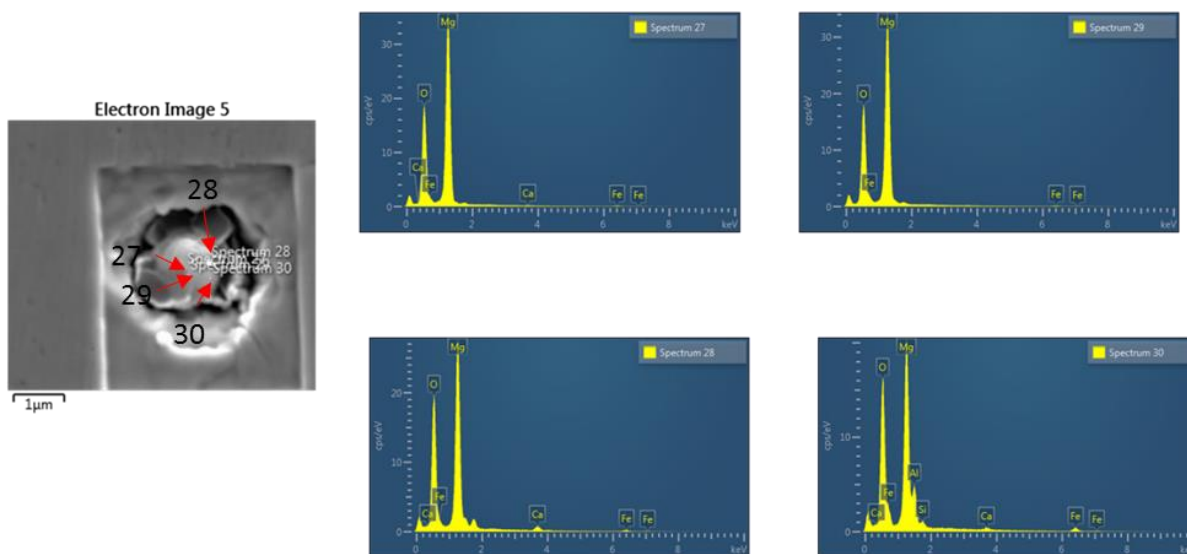


Figure 183 Inclusion composition after FIB milling

10.5.1.2 Serial sectioning of an inclusion using plasma-FIB (PFIB)

The PFIB instrument at Carnegie Mellon is equipped with EDS and can be used to section through an inclusion with better precision than the Ga-FIB instrument. It can also save images during the sectioning process and create EDS maps of the region of interest. In this case, a sample taken one minute after calcium treatment of a laboratory scale aluminum-deoxidized induction furnace heat was taken, polished, and mounted on a stub. A relatively large inclusion was first located on a polished cross-section of the sample, as shown in Figure 184. The inclusion was subsequently platinum coated in the microscope chamber before exposing it to a Xenon ion beam as shown in Figure 185. Platinum coating was achieved by flowing a platinum containing hydrocarbon gas over the sample. The hydrocarbon was decomposed by the electron beam and platinum was released coating the inclusion. A U-shaped trench was created around the platinum-coated inclusion using the ion-beam. A sectioning and EDS program was created to mill through the inclusion from bottom to top of the image shown in Figure 186. Figure 187 shows the initial section of the inclusion revealed during the milling process.

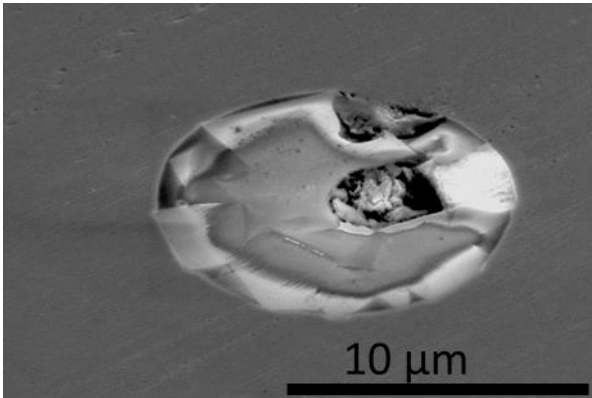


Figure 184. Secondary electron image of an inclusion on a polished cross-section of the sample

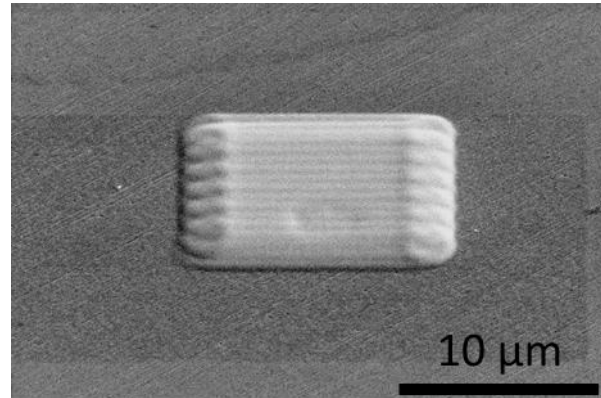


Figure 185. Platinum coating of the inclusion to protect it from ion beam exposure

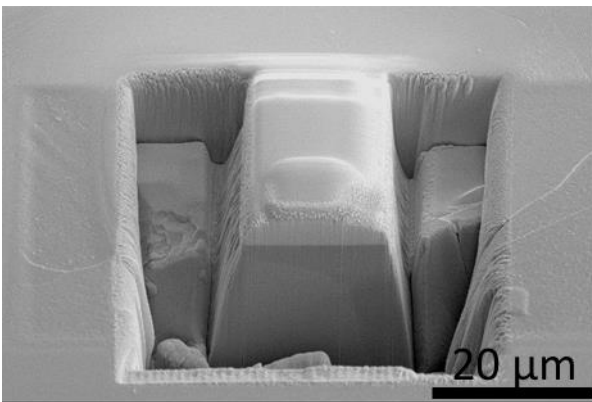


Figure 186. A U-shape trench around platinum coated inclusion

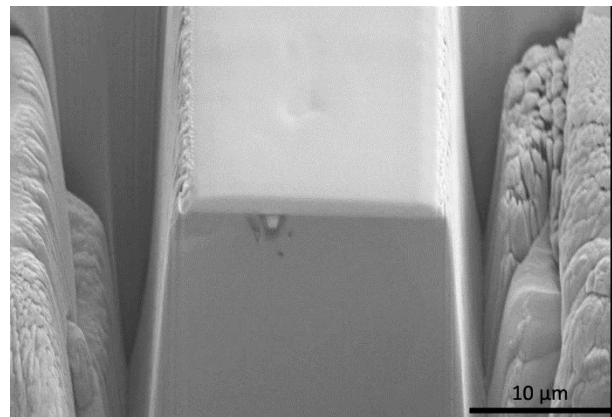


Figure 187. Section of the target inclusion revealed during the milling

Figure 188 shows the inside of the inclusion revealing that the inclusion was indeed a cluster of smaller phases. EDS map of the same section shows that it contained calcium-aluminate, alumina, spinel and MgO. 391 slices were created and corresponding secondary electron image and EDS maps were saved. The entire process took 3 days. This experiment showed that PFIB can be a powerful tool in understanding the chemical and morphological variation inside the inclusion and can help in developing a better understanding of the process.

