Equilibrium and Kinetic Considerations in Refining of Silicon

Jesse Franklin White

Doctoral Thesis

Royal Institute of Technology
School of Industrial Engineering and Management
Department of Materials Science and Engineering
Division of Micro-Modelling
SE-100 44 Stockholm
Sweden

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Department of Materials Science and Engineering  
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ABSTRACT

The purity requirements for photovoltaic-grade (PV) silicon are very stringent. In PV applications, purified silicon is either doped with boron or phosphorous, so the levels of these particular elements have to be tightly controlled. An alternative process route to photovoltaic-grade silicon that has been successfully implemented on an industrial scale is a multi-step process comprising carbothermic reduction, slag refining, hydrometallurgical extraction, and finally directional solidification. There are many fundamental aspects of the process that are not fully understood and need to be defined.

In the refining of silicon using slag treatment, boron dissolved in the silicon is oxidized and rejected to a liquid oxide (slag) phase. The partitioning of boron between liquid silicon and SiO$_2$–CaO–MgO slags was examined at 1873 K. It was found that the distribution of boron is strongly dependent on the oxygen partial pressure and nitrogen partial pressure, as well as the slag composition. The concentration of MgO seems to have little impact on the partition ratio. The greatest partition ratios were achieved at 0.6 atm CO / 0.4 atm N$_2$ with low silica content in the slag.

Experiments were carried out to study mass transfer rates between liquid silicon and CaO–SiO$_2$ slag using mechanical stirring at 1823 K. The evidence suggests that the reduction of calcium oxide at the interface leads to a rapid, temporary drop in the apparent interfacial tension. At low apparent interfacial tension, mechanical agitation facilitates the dispersion of metal into the slag phase, which dramatically increases the interfacial area; here it has been estimated to increase by at least one order of magnitude. As the reaction rate slows down, the apparent interfacial tension increases and the metal re-coalesces. The rates of mass transfer of both Ca and B were found to increase by agitating the melt, which shows that without forced convection, the overall kinetic rates are mass-transfer controlled. From a reactor design perspective, this is ideal since it should be simpler to achieve optimal mixing conditions with less kinetic energy input into the melt.

The infiltration of silicon into graphite was found to be highly dependent on the internal structure of the graphite substrate. It was confirmed that the heating history of silicon in contact with a graphite substrate strongly influences the melting behavior, which is likely attributed to a gas-solid reaction that forms SiC below the liquidus temperature of silicon and alters the surface properties of the graphite. It was also observed that a partial pressure of CO greater than 0.05 atm in the inlet gas leads to SiC formation on the surface of the silicon and severely hinders proper melting.
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Kristiansand, October 2013

Jesse White
SUPPLEMENTS

The thesis is based on the following supplements:

Supplement 1: “The thermodynamics of boron extraction from liquid silicon using SiO$_2$–CaO–MgO slag treatment”

Jesse F. White, Carl Allertz, and Sichen Du


Supplement 2: “Boron partitioning between SiO$_2$–CaO–MgO slags and liquid silicon at controlled nitrogen potential”

Jesse F. White, Carl Allertz, and Du Sichen


Supplement 3: “Mass Transfer in Slag Refining of Silicon with Mechanical Stirring: Transient Interfacial Phenomena”

Jesse F. White and Du Sichen

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Supplement 4: “Mass Transfer in Slag Refining of Silicon with Mechanical Stirring: Rates of Ca and B Transfer”

Jesse F. White and Du Sichen

To be submitted for publication

Supplement 5: “Reactions between Silicon and Graphite Substrates at High Temperature: *In Situ* Observations”

Jesse F. White, Luyao Ma, Karl Forwald, and Du Sichen

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INTRODUCTION

At this point in the history of technological development, perhaps we take silicon for granted. Maybe even many consider silicon an unremarkable element. However, after some reflection, one can see that silicon’s unique properties have transformed our world. The development of the silicon transistor ushered in the digital age. From ceramics to silicone polymers to integrated circuits, silicon is woven into our everyday lives.

Yet silicon has another great potential for humankind that has not been fully realized: the generation of plentiful renewable energy. Silicon has the ability to convert photons into electric current, a phenomenon that is commonly termed the photovoltaic (PV) effect. Bell Laboratories built the first silicon solar cell already in 1954 [1]. As the population of earth increases and is steadily lifted from subsistence living, the demand for energy will continue to rise. Solar power will undoubtedly be part of the equation to fulfill this energy demand; it is calculated that over 170 000 terawatts of energy strike the surface of the earth continuously [2]. How to harness even a small fraction of this energy is the engineering conundrum.

Why aren’t silicon solar panels on every rooftop? After all, silicon is the second most abundant element in the earth’s crust – it is incorporated into countless silicate minerals [3]. It comes down to a matter of economics: The unit cost of PV silicon material, fabrication costs for solar cell arrays and installation costs, combined with silicon’s relatively low efficiency of energy conversion make PV energy more costly per kilowatt-hour than conventional energy sources. Solar energy is an intermittent and diffuse energy source that requires clever engineering solutions if we are to realize the full potential of PV electricity production. Up until the present time, growth of the PV market has relied heavily on government subsidies to promote solar panel installation.

To use silicon in semiconductor applications, it has to be refined to a very pure level. The current standard technology for refining of silicon is the Siemens process, which yields extremely pure silicon called semiconductor-grade (SG) silicon. The Siemens process is costly. For photovoltaic applications, however, this extreme level of purity is unwarranted. There is considerable economic driving force for developing alternative refining processes. It has long been an ambition of Elkem to develop a less cost-intensive metallurgical process for the refining of PV silicon [4].

The metallurgical refining of silicon as an industrial process is just getting on its feet. Elkem committed a large capital expenditure to building the first metallurgical solar silicon production plant, which successfully reached full design operational capacity when the economic downturn set in and dampened the entire solar cell market. The process has been proven technically viable, and this is a major step forward. As an industry, we will likely be making continual improvements along the way, and there will surely be some major leaps in innovation that make for more efficient operations. Let us just say there is plenty of potential for several fundamental PhD studies in the future to improve our scientific knowledge base.
2 BACKGROUND

Silicon is a brittle metalloid with a blue-grey metallic luster that belongs to the Group 14 in the periodic table of elements. Like carbon, silicon is tetravalent, which gives it unique chemical properties. In crystalline form, silicon has a diamond cubic crystal structure. Compared to common metals such as iron, the density of pure silicon at its melting point is rather low at 2.293 g·cm$^{-3}$ [5]. Silicon melts at 1687 K (1414 °C), and upon fusing, silicon does a remarkable thing: it contracts – the density of liquid silicon at the melting point is 2.56 g·cm$^{-3}$ [5]. Another rather unusual property of silicon is a large enthalpy of fusion, 1787 J/g as compared to most metallic elements such as iron with 247 J/g [6]. These unusual physical characteristics have implications for the production and refining of silicon.

2.1 Production of Metallurgical-Grade (MG) Silicon

Silicon metal is produced on an industrial scale by the reduction of quartz (SiO$_2$) with carbon in a submerged electric-arc furnace. A schematic of the overall process is presented in Figure 2-1. Metallurgical coke and quartz are charged to the furnace, where quartz is reduced at about 2000 °C (2273 K) in the “crater” of the furnace just below the electrodes. The silicon is intermittently tapped from the bottom of the furnace into ladles. This relatively impure silicon is called metallurgical-grade (MG) silicon.

An interesting characteristic of the Si–O–C system is the generation of SiO(g); this vapor species has a relatively high partial pressure, and combusts to form silica fume in the freeboard of the furnace. This amorphous silica fume is very fine, and must be collected from the off-gas using bag filters. The fume has a very large specific surface area (20 m$^2$/g), and is a valuable by-product of silicon production [7]. The enthalpy generated by the combustion of SiO(g) is partially recovered by a heat exchanger, and is important to the overall energy balance of the process.

![Figure 2-1. Process schematic depicting the carbothermic silicon process, from [7].](image-url)
2.2 Elkem Solar Process

Silicon for semiconductors must be very pure: impurities must be in the low parts per billion (ppb) range. The purity requirements for solar-grade silicon, although very stringent, are not as demanding as for semiconductor-grade silicon. In both semiconductor and PV applications, silicon is either doped with boron or phosphorous, so the levels of these particular elements have to be tightly controlled.

The Elkem Solar process is an alternative route to photovoltaic-grade silicon. In 2009, after many years of research and development at Elkem, full-scale operation was commenced to produce solar-grade silicon by the subsidiary company Elkem Solar in Kristiansand, Norway. This is a multi-step process comprising carbothermic reduction, slag refining, hydrometallurgical extraction, and finally directional solidification. Figure 2-2 is a simplified flow diagram of the process [4].

![Flow diagram](image)

Figure 2-2. Flow diagram for the Elkem Solar production of photovoltaic-grade silicon.

The first step is carbothermic reduction, as already described in Section 2.1. The furnace technology used at Elkem Solar is essentially the same as for the production of standard metallurgical-grade silicon; the primary difference here is that purer raw materials are used to control ingoing levels of boron and phosphorous downstream in the refining steps.

In the following step, boron is extracted from the liquid silicon using a high-temperature slag refining process, and is then cast and crushed. Phosphorous is removed in the next step via leaching. A final step of directional solidification removes remaining impurities. These process steps are further detailed below.

2.2.1 Slag Treatment of Silicon

Slag treatment, or slag refining as is it sometimes called, works by contacting a liquid oxide (slag) phase with the liquid silicon at temperatures between 1550 and 1650 °C (1823 and 1923 K). The thermodynamic conditions conveniently favor removal of boron from silicon into the slag phase using a relatively simple and stable slag composition. Slag treatment is really only effective for the removal of elemental boron dissolved in the silicon; it is not possible to efficiently remove phosphorous or any other key impurities with this method at the present time. The boron level in the silicon can be reduced to below 0.3 ppm with this methodology. Boron oxidizes and reports to the slag phase, and the reaction can be written as:

\[ 2B(l) + \frac{3}{2}O_2(g) = B_2O_3(l) \]  

(Eq. 2.1)

\[ \Delta G^\circ = -1329300 + 380.0T \]  

(Eq. 2.2)

where the above value, in joules, is taken from Turkdogan [8].
The slag utilized in the process is fused in an electric furnace. The slag density is about 2.7 g·cm$^{-3}$, making it denser than liquid silicon [9]; as a consequence during slag treatment the silicon phase is on top of the slag phase. After slag treatment is complete, the silicon is cast into thin layers by pouring in to cast iron forms, and crushed and sent to the hydrometallurgical step.

2.2.2 Leaching

During casting of the silicon product from the pyrometallurgical step, an intermetallic CaSi$_2$ phase is formed at the silicon grain boundaries. As solidification occurs, certain impurities are collected in the liquid phase as the silicon crystallizes. The remaining liquid phase forms a phase rich in CaSi$_2$(s). In the leaching step the CaSi$_2$ phase is dissolved from around the grain boundaries of the silicon. The resulting product after leaching is an even purer, fine-grained silicon.

2.2.3 Directional Solidification of Silicon

By the end of the leaching operation, the amounts of phosphorous and boron in the silicon are reduced to very low levels. However, there still are some key impurities left in the silicon, and the only effective means to remove these remaining elements is by directional solidification.

Directional solidification takes advantage of that during the crystallization of silicon, impurities are rejected to the liquid phase. By controlling the rate of propagation of the solidification front, the impurities can be collected in the top of the ingot. This is a well-known technique in materials engineering, and will not be elaborated upon in detail here. What determines the efficacy of this technique for a given impurity element is the segregation coefficient of the element – the lower the better. Boron and phosphorous have high segregation coefficients, meaning that directional solidification does not effectively remove these elements (thus justifying the previous two costly process steps). Other key impurities in silicon, however, such as Fe, Cu, Cr are readily removed by this technique.

2.2.4 Refractory Materials for Silicon Refining

A commonly heard aphorism in high-temperature metallurgy is that the crucible containing the melt is part of the system – i.e. the crucible cannot be considered a separate, inert entity since it reacts with the melt. Fortunately, there is a material that is of the utmost suitability for the melting and refining of silicon, and that is graphite.

As a refractory material, graphite has outstanding thermophysical and chemical properties. High chemical purity, compatible thermal expansion with Si, good thermal shock resistance, high thermal conductivity, and excellent machinability make graphite one of the most commonly used refractory materials in the refining of silicon, and it is used throughout the Elkem Solar process. Large monolithic graphite crucibles are exclusively used in slag refining. There is a wide array of graphite grades available on the market, and some grades are marketed specifically for the solar silicon industry. The compositions, thermophysical properties (and cost) of these different graphite grades vary enormously.

2.3 Impetus for Research

In comparison to mature metallurgical industries such as iron or copper production, the industrial metallurgical refining of solar silicon is in a nascent stage of technological development. As described above, the process in its current form has several diverse unit
operations. Surely there is room for improvement and simplification of the process, and this is what makes the job of a metallurgical engineer exciting. From a scientific perspective, there is still a lot to be understood about many fundamental aspects of the silicon refining unit operations. This thesis attempts to address some of the more pertinent areas where we lack key knowledge.

