An Investigation of Metallurgical Reactions with Levitated Droplets

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Department of Materials Science and Engineering
University of Toronto

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Abstract

The study of gas-metal interactions has industrial significance in metallurgical processes. Despite the vast production volume, the high temperature kinetics of these processes are far from fully understood. The difficulty in accounting for the effects brought by the large temperature gradients that commonly exist between gas and liquid metal phases remains a major challenge. It is therefore essential to understand and quantify the influence of these conditions on mass transfer during metallurgical reactions.

In the production of stainless steel, one of the main objectives is to minimize oxidative loss of valuable alloying elements such as chromium during the decarburization process. Carbon dioxide has a lower oxidizing potential compared to oxygen gas, and could provide a potential solution to the problem of alloy loss during the oxidation refining of stainless steel. From an economic standpoint, in order to fully utilize the advantages associated with using CO$_2$ as an alternative oxidant, decarburization should be carried out with alloy melts having high initial carbon contents. As a consequence of these considerations, an understanding of the oxidation kinetics of high carbon melts containing chromium is of fundamental importance in facilitating the implementation of a carbon dioxide based refining process.
In the present thesis, several specific experimental investigations were carried out, using electromagnetic levitation, to study the decarburization of Fe-Cr-C_{sat} alloys by carbon dioxide. However, a significant discrepancy was found between the measured decarburization rates and those predicted from models based on conventional formulations for evaluating mass transport behaviour. Although the well-established models offer accurate predictions for systems with small temperature gradients, evidence suggests that they are not suitable for the system in question. As a result of this work, new dimensionless equations for mass transport have been developed, to account for the large thermal gradients that exist between the gas and liquid metal phases. The effects of thermal diffusion on the mass transfer of gases across the boundary layer have also been explored. In this context, for the first time, thermal diffusion factors for two binary gas mixtures (CO\textsubscript{2}-Ar and O\textsubscript{2}-Ar) at 1873\textdegree{}K (1600\textdegree{}C) have been determined.

Based on the experience generated with the levitation of iron alloy droplets, an experimental methodology was developed for non-conductive silicon heating and conductive silicon levitation. Results are presented for the effects of specimen weight and applied power on the heating behaviour and temperature control of levitated silicon and silicon-iron alloy droplets. While extensive fundamental research is required to optimize the metallurgical processing of silicon and its alloys, this preliminary work provides a foundation for future studies involving the refining of metallurgical grade silicon in order to provide material which could then be used for solar grade applications.
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# Table of Contents

Abstract .................................................................................................................................................. ii

Acknowledgments ................................................................................................................................... iv

Table of Contents .................................................................................................................................. v

List of Tables .......................................................................................................................................... ix

List of Figures ......................................................................................................................................... x

1 Introduction ....................................................................................................................................... 1

1.1 Motivation ....................................................................................................................................... 1

1.2 Importance of the Present Work ................................................................................................. 1

1.2.1 Alloy retention during decarburization .................................................................................. 1

1.2.2 High temperature transport phenomena ............................................................................... 2

1.2.3 Refining of silicon for photovoltaic application ..................................................................... 2

1.3 Outline .......................................................................................................................................... 2

2 Background for the Proposed Research ........................................................................................... 4

2.1 The Levitation Technique .............................................................................................................. 4

2.1.1 Principle of electromagnetic levitation .................................................................................. 4

2.1.2 Applications of electromagnetic levitation ........................................................................... 6

2.1.3 Advantages of levitation melting ........................................................................................... 9

2.1.4 Limitations of levitation melting .......................................................................................... 10

2.2 Stainless Steel Refining ................................................................................................................. 12

2.2.1 Carbon dioxide as oxidant .................................................................................................... 13

2.3 Refining of Metallurgical Grade Silicon for the Production of Solar Cells ................................ 14

2.3.1 Metallurgical grade silicon .................................................................................................... 15

2.3.2 Impurities in silicon ................................................................................................................ 15

2.4 References ...................................................................................................................................... 17

3 Experimental Considerations ........................................................................................................... 21
3.1 Design and Construction of the Electromagnetic Levitation Facility

3.1.1 Power supply and coil design

3.1.2 IR pyrometer calibration

3.1.3 Gas train

3.1.4 General operating procedure

3.2 Specimen Preparation

3.3 References

4 Decarburization of Levitated Fe-Cr-C Droplets by Carbon Dioxide

4.1 Background

4.2 Fundamental Considerations

4.2.1 Interfacial reaction as the rate-controlling step

4.2.2 Mass transport of carbon in the liquid phase

4.2.3 Mass transport of carbon dioxide in the gas phase

4.3 Experimental Aspects

4.4 Results and Discussion

4.4.1 Effect of partial pressure of carbon dioxide

4.4.2 Natural convection

4.4.3 Effect of gas flow rate

4.4.4 Development of a new correlation for decarburization of levitated droplets

4.5 Summary and Conclusions

4.6 References

5 The Effect of Thermal Diffusion on Decarburization Kinetics

5.1 Background

5.2 The Effects of Thermal Diffusion on Mass Transfer

5.3 Evaluation of the Thermal Diffusion Factor

5.4 Development of a New Mass Transport Correlation
5.5 Thermal Diffusion in the Oxidation Behavior of Fe-Cr-C by O₂-Ar Gas Mixtures ........ 61
  5.5.1 Decarburization experiments using O₂-Ar gases .............................................. 62
  5.5.2 Effect of oxidant partial pressure ........................................................................... 62
  5.5.3 Thermal diffusion in mass transfer ......................................................................... 64
5.6 Summary and Conclusions .......................................................................................... 66
5.7 References .................................................................................................................. 67

6 Effect of Chromium-Sulphur Interactions on the Rate of Decarburization by CO₂-Ar Gas Mixtures .......................................................... 69
  6.1 Development of Rate Equation .................................................................................. 70
  6.2 Effect of Chromium .................................................................................................... 71
  6.3 Summary and Conclusions ........................................................................................ 73
  6.4 References .................................................................................................................. 73

7 Thermodynamic and Kinetic Aspects of Sulphur Evaporation from Fe-C Alloy Droplets .... 74
  7.1 Background ................................................................................................................ 74
  7.2 Experimental Aspects ................................................................................................. 75
  7.3 Results and Discussion ............................................................................................... 75
    7.3.1 Kinetics of sulphur removal .................................................................................. 76
    7.3.2 Thermodynamic considerations .......................................................................... 82
    7.3.3 Integrated rate analysis ....................................................................................... 85
  7.4 Summary and Conclusions ........................................................................................ 86
  7.5 References .................................................................................................................. 87

8 Electromagnetic Levitation of Silicon and Silicon-Iron Alloy Droplets ......................... 88
  8.1 Background ................................................................................................................ 88
  8.2 Levitation of Silicon and Silicon-Iron Alloy Droplets ............................................... 89
  8.3 Effect of Operating Parameters on Temperature Control ........................................... 91
    8.3.1 Effect of specimen mass ........................................................................................ 91
8.3.2 Effect of applied power ................................................................. 91
8.4 Conclusions .................................................................................... 93
8.5 References ....................................................................................... 94
9 Summary and Conclusions .................................................................. 95
  9.1 Summary ....................................................................................... 95
  9.2 Contributions ................................................................................. 97
    9.2.1 Contributions of impact .............................................................. 97
    9.2.2 Other contributions ................................................................... 98
  9.3 Future Work ................................................................................... 99
List of Symbols - English ........................................................................ 100
List of Symbols - Greek .......................................................................... 103
Appendix A ........................................................................................... 104
  A.1 Physical Properties ......................................................................... 104
  A.2 Material Chemical Composition ..................................................... 105
Appendix B ............................................................................................. 106
  B.1 Publications Resulting from the Thesis ........................................... 106
  B.2 Other Related Publications ............................................................. 106
  B.3 Conference Presentations ............................................................... 107
  B.4 Poster Presentations ....................................................................... 107
List of Tables

Table 3.1 Chemical composition of chromium chips from ESPI Metals (wt pct) ..................... 27

Table 3.2 Impurity concentrations of electrolytic iron from Allied Metals (wt pct) ............... 27

Table 3.3 Impurity concentrations of silicon (6N purity) pellets from ESPI Metals – supplier’s analysis (ppm) ................................................................................................................................. 27

Table 4.1 Alloy composition ........................................................................................................ 38

Table 4.2 Experimental results for decarburization using CO$_2$-Ar at low gas flow ............. 41

Table 4.3 Experimental results for decarburization using CO$_2$-Ar at higher gas flow .......... 41

Table 4.4 Comparison of experimental conditions ..................................................................... 46

Table 5.1 Experimental results for decarburization using CO$_2$-Ar at flow rate of 0.1L/min .... 56

Table 5.2 Experimental results for decarburization using O$_2$-Ar at 1873K ......................... 63

Table 7.1 Experimental results .................................................................................................. 77

Table 7.2 Equilibrium vapor pressures of sulphur-bearing gases over Fe-C-0.1 wt pct S alloys at 1873K ............................................................................................................................................... 79
List of Figures

Figure 2.1 Effect of temperature on equilibrium concentrations of carbon and chromium in molten steel ($P_{CO}=1$ atm). ............................................................. 13

Figure 2.2 Effect of temperature on the oxidation of chromium by $O_2$ and $CO_2$. .................... 14

Figure 3.1 Schematic representation of the electromagnetic levitation apparatus. ......................... 22

Figure 3.2 Schematic diagram of the levitation coil. .................................................................... 23

Figure 3.3 Schematic diagram of the induction furnace system for pyrometer calibration and preparation of alloys. ................................................................. 24

Figure 3.4 Pyrometer calibration results obtained using the assembly shown in Fig. 3.3. .............. 24

Figure 3.5 Pyrometer calibration results with different copper droplets. .................................... 25

Figure 3.6 Schematic diagram of the gas train system. ................................................................. 26

Figure 4.1 Chromium loss during decarburization in induction furnace at 1873K (1600°C)$^{[5]}$. 29

Figure 4.2 Flux of reactants arriving at the gas-metal interface as a function of carbon concentration in the metal. ............................................................. 38

Figure 4.3 Variation of carbon, sulphur and chromium contents with exposure time. ................. 40

Figure 4.4 Effect of oxidant partial pressure on decarburization rate. ........................................ 42

Figure 4.5 Comparison of observed and predicted Sherwood numbers as a function of the Rayleigh number. ........................................................................ 43

Figure 4.6 Linear regression of the data as represented by Eq. (4.13) from present work. ........... 44

Figure 4.7 Effect of flow rate on the rate of decarburization for Fe-20Cr-C alloy. ....................... 45

Figure 4.8 Comparison of observed and predicted Sherwood numbers as a function of the Reynolds number. ........................................................................ 46
Figure 4.9 Linear regression of the data expressed in terms of Eq. (4.19) from present work.

Figure 4.10 Comparison of correlation data derived from previous decarburization studies[^18,20] with Eq. (4.20) from the present work.

Figure 5.1 Evaluation of \( \alpha \) for the Ar-CO\(_2\) system at 1873K (1600°C).

Figure 5.2 Linear regression of the data expressed in terms of Eq. (5.12) from present work.

Figure 5.3 Comparison of correlation data derived from previous decarburization studies[^12,13] with Eq. (5.13) from present work.

Figure 5.4 Comparison of experimental data with the Ranz-Marshall equation and the Whitaker equation.

Figure 5.5 Change of carbon concentration with reaction time at different oxygen partial pressures for droplets containing a) \([\text{Cr}]=10\) wt pct and b) \([\text{Cr}]=17\) wt pct.

Figure 5.6 Effect of oxidant partial pressure on decarburization rate.

Figure 5.7 Composition dependence of \( \alpha \) for Ar-O\(_2\) system at 1873K.

Figure 5.8 Temperature dependence of \( \alpha \) for Ar-O\(_2\) gas mixtures.

Figure 6.1 Effects of gas flow characteristics and melt sulphur content on the rate of carbon removal.

Figure 6.2 Effect of melt sulphur content on decarburization rate.

Figure 6.3 Change of available surface sites with melt sulphur and chromium contents.

Figure 7.1 Change in sulphur concentration with time.

Figure 7.2 Change in carbon concentration with time.

Figure 7.3 Desulphurization of Fe-C-S alloys at 1873K.

Figure 7.4 Equilibrium vapor pressures over Fe-C-0.1 wt pct S alloys at 1873K.
Figure 7.5 Results for desulphurization of Fe-C-S alloys \( (e_S^C = 0.11, r_S^C = 0.0058) \) .............. 82

Figure 7.6 Comparison of the measured equilibrium sulphur concentration with thermodynamic prediction. ................................................................. 85

Figure 7.7 Kinetic analysis using the proposed interaction parameters.............................. 86

Figure 8.1 Schematic diagram of the electromagnetic levitation assembly......................... 90

Figure 8.2 Levitation of a silicon alloy droplet.............................................................. 90

Figure 8.3 Quenched silicon sample.......................................................................... 90

Figure 8.4 Heating profiles for silicon-iron droplets containing 15% iron......................... 91

Figure 8.5 Heating behavior of silicon-iron alloy droplets at two levels of applied power.... 92

Figure 8.6 Effect of applied power on the steady state temperature of Si-Fe alloy droplet. .... 93

Figure 8.7 Effect of specimen mass on droplet temperature. ........................................ 93
1 Introduction

1.1 Motivation

Reactions between gas and molten metal droplets have been an important topic in many metallurgical applications. In many processes of interest, transfer of mass between spherical surfaces and flowing fluids are extremely important. In ironmaking, for instance, high intensity bath smelting generates large quantities of metal and slag droplets. The reactions between these drops and the post-combusted gases can greatly influence the process efficiency. Similarly, in a certain spray degassing process developed for steelmaking, the operating parameters such as droplet size, droplet velocity, inert gas flow rate, and system pressure largely determine the productivity. More recently, emphasis on process sustainability has encouraged the metallurgical industries to develop heat recovery technologies for metallurgical slags. The feasibility of these energy-saving technologies relies on the reaction characteristics between the finely dispersed molten slags and the rising gases with which it may react to produce steam or syngas.

Metallurgical processes benefit greatly from the improved reaction rates at elevated temperatures. However, the kinetic aspects of these reactions are not fully understood. Electromagnetic levitation is an excellent tool for conducting these fundamental investigations without the complications arising from the presence of a solid container made from refractory materials and is chosen as the principal experimental technique for the present study.

1.2 Importance of the Present Work

1.2.1 Alloy retention during decarburization

Oxidative loss of valuable alloy elements such as chromium during the last stages of decarburization in refining stainless steels poses economic and environmental challenges. Even with argon dilution, decarburization by oxygen leads to extensive oxidation of alloying metals. Thus, development of methods to achieve alloy retention is indispensable for the production of high alloy melts. The present work explores the viability of utilizing carbon dioxide, instead of oxygen, as the oxidant gas for decarburization so that chromium loss is minimized.
1.2.2 High temperature transport phenomena

Steel decarburization by carbon dioxide is one system that has particular implications for the ferrous industry. In order to realize the benefit of valuable metal retention associated with the process and to improve its industrial feasibility, it is essential to gain a fundamental understanding of the reaction and related transport mechanisms. Although rate data on decarburization by carbon dioxide have been reported in some detail, there is still uncertainty concerning an appropriate mass transport correlation that would be applicable to describe the kinetic conditions. The presence of a steep temperature gradient near the gas-metal interface, an inherent feature of metallurgical processes, gives rise to variation in gas properties and flow patterns across the boundary layer and as a result, quantification of mass flux of this origin becomes important. However, values for transport coefficients, particularly thermal diffusion factors, are sparse at high temperatures.

Accordingly, this thesis mainly focuses on the study of mass transport by convection, mass transport by thermal diffusion, and control mechanism by surface adsorption that is frequently associated with steel decarburization by carbon dioxide or oxygen. A series of investigations were devised and performed to better our understanding of gas-metal reactions at high temperatures.

1.2.3 Refining of silicon for photovoltaic application

Solar power is an emerging source of energy. Refining of solar-grade silicon through metallurgical routes, from both economic and environmental perspectives, is an appealing alternative to the traditional chemical methods. However, unlike the already established ferrous industry, where thermodynamic data are readily available, extensive fundamental research is required to optimize the metallurgical processing of silicon and its alloys. Therefore, preliminary work on levitation of silicon and silicon-iron alloys was carried out with the goal of setting the groundwork for future studies.

1.3 Outline

The remainder of this thesis is structured as follows: Chapter 2 covers background aspects on the levitation technique, refining of stainless steel, and refining of solar grade silicon. Chapter 3 discusses the specifics of the experimental methods, which include the design and construction
of the electromagnetic levitation apparatus, general operating procedure, specimen preparation and chemical analysis of samples. Chapter 4 presents experimental results for the decarburization with CO$_2$ at 1873K. To express the kinetics of decarburization, a new mass transfer correlation to take account of contributions from molecular diffusion, natural convection, and forced convection has been proposed. In Chapter 5, based on the concept of thermal diffusion, an alternate interpretation is developed for the kinetic data presented in Chapter 4. In addition, details are provided of the experimental evaluation of the thermal diffusion factors for CO$_2$-Ar and O$_2$-Ar gas mixtures at 1873K. Chapter 6 provides a comprehensive evaluation of the influence of chromium on the decarburization kinetics for systems involving CO$_2$ as the oxidant in the presence of the surface active element sulphur. Chapter 7 presents the results of an experimental investigation on the cause of sulphur loss during the decarburization experiments with CO$_2$. The development of an experimental methodology for the electromagnetic levitation of silicon and ferrosilicon alloys is presented in Chapter 8. Finally, Chapter 9 reviews the major findings of the thesis and presents suggestions for future work.
2 Background for the Proposed Research

This chapter presents details of the relevant literature and background information pertaining to the scope of the thesis. The first section provides a comprehensive review of the levitation technique and its applications in high temperature studies. The fundamental aspects of stainless steel decarburization and solar-grade silicon refining are discussed in the subsequent sections.

2.1 The Levitation Technique

A conductor can be made to levitate when placed in a varying electromagnetic field. The electromagnetic field is usually created by passing large alternating currents through a water-cooled copper coil, which is specifically designed to produce field patterns that offer predictable temperature control and droplet stability. When a conductor, in this case a metallic specimen, experiences change in the magnetic field, eddy current is induced on the surface of the specimen. In addition to heating the specimen by induction, the presence of circulating eddy current will generate a magnetic field on the surface of the specimen. The induced magnetic field opposes the applied magnetic field thereby providing a repulsive effect, or lifting force. The strength of induced eddy current and magnetic field will depend on the following factors:

- Strength of the applied magnetic field
- Electrical conductivity of the specimen
- Rate of change in applied magnetic field, or frequency of applied alternating current

2.1.1 Principle of electromagnetic levitation

A conductor can be made to levitate by balancing the electromagnetic body force (Lorentz force) and the gravity force which can be described using the governing equation[1]:

\[ J \times B = \rho g \]  \hspace{1cm} (2.1)

where \( J \) is the eddy current induced by the alternating magnetic field \( B \), \( \rho \) is the density of the levitated material and \( g \) is the gravitational constant. For a levitation (or solenoid) coil, the \( B \) function can be obtained by solving the Biot-Savart equation[2]:
\[ dB = \frac{\mu_m I}{4\pi} \frac{dl \times r}{r^3} \] (2.2)

where \( \mu_m \) is the magnetic permeability of the material, \( I \) is the coil current (power), \( r \) is the radial position, and \( dl \) is the length element along the current path. The direction of the field \( dB \) is normal to a plane containing \( dl \).

The eddy current \( J \) flows in an electrically conductive media, in this case molten metal, and has two main contribution sources 1) current induced by an alternating magnetic field and 2) current induced by the motion of an electrically conductive fluid under a magnetic field which can be expressed mathematically as follows\(^{[1]}\):

\[
J = \sigma \left[ \left( -\frac{\partial A_v}{\partial t} \right) + (\nu \times B) \right]
\] (2.3)

where \( \sigma \) is the electrical conductivity of the molten metal, \( \nu \) is the flow velocity, and \( A_v \) is the vector potential of a magnetic flux, defined as \( B = \nabla \times A_v, \nabla \cdot A_v = 0 \).

Although a full solution of the system may not be trivial, it is still possible to relate the coil current (applied power) to the gravity force (sample mass) by solving the above equations while taking account of joule heating, and heat dissipation through radiation loss. A conventional solution\(^{[3]}\) of the system can be found in the fundamental principle of electromagnetic casting which utilizes the following relation:

\[
\rho gh_z = \frac{B^2}{2\mu_m}
\] (2.4)

The magnetic field inside a levitation coil can be approximated with a solenoid infinite in length. A simplified solution to the Biot-Savart equation is\(^{[3]}\):

\[
B = \mu_0 \frac{N}{L} I
\] (2.5)

where \( \mu_0 \) is the magnetic constant, \( N \) is the number of turns and \( L \) is the length of the solenoid. This solution, however, implies that \( B \) is independent of the length and diameter of the solenoid.
and is uniform over the cross-section of the solenoid. Upon combining the two equations, the following relationship is obtained:

\[
\rho g h_z = \frac{\mu_0^2}{2\mu_m} \left( \frac{N}{L} \right)^2 I^2
\]  

(2.6)

This expression served as a useful tool in the initial development of the coil design used in the present work.