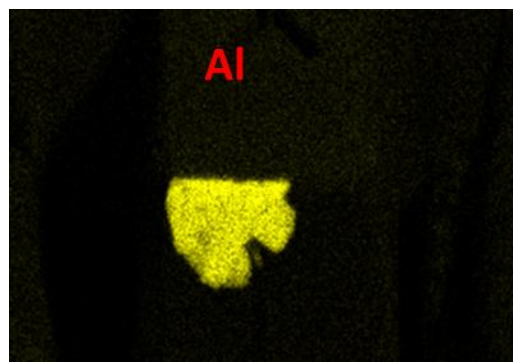
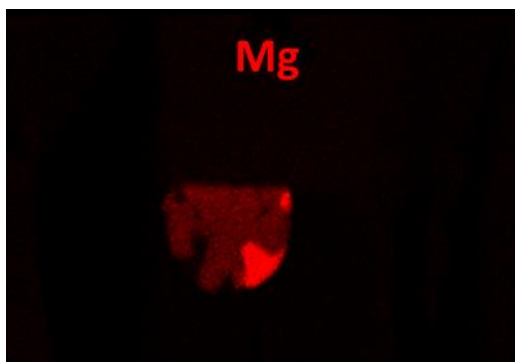
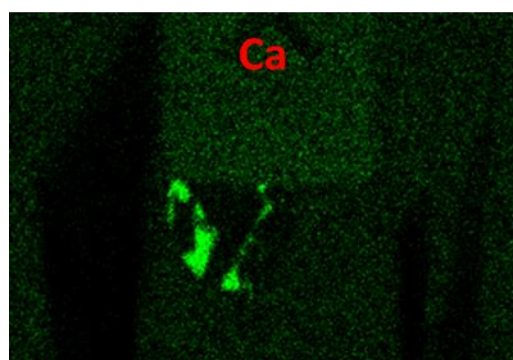
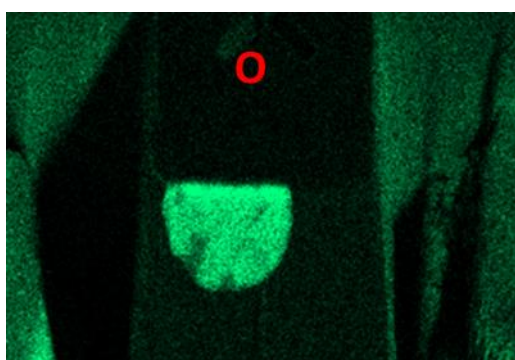
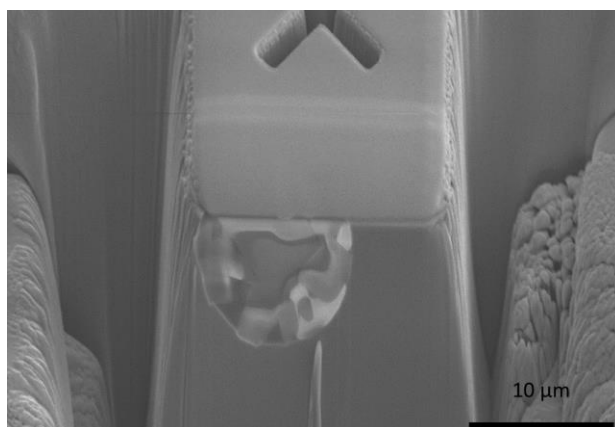


Figure 188. Inside of inclusion and corresponding EDS maps

11 Conclusions and suggestions

The following conclusions can be drawn from current experimental and modeling work:

- I. The inclusion removal under laboratory conditions can be considered to have regimes: one corresponding to initial large inclusions or clusters after aluminum deoxidation followed by slower inclusion removal regime. The inclusion removal in each regime followed a first order decrease in inclusion removal with rate constants as β_1 and β_2 .
- II. The presence of spinel layer on the crucible at the steel-MgO crucible interface can significantly reduce the rate of magnesium transfer compared to the presence of a slag like layer.
- III. The kinetic model can be used to find the rate of magnesium pick-up in steel and to oxide inclusions in steel considering steel-MgO crucible reaction, magnesium evaporation and inclusion removal. The effective magnesium transfer rate in steel was 4.5×10^{-5} m/s when inner surface of the MgO crucible was coated with a slag like layer (due to impurities in MgO crucible). The magnesium transfer rate was about 10-times smaller when crucible wall was coated with a solid spinel layer.
- IV. The MgO pickup in alumina inclusions was simulated for different total oxygen concentrations along with the effect of steel-MgO-C refractory reactions under industrial steelmaking conditions. Following conclusions can be made from this set of simulations:
 - a. For lower total oxygen concentration, the transformation of alumina to spinel and beyond was much quicker.
 - b. When steel picks up magnesium due to both steel-slag and steel-refractory reactions, inclusions may transform to MgO for both high and low inclusion concentrations.

- c. The dissolved magnesium concentration in steel was much lower until alumina inclusions completely transformed to alumina saturated spinel inclusions indicating the calcium modification of partially transformed spinel inclusions may be beneficial in avoiding the re-appearance of spinel inclusions upon a reoxidation event at a later stage.
- V. Targeted laboratory scale induction furnace experiments were conducted to develop a kinetic model that can predict change in steel, slag and inclusion composition during the experiments. The model could fairly predict these changes. The deviation between calculated and observed inclusion composition was due to higher predicted calcium pick-up in steel due to steel-slag reaction. The deviation between calculated and measured steel composition was due to experimental difficulties especially initial oxygen concentration in electrolytic iron and re-oxidation during slag addition.
- VI. A two-parameter based kinetic model was developed to simulate the changes in steel, slag and inclusion composition changes during ladle refining operation. The fitted mass transfer coefficient was much smaller than that calculated from published steel mass transfer correlations. The difference was likely due to the presence of solid slag.
- VII. Induction furnace experiments were carefully designed to clarify the effect of silicon addition on the calcium modification of spinel inclusions due to steel-slag reaction. The use of electronic grade silicon clarified that the source of calcium can be steel-slag reaction in addition to calcium impurities in ferrosilicon.
- VIII. The extent of calcium transfer to oxide inclusions was limited compared to magnesium transfer when experiment was conducted in MgO crucibles. Following methods could improve calcium transfer to oxide inclusions without calcium treatment:

- a. Use of ZrO_2 or CaO crucible when steel was reacted with slag close to CaO saturation.
 - b. Steel-CaO crucible reaction
 - c. Use of reducing slag (SiO_2 free) and 1 wt% silicon addition
- IX. The dissolved calcium was estimated from the CaO precipitated as inclusions in the sample taken just after reoxidizing liquid steel after it was equilibrated with CaO crucible.
- X. The relationship between dissolved [%O] and dissolved [%Ca] was calculated using Ca-O interaction parameter ($e_{\text{Ca}}^{\text{O}} = -994$) estimated from the reoxidation experiments mentioned above. For typical steelmaking conditions (0.05% Al, few ppm O), the calculated relationship was almost same as the condition without any Ca-O interaction.
- XI. An interaction parameter based private database for liquid steel was developed using Ca-O interaction parameter. The private database can be used in the kinetic model developed in the present work.
- XII. The magnesium and calcium evaporation was observed during steel-crucible reaction when experiments were conducted using MgO and CaO crucibles respectively. These should be included in the kinetic model. Magnesium transfer was included in the steel-MgO crucible kinetic model.
- XIII. The growth mechanism of MgO whiskers on MgO crucible was found to be catalyzed by the liquid slag through vapor-liquid-slag (VLS) mechanism.
- XIV. The agglomeration behavior of alumina, spinel, solid and liquid calcium aluminate inclusions at the steel-argon interface was observed. Similar agglomeration behavior of solid inclusions was observed for all three types of samples. Alumina, solid CaO- Al_2O_3 -MgO and spinel inclusions agglomerated in all three types of samples with significant

sintering of the former two types of inclusions; spinel formed a loosely connected network. Agglomeration of fully liquid inclusions was not observed in CLSM experiments but it occurred in bulk samples.