One unit operation that has great potential for improvement is slag treatment; as described in Section 2.2.1, this is a complex operation in itself. Although the current batch slag treatment configuration is quite an effective means to reduce the boron level in the silicon, operational throughput is inherently restricted by cycle times, decanting operations, and logistics. As an incremental improvement, faster mass transfer rates for boron extraction could possibly be achieved by employing mechanical stirring. Ultimately, such an operation could even be conducted using a continuous, counter-current reactor, and this is the Holy Grail of slag treatment. The design of such a reactor would be rather complex and influenced by many factors. Before any of this is technically achievable, it is imperative that the thermodynamics and kinetics of boron oxidation are better understood. The use of graphite as a refractory material opens up exciting possibilities for sophisticated reactor designs that are not conceivable with traditional ceramic refractory materials.

To this end, silicon–graphite–gas interactions are also important to understand. It is known from industrial experience that the heating rate and furnace atmosphere influence the melting behavior of silicon. The formation of carbide and nitride accretions is an issue that plagues operation. In fact, these phenomena are important for all high-temperature operations involving silicon melting.

2.4 Scope of Current Study

The current body of work covered the study of key fundamental aspects related to the slag refining of silicon, and reactions between silicon and graphite that influence silicon melting and accretion formation. The scope of the research that was undertaken is outlined below:

1. The thermodynamics of slag refining of silicon. Prior to this investigation, other researchers have measured the partitioning of boron between liquid silicon and a wide array of slag compositions, but unfortunately, the results are in substantial discordance. Moreover, the values of boron partition ratios reported in the literature differ greatly from actual, measured values in the industrial slag refining process. Equilibrium experiments were undertaken to gain a better understanding of the thermodynamics of boron extraction: In Supplement 1, the partitioning of boron as a function of the oxygen potential and slag composition at 1873 K was examined. In Supplement 2, the impact of the nitrogen potential on the boron partition ratio was documented.

2. Mass transfer rates in slag refining. Little is truly known about the interfacial reactions that occur during slag refining of silicon. Even a semi-quantitative understanding of mass transfer rates could lead to a much more efficient and cost-effective reactor design. An experimental apparatus was specially designed to study the impact of mechanical stirring on the mass transfer rates of boron and calcium. In Supplement 3, interfacial phenomena occurring due to calcium transfer that greatly impact mass transfer rates were observed. In Supplement 4, the effects of calcium concentration and stirring speed on the rates of calcium and boron transfer were delineated.
3. **Interactions of silicon with graphite and furnace atmosphere.** How graphite, silicon, and the furnace atmosphere interact during silicon melting and processing has many practical implications that potentially affect reactor design due to infiltration by silicon, accretion formation, and graphite wear. A sessile drop apparatus was used to study the affect of graphite substrate type, atmosphere, and heating rate on the spreading of silicon on graphite. This is covered in Supplement 5.

3 **THEORETICAL CONSIDERATIONS**

In the metallurgical refining of silicon for PV applications, the principle impurities that have a process impact are boron, phosphorous, calcium, carbon, oxygen and nitrogen. Boron is the element of primary interest in this study. Carbon, oxygen, and nitrogen can be problematic since silicon has a large affinity for these elements and can lead to undesirable events such as inclusion formation or accretions.

In this section, some relevant theoretical aspects of silicon refining are described. Firstly, the basic systems Si–O, Si–O–C, and Si–O–N are described thermodynamically. The properties of infinitely dilute solutions will also be reviewed.

3.1 The Si–O System

In the silicon-oxygen system, the condensed species are Si(s,l) and silica (SiO$_2$). Silica has several polymorphs; here the cristobalite SiO$_2$(cr) phase is taken into consideration since we are considering a high-temperature system. Actually, this system is quite complex due to the formation of a multitude of vapor species at elevated temperatures. Although the predominant vapor species is silicon monoxide vapor, SiO(g), other species can be present at significant partial pressures. The species SiO$_2$(g), and Si$_2$O$_2$(g) are known to form. In addition to the monomer gas species Si(g), the polymer vapor species Si$_2$(g) and Si$_3$(g) exist.

The partial pressures of these silicon-bearing vapor species are dependent on the temperature and the oxygen partial pressure of oxygen. Presented in Figure 3-1 is a vapor pressure / phase stability diagram was constructed using data from Turkdogan [8], together with values from Rosenqvist and Tuset [10]. The vapor pressure of SiO(g) in the system, even at 1573 K (1300 °C), is significant and highest at an oxygen partial pressure value corresponding to the equilibrium between the condensed phases. The next highest vapor pressure is that of Si(g). As shown by Kellogg [11], one can consider a total effective pressure of silicon by:

$$P_{Si,eff} = p_{Si(g)} + 2p_{Si_2(g)} + 3p_{Si_3(g)} + p_{SiO(g)} + p_{SiO_2(g)} + 2p_{Si_2O_2(g)} \quad (Eq. \ 3.1)$$

As can be seen in the figure, the highest total effective vapor pressure of silicon is $7.0 \times 10^{-2}$ atm, which is a significant value considering that 1573 K is well below the liquidus temperature of silicon.
Figure 3-1. Vapor pressure / phase stability diagram for the Si–O system at 1573 K.

Figure 3-2. Effective total vapor pressure of Si in the system Si–O at increasing temperature.
The total effective vapor pressure of silicon is highly dependent on the system temperature and oxygen potential, as illustrated in Figure 3-2. At 1687 K (1414 °C), the liquidus temperature of silicon at 1 atm, the maximum total effective vapor pressure of silicon ($P_{Si,eff}$) is 0.15 atm. At 2073 K (1800 °C), the maximum $P_{Si,eff}$ is 1 atm; this not an extreme temperature in the production of silicon. The generation of silicon-bearing vapor species has considerable practical implications. In an open system with a constant flow of gas, the transport of silicon out of the system via the gas phase can become significant.

3.2 The Si–O–C System

The condensed phases in the Si–O–C system in the temperature range of interest are Si(s,l), SiO$_2$(cr), and SiC(β). Figure 3-3 is a phase stability diagram of the Si–O–C system at 1687 K (the liquidus temperature of silicon) and 1873 K, which was constructed using data from Turkdogan [8].

![Phase Stability Diagram Si–O–C System](image)

Figure 3-3. Vapor pressure / phase stability diagram for the Si–O–C system at 1687 K and 1873 K.

3.3 The Si–O–N System

In the Si–O–N system there are more phases to consider. Si$_3$N$_4$(α), the oxynitride Si$_2$N$_2$O(s), Si(l), and SiO$_2$(cr) exist. Figure 3-4 is a phase stability diagram of the Si–O–N system at 1873 K, which was constructed using data from Turkdogan [8]. According to this data at 1873 K, Si$_3$N$_4$(s) forms at a partial pressure of nitrogen greater than 0.02 atm below $10^{-20}$ atm oxygen partial pressure; greater than this pressure and Si$_2$N$_2$O(s) is formed.
3.4 Infinitely Dilute Solutions

For a solute B in A over an initial range of concentration, the partial pressure of B approximates the mole fraction of B multiplied by a constant:

\[ p_B = \text{constant} \cdot x_B \]  
(Eq. 3.2)

This initial range of concentration is termed as the “infinitely dilute” range. This is known as Henry’s Law. Since

\[ a_B = \frac{p_B}{p^\circ_B} \]  
(Eq. 3.3)

it follows that

\[ a_B = k_B \cdot x_B \]  
(Eq. 3.4)

The activity of B is linearly proportional to the mole fraction of B in this range of concentration. This is an alternative expression of Henry’s law. The constant, \( k_B \), is the slope of the tangent line to the activity curve at zero concentration of B, and is the Raoultian activity coefficient of B at infinite dilution, designated by \( \gamma^\circ_B \) (see Figure 3-5). So,

\[ a_B = \gamma^\circ_B \cdot x_B \]  
(Eq. 3.5)
Figure 3-5. The activity of solute B in an A–B solution exhibiting negative deviation from Raoult’s law.

In the infinitely dilute range, the B atoms are mostly surrounded by A atoms. If the magnitude of the A–B interaction is stronger than A–A or B–B interactions, then the Henry’s law tangent has negative deviation from that of an ideal solution (Raoult’s law). Oppositely, if A–B interactions are weaker, then the Henry’s law tangent has positive deviation from that of an ideal solution. When the concentration of B is increased above a critical amount in an A–B solution, B atoms begin to interact with other B atoms, and $a_B$ is no longer linear with the mole fraction of B.

Sometimes it is more convenient computationally to use alternative standard states for dilute solutions. Traditionally, there are two such alternative states based on Henry’s law: the Henrian standard state (mole fraction) and the one mass percent (1 mass %) standard state.

The Henrian standard state is defined such that the value of the Henrian activity, $h_B$, approaches the mole fraction of B at infinite dilution. As $x_B$ approaches zero,

$$h_B = x_B \quad \text{(Eq. 3.6)}$$

Outside of the infinitely dilute range of concentration,

$$h_B = f_B \cdot x_B \quad \text{(Eq. 3.7)}$$

defining $f_B$ as the Henrian activity coefficient of B (at infinite dilution). By definition, in the Henrian range $f_B$ is unity. The Gibbs energy for the change from the Raoultian standard state (with respect to pure liquid or solid B) to the Henrian standard state is:

$$\Delta G^\circ_{B(R\to H)} = RT \ln \gamma_B^\circ \quad \text{(Eq. 3.8)}$$
The other commonly employed alternative standard state is the one mass percent standard state. It is defined as unity when the Henrian activity approaches the mass percent of B at infinite dilution. Thus,

\[ h_B(\text{1 mass \%}) = f_B(\text{1 mass \%}) \cdot \text{mass \% B} \quad \text{(Eq. 3.9)} \]

where \( f_B(\text{1 mass \%}) \) is the 1 mass \% activity coefficient. In the Henrian range, this value is unity so that

\[ h_B(\text{1 mass \%}) = \text{mass \% B} \quad \text{(Eq. 3.10)} \]

For a dilute solute B, the mole fraction is nearly proportional to the mass percentage of B:

\[ x_B = \frac{\text{mass \% B} \cdot M_A}{100 \cdot M_B} \quad \text{(Eq. 3.11)} \]

The Gibbs energy for the change from the Raoultian standard state to the one mass percent standard state is:

\[ \Delta G^\circ_B(\text{R \rightarrow 1 mass \%}) = RT \ln \frac{\gamma_B^\circ M_A}{100 M_B} \quad \text{(Eq. 3.12)} \]

where \( M_A \) and \( M_B \) are the molecular weights of the solvent A and solute B.

### 3.5 Multicomponent Dilute Solutions

Multicomponent solutions are more complex, and there exist today many different solution models. Here we will discuss a simple solution model for dilute metallic solutions that is commonly used. Consider a solvent A with solutes B, C, and D. To accurately quantify the activity of say, solute B, the impact of the other solutes C and D must be taken into account. The concept of “interaction parameters” was devised by Chipman [12] and Wagner [13]. The Henrian activity coefficient of B may be expressed as the product of these interaction coefficients as follows:

\[ f_B = f_B^B \cdot f_B^C \cdot f_B^D \quad \text{(Eq. 3.13)} \]

The activity coefficient of B in a binary solution A–B is \( f_B^A \). This is known as the self-interaction coefficient. The influence of solute C on the activity coefficient of B is thus designated \( f_B^C \), and the influence of D on B is \( f_B^D \).

This however, is only truly valid if \( f_B^C \) is not influenced by the concentration of D, and \( f_B^D \) is not influenced by the concentration of C. The concept was further developed by invoking a Taylor series of the natural logarithm of \( f \) as a function of the solute concentrations [13]. For \( f_B \) in the alloy A–B–C–D it looks like:
\[
\ln f_B = \ln f_B^\circ + \left( \frac{\partial \ln f_B}{\partial x_B} \right)_{x_B=0} x_B + \left( \frac{\partial \ln f_B}{\partial x_C} \right)_{x_C=0} x_C + \left( \frac{\partial \ln f_B}{\partial x_D} \right)_{x_D=0} x_D 
+ \frac{1}{2} \left( \frac{\partial^2 \ln f_B}{\partial x_B^2} \right)_{x_B=0} x_B^2 + \left( \frac{\partial^2 \ln f_B}{\partial x_B \partial x_C} \right)_{x_B=x_C=0} x_B x_C + \ldots 
\]

(Eq. 3.14)

The derivative terms are symbolized by \( \varepsilon \) as follows:

\[
\varepsilon_B = \left( \frac{\partial \ln f_B}{\partial x_B} \right)_{x_B=0}, \quad \varepsilon_C = \left( \frac{\partial \ln f_B}{\partial x_C} \right)_{x_C=0}, \quad \varepsilon_D = \left( \frac{\partial \ln f_B}{\partial x_D} \right)_{x_D=0}, \quad \text{etc.}
\]

In the Henrian standard state, \( f_B^\circ = 1 \). The second-order terms are often neglected. Rewriting the above equation:

\[
\ln f_B = \varepsilon_B x_B + \varepsilon_C x_C + \varepsilon_D x_D \quad \text{(Eq. 3.15)}
\]

It should be noted that:

\[
\varepsilon_C = \varepsilon_B. \quad \text{(Eq. 3.16)}
\]

Using base ten logarithms and weight percentages:

\[
\log f_B = \varepsilon_B^{\% B} + \varepsilon_C^{\% C} + \varepsilon_D^{\% D} \quad \text{(Eq. 3.17)}
\]

However, to convert from one type of interaction parameter to the other:

\[
\varepsilon_C = \frac{M_B}{230.3 \cdot M_C} \cdot \varepsilon_B \quad \text{(Eq. 3.18)}
\]

\[
\varepsilon_B = \frac{M_B}{M_C} \cdot \varepsilon_C \quad \text{(Eq. 3.19)}
\]

where \( M_B \) and \( M_C \) are the molecular weights of B and C.