2.1.2 Applications of electromagnetic levitation

As both laboratory and industrial tool, the levitated droplet technique has served in many areas of research and application such as:

- Alloy preparation
- Material synthesis and casting
- Metal purification
- Measurement of physical properties
- Determination of thermodynamic properties
- Evaluation of reaction kinetics

Containerless levitation melting is an ideal technique for preparation of reference alloys that require precise control of homogeneity and chemical composition, and are often sensitive to contaminants such as materials for nuclear applications\cite{4}. Morita et al.\cite{5} successfully produced a titanium-tantalum alloy for biomedical applications from pure metals using the cold-crucible electromagnetic levitation melting approach. Due to the highly reactive nature of the alloying components as well as significant difference in the corresponding melting points and specific gravity, uniform Ti-Ta alloy synthesis was difficult to achieve using conventional furnaces. However, good composition homogeneity was found within the 1 kg Ti-15wt pct Ta alloy produced by a cold-crucible arrangement, a variation of the electromagnetic melting setup. Sypien et al.\cite{6} prepared Ti-Ni-Fe alloys using an electromagnetic levitation facility in their investigation of the crystallization process and associated intermetallic microstructures.
In addition to alloy preparation, the levitated droplet technique has recently found application in the synthesis of new materials. Nanoparticles of pure Fe were produced in bulk quantity by Kermanpur *et al.*[7] using electromagnetic levitation in conjunction with He-20%Ar gas condensation.

Purification of niobium by impurity evaporation under vacuum using electromagnetic levitation was first reported by Begley *et al.*[8]. Recently, Beaudhuin *et al.*[9] utilized a levitation technique to achieve impurity solute rejection in undercooled molten silicon.

Levitation melting has also been used extensively in the determination of physical properties including surface tension, density, viscosity, electrical resistivity, thermal conductivity and specific heat.

Several studies have been made of surface tension measurement for molten metals, first pioneered by Lu and his co-workers[10,11], by relating the frequency of droplet surface oscillation through the Rayleigh equation. This technique has subsequently led to the measurement of surface tension and its temperature dependence of common liquid metals including Fe[10-13], Ni[11-13], Co[12,13], Cr[13], Cu[12,14,15], Ag[12], Zn[12], Pb[12], Cd[12], and Sn[12]. However, it was recognized[12] that the surface tension values obtained by the oscillating drops, a dynamic method, were noticeably higher than those obtained by the sessile drops, which is considered a static method. Later, Keene *et al.*[16] concluded that the levitating drop is a suitable technique for yielding reliable measurements by comparing the data from two independent sources. As pointed out by Soda *et al.*[17], the reported discrepancy is attributed to the high sensitivity of the oscillation amplitude.

In the absence of container-induced heterogeneous nucleation, surface tension measurements at high degrees of undercooling were also achieved[11,13]. Zhou *et al.*[18] recorded the oscillation of undercooled liquid Ti-51 at. pct Al with photodetector viewing from above the droplet in an electromagnetic levitation facility. Similar measurements were performed by Wang *et al.*[19] on monotectic Fe-Cu-Mo alloys. The work by Nogi *et al.*[20] detailed the effects of several alloying elements on the surface tension of Ni-based and Fe-based alloys. Comprehensive investigations were also carried out to study the effect of dissolved oxygen on the surface tension of Cr[21] and Fe[22,23]. More recently, Egry, Brillo and co-workers[24-29] studied the surface tension and density of pure copper, nickel, iron, titanium, aluminum, and their binary alloys. Further, Brillo *et al.*
reported surface tension data over a wide temperature range on Al-Cu-Ag, Cu-Co-Fe, and Ni-Cu-Fe ternary alloys.

The effect of different oxygen partial pressure on the surface tension of molten Ag, Si, and Fe-18Cr-8Ni was determined using the electromagnetic levitation technique under controlled atmosphere. Generally, under low oxygen partial pressure, it was observed that surface tension increases with decreasing temperature. However, the slope of the surface tension-temperature plot, often referred to as the temperature coefficient, varies with oxygen partial pressure. For silver and stainless steel, the temperature coefficient changes from negative to positive as the partial pressure of oxygen increases. Whereas results indicated that the surface tension of silicon decreases with increasing oxygen partial pressure and the sign of the temperature coefficient does not change. Under equilibrium conditions for SiO2 formation, the thin oxide layer on the surface of the Si droplet may have contributed to this finding.

The levitated droplet technique has long been a prominent method for density measurement. Ward and his co-workers calculated the density of Cu and Ni from an optically projected profile of a droplet of known weight. On the basis of this technique, Egry, Brillo and co-workers measured the density of various binary alloys: Al-Si, Al-Fe, Al-Ni, Al-Ag, Al-Cu, Cu-Ni, Ag-Cu, Ag-Au, Au-Cu. To further improve the accuracy of this method, Inatomi et al. utilized a static magnetic field to suppress surface oscillation on pure silicon droplets during density measurements. Adachi et al., using similar methodology, measured the density of Si-Ge alloys at temperatures from 1350K to 1650K.

The heat capacity of titanium and zirconium has been measured by Guo et al., using electromagnetic levitation and a modulated power method. The modulated power method takes account of delayed temperature response as a result of heating by slowly modulating the applied power in sinusoidal profile; with known emissivity of the samples, specific heat of the sample can be deduced using the Stefan-Boltzmann relation. Utilizing the crucible-free advantage, Barth et al. studied the temperature dependence of enthalpy and specific heat of undercooled Ni and Fe melts using combined electromagnetic levitation and drop calorimetry techniques.

The levitation technique is particularly suited for thermodynamic studies involving gas-metal reactions since errors caused by reaction with crucible material can be avoided. Gomersall et al. have reported data for the solution of nitrogen in levitated Fe-C droplets and provided
values for first and second order carbon-nitrogen interaction parameters. Using a similar
technique, Kershaw et al.\textsuperscript{48} studied the effect of vanadium on oxygen activity by equilibrating
Fe-V droplets with H\textsubscript{2}O/H\textsubscript{2} gas mixtures. However, it was noted\textsuperscript{48,49} that corrections are needed
to account for the observed thermal diffusion effects when H\textsubscript{2}O/H\textsubscript{2} gas mixtures are employed in
levitated droplet studies to determine values for equilibrium constants. The errors caused by
thermal diffusion can be greatly reduced by increasing the mean square root of the molecular
weight of the gas mixture. Hence, in a study of interactions between chromium and oxygen in
liquid iron, Larché and McLean\textsuperscript{50} conducted their droplet experiments with CO/CO\textsubscript{2} gas
mixtures to control the oxygen potential. Based on this knowledge, sulphurization studies were
carried out by Sunderland et al.\textsuperscript{51} using H\textsubscript{2}S/H\textsubscript{2} gas mixtures to quantify the influence of
thermal diffusion, which in turn, can be applied to thermodynamic and kinetic data obtained
from levitation experiments.

In their work on equilibrium distribution of Mn between liquid iron and slag, Caryll and Ward\textsuperscript{52}
have demonstrated that this technique can be further extended to study interactions between slag
and molten metal phases.

Since the geometry of the levitated droplet system is accurately known, a number of studies have
been conducted to investigate the kinetic aspects of nitrogen absorption\textsuperscript{53} and oxidation
reactions\textsuperscript{54} during steelmaking operations.

2.1.3 Advantages of levitation melting

Applications discussed in section 2.1.2 utilize many of the advantages associated with the
levitation melting technique, which are summarized below:

\textit{Lack of melt contamination:} The absence of crucible contact with the molten specimen
effectively rules out contamination from refractory materials. The containerless approach also
permits studies that involve aggressive materials such as titanium, zirconium, etc.

\textit{Rapid melting:} Generally, the time required to heat a metal specimen to the desired temperature
is less than a minute. In addition, enhanced consistency of experimental data is expected due to
increased number of experiments per unit time. The elimination of contact with physical support
also prevents the need to pre-heat refractory materials that are sensitive to thermal shock.
Wide temperature range: A wide temperature range is available for levitation experiments. The upper limit depends on the extent of specimen vaporization, which can be circumvented by pressurizing the system. Given the absence of potential heterogeneous nucleation sites, considerable undercooling may be achieved. Undercooling of liquid iron by 400 degrees has been reported by Gomersall et al.\textsuperscript{[55]}

Melt stirring: Vigorous inductive stirring as a result of the applied electromagnetic field ensures that the melt is homogenous throughout an experiment. In addition to uniform droplet temperature, the melt stirring effectively removes the solute-depleted layer near the surface and therefore increases the rate of mass transfer for liquid-gas interactions, as well as solute evaporation.

Spherical melt geometry: The well-defined melt geometry facilitates mathematical modeling of liquid-gas interactions. When compared with the melt geometry found in experiments conducted using crucibles, spherical melt geometry presents benefit in surface area to volume ratio, which is advantageous in studies of phenomena such as impurity evaporation.

2.1.4 Limitations of levitation melting

While levitation melting has several advantages, there are also certain limitations:

Non-conductors: The specimen to be levitated needs to be an electrical conductor.

Temperature control: In many studies, it is necessary to obtain precise control of temperature. Electromagnetic levitation, however, often requires external efforts to maintain stable droplet temperature since the applied alternating current to the coil provides both lifting force and heating energy to the specimen. The required electromagnetic field, while sufficient to levitate the specimen, is sometimes found to provide excessive heat and the specimen must be cooled by convection with controlled flow rate of high purity inert gas. Zuliani\textsuperscript{[56]} summarized five parameters that affect the droplet temperature during levitation:

- Electrical power to the coil: The magnitude of power applied to the coil controls the vertical position of the droplet within the electromagnetic field, which, in turn determines the density of electromagnetic field lines that interact with the droplet. Reducing the lift force by decreasing the power will allow the droplet to position lower within the coil, where the field
flux is higher. As a result, the droplet temperature increases. Conversely, the droplet temperature decreases if the droplet sits higher within the electromagnetic field by applying increased power to the coil.

- Frequency of applied current: In high frequency AC powered levitation, the induced eddy current is largely found on the near-surface of the specimen. Known as the skin-effect, this increases the effective electrical resistance and therefore increases the efficiency of heating the specimen inductively. The extent of the skin-effect is measured by the penetration depth of the eddy current, which is found to decrease with increasing frequency of the applied current. In other words, the droplet temperature tends to increase with increasing current frequency at the expense of a decrease in the lifting force.

- Physical properties of the specimen: Material properties such as density, electrical conductivity and magnetic permeability can inherently influence the vertical position of the droplet within the coil. While directly proportional to the droplet lifting force, the depth of eddy current penetration decreases with increasing electrical conductivity and magnetic permeability of the material. Accordingly, droplets with higher density, electrical conductivity and magnetic permeability will sit lower within the electromagnetic field and receive greater heat generation.

- Coil-droplet coupling distance: The density of field flux lines passing through the droplet increases with decreasing coil-droplet separation distance. As the distance separating the excitation coil and specimen decreases, the current generated in the droplet increases thus leading to increased temperature.

- Atmosphere: The presence of a continuous gas flow will decrease the droplet temperature through convective cooling. Since thermal conductivity of a gas varies as the reciprocal of the molecular weight, gases such as hydrogen and helium are effective cooling agents.

Large temperature gradient within the gas boundary layer: Gases for the purpose of reaction with the droplet or simply for cooling will experience abrupt temperature difference at the droplet-gas interface. A steep temperature gradient exists when gases at room temperature interact with the surface of the droplet at elevated temperature. The wide variation of physical properties in the vicinity of the droplet-gas interface often poses complexity in evaluating
diffusivity data obtained in the presence of thermal diffusion effects caused by the steep temperature gradient.

### 2.2 Stainless Steel Refining

Stainless steel is primarily an iron-chromium-carbon alloy that, depending on the intended applications, may contain varying amounts of nickel, molybdenum, titanium, niobium etc. The challenges involved in the making of stainless steel lie in the retention of chromium while achieving sufficiently low carbon concentration. If typical electric arc furnace or basic oxygen furnace operations for carbon steel refining were used to produce stainless steel, considerable amounts of chromium will be oxidized before the target carbon concentrations can be reached. The chromium-carbon relationship can be described with the following reaction:

\[
Cr_2O_3(s) + 3C = 3CO(g) + 2Cr
\]  
(2.7)

The standard state for the activities of dissolved species (Cr and C) is chosen to be 1 wt pct. For the activity of Cr$_2$O$_3$ in the slag, the pure substance is taken as the standard state. The standard state of 1 atm is designated for CO. The equilibrium constant and of Equation (2.7) may be defined as:

\[
K = \frac{p_{CO}^3a_{Cr}^2}{a_{Cr_2O_3}a_C^3}
\]  
(2.8)

\[
\Delta G^0 = 776500 - 486.82T\left(\frac{J}{mol}\right)
\]  
(2.9)

In 1973, Krivsky[57] found that oxygen, with argon dilution, can effectively decarburize the melt without incurring excessive oxidative loss of chromium to the slag. This observation subsequently prompted the development of the Argon-Oxygen Decarburization (AOD) process that revolutionized stainless steelmaking. The working principle of the AOD process is based on the concept that the partial pressure of CO is decreased when oxygen is injected with argon as a diluent. Reaction will thus proceed forward according to Equation (2.7), thereby allowing higher chromium concentrations to be in equilibrium with lower carbon contents. However, in the final stages of decarburization, even with elevated argon dilution, chromium oxidation will nonetheless take place due to the scarce supply of carbon and the high affinity of chromium for
oxygen. Therefore, ferrosilicon is normally added to recover chromium from the slag at the end of the decarburization process.

2.2.1 Carbon dioxide as oxidant

Since the advent of the AOD process, many investigations were undertaken to study and improve the various process routes for stainless steelmaking. The processes are often developed based on manipulation of temperature, gas dilution and pressure in which the latter is the basis for the Vacuum Oxygen Decarburization (VOD) process.

As shown in Figure 2.1 the carbon concentrations in equilibrium with specific chromium contents can be significantly lowered by simply raising the melt temperature. However, this approach is not without problems. In particular, refractory life is greatly compromised.

![Figure 2.1 Effect of temperature on equilibrium concentrations of carbon and chromium in molten steel (P_{CO}=1 atm).](image)

In general, the gas mixture injected through the tuyeres during decarburization mainly consists of oxygen as the oxidant with nitrogen or argon as the diluents. However, it has been recently demonstrated[58] that using CO$_2$ in steel decarburization is a promising approach for the retention of valuable alloying elements. In principle, CO$_2$ decarburization is similar to both the dilution (AOD) and vacuum (VOD) processes in that it lowers the oxygen potential in the steel bath, thus giving preference to the oxidation of carbon rather than chromium. The oxidation of chromium by oxygen can be described by:
\[ 2Cr + \frac{3}{2} O_2(g) = Cr_2O_3(s) \]

\[ \Delta G^0 = -1190350 + 357.91T \] (2.10)

For comparison, the reaction involving carbon dioxide is:

\[ 2Cr + 3CO_2(g) = Cr_2O_3(s) + 3CO(g) \]

\[ \Delta G^0 = -342400 + 98.32T \] (2.11)

Based on these relationships, Figure 2.2, shows that carbon dioxide has a weaker tendency to oxidize chromium compared to oxygen. Thus it would appear that CO\textsubscript{2} may be an advantageous oxidizing agent for stainless steel decarburization.

![Figure 2.2 Effect of temperature on the oxidation of chromium by O\textsubscript{2} and CO\textsubscript{2}](image)

**2.3 Refining of Metallurgical Grade Silicon for the Production of Solar Cells**

In the search for sustainable energy, it is expected that solar energy will increasingly become an alternative primary source for replacement of fossil fuels. In recent years, the growing demand for green energy together with the diminishing supply of fossil fuels have increased solar research as well as the production of solar cells\textsuperscript{[59]}. However, the cost for solar power generation is still significantly more than that from fossil fuels. The solar-grade silicon (SOG-Si), used in the production of solar cells accounts for 20% of the manufacturing cost. In order to satisfy the economic constraints related to mass-production of solar power generation devices, it is
important to explore alternative sources for the generation of SOG-Si.

Presently, raw materials for solar cell production are obtained from off-grade silicon from the semiconductor industry\textsuperscript{[59]}. Since greater volumes of silicon raw materials will be necessary to meet future solar power requirements, a cost-effective manufacturing route must be devised for SOG-Si production. A possible approach is to upgrade metallurgical grade silicon (MG-Si) by reducing impurities to the levels required for SOG-Si. Johnston \textit{et al.}\textsuperscript{[60]}, in their comprehensive report, have described recent developments for SOG-Si production by metallurgical processing routes.

\subsection*{2.3.1 Metallurgical grade silicon}
As the second most abundant element in the earth’s crust, silicon, due to its high affinity for oxygen, exists in nature either as silica (SiO\textsubscript{2}) or in the form of silicates (MeSiO\textsubscript{x}).\textsuperscript{[61]} High purity, silicon-containing ores (less than 100 ppm impurity) are used as raw materials for the production of MG-Si. Coke reduction of the oxide ores takes place in an electric arc furnace at temperatures above 2000 degrees Celsius. Silicon oxide reduction by carbon can be represented by the reaction:

\[
\text{SiO}_2 + 2\text{C} + \text{O}_2 = \text{Si} + 2\text{CO}_2 \quad (2.12)
\]

MG-Si is mostly used for alloying and deoxidizing steel. A small fraction of the supply is further purified using chemical methods to provide raw materials for the semiconductor industry.

\subsection*{2.3.2 Impurities in silicon}
The power conversion efficiency of solar cells depends largely on the impurity level in the silicon raw materials. Since the presence of impurities will adversely influence the solar cell performance, the refining of MG-Si to produce SOG-Si mainly involves the reduction of impurities by several different processes.

It was found that most impurities have extremely low solubility limits in solid silicon compared to that in the liquid phase. Given that the impurity concentrations vary greatly between solid and liquid silicon, directional solidification refining can prove advantageous. During such a process, the homogenously dispersed solute (impurity), upon cooling just below the melting point of silicon, will redistribute disproportionately between the solid and liquid phase. At the advancing
solid-liquid front, the impurities, which are less soluble in the solid phase, will be retained within the liquid phase. Consequently, the impurities will be concentrated within the last-to-solidify liquid, while the first-to-solidify material will have fewer impurities than the initial liquid phase. The solute distribution behaviour for each impurity, i, can be represented by the segregation coefficient, \( k_i \), defined as:

\[
k_i = \frac{C_i^S}{C_i^L}
\]  

(2.13)

where \( C_i^S \) and \( C_i^L \) are the impurity concentrations in the solid phase and liquid phase respectively.

The concentration of impurities with a small segregation coefficient, typically less than \( 10^{-5} \), will be reduced significantly after the first solidification. Repeated directional solidification is often employed to ensure impurities with slightly larger segregation coefficients (up to \( 10^{-2} \)) are reduced to an acceptable level. Most impurities in silicon can be removed by directional solidification except for phosphorus and boron whose segregation coefficients are 0.35 and 0.8 respectively. The amount of boron and phosphorus in MG-Si ranges from 10 to 50 ppm, and is intrinsically related to the process of ore reduction with coke in the electric arc furnace. Morita and Miki\[62\] have suggested boron removal by plasma-assisted oxidation as an effective approach. Hu et al.\[63\] have shown that more than 88% reduction in boron, to levels less than 7 ppmw, can be achieved by an oxidation slagging method. Miki et al.\[64\] confirmed that phosphorus has a relatively high vapor pressure, and could be removed by vacuum refining. Several studies have shown that dephosphorization by vacuum distillation\[65-67\] and electron beam remelting\[68\] are feasible routes for phosphorus removal from molten silicon.

Vapour pressure of silicon at 1700 K, slightly above its melting point, is approximately 0.0689 Pa\[64\]. At the same temperature, impurities with higher vapour pressure such as phosphorus, aluminum, and calcium, are likely to be removed by surface evaporation. The work by Wei et al.\[67\] utilized the difference in vapour pressure between species to remove phosphorus from molten silicon under vacuum conditions. The results indicated that removal of phosphorus from molten silicon using vacuum distillation is a feasible approach provided attention is given to the importance of kinetic conditions.
2.4 References

753-757.


3 Experimental Considerations

3.1 Design and Construction of the Electromagnetic Levitation Facility

A schematic representation of the electromagnetic levitation facility is shown in Figure 3.1. The equipment consists of a quartz tube, a levitation coil, an aluminum rotatable platform, a copper mold and a specimen charging rod. The quartz tube, 15 mm in outer diameter, 13 mm in inner diameter and 304 mm in length, is sealed at the upper end with O-rings and a quartz window to permit temperature measurement using a two-colour IR pyrometer. Due to potential heating of metallic components as a result of the alternating electromagnetic field, polycarbonate and polyvinylchloride were used for the making of various parts with the exception of the aluminum base plate. The O-ring sealed, rotatable aluminum base plate was located at the lower end of the chamber. This platform was fitted with a copper mold for droplet quenching and an alumina charging rod for loading solid specimens into the electromagnetic field within the levitation coil. The rotating action of the platform allowed either the copper mold or the charging rod to be aligned directly below the levitation zone within the quartz tube. The water-cooled levitation coil was wound from copper tubing of 1/8 inch in outer diameter. After levitation, the liquid metal samples are quenched by dropping into the copper mold and subsequently analyzed.