Some suggestions for the future work are in the following:

- a) The two parameter based kinetic model can be tested for other industrial conditions.
- b) The effect of silicon on calcium transfer can be tested by varying silicon concentration in steel and with different slag compositions.
- c) The accuracy of reoxidation method to estimate Ca-O interaction parameter can be improved by using ZrO_2 and MgO free CaO crucible.
- d) The X-ray μCT can be used to study the flotation behavior of inclusion cluster. The morphology of inclusions can be exported to a CFD software like ANSYS-FLUENT and the effect of cluster morphology on the inclusion flotation can be studied.

12 References

- [1] E. B. Pretorius, H. G. Oltmann, and B. T. Schart, “An Overview of Steel Cleanliness From an Industry Perspective,” *AISTech 2013 Proc.*, pp. 993–1026, 2013.
- [2] N. Verma, P. C. Pistorius, R. J. Fruehan, M. S. Potter, H. G. Oltmann, and E. B. Pretorius, “Calcium Modification of Spinel Inclusions in Aluminum-Killed Steel: Reaction Steps,” *Metall. Mater. Trans. B*, vol. 43, no. 4, pp. 830–840, Apr. 2012.
- [3] N. Verma, P. C. Pistorius, R. J. Fruehan, M. Potter, M. Lind, and S. Story, “Transient Inclusion Evolution During Modification of Alumina Inclusions by Calcium in Liquid Steel: Part I. Background, Experimental Techniques and Analysis Methods,” *Metall. Mater. Trans. B*, vol. 42, no. 4, pp. 711–719, Apr. 2011.
- [4] H. Mu, “Reduction of CaO and MgO by Al in Steel and Inclusion Modification,” Carnegie Mellon University, 2016.
- [5] J. Poirier, “A review: influence of refractories on steel quality,” *Metall. Res. Technol.*, vol. 112, no. 4, p. 410, 2015.
- [6] A. Harada, N. Maruoka, H. Shibata, and S. Kitamura, “A Kinetic Model to Predict the Compositions of Metal, Slag and Inclusions during Ladle Refining: Part2. Condition to Control the Inclusion Composition,” *ISIJ Int.*, vol. 53, no. 12, pp. 2118–2125, 2013.
- [7] M. A. van Ende and I. H. Jung, “A Kinetic Ladle Furnace Process Simulation Model: Effective Equilibrium Reaction Zone Model Using FactSage Macro Processing,” *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.*, pp. 1–9, 2016.
- [8] J. H. Shin, Y. Chung, and J. H. Park, “Refractory–Slag–Metal–Inclusion Multiphase

- Reactions Modeling Using Computational Thermodynamics: Kinetic Model for Prediction of Inclusion Evolution in Molten Steel,” *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.*, pp. 1–14, 2016.
- [9] J. Tan and P. C. Pistorius, “Comparison of Three Approaches to Study Inclusions in Al-Si Deoxidized Steel and Al-killed Steel,” *AISTech 2013 Proc.*, pp. 1301–1311, 2013.
- [10] C. Merlet, “Evaluation and description of a new correction procedure for quantitative electron probe microanalysis,” *Int. Congr. X-ray Opt. Microanal.*, no. September 1992, pp. 123–126, 1992.
- [11] C. Merlet, “An accurate computer correction program for quantitative electron probe microanalysis,” *Mikrochim. Acta*, vol. 114–115, no. 1, pp. 363–376, 1994.
- [12] K. Shibata, Y. Mizukami, and T. Kitamura, “Effect of Stirring Energy, Temperature and Flux Composition on Hot Metal Dephosphorization Kinetics,” *ISIJ Int.*, vol. 31, no. 11, pp. 1322–1328, 1991.
- [13] S.-H. Kim and R. J. Fruehan, “Physical modeling of liquid/liquid mass transfer in a gas stirred ladle,” *Metall. Trans. B*, vol. 18, no. 4, pp. 673–680, 1987.
- [14] D. Roy, P. C. Pistorius, and R. J. Fruehan, “Effect of silicon on the desulfurization of Al-killed steels: Part I. Mathematical model,” *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.*, vol. 44, no. 5, pp. 1086–1094, 2013.
- [15] D. Roy, P. C. Pistorius, and R. J. Fruehan, “Effect of silicon on the desulfurization of Al-killed steels: Part II. Experimental results and plant trials,” *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.*, vol. 44, no. 5, pp. 1095–1104, 2013.

- [16] K. J. Graham and G. A. Irons, “Towards Integrated Ladle Metallurgy Control,” in *Proceedings of AISTech 2008*, 2008, pp. 1181–1194.
- [17] P. K. Iwamasa and R. J. Fruehan, “Effect of FeO in the slag and silicon in the metal on the desulfurization of hot metal,” *Metall. Mater. Trans. B*, vol. 28, no. February, pp. 47–57, 1997.
- [18] T. Kargul and J. Falkus, “A hybrid model of steel refining in the ladle furnace,” *Steel Res. Int.*, vol. 81, no. 11, pp. 953–958, 2010.
- [19] J. Peter, K. D. Peaslee, D. G. C. Robertson, M. Hall, and B. G. Thomas, “Experimental Study of Kinetic Processes During the Steel Treatment at two LMF ’ s,” *AISTech*, vol. 1, pp. 959–967, 2005.
- [20] C. Cicutti, C. Capurro, and C. Cerrutti, “Development of a kinetic model to predict the evolution of inclusions composition during the production of aluminum killed, calcium treated steels,” in *9th International Conference and Exhibition on Clean Steel*, 2015.
- [21] G. Okuyama, K. Yamaguchi, S. Takeuchi, and K. Sorimachi, “Effect of Slag Composition on the Kinetics of Formation of $\text{Al}_2\text{O}_3\cdot\text{MgO}$ Inclusions in Aluminum Killed Ferritic Stainless Steel,” *ISIJ Int.*, vol. 40, no. 2, pp. 121–128, 2000.
- [22] J. H. Shin, Y. Chung, and J. H. Park, “Refractory–Slag–Metal–Inclusion Multiphase Reactions Modeling Using Computational Thermodynamics: Kinetic Model for Prediction of Inclusion Evolution in Molten Steel,” *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.*, pp. 1–14, 2016.
- [23] A. Harada, N. Maruoka, H. Shibata, and S. Kitamura, “A Kinetic Model to Predict the

- Compositions of Metal, Slag and Inclusions during Ladle Refining: Part 1. Basic Concept and Application,” *ISIJ Int.*, vol. 53, no. 12, pp. 2110–2117, 2013.
- [24] A. Harada *et al.*, “Kinetic Analysis of Compositional Changes in Inclusions during Ladle Refining,” *ISIJ Int.*, vol. 54, no. 11, pp. 2569–2577, 2014.
- [25] M. Järvinen *et al.*, “Law of Mass Action Based Kinetic Approach for the Modelling of Parallel Mass Transfer Limited Reactions : Application to Metallurgical Systems,” *ISIJ Int.*, vol. 56, no. 9, pp. 1543–1552, 2016.
- [26] P. Yan, B. A. Webler, P. C. Pistorius, and R. J. Fruehan, “Nature of MgO and Al₂O₃ Dissolution in Metallurgical Slags,” *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.*, vol. 46, no. 6, pp. 2414–2418, 2015.
- [27] S. Ohguchi, D. G. C. Robertson, B. Deo, P. Grieveson, and J. H. E. Jeffes, “Simultaneous dephosphorization and desulphurization of molten pig iron,” *Ironm*, vol. 11, no. 4, pp. 202–213, 1984.
- [28] A. Harada, G. Miyano, N. Maruoka, H. Shibata, and S. Kitamura, “Dissolution Behavior of Mg from MgO into Molten Steel Deoxidized by Al,” *ISIJ Int.*, vol. 54, no. 10, pp. 2230–2238, 2014.
- [29] K. Schwerdtfeger, “Present state of oxygen control in alumium deoxidized steel,” *Arch. Eisenhüttenwes.*, vol. 54, no. 3, pp. 87–98, 1983.
- [30] Z. Deng and M. Zhu, “Evolution mechanism of non-metallic inclusions in Al-killed alloyed steel during secondary refining process,” *ISIJ Int.*, vol. 53, no. 3, pp. 450–458, 2013.
- [31] S. Yang, Q. Wang, L. Zhang, J. Li, and K. Peaslee, “Formation and Modification of