### 3.6 Partition Coefficient of a Dilute Solute

In metal refining, the concept of the “partition coefficient” or “partition ratio” of a solute is often invoked. Consider a general oxidation reaction for a metal M:

\[
[M] + \frac{1}{2} O_2(g) = (MO) \quad \text{(Eq. 3.20)}
\]
where the brackets [ ] signify the metallic phase, and the oval brackets ( ) signify the slag phase; this will be the convention used throughout this text. The equilibrium constant for the above reaction would be written as

$$K = \frac{a_{(MO)}}{a_{[M]} \cdot p_{O_2}^{1/2}}$$  \hspace{1cm} (Eq. 3.21)

which can be expanded to:

$$K = \frac{\gamma_{(MO)} \cdot x_{(MO)}}{\gamma_{[M]} \cdot x_{[M]} \cdot p_{O_2}^{1/2}}$$  \hspace{1cm} (Eq. 3.22)

Rearrangement yields:

$$K = \left( \frac{\gamma_{(MO)}}{\gamma_{[M]}} \right) \cdot \left( \frac{x_{(MO)}}{x_{[M]}} \right) \cdot p_{O_2}^{-1/2}$$  \hspace{1cm} (Eq. 3.23)

and it follows that

$$\left( \frac{x_{(MO)}}{x_{[M]}} \right) = K \cdot \left( \frac{\gamma_{[M]}}{\gamma_{(MO)}} \right) \cdot p_{O_2}^{1/2}$$  \hspace{1cm} (Eq. 3.24)

The partition coefficient $L_M$, we define as the equilibrium mass ratio of M in the slag to M present in the metal. The mole fraction of a solute is proportional its mass percentage as seen in Eq. 3.11. Accordingly,

$$L_M \propto K \cdot \left( \frac{\gamma_{[M]}}{\gamma_{(MO)}} \right) \cdot p_{O_2}^{1/2}$$  \hspace{1cm} (Eq. 3.25)

By this reasoning, the partition coefficient of M should be dependent on the reaction equilibrium constant, the partial pressure of oxygen in the system, and the activity coefficient ratio between the slag and metal phases. In the infinitely dilute range, the partition coefficient of the solute should be independent of concentration.

The equilibrium constant is solely a function of temperature. The effect of temperature on the equilibrium constant is embodied in the van’t Hoff equation:

$$\frac{\partial \ln K}{\partial (1/T)} = -\frac{\Delta H^\circ}{R}$$  \hspace{1cm} (Eq. 3.26)

Therefore, if the reaction is endothermic, i.e. $\Delta H^\circ$ is positive, then $K$ increases with increasing temperature. In contrast, if the reaction is exothermic and $\Delta H^\circ$ is negative, then $K$ would decrease with increasing temperature. Taking it a step further, with an exothermic reaction such as oxidation of M, increasing temperature should lead to a reduction in the partition coefficient, $L_M$, with the extent of change dependent on the change in temperature and the magnitude of $\Delta H^\circ$.  

13
3.7 Kinetics of Slag–Metal Reactions

Reaction rate theory of interfacial reactions is not nearly as rigorously developed in comparison with the immutable laws of thermodynamics. This is a field still very ripe with research opportunities. Many classic metallurgical textbooks cover the area of slag–metal reaction kinetics such as Richardson [16], and Turkdogan [8]. A landmark review paper that covered developments in this subject was published in 1983 by Pomfret and Grieveson [14], and very recently the subject was revisited in a review paper by Coley [15].

The transfer of a solute element between a metal phase and a slag phase is a heterogeneous liquid/liquid reaction that occurs at the interface. Slags and molten salts are primarily ionic melts, and the reaction mechanisms are generally considered to be electrochemical in nature [16a], i.e. the oxidation and reduction reactions involve the transfer of electrons greater than atomic distances. Consider the overall exchange reaction between divalent A and B:

\[ [A] + (BO) = [B] + (AO) \] (Eq. 3.27)

The anodic reaction would be:

\[ [A] = (A^{2+}O^{2−}) + 2e^- \] (Eq. 3.28)

and the cathodic reaction:

\[ (B^{2+}O^{2−}) + 2e^- = [B] \] (Eq. 3.29)

Thus the reaction sequence for the oxidation of A could be considered as a series of resistance steps:

1. Transfer of solute [A] from the bulk of the metal phase to the slag–metal interface
2. Transfer of \((O^{2−})\) ions from the bulk slag phase to the interface
3. Chemical reaction (oxidation) at the interface
4. Transfer of dissolved oxygen [O] from the interface to the bulk metal phase
5. Transfer of \((A^{2+})\) ions from the interface to the bulk slag phase

Charge neutrality must be maintained, so the generation and consumption of electrons and oxygen ions are balanced. Any one of these steps may control the overall reaction rate, or there may be mixed control.

3.7.1 Chemical Reaction at the Interface

Many slag–metal reactions are characterized by first-order kinetics with respect to the solute element in the metal phase. A first-order reaction is when the rate of reaction depends only on the concentration of one reactant. Let A be the reactant:

\[ A \rightarrow \text{products} \]

The rate equation would look like:

\[ R = -\frac{1}{a} \frac{d[A]}{dt} = k[A]^t \] (Eq. 3.30)
Here $k$ is a reaction rate constant. Since only one $A$ molecule disappears to produce one product molecule, $a = 1$ and

$$\frac{-d[A]}{dt} = k[A]. \quad (\text{Eq. 3.31})$$

At $t = 0$, $[A] = [A]_0$. Upon separating variables and integrating:

$$[A] = -[A]_0 e^{-kt}. \quad (\text{Eq. 3.32})$$

### 3.7.2 Mass Transfer as the Rate-Limiting Step

In many cases slag–metal reactions are mass-transport controlled. The interfacial reaction is so rapid that chemical equilibrium is achieved at the interface, and it is the transport of the reactants or the products to and away from the interface that limits the rate of the overall reaction sequence. The mass flux for a solute Me from the metal phase is expressed as:

$$J_{Me} = \frac{k \cdot A}{V_M} \left(\frac{\% \text{ Me}}{\% \text{ Me}_{eq}}\right) \quad (\text{Eq. 3.33})$$

where $k$ is a mass transfer coefficient, and $A$ is the interfacial area. The driving force for mass transport is the concentration gradient of the solute between the interface and the bulk metal phase.

Traditionally in laboratory investigations of a given system, the quest has been to determine the value of a mass transfer coefficient value to quantitatively describe the mass transfer rate in a given system. The magnitude of a mass transfer coefficient is system-dependent and related to factors such as the vessel geometry, mixing conditions, fluid properties such as viscosity and density, and the diffusivity of the solute [16b].

In metallurgical reactors, mass transfer is often facilitated by dispersing one phase as droplets into the other, either by mechanical means or by using gas stirring. This complicates matters considerably. Fluid flow is often turbulent, and temperature and viscosity gradients can be large. One severe limitation is to quantify the interfacial area, particularly when the interfacial area is time-dependent due to the progress of interfacial reactions [15]. As such it can be dubious to extrapolate measured $k$ values from static laboratory studies to full-scale reactors with turbulent flow regimes.

Much effort has been devoted to describing such systems mathematically using empirical models employing dimensionless correlations. Under conditions of forced convection, one often-cited correlation is [17]:

$$Sh = f(\text{Re,Sc}) \quad (\text{Eq. 3.34})$$

Re is the Reynolds number, and Sh is the Sherwood number, which is the ratio of the convective mass flow to the conductive mass flow:

$$Sh = \frac{kL}{D} \quad (\text{Eq. 3.35})$$
where $k$ is the mass transfer coefficient, $L$ is a characteristic length, and $D$ is the diffusivity of the solute. $Sc$ is the Schmidt number:

$$Sc = \frac{\nu}{D}$$

(Eq. 3.36)

which is the kinematic viscosity $\nu$ divided by the diffusivity of the solute. This correlation is the ratio of momentum diffusivity to molecular diffusivity.

These are all approximations for describing very complex conditions that were developed well before the advent of computer modeling. In the future of metallurgical reactor design, there is little doubt that increasingly sophisticated computer models will be employed to more satisfactorily describe the mass transfer in real metallurgical systems with complex flow conditions.

4 LITERATURE SURVEY

A rather comprehensive literature survey was undertaken during the course of this research study, and is presented in this chapter. The first area of focus was the thermodynamic data for dilute Si solutions and slag refining of silicon. Thereafter, a literature review of the kinetics of slag–metal reactions was conducted, with an emphasis on experimental technique. Finally, literature on silicon–graphite interactions was reviewed.

4.1 Data for Dilute Liquid Si Solutions

Activity coefficients and interaction parameters are gathered empirically. Data from several researchers for dilute liquid silicon solutions have been compiled in this study. Experimental research in this area has been predominantly conducted by Japanese researchers. Although a good deal of the data presented here were conveniently compiled and presented in earlier works [18,19], the years pass by and new data have been generated. Here also, the data for boron activity in silicon at infinite dilution is of paramount interest, so an effort has been made to evaluate these particular data. Table 4-1 lists published activity coefficients at infinite dilution for selected impurity elements in liquid silicon.

As seen in Table 4-1, the data for the activity coefficient of boron at infinite dilution in silicon with reference to B(s) agree well. As seen in Figure 4-1, however, the values for the activity coefficient of boron at infinite dilution with reference to B(l) do not agree so well. It is immediately apparent that there is a large variation in the reported values. In the temperature range of interest, the only available data for the activity coefficient of boron at infinite dilution seems to be from Yoshikawa and Morita [20]. The caveat is that the stated error amounts to $\pm 37\%$. This expression is a linear regression based on their own data and re-evaluated data from Noguchi [21], where it was taken into consideration the equilibrium of $\text{Si}_3\text{N}_4$ with Si and BN. Still, taking into account the stated error, which, $\gamma^{0}_{B0}$ spans from 2.3 to 6.26 at 1873 K. This is an unsatisfactorily large range nonetheless.

Table 4-2 lists self-interaction parameters, while Table 4-3 is a tabulation of first-order interaction parameters. The data for boron in particular are sparse and have wide variation. To compound matters, most of the data is for well below the temperature range of interest in this study (1823 to 1923 K).
Table 4-1. Activity coefficients at infinite dilution in liquid silicon of selected impurity elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>( \ln \gamma^o_i )</th>
<th>Std. State</th>
<th>Temp. [K]</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>289±450/T + 1.19 ±0.25</td>
<td>Pure liquid</td>
<td>1693–1923</td>
<td>Equilibration of Si with BN in a Si₃N₄ crucible. N₂-10% H₂ atmosphere.</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td>−2.56×10⁴/T + 13.40</td>
<td>Pure liquid</td>
<td>1723–1923</td>
<td>BN crucible</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>Pure liquid</td>
<td>1850</td>
<td>Knudsen cell. TiB₂, ZrO₂ coated, siliconized Mo cells.</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>2.27 ± 0.010</td>
<td>Pure solid</td>
<td>1723</td>
<td>Equilibration of Si-B-Ca alloy with BN in a Si₃N₄ crucible. N₂-10% H₂ atmosphere.</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>2.5 ± 0.2</td>
<td>Pure solid</td>
<td>1723</td>
<td>MgO equilibrated with BN or Si₃N₄</td>
<td>[24]</td>
</tr>
<tr>
<td>C</td>
<td>8666/T – 1.37logT + 4.513</td>
<td>Graphite</td>
<td>1723–1873</td>
<td>SiC crucible</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>7672/T + 0.086</td>
<td>Graphite</td>
<td>1693–1923</td>
<td></td>
<td>[19]</td>
</tr>
<tr>
<td>Ca</td>
<td>−23006/T + 5.45</td>
<td>Pure liquid</td>
<td>1693–1923</td>
<td>Knudsen effusion, vitreous C crucible</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>−15634/T + 1.52</td>
<td>Pure liquid</td>
<td>1687–1900</td>
<td>Knudsen effusion, vitreous C crucible</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>−17664/T + 3.52</td>
<td>Pure liquid</td>
<td>1723–1823</td>
<td>Equilibration of Si(l) and CaO-SiO₂ slag in silica crucible</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>−6.03</td>
<td>Pure liquid</td>
<td>1773</td>
<td>Graphite crucible, CaO-SiO₂ slag</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>−14300/T + 1.55</td>
<td>Pure liquid</td>
<td>1723–1823</td>
<td>Knudsen effusion, BN crucible</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>−15427/T + 1.02</td>
<td>Pure liquid</td>
<td>1823–1923</td>
<td>Equilibration of Si(l) and CaO-SiO₂ slag in a silica crucible</td>
<td>[29]</td>
</tr>
<tr>
<td>Mg</td>
<td>−11284/T + 4.51</td>
<td>Pure liquid</td>
<td>1698–1798</td>
<td>SiO₂/MgSiO₂-sat crucible. MgO-SiO₂-Al₂O₃ slag</td>
<td>[26]</td>
</tr>
</tbody>
</table>

Table 4-2. Self-interaction parameters for impurities in liquid silicon, updated from Bakke [19].