3.1.1 Power supply and coil design

For any given experiment, the parameters that influence droplet temperature and droplet stability are the magnitude of the applied current, the coil geometry, the gas composition and flow rate, the specimen material and specimen mass. The power supply used in this investigation was a high frequency induction heating system by Ameritherm-Ambrell with a rated terminal output of 10 kW and a frequency range from 150 to 400 kHz. The magnitude of the applied current allows the manipulation of the droplet position within the levitation coil. There exists, however, a minimum working current that is required to support the droplet and this is influenced by the specimen material and mass, gas direction and flow rate as well as the coil design.
Droplet stability depends to a large extent on the coil design, which may be cylindrical or conical in shape with different coil angles. Levitation coils are generally derived empirically based on the design used by Harris and Jenkins. Kermanpur et al. have carried out detailed investigations in an attempt to provide a theoretical background for coil design by studying the effect of coil angle, number of horizontal turns, charge weight, and droplet vertical position, on lifting force and temperature profile within the droplet. A numerical model was developed to simulate the field generated by the coil using the finite element method. It was concluded that increase in coil angle (deviation from cylindrical geometry) will lead to a decrease in lifting force and in turn cause droplet temperature to increase as a result of the droplet location shifting to a lower position within the coil where the heating effect is stronger. As a design constraint, the oscillation frequency of the coil must match that of the power generator via mutual inductance. The coil’s inductance, which varies with distance that separates each coil turn, may be altered to match the specified working range set by the generator. Generally, the coil’s inductance decreases with increasing distance between the turns.
The design for the levitation coil used in this investigation is shown in Figure 3.2. After numerous tests, the selected coil consisted of a low-angle conical configuration that provides sufficient lift force, good droplet stability and appropriate droplet temperatures. The coil consists of two segments with the lower cone having three turns and the upper inverted cone having two reverse turns. The lower cone is responsible for providing the droplet with lifting force and heat while the upper inverted cone controls the vertical and lateral stability of the levitated droplet.

![Figure 3.2 Schematic diagram of the levitation coil.](image)

3.1.2 IR pyrometer calibration

Droplet temperature measurement by immersed thermocouple is not feasible due to the small volume of the melt. Therefore a non-contact technique such as infrared (IR) pyrometry must be used. An IR pyrometer determines an object’s surface temperature by relating measured radiations emitted from the high temperature surface with the emissivity of the object. However, emissivity of an object varies greatly with chemical composition, surface roughness, and temperature range. For this reason, the challenge associated with lack of complete emissivity data beyond pure substances has led to the development of a two-color IR pyrometer, which consists of two regular brightness pyrometers placed in one device. The two-color pyrometer gathers intensity readings at two individual wavelengths and upon division of the two intensity
equations, a ratio is obtained, which is dependent on temperature. The principle at work essentially assumes that emissivity remains the same at different wavelengths. Despite the fact that two-color pyrometry offers improved reliability and practicality, frequent calibration of a two-color pyrometer is deemed necessary as a precaution measure for specific conditions where the emissivity values differ and do not cancel upon division.

To measure temperature, a pyrometer was focused on the droplet in the levitation chamber or on the surface of the melt contained in the crucible within the induction furnace. An optical grade fused silica window (2 mm in thickness) and prism were used in order to minimize potential spectral loss during temperature measurements. Two calibration tests were carried out. For the first calibration, reference temperature measurements obtained with the thermocouple were used to calibrate the pyrometer readings using the furnace arrangement shown in Figure 3.3 with molten iron contained in an alumina crucible. Since temperature measurements made by thermocouples are not considered standard reference temperatures, two alumina-sheathed type B thermocouples were used to verify against each other while providing validation to the pyrometer reading. Rated to measure temperature up to 1973K (1700°C), Type B thermocouple
has one conductor made of platinum – 30% rhodium alloy while the other conductor is made from platinum – 6% rhodium alloy. During the calibration tests a hydrogen-argon atmosphere was maintained within the induction unit to prevent oxidation of the molten iron. The results obtained in this way are shown in Figure 3.4. A second calibration was carried out using the electromagnetic levitation facility to measure the melting point of copper droplets with different mass. The results are shown in Figure 3.5. In this work, temperature measurements were obtained using a Chino (IR-CAQ3300) two-color pyrometer having an uncertainty of ±15 degrees.

![Figure 3.5 Pyrometer calibration results with different copper droplets.](image)

3.1.3 Gas train

A schematic of the gas train used in this work is shown in Figure 3.6. Moisture in high purity argon, oxygen and carbon dioxide was first removed by passing through drierite columns. The argon gas was also passed through a heated chamber containing titanium pellets at 433K (160°C) prior to merger with the oxidant gas in a gas mixer. Volumetric flow of the gases was monitored by flow meters. Using respective gas species, each flow meter was standardized with a graduated calibration column.
3.1.4 General operating procedure

At the beginning of each experiment, the levitation chamber was purged with purified argon for two minutes. The metal specimen, placed on the alumina charging rod, was raised to a vertical position between the upper and lower sections of the coil. Upon application of high frequency electrical power to the levitation coil, the solid specimen would begin to levitate. Depending on the intensity of applied current, the specimen would become molten in, typically, less than 30 seconds. Once the droplet temperature has stabilized, the appropriate reaction gas was introduced into the reaction chamber at specific flow rates. After a given reaction time, the power was turned off, at which point the droplet would fall and be quenched by the copper mold.

3.2 Specimen Preparation

In preparation of homogenized molten alloys, predetermined amounts of high purity reagents were placed in a high purity graphite crucible (for the making of Fe-Cr-C alloys) or in a high purity alumina crucible (for the making of Fe-C-S alloys and Fe-Si alloys). The crucible and its
contents were heated in the induction unit shown in Figure 3.3. Inside the furnace, an inert atmosphere was maintained by a constant flow of purified argon gas. After about five minutes for the melt to reach homogeneity, alloy samples were taken by suction through a quartz tube, thereby producing rod-shaped specimens with diameter of 4 mm. These rods were then sectioned into equal length pieces where each piece weighs about 0.7 gram. Fe-Cr-C and Fe-C-S samples were analyzed for carbon and sulphur using a LECO CS-244 analyzer and for chromium by X-ray fluorescence. The chemical compositions of reagents used are detailed in the Table 3.1, Table 3.2 and Table 3.3.

Table 3.1 Chemical composition of chromium chips from ESPI Metals (wt pct)

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<th>N</th>
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Table 3.2 Impurity concentrations of electrolytic iron from Allied Metals (wt pct)

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<th>S</th>
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Table 3.3 Impurity concentrations of silicon (6N purity) pellets from ESPI Metals – supplier’s analysis (ppm)

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3.3 References
4 Decarburization of Levitated Fe-Cr-C Droplets by Carbon Dioxide*

Experiments have been conducted at 1873K (1600°C) to study the kinetics of decarburization of Fe-Cr-C levitated droplets containing 10, 17 and 20 wt pct Cr using argon-carbon dioxide gas mixtures containing up to 30 pct CO₂, at flow rates of 100, 1000, 3000 and 12200 mL per min. It was found that chromium did not have a strong influence on the kinetics of decarburization while showing only minor effects on the extent of carbon removal. The results indicate that, for high carbon concentrations in the melt, the decarburization rates were controlled by mass transfer in the gas phase. Conventional formulation of governing mass transport numbers did not adequately describe the experimental observations made in this work. The observed rates are consistently higher than the values predicted using either the Ranz-Marshall correlation or the Steinberger-Treybal equation. A new correlation has been proposed to express the decarburization kinetics of levitated droplets for gas-flows in the range of Reynolds numbers between 2 and 100. The experimentally-derived model was found to be in excellent agreement with rate data derived from studies conducted by other researchers using levitated droplets.

4.1 Background

It has been almost three decades[1] since argon was first replaced by CO₂ as the stirring gas in bottom blowing. Recent research[2] suggests the use of CO₂-O₂ as the top gas and CO₂ as the bottom gas during combined blowing in a converter. Over the years, CO₂ has also found applications in shrouding and mold purging.[3,4]

In stainless steelmaking, traditionally argon-oxygen gas mixtures were used in the Argon Oxygen Decarburization (AOD) process as a means to minimize the loss of alloying elements such as chromium. However, significant chromium loss is often still observed in stainless steelmaking practice today. Previous studies[5,6] have indicated that using CO₂ to replace O₂ as an oxidising agent for decarburization is a viable alternative to optimize the retention of alloying elements as shown in Figure 4.1. This substitution promotes the oxidation of carbon in preference to chromium. It was proposed that in this process, lower cost high-carbon ferroalloys

* The content of this chapter has been published in Metall. Mater. Trans. B, 2014, v 45, n 6, pp. 2211-2221.
can be used in favour of high-cost low-carbon ferroalloys since the decarburization process can now start at a higher carbon content and still be economically feasible.

Figure 4.1 Chromium loss during decarburization in induction furnace at 1873K (1600°C)[5].

The kinetics of CO\(_2\) decarburization has been an important subject for many previous investigations due to its industrial importance in steel-making operations. Sain and Belton[7] carried out their experiments at extremely high gas flow rates to reduce the influence of gas phase mass transport, permitting other modes of controlling step to become dominant. In the flow rate independent regime, they proposed that chemical control governed by CO\(_2\) dissociation is rate-limiting. Results of a subsequent study[8] by the same authors demonstrated that the rate of reaction is greatly influenced by the presence of surface active elements such as sulphur. More recently, Mannion and Fruehan[9] have shown that the presence of tin can have a minor effect on CO\(_2\) dissociation while phosphorus and lead have negligible effects on the dissociation rate constant. Later work by Petit and Fruehan[10] indicated that the effect of chromium and nickel on the kinetics of CO\(_2\) dissociation is minimal. Ito et al.[11] found that the rate of C and O transfer between a levitated pure iron droplet and CO-CO\(_2\) gas mixtures, is characterized by two controlling mechanisms. During the initial period, the rate is controlled by mass transfer in the liquid phase, whereas the transport of CO and CO\(_2\) in the gas phase controls the overall rate in the later stage. Fruehan and Martonik[12] found that decarburization rate is controlled only by gas phase diffusion in the gas boundary layer when flows of CO-CO\(_2\) or H\(_2\) gas were applied to the surface of liquid iron at 1800K (1527°C).
The experimental techniques used in decarburization studies frequently involve a crucible in combination with gas blowing on to the surface of a continuously carbon-saturated melt via a lance.\textsuperscript{[7-10]} However, accurate mass transport modeling of high velocity impinging gas on the melt surface, involved with the crucible approach, can be particularly challenging without reliable information on cavity dimension and effective temperature in the gas phase.

Over the last five decades, there have been a number of investigations on topics associated with the oxidation behavior of iron-carbon alloys using the levitation melting technique. In general, two different oxidants, CO\textsubscript{2} and O\textsubscript{2}, with various combinations of diluent gases such as CO, N\textsubscript{2}, He, or Ar were utilized.

One of the earliest investigations was by Baker \textit{et al.}\textsuperscript{[13]} using CO\textsubscript{2} as the oxidizing gas. Iron-carbon droplets with 0 to 5.5 wt pct C were levitated in an inert atmosphere, then subjected to constant flow of CO\textsubscript{2}-CO/He mixtures containing up to 100 pct CO\textsubscript{2}. The rate of decarburization at 1933K was found to be independent of carbon content in the melt and the rate varied considerably with oxidant partial pressure in the gas phase. It was therefore concluded that decarburization by CO\textsubscript{2} is controlled wholly by diffusion in the gas phase at high carbon concentrations.

Later, the same authors\textsuperscript{[14]} also studied the decarburization kinetics of Fe-C droplets weighing 0.7g in O\textsubscript{2}-He gases with flow rates between 1 and 5 L/min. They found that the rates remain constant down to a carbon concentration of 0.5 wt pct. Gas phase mass transfer was thus considered the rate controlling step in high carbon melts. However, it was proposed that liquid phase mass transfer will become significant at low carbon levels.

In the experiments conducted by Baker and Ward\textsuperscript{[15]}, the Fe-C droplets were first levitated in He-Ar gas mixtures and subsequently allowed to fall through oxygen. In this case, the relative velocity between the droplet and the gas phase increases drastically with time. With the transient Reynolds number accounted for, they found that the measured rates of decarburization were noticeably higher than those predicted by a gas phase diffusion model. In the absence of inductive stirring during the fall, depletion of carbon at the droplet surface will likely occur and therefore, liquid phase diffusion in the metal should be considered in the rate analysis.
Detailed studies on the decarburization of Fe-4 wt pct C alloys, using the levitation technique, in oxygen, carbon dioxide and water vapor were undertaken by Distin et al.\textsuperscript{[16]}. Since the rate did not decrease with decreasing carbon concentrations, it was suggested that neither mass transfer in the metal nor the rate of chemical reaction at the surface of the droplets are rate controlling. The results also showed that the rate of carbon loss increased with increasing gas flow rate from 0.1 to 1.2 L/min. This observation led them to conclude that decarburization was controlled primarily by gaseous diffusion. Transport of oxidants from the bulk gas to the droplet surface was found to be in good agreement with predictions developed using the Steinberger and Treybal correlation.

In their investigation involving elevated pressure of 40 atm., El-Kaddah and Robertson\textsuperscript{[17]} demonstrated that both decarburization and carburization of Fe-C liquid alloys by CO\textsubscript{2}-CO gas mixtures can be achieved. The kinetics of decarburization, for 1 g droplets containing 5 and 5.5 wt pct C, was found to obey a model developed for convective mass transfer in the gas phase. Their assessment of the carburization results, on the other hand, revealed that liquid phase resistance is significant at the reaction temperature of 1923K. For the gas composition studied, 1.1 or 2.15 pct CO\textsubscript{2}, the carburization rate was controlled by mixed transport of gas and liquid phase diffusion.

Lee and Rao\textsuperscript{[18,19]} carried out decarburization of levitated Fe-C-S droplets in a flowing CO-CO\textsubscript{2} gas stream at 1973K. The rate decreases significantly with increase in sulphur concentrations in the melt. Sulphur, being surface active, was responsible for blocking available sites for CO\textsubscript{2} dissociation. However, it was found that for gas streams containing 10 pct CO\textsubscript{2} and flowing at 1 L/min, the retarding effect of sulphur diminishes as sulphur concentration increases past 0.05 wt pct. They observed that flow rate of the gas mixture has a relatively small effect on the decarburization rate compared to the oxidant partial pressure in the gas mixture. It was thus concluded that the process is a mixed controlled scenario of both gas phase mass transfer and dissociative chemisorption of carbon dioxide.

Sun and Pehlke\textsuperscript{[20]} have studied the kinetics of carbon oxidation in the presence of silicon and manganese in iron. They observed preferential oxidation of carbon when the alloy (3.35 wt pct C, 2 wt pct Si, 0.36 wt pct Mn) was exposed to 20 pct CO\textsubscript{2}-80 pct N\textsubscript{2} gases. Oxidation of Mn and Si only began when carbon levels were sufficiently low and the rate limiting step changed from
CO₂ transport in the boundary layer to solute diffusion in the liquid metal. It was found that sulphur, in the range of 0.002 to 0.5 wt pct has negligible effect on the decarburization rate.

Work by Simento et al.[21] has shown that the rate of decarburization of Fe-C, with initial carbon concentrations between 3.38 and 4.18 wt pct, by CO₂-N₂ gas mixtures is jointly controlled by CO₂ diffusion in the gas phase and subsequent dissociative chemisorption at the gas-metal interface. Small amounts of P (0.1 wt pct), Cr (0.5 wt pct), and S (up to 0.27 wt pct) were alloyed with the Fe-C melt to determine their effect on the decarburization behavior. From their experimental results, mostly at 1723K, the effect of sulphur on the rate was found to obey the Langmuir isotherm for sulphur adsorption. For the melt compositions pertaining to their work, both chromium and phosphorus did not exhibit a noticeable effect on the rate.

The preceding authors[22] also investigated decarburization of Fe-C-S alloys in flowing O₂-N₂-He gases. The experimental results indicated that sulphur, in the range of <5 ppm to 0.27 wt pct, had only a small effect on the rate at 1723K. It was found that the rate of decarburization is first order with respect to oxygen partial pressure in the bulk gas. They concluded that mass transfer through the gas boundary layer near the surface of the liquid droplet is controlling the overall rate. However, results from additional experiments have shown consistent decrease in the decarburization rate at higher gas flow rates. Furthermore, predictions using the Steinberger and Treybal correlation were unable to provide a meaningful description of this observation. The authors suggested that flow field interference due to the presence of coil around the droplet is responsible for this abnormal behavior.

Simento et al.[23] later examined the simultaneous reactions of O₂ and CO₂ with liquid Fe-C alloys. The observed decarburization rates were adequately described by the simple addition of the rates of the individual reactions, where the behavior of O₂ and CO₂ was identical with that previously reported.

Widlund et al.[24] have recently studied the oxidation behavior of Fe-C-Si droplets in O₂-He gas stream flowing at 5 L/min. For droplet temperatures between 1673K and 1903K, they reported that the rate of decarburization is only influenced by the partial pressure of oxygen in the gas phase. The observed rates as well as the silicon concentrations were found to remain constant until carbon contents were less than 0.5 wt pct, at which point the decarburization rate declined while desiliconization commenced.
It is clear from the above that, for high carbon melts, the rates of CO$_2$ decarburization were found to be controlled by either diffusion in the gas phase, surface chemical kinetics, or a mix of both. However, limited mention was made with regard to the effects of other alloying elements commonly found in high alloy steel grades on the kinetics of decarburization by CO$_2$. On the other hand, there is consensus among investigators that, for O$_2$ decarburization, the rate is controlled solely by gas phase mass transfer at high carbon concentrations. In both cases, as carbon content decreases below a certain critical level, mass diffusion in the liquid phase becomes significant.

Although data on decarburization rate and the associated limiting step have been discussed in some detail, there is still uncertainty concerning an appropriate mass transport correlation that would be applicable to levitated droplet studies. The present investigation is aimed at addressing this particular aspect.

4.2 Fundamental Considerations

The decarburization reaction by carbon dioxide is usually given by the overall chemical reaction,

$$\text{CO}_2(g) + \text{C} = 2\text{CO}_2(g) \quad (4.1)$$

The kinetics of the decarburization reaction can be described in terms of the following steps:

1. Gaseous diffusion within the gas boundary layer.
2. Surface adsorption of CO$_2$.
3. CO$_2$ dissociation.
5. Surface desorption of CO.

4.2.1 Interfacial reaction as the rate-controlling step

The rate of interfacial reaction in the present study is considered to be much higher than the transport of oxidants in the gas phase and carbon atoms in the liquid phase. According to the work by Sain and Belton$^7$, the decarburization rate is first order with respect to CO$_2$ partial pressure. In their work, a gas jet at flow rates up to 40 L/min was imposed on an inductively stirred melt to avoid both gaseous and liquid mass transfer limitations, thereby forcing the interfacial reaction to become rate-limiting. Their analysis indicates that neither desorption of
CO or dissociation of CO$_2$ play a significant role in the kinetics of the decarburization process. It was suggested that the rate of CO$_2$ chemisorption represents the rate controlling step with $1.20 \times 10^{-3}$ mol cm$^{-2}$ s$^{-1}$ atm$^{-1}$ as the rate constant at 1873K (1600°C) which is approximately two orders of magnitude higher than that for mass transport in the gas phase found in the present work. Therefore interfacial reactions could not have contributed to the rate limiting step in the current investigation.

### 4.2.2 Mass transport of carbon in the liquid phase

The liquid phase transport behaviour within the droplet is largely controlled by the intensity of internal flow. Flow of liquid in an electromagnetically levitated droplet is driven by both convection and magnetic field$^{[25]}$. Mathematical modelling work by Hyers$^{[26]}$ suggests that the stirring velocity in a 1g (dp= 0.64 cm) ferrous alloy drop can reach 32 cm s$^{-1}$. Thus, mass transport within an EML droplet is widely accepted as a rapid process. For an inductively stirred melt, previous studies$^{[7,17]}$ suggested that the transfer coefficient for carbon in molten iron, $k_l$, is in the range 0.027 to 0.035 cm s$^{-1}$. Taking the mean value of $3.1 \times 10^{-2}$ cm s$^{-1}$, one can readily deduce the flux of carbon atoms arriving at the gas-liquid interface with the following relationship:

$$J_C = k_l \frac{\rho}{100M_C} (C_{bulk} - C_{surface})$$  \hspace{1cm} (4.2)

where $\rho$ is the melt density, $M_C$ is the atomic weight of carbon, $C_{bulk}$ is the carbon concentration in bulk metal and $C_{surface}$ is the carbon concentration at the gas-metal interface. Using a similar experimental approach, Sun and Pehlke$^{[20]}$ have demonstrated that chemical reactions at the gas-metal interface can be considered to be at equilibrium. Given chemical equilibrium at the surface of the droplet, wt pctl $C_{bulk}$ is much greater than wt pctl $C_{surface}$. Hence the relationship shown by Eq. (4.2) becomes:

$$J_C = k_l \frac{\rho}{100M_C} C_{bulk}$$  \hspace{1cm} (4.3)

and the decarburization rate,
\[
\frac{d[C]}{dt_s} = -\frac{1200A}{W}J_C
\]  

(4.4)

where \(A\) and \(W\) correspond to the surface area and mass of the droplet respectively.