- MgO·Al₂O₃-Based Inclusions in Alloy Steels,” *Metall. Mater. Trans. B*, vol. 43, no. 4, pp. 731–750, 2012.
- [32] Z. Deng, M. Zhu, and D. Sichen, “Effect of Refractory on Nonmetallic Inclusions in Al-Killed Steel,” *Metall. Mater. Trans. B*, vol. 47, no. 5, pp. 3158–3167, 2016.
- [33] C. Liu, F. Huang, J. Suo, and X. Wang, “Effect of Magnesite-Carbon Refractory on the Kinetics of MgO·Al₂O₃ Spinel Inclusion Generation in Extra-Low Oxygen Steels,” *Metall. Mater. Trans. B*, vol. 47, no. 2, pp. 989–998, 2016.
- [34] J. Tan and B. A. Webler, “Study of Spinel Inclusions Formed From Deoxidation and Reoxidation in Al-Killed Steel,” *AISTech 2016 Proc.*, no. 412, pp. 2485–2496, 2016.
- [35] N. Verma, P. C. Pistorius, R. J. Fruehan, and M. Potter, “Modification of Spinel Inclusions by Calcium in Liquid Steel,” *Iron Steel Technol.*, vol. 7, no. 1, pp. 189–197, 2010.
- [36] S. P. T. Piva, D. Kumar, and P. C. Pistorius, “Modeling Manganese Silicate Inclusion Composition Changes during Ladle Treatment Using FactSage Macros,” *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.*, pp. 1–9, 2016.
- [37] K. H. Javed, *Science and Practice of Liquid-Liquid Extraction, Chapter-4*. Clarendon Press, Oxford, 1992.
- [38] I.-H. Jung, S. A. Decterov, and A. D. Pelton, “A thermodynamic model for deoxidation equilibria in steel,” *Metall. Mater. Trans. B*, vol. 35, no. June, pp. 493–507, 2004.
- [39] A. Costa e Silva, “Calcium and magnesium thermodynamics in steel and its impacts on secondary steelmaking: a computational thermodynamics approach,” *Rev. Metall.*, vol. 105, no. 4, pp. 181–193, 2008.

- [40] M. Berg, J. Lee, and D. Sichen, “Study on the Equilibrium Between Liquid Iron and Calcium Vapor,” *Metall. Mater. Trans. B*, 2017.
- [41] J. Gran and D. Sichen, “Experimental determination of Mg activities in Fe-Mg solutions,” *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.*, vol. 42, no. October, pp. 921–924, 2011.
- [42] M. Hino and K. Ito, Eds., *Thermodynamic Data for Steelmaking*. Sendai: Tohoku University Press, 2010.
- [43] X. Zhang, Q. Han, and D. Chen, “Dissolution equilibrium of magnesium Vapor in liquid iron,” *Metall. Trans. B*, vol. 22, no. 6, pp. 918–921, 1991.
- [44] C. W. Bale *et al.*, “FactSage thermochemical software and databases, 2010-2016,” *Calphad Comput. Coupling Phase Diagrams Thermochem.*, vol. 54, pp. 35–53, 2016.
- [45] H. Itoh, M. Hino, and S. Ban-Ya, “Thermodynamics on the formation of spinel nonmetallic inclusion in liquid steel,” *Metall. Mater. Trans. B*, vol. 28, pp. 953–956, 1997.
- [46] W.-G. Seo, W.-H. Han, J.-S. Kim, and J.-J. Pak, “Deoxidation Equilibria among Mg, Al and O in Liquid Iron in the Presence of MgO Al₂O₃ Spinel,” *ISIJ Int.*, vol. 43, no. 2, pp. 201–208, 2003.
- [47] H. Ohta and H. Suito, “Deoxidation equilibria of calcium and magnesium in liquid iron,” *Metall. Mater. Trans. B*, vol. 28, no. 6, pp. 1131–1139, 1997.
- [48] R. Inoue and H. Suito, “Thermodynamics of O, N, and S in liquid Fe equilibrated with CaO-Al₂O₃-MgO slags,” *Metall. Mater. Trans. B*, vol. 25, no. 2, pp. 235–244, 1994.
- [49] T. Kimura and H. Suito, “Calcium deoxidation equilibrium in liquid iron,” *Metall. Mater.*

- Trans. B*, vol. 25, no. 1, pp. 33–42, 1994.
- [50] M. Nadif and C. Gatellier, “Influence of Calcium and Magnesium on the Solubility of Oxygen and Sulphur in Liquid Steel (Laboratory Results),” *Rev. Metall.*, vol. 83, no. 5, pp. 377–394, 1986.
 - [51] E. T. Turkdogan, “Possible failure of emf sensor in liquid iron containing dissolved calcium or magnesium,” *Steel Res. Int.*, vol. 62, no. 9, pp. 379–384, 1991.
 - [52] D. Kumar and P. C. Pistorius, “Understanding Transient Composition of Inclusions in Ladle Furnace : Modeling Approach,” *AISTech 2016 Proc.*, pp. 1151–1160, 2016.
 - [53] H. Mitsutaka, S. Wang, T. Nagsaka, and S. Ban-ya, “Evaporation Rate of Zinc in Liquid Iron,” *ISIJ Int.*, vol. 34, no. 6, pp. 491–497, 1994.
 - [54] J. R. Lloyd and W. R. Moran, “Natural-convection adjacent to horizontal surface of various planforms,” *J. Heat Transfer*, vol. 96, no. 4, pp. 443–447, 1974.
 - [55] B. E. Poling, J. M. Prausnitz, and J. P. O’Connell, *Properties of Gases and Liquids, Fifth Edition*. McGraw-Hill Education, 2001.
 - [56] D. Kumar and P. C. Pistorius, “Kinetics of Transient Inclusion Reactions: Modeling Approach,” Pittsburgh.
 - [57] M.-A. Van Ende, M. Guo, E. Zinngrebe, B. Blanpain, and I.-H. Jung, “Evolution of Non-Metallic Inclusions in Secondary Steelmaking: Learning from Inclusion Size Distributions,” *ISIJ Int.*, vol. 53, no. 11, pp. 1974–1982, 2013.
 - [58] S. P. T. Piva, D. Kumar, and P. C. Pistorius, “Modeling Manganese Silicate Inclusion Composition Changes during Ladle Treatment Using FactSage Macros,” *Metall. Mater.*