<table>
<thead>
<tr>
<th>Element</th>
<th>( \varepsilon'_{ij} )</th>
<th>Temp. [K]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>-164</td>
<td>1723</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td>-105</td>
<td>1773</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1850</td>
<td>[22]</td>
</tr>
<tr>
<td>Ca</td>
<td>55600/T -22.1</td>
<td>1723-1823</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>3.17</td>
<td>1723</td>
<td>[30]</td>
</tr>
<tr>
<td>Mg</td>
<td>6.02</td>
<td>1723</td>
<td>[28]</td>
</tr>
</tbody>
</table>
Table 4-3. First-order interaction parameters for impurities in liquid silicon, updated from Lynch [18].

<table>
<thead>
<tr>
<th>Element $i$</th>
<th>Element $j$</th>
<th>Temp. [K]</th>
<th>$\epsilon_i^j$</th>
<th>$\epsilon_j^i$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>N</td>
<td>1723</td>
<td>600 ±55</td>
<td>6.8 ±0.8</td>
<td>[23]</td>
</tr>
<tr>
<td>Ca</td>
<td>B</td>
<td>1723</td>
<td>80 ±20</td>
<td>0.9 ±0.2</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1773</td>
<td>73 ±1</td>
<td>0.82 ±0.01</td>
<td>[24]</td>
</tr>
<tr>
<td>C</td>
<td>Al</td>
<td>1693-1923</td>
<td>38610/T +6.76</td>
<td>-174.54/T+0.0304</td>
<td>[19]</td>
</tr>
<tr>
<td>Ca</td>
<td></td>
<td></td>
<td>0</td>
<td>0.0013</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>B</td>
<td>1723-1873</td>
<td>-6980/T+6.56</td>
<td>-22.62/T+0.0249</td>
<td>[31]</td>
</tr>
<tr>
<td>N</td>
<td>Ca</td>
<td>1723</td>
<td>-140</td>
<td>-0.63</td>
<td>[23]</td>
</tr>
<tr>
<td>O</td>
<td>Al</td>
<td>1773</td>
<td>-126</td>
<td>-0.57</td>
<td>[27]</td>
</tr>
<tr>
<td>Ca</td>
<td></td>
<td>1773</td>
<td>-690</td>
<td>-2.1</td>
<td>[24]</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>1693-1723</td>
<td>-2.04</td>
<td>-0.03</td>
<td>[19]</td>
</tr>
</tbody>
</table>

Figure 4-1. Comparison of values from the literature for the activity coefficient of boron in liquid silicon at infinite dilution.

Figure 4-2 examines the influence of co-impurities on the activity coefficient of boron in liquid silicon. What is of interest here is that calcium and carbon seem to have little interaction with boron in liquid silicon. Although there are considerable discrepancies in published interaction parameters for the effect of nitrogen on boron, the effect on the activity coefficient is pronounced: nitrogen increases the activity coefficient of boron in liquid silicon.
Figure 4.2. The relative influence of co-impurities on the activity coefficient of boron in liquid silicon at 1723 K.

4.2 The Silicon–Calcium System

The silicon-calcium system has particular relevance to silicon refining. Figure 4-3 is a phase diagram of the Ca–Si system [32]. As can be seen, calcium and silicon form many intermediate phases.
Data for the activity of calcium in liquid binary silicon-calcium alloys are sparse. Indeed, it is a difficult system to study at elevated temperatures due to the volatility of calcium and the highly exothermic enthalpy of mixing. There are two landmark studies that will be described in detail below.

The first study is from 1971 by Wynnyckyj and Pidgeon [33]. They measured the partial pressures of calcium vapor in a Knudsen cell from 1203 K (930 °C) to 1493 K (1220 °C) over a range of 0.24 to 0.49 mole fraction of calcium. A relation for the partial pressure of calcium as a function of temperature was determined for several alloy compositions. Using these functions, the partial pressure of Ca was calculated at 1323, 1373, 1423, and 1473 K. With these values the activity of calcium with respect to pure liquid calcium was calculated via the relationship:

\[ a_{\text{Ca}(l)} = \frac{p_{\text{Cal}(l)}}{p^o_{\text{Ca}(l)}} \]  

(Eq. 4.1)

Data for the partial pressure over pure liquid calcium, \( p^o_{\text{Ca}(l)} \), was taken from Hultgren [34].

The second study was by Schürmann, Fünders, and Litterscheidt from 1975 using the boiling point determination method at the temperatures 1483 K and 1623 K [35]. Using a function for the vapor pressure of calcium above pure liquid calcium, they calculated the activity of calcium using the above equation. By integrating a form of the Gibbs-Helmholtz equation, the partial molar enthalpy of mixing for calcium was calculated:

\[ \frac{\partial \left( R \ln \gamma_{\text{Ca}} \right)}{\partial \left( 1/T \right)} = \Delta H^M_{\text{Ca}} \]  

(Eq. 4.2)

These data are plotted as open circles in Figure 4-4. The line is a fitted curve to the data extrapolated to zero mole fraction calcium.

Unfortunately, both of these studies were conducted at temperatures below the range of interest for silicon refining. Using the fitted curve to the partial molar enthalpy data shown in Figure 4-4, these two datasets were adjusted to a common temperature of 1873 K using Eq. 4.2 and are plotted as the line in Figure 4-5. The system exhibits a very negative deviation from Raoult’s law. As evident in the plot, the activity curve does not change considerably with increased temperature.

### 4.2.1 Activity Coefficient of Ca in Si at Infinite Dilution

Figure 4-6 and Table 4-4 compare the values from the literature for the activity coefficient of Ca in liquid silicon at infinite dilution, \( \gamma^o_{\text{Ca(l)} \text{in Si}} \), (listed in Table 4-1). As can be seen, there is a wide range in the values. The results of Miki et al. [26,28] are fairly self-consistent, particularly since two quite different experimental techniques were used in these studies (Si–slag equilibration vs. Knudsen effusion cell, respectively). Similarly, Dumay et al. [25] also employed Knudsen effusion, although as can be seen, their results are in closer agreement with Bakke and Klevan [19] and Pinto and Takano [29]. Table 4-1 shows calculated values of \( \gamma^o_{\text{Ca(l)} \text{in Si}} \) at 1773, 1823, and 1873 K.
Figure 4-4. Partial molar enthalpy of Ca in J mol\(^{-1}\) in the binary alloy Si–Ca at 1623 K, data from Schürmann \textit{et al.} [35].

Figure 4-5. Activity of Ca(l) in the Si–Ca system at 1873 K, with data from Wynnyckyj and Pidgeon [33], and Schürmann \textit{et al.} [35].
Figure 4-6. Comparison of values from literature for activity coefficient of Ca(l) in Si(l) at infinite dilution.

Table 4-4. Calculated values of $\gamma^{\circ}_{\text{Ca(l) in Si}}$ at different temperatures.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\gamma^{\circ}_{\text{Ca(l) in Si}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1773 K</td>
</tr>
<tr>
<td>[19]</td>
<td>$5.39\times10^{-4}$</td>
</tr>
<tr>
<td>[25]</td>
<td>$6.77\times10^{-4}$</td>
</tr>
<tr>
<td>[26]</td>
<td>$1.60\times10^{-3}$</td>
</tr>
<tr>
<td>[27]</td>
<td>$2.40\times10^{-3}$</td>
</tr>
<tr>
<td>[28]</td>
<td>$1.50\times10^{-3}$</td>
</tr>
<tr>
<td>[29]</td>
<td>$4.61\times10^{-4}$</td>
</tr>
</tbody>
</table>

4.3 Thermodynamics of Slag Refining

Several researchers have measured the partition coefficient of boron between liquid silicon and slag. These studies are of particular relevance to the current study and will be described in more detail.

In slag refining, the boron partition ratio, $L_B$, is defined as the equilibrium mass ratio of boron in the slag to boron present in the silicon:
\[ L_B = \frac{\text{(mass \% B)}}{\text{[mass \% B]}} \quad \text{(Eq. 4.3)} \]

In the slag refining of silicon, a high partition ratio is desirable (more boron rejected to the oxide phase).

4.3.1 Suzuki 1990

Suzuki, Sugiyama, Takano, and Sano studied the equilibrium distributions of boron between silicon and CaO−SiO₂, CaO−CaF₂−SiO₂, CaO−MgO−SiO₂−(CaF₂) and CaO−BaO−SiO₂−(CaF₂) slags from 1723 to 1823 K [36]. Ten grams of silicon and 10 grams of slag of varying composition were held in graphite crucibles for 2 hours under atmospheres of Ar, CO, and Ar/12.5 % CO₂. The starting concentration of boron in the silicon was between 30–90 ppm.

They give evidence that the partition coefficient, \( L_B \), is a function of the slag basicity of the slag as apparent in Figure 4.7. According to their results, the partition coefficient increases with increasing basicity, and reaches a maximum at a CaO/SiO₂ ratio of around 0.8–1.0. The maximum \( L_B \) of 1.6 was attained with a CaO−SiO₂−10 % MgO slag at a CaO/SiO₂ ratio of 0.8 was about 1.6.

![Figure 4.7. Relationship between \( L_B \) and basicity at 1723 K [36].](image)

Their assertion is that the data show that \( L_B \) is independent of the gas composition. Thus they reasoned that the oxygen partial pressure of the system is controlled by the Si−SiO₂ equilibrium.

4.3.2 Noguchi 1994

Noguchi, Suzuki, Tsukihashi, and Sano [21] followed up the previous publication with a study of the equilibrium between B-containing silicon, \( \text{N}_2 \) and BN according to the reaction:

\[ [\text{B}]+\frac{1}{2}\text{N}_2(g) = \text{BN(s)} \quad \text{(Eq. 4.4)} \]
They calculated \( L_B \) based on data for \( \gamma^\circ_B \) in liquid silicon. Values of \( \gamma_{BO_1,5} \) were estimated. Assuming that the Si–SiO\(_2\) equilibrium determined the oxygen potential, and a regular solution model approximation of \( a_{SiO_2} \), values of \( L_B \) were calculated.

This study, it appears, generated spurious results due to \( Si_3N_4 \) formation. This is anyway the conclusion of other researchers [18,20] (see Section 4.1).

4.3.3 Teixeira 2007

Teixeira, and Morita equilibrated silicon and various slags in graphite crucibles under an argon atmosphere in an induction furnace at 1823 K [37]. The duration of the experiments was 18 hours – considerably longer than Suzuki’s experiments. The starting concentration of boron metal in the silicon was 150 ppm. Their results, seen in Figure 4-8, show \( L_B \) to be strongly affected by slag basicity, yet the shape of the curve is unusual and shows a distinct minimum value at a neutral slag composition.

![Figure 4-8. Boron partition ratio for silicate slags as a function of basicity at 1823 K [37].](image)

4.3.4 Teixeira 2009

Teixeira et al. [38] conducted experiments where the boron in the Si phase varied between 150 ppm and 1.0 mass %. The maximum attainable concentration of boron in the slag phase was below 0.25 mass %. Boron oxide in the slag could be regarded as a Henrian solution as seen by the linear relationship in Figure 4-9.
4.3.5 Johnston 2010

Johnston and Barati [39] conducted a similar study equilibrating silicon and slags up to 7 hours in a magnesia or alumina crucible in a vertical tube furnace. The atmosphere used was pure argon. The absolute values of $L_B$ were similar to that of Suzuki et al. The variation is fairly large – spanning from 1.0 to 1.4 at a 0.4 CaO/SiO$_2$ ratio (if one excludes the outlying value of 1.8). They sketch a dashed line showing the perceived relationship of $L_B$ to the slag basicity, indicating a maximum level at 0.8 basicity. Here, pure argon was used as the furnace atmosphere, leading to questions about how the prevailing oxygen potential was controlled during the runs.

![Figure 4-9. Boron concentration in silicon and CaO–SiO$_2$ slag phases at 1823 K [38].](image)

Figure 4-9. Boron concentration in silicon and CaO–SiO$_2$ slag phases at 1823 K [38].

4.4 Kinetics of Slag–Metal Reactions

There are no well-established experimental techniques that can be used to study the kinetics
of a high temperature slag–metal system. A literature survey was undertaken, and the greatest body of data is for slag–metal reactions in steelmaking. Unfortunately it seems there are as many experimental methods as there are studies.