### 4.2.3 Mass transport of carbon dioxide in the gas phase

In the high carbon regime, the transfer of carbon is faster than the flux of oxidant species arriving at the gas-metal interface. Under these conditions it will be shown that the decarburization rate is controlled by gas diffusion.

The reaction geometry, facilitated by the levitation technique, consists of gas mixtures flowing over the surface of a liquid sphere. The decarburization rate can be related to the flux of arriving gaseous oxidant, \(J_{CO_2}\), using the expression:

\[
\frac{d[C]}{dt_s} = -\frac{1200A}{W}J_{CO_2} = -\frac{1200A}{W}k_x(X_{CO_2}^b - X_{CO_2}^l)
\]

(4.5)

where \(k_x\) is the mass transfer coefficient, \(X_{CO_2}^b\) is the mole fraction of CO\(_2\) in the bulk gas on the edge of the boundary layer and \(X_{CO_2}^l\) is the mole fraction of CO\(_2\) at the surface of the liquid sphere. In the gas phase controlled scenario, the mole fraction of CO\(_2\) at the gas-metal interface is negligibly low. For convective mass transfer, the Sherwood number is defined as

\[
Sh = \frac{d_p k_g}{D_{AB}}; \quad k_x = C_t k_g
\]

(4.6)

where \(d_p\) is the diameter of the metal droplet, \(k_g\) is the gas transfer coefficient, \(D_{AB}\) is the mutual diffusion coefficient, and \(C_t\) is the total molar concentration in the gas phase. Combining Eqs. (4.5) and (4.6) and replacing \(k_x\):

\[
\frac{d[C]}{dt_s} = -\frac{1200A}{W}ShD_{AB}P\frac{d_p}{d_pRT_f}X_{CO_2}^b
\]

(4.7)

Assuming an ideal gas mixture, \(C_t\) can be replaced by \(P/RT\) where \(P\) is the total pressure, \(R\) is the gas constant with a value of 82.05 \(cm^3\ atm\ mol^{-1}K^{-1}\) and \(T_f\) is the film temperature.
In 1938, Frössling\cite{27} introduced the following equation for the Sherwood number expressed in terms of the Reynolds and Schmidt numbers to account for the effects of forced convection:

$$Sh = 2 + 0.552Re^{\frac{1}{2}}Sc^{\frac{1}{3}}$$

(4.8)

For mass transport in the presence of a high temperature gradient, contributions from both natural convection and forced convection must be taken into account. The Sherwood number is then expressed by the generalized form of the Frössling equation as a function of the Rayleigh, Reynolds and Schmidt numbers:

$$Sh = 2 + \gamma Ra^f + \beta Re^m Sc^n$$

(4.9)

where $\gamma$, $\beta$ and $m$ are experimentally determined coefficients. For $Ra$ less than $10^9$, coefficient $f$ is commonly taken as $1/4$. For $Sc$ less than 250, coefficient $n$ is commonly taken as $1/3$. The constant 2 represents the molecular diffusion contribution for a spherical droplet, which is the minimum expected value for $Sh$ as in the case of a droplet immersed in a stagnant fluid. The second and third terms represent the effects of natural and forced convection respectively. There are two notable utilizations of Eq. (4.9). The Ranz-Marshall\cite{28} equation is used for cases where natural convection can be ignored:

$$Sh = 2 + 0.6Re^{\frac{1}{2}}Sc^{\frac{1}{3}}$$

(4.10)

while the Steinberger and Treybal\cite{29} correlation, takes account of contributions from both natural and forced convection:

$$Sh = 2 + 0.569Ra^{0.25} + 0.347Re^{0.62}Sc^{0.31}$$

(4.11)

While both correlations are excellent for describing systems with temperature gradients of less than 200 degrees, it will be shown that neither are suitable for metallurgical processes where temperature gradients greater than 1000 degrees are not uncommon.

As mentioned above, at carbon saturation, the carbon diffusion flux is much greater than the flux of oxidant species arriving at the gas-metal interface and under these circumstances the decarburization rate is controlled by gas diffusion. As the carbon concentration in the melt decreases there is a transition from gas phase control to liquid phase control due to a
progressively scarcer supply of carbon atoms from the bulk metal arriving at the gas-metal interface. This shift in rate limiting step occurs at a specific carbon content, $C_{\text{critical}}$. The flux of carbon dioxide molecules arriving at the gas-liquid interface can be obtained by combining Eqs. (4.5) and (4.7) to give:

$$J_{CO_2} = \frac{ShD_{AB}P}{d_\rho RT_f} (X_{CO_2}^b)$$  \hspace{1cm} (4.12)

If the Sherwood number is estimated using the Ranz-Marshall equation, $J_{CO_2}$ can be evaluated at $T_f$. The flux of carbon atoms arriving at the gas-liquid interface is given by Eq. (4.3). Taking $3.1 \times 10^{-2} \text{ cm s}^{-1}$ as the value\textsuperscript{[7,17]} for $k_1$, $J_C$ can be evaluated. The results are presented in Figure 4.2. The critical carbon contents for various experimental conditions correspond to the intersections of the carbon transport line and the CO$_2$ transport lines. Based on these findings, in the range of carbon concentrations for which the rate analysis was performed, between carbon saturation and 1 wt pct C, the decarburization rate is controlled by diffusion in the gas phase rather than carbon transport within the liquid phase. This is consistent with the data discussed later and shown in Figures 4.4 and 4.7 which indicate that the decarburization rate is proportional to the oxidant concentration in the gas phase and increases with the gas flow rate.
Figure 4.2 Flux of reactants arriving at the gas-metal interface as a function of carbon concentration in the metal.

4.3 Experimental Aspects

Fe-Cr-C<sub>sat</sub> alloys with three different chromium contents were used for the present investigation. The alloy compositions are shown in Table I. Sulphur was added to replicate the composition of stainless steel.

<table>
<thead>
<tr>
<th>Alloy #</th>
<th>[Cr] &lt;sub&gt;i&lt;/sub&gt; (wt pct)</th>
<th>[C] &lt;sub&gt;i&lt;/sub&gt; (wt pct)</th>
<th>[S] &lt;sub&gt;i&lt;/sub&gt; (wt pct)</th>
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</table>

Experiments using very low flow rates, with Reynolds numbers in the range 0.3~0.6, were performed in order to determine the contribution from natural convection. In this regime where the Archimedes number (Ar) >>1, the predominant mode of mass transfer is natural convection and the contribution of forced convection will be minimal. The coefficient γ can be experimentally deduced by varying the gas composition. Taking the coefficients determined from experiments dominated by natural convection, a second set of experiments was designed to
focus on forced convection. The coefficients $\beta$ and $m$ can be deduced by varying the gas flow rate.

### 4.4 Results and Discussion

Figure 4.3 shows typical results for the decarburization experiments. The data are presented here in terms of changing solute concentration as a function of exposure time to different flow rates of CO$_2$-Ar gas mixtures. Under the various conditions, the chromium concentration remains virtually constant throughout the experiments. This observation is consistent with the predicted partial pressure of oxygen, which is sufficiently low at approximately $5.7 \times 10^{-10}$ atm. The effect of chromium on the kinetics of decarburization is discussed in Chapter 6. On the other hand, for experiments with high residual carbon content and low CO$_2$ partial pressure in the gas phase, up to 64 pct reduction in sulphur content, from 0.0108 wt pct to 0.0044 wt pct, was observed. This observation is in accord with that of Sain and Belton$^{[8]}$, who found significant sulphur loss in their experiments with continuously carbon saturated iron melts contained in an alumina crucible with a graphite disc cemented to the bottom. For the present experiments with high oxidant partial pressure, hence low residual carbon content, up to 18 pct sulphur reduction was observed. However, Lee and Rao$^{[18]}$ found no sulphur loss in their levitated iron droplet experiments with initial carbon contents less than 2.5 wt pct. The behavior of sulphur during decarburization of iron-chromium alloy droplets with carbon dioxide is discussed in Chapter 7.
Figure 4.3 Variation of carbon, sulphur and chromium contents with exposure time.
Table 4.2 Experimental results for decarburization using CO\textsubscript{2}-Ar at low gas flow

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition (pct CO\textsubscript{2})</th>
<th>Flow Rate (mL/min)</th>
<th>Droplet mass (g)</th>
<th>-d[C]/dt (wt pct/sec)</th>
<th>Sh (Observed)</th>
<th>Sh\textsubscript{R-M} (%)</th>
<th>Sh\textsubscript{S-T} (%)</th>
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Table 4.3 Experimental results for decarburization using CO\textsubscript{2}-Ar at higher gas flow

<table>
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<tr>
<th>Alloy</th>
<th>Composition (pct CO\textsubscript{2})</th>
<th>Flow Rate (mL/min)</th>
<th>Droplet mass (g)</th>
<th>-d[C]/dt (wt pct/sec)</th>
<th>Sh (Observed)</th>
<th>Sh (R-M)</th>
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4.4.1 Effect of partial pressure of carbon dioxide

To illustrate the effect of gas composition on decarburization behavior, results from the low gas flow rate experiments using different partial pressures of gaseous oxidants are shown in Figure 4.4. The reaction rate is first order with oxidant partial pressure, which is in accord with previous studies\cite{7,20}. In this investigation, for a flow rate of 100 mL/min, the value of the mass transfer coefficient for CO\textsubscript{2}-Ar is found to be $k_{CO_2} = 3.37 \times 10^{-5} \text{ mol cm}^{-2} \text{s}^{-1} \text{atm}^{-1}$. It was found
that chromium, while showing minor effects on the extent of carbon removal, did not have a strong influence on the kinetics of decarburization.

4.4.2 Natural convection

At low gas flow rates, the predominant mode of mass transport is by natural convection, as indicated by a high Archimedes number averaging a value of 829. From Table 4.2 and Figure 4.5, it can be seen that the experimentally determined Sherwood numbers are consistently lower than those predicted using the Steinberger-Treybal equation.
Figure 4.5 Comparison of observed and predicted Sherwood numbers as a function of the Rayleigh number.

More importantly, the observed Sherwood numbers are less than the minimum expected value of 2 from molecular diffusion, which suggests a negative contribution from natural convection. For mass transport under natural convection conditions, the Sherwood number takes the following general form where the Rayleigh number is expressed by the product of the mean Grashof number and the Schmidt number:

$$Sh = 2 + \gamma (Gr'Sc)^{\frac{1}{4}}$$  \hspace{1cm} (4.13)

This modified form of the Steinberger-Treybal equation utilizing the mean Grashof number was introduced by Mathers et al.\textsuperscript{[30]} and was subsequently used by Baker et al.\textsuperscript{[14]} and Distin et al.\textsuperscript{[16]}. It was also later used by Lee and Rao\textsuperscript{[19]} as well as Simento et al.\textsuperscript{[31]}. In the present work, with mean Grashof numbers and Schmidt numbers determined from experimental conditions, as well as Sherwood numbers deduced from the observed decarburization rates, it is then possible to plot $Sh-2$ against $(Gr'Sc)^{\frac{1}{4}}$, where the linear slope corresponds to the coefficient $\gamma$, Figure 4.6. Upon evaluation of the data, Eq. (4.13) becomes:

$$Sh = 2 - 0.317(Gr'Sc)^{\frac{1}{4}}$$  \hspace{1cm} (4.14)
Within the current data set, the outlier point (Ra=10.4) in Figure 4.6, is possibly the result of experimental error. However, it could also imply that the lower applicability limit of Rayleigh number, for the proposed correlation, has been reached. Additional data in the low Ra range are needed to reach a more definitive conclusion.

While it is true that natural convection may assist with mass transport from the droplet to the surroundings in a shrinking-sphere experiment as in the case of the Steinberger-Treybal experiments\[29\], it may hinder the process, as indicated by the negative sign in Eq. (4.14), if mass is being transported to a warm droplet from cold surroundings under a steep temperature gradient. To add to the matter, based on the decarburization reaction (Eq. 4.1), there are two departing molecules of CO for every molecule of CO\(_2\) approaching the gas-metal interface. This added resistance is therefore expected to, partly, contribute to the observed phenomena.

![Figure 4.6 Linear regression of the data as represented by Eq. (4.13) from present work.](image)

4.4.3 Effect of gas flow rate

The effect of gas flow rate on the decarburization of iron-carbon alloys containing 20 wt pct chromium was evaluated. At constant gas composition (10 pct CO\(_2\)-Ar), the change in gas flow rate is responsible for the difference in mass transfer behavior within the gas-metal boundary layer which ultimately influenced the decarburization rate, as shown in Figure 4.7.
4.4.4 Development of a new correlation for decarburization of levitated droplets

Interpretation of data from the current work using either the Ranz-Marshall equation or the Steinberger-Treybal equation does not adequately represent the trend observed in the experimental measurements despite the Reynolds and Schmidt numbers being in the appropriate range. Figure 4.8 shows a plot comparing the experimentally observed Sherwood numbers with those predicted from the well-established models. The deviation from both models increases with increasing Reynolds number. The observed values differ from the values predicted by the Steinberger-Treybal equation and the Ranz-Marshall equation, by a factor of approximately 1.4 and 2 respectively. This finding is in accord with the observation made by Baker and Ward\textsuperscript{[15]} in their study involving decarburization of iron-carbon droplets falling through oxygen. They found the measured rates to be approximately twice as great as those estimated by a model for gas diffusion control. The expression given by Ranz-Marshall was deduced using data for the evaporation rates of water droplets exposed to air at temperatures up to 493K (220°C). The Steinberger-Treybal equation was determined by measuring the rate of dissolution of spherical benzoic acid droplets into flowing water at 288-303K (15-30°C) or into aqueous propylene glycol at 288-298K (15-25°C). In the present work, it is hypothesized that the steep temperature gradient of approximately 1550 degrees between the incoming CO\textsubscript{2} and the surface of the alloy droplet, is responsible for the difference observed between the well-established mass transfer
models and the experimental data obtained with levitated droplets. This suggests that an alternative correlation should be established for the conditions prevailing in the current work.

Figure 4.8 Comparison of observed and predicted Sherwood numbers as a function of the Reynolds number.

Table 4.4 Comparison of experimental conditions

<table>
<thead>
<tr>
<th></th>
<th>Experimental Re and Sc</th>
<th>Droplet diameter (mm)</th>
<th>Sphere- to column-diameter ratio (dp/dc)</th>
<th>Temperature gradient (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Current work</strong></td>
<td>2.75≤Re≤97.2, 0.71≤Sc≤0.73</td>
<td>2.5≤dp≤2.8</td>
<td>0.192≤dp/dc≤0.215</td>
<td>~1550</td>
</tr>
<tr>
<td><strong>Ranz-Marshall</strong></td>
<td>2≤Re≤200, 0.6≤Sc≤2.7</td>
<td>0.6≤dp≤1.1</td>
<td>0.024≤dp/dc≤0.044</td>
<td>~200</td>
</tr>
<tr>
<td><strong>Steinberger-Treybal</strong></td>
<td>2≤Re≤16,900, 0.6≤Sc≤3200</td>
<td>12.7≤dp≤25.4</td>
<td>0.123≤dp/dc≤0.497</td>
<td>15-30</td>
</tr>
</tbody>
</table>

The experimental conditions for the present work and those pertaining to the derivation of previous empirical relationships are summarized in Table 4.4. The difference between droplet sizes is not expected to influence the observed behavior since change in droplet size mostly modifies the Reynolds number. Provided the Reynolds number stays within the appropriate range, both the comparison and the derived correlation should be valid. However, the sphere-to
column-diameter ratio could have a greater impact if not carefully controlled. Within the range of sample weights used in this investigation, the shape of droplets is near-spherical although the dominance of surface tension in holding the droplet’s spherical shape is expected to diminish if the sample weights were to increase, in which case the droplet will tend to become ellipsoidal.

Paterson and Hayhurst\textsuperscript{[32]} have emphasized the importance of accurately evaluating the characteristics of gases within the boundary layer surrounding the liquid droplet when interpreting experimental measurements. Hamielec, Lu, and McLean\textsuperscript{[33]} have pointed out the complexities in defining the physical properties of gases in the boundary layer surrounding liquid steel droplets due to the considerable temperature gradient as well as the multi-component nature of the system. The difficulty is mainly attributed to the proper choice of effective film temperature, which can greatly influence the estimation of density, viscosity, heat capacity, thermal conductivity, and the diffusion coefficient of gases. For evaluation of gas properties and mutual diffusion coefficients within the boundary layer, Greenberg and McLean\textsuperscript{[34]}, who studied the oxidation rate of iron alloy droplets falling through air, proposed the use of an effective temperature defined as:

\[
T_E = 0.83T_f = 0.83\left(\frac{T_i + T_b}{2}\right)
\]  \hspace{1cm} (4.15)

Although the justification for using a single temperature (\(T_f\) or \(T_E\)) to approximate such a large temperature gradient in these systems is lacking, there is a need to use a “film” temperature that is appropriate for the system of interest. In the case of high-temperature levitated droplet experiments, Eq. (4.15) is the most appropriate. Values for properties of the gas phase at \(T_f\) and \(T_E\) for use in the appropriate equations are listed in the appended tables.

Combining Eqs. (4.9) and (4.14) yields:

\[
Sh = 2 - 0.317(Gr'Sc)^{\frac{1}{4}} + \beta Re^mSc^n
\]  \hspace{1cm} (4.16)

Rearranging,

\[
Sh - 2 + 0.317(Gr'Sc)^{\frac{1}{4}} = \beta Re^mSc^n
\]  \hspace{1cm} (4.17)

Taking logarithms and rearranging,
\[ \log(Sh - 2 + 0.317(Gr'Sc)^{\frac{1}{3}}) - n \log Sc = m \log Re + \log \beta \]  

(4.18)

For Sc values less than 250, the coefficient \( n \) is commonly taken as 1/3 and thus Eq. (4.19) is obtained:

\[ \log(Sh - 2 + 0.317(Gr'Sc)^{\frac{1}{3}}) - \frac{1}{3} \log Sc = m \log Re + \log \beta \]  

(4.19)

The Schmidt number takes account of the fluid transfer characteristics and remains largely unchanged given the gas compositions and a fixed effective temperature in the boundary layer. Therefore, the Schmidt number is not a variable in this investigation. In the present study, contribution of the Reynolds number to the Sherwood number, pertains to the relative velocity \( \nu \) between the droplet and the gas stream. In the case of stationary levitated droplets \( \nu \) can be directly related to the gas flow rate. With values determined from the experimental conditions for the Grashof, Schmidt and Reynolds numbers in Eq. (4.19), coefficients \( m \) and \( \beta \) can be readily determined from a plot of \( \log(Sh - 2 + 0.317(Gr'Sc)^{\frac{1}{3}}) - \frac{1}{3} \log Sc \) against \( \log Re \) where the linear slope corresponds to the constant \( m \) and the y-intercept can be used to calculate the constant \( \beta \), Figure 4.9. Upon evaluation, Eq. (4.9) becomes:

\[ Sh = 2 - 0.317(Gr'Sc)^{\frac{1}{3}} + 3Re^{0.415}Sc^{\frac{1}{3}} \]  

(4.20)

Figure 4.9 Linear regression of the data expressed in terms of Eq. (4.19) from present work.
A comparison of correlation data derived from previous decarburization studies\textsuperscript{[18,20]} with Eq. (4.20) from the present work, is shown in Figure 4.10. Both previous studies were conducted using the electromagnetic levitation method under comparable experimental conditions. Sun and Pehlke\textsuperscript{[20]} carried out decarburization of Fe-C-Si-Mn alloy droplets with N\textsubscript{2}-CO\textsubscript{2} gas mixtures with $P_{CO_2}$ ranging from 0.1 to 0.2 atm at flow rates of 200, 500, 1000 and 2000 mL min\textsuperscript{-1}. The internal diameter of the levitation reaction tube was identical to that used in the present study. The work by Lee and Rao\textsuperscript{[18]} involved decarburization of Fe-C droplets containing various amount of sulphur by CO-CO\textsubscript{2} gas mixtures with $P_{CO_2}$ ranging from 0.1 to 0.2 atm at flow rates of 1000, 1300 and 1500 mL min\textsuperscript{-1}. In this case, the gas was injected through a silica lance located directly above the levitated droplet. Results from experiments involving high sulphur content were not included in the data shown in Figure 4.10 since the application of correction factors is often required to account for the effect of surface active sulphur on the reaction rate. With this proviso, it is evident from Figure 4.10 that the data sets from past studies with Reynolds number as low as 2, are well characterized by the correlation derived from the present investigation.