- Trans. B Process Metall. Mater. Process. Sci.*, vol. 48B, no. February 2017, pp. 37–45, 2017.
- [59] D. Kumar, K. C. Ahlborg, and P. C. Pistorius, “Application of Kinetic Model for Industrial Scale Ladle Refining Process,” in *AISTech 2017 Proceedings*, 2017, pp. 2693–2706.
- [60] D. Kumar and P. C. Pistorius, “A Study on Calcium Transfer From Slag To Steel and Its Effect on Modification of Alumina and Spinel Inclusions,” in *Advances in Molten Slags, Fluxes, and Salts: Proceedings of The 10th International Conference on Molten Slags, Fluxes and Salts (MOLTEN16)*, 2016, pp. 145–154.
- [61] N. Bannenberg, B. Bergmann, and H. Gaye, “Combined decrease of sulfur, nitrogen, hydrogen and total oxygen in only one secondary steelmaking operation,” *Steel Res. Int.*, vol. 63, no. 10, pp. 431–437, 1992.
- [62] Y. Miki, B. G. Thomas, A. Denissov, and Y. Shimada, “Model of Inclusion Removal during RH Degassing of Steel,” *Iron Steelmak.*, vol. 24, no. 8, pp. 31–38, 1997.
- [63] S. Yngve, “Mechanical Stirring Power in Molten metal in Ladles Obtained by Induction Stirring and Gas Blowing,” *Scand. J. Metall.*, vol. 7, pp. 81–87, 1978.
- [64] C. A. Abel, R. J. Fruehan, and A. Vassilicos, “Physical Modeling of Bottom-Blown Continuous Steelmaking, Part-II: DEvelopment of Mass Transfer Correlations and Process Feasibility,” *Trans. Iron Steel Soc.*, vol. 49, no. August, pp. 49–64, 1995.
- [65] E. B. Pretorius, H. G. Oltmann, and T. Cash, “The effective modification of spinel inclusions by Ca treatment in LCAK steel,” *Iron Steel Technol.*, vol. 7, no. 7, pp. 31–44, 2010.

- [66] M. E. Ferreira, P. C. Pistorius, and R. J. Fruehan, "Inclusion Size Distributions After Calcium Addition in LCAK Steels," in *AISTech 2017 Proceedings*, 2017, pp. 2837–2846.
- [67] A. Parrish, R. O. Campbell, P. B. Mobley, and G. McCarthy, "REFINER BLEACHING WITH MAGNESIUM OXIDE AND HYDROGEN PEROXIDE," US 6,881,299 B2, 2005.
- [68] N. Verma, P. C. Pistorius, R. J. Fruehan, M. Potter, M. Lind, and S. R. Story, "Transient Inclusion Evolution During Modification of Alumina Inclusions by Calcium in Liquid Steel: Part II. Results and Discussion," *Metall. Mater. Trans. B*, vol. 42, no. 4, pp. 720–729, 2011.
- [69] D. L. S. and R.A.Flinn, "The solubility of calcium in liquid iron and third element interaction effects," *Trans AIME* 230, vol. 21, no. June, pp. 876–887, 1964.
- [70] B. Song and Q. Han, "Equilibrium of calcium vapor with liquid iron and the interaction of third elements," *Metall. Mater. Trans. B*, vol. 29, no. 2, pp. 415–420, 1998.
- [71] Q. Han, X. Zhang, D. Chen, and P. Wang, "The calcium-phosphorus and the simultaneous calcium-oxygen and calcium-sulfur equilibria in liquid iron," *Metall. Trans. B*, vol. 19, no. 4, pp. 617–622, 1988.
- [72] G. K. Sigworth and Elliot J. F., "The Thermodynamics of Liquid Iron Alloys," *Met. Sci.*, vol. B, pp. 298–310, 1974.
- [73] H. Suito and S. Cho, "Assessment Calcium-Oxygen Equilibrium in Liquid Iron," *ISIJ Int.*, vol. 34, no. 3, pp. 265–269, 1994.
- [74] D. R. Askeland and P. P. Phulé, "Atomic and Ionic Arrangements," in *The Science and Engineering of Materials*, 5th editio., Ontario, Canada: Thomson, 2006, p. 78.

- [75] K. P. Kalyanikutty, F. L. Deepak, C. Edem, A. Govindaraj, and C. N. R. Rao, "Carbon-assisted synthesis of nanowires and related nanostructures of MgO," *Mater. Res. Bull.*, vol. 40, no. 5, pp. 831–839, 2005.
- [76] Z. Xie and F. Ye, "In-situ formation of spinel fibers in MgO-C refractory matrixes," *J. Wuhan Univ. Technol. Mater. Sci. Ed.*, vol. 24, no. 6, pp. 896–902, 2009.
- [77] W. Luo, B. Zhu, X. Li, P. Chen, Z. Ma, and X. Wang, "In-situ formation of MgO whiskers and CNTs and their influence on the mechanical properties of low-carbon MgO-C refractory composites," *Int. J. Mater. Res.*, vol. 107, no. 4, pp. 333–339, 2016.
- [78] M. Zhao, X. L. Chen, W. J. Wang, Y. J. Ma, Y. P. Xu, and H. Z. Zhao, "Self-catalyzed growth of magnesium oxide nanorods," *Mater. Lett.*, vol. 60, no. 16, pp. 2017–2019, 2006.
- [79] Q. Shi, Y. Liu, Z. Gao, and Q. Zhao, "Formation of MgO whiskers on the surface of bulk MgB₂ superconductors during in situ sintering," *J. Mater. Sci.*, vol. 43, no. 4, pp. 1438–1443, 2008.
- [80] T. Yanagida, K. Nagashima, H. Tanaka, and T. Kawai, "Mechanism of catalyst diffusion on magnesium oxide nanowire growth," *Appl. Phys. Lett.*, vol. 91, no. 6, pp. 1–4, 2007.
- [81] Y. Chen, J. Li, Y. Han, X. Yang, and J. Dai, "The effect of Mg vapor source on the formation of MgO whiskers and sheets," *J. Cryst. Growth*, vol. 245, no. 1–2, pp. 163–170, 2002.
- [82] A. Yamaguchi and S. Hashimoto, "Growth of magnesia whiskers," *Ceram. Int.*, vol. 18, no. 5, pp. 301–305, 1992.
- [83] T. Zhu, Y. Li, S. Jin, S. Sang, and N. Liao, "Catalytic formation of one-dimensional nanocarbon and MgO whiskers in low carbon MgO–C refractories," *Ceram. Int.*, vol. 41,

- no. 3, pp. 3541–3548, 2015.
- [84] T. Zhu, Y. Li, S. Sang, S. Jin, and H. Wang, “Formation of hollow MgO-rich spinel whiskers in low carbon MgO-C refractories with Al additives,” *J. Eur. Ceram. Soc.*, vol. 34, no. 16, pp. 4425–4432, 2014.
- [85] S. N. Singh, “Mechanism of alumina buildup in tundish nozzles during continuous casting of aluminum-killed steels,” *Metall. Trans.*, vol. 5, no. 10, pp. 2165–2178, 1974.
- [86] L. Zhang and B. G. G. Thomas, “Alumina Inclusion Behavior During Steel Deoxidation,” *7th Eur. Electr. Steelmak. Conf. 26-29, 2002, Venice, Italy*, Assoc. Ital. di Metall. Milano, Italy, vol. 2, pp. 2–77, 2002.
- [87] H. Yin, H. Shibata, T. Emi, and M. Suzuki, “‘In-situ’ Observation of Collision, Agglomeration and Cluster Formation of Alumina Inclusion Particles on Steel Melts,” *ISIJ Int.*, vol. 37, no. 10, pp. 936–945, 1997.
- [88] H. Yin, H. Shibata, T. Emi, and M. Suzuki, “Characteristics of Agglomeration of Various Inclusion Particles on Molten Steel Surface,” *ISIJ Int.*, vol. 37, no. 10, pp. 946–955, 1997.
- [89] Y. Kang, B. Sahebkar, P. R. Scheller, K. Morita, and D. Sichen, “Observation on Physical Growth of Nonmetallic Inclusion in Liquid Steel During Ladle Treatment,” *Metall. Mater. Trans. B*, vol. 42, no. 3, pp. 522–534, 2011.
- [90] H. Shibata, H. Yin, and T. Emi, “The Capillary Effect Promoting Collision and Agglomeration of Inclusion Particles at the Inert Gas-Steel Interface,” *Philos. Trans. Math. Phys. Eng. Sci.*, vol. 356, pp. 957–966, 1998.
- [91] S. Kimura, K. Nakajima, and S. Mizoguchi, “Behavior of Alumina-Magnesia Complex