One method, with different variations, is to bring liquid slag and metal into contact for determined time intervals, and then to measure resulting concentration profiles as a function of time. A handful of unrelated kinetic studies have employed mechanical stirring to study mass transfer rates between liquid slag and metal. The experimental difficulty lies in accurately controlling the contact time – quickly bringing the liquid phases into contact and then rapid cooling or quenching to halt the reaction. Some of the more relevant studies are described here, with the focus on experimental technique.

4.4.1 Fulton 1953

Fulton, Grant and Chipman [40] measured the transfer of silicon between carbon-saturated iron and CaO–SiO$_2$–Al$_2$O$_3$ slags in an induction furnace at 1873 K under 1 atm CO. A graphite crucible and stirrer were employed in the study. An optical pyrometer was used to measure the temperature of the melt through the hollow stirring rod. The iron was first melted in the crucible and allowed to reach carbon saturation. Then the prefused slag components were added on top. Zero-time was considered when the melt reached the target temperature. The stirring rate was varied from 0 to 500 rpm. Samples were aspirated out of the melt with a Vycor tube and suction bulb.

4.4.2 Daines 1968

Daines and Pehlke [41] studied the kinetics of manganese oxide reduction using a zirconia crucible and a graphite stirring rod to mix the melt. A variable speed motor was employed to rotate the stirring rod over a range of 0 to 100 rpm. Figure 4-11 is a schematic of their experimental system. Like in the aforementioned study, samples were taken out of the melt at regular intervals with a Vycor tube and suction bulb. The zero-time for the study was when MnO was introduced into the melt (via a Vycor tube extending into the melt). The stirring rate was found to have a significant effect on the mass transfer rate of Mn.
4.4.3 Wei 1988

Wei, Sano, Hirasawa and Mori [42] studied the kinetics of silicon oxidation of liquid iron with Li2O-CaO-SiO2-FeO slags at 1573 K. Alumina crucibles and a CO atmosphere were used. The experiment commenced by adding FeO to the slag. An eccentrically rotating stirring rod was used to agitate the liquids from 50 to 400 rpm. Slag and metal samples were taken periodically with a nickel wire and quartz tube.
4.4.4 Nishimoto 2012

To the author’s knowledge, Nishimoto and Morita [43] conducted the first published study on the deboronization rate of silicon. The experimental system consisted of a vertical tube furnace with a mullite reaction tube sealed on both ends. High-purity argon gas was used as the atmosphere. Silicon doped with 300 ppm boron and CaO–SiO$_2$ slag in a graphite crucible and introduced into the hot zone of the furnace, which was designated $t = 0$. The sample was removed from the furnace at a given time, quenched with Ar, and analyzed. No stirring was used.

Figure 4-13 shows the rate of boron rejection from the silicon. Their analysis of the data yielded the conclusion that deboronization is a first-order reaction. By conducting experiments with varying slag/metal ratios and comparing to analytical models, it was deduced that mass transport in the slag phase is the rate-controlling step (see Figure 4-14, where $Y$ is the slag/metal mass ratio). A mass transfer coefficient of $k_s = 1.4 \times 10^{-6}$ m/s was calculated.

![Figure 4-13. Deboronization rate of liquid silicon with CaO-SiO$_2$ slag [43].](image)

![Figure 4-14. Integrated rate plots for deboronization showing (a) metal mass-transport control, and (b) slag mass-transfer control [43].](image)
4.5 Reactivity of Graphite with Silicon

A number of studies have investigated the wettability and reaction of liquid silicon with different substrates, including graphite and vitreous carbon [44,45,46,47,48,49]. The physical properties such as open porosity and surface roughness have been shown to greatly influence the “dynamic wetting” of liquid silicon on graphite. By dynamic wetting it is implied that the system is not in a state of chemical equilibrium; liquid silicon rapidly reacts with carbon to form silicon carbide according to the reaction:

\[
\text{Si(l)} + \text{C(gr)} = \text{SiC(\beta)}
\]  
(Eq. 4.5)

\[
\Delta G^\circ_{\text{Eq. 4.5, 1687 K}} = -60124 \text{ J/mol}[8]
\]  
(Eq. 4.6)

and in doing so the apparent contact angle between a droplet of molten silicon and a carbon substrate rapidly decreases with time until either the melt is completely absorbed by the porous graphite substrate, or an intermediate layer of SiC is formed, and the wetting reaches equilibrium. In all of these studies the experimental technique was essentially the same: A high-temperature sessile drop apparatus was used to visually document the change in apparent contact angle over time of a molten silicon droplet on a substrate under high-purity argon atmosphere or vacuum, followed by scanning electron microscopy (SEM) of the specimens to analyze the condition at the reaction interface. In some studies, oxygen concentration in the furnace inlet gas was maintained at low levels by scrubbing the argon with heated Mg chips [45,46]. Liquid silicon is known to wet silicon carbide, and the equilibrium apparent contact angle of liquid silicon on SiC is reported to be approximately 8 degrees at 1693 K (1420 °C) and an oxygen partial pressure of 10^-21 MPa [47]. Li and Hausner [45] documented the effect of surface roughness on the equilibrium apparent contact angle of liquid silicon on graphite (after reaction to a SiC layer). The work of Ciftja et al. confirms that the surface roughness affects the equilibrium contact angle, but not the initial rate of spreading [46].

A few studies took a more fundamental approach and focused on the kinetics and mechanisms of the Si–C reaction at the liquid-solid interface. Deike and Schwerdtfeger [50] studied the kinetics of growth of SiC layers in silicon-containing graphite crucibles at 1773 K (1500 °C). They identified two distinct morphologies that form: one is a heterogeneous mixture of very fine SiC particles dispersed in silicon at the interface and in the pores of the graphite; the other is large SiC crystals formed at the interface. No simple rate law is obeyed. Israel et al. [51] studied the infiltration of graphite by liquid silicon under He atmosphere up to 1733 K (1460 °C), and found that the infiltration rate is linear with time and is strongly dependent on the tortuosity of the graphite.

5 EXPERIMENTAL METHODS

5.1 Control of Oxygen Potential

In some of the experiments it was desired to set the oxygen potential in the system. In this case the oxygen potential was controlled using an “open circuit”, gas-condensed phase equilibration technique, where a continuous flow of inlet gas is reacted with a condensed phase to establish a fixed chemical potential in the system [52]. In these experiments, carbon monoxide was blended into the reaction gas at various ratios using a mixing column filled with glass beads. This continuous stream of reaction gas with a fixed partial pressure of CO was passed over a surplus of carbon (graphite crucibles) in the system at the reaction
temperature [16c]. Other previous studies also employed this methodology [53,54,55,56]. The flow rate of gas was very low at 0.05 l/min, and holes in the bottom of the graphite holding crucible ensured a long contact time between the inlet gas and the graphite to ensure the establishment of equilibrium as per the reaction:

$$\text{C(gr)} + \frac{1}{2} \text{O}_2(g) = \text{CO(g)} \quad \text{(Eq. 5.1)}$$

$$\Delta G^\circ_{\text{Eq. 5.1}} = -114400 - 85.75T \text{ J/mol} \quad \text{(Eq. 5.2)}$$

where $\Delta G^\circ$ is given in joules per mole [8]. Since the stream of reaction gas in contact with the slag/Si samples was continuous, a constant oxygen partial pressure was maintained in the system. By doing this, the Si–SiO$_2$ equilibrium was forced to adjust to the prevailing oxygen partial pressure (i.e. the activity of SiO$_2$ in the slag adjusts). It should also be pointed out that in the case of using 100 % argon as the inlet gas and graphite crucibles, the oxygen potential would be an unknown quantity since leakage of air into the system is unquantifiable, and could fluctuate.

In the presence of graphite at 1873 K, it is not thermodynamically feasible to use mixtures of CO and CO$_2$ to set the oxygen potential in the gas phase, as illustrated in Figure 5-1. This is a plot of the equilibrium CO/CO$_2$ ratio as a function of temperature in the C–CO–CO$_2$ system at 1 atmosphere total pressure, which was constructed using data from Turkdogan [8]. As can be seen, the equilibrium CO/CO$_2$ ratio increases with increasing temperature. At 1873 K, CO is predominant; log($p_{\text{CO}} / p_{\text{CO}_2}$) at 1873 K is 4.29, which corresponds to $p_{\text{CO}_2} = 5.14 \times 10^{-5}$ atm. This implies that if CO$_2$ is added in any appreciable quantity to the inlet gas stream at this temperature, the gas phase will not be in thermodynamic equilibrium since CO$_2$ will react with graphite to form CO until the CO$_2$ concentration is lowered to this very low equilibrium partial pressure. Figure 5-2 plots the equilibrium partial pressure of oxygen with increasing partial pressure of CO in accordance with Eq. 5.1 at 1698 K, 1773 K, and 1873 K.
Equilibrium partial pressures of CO and CO\(_2\) (g) in equilibrium with graphite with increasing temperature at 1 atm total pressure. The dashed lines represent the \(p_{O_2}\) isobars.

Partial pressure of oxygen as a function of the partial pressure of CO(g), in accordance with Eq. 5.1.
5.2 Control of Nitrogen Potential

In some experiments, a fixed nitrogen potential was imposed on the system by continuously supplying nitrogen to the system at a fixed partial pressure in the inlet gas. As in industrial practice, the partial pressures of nitrogen employed in these experiments were well above the equilibrium partial pressure for the formation of Si₃N₄(s) at 1873 K; in a closed system, the nitrogen partial pressure would be 0.02 atm at 1873 K in the presence of Si₃N₄(s) as described by Tanahashi et al. [24], and Yoshikawa and Morita [20]. See also Section 3.3.

5.3 Equilibrium Studies

The experimental setup used in the equilibrium studies is illustrated in Figure 5-3. The primary component of the setup was a vertical, electrical tube furnace with Kanthal Super heating elements and an alumina reaction tube (64 mm inner diameter). The reaction tube was sealed with o-rings on its ends by a brass, water-cooled quenching chamber on the top, and a water-cooled cap on the bottom. The reaction gas entered the bottom of the tube and exited the quenching chamber on the top. A suspension rod fastened to a motorized screw-drive was used to position a holding crucible (containing up to six smaller sample crucibles) in the hot zone of the furnace. A Eurotherm controller set and maintained the target furnace temperature; the temperature was 1873 ± 2 K in the even temperature zone of the furnace. The control thermocouple was a Type B (Pt–6 % Rh / Pt–30 % Rh) thermocouple mounted in the wall of the furnace, which was positioned external to the reaction tube. The measurement thermocouple was also Type B, with a sapphire thermocouple sheath to protect against degradation from SiO(g) penetration. As can be seen in the figure, the tip of the measurement thermocouple was positioned just below the holding crucible. The reaction gas mixture was metered into the reaction tube using a gas train equipped with Bronkhorst mass flow meters (± 0.5 % accuracy) connected to a mixing column filled with glass beads.

5.3.1 Materials Preparation

Several different slag compositions were tested in each run. A eutectic CaO–SiO₂ master slag was prepared prior to the experiments, and was comprised of high-purity fused silica, and calcium oxide prepared by calcining precipitated calcium hydroxide. The composition of each slag sample was adjusted by blending small amounts of reagent-grade silica, calcium oxide, and magnesia with the master slag to achieve the desired slag compositions. Boron oxide was admixed with the slag constituents in the form of H₃BO₃. Higher concentrations of boron in the slag were used in this study compared to most of the previous investigations in order to facilitate more reliable chemical analyses. The equilibrium boron concentration levels were still well in the infinitely dilute range in both phases.

For each run, up to six small graphite crucibles were filled with silicon and the slag constituents in varying proportions. The small crucibles, fabricated out of high-purity, isostatically-pressed graphite, had dimensions of 41 mm inner height and 18 mm inner diameter. The silicon used in this study was polycrystalline, electronic-grade purity. Large chips of silicon were placed in the bottom of the graphite crucible. The slag components were placed in each small crucible above the silicon chips. Each crucible contained 10 grams of slag components and 3 grams of silicon.
5.3.2 Experimental Procedure

The sample crucibles were placed in a larger graphite holding crucible, mounted on the end of the suspension rod, and lowered into the center of the furnace. After lowering the holding crucible into position, the reaction tube was sealed, and the measurement thermocouple was positioned just below the holding crucible. The reaction tube was then evacuated and back-filled with argon several times. To commence the run, flow of reaction gas was commenced and the furnace controller was started. The flow rate of the inlet gas was 0.05 l/min. The temperature was ramped up to 1873 K at 4 to 5 degrees per minute. According to the CaO–SiO$_2$–MgO phase diagram, all the ingoing slag compositions were completely in the liquidus range at this temperature. The gas and condensed phases were equilibrated for 48 hours.

At the end of the experiment, the holding crucible was rapidly pulled out of the furnace into the water-cooled quenching chamber by raising the suspension rod. A flow of argon gas into the quenching chamber was immediately initiated to facilitate quenching of the samples. After cooling, the samples were removed from the quenching chamber, and the slag and silicon were carefully separated and cleaned. Special care was taken to remove any residual pieces of slag on the silicon samples.