4.5 Summary and Conclusions

Decarburization of Fe-Cr-C\textsubscript{sat} alloys containing 10 wt pct, 17 wt pct, and 20 wt pct chromium, was carried out using different flow rates of CO\textsubscript{2}-Ar gas mixtures. The flow regime investigated
was between creeping flow (Stokes flow) and Reynolds number of 100. No significant chromium loss was observed even after the carbon concentration had been reduced to as low as 0.02 wt pct. The reaction rate is first order with oxidant partial pressure, which is in accord with previous studies. On the basis of gas transport control, a new correlation has been proposed to describe the decarburization kinetics of levitated droplets at low to moderate gas flow rates. The experimentally-derived model was found to be in excellent agreement with rate data from other decarburization studies using a similar experimental approach involving levitated droplets.

4.6 References

5 The Effect of Thermal Diffusion on Decarburization Kinetics*

The influence of thermal diffusion on the kinetics of decarburization of Fe-Cr-C droplets with CO₂-Ar gas mixtures was investigated. Interpretation of the results indicates that the decarburization rate has been retarded by thermal diffusion. With incorporation of the effect of thermal diffusion, a new correlation has been proposed to express the decarburization kinetics of levitated droplets for flows in the range of Reynolds number between 2 to 100. A thermal diffusion factor of 0.228 was evaluated for CO₂-Ar gas mixtures at 1873K (1600°C). Decarburization experiments of Fe-Cr-C droplets with O₂-Ar gas mixtures containing up to 10% oxygen were also carried out at 1873K and a thermal diffusion factor of 0.21 was determined from analysis of the rate data.

5.1 Background

Based on the study described in the previous chapter, results were reported[1] for the decarburization of Fe-Cr-C levitated droplets with CO₂-Ar gas mixtures. It was found that mass transfer correlations such as the Ranz-Marshall[2] and Steinberger-Treybal[3] equations, while widely employed, do not describe the data obtained from the droplet experiments. Based on analysis of the rate data a new correlation was proposed that accounts for contributions from both natural and forced convection and is appropriate for mass transfer involving levitated droplets:

\[
Sh = 2 - 0.317 (Gr'Sc)\frac{1}{3} + 3Re^{0.415}Sc^{\frac{1}{3}}
\]  (5.1)

where \(Sh\), \(Gr'\), \(Sc\) and \(Re\) correspond to the Sherwood, Mean Grashof, Schmidt and Reynolds numbers respectively.

The presence of a steep temperature gradient near the gas-metal interface, an inherent feature of the levitation technique, gives rise to variation in gas properties and flow patterns across the boundary layer and as a result, mass flux due to thermal diffusion becomes significant. The

objective of the present discussion is to provide an alternative approach to rationalize the reported discrepancy between the existing models and the experimental measurements by considering the implications of the effect of thermal diffusion on reaction kinetics in the presence of large temperature differences between the two phases.

5.2 The Effects of Thermal Diffusion on Mass Transfer

The work by Sain and Belton\textsuperscript{[4]} suggests that interfacial reactions are faster than both liquid transport and gas transport. In the high carbon regime, the transfer of carbon is faster than the flux of oxidant species arriving at the gas-metal interface. Therefore at high carbon content the experimental reaction rate is controlled by gas diffusion. The reaction geometry associated with the levitation technique, consists of gas mixtures flowing over a liquid sphere of surface area $A$ with weight $W$. As shown in the previous chapter, the decarburization rate can be related to the flux of arriving gaseous oxidant, $J_{CO_2}$, using the expression:

$$\frac{d}{dt_s}\left(\frac{wt\text{ pct } C}{P}\right) = -\frac{1200A}{W} J_{CO_2} = -\frac{1200A ShD_{AB}P}{d_pRT_f} \left(X_{CO_2}^b - X_{CO_2}^l\right)$$  \hspace{1cm} (5.2)

where $D_{AB}$ is the mutual diffusion coefficient, $P$ is the total pressure, $d_p$ is the diameter of metal droplet, $R$ is the gas constant and $T_f$ is the film temperature, $X_{CO_2}^b$ is the mole fraction of CO$_2$ in the bulk gas at the edge of the boundary layer and $X_{CO_2}^l$ is the mole fraction of CO$_2$ at the surface of the liquid sphere. In the gas phase controlled regime, the mole fraction of CO$_2$ at the gas-metal interface is negligibly low.

In a levitated droplet experiment, thermal equilibrium is reached when the heat dissipation through radiation and convection equals the heat gain through induction by the applied electromagnetic field. The steep temperature gradient between the droplet surface and the incoming reaction gas may cause mass flux by thermal diffusion. Therefore, the net flux of a species has contributions from molecular diffusion, thermal diffusion and convection, which may be written as:

$$J_{CO_2} = \frac{ShD_{AB}P}{d_pRT_f} X_{CO_2}^b + J_T$$  \hspace{1cm} (5.3)
where \( J_T \) represents the contribution to the net flux due to thermal diffusion effects. The process of thermal diffusion depends greatly on the gas composition. This dependence is reflected in the expression for the thermal diffusion term defined\[^5\] as:

\[
J_T = k_T \nabla \ln T = \left( \frac{D_{AB} \alpha X_{CO_2}^b X_{Ar}^b}{T} \frac{dT}{dr} \right)_i
\]  

(5.4)

where \( k_T \) is the thermal diffusion ratio, \( C \) is the total molar concentration in the gas phase, \( \alpha \) is the binary thermal diffusion factor, which is independent of the mole fractions of the binary gas mixture and \( r \) is the radial distance from the droplet surface. Combining Eqs. (5.2), (5.3) and (5.4):

\[
\frac{W}{-1200A} \frac{d(\text{wt pct } C)}{dt_s} = ShD_{AB}P \frac{d_p}{d_p RT_f} X_{CO_2}^b + \left( \frac{D_{AB} \alpha X_{CO_2}^b X_{Ar}^b}{T} \frac{dT}{dr} \right)_i
\]

(5.5)

In order to utilize Eq. (5.5) to assess the decarburization data described in the current work, \( Sh \) and \( \frac{dT}{dr} \) must both be known. Following the approach of El-Kaddah and Szekely\[^6\] the \( \frac{dT}{dr} \) term can be expressed as:

\[
\frac{dT}{dr} = - \frac{Nu}{d_p} (T_i - T_b) - \frac{\sigma_{SB} \varepsilon}{k} (T_i^4 - T_b^4)
\]

(5.6)

where \( Nu \) is the Nusselt number, \( \sigma_{SB} \) is the Stefan-Boltzmann constant, \( \varepsilon \) is the emissivity of the metal drop and \( k \) is the thermal conductivity of the gas phase. The Nusselt number can be expressed in terms of natural and forced convection using the Grashof number for heat transfer, \( Gr_H \), the Prandtl number \( Pr \) and the Reynolds Number:

\[
Nu = 0.78(Gr_H Pr)^{1/4} + 0.8Re^{1/2}Pr^{1/3}
\]

(5.7)

### 5.3 Evaluation of the Thermal Diffusion Factor

The thermal diffusion factor is used to express the ratio of contributions from the mutual diffusion coefficient \( (D_{AB}) \) and the thermal diffusion coefficient \( (D_T) \), in non-equilibrium steady state\[^7\]:

...
\[ \alpha_i = T \frac{D_T}{D_{AB}} = -\frac{T}{X_i(1 - X_i)} \frac{\nabla X_i}{\nabla T} \]  

\[ (5.8) \]

\( \alpha_i \) is often used to estimate \( D_T \), which is otherwise difficult to measure. Although \( D_T \) shares some similarity with \( D_{AB} \), \( D_T \) also depends on composition whereas \( D_{AB} \) does not.

Over the past five decades, there have been a number of studies on the measurement of the thermal diffusion factor, \( \alpha \) for Ar-CO\(_2\) gas mixtures. Perhaps due to experimental limitations, none of these studies have reported values of \( \alpha \) for temperatures greater than 700K (427°C). Shashkov \textit{et al.}\textsuperscript{[8]} reported values for several temperatures averaged at 326K (53°C) from measurements made in a two-bulb apparatus. Recent work by McCourt\textsuperscript{[9]} proposed an expression for temperature dependence of \( \alpha \) using experimental data by Taylor and Pickett\textsuperscript{[10]}, up to 550K (277°C). Sunderland \textit{et al.}\textsuperscript{[5]} suggested the levitation melting technique could be an appropriate method for measurements of \( \alpha \) at temperatures of about 1900K (1627°C).

The experimental data presented in the previous chapter for decarburization with CO\(_2\)-Ar gas mixtures at very low flow rates (0.1L min\(^{-1}\)) and Reynolds numbers in the range 0.3–0.6, were used here in order to determine the contribution from thermal diffusion, Table 5.1. In this regime where the Archimedes number (\( Ar \)) >>1, the predominant mode of mass transfer is natural convection and the contribution of forced convection is minimal. The thermal diffusion factor \( \alpha \) can be experimentally deduced by varying the gas composition.
<table>
<thead>
<tr>
<th>[Cr] (wt pct)</th>
<th>Composition (pct CO₂)</th>
<th>Droplet mass (g)</th>
<th>-d[C]/dt (wt pct/sec)</th>
<th>Sh (Observed)</th>
<th>Sh (S-T)</th>
<th>α</th>
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<tbody>
<tr>
<td>10</td>
<td>2</td>
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<td>0.0141</td>
<td>1.15</td>
<td>3.60</td>
<td>0.223</td>
</tr>
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</table>

From Table 5.1, it can be seen that the experimentally determined Sherwood numbers are consistently lower than those calculated, $Sh(S-T)$, from the Steinberger-Treybal equation using only the first two terms which account for molecular diffusion and natural convection respectively:

$$Sh = 2 + 0.569(Gr’Sc)^{0.25} + 0.347Re^{0.62}Sc^{0.31} \quad (5.9)$$

More importantly, the observed Sherwood numbers are even smaller than the minimum expected value of 2 from molecular diffusion. The effect of thermal diffusion may account at least in part for this difference. The observed decarburization rate may be used to determine the thermal diffusion factor by rearranging Eq. (5.5):

$$\frac{W}{-1200A} \frac{d(\text{wt pct C})}{dt_s} = \frac{ShD_{AB}P}{d_pRT_f}X_{CO_2}^{b} = \left(\frac{D_{AB}C_\alpha X_{CO_2}X_{Ar} dT}{T} \frac{dT}{dr}\right)_i \quad (5.10)$$
When evaluated at the film temperature, molecular diffusion and natural convection terms in the Steinberger-Treybal equation can be used to estimate the Sherwood number; allowing $\alpha$ to be found when $dT/dr$ is calculated using Eqs. (5.6) and (5.7). The results are plotted against composition in Figure 5.1 and it is evident that the mole fraction of CO$_2$ has little influence on the value of the thermal diffusion factor. At 1873K (1600°C), $\alpha$ is found to have an average value of 0.228.

![Graph showing binary thermal diffusion factor vs. mole fraction CO$_2$.](image)

**Figure 5.1 Evaluation of $\alpha$ for the Ar-CO$_2$ system at 1873K (1600°C).**

### 5.4 Development of a New Mass Transport Correlation

As mentioned in the previous chapter, the inability to utilize Ranz-Marshall or Steinberger-Treybal correlations to describe the mass transport behavior associated with the levitated droplets is largely influenced by the difference in experimental conditions. For the conditions prevailing in the development of Ranz-Marshall and Steinberger-Treybal correlations, where the temperature difference between the reacting phases was about 200 degrees, the contribution from thermal diffusion would be insignificant compared to natural and forced convection. In contrast however, analysis of the rate data from levitated droplet studies, suggests thermal diffusion effects should not be ignored in systems characterized by large temperature gradients, such as the present system with $\Delta T \approx 1550$ degrees. Thus when assessing transport phenomena within a particular system, it is important to take into consideration the specific conditions in order to apply the most appropriate correlation model.
In the case of the rate data taken from higher gas flow rate regimes (0.385, 1, 3, and 12.2L min\(^{-1}\)), conditions where the Archimedes number \( Ar \ll 1 \), the predominant mode of mass transfer is forced convection. The Sherwood number takes the general form\(^{[11]}\):

\[
Sh = 2 + \beta Re^m Sc^n
\]  

(5.11)

The Schmidt number \( Sc \) takes account of the fluid transfer characteristics and remains largely unchanged given the gas compositions and a fixed effective temperature in the boundary layer. Therefore, the Schmidt number is not a variable in this investigation. For values of \( Sc \) less than 250, the coefficient \( n \) is commonly taken as 1/3. As mentioned in the previous chapter, the contribution of the Reynolds number to the Sherwood number pertains to the relative velocity between the droplet and the gas stream. In the case of stationary levitated droplets this can be directly related to the gas flow rate. Combining Eqs. (5.3) and (5.11):

\[
(J_{CO_2} - J_T) \frac{d_p RT_E}{D_{AB} p_{CO_2}} = 2 + \beta Re^m Sc^{1/3}
\]  

(5.12)

It should be noted that effective film temperature \( T_E \) is used in place of the common film temperature \( T_f \) for reasons detailed in the previous chapter. With the Reynolds number and Schmidt number determined from experimental conditions on the right hand side of Eq. (5.12) and the Sherwood number, taking into account the effect of thermal diffusion, on the left hand side of the equation, coefficients \( \beta \) and \( m \) can be readily determined. Figure 5.2 shows a logarithmic plot of the relationship represented by Eq. (5.12) where the linear slope corresponds to the constant \( m \) and the y-intercept value can be used to calculate the constant \( \beta \). Upon evaluation, Eq. (5.11) becomes:

\[
Sh = 2 + 4.32 Re^{0.363} Sc^{1/3}
\]  

(5.13)
As shown in Figure 5.3, good agreement was found between data available in the literature\textsuperscript{[12,13]} for the rate of CO\textsubscript{2} decarburization of molten steel droplets and Eq. (5.13) from the present investigation. As described in more detail in the previous chapter, these two earlier studies were also conducted using the electromagnetic levitation method. The work by Lee and Rao\textsuperscript{[12]} involved decarburization of Fe-C droplets with CO-CO\textsubscript{2} gas mixtures while Sun and Pehlke\textsuperscript{[13]} carried out decarburization with N\textsubscript{2}-CO\textsubscript{2} gas mixtures, in each case with $P_{\text{CO}_2}$ ranging from 0.1 to 0.2 atm and flow rates between 200 and 2000 mL min\textsuperscript{-1}. It is evident from Figure 5.3 that the data from past studies with Reynolds numbers as low as 2, are well characterized by the correlation derived during the present investigation.
Figure 5.3 Comparison of correlation data derived from previous decarburization studies\textsuperscript{12,13} with Eq. (5.13) from present work.

For comparison purposes the Sherwood number predicted by the Ranz-Marshall equation using an average Schmidt number of 0.7, is included in Figure 5.3. It is evident that there is a significant difference between the relationship represented by the Ranz-Marshall equation and the published experimental data which are in accord with the proposed model from the present work. A noticeable difference between the two correlations is the weaker dependence of $Sh$ on $Re$ in the presence of a large $\Delta T$. This may be expected noting that the steeper temperature gradient between the two phases promotes turbulence in the boundary layer, resulting in an enhanced effective $Re$ in the vicinity of the droplet, while the apparent $Re$ calculated based on the average gas velocity is constant. It is suggested that the temperature gradient, $\Delta T$, between the gas stream and the liquid droplet has a strong influence on models describing and predicting mass transfer numbers such as $Sh$. It is therefore speculated that the experimentally derived coefficients in Eq. (5.11), $\beta$ and $m$, are dependent on the temperature gradient. To validate this suggestion, additional droplet experiments using systems with different temperature gradients would be of value.
Another well-known dimensionless equation, developed by Whitaker\textsuperscript{[14]}, was established to describe heat transfer, by forced convection, to fluids flowing past a single heated sphere. The analogous form of the Whitaker correlation for mass transport, is given as:

\[
Sh = 2 + \left(0.4Re^2 + 0.06Re^3\right)Sc^{0.4}\left(\frac{\mu_b}{\mu_i}\right)^{0.14}
\]  

(5.14)

This equation is recommended for $3.5<Re<7.6 \times 10^4$, $0.71<Sc<380$, and $1.0<\mu_b/\mu_i<3.2$. For conditions prevailing in the current work, the viscosity ratio, $\mu_b/\mu_i$, falls outside of the recommended range, at approximately 0.27. Nonetheless, the Sherwood number predicted by the Whitaker equation using an average Schmidt number of 0.7 is included in Figure 5.4. The model predictions, using either the Whitaker or the Ranz-Marshall equation, offer matching estimations. The reason for this similarity is that both correlations were deduced using experimental data characterized by $\Delta T <200^\circ C$.

![Figure 5.4](image)

Figure 5.4 Comparison of experimental data with the Ranz-Marshall equation and the Whitaker equation.

### 5.5 Thermal Diffusion in the Oxidation Behavior of Fe-Cr-C by O\textsubscript{2}-Ar Gas Mixtures

The effects of thermal diffusion on decarburization using O\textsubscript{2}-Ar gas mixtures do not appear to have been reported previously. Accordingly, this is the purpose of the present investigation.
5.5.1 Decarburization experiments using O$_2$-Ar gases

The experimental procedure is similar to that previously discussed. Once the droplet temperature is stabilized, reaction gas containing 1 pct, 2 pct, 5 pct, or 10 pct O$_2$ was introduced into the reaction chamber at a constant flow rate of 100 mL/min.

5.5.2 Effect of oxidant partial pressure

Typical decarburization results are given in Figure 5.5. It can be seen that carbon contents decrease linearly with respect to reaction time. This linear relationship was found for all oxygen partial pressures employed in this study.

![Graph showing change of carbon concentration with reaction time at different oxygen partial pressures for droplets containing a) [Cr]=10 wt pct and b) [Cr]=17 wt pct.]

To illustrate the effect of gas composition on decarburization behavior, the rate data from experiments using different oxidant partial pressures are shown in Figure 5.6. The decarburization rate for each experimental condition was deduced by linear regression of the change in carbon content with time. The rate data for the various experimental conditions are summarized in Table 5.2. The reaction rate is first order with oxidant partial pressure, which is in accord with previous studies$^{[4,13]}$. 
Table 5.2 Experimental results for decarburization using O\textsubscript{2}-Ar at 1873K

<table>
<thead>
<tr>
<th>[Cr] (wt pct)</th>
<th>$X_{\text{O}_2}^b$ (wt pct)</th>
<th>[C] (wt pct)</th>
<th>Droplet mass (g)</th>
<th>-d[C]/dt (wt pct/sec)</th>
<th>Sh</th>
<th>$\alpha_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>.01</td>
<td>5.47</td>
<td>0.62</td>
<td>0.000733</td>
<td>3.70</td>
<td>0.198</td>
</tr>
<tr>
<td>10</td>
<td>.05</td>
<td>5.47</td>
<td>0.61</td>
<td>0.00707</td>
<td>3.78</td>
<td>0.215</td>
</tr>
<tr>
<td>10</td>
<td>.10</td>
<td>5.47</td>
<td>0.65</td>
<td>0.00904</td>
<td>3.80</td>
<td>0.188</td>
</tr>
<tr>
<td>10</td>
<td>.10</td>
<td>5.47</td>
<td>0.66</td>
<td>0.0163</td>
<td>3.71</td>
<td>0.204</td>
</tr>
<tr>
<td>10</td>
<td>.10</td>
<td>5.47</td>
<td>0.67</td>
<td>0.0125</td>
<td>3.72</td>
<td>0.225</td>
</tr>
<tr>
<td>17</td>
<td>.01</td>
<td>6.00</td>
<td>0.61</td>
<td>0.00116</td>
<td>3.69</td>
<td>0.180</td>
</tr>
<tr>
<td>17</td>
<td>.02</td>
<td>6.00</td>
<td>0.57</td>
<td>0.00191</td>
<td>3.79</td>
<td>0.239</td>
</tr>
<tr>
<td>17</td>
<td>.02</td>
<td>6.00</td>
<td>0.58</td>
<td>0.00356</td>
<td>3.80</td>
<td>0.196</td>
</tr>
<tr>
<td>17</td>
<td>.05</td>
<td>6.00</td>
<td>0.63</td>
<td>0.00555</td>
<td>3.79</td>
<td>0.228</td>
</tr>
<tr>
<td>17</td>
<td>.10</td>
<td>6.00</td>
<td>0.61</td>
<td>0.0129</td>
<td>3.68</td>
<td>0.230</td>
</tr>
</tbody>
</table>

For comparison, the decarburization rate data with CO\textsubscript{2}-Ar gas mixtures are also plotted in Figure 5.6. It can be seen that experiments using oxygen-containing gas mixtures were able to achieve 2.3 times the decarburization rates compared to those with carbon dioxide-containing gas mixtures, given the same oxidant partial pressure and gas flow rate. This finding agrees with the observations made by Distin et al.\cite{15}, who also found that at a gas flow rate of 1.2 L/min, the measured rate for oxygen decarburization was 2.3 times faster than that obtained with carbon dioxide. This is also very similar to the results obtained by Baker et al.\cite{16,17}, who indicated that oxygen is 2.5 times more effective than carbon dioxide for decarburization of iron melts.