- Inclusions and Magnesia Inclusions on the Surface of Molten Low-Carbon Steels,” *Metall. Mater. Trans. B*, vol. 32B, no. 1, pp. 79–85, 2001.
- [92] W. Mu, N. Dogan, and K. S. Coley, “Agglomeration of Non-metallic Inclusions at the Steel/Ar Interface: Model Application,” *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.*, vol. 48, no. 4, pp. 2092–2103, 2017.
- [93] W. Yang, L. Zhang, X. Wang, Y. Ren, X. Liu, and Q. Shan, “Characteristics of Inclusions in Low Carbon Al-Killed Steel during Ladle Furnace Refining and Calcium Treatment,” *ISIJ Int.*, vol. 53, no. 8, pp. 1401–1410, 2013.
- [94] J. Spring, M. Paliwal, and I. Jung, “Numerical Model for the Nucleation , Growth and Removal of Deoxidation Inclusions,” in *AISTech 2016 Proceedings*, 2016, pp. 1179–1186.
- [95] H. Tozawa, Y. Kato, K. Sorimachi, and T. Nakanishi, “Agglomeration and Flotation of Alumina Clusters in Molten Steel,” *ISIJ Int.*, vol. 39, no. 5, pp. 426–434, 1999.
- [96] L. Guo, Y. Wang, L. Hong, and L. Hai-tao, “Floating Properties of Agglomerated Inclusion in Liquid Steel,” *J. Iron Steel Res. Int.*, vol. 20, no. 7, pp. 35–39, 2013.
- [97] T. Li, S. Shimasaki, S. Taniguchi, K. Uesugi, and S. Narita, “Particle Coagulation in Molten Metal Based on Three-Dimensional Analysis of Cluster by X-Ray Micro-Computer Tomography (CT),” *ISIJ Int.*, vol. 53, no. 11, pp. 1958–1967, 2013.
- [98] T. Li, S. Shimasaki, S. Taniguchi, S. Narita, and K. Uesugi, “Three-dimensional Observation of Nonmetallic Inclusion Clusters in Solid Metal by X-ray Micro-CT,” *ISIJ Int.*, vol. 56, no. 11, pp. 1989–1995, 2016.
- [99] P. Kaushik, J. Lehmann, and M. Nadif, “State of the art in control of inclusions, their

- characterization, and future requirements,” *Metall. Mater. Trans. B*, vol. 43, no. 4, pp. 710–725, 2012.
- [100] E. B. Pretorius, H. G. Oltmann, and B. T. Schart, “An overview of steel cleanliness from an industry perspective,” *Iron Steel Technol.*, vol. 12, no. 3, pp. 333–345, 2015.
- [101] D. Tang, M. E. Ferreira, and P. C. Pistorius, “Automated Inclusion Microanalysis in Steel by Computer-Based Scanning Electron Microscopy: Accelerating Voltage, Backscattered Electron Image Quality, and Analysis Time,” *Microsc. Microanal.*, pp. 1–9, 2017.
- [102] D. Gürsoy, F. De Carlo, X. Xiao, and C. Jacobsen, “TomoPy: A framework for the analysis of synchrotron tomographic data,” *J. Synchrotron Radiat.*, vol. 21, no. 5, pp. 1188–1193, 2014.
- [103] Z. Wei, S. Wiebe, and D. Chapman, “Ring artifacts removal from synchrotron CT image slices,” *J. Instrum.*, vol. 8, no. C06006, 2013.
- [104] F. C. Clark, Philip J. and Evans, “Distance to Nearest Neighbor as a Measure of Spatial Relationships in Populations,” *Ecology*, vol. 35, no. 4, pp. 445–453, 1954.

Appendix A Challenges in induction furnace experiments

In total 41 steel deoxidation experiments were conducted with or without slag using the induction furnace out of which 13 experiments failed. The common operational causes of failure are described in the following section. Sometimes, a new experimental setup required a few iterations and those are not described here.

- a) Temperature measurement: There are two factors that can affect temperature measurement in the induction furnace setup. The top of graphite crucible was insulated using an alumina cap. In the absence of the cap or breaking of cap the radiation loss from top of the melt surface to top cap/flange becomes significant resulting in a large temperature difference between melt and thermocouple tip. In this case, the temperature reading can be well below the actual temperature of the melt surface. The steel may be molten at a temperature reading 100s of Celsius lower than melting temperature. A second issue may arise due to interaction of the thermocouple sheath (alumina) with crucible or slag. A CaO crucible or CaO-Al₂O₃-MgO slag may easily dissolve tip of thermocouple sheath during the experiment. Sometime, sheath may pierce the CaO crucible resulting in crucible fracture.
- b) Sampling contamination: The steel samples from liquid steel melt were taken using fused-quartz tubes (o.d. = 6 mm and i.d. = 4 mm) and a pipette. Liquid steel may react with the fused quartz tube during sampling resulting in formation of aluminosilicate inclusions at the edge of sample as shown in Figure 189. Therefore, the edge of the sample should be avoided while setting up inclusion analysis area using SEM automated feature analysis.
- c) Improper insulation: The side, top and bottom of the crucible must be well insulated using high temperature refractory. Low temperature refractory may break/decompose during the experiment. Improper insulation also results in heat loss during the experiment.

- d) Cooling in induction furnace with stainless steel chamber: The water cooling is used to cool the induction coil, stainless steel chamber and heat station. The water temperature should not be too low inside the heat station as it may result in condensation of moisture on the electric circuit which may cause short-circuit and failure of equipment. During the experiment, the water must be cooled using a chilled water supply to avoid water boiling inside copper coils.
- e) Placing crucible: The entire length of the graphite crucible must be within the coil. If needed, high temperature refractory support should be placed beneath the crucible. If the bottom of the crucible is outside coil, electrolytic iron may remain solid in the bottom.

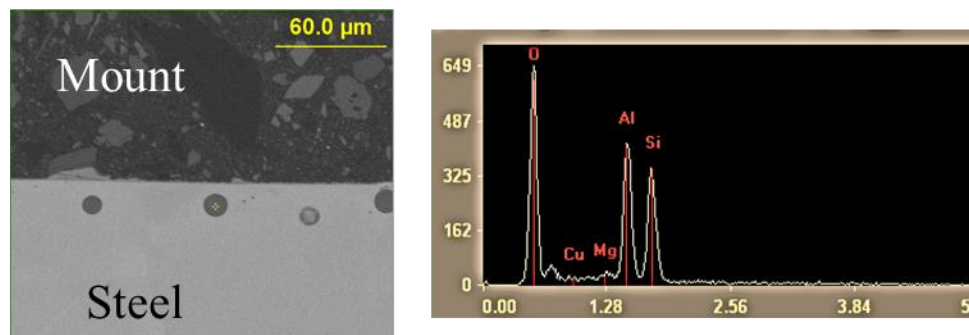


Figure 189. Aluminosilicate inclusion at the edge of sample

Appendix B Developing private database for liquid steel

FactSage allows users to create private databases using its “Solution module”. The solution database can be created based on different models like uniform interaction parameter model, associate solution model etc. However, it does not allow to create a database based on associate solution model. In this work, the uniform interaction parameter model was used to create a private database for liquid steel that could be used with other databases available in FactSage (for example slag and pure substance). Thermodynamic data of elements/compounds in reference states (known as functions) was imported from the compound database. A solution model of interest was selected (unified interaction parameter in this case). In the Solution module, sublattice, end members and interaction parameters were entered. The Gibbs free energy function for each end member was entered as shown in Figure 190 and Figure 191 (O#Gas_1 for oxygen in Gas_1 form as shown in Functions).