5.4 Kinetic Studies

In the mass transfer investigation, a specially designed impeller system was constructed to agitate the melts. The design of the impeller and crucible was done using a 1:1 cold model made of Plexiglas. The mixing crucibles and impellers were machined out of Mersen 2020 graphite. The impeller had a simple flat blade geometry, 45 mm high by 15 mm wide, as shown in Figure 5-4(a). As can be seen in Figure 5-4(b), the mixing crucible was fabricated by boring four 18-mm diameter holes into a graphite blank in such a manner as to create an internal volume with a quatrefoil profile. The resulting four vertical protrusions acted as baffles to prevent bulk rotation of the melt and consequent vortex formation. Figure 5-5 is an isometric illustration of the graphite crucible assembly, comprised of a mixing crucible, a holding crucible, and a graphite support cap mounted onto a threaded graphite support tube. One mixing crucible and impeller were used for each heat. The graphite support tube was fastened onto the lower end of the stainless steel support tube with a threaded stainless steel coupling.

Photographs of the experimental apparatus are shown in Figure 5-6, while a schematic diagram of the setup is provided in Figure 5-7. The setup was essentially the same basic setup as shown in Figure 5-3 used for the equilibrium experiments; only it was modified to incorporate impeller mixing. As depicted in Figure 5-7, a Eurostar variable-speed stirring motor was used to drive a graphite impeller that stirred the melt. The main impeller shaft, made of stainless steel, was 1550 mm long and 10 mm in diameter. Threaded into the bottom end of the main impeller shaft was a 250 mm long, 8 mm diameter graphite extension rod and at its tip a graphite, blade-shaped impeller. A steel support tube with a 30 mm outer diameter housed the impeller shaft and supported the crucible assembly (described later). The upper end of the steel impeller shaft extended out of the support tube, and was connected to the stirring motor. The stirring motor and support tube were fastened to a motorized belt drive that allowed the vertical movement of the crucible assembly in and out of the hot zone of the furnace. To seal the moving mechanical components, radial shaft seals were used between the impeller shaft and support tube, and between the support tube and the cooling chamber.
Figure 5-4. The dimensions of the impeller and crucible.

(a) Impeller design

(b) Crucible design

Figure 5-5. Isometric illustration of the crucible assembly showing all the parts made of graphite.
5.4.1 Materials Preparation

Three different CaO–SiO$_2$ master slags, designated Slag A, B, and C were prepared prior to the experiments by fusing high-purity fused silica and calcium oxide (which was prepared by calcining precipitated calcium hydroxide) in a graphite crucible, and then granulated in water. Table 5-1 lists the compositions of the slags.

The silicon was polycrystalline, semiconductor-grade purity. Large chips of silicon were used in order to minimize surface area. Boron was added either to the slag phase or to the metal phase at an initial concentration of approximately 436 ppm. A small amount of highly doped silicon with silicon hexaboride (SiB$_6$) was made prior to the runs, and this was added in small amounts to the silicon phase in some of the runs. In other runs the slag phase was doped with boric acid (H$_3$BO$_3$), which was admixed with the slag granules. The concentration of boron in both phases was well in the infinitely dilute range in this study (see Figure 4-9).

Table 5-1. Slag compositions used in the experimental study.

<table>
<thead>
<tr>
<th>Slag</th>
<th>CaO, [mass %]</th>
<th>SiO$_2$, [mass %]</th>
<th>Viscosity at 1873 K [9] [Pa·s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>54</td>
<td>46</td>
<td>0.15</td>
</tr>
<tr>
<td>B</td>
<td>46</td>
<td>54</td>
<td>0.30</td>
</tr>
<tr>
<td>C</td>
<td>37</td>
<td>63</td>
<td>1</td>
</tr>
</tbody>
</table>
5.4.2 Experimental Procedure

In preparation for each heat, 40 grams of silicon chips were placed in the bottom of the mixing crucible, and 40 grams of slag constituents were placed on the top. The slag to metal ratio was 1:1 in all experiments. The mixing crucible was then placed into the holding crucible and the whole assembly was fastened onto the end of the stainless steel support tube. The impeller blade was lowered until it rested on the top of the material in the mixing crucible. The reaction tube was then sealed, evacuated and back-filled with argon. The crucible assembly resided in the quenching chamber until commencement of the run. The
furnace temperature was ramped up to 1823 K at 2 to 3 degrees per minute, flow of argon gas was commenced, and the furnace controller was started. The flow rate of the inlet gas was 0.05 l/min. When the target temperature in the hot zone of the furnace was reached, the crucible assembly was lowered to rest at a position in the reaction tube at about 1573 K to preheat the crucible to minimize thermal shock to the alumina reaction tube. After 15 minutes the crucible assembly was lowered all the way into final position in the hot zone of the furnace. It took approximately 6 minutes to melt the slag and silicon; this was determined by pushing the impeller down until it was possible to touch the bottom of the mixing crucible. The final impeller position was 10 mm above the bottom of the mixing crucible. After fusing, the crucible was half-filled with melt. When the impeller was in position, the stirring motor was engaged. The zero-time \((t = 0)\) for the run was when stirring was initiated.

At the end of an experiment, the crucible assembly was rapidly retracted out of the furnace into the water-cooled quenching chamber by raising the stainless steel support tube with the motorized belt drive. A high flow of argon gas into nozzles in the quenching chamber was immediately initiated to expedite quenching of the samples. After cooling, the crucible was removed from the quenching chamber, and cross-sectioned longitudinally using a diamond saw. Photographs and micrographs were taken of the crucible cross-sections. Samples of slag and metal were then extracted from the cross-sections and carefully separated and cleaned. Special care was taken to remove any residual slag on the metal samples.

5.5 **Silicon–Graphite Interactions**

The experimental apparatus used in the study was a high-temperature sessile drop apparatus as depicted in Figure 5-8, while Figure 5-9 shows photographs of the setup. The main component of the setup was a horizontal Entech electrical tube furnace with Kanthal Super heating elements and an alumina reaction tube (70 mm inner diameter). The reaction tube was sealed with o-rings on its ends by an internally water-cooled quenching chamber on one end, and the other end had a water-cooled aluminum cap with a sealed quartz glass window. The reaction gas entered on the window end and exited the quenching chamber. A carriage made of graphite held the specimen in the hot zone of the furnace. The carriage was threaded onto a water-cooled pushrod (sealed with a packing). The pushrod was fastened to a motorized screw drive that enabled the precise positioning and movement of the specimen to reproducibly control heating rates. A Eurotherm controller set and maintained the target furnace temperature, and the even temperature zone was defined as ± 2 K from the target temperature. The control thermocouple was a Type B (Pt–6 % Rh / Pt–30 % Rh) thermocouple (mounted in the wall of the furnace), which was positioned external to the reaction tube. The measurement thermocouple was a Type C (W / W–5 % Re), and was mounted axially in the pushrod and carriage, with the tip inside the carriage body positioned directly under the substrate. A gas train, as shown in Figure 5-8, prepared the reaction gas mixture. High-purity argon gas was metered using a Bronkhorst mass flow meter (± 0.5 % accuracy). The argon was first passed through a silica gel column to absorb water vapor, a column of ascarite removed CO₂, and then a magnesium perchlorate column was used to further reduce water vapor. After that the argon was passed through three furnaces with copper turnings at 723 K (450 °C) connected in series to reduce the oxygen level.

5.5.1 **Materials Preparation**

The silicon used in the study was polycrystalline, electronic grade purity. The silicon was broken into ~ 2.5 g pieces prior to the experiments.
Graphite substrate disks were milled out of various grades of graphite listed in Table 5-2. The grades were chosen according to industrial relevance, and as can be seen from the table, there is a large difference in the physical characteristics of the graphite grades. The substrates were 38 mm in diameter, and 8 mm thick. The surfaces of the substrates were not modified after machining; the effect of roughness has been documented by other researchers, and is shown to only influence the equilibrium apparent contact angle and not the initial spreading rate, [45,46] so it was not a focus of this study. Prior to the runs, the disks were heated at 393 K (120 °C) for several hours to remove any adsorbed water on the surfaces.

Table 5-2. Characteristics of the graphite substrates used in this study.

<table>
<thead>
<tr>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Isostatically pressed</td>
<td>1.77</td>
<td>4.3</td>
<td>15 µm</td>
<td>11</td>
</tr>
<tr>
<td>B</td>
<td>Vibration molded</td>
<td>1.73</td>
<td>2.2 / 2.5</td>
<td>0.8 mm</td>
<td>15</td>
</tr>
<tr>
<td>C</td>
<td>Extruded</td>
<td>1.70</td>
<td>2.1 / 3.1</td>
<td>0.8 mm</td>
<td>17</td>
</tr>
</tbody>
</table>

5.5.2 Experimental Procedure

In preparation for each experiment, the silicon piece and the graphite substrate were first cleaned with ethanol and then placed on the carriage. The carriage was positioned in the quenching chamber, and the whole system was then sealed. The reaction tube was evacuated with a vacuum pump and back-filled with argon. To start the run, a flow of reaction gas and the furnace control sequence were initiated. The flow rate of the inlet gas was fixed at 0.02 l/min. The temperature was ramped up to 1703 K (1430 °C) at 2 degrees per minute.

At the end of each experiment, the carriage was rapidly withdrawn from the furnace into the water-cooled quenching chamber by activating the mechanical drive. In some of the tests the specimens were quenched shortly after melting started, while in other tests the silicon was
given time to completely wet the graphite substrate so that dynamic changes in infiltration could be observed. The specimens were then prepared for scanning electron microscopy (SEM) analysis and electron dispersive spectroscopy (EDS) using a Hitachi S-3700N coupled with a Bruker XFlash Detector 4010. Still images were extracted from the video files, and from these the rate of spreading of silicon (apparent contact angle) on the graphite substrate was quantified.

The heating history was an important variable in this study. In the “rapid” heating tests, the furnace was ramped to the target temperature of 1703 K (1430 °C) while the specimen resided in the water-cooled quenching chamber. The carriage holding the silicon + graphite substrate (hereafter collectively referred to as the “specimen”) was pushed into the quenching chamber at a programmed velocity by means of the mechanical screw drive system. In this manner the heating rate was reproducible from one experiment to the next. In the tests with long heating times (SD5, SD6, and SD9), the specimen was positioned in the hot zone of the furnace and was slowly heated up at the normal ramp-up rate for the furnace of 2 K per minute up to 1573 K (1300 °C), where the specimen was allowed to soak for either 3 or 7 hours before finally increasing up to the maximum target temperature of 1703 K (1430 °C).

Video recording with the digital camera was started as the melting temperature of the silicon (1687 K) was approached.

5.6 Chemical Analyses

Calculating the partition ratios of boron requires attaining accurate boron analyses of two phases to generate one data point. Moreover, the concentration levels of boron are in the infinitely dilute range in both phases. In this study it was chosen to operate with higher levels of boron than in earlier studies to help reduce analytical uncertainty.

All of the silicon samples generated by these experiments were analyzed at the Elkem Technology analytical laboratory. They specialize in silicon and have developed advanced techniques and good routines for this work. Most of the boron assays for the slag and silicon samples were conducted with a Spectro Arcos Simultan inductively coupled plasma optical emission spectrometry (ICP-OES) instrument. For silicon Samples B8-1 through B11-6, however, analyses were conducted by atomic adsorption spectroscopy (AAS), using a Varian AA 280 FS. The estimated relative uncertainty for the ICP-OES and AAS analyses are ± 5% and ± 3 %, respectively.

Most of the slag samples were analyzed at Elkem Technology as well. The boron analyses were conducted by atomic adsorption spectroscopy (AAS), using a Varian AA 280 FS instrument. Some of the slag samples in the equilibrium studies were analyzed at an external laboratory using a Perkin-Elmer AAnalyst 300. The estimated relative uncertainty for these slag analyses is given at ± 5 %. The metallic Si contents of the slag samples were determined using the Fedorov method, with a relative uncertainty of ± 1 %.

The total nitrogen contents in the silicon and slag phases were quantified using a LECO TCH 600 instrument.
6 EXPERIMENTAL RESULTS

6.1 Equilibrium Studies

The equilibrium experiments were conducted at 1873 K. According to the CaO–SiO$_2$–MgO phase diagram, all the slag compositions studied were completely in the liquidus range at this temperature.

The equilibrium slag compositions, nitrogen contents, and partition ratios of boron are presented in Table A-1 and Table A-2 in Appendix A. Runs B1 to B11 were conducted with CO–Ar gas mixtures; Runs N1 to N9 had CO–N$_2$ gas mixtures, ranging from 0.1 to 0.99 atm nitrogen. The oxygen partial pressure values listed in the table were calculated using Eq. 5.1 and Eq. 5.2.

The values of $L_B$ were directly determined from the chemical analyses. In general, the highest boron partition ratios were attained with N$_2$–CO atmospheres; although the lowest $L_B$ values, however, were clearly from Runs N9-1 to N9-4, which were conducted with 0.99 atm N$_2$ and 0.01 atm CO.

The nitrogen concentrations in the silicon and slag phases are also reported in Table A-1. A few of the samples yielded unreasonably high nitrogen values, likely due to contamination, so these were omitted from the dataset.