![Figure 5.6 Effect of oxidant partial pressure on decarburization rate.](image_url)
5.5.3 Thermal diffusion in mass transfer

The decarburization reaction by oxygen is usually represented by the overall chemical reaction:

\[ O_{2(g)} + 2C = 2CO_{(g)} \]  

(5.14)

For conditions characterized by electromagnetic stirring of the melt, high carbon and low gas flow rate such as those in the current work, the transport of carbon within the melt is faster than oxygen arriving at the gas-metal interface. Therefore at high carbon content the reaction rate is controlled by gas diffusion.

Following the approach detailed in Section 5.3, the thermal diffusion factor \( \alpha \) for \( O_2\)-Ar gas mixtures can be evaluated using:

\[
\alpha = \left( \frac{W}{-2400A} \frac{d(wt\ pct\ C)}{dt_s} - \frac{ShD_{AB}P}{d_pRT_f}X_{O_2}^b \right) \cdot \left( \frac{RT^2}{D_{AB}P} \frac{1}{X_{O_2}^b X_{Ar}^b} \frac{dT}{dr} \right)_{i} 
\]

(5.15)

The numerical values of thermal diffusion factors calculated from Equation (5.15) are reported in Table 5.2. As shown in Figure 5.7, with an average value of 0.210, \( \alpha \) seems to be largely unaffected by the increasing proportion of oxygen, up to 10 pct, in the mixture. The thermal diffusion factor is a quantitative measure of the degree of separation between components in a mixture when subjected to a thermal gradient. The sign of \( \alpha \) is related to the direction of separation. Positive \( \alpha \) suggests that mass fluxes, driven by thermophoretic forces, will travel down the thermal gradient, to the cool region. The opposite is true for negative \( \alpha \).
Measurement of the thermal diffusion factor for O\textsubscript{2}-Ar gas mixtures has not been widely reported. Comprehensive work by Grew et al.\cite{grew1988} was one of the first detailed studies to document the effect of temperature on thermal diffusion factors of eight different binary gas systems. The measurements for the various systems, taken within the temperature range of 73.6-1167K, were made using a two-bulb diffusion apparatus. However, possibly due to the constraints in materials or equipment, no experimental data were listed for the Ar-O\textsubscript{2} system at temperatures in excess of 500K. The results by Grew et al. are shown in Figure 5.8 as a function of temperature. A trend line, extrapolated to higher temperatures by means of trend extension, was drawn in relation to these data points. It can be seen that the average $\alpha$ value determined at 1873K, which was superimposed on the plot, is in fair agreement with the projection that was based on measurements obtained using a technique vastly different from that of the present work. This finding is significant and provides compelling evidence that the electromagnetic levitation technique is appropriate for measurements of the thermal diffusion factor at elevated temperatures, measurements which might be difficult to generate with other techniques.
In the present scenario, mass (O₂ molecule) is being transported to a warm droplet from cold surroundings under a steep temperature gradient, which is in the opposite direction to that of the concentration gradient. Physically, the gas mixture (CO and Ar) leaving the reaction site will be flowing away from the gas-metal interface down the thermal gradient at a rapid rate. In the eventual collision with heavier gas molecules (O₂ and Ar) from the bulk gas, the fast-moving “product” molecules with higher kinetic energy will push away the slow-moving “reactant” molecules. From a macro point of view, the relative high temperature in the droplet’s vicinity creates a flow field that effectively acts as a wall of resistance to the approaching, oxygen-carrying, cold gas mixtures.

5.6 Summary and Conclusions

Electromagnetic levitation is a useful technique for measuring thermal diffusion effects at elevated temperatures. In this study, a forced convection model that incorporates the effects of thermal diffusion has been developed to describe the decarburization kinetics of levitated iron-alloy droplets for Reynolds numbers between 2 and 100. The thermal diffusion factor for CO₂-Ar gas mixtures at 1873K (1600°C) was found to have a value of 0.228. Both Sherwood number expressions derived from the results of the present work, \( Sh = 2 + 4.32Re^{0.363}Sc^{\frac{1}{3}} \) and \( Sh = 2 - 0.317(Gr'Sc)^{\frac{1}{4}} + 3Re^{0.415}Sc^{\frac{1}{3}} \), were found to be in excellent agreement with rate data from other decarburization studies using a similar experimental approach involving levitated droplets.

![Figure 5.8 Temperature dependence of α for Ar-O₂ gas mixtures.](image)
However, there was a significant difference between the relationships represented by the proposed models and those corresponding to the Ranz-Marshall and the Steinberger-Treybal equations. It is therefore recommended that such mass transfer correlations should only be used after taking into account the specific experimental conditions. It is speculated that the experimentally determined coefficients in the different mass transfer relationships have temperature gradient dependence. Quantification of this aspect requires further investigation.

An investigation on the rate of decarburization of Fe-Cr-C alloys in O₂-Ar gas mixtures using the electromagnetic levitation technique has also been made. The rate data obtained at low gas flow rates were used to obtain the thermal diffusion factor for O₂-Ar systems at 1873K, which was found to have a value of 0.21. Electromagnetic levitation has been demonstrated to be a viable alternative technique for measuring thermal diffusion effects at elevated temperatures. It is recommended that this technique be used to study the effect of thermal diffusion in other gas systems.

5.7 References
6 Effect of Chromium-Sulphur Interactions on the Rate of Decarburization by CO$_2$-Ar Gas Mixtures

This part of the research is aimed at providing some insight into the effects of chromium in the presence of sulphur on the decarburization kinetics involving CO$_2$ as the oxidant gas.

It has been indicated$^{[1-4]}$ that sulphur plays an important role in the kinetics of decarburization by CO$_2$. The presence of sulphur, even in low concentrations, was found to significantly decrease the decarburization rate. It is generally understood that the blocking of available reaction sites by chemisorbed sulphur is responsible for the rate retardation. As shown in Figure 6.1, decarburization rate is hampered by the increasing sulphur concentration in the melt. However, the results from the present research suggest that 0.01 wt pct sulphur in the presence of 20% Cr, did not have an adverse effect on the decarburization rate of Fe-Cr-C droplets. It can be seen from Figure 6.1 that chromium-containing melts with 0.01 wt pct sulphur (□) have similar behavior to that of essentially sulphur-free melts (Δ). This trend is consistently observed within a range of gas flow rates, specifically, between 500 mL/min and 1500 mL/min.

![Figure 6.1 Effects of gas flow characteristics and melt sulphur content on the rate of carbon removal.](image)

The presence of chromium in significant concentrations may have contributed to this observation due to its effect on reducing the sulphur activity at steelmaking temperatures. This would imply
that chromium can mitigate the effect of sulphur coverage. In order to gain some insight into the specific mechanism, re-examination of the rate data was performed.

6.1 Development of Rate Equation

As discussed earlier, the rate of carbon loss is linear down to about 1 wt pct C, which suggests that mass transport in the liquid phase is not the rate-limiting step. If decarburization is limited solely by the transport of CO$_2$ from the bulk gas to the interface, the rate can be expressed as follows:

$$\frac{d(\text{wt pct C})}{dt_s} = \frac{-1200A}{W} \frac{k_g}{RT_f} \left(p_{\text{CO}_2}^b - p_{\text{CO}_2}^i\right)$$  \hspace{1cm} (6.1)

where $k_g$ is the gas phase mass transfer coefficient, $p_{\text{CO}_2}^b$ is the CO$_2$ partial pressure in the bulk gas on the edge of the boundary layer and $p_{\text{CO}_2}^i$ is the CO$_2$ partial pressure at the interface. In the gas phase controlled scenario, $p_{\text{CO}_2}^i$ is expected to approach zero.

The interfacial reaction for dissociative chemisorption of CO$_2$ can be written as:

$$\text{CO}_2^i + v = \text{CO}^* + O^*$$  \hspace{1cm} (6.2)

where $v$ represents a vacant reaction site at the droplet surface and the superscript $i$ and * denote interface and adsorbed species, respectively. Ignoring the reverse reaction, the rate of decarburization is given by:

$$\frac{d(\text{wt pct C})}{dt_s} = \frac{-1200A}{W} k_c (1 - \theta_S) p_{\text{CO}_2}^i$$  \hspace{1cm} (6.3)

where $k_c$ is the chemical rate constant for the forward reaction described in Equation (6.2). The fractional surface coverage by sulphur, $\theta_S$, can be described using the Langmuir adsorption model:

$$K_S = \frac{\theta_S f^*_S}{(1 - \theta_S - \theta_u) a_S}$$  \hspace{1cm} (6.4)

where $K_S$ is the sulphur adsorption coefficient, $a_S$ is the activity of sulphur in the melt, $\theta_u$ represents the fraction of surface sites that cannot be occupied by sulphur, and $f^*_S$ is the activity
coefficient of sulphur in the adsorbed layer, which can be taken as unity at carbon saturation\textsuperscript{[2]}. For carbon saturated alloys, Sain and Belton\textsuperscript{[2]} provided an expression for $K_S$, in wt pct$^{-1}$, which was based on measurements taken between 1553K and 1873K:

$$\log K_S = \frac{3600}{T} + 0.57 \quad (6.5)$$

The $\theta_u$ term was introduced to account for the residual rates observed by many investigators\textsuperscript{[2,5,6]} who noted that increase in sulphur content beyond 0.1 wt pct does not further decrease the decarburization rate. Lee and Rao\textsuperscript{[5]} have obtained a value of 0.085 for $\theta_u$ from kinetics analysis of their study involving levitated droplets. For convenience, Equation (6.4) can be rearranged in terms of available reaction sites:

$$(1 - \theta_S) = \frac{f_S^* + a_sK_S\theta_u}{f_S^* + a_sK_S} \quad (6.6)$$

When the process of decarburization is jointly controlled by both the gas phase mass transfer and the interfacial reaction, the overall rate may be derived by combining Equations (6.1) and (6.3). The resulting expression takes the form:

$$\frac{d(\text{wt pct } C)}{dt_s} = \frac{-1200A}{W} \frac{k_gk_c(1 - \theta_S)p_{CO_2}^b}{RT_fk_c(1 - \theta_S) + k_g}$$ \quad (6.7)

### 6.2 Effect of Chromium

As shown in Figure 6.2, experimental measurements by Lee and Rao\textsuperscript{[7]} has demonstrated the effect of sulphur concentration on the overall rate. The result from present work, obtained under similar experimental conditions, is also superimposed on the plot. It can be seen that the process of decarburization of Fe-C alloys containing 20 wt pct chromium (represented by ■) is 33 pct faster than chromium-free melts (represented by ○) containing the equivalent amount of sulphur, based on the experimental results by Lee and Rao\textsuperscript{[7]}.
According to Equation (6.7), the fractional surface sites available for the CO₂ dissociative reaction, \((1 - \theta_S)\), is an important parameter in decarburization kinetics. It is evident from Equations (6.6) and (6.7) that the rate would become a sole function of \(a_S\) if parameters such as droplet weight, temperature, gas composition and flow rate remain constant. Hence the effect of an alloying element such as chromium on the decarburization rate is reflected by virtue of the effect on the sulphur activity coefficient, and consequently \((1 - \theta_S)\). The interaction parameter for effect of Cr on S as a function of temperature is given by the equation[8]:

\[
e_{S}^{Cr} = \frac{-94.2}{T} + 0.040
\]  

(6.8)

At 1873K, \(e_{S}^{Cr}\) has a value of -0.0103. Using this figure, the effect of chromium on surface coverage by sulphur can be computed using Equation (6.6). Results of the calculations are summarized in Figure 6.3. For instance, melts with identical sulphur concentration of 0.01 wt pct, the fraction of available sites is approximately 31 pct higher in the melts containing 20 wt pct chromium compared with chromium-free melts. With more available sites on the surface of the droplet, the contribution from chemical rate to the overall rate equation is expected to increase. Since the interfacial reaction takes place much faster than the transfer of gaseous oxidant across the boundary layer, this phenomenon translates to an enhanced rate as indicated by Figure 6.2. In other words, melts containing 0.01 wt pct sulphur and 20 wt pct chromium can exhibit decarburization behavior that is similar to melts which are essentially free of sulphur.
This finding is particularly significant to the industrial development of decarburization of stainless steels by \( \text{CO}_2 \).

![Figure 6.3 Change of available surface sites with melt sulphur and chromium contents.](image)

### 6.3 Summary and Conclusions

This work provides an explanation for the influence of chromium on the decarburization kinetics for systems involving \( \text{CO}_2 \) as the oxidant. The increase in decarburization rate of iron-chromium droplets, compared to chromium-free droplets containing the same amount of sulphur, can be accounted for by the solute interaction effects between chromium and sulphur in the liquid phase that resulted in a decrease of surface site occupation by sulphur.

### 6.4 References

7 Thermodynamic and Kinetic Aspects of Sulphur Evaporation from Fe-C Alloy Droplets*

The aim of this study was to investigate the physical chemistry aspects of sulphur behaviour that was observed during the decarburization experiments with CO\(_2\). With this in mind, the loss of sulphur from Fe-C-0.1 wt pct S alloys at 1873K was determined using electromagnetic levitation and an inert atmosphere of purified argon. The influence of carbon concentration, up to carbon saturation, on the reaction kinetics was examined and the effect of carbon on the activity coefficient of sulphur in liquid iron was also evaluated.

7.1 Background

Electromagnetic levitation is a technique well suited for the study of vaporization of solute elements from liquid metals. The vigorous inductive stirring ensures melt homogeneity and refreshes the solute-depleted layer close to the liquid metal surface thereby increasing the rate of liquid phase mass transport. Due to rapid kinetics, the time required to reach thermal and chemical equilibrium is particularly short. With levitated droplets, the spherical geometry provides the additional benefits of well–defined and high surface area to volume ratio, which is important in surface controlled processes such as impurity evaporation.

As discussed in Chapter 4, sulphur loss was observed during the decarburization of Fe-Cr-C-S levitated droplets with CO\(_2\)-Ar gas mixtures\(^{[1]}\). Similar behaviour has been reported elsewhere. For example, Nagasaka and Fruehan\(^{[2]}\) found that sulphur loss was 5-12 % during decarburization of levitated Fe-C-S droplets when exposed to CO\(_2\)-Ar, CO\(_2\)-H\(_2\)O and CO\(_2\)-H\(_2\)O-Ar atmospheres. Sain and Belton\(^{[3]}\) have also reported sulphur loss, of up to 22 %, during decarburization of Fe-C-S melts in alumina crucibles with an impinging jet of CO\(_2\)-Ar. While it is well known that sulphur removal from steel by molten slag is most effective under reducing conditions, a number of studies\(^{[4-6]}\) have shown that steel desulphurization can also be achieved by vaporization. More recently, investigations\(^{[7,8]}\) were carried out to study sulphur removal during ladle vacuum degassing. Fruehan and Turkdogan\(^{[4]}\), in their study on the formation of SiS vapor, indicate that rapid desulphurization during vacuum degassing is likely due to the

* Material from this chapter has been submitted to ISIJ Int., 2014.
formation of sulphur-bearing volatile species, which significantly improve the sulphur transfer between steel and slag. It is therefore speculated that, in the absence of a slag phase, sulphur volatilization may be responsible for the loss observed from levitated droplets exposed to the CO$_2$-Ar atmosphere.

As noted in Chapter 4, depending on the carbon concentration in the melt, sulphur loss varies between 18 and 64%. The detailed study on the kinetics of sulphur evaporation by Sehgal et al.\cite{6} found that sulphur removal rate was increased by 40% when the carbon concentration was increased by approximately 1 wt pct. These authors went on to suggest that carbon affects the desulphurization rate only through activity interaction effects within the metal phase. Since carbon substantially increases the activity of sulphur in liquid iron, most desulphurization practices are performed during hot metal pretreatment. The purpose of the present investigation is to examine the thermodynamic and kinetic aspects associated with the effect of carbon on sulphur removal from levitated iron droplets exposed to an inert argon atmosphere.

### 7.2 Experimental Aspects

Fe-C-0.1 wt pct S alloys with various carbon contents were levitated in an inert atmosphere, which was maintained with a constant argon gas flow rate of 1 L/min. Moisture was removed from high purity argon gas with drierite columns and the dried argon then deoxidized by passing through heated titanium pellets. After exposing the liquid metal samples to the purified argon atmosphere for a predetermined time, power was turned off, allowing the droplet to fall into the copper mold and be quenched. Metal samples were analyzed for carbon and sulphur using a LECO CS-244 analyzer.

### 7.3 Results and Discussion

Experimental results presented in Figure 7.1 show the decrease in sulphur concentration as a function of time. The carbon concentration remains virtually constant throughout the experiments as shown in Figure 7.2. Two noticeable features can be observed from the desulphurization behavior: i) The rate of sulphur removal is consistent with a first-order reaction relative to sulphur concentration in the melt, and ii) The rate increases with increasing carbon content of the melt.
7.3.1 Kinetics of sulphur removal

Sulphur removal from the molten alloy follows first order kinetics, according to the relationship:
\[
\frac{d[S]}{dt_m} = k_a \frac{A}{V} \text{(wt pct S)} \tag{7.1}
\]

Upon integration:

\[
\ln \frac{S_t}{S_o} = k_a \frac{A}{V} t_m \tag{7.2}
\]

The apparent rate constants, \(k_a\), can be obtained from the linear slopes of \(\ln S_t/S_o\) vs \(t_m\) plots, as shown in Figure 7.3, where \(S_o\) is the initial sulphur concentration of the alloy and \(S_t\) is the sulphur concentration at time \(t_m\). The compositions of the alloys and values of \(k_a\) are summarized in Table 7.1.

![Figure 7.3 Desulphurization of Fe-C-S alloys at 1873K.](image)

**Table 7.1 Experimental results**

<table>
<thead>
<tr>
<th>Droplet mass (g)</th>
<th>Initial [C] (wt pct)</th>
<th>Initial [S] (wt pct)</th>
<th>[S] at (t_m=40\text{min}) (wt pct)</th>
<th>(k_a) (cm min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.726</td>
<td>0.063</td>
<td>0.131</td>
<td>0.0794</td>
<td>-0.00114</td>
</tr>
<tr>
<td>0.683</td>
<td>0.704</td>
<td>0.119</td>
<td>0.0584</td>
<td>-0.00171</td>
</tr>
<tr>
<td>0.750</td>
<td>1.76</td>
<td>0.112</td>
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</tr>
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<td>0.120</td>
<td>0.0283</td>
<td>-0.00429</td>
</tr>
<tr>
<td>0.674</td>
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</tr>
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</tr>
<tr>
<td>0.704</td>
<td>5.06</td>
<td>0.104</td>
<td>0.0039</td>
<td>-0.0286</td>
</tr>
</tbody>
</table>
In the absence of a slag phase, sulphur is expected to leave the droplet in gaseous form. The kinetics of sulphur removal involves the following steps:

1. Liquid phase transport of sulphur to the metal-gas interface.
2. Surface reaction involving desorption of the sulphur species at the interface.
3. Gaseous diffusion within the gas boundary layer.

Due to the relatively high argon flow, the transport of gaseous product across the boundary layer is not expected to hinder the desulphurization rate. With induction stirring of the melt and constant surface renewal, the rate of sulphur removal should not be impeded by sulphur transport in the liquid phase. Therefore mass transport should not have been rate-limiting under the conditions prevailing in the current work. This is further substantiated by the fact that carbon concentration in the melt exhibits a beneficial effect on the desulphurization rate whereas, in fact, Kawai[9] found that carbon decreases the diffusion coefficient of sulphur in steel. This argument is consistent with observations made by previous investigators[4,5], which also suggest that the rate is controlled by a surface reaction.

Based on the investigation by Mukawa et al.[10], at 1873K, oxygen is approximately three times more surface active than sulfur in liquid steel. However, due to the relatively high carbon contents studied in the present work, the dissolved oxygen concentration is expected to be less than 50 ppmw. In contrast, sulfur concentration (0.1 wt pct) is at least 20 times greater. Thus, formation of COS and surface coverage by oxygen are considered negligible. The volatile sulphur-bearing species relevant to the current work are listed in Table 7.2. It can be seen from Figure 7.4 that the equilibrium vapor pressure for monatomic sulphur above Fe-C-0.1 wt pct S alloys is several orders of magnitude higher than other co-existing species. This is in good agreement with the mass spectrometric study by Kato and Fukube[11], which indicated that monatomic sulphur is the principal sulphur-bearing species leaving the surface of Fe-C-S melts. At 1873K, evaporation of sulphur in the form of S(g) is more favorable[4] and is therefore taken as the dominant species for subsequent evaluations of kinetics and thermodynamics in the present work.
Table 7.2 Equilibrium vapor pressures of sulphur-bearing gases over Fe-C-0.1 wt pct S alloys at 1873K

<table>
<thead>
<tr>
<th>Species</th>
<th>Gibbs Energy Change (J/mol)</th>
<th>Equilibrium vapor pressure at 1873K (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S = S_{(g)} )</td>
<td>341988-79.19T( ^\dagger )</td>
<td>4.0 ( \times 10^{-7}f_s )</td>
</tr>
<tr>
<td>( S = \frac{1}{2}S_{2(g)} )</td>
<td>125100-18.50T( ^\dagger )</td>
<td>9.0 ( \times 10^{-8}f_s^2 )</td>
</tr>
<tr>
<td>( C + S = CS_{(g)} )</td>
<td>324093-68.52T( ^\dagger )</td>
<td>3.5 ( \times 10^{-7}a_cf_S )</td>
</tr>
<tr>
<td>( C + 2S = CS_{2(g)} )</td>
<td>236948-11.40T( ^\dagger )</td>
<td>9.7 ( \times 10^{-9}a_cf_S^2 )</td>
</tr>
<tr>
<td>( Fe_{(l)} + S = FeS_{(g)} )</td>
<td>428540-111.36T( ^\dagger )</td>
<td>7.3 ( \times 10^{-8}f_S )</td>
</tr>
</tbody>
</table>

\( f_S \): Activity coefficient of sulphur.
\( a_c \): Activity of carbon.
\( ^\dagger \): NIST-JANAF Thermochemical Tables (Fourth Edition)\([12]\)
\( ^\ddagger \): Thermodynamic Data For Steelmaking\([13]\)

Figure 7.4 Equilibrium vapor pressures over Fe-C-0.1 wt pct S alloys at 1873K.