Interaction parameters were entered as shown in Figure 192. The appropriate reference state must be considered while specifying the value of $\ln\gamma^o$. It was necessary to select monatomic gaseous species (particularly for O and S) as functions to allow them to be directly used as end members and define interactions.

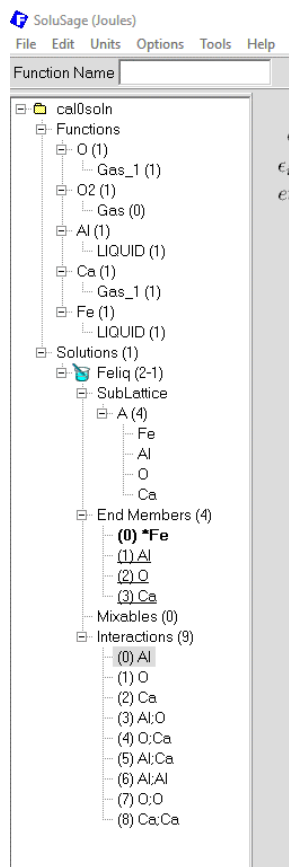


Figure 190 Structure of database

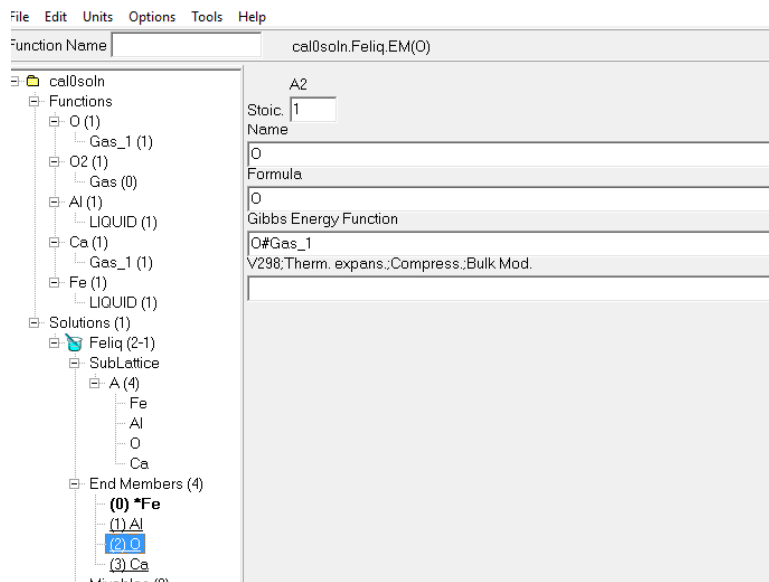


Figure 191 Writing Gibbs Energy Function for end members

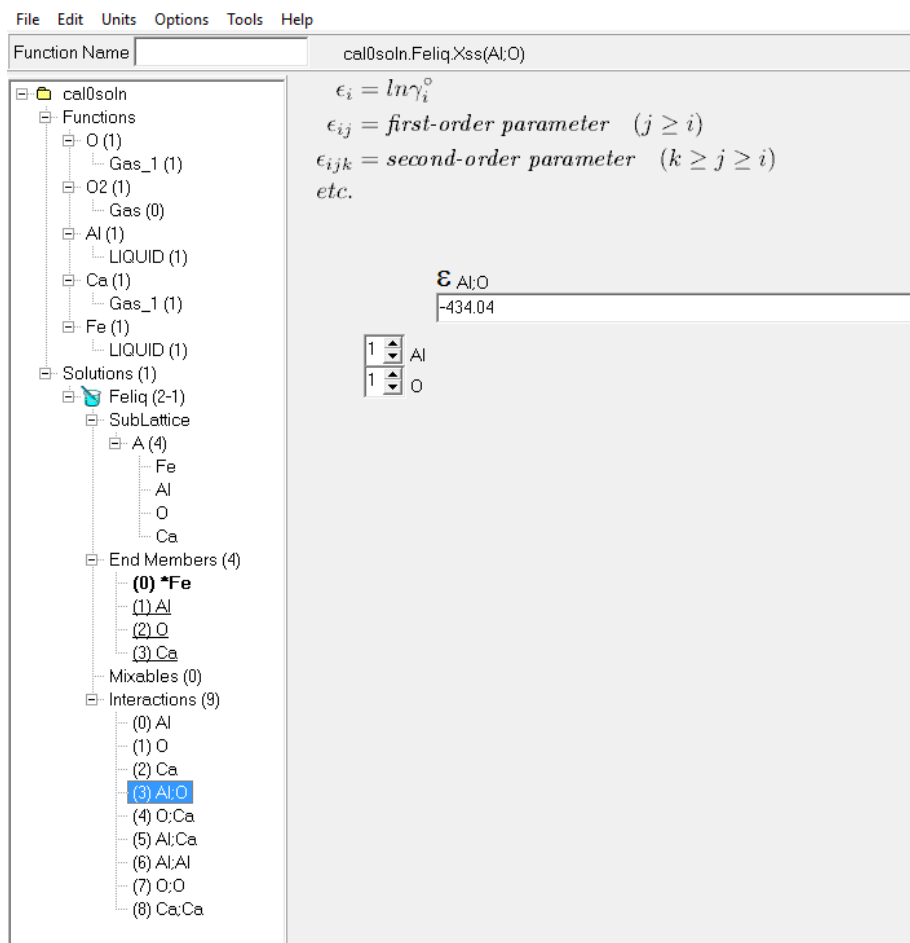


Figure 192 Entering interaction parameter

The first and second order interactions were also assessed using FTmisc (liquid steel database) and FactPS (pure substance database). The method and results of the assessment is described in Appendix C. It was important to use FactSage to derive these interaction parameters for better accuracy when private database was aimed to be used along with other databases (specifically pure substance database) for kinetic models.

Appendix C Assessing Fe-X-O using FactSage

Standard activity coefficient

The standard activity coefficient was calculated for Al, Si, Ca, O, S and Mg by plotting activity with mole fraction in steel as shown in Figure 193 using data from FactSage. All values are tabulated in Table 59. Self-interaction parameter for silicon and Ca-Al (-6.98), and Ca-Si (-12.58) interaction parameter was also calculated from similar method.

Table 59 . Standard activity coefficients of elements in liquid steel calculated using FactSage

Element	Ref. state	$\ln(\gamma^0)$
Al	Liquid	-2.85
Si	Liquid	-6.28
Ca	Vapor	7.95
O	Vapor	-13.12
S	Vapor	-8.52
Mg	Vapor	7.35