6.2 Kinetic Studies

Table A-3 lists the conditions and the results of the experiments. Heats were conducted at 0, 50, 100, 200, and 400 rpm mixing speed at 1823 K. Experimental times ranged from 30 to 600 seconds. Either the slag phase was doped, or the metal phase was doped, as designated accordingly in the table. In all the heats pure argon gas was used as the atmosphere. Runs were conducted with the three slag compositions A, B, and C as described in Table 5-1.

Figure 6-1 shows photographs of the crucible cross-sections for the heats at 100 rpm mixing where boron was added to the slag phase. Keep in mind that mixing was stopped prior to quenching, and that the mixing conditions were kept constant in all the experiments. At short reaction times of $t = 30$ seconds and $t = 60$ seconds seen in (a) and (b), it can be seen with the naked eye that the interfacial boundary between the metal phase and slag phase is markedly irregular, and that there are countless small yet visible metal droplets entrained in the slag phase. By 300 seconds of reaction time as seen in (c), the interface is smooth, and the slag phase color has transformed from grey to green.
Figure 6-1. Changes in characteristics of slag–metal interface with increasing reaction time at 100 rpm mixing speed, slag phase doped with boron.

Figure 6-2 shows optical micrographs at 50× magnification of the bulk slag phase at $t = 30$ s and $t = 300$ s. All of these runs were conducted at 100 rpm mixing speed. At 30 seconds reaction time as seen in (a), metal is finely dispersed in the slag phase as irregularly formed droplets of varying size. It is apparent that the interfacial area is very large at this stage. In (b) at 500× magnification metal droplets ranging in size from 10 to 50 micrometers can be seen. In contrast, under the same mixing conditions at $t = 300$ s as seen in (c), the slag phase is nearly devoid of metal droplets. Higher magnification in (d) reveals only very tiny metal droplets less than 5 micrometers in diameter are left in the slag phase.

This is clear visual evidence that the interfacial area is highly variable and is strongly a function of reaction time. The grey appearance of the slag phase at short reaction times is attributed to emulsified metal droplets. It is expected that it is much easier to form an emulsion in the slag phase due to its much higher viscosity, about 150 mPa·s at 1873 K [9], as compared to liquid silicon, which has a viscosity of about 0.51 mPa·s at the same temperature [5]. In fact it was very difficult to obtain clean slag samples from the runs conducted at short reaction times due to emulsification.
Figure 6-2. Optical micrographs of the slag phase with increasing mixing time showing emulsification in the slag phase.

Figure 6-3 shows the rate of change in the amount of metallic silicon that is emulsified in the slag phase as determined by chemical analyses. As can be seen, the percentage of metal in the slag increases very quickly, peaks as high as 18.3 mass percent, and then decreases very rapidly with reaction time. By $t = 300$ s, the amount of metal entrained in the slag appears to reach a steady-state value below 2 mass percent Si metal. In the heats where the slag was doped with boron, the quantity of emulsified metal is lower, and this can at least partially be explained by the difficulty of taking representative samples of the slag phase before re-coalescence occurs. By $t = 300$ seconds, however, the quantity of metal in the slag after 180 seconds have reached stable values for both series. This corroborates with the visual evidence for the rapid changes in interfacial area in Figure 6-1 and Figure 6-2.
Figure 6-3. Change in amount of metallic Si in the slag phase with mixing time, 100 rpm mixing speed.

Figure 6-4 shows the change in boron concentration with increasing reaction time for the two cases when the slag was doped with boron, or when the metal phase was doped with boron. When the boron was added to the metal phase, the concentration decreased exponentially and leveled out by about 300 seconds. When boron was added to the slag phase, the concentration in the metal phase increased and leveled out. Since the total amount of boron was added to the system was equal in each case, these two curves converge at 300 seconds. No change in concentration is observed beyond 300 seconds of reaction time.

Figure 6-5 shows the change in calcium concentration in the metal phase as a function of reaction time and mixing speed in revolutions per minute (rpm). The calcium concentration in the silicon increases with time as CaO in the slag is reduced. With mechanical stirring, it can be seen that the rate of calcium transfer increases. However, it is readily apparent from the figure that a stirring speed greater than 100 rpm does not appear to increase the rate of calcium transfer. With stirring, by 600 seconds the calcium concentration in the slag reaches around 0.5 mass % Ca. The lines shown in the figure are simple power function curve fits to the 0 and 100 rpm data.
Figure 6-4. Concentration of boron in the metal phase as a function of time, 100 rpm mixing speed.

Figure 6-5. Concentration of calcium in the metal phase as a function of time with increasing mixing speed; Slag A (54 % CaO)
Figure 6-6 plots the change in boron concentration in the metal phase as a function of reaction time and mixing speed. These results are for heats where the slag phase was doped with boron, so the concentration of boron increases with reaction time. In this case, the boron oxide is being reduced at the interface and transferred to the metal phase. Again, mechanical stirring is seen to increase the rate of boron transfer from the slag phase to the metal phase. Without stirring at 0 rpm, the boron concentration in the metal by 500 seconds is only 81 ppm. With 100 rpm stirring, it appears that equilibrium is nearly reached by 300 seconds to about 120 ppm boron in the metal phase. Similar to the results with calcium, a stirring speed greater than 100 rpm does not improve the mass transfer rate of boron. The lines shown in the figure are simple power function curve fits to the 0 and 100 rpm data.

![Graph showing boron concentration over time with varying mixing speeds.]

Figure 6-6. Concentration of boron in the metal phase as a function of time with increasing mixing speed, slag phase doped with boron, Slag A (54 % CaO).

Figure 6-7 shows the concentration of calcium in the metal phase as a function of time with decreasing CaO content in the slag. As can be seen, the large reduction in the rate of calcium transfer is dramatic from Slag A (54 % CaO) to Slag B (46 % CaO); the decrease is disproportionately large considering the relatively modest viscosity difference (see Table 5-1). The rate of calcium transfer with Slag C (37 % CaO) is lowered even further, although the incremental change is relatively low compared despite a very large increase in slag viscosity between these two slag compositions. The lines shown in the figure are simple power function curve fits (for use in later calculations).

Figure 6-8 shows the changes in characteristics of the slag–metal interface at $t = 90$ s at 100 rpm with decreasing CaO content in the slag. At the highest CaO content in the slag, Slag A, shown in (a), emulsification of metal in the slag phase is clearly visible. For Slag B seen in (b) and for Slag C shown in (c), emulsification is not apparent.
Figure 6-7. Concentration of calcium in the metal phase as a function of time with decreasing CaO content in the slag.

Figure 6-8. Changes in characteristics of slag–metal interface at \( t = 90 \) s with decreasing CaO content in the slag, 100 rpm mixing speed.
6.3 Silicon–Graphite Interactions

Table A-4 outlines the experiments that were conducted. The three types of graphite described in Table 5-2 were tested. All of the tests were conducted at a maximum temperature of 1703 K (1430 °C). Most of the tests used purified argon as the furnace atmosphere, though Test SD3 used 0.05 atm CO(g), and Tests SD12–14 were run with a mixture of CO(g) and Ar–6 % H₂ mixture.

6.3.1 Wetting

As an example, still images extracted from the video recording of Test SD4 are shown in sequence in Figure 6-9. The starting time, \( t = 0 \) (designated \( t_0 \)) was assigned to when the silicon was completely molten. It did not take long – only a few minutes – for the molten silicon to completely spread and infiltrate the graphite. In this case, the substrate actually fractured during infiltration due to internal stresses as also described by Israel et al. [51].

It should be mentioned that the “contact angle” observed in a non-equilibrium system is not a fundamental property but a reaction of the system and its tendency to go towards equilibrium. This aspect is addressed in detail in the discussion section. Hence, the term “apparent contact angle” is used in the current study for all further discussions.

![Figure 6-9. The wetting of Si(l) on Grade C graphite as a function of contact time (SD4).](image)

The change in apparent contact angle as a function of time for each of the three different graphite grades at rapid heating rate are presented in Figure 6-10. In every one of these runs, the specimen was pushed at the same velocity (corresponding to a rate of temperature increase calculated to be 6.6 K/s) into the hot zone of the furnace at 1703 K (1430 °C). It is evident from this figure that there are clear differences in the dynamic wetting behavior of these graphite grades. For all of the graphite grades tested, the apparent contact angle decreased linearly with time until approaching equilibrium, corroborating the observation of Israel et al. [51]. Linear regression models were fitted to the data points in the linear regions as shown in the figure. The initial apparent contact angles, \( \theta_0 \), and the rate of spreading, \( d\theta/dt \), for each of
the grades were thusly determined. These values are shown in the inset table in the figure, along with corresponding r-squared values for the linear regression lines.

Silicon melting on Grade A in Test SD1 started out at a high apparent contact angle and did not attain an equilibrium contact angle until after over 250 seconds; this is expected since this is an isostatically pressed, dense graphite grade with low open porosity. The initial apparent contact angle for Grade C, surprisingly, was quite similar to Grade A grade despite having the highest open porosity since it is an extruded graphite quality. Melting on Grade B (the vibration molded quality), in contrast, started at a low apparent contact angle and was completely wetted in just under 150 seconds, although the initial rate of spreading differed.

![Figure 6-10. The contact angle of Si(l) on different graphite substrates as a function of time.](image)

The changes in spreading rates and initial apparent contact angles of liquid silicon with varying heating histories are compared in Figure 6-11. As seen in the figure, for the Grade A graphite, there are striking differences in the melting behavior with different heating histories. At a rapid heating rate, the starting apparent contact angle upon melting was high and leveled off after over 500 seconds of reaction time. It can be seen a satisfactory degree of reproducibility between Runs SD1 and SD8, which were replicate experiments. At the intermediate heating time of 3 hours, the initial apparent contact angle at \( t_0 \) was considerably lower, and the rate of wetting decreased substantially. The initial apparent contact angle with the longest heating history was much lower – only 11 degrees, and reached a final apparent contact angle of 7–8 degrees after just over 150 seconds. This final value is in good agreement with the equilibrium contact angle of silicon on SiC reported by Yuan et al. [47]. These results strongly suggest that something must be occurring on the graphite surface during slow heating (below the liquidus temperature of silicon) which modifies its properties and reduces the initial apparent contact angle.
In this study the presence of CO(g) into the furnace atmosphere was also tested and, interestingly, at partial pressures greater than about 0.05 atm this led to a very rapid surface reaction and disruption in the melting of silicon and wetting of the graphite substrate. In fact, the silicon pieces in Runs SD3 and SD12–14 did not appear to melt at all. In the latter tests, hydrogen was added to the furnace atmosphere in a failed attempt to reduce the surface reaction layer. Analysis of this phenomenon will be developed later in the discussion section.

6.3.2 Infiltration

Scanning electron microscopy and electron dispersive spectroscopy were conducted to examine the extent of infiltration of the graphite substrates. For brevity, only the infiltration of Grade A graphite is shown here. The extent of infiltration in Grade A graphite after 260 seconds is shown in Figure 6-12. In this test (SD1) the droplet was quenched before complete wetting. This is an isostatically-pressed graphite grade with a very fine average grain size. The infiltration of silicon reveals the internal structure of the graphite: in (a) it can be seen many fine pores fairly uniform in size, and penetration to a depth of about 500 microns. Higher magnifications in (b) and (c) show a darker, distinct phase at the interface and filling the pores, which was confirmed by EDS to be silicon carbide. An irregular, coherent layer of silicon carbide only a few microns thick is confirmed at the silicon-graphite interface.

Figure 6-11. The contact angle of Si(l) on Grade A graphite as a function of heating history.
7 DISCUSSION

7.1 Equilibrium Studies

It is conceived that boron dissolved in molten silicon is rejected to the slag phase following the oxidation as per Eq. 2.1. To simplify calculations this equation is recast as:

\[
\text{B(l)} + \frac{3}{4}\text{O}_2(g) = \text{BO}_{1.5}(l)
\]  

(Eq. 7.1)

\[
\Delta G^{\circ}_{\text{Eq. 7.1}, 1873K} = -427000
\]  

(Eq. 7.2)

where Eq. 7.2 is given in joules per mole [8], with the standard states pure liquid B, pure liquid BO\textsubscript{1.5}, and 1 atm oxygen gas. The equilibrium constant for Eq. 7.1 is written:

\[
K_{\text{Eq. 7.1}} = \frac{a_{\text{BO}_{1.5}(0)}}{a_{\text{B}(0)} \cdot p_{\text{O}_2}^{\frac{3}{4}}}
\]  

(Eq. 7.3)

where \(a_{\text{BO}_{1.5}}\) and \(a_{\text{B}}\) are the activities of liquid BO\textsubscript{1.5} and liquid B, respectively, and \(p_{\text{O}_2}\) is the partial pressure of oxygen. Following the development in Section 3.6 it can be established that:

\[
L_B \propto K_{\text{Eq. 7.1}} \cdot p_{\text{O}_2}^{\frac{3}{4}} \left( \frac{\gamma_{\text{B}(l)}}{\gamma_{\text{BO}_{1.5}(l)}} \right)
\]  

(Eq. 7.4)
In the presence of nitrogen, it is also reasonable to postulate that boron dissolved in molten silicon can be rejected to the slag phase following the reaction:

\[
\text{B(l)} + \frac{1}{2}\text{N}_2(g) = \text{BN (s)} \quad \text{(Eq. 7.5)}
\]

\[
\Delta G^\circ_{\text{Eq. 7.5}, 1873 K} = -95800 \quad \text{(Eq. 7.6)}
\]

where Eq. 7.6 is given in joules per mole [8]. The standard states for the above reaction are pure liquid B, pure solid BN and 1 atm nitrogen. For a system with only nitrogen and no oxygen, one could similarly deduce that

\[
L_B \propto K_{\text{Eq. 7.5}} \cdot p_{\text{N}_2}^{\frac{1}{2}} \left( \frac{\gamma_{\text{B(l)}}}{\gamma_{\text{BN(s)}}} \right) \quad \text{(Eq. 7.7)}
\]

where \(\gamma_{\text{B}}\) and \(\gamma_{\text{BN}}\) are the activity coefficients of pure liquid B, pure solid BN, respectively, and \(p_{\text{N}_2}\) is the partial pressure of nitrogen. Therefore, the partition ratio of boron should be dependent on nitrogen partial pressure and the nitride capacity of the slag phase.