From the transition state theory, where quasi-equilibrium exists between reactants and activated complexes, the reaction involving sulphur vaporization is written as:

\[
x_S = (S_x)^\ddagger
\]  
(7.3)

The corresponding equilibrium constant is given by:

\[
K_3 = \frac{a_x}{a_S^2}
\]  
(7.4)
where \( a_\dagger \) is the activity of the complex \((S_x)\dagger\) and \( a_S \) is the sulphur activity in the melt. Following the approach of Fruehan and Turkdogan\[^4\], the rate equation is represented by:

\[
\frac{d(\text{wt ppt } S)}{dt_m} = \frac{-100A k_B T}{\rho V h_p} M_S \Gamma_o \theta^\dagger
\] (7.5)

where \( \rho \) is the density of liquid iron, \( A \) is the surface area of the droplet, \( V \) is the volume of the melt, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( h_p \) is Planck’s constant, \( M_S \) is the molecular mass of sulphur, \( \Gamma_o \) is the total available sites for chemisorption, and \( \theta^\dagger \) is the fractional coverage occupied by the activated complexes. Since sulphur is highly surface active, the effect of fractional surface coverage by sulphur, \( \theta_S \), on \( \theta^\dagger \) must also be considered when interpreting the rate data. \( \theta_S \) can be expressed using the Langmuir adsorption equation:

\[
K_S = \frac{\theta_S f_S^\ast}{(1 - \theta_S) a_S}
\] (7.6)

where \( f_S^\ast \) is the activity coefficient of sulphur in the adsorbed layer and \( a_S \) is the activity of sulphur in the melt. \( K_S \) is known as the sulphur adsorption coefficient. For carbon saturated alloys, Sain and Belton\[^3\] provided an expression for the effect of temperature on the adsorption coefficient, which was based on measurements taken between 1553K and 1873K.

\[
\log K_S = \frac{3600}{T} + 0.57
\] (7.7)

For the composition range studied in the present work, the surface coverage by adsorbed sulphur is within the range \( 0.95 < \theta_S < 1 \). Hence it is reasonable to assume the limiting case of \( \theta_S \to 1 \), where \( \theta^\dagger \) simplifies\[^4\] to:

\[
\theta^\dagger = K_3 a_\dagger f_\dagger \left(1 - \theta_S \right)
\] (7.8)

where \( f_\dagger \) is the activity coefficient of the complexes. For the limiting case of \( \theta_S \to 1 \), \( (1 - \theta_S) \) can be represented by \( f_S^\ast / a_S \). Considering the diatomic nature of the activated complexes, which has been expounded by Fruehan and Turkdogan\[^4\], Eq. (7.8) becomes:
\[ \theta^\ddagger = \frac{K_3 f_s^*}{f^\ddagger} a_S \]  

(7.9)

Combining Eqs. (7.5) and (7.9) and replacing \( a_S \) for dilute solution:

\[
\frac{d(\text{wt pct } S)}{dt_m} = \frac{-100A k_B T}{\rho V} \frac{K_3 f_s^*}{h_p \Gamma_o} \frac{K_3 f_s^*}{f^\ddagger} M_S f_S (\text{wt pct } S) \]  

(7.10)

Upon integration, the rate equation can be expressed as:

\[
\ln \frac{S_t}{S_o} = \frac{-100A k_B T}{W} \frac{K_3 f_s^*}{h_p \Gamma_o} \frac{K_3 f_s^*}{f^\ddagger} M_S f_S t_m \]  

(7.11)

where \( W \) is the weight of the droplet.

Kozakevitch et al.\(^{[14]}\) found that the surface tension of molten Fe-C-S alloys at 1723K is solely a function of sulphur concentration, which implies that the activity coefficient of adsorbed sulphur is not a function of carbon concentration. In the present work, the influence of carbon on the desulphurization rate is thus reflected only by virtue of the sulphur activity coefficient, \( f_S \). Therefore, the rate data are expected to be represented by a single straight line on a plot of \( \ln S_t / S_o \) vs. \( A \cdot f_S \cdot t_m / W \). However, as indicated by Figure 7.5, the slopes of the lines were found to vary with different carbon concentrations. This difference may be due to errors in the estimation of carbon’s effect on sulphur behavior. A similar discrepancy was also reported by Belton et al.\(^{[5]}\). In their analysis they found the experimental desulphurization rate to be consistently higher than the theoretical maximum by approximately 20% for carbon concentrations between 0 and 4.9 wt pct. Inaccurate description of solution thermodynamics was postulated to be one of the potential causes for this observed discrepancy.
7.3.2 Thermodynamic considerations

Studies\textsuperscript{[15,16]} on the thermodynamic behavior of sulphur in the presence of carbon often utilize the solute dissolution method, where a binary gas mixture such as H\textsubscript{2}-H\textsubscript{2}S of known ratio is passed over or bubbled through molten iron-carbon alloys. In the work of Ban-ya \textit{et al.}\textsuperscript{[16]}, it was concluded that while this experimental technique is appropriate for studying most other alloying elements, the results for Fe-S-C obtained in this manner are possibly less dependable than measurements made using other techniques. Formation of volatile sulfides during the experiments is thought to have an impact on the reliability of measurements. Also, as pointed out by Sunderland \textit{et al.}\textsuperscript{[17]}, when gas mixtures are passed over molten alloys during gas dissolution experiments, the measured steady-state solubilities may differ from the true equilibrium values due to the presence of thermal diffusion effects. By contrast, thermal diffusion may be less relevant in the case of thermodynamic measurements based on sulphur evaporation in vacuum or inert atmosphere with a levitated droplet. Hence this approach could prove useful in determining interaction parameters for solutes in liquid iron alloys.

The effect of carbon on the activity coefficient of sulphur in liquid iron is given by:

\[ \log f_s = e_s^C \text{ (wt pct C)} + r_s^C \text{ (wt pct C)}^2 + e_s^S \text{ (wt pct S)} \]  \hspace{1cm} (7.12)
where $e^C_S$ and $r^C_S$ are respectively the first-order and second-order interaction parameters for the effect of carbon on the activity coefficient of sulphur. The self-interaction parameter for sulphur $e^S_S$ is given\textsuperscript{13} as:

$$e^S_S = \frac{-120}{T} + 0.018$$  \hspace{1cm} (7.13)

At 1873K, the commonly quoted values for $e^C_S$ and $r^C_S$ are 0.11\textsuperscript{13,18} and 0.0058\textsuperscript{18}, respectively; both of which were derived from experimental data\textsuperscript{15,16}. Due to the relatively high carbon and low sulphur concentrations studied in the present work, the contribution from the self-interaction parameter to the sulphur activity coefficient is negligible. Eq. (7.12) is therefore reduced to:

$$\log f_S = e^C_S(\text{wt pct } C) + r^C_S(\text{wt pct } C)^2$$  \hspace{1cm} (7.14)

In order to confirm the validity of the kinetics analysis discussed in the present work, it is essential to verify the values used for the interaction parameters and hence the sulphur activity coefficients. Values for $e^C_S$ and $r^C_S$ can be obtained by examining the extent of desulphurization as a function of melt carbon concentration. As shown in Figure 7.1, due to the rapid kinetics associated with the levitation technique, sulfur concentrations in the high-carbon samples approached steady-state after about 30 minutes of exposure to the argon gas flow. Desulfurization behavior of the low-carbon samples suggest that steady-state is not far beyond the 40-minute mark. Thus, droplets at 40 minutes are considered to be in a near-equilibrium state. The overall reaction for sulphur vaporization from liquid iron alloys can be represented by the following:

$$S = S'(C)$$  \hspace{1cm} (7.15)

for which the equilibrium constant is:

$$K = \frac{P_S}{(\text{wt pct } S)f_S}$$  \hspace{1cm} (7.16)

where $P_S$ is the equilibrium partial pressure of monatomic sulphur. Combining Eqs. (7.14) and (7.16) and rearranging the terms:
\[
\frac{\log P_S - \log K - \log(\text{wt pct } S)}{\text{wt pct } C} = r_S^C (\text{wt pct } C) + e_S^C
\]  
(7.17)

From Eq. (7.17), the common practice for determining values for \(e_S^C\) and \(r_S^C\) is by plotting the left hand side of Eq. (7.17) against carbon concentration in the melt. This approach requires \(K\) and \(P_S\) to be known. Since the present experiments were conducted at a fixed temperature of 1873K, the value of \(K\) is a constant for all conditions. In the case of measurements made in an inert atmosphere or vacuum, an accurate value for the effective \(P_S\) is not available. However, the atmospheric conditions imposed on the droplets by constant argon flow are identical among the various trials. Therefore, the applied \(P_S\) is not a variable in this investigation. Rearranging Eq. (7.17), Eq. (7.18) is obtained:

\[
-\log(\text{wt pct } S) = r_S^C (\text{wt pct } C)^2 + e_S^C (\text{wt pct } C) + \log K - \log P_S
\]  
(7.18)

A plot of the present results expressed in terms of Eq. (7.18) is shown in Figure 7.6. The y-intercept corresponds to the combination of \(\log K\) and \(\log P_S\). By calculating the value of \(K\) at 1873K using the free energy expression shown in Table 7.2, together with the intercept value from Figure 7.6, the value of \(P_S\) can be deduced. For the current experimental conditions, the effective partial pressure of monatomic sulphur experienced by the metal droplets is calculated to be \(2.6 \times 10^{-7} \text{ atm}\), which is in accord with the thermodynamic prediction listed in Table 7.2.

For comparison purposes, a predicted equilibrium line based on the previously reported interaction parameter values is included in Figure 7.6. It can be seen that, at carbon concentrations less than approximately 2 wt pct, the present experimental data are in good agreement with the predicted equilibrium line. However as carbon concentration increases beyond 2 wt pct, the measured values begin to deviate from the prediction; suggesting a substantial contribution from the second-order term may be important.
Upon evaluation by polynomial regression, it is found that $e_S^C = 0.113$ and $r_S^C = 0.028$. The value obtained for $e_S^C$ agrees well with those reported in the literature: 0.114$^{[16]}$, 0.11$^{[13,18]}$, 0.12$^{[19,20]}$. However, for the second-order interaction coefficient ($r_S^C$), the value determined in the present work is appreciably higher than those found in previous studies that utilized the solute dissolution approach. It should be noted that there are large discrepancies among the reported values: 0.0058$^{[18]}$, 0.0091$^{[16]}$, 0.013$^{[21]}$. This relatively wide range of values seems to indicate that, for experiments conducted in a H$_2$-H$_2$S atmosphere, the measurements are more susceptible to errors that may arise from the effects of thermal diffusion$^{[17]}$.

7.3.3 Integrated rate analysis

The parameters determined from the equilibrium study permit reevaluation of the sulphur activity coefficients from the kinetic analysis. On a plot of $\ln S_t/S_o$ vs. $A \cdot f_S \cdot t_m/W$, as shown in Figure 7.7, the desulphurization data are well-described by a single straight line. The gradient of the line, based on Eq. (7.19), can be used to compute the desulphurization rate constant, $k_a'$.

$$-\ln \frac{S_t}{S_o} = k_a' \frac{100A}{W} f_s t_m$$  \hspace{1cm} (7.19)

For the experimental conditions prevailing in the present work, specifically $T=1873K$ and $\theta_S > 0.95$, the desulphurization rate constant is found to be $1.33 \times 10^{-4} g \ cm^{-2} \ min^{-1}$. To put
this value in perspective, experimental data\(^{[4]}\) for free evaporation of sulphur from Fe-C-S melts at 1873K and 1.333 Pa pressure reveals \(k_a' = 2.07 \times 10^{-3} \text{ g cm}^{-2} \text{ min}^{-1}\). Thus it would appear that the rate of evaporative loss of sulphur from Fe-C-S melts at atmospheric pressure is approximately one order of magnitude less than that in vacuum.

\[
\frac{dy}{dx} = -0.0133 \\
R^2 = 0.971319
\]

Figure 7.7 Kinetic analysis using the proposed interaction parameters.

In view of the fact that the thermodynamic analysis described in the previous section was based on measurements pertaining to equilibrium conditions and was uninfluenced by reaction kinetics, the validity of the values for the interaction parameters derived in the present work is further supported by their ability to provide an excellent description of the desulphurization rates.

### 7.4 Summary and Conclusions

Sulphur loss from levitated Fe-C-S alloys exposed to an inert atmosphere at 1873K is attributed to the formation of monatomic sulphur vapor. Within the composition range studied, the rate of sulphur removal was found to be in accord with a first-order type reaction with respect to sulphur concentration in the melt. Carbon exerted a positive effect on the rate, by increasing the activity of sulphur. It was found that the values reported in the literature for the second order interaction parameter \(r_S^C\) consistently underestimated the influence of carbon on the sulphur activity coefficient. This led to erroneous assessment of the rate data. Based on a thermodynamic evaluation of the results from the present work, values were determined for the first and second
order parameters $e^C_S$ and $r^C_S$. While the value obtained for $e^C_S$ of 0.113 is in excellent agreement with literature data, the value for $r^C_S$ of 0.028 is significantly higher. Using the proposed new values for the parameters, the desulphurization behavior is well represented by a rate equation describing interfacial reaction as the rate-determining step.

7.5 References
8 Electromagnetic Levitation of Silicon and Silicon-Iron Alloy Droplets*

In this chapter, a technique for non-conductive silicon heating and conductive silicon levitation is described. Results are presented for the effects of specimen weight and applied power on the heating behaviour and temperature control of levitated silicon and silicon-iron alloy droplets.

8.1 Background

In recent years, the world's photovoltaic (PV) industry has experienced rapid development and expansion, attracting considerable attention from different industrial sectors. However, a shortage of raw materials with high purity and low cost restricts major development of this clean energy industry. At present, expensive semiconductor grade silicon (SEG-Si) is used for the manufacture of cells to convert solar energy into electricity. This results in a high cost for photovoltaic electricity compared to electricity derived from conventional sources. Since the amount of SEG-Si scrap supply is limited, an innovative process for silicon production using relatively inexpensive metallurgical grade silicon (MG-Si) as a starting material could provide a more economical route for the manufacture of solar cells.

A number of research studies have been carried out to upgrade metallurgical grade silicon to solar grade silicon\[1-6\]. For example, acid leaching, slag refining, thermal plasma processing, controlled solidification and vacuum melting have all been investigated. While solidification refining is an effective way to remove most of the impurities and does not require chemical processing, phosphorus and boron are not removed by this approach. There is therefore considerable interest in developing new processes for dephosphorization of silicon, as well as the removal of boron, in order to provide material which could then be used for solar grade applications. A potential method for the removal of phosphorus is to apply reduced pressure.

As discussed in previous chapters, electromagnetic levitation is an ideal tool to study gas-metal interactions and related kinetics owing to inherent advantages such as inductive stirring and approximate spherical geometry of the levitated droplet with associated high specific surface

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area. In addition, unlike other processes which use containers, levitation refining avoids potential contamination of the molten silicon by container materials. The aim of this work is to develop an electromagnetic levitation technique that would be suitable for the investigation of the thermodynamic and kinetic factors that affect the removal of phosphorus from metallurgical grade silicon or ferrosilicon alloys.

In the following sections, details are provided concerning some fundamental considerations pertaining to the levitation and temperature control of silicon and silicon-iron alloy droplets.

8.2 Levitation of Silicon and Silicon-Iron Alloy Droplets

Since the resistivity of pure silicon is too high for samples to be electromagnetically levitated at temperatures below 1100K, an additional pre-heating step is required. There are several preheating techniques reported in the literature associated with investigations of crystallization behavior and physical property measurements of highly undercooled silicon melts. Kuribayashi et al.\textsuperscript{[7-9]} transmitted a CO\textsubscript{2} laser beam with wavelength of 10.6 µm onto the silicon specimen to increase temperature high enough so that the droplet conductivity reaches the working range for levitation. For drop-shaft microgravity experiments\textsuperscript{[10,11]} an infrared heating device was implemented for preheating the metal specimen. Li et al.\textsuperscript{[12]} suggested preheating be carried out in a resistance furnace positioned directly above the levitation coil. The work by Przyborowski et al.\textsuperscript{[13]} has demonstrated the possibility of levitating single crystal silicon without preheating. It has been shown that B and Sb doped silicon displayed significantly lower resistivity than pure silicon and that levitation and subsequent melting was achieved.

In the present work, a silicon specimen was first placed on a high purity graphite disc located on the alumina charging rod as shown in Figure 8.1. The approach is similar to that by Li and Herlach\textsuperscript{[14]} where a graphite heating element was encapsulated by an alumina shell. The graphite disc is then heated by induction as a result of the applied electromagnetic field. The resulting thermal energy is transferred from the graphite disc to the solid silicon by conduction. Decreased resistivity causes the solid specimen to respond to the applied field and begin to gain heat and ultimately levitate. The alumina charging rod is retracted as soon as a stable levitation condition is attained. In the case of silicon-iron specimens, pre-heating is also necessary but this can be achieved without utilizing the graphite disc. Iron within the silicon-iron alloy is responsible for providing inductive heating to the entire specimen. In the vicinity of 900K, silicon-iron
specimens respond to the applied field and begin to levitate. Photographs of a levitated silicon alloy droplet and as-quenched silicon sample are shown in Figure 8.2 and Figure 8.3, respectively.

Figure 8.1 Schematic diagram of the electromagnetic levitation assembly.

Figure 8.2 Levitation of a silicon alloy droplet.  
Figure 8.3 Quenched silicon sample.
8.3 Effect of Operating Parameters on Temperature Control

8.3.1 Effect of specimen mass

Heating profiles of silicon-iron specimens containing 15 wt pct iron, are shown in Figure 8.4. The levitation facility provides rapid heating and permits most specimens to reach a molten state in less than 100 seconds. Under a constant applied power and frequency, the droplet heating rate increases with increasing specimen mass, which adds to the absolute amount of iron in the silicon alloy specimen, resulting in additional heat gain through induction. Temperatures more than 200K above the melting point can be achieved using heavier specimens.

![Figure 8.4 Heating profiles for silicon-iron droplets containing 15% iron.](image)

8.3.2 Effect of applied power

The magnitude of power applied to the coil controls the vertical position of the droplet within the electromagnetic field, which, in turn determines the density of electromagnetic field lines that interact with the droplet. The effect of applied power on droplet heating behavior is shown in Figure 8.5. The increase in heating rate at approximately 900K is attributed to the silicon responding to the applied field and beginning to generate heat by induction.
By decreasing the power supplied to the coil, the lifting force is reduced and the droplet is located lower within the bottom coil, where the field flux is higher. As a result, the droplet temperature increases. Conversely, by increasing power to the coil, the droplet sits higher within the electromagnetic field where the flux is weaker and consequently lower temperatures are achieved. However, upon reaching a minimum temperature, further increase in applied power will lift the droplet higher into the electromagnetic field associated with the upper coil where the flux is greater and this will cause the droplet temperature to increase again, as shown in Figure 8.6. The effect of specimen mass on droplet temperature at fixed power input is shown in Figure 8.7. By controlling these parameters precise droplet temperatures within the desired range can be achieved.

Figure 8.5 Heating behavior of silicon-iron alloy droplets at two levels of applied power.
8.4 Conclusions

(1) Electromagnetic levitation of silicon was achieved using a pre-heating procedure by means of which solid silicon was heated by conduction while positioned on a high purity graphite disc which in turn was located within the electromagnetic field. With increasing temperature, the resistivity of the silicon is decreased and at approximately 1100K the solid silicon responds to the applied field and begins to levitate.

(2) Pre-heating is also necessary with silicon-iron alloys but this can be achieved without utilizing the graphite disc. Iron within the silicon alloy is responsible for providing induction heating to the entire specimen. At temperatures in the vicinity of 900K, silicon-iron specimens respond to the applied field and begin to levitate.

(3) With the aid of an appropriate coil design the effect of specimen weight and applied power on droplet temperature was investigated. Under a constant applied power and frequency, the droplet heating rate increases with increasing specimen mass. Reducing the lift force by decreasing the power will allow the droplet to position lower within the coil, where the field flux is stronger. As a result, the droplet temperature increases. Conversely, the droplet temperature is able to remain at the lower end of the temperature range if the droplet sits
higher within the electromagnetic field. This is achieved by increasing power to the coil. However, upon reaching a minimum temperature, further increase in applied power will increase the droplet temperature due to positioning of the sample within the reversed turn region of the coil where the flux density again increases.