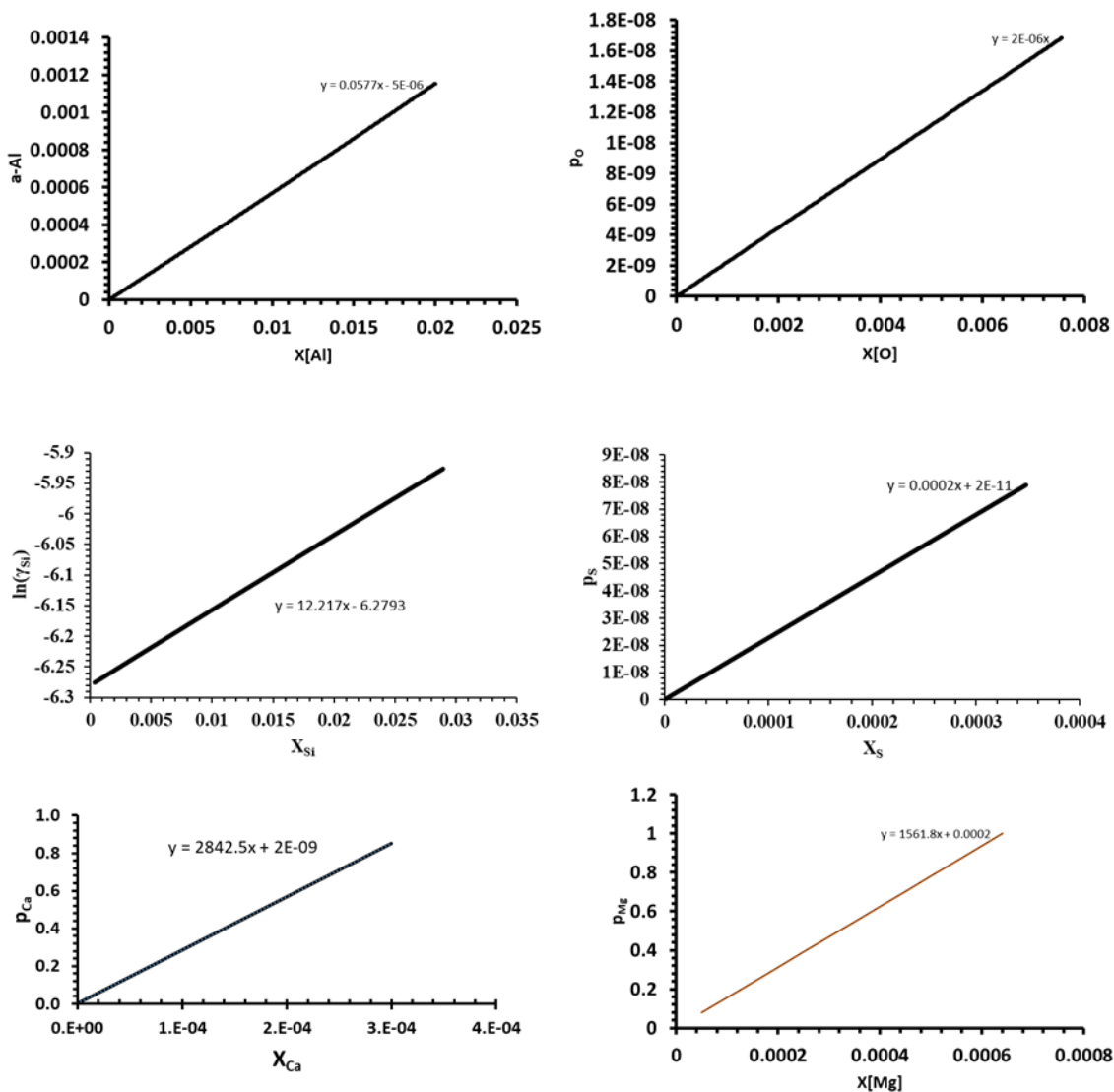


Figure 193. Extracting standard activity coefficient from FactSage

Interaction parameters for Fe-X-O system

The first and second order (where needed) interaction parameter of X (X=Al, Si, Ca, S and Mg) was calculated by plotting $\ln(\gamma_X)$ vs X_{O} . The plot was fitted to a second order polynomial and the intercept was same (or approximately same) as $\ln(\gamma_X^0)$. The coefficients of the polynomial can be considered as interaction parameters as shown by Equation 43.

$$\ln \gamma_X = \ln \gamma_X^0 + \epsilon_X^O X_O + \rho_X^O X_{Al}^2$$

Equation 43

It should be noted that the liquid steel solution is modeled using associate solution model in FactSage. While extracting first and second interaction parameter using the method described above, in some cases it was necessary to change interaction parameters for different range of concentrations as shown in Figure 194.

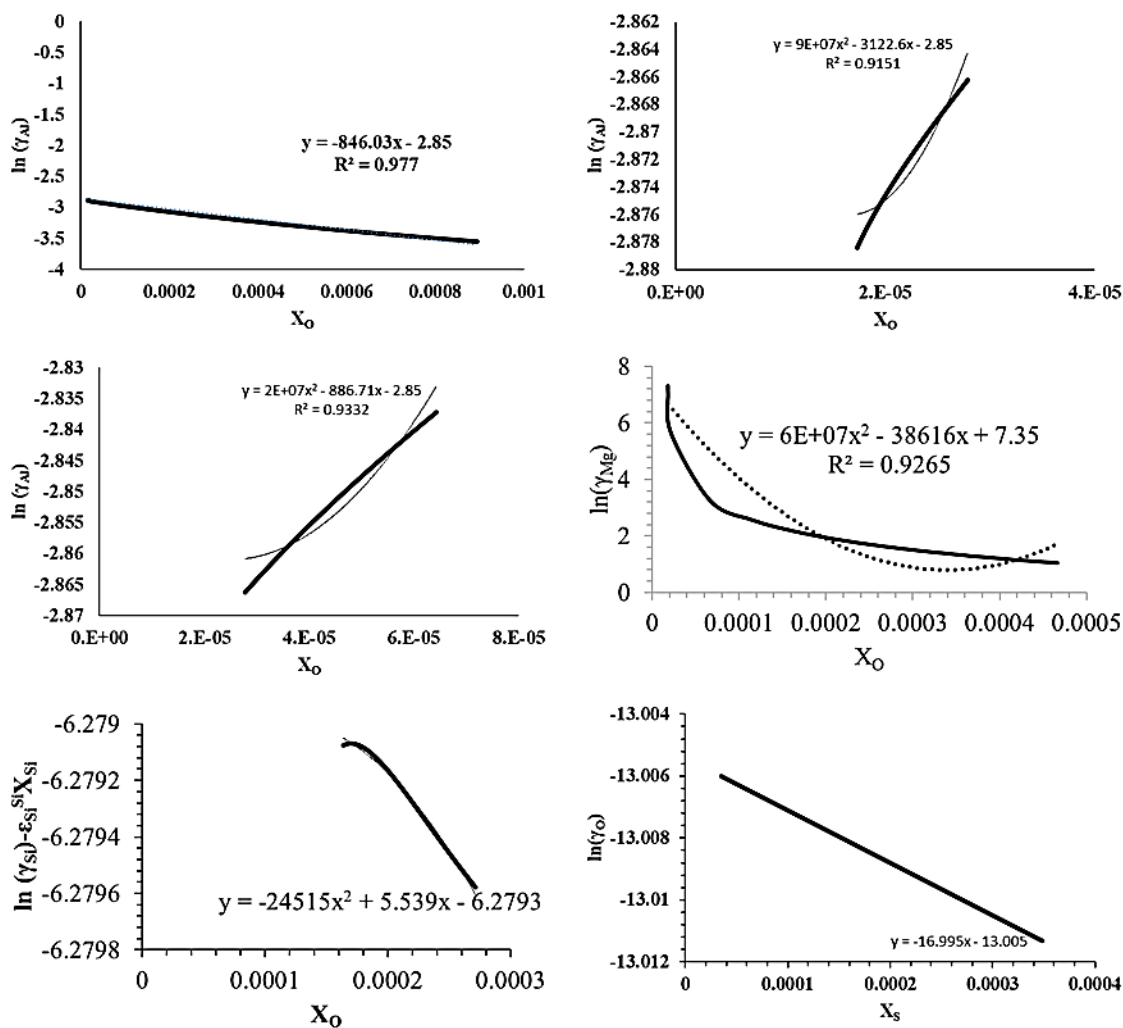


Figure 194. Extracting first and second interaction parameters for Fe-X-O system

Element	ϵ_X^O	ρ_X^O
Al (for Al<0.13 wt%)	-846	0
Al (0.13%-0.36%)	-3122.6	9×10^7
Al (0.36%-0.96%)	-886.7	2×10^7
Mg	-38616	6×10^7
Si	5.54	-24515
S	-17	0