(4) The rapid heating nature of electromagnetic levitation permits most silicon and silicon-iron specimens to reach the molten state in less than 100 seconds.

8.5 References

9 Summary and Conclusions

9.1 Summary

1. An electromagnetic levitation melting facility has been designed and constructed and a series of controlled experiments performed to evaluate the effects of coil geometry and associated parameters such as droplet size and applied current on droplet stability, heating behaviour and temperature control.

2. Using the levitation facility, the decarburization of Fe-Cr-Csat alloy droplets containing 10%, 17%, and 20% chromium, by weight, was carried out at 1873K (1600°C) with CO₂-Ar gas mixtures at flow rates between 100 and 12,200 mL per min. which is within the regime between creeping flow (Stokes flow) and a Reynolds number of 100.

3. The reaction rate was found to be first order with oxidant partial pressure, which is in accord with previous studies. However, conventional formulation of governing mass transport numbers did not describe the experimental observations made during this study. The observed decarburization rates are consistently higher than those predicted using either the Ranz-Marshall correlation or the Steinberger-Treybal equation. It is hypothesized that the steep temperature gradient (~1550 degrees) between the incoming gas stream and the surface of the droplet, is responsible for the offset observed between well-established mass transfer models and the experimental data. This finding has important implications with respect to the application of appropriate mass/heat transport equations that should be employed when using commercial software to model pyro-metallurgical processes, where large temperature gradients are an inherent component of the system.

4. In a system where a steep temperature gradient exists, the contribution from natural convection should not be neglected; even although in some cases the Archimedes number may be less than 1. If thermal diffusion, rather than natural convection, is considered to be the dominant form of mass transport at low Reynolds number, then a different interpretation of the decarburization rate data is possible. On the basis of gas diffusion control, mass transport correlations have been proposed to express decarburization kinetics involving levitated droplets at low to moderate gas flow rates.
5. Based on the current research studies, it has been demonstrated that the electromagnetic levitation technique is a suitable experimental method for determining thermal diffusion factors for gas mixtures at elevated temperatures.

6. A series of experiments was performed aimed at providing some insights into the effects of chromium, at higher concentrations, on the decarburization kinetics involving CO$_2$ as the oxidant gas. It was observed that the rate for Fe-20Cr-C alloys containing 0.01 wt. pct. S was 33pct faster than that reported for chromium-free melts with the same sulphur content and essentially the same as that for Fe-C alloys containing zero sulphur and zero chromium. The increase in decarburization rate of iron-chromium-carbon-sulphur droplets can be explained by the attraction between chromium and sulphur solutes in the liquid phase which decreases the sulphur activity and results in fewer surface sites occupied by surface active sulphur.

7. A study was also conducted to investigate the loss of sulphur that was observed during the decarburization experiments with CO$_2$. It was concluded that evaporative loss in the form of monatomic sulphur gas is responsible for the observed phenomenon. In the presence of an inert argon atmosphere at 1873K, the rate of sulphur loss increases with higher carbon concentrations, mainly due to the fact that carbon increases the sulphur activity through a positive interaction effect.

8. Using an adaptation of the levitation technique an experimental study was conducted to determine appropriate conditions for the levitation and temperature control of silicon and silicon-iron alloy droplets. Levitation of silicon was achieved using a pre-heating procedure by means of which solid silicon was heated by conduction while positioned on a high purity graphite disc which in turn was located within the electromagnetic field. With increasing temperature, the resistivity of the silicon decreases and at approximately 1100K the solid silicon responds to the applied field and begins to levitate.

9. Pre-heating is also necessary with silicon-iron alloys but this can be achieved without utilizing the graphite disc. Iron within the silicon alloy is responsible for providing induction heating to the entire specimen. At temperatures in the vicinity of 900K, silicon-iron
specimens respond to the applied field and begin to levitate. The rapid heating associated with electromagnetic levitation permits most silicon and silicon-iron specimens to reach the molten state in less than 100 seconds.

10. With the aid of an appropriate coil design the effects of specimen weight and applied power on droplet temperature was investigated. Under a constant applied power and frequency, the droplet heating rate increases with increasing specimen mass. Reducing the lift force by decreasing the power will allow the droplet to position lower within the coil, where the field flux is stronger. As a result, the droplet temperature increases. Conversely, the droplet temperature is able to remain at the lower end of the temperature range if the droplet sits higher within the electromagnetic field. This is achieved by increasing power to the coil. However, upon reaching a minimum temperature, further increase in applied power will increase the droplet temperature due to positioning of the sample within the reversed turn region of the coil where the flux density again increases.

9.2 Contributions

9.2.1 Contributions of impact

1. New non-dimensional equations have been proposed to describe mass transfer from a flowing fluid to a sphere under conditions characterized by steep temperature gradients.

The combined convective mass transport correlation is given by the following expression:

$$ Sh = 2 - 0.317(Gr'Sc)^{1/4} + 3Re^{0.415}Sc^{1/3} $$

The forced convection model that incorporates the effects of thermal diffusion is represented by the following correlation:

$$ Sh = 2 + 4.32Re^{0.363}Sc^{1/3} $$

These experimental-based models were able to appropriately describe decarburization rate data from previous studies by other researchers who had also used the levitated droplet technique.
This particular finding paves the way towards a better understanding of the physical significance associated with each of the experimentally determined coefficients in the non-dimensional transport equations. Furthermore, evidence suggests that accurate predictions of these coefficients can be made with sufficient data and knowledge. Ultimately, specific correlations can be developed to describe transport phenomena under given conditions.

2. For the first time, values were determined for the thermal diffusion factors for CO₂-Ar and O₂-Ar mixtures at 1873K. These values were found to be 0.228 and 0.210, respectively.

3. During the decarburization process with CO₂, no significant chromium loss was observed even after the carbon concentration had been reduced to as low as 0.02 wt pct. This is an important observation and has profound practical implications, from both economic and environmental perspectives, for stainless steel refining with carbon dioxide rather than oxygen.

9.2.2 Other contributions

1. Based on the study of sulphur loss from iron-carbon alloys exposed to an argon atmosphere, the first-order carbon-sulphur interaction parameter was found to be 0.113 which is in good agreement with values reported in the literature. However, the value of 0.028 determined for the second-order carbon-sulphur interaction parameter is appreciably higher than values previously reported. Using the proposed values for the parameters, the desulphurization behavior is well represented by the following rate equation which is based on interfacial reaction as the rate-determining step:

\[
\ln \frac{S_t}{S_o} = \frac{-100A k_B T}{W h_p} \frac{K f^*}{\Gamma_o f^{**}} M_S S_t t_m
\]

2. It is postulated that chromium will mitigate the retarding effect of sulphur on the decarburization reaction by carbon dioxide. This in turn has important implications with regard to preferential oxidation of carbon rather than chromium if stainless steel is refined with carbon dioxide rather than oxygen.

3. The results obtained for the effects of specimen weight and applied power on the heating behaviour and temperature control of silicon and silicon alloy droplets provide a foundation
for future studies involving the refining of metallurgical grade silicon in order to generate material which could then be used for solar grade applications.

### 9.3 Future Work

1. Experimental results suggested that the presence of chromium alleviated the retardation of decarburization due to surface site coverage by sulphur when carbon dioxide is used as the oxidant gas. In view of the important practical implications, a systematic investigation with different sulphur and chromium contents should be conducted to verify this observation and develop further information.

2. It is speculated that the experimentally determined coefficients in the non-dimensional correlations may have a temperature gradient dependence. This requires further investigations with experiments conducted at temperatures significantly different from 1873K (1600°C).

3. A detailed study should be carried out to quantify the effect of temperature on thermal diffusion factors, at temperatures of 700K or higher. The results can then be used to compare with published data obtained at lower temperatures using a two-bulb method.

4. Equipped with the knowledge generated during this study for levitation and temperature control of Si and Si-Fe droplets, an extensive investigation should be carried out to study the thermodynamic behaviour of phosphorus dissolution in silicon and silicon-iron alloys. Factors affecting the removal of phosphorus from silicon and silicon-iron alloys can be examined by exposing the levitated droplets to controlled atmospheres under reduced pressure. The experiments will provide a foundation of fundamental knowledge which could ultimately lead to the development of a new method for the mass production of solar grade silicon at a relatively low cost.
List of Symbols - English

\( A \)  Area of droplet surface (\( \text{cm}^2 \))
\( A_v \)  Vector potential (\( \text{V} \text{s} \text{m}^{-1} \))
\( a_C \)  Henrian activity of carbon based on the hypothetical 1 wt pct standard state
\( a_S \)  Henrian activity of sulphur based on the hypothetical 1 wt pct standard state
\( a_* \)  Activity of activated complex
\( A_r \)  Archimedes number (\( = \frac{Gr}{Re^2} \))
\( B \)  Magnetic field (\( A \text{m}^{-1} \))
\( C_{bulk} \)  Carbon concentration in bulk metal (\( \text{wt pct} \))
\( C_{surface} \)  Carbon concentration at the gas-metal interface (\( \text{wt pct} \))
\( C_b \)  Carbon concentration in bulk metal (\( \text{wt pct} \))
\( C_i \)  Carbon concentration at the gas-metal interface (\( \text{wt pct} \))
\( C_{iS} \)  Impurity concentrations in the solid phase
\( C_{iL} \)  Impurity concentrations in the liquid phase
\( C_t \)  Total molar concentration in gas phase (\( \text{mol cm}^{-3} \))
\( C_p \)  Heat capacity of gas (\( J \text{g}^{-1}K^{-1} \))
\( D_{AB} \)  Mutual diffusion coefficient in gas phase (\( \text{cm}^2\text{s}^{-1} \))
\( D_T \)  Thermal diffusion coefficient (\( \text{cm}^2\text{s}^{-1} \))
\( d_p \)  Diameter of the droplet (\( \text{cm} \))
\( e_{SC} \)  First order interaction parameter for effect of carbon on sulphur
\( e_{SCr} \)  First order interaction parameter for effect of chromium on sulphur
\( e_{SS} \)  Self-interaction parameter for sulphur
\( f \)  Coefficient in dimensionless mass transfer equation
\( f_S \)  Activity coefficient of sulphur (\( \text{wt pct} \) \( S^{-1} \))
\( f_{S^*} \)  Activity coefficient of adsorbed sulphur
\( f_{*} \)  Activity coefficient of activated complex
\( g \)  Standard gravity (9.80665 \( m \text{s}^{-2} \))
\( Gr' \)  Mean Grashof number (\( = Gr_m + Gr_H(Sc/Pr)^{0.5} \))
\( Gr_m \)  Grashof number for mass transfer (\( = \frac{\rho g d_p^3 (C_i-C_b)}{\mu g^2} \))
\( Gr_H \)  Grashof number for heat transfer (\( = \frac{g d_p^3 (T_i-T_b)}{T_f \mu g^2} \))
\( h \)  Heat transfer coefficient (\( J \text{cm}^{-2}\text{s}^{-1}K^{-1} \))
\( h_z \)  Height (\( m \))
Planck constant \( (3.97564 \times 10^{-32} m^2 kg min^{-1}) \)

Coil current \( (A) \)

Eddy current \( (A) \)

Flux of diffusion species \( i \) \( (mol cm^{-2}s^{-1}) \)

Equilibrium constant

Thermal conductivity of gas \( (J cm^{-1}s^{-1}K^{-1}) \)

Apparent rate constant \( (cm min^{-1}) \)

Desulphurization rate constant \( (g cm^{-2} min^{-1}) \)

Boltzmann constant \( (4.97034 \times 10^{-20} m^2 kg min^{-2} K^{-1}) \)

Chemical rate constant \( (mol cm^{-2}s^{-1} atm^{-1}) \)

Gas transfer coefficient \( (cm s^{-1}) \)

Segregation coefficient

Liquid transfer coefficient \( (cm s^{-1}) \)

Sulphur adsorption coefficient

Thermal diffusion ratio

Mass transfer coefficient \( (mol cm^{-2}s^{-1} atm^{-1}) \)

Length of the solenoid \( (m) \)

Molecular weight of gas mixture \( (g mol^{-1}) \)

Coefficient in dimensionless mass transfer equation

Atomic weight of carbon \( (g mol^{-1}) \)

Atomic weight of sulphur \( (g mol^{-1}) \)

Number of turns in the solenoid

Coefficient in dimensionless mass transfer equation

Nusselt number \( \left( \frac{d_p h}{k} \right) \)

Total pressure \( (atm) \)

Prandtl number \( \left( \frac{\mu g C_p}{k} \right) \)

Equilibrium partial pressure of monatomic sulphur \( (atm) \)

Gas constant \( (cm^3 atm mol^{-1}K^{-1}) \)

Radial distance from the droplet surface \( (cm) \)

Rayleigh number \( (= Gr'Sc) \)

Reynolds number \( \left( \frac{d_p \nu \rho g}{\mu g} \right) \)

Second order interaction parameter for effect of carbon on sulphur
\( S_0 \)  Initial sulphur concentration (wt pct)
\( S_t \)  Sulphur concentration at time \( t \) (wt pct)
\( Sc \)  Schmidt number \( \left( = \frac{\mu_g}{\rho g D_{AB}} \right) \)
\( Sh \)  Sherwood number \( \left( = \frac{d_p k_g}{D_{AB}} \right) \)
\( T \)  Absolute temperature \( (K) \)
\( t_m \)  Time \( (min) \)
\( t_s \)  Time \( (s) \)
\( T_b \)  Bulk gas temperature \( (K) \)
\( T_E \)  Effective temperature of gases \( (K) \) \( (= 0.83 T_f) \)
\( T_f \)  Film temperature \( (K) \) \( \left( = \frac{T_i + T_b}{2} \right) \)
\( T_i \)  Gas-metal interface temperature \( (K) \)
\( V \)  Volume of droplet \( (cm^3) \)
\( W \)  Mass of the droplet \( (g) \)
\( X_i^b \)  Mole fraction of \( i \) in the bulk gas
\( X_i^l \)  Mole fraction of \( i \) at the gas-metal interface
\( X_i \)  Mole fraction of component \( i \)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Binary thermal diffusion factor</td>
</tr>
<tr>
<td>$\alpha_i$</td>
<td>Thermal diffusion factor of component $i$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Coefficient in dimensionless mass transfer equation</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Coefficient in dimensionless mass transfer equation</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Emissivity of metal</td>
</tr>
<tr>
<td>$\theta_s$</td>
<td>Fractional surface coverage by adsorbed sulphur</td>
</tr>
<tr>
<td>$\theta_u$</td>
<td>Fractional surface sites that cannot be occupied by sulphur</td>
</tr>
<tr>
<td>$\theta^*$</td>
<td>Fractional surface coverage by activated complexes</td>
</tr>
<tr>
<td>$v$</td>
<td>Relative velocity between gas and droplet ($cm \ s^{-1}$)</td>
</tr>
<tr>
<td>$\mu_g$</td>
<td>Gas viscosity ($g \ cm^{-1} \ s^{-1}$)</td>
</tr>
<tr>
<td>$\mu_m$</td>
<td>Magnetic permeability ($H \ m^{-1}$)</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>Magnetic constant ($4\pi \times 10^{-7} \ H \ m^{-1}$)</td>
</tr>
<tr>
<td>$\Gamma_0$</td>
<td>Total available sites for chemisorption ($site \ cm^{-2}$)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Melt density ($g \ cm^{-3}$)</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>Gas density ($g \ cm^{-3}$)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Electrical conductivity ($S \ m^{-1}$)</td>
</tr>
<tr>
<td>$\sigma_{SB}$</td>
<td>Stefan-Boltzmann constant ($= 5.67037 \times 10^{-12} \ J \ cm^{-2} \ s^{-1} \ K^{-4}$)</td>
</tr>
</tbody>
</table>
Appendix A

A.1 Physical Properties

Assuming an ideal gas phase, the density is calculated from the relationship:

$$\rho_g = \frac{MP}{RT}$$

Data for viscosity, inter-diffusivity, heat capacity and thermal conductivity are available from AspenONE Engineering Suite – Heat Exchanger Design.

\(T_f=1079K\ (806^\circ C);\ \text{D}_{\text{AB}}=1.520\ \text{cm}^2/\text{s}\)

<table>
<thead>
<tr>
<th>% CO₂</th>
<th>(\rho_g), Density at (T_f)</th>
<th>(\mu_g), Viscosity at (T_f)</th>
<th>(C_p), Heat capacity at (T_f)</th>
<th>(k), Thermal conductivity of gas at (T_f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.52 x10⁻⁴</td>
<td>5.58 x10⁻⁴</td>
<td>0.532</td>
<td>4.60 x10⁻⁴</td>
</tr>
<tr>
<td>6</td>
<td>4.54 x10⁻⁴</td>
<td>5.61 x10⁻⁴</td>
<td>0.560</td>
<td>4.64 x10⁻⁴</td>
</tr>
<tr>
<td>10</td>
<td>4.56 x10⁻⁴</td>
<td>5.52 x10⁻⁴</td>
<td>0.600</td>
<td>4.61 x10⁻⁴</td>
</tr>
<tr>
<td>15</td>
<td>4.58 x10⁻⁴</td>
<td>5.60 x10⁻⁴</td>
<td>0.636</td>
<td>4.62 x10⁻⁴</td>
</tr>
<tr>
<td>20</td>
<td>4.60 x10⁻⁴</td>
<td>5.37 x10⁻⁴</td>
<td>0.679</td>
<td>4.64 x10⁻⁴</td>
</tr>
<tr>
<td>25</td>
<td>4.63 x10⁻⁴</td>
<td>5.29 x10⁻⁴</td>
<td>0.717</td>
<td>4.70 x10⁻⁴</td>
</tr>
<tr>
<td>30</td>
<td>4.65 x10⁻⁴</td>
<td>5.22 x10⁻⁴</td>
<td>0.755</td>
<td>4.82 x10⁻⁴</td>
</tr>
</tbody>
</table>

\(T_E=896K\ (623^\circ C);\ \text{D}_{\text{AB}}=1.247\ \text{cm}^2/\text{s}\)

<table>
<thead>
<tr>
<th>% CO₂</th>
<th>(\rho_g), Density at (T_E)</th>
<th>(\mu_g), Viscosity at (T_E)</th>
<th>(C_p), Heat capacity at (T_E)</th>
<th>(k), Thermal conductivity of gas at (T_E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5.47 x10⁻⁴</td>
<td>4.90 x10⁻⁴</td>
<td>0.594</td>
<td>3.93 x10⁻⁴</td>
</tr>
<tr>
<td>30</td>
<td>5.58 x10⁻⁴</td>
<td>4.62 x10⁻⁴</td>
<td>0.738</td>
<td>4.11 x10⁻⁴</td>
</tr>
</tbody>
</table>
\( T_E = 896\,K \) \( (623^\circ C) \); \( D_{AB} = 1.42\, \text{cm}^2/\text{s} \)

\[
\begin{array}{|c|c|c|c|c|}
\hline
\% O_2 & \rho_g, \text{ Density at } T_E & \mu_g, \text{ Viscosity at } T_E & C_p, \text{ Heat capacity at } T_E & k, \text{ Thermal conductivity of gas at } T_E \\
\hline
1 & 5.4 \times 10^{-4} & 5.05 \times 10^{-4} & 0.524 & 4.00 \times 10^{-4} \\
2 & 5.37 \times 10^{-4} & 5.04 \times 10^{-4} & 0.529 & 4.01 \times 10^{-4} \\
5 & 5.27 \times 10^{-4} & 5.03 \times 10^{-4} & 0.543 & 4.05 \times 10^{-4} \\
10 & 5.11 \times 10^{-4} & 5.00 \times 10^{-4} & 0.566 & 4.11 \times 10^{-4} \\
\hline
\end{array}
\]

A.2 Material Chemical Composition

Impurity concentrations of Si-Fe alloys studied in Ch. 8 – XRF analysis (wt pct)

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
\text{Si} & \text{Fe} & \text{Ca} & \text{P} & \text{Cu} & \text{Nb} & \text{Sr} \\
\hline
83.11 & 14.93 & 0.83 & 0.02 & 0.06 & 0.001 & 0.008 \\
\hline
\text{Al} & \text{Ti} & \text{Cr} & \text{Mn} & \text{Ni} & \text{Mo} & \text{Y} \\
\hline
0.59 & 0.09 & 0.12 & 0.17 & 0.05 & 0.02 & 0.004 \\
\hline
\end{array}
\]
Appendix B

B.1 Publications Resulting from the Thesis

B.2 Other Related Publications
B.3 Conference Presentations


B.4 Poster Presentations

1. P. Wu, Y.D. Yang, M. Barati, and A. McLean: “Possibility of Simultaneous Removal of Carbon and Sulfur from Fe-Cr-C Melt in CO₂-Ar Gas Mixture”, May 2014, AISTech, Indianapolis, IN. (Graduate Student Poster Competition – First prize)


3. P. Wu, Y.D. Yang, M. Barati, and A. McLean: “Decarburization of Liquid Stainless Steel by Carbon Dioxide”, September 2012, Conference of Metallurgists, Niagara Falls, ON. (Best Poster prize)