7.1.1 Comparison with Literature

For comparison with the literature, Figure 7-1 is a plot of \(L_B\) as a function of the CaO:SiO\(_2\) ratio (basicity) of the slag. The values of \(L_B\) at 1 atm CO from the present work are shown here, and were categorized according to the MgO content in the slag. It is apparent that the results differ considerably from previous studies.

![Figure 7-1. The partition ratio of boron, \(L_B\), as a function of the CaO:SiO\(_2\) ratio in the slag at 1 atm CO, and comparison with previous studies.](image-url)
The values of Suzuki et al. [36] shown in Figure 7-1 were attained at 1 atm CO at a temperature of 1723 K. They show a maximum $L_B$ of 1.6, which is considerably lower than the present work. The lower temperature does not explain lower $L_B$ values compared to the present study. One would expect the value of $L_B$ to be greater at lower temperature, since the oxidation reaction of boron is exothermic (see Eq. 7.2) and thus the equilibrium constant should be larger in magnitude at lower temperature, which should raise $L_B$ according to Eq. 7.4.

As can be seen in Figure 7-1, the findings of Teixeira and Morita [37] are in marked contrast to the other studies: their $L_B$ values exhibit a much stronger dependence on the slag basicity, as well as show a distinct minimum. Their values in the middle range of basicity agree reasonably well with the current study, but at both high and low basicities the $L_B$ values are unreasonably large. Their highest reported value of $L_B$ is about 5.5 at a basicity of 1.2.

Even though they studied quite different slag compositions, the data of Johnston and Barati [39] were included in Figure 7-1, since they did not use graphite crucibles, and they flushed with pure Ar in the experiments. Their reported $L_B$ values are also considerably lower than the results of the present work.

7.1.2 Effect of Equilibration Time

Both Suzuki et al. and Johnston and Barati used very short run times of 2 hours [36, 39]. Teixeira and Morita [38] used equilibration times of 18 hours. According to experience from previous work, an equilibration time of at least 24 hours is necessary for this type of measurement. To ensure equilibrium with the gas phase, the present work employed a 48-hour run time. This may help explain the difference in the results of the current study as compared to others.

7.1.3 Dependence of $L_B$ on Oxygen Potential

Suzuki et al. [36] conducted experiments using pure Ar, pure CO and Ar/12.5 % CO$_2$ mixtures. Their assertion is that $L_B$ is independent of the gas composition. Thus they reasoned that the oxygen partial pressure of the system is actually controlled by the Si–SiO$_2$ equilibrium. They also conducted some experiments using Ar–CO$_2$ mixtures, and it should be questioned whether the oxygen partial pressures were in equilibrium in these particular experiments (see Figure 5-1).

The dependence of $L_B$ on the partial pressure of oxygen is indeed somewhat difficult to delineate from the effect of slag composition. Most of the runs were conducted at 1 atm CO (to examine the impact of slag composition), so there are fewer data points at lower CO partial pressures. It was possible to group several of the data into three groups with very similar slag compositions, but equilibrated under different oxygen partial pressures, as listed in the figure inset. Figure 7-2 is a plot of the dependence of $L_B$ on the partial pressure of oxygen and slag composition. This figure shows that at constant slag composition, $L_B$ increases with increasing oxygen partial pressure for all three slag compositions.
7.1.4 Activity Coefficient of Boron Oxide

The activity coefficient of boron oxide in the slag phase can be calculated by route of Eq. 7.3. A reliable value for the activity coefficient of boron at infinite dilution in silicon, together with the current experimental data, is needed in order to calculate the activity coefficient of boron oxide. From Yoshikawa and Morita [20], the activity coefficient of boron at infinite dilution is:

\[
\log \gamma^\circ_{B(0)_{\text{in Si}}} = \frac{126}{T} + 0.517
\]  

(Eq. 7.8)

The activity of boron in liquid silicon deviates positively from Raoult’s law. At 1873 K, \(\gamma^\circ_B\) has a value of 3.84. We neglect the interaction of B with Ca and Mg dissolved in the liquid silicon.

The calculated activity coefficients of boron oxide, \(\gamma_{\text{BO}_{1.5}}\), with respect to pure liquid BO\(_{1.5}\), are listed in Table A-1. The magnitudes and span of these values are reasonable; at 1 atm CO, the activity coefficient values range from 1.36 to 2.05. The only other reported activity coefficient values for boron oxide at infinite dilution in slag are reported by Teixeira and Morita [37], although they are calculated based on the assumption that the oxygen potential is controlled by the Si–SiO\(_2\) equilibrium.

7.1.5 Dependence of \(L_B\) on Nitrogen Potential

Figure 7-3 is a plot of the partition ratio of boron with increasing nitrogen partial pressure. The partition ratio clearly increases with increasing nitrogen content in the gas at constant oxygen potential. The highest boron partition ratios were reached at 0.4 atm N\(_2\). What is also
clear from the figure is the effect of the slag composition: the highest partition ratios are yielded at the lowest SiO$_2$ concentrations. Secondly, it is evident that a wide variance in the concentration of MgO in the slag does not negatively impact the partition ratio of boron.

![Graph](image)

Figure 7-3. The dependence of the partition ratio of boron on the nitrogen partial pressure at 1873 K.

The observation that a high CO partial pressure combined with high nitrogen potential facilitates the greatest rejection of boron to the slag phase also leads to the conclusion that oxidation and nitridization are occurring in parallel. Both reactions are spontaneous at 1873 K at the given standard states as seen in Eqs. 7.1 and 7.5, although there is a greater driving force for oxidation of boron to occur. The lowest $L_B$ values were actually attained under 0.99 atm nitrogen, which underscores the significant role of the oxidation reaction (Eq. 7.1) in boron rejection to the slag phase. It is indeed possible that the optimum nitrogen partial pressure is between 0.4 atm and 1 atm $N_2$. More study is needed to find the optimum reaction gas composition in order to maximize the boron partition ratio.

7.1.6 Nitrogen Capacity in the Slag

Nitrogen is known to dissolve in slag according to the following reaction:

$$\frac{1}{2}N_2(g) + \frac{3}{2}O^2- = N^{3+} + \frac{3}{4}O_2(g) \quad (Eq. 7.9)$$

Nitride capacity is defined as:
\[
C_{N^3-} = \left(\text{mass\% N}^3-\right) \frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} \tag{Eq. 7.10}
\]

The presence of carbon, as in the case of industrial slag treatment of silicon (graphite crucibles), complicates matters. Nitrogen is also known to exist in slags as CN\(^-\) ions in significant concentrations, forming by the reaction:

\[
\frac{1}{2} \text{N}_2(g) + \text{C}(s) + \frac{1}{2} \text{O}^{2-} = \text{CN}^- + \frac{1}{4} \text{O}_2(g) \tag{Eq. 7.11}
\]

\[
C_{CN^-} = \left(\text{mass\% CN}^-\right) \frac{P_{O_2}^{3/4}}{P_{N_2}^{1/2}} \tag{Eq. 7.12}
\]

Therefore, both the \(N^3-\) and \(CN^-\) concentrations in the slag are related to the free oxygen ion concentration in the slag, as well as the partial pressures of oxygen and nitrogen. Carbon, of course, is also known to exist as a carbide ion (\(C_2^2-\)), and carbonate ion (\(CO^3-\)) in slags as well.

A fair amount of research has been done concerning nitrogen dissolution in slags, mostly pertaining to steelmaking slags \([53,54,55,56,57]\). The solubility of nitrogen is strongly influenced by the oxygen partial pressure, the nitrogen partial pressure, and the composition of the slag. There are few particular studies of the solubility of nitrogen in \(\text{CaO-SiO}_2\) and \(\text{CaO-MgO-SiO}_2\) slags \([55,56]\). It is reasonable to assume that at low oxygen potential and carbon saturation, the nitrogen present in the slag is largely in the form of cyanide; Shimoo et al. \([57]\) show that this is indeed the case below 0.4 atm nitrogen. However, from Eq. 7.5, boron is expected to react with nitride ions to form BN. The concentration of boron in the silicon is in the infinitely dilute range (below 150 ppm), so even a relatively small fraction of free nitride ions in the slag would substantially increase the partition ratio of boron.

Figure 7-4 shows the total nitrogen content with increasing mole fraction of \(\text{SiO}_2\) in the slag, at a constant \(\text{CO-N}_2\) ratio of 0.9 to 0.1. The nitrogen content is seen to diminish with increasing \(\text{SiO}_2\) content, which agrees reasonably well with Martinez and Sano \([56]\), where they show a distinct maximum total nitrogen solubility at about \(x_{\text{SiO}_2} = 0.55\) and thereafter a decrease in the nitrogen content of the slag. Here they distinguish between incorporated and free nitride ions, and give the explanation that the free nitride ion concentration decreases as the free oxygen ions become deficient with increasing silica content in the slag (as supported by Eq. 7.11). The present results also follow the trend shown by Shimoo et al. \([57]\), for \(\text{CaO-Al}_2\text{O}_3-\text{SiO}_2\) slag compositions at nearly the same nitrogen and oxygen partial pressures.
Figure 7-4. The total nitrogen content as a function of the mole fraction of SiO$_2$ in the slag.

Figure 7-5. The calculated nitride capacity as a function of the mole fraction of SiO$_2$ in the slag.

Even though it is likely that most of the nitrogen in the slag exists as cyanide under the experimental conditions of the present study, nitride capacities were calculated as per Eq. 7.10 for purposes of qualitative analysis. This is also advantageous because calculating capacity
values incorporates the oxygen and nitrogen partial pressures so that all of the current data may be analyzed simultaneously. Figure 7-5 shows a plot of nitride capacity with increasing SiO$_2$ mole fraction. The trend of decreasing nitride capacity with increasing SiO$_2$ concentration corroborates the trend shown in Figure 7-4. This could explain why the boron partition ratio also decreases with increasing SiO$_2$ content in the slag.

In light of this evidence, it makes little sense to calculate the activity of BN in the slag phase as per Eq. 7.5 with the given data, since boron is likely simultaneously associated with both oxygen and nitrogen in the slag phase.

### 7.2 Kinetic Studies

#### 7.2.1 Estimation of Dynamic Interfacial Area

It is illustrative to make a rough estimate of the interfacial area based on the experimental data. Figure 7-6 shows a spline function fitted to the data from experiments at 100 rpm mixing speed presented earlier in Figure 6-3. Assuming a uniform droplet diameter of 0.5 mm, the starting interfacial area, with a spherical 40 g of liquid silicon, is 16 cm$^2$. Since the mass percent metal in the slag phase with time is known, the change in interfacial area can be calculated. Figure 7-6 is also a plot of the estimated total interfacial area versus time. As can be seen in the plot, the interfacial area is very large – in this estimation as high 420 square centimeters. This is more than an order of magnitude greater than the starting interfacial area.

![Figure 7-6](image)

**Figure 7-6.** Fitted curve for metallic Si present in slag, and estimation of magnitude of interfacial area as a function of time.

Dynamic interfacial phenomena have been documented in liquid iron–slag systems containing Al and Ti, and S as solutes [16d,58,59,60,61]. Riboud and Lucas provide compelling micrographs of the slag–metal boundary exhibiting what they describe as a “serrated”
interface due to the mass flux of aluminum [59]. Temporary interfacial instability due to the mass flux of surface-active solute elements across the interface is sometimes referred to as “interfacial turbulence”, which is theorized to be a combination of thermocapillary, solutocapillary (Marangoni flow), and electrocapillary effects [16d,60,61]. Boron oxide is known to be surface active in slag systems [62]. To determine whether or not this is the case here, Heat 22 was undertaken, in which no boron at all was added. The melt was mixed at 100 rpm and quenched after only 30 seconds. As evident in Figure 7-7, the irregularity of the slag–metal interface and emulsification is just as pronounced as in the runs conducted with boron addition. This result implies that the decrease in \( \gamma \) cannot be the dominating factor for the large interfacial area generated in the system at the initial stages of the reaction.

![Figure 7-7. Characteristics of the slag–metal interface for Heat 22, \( t = 30 \) s reaction time and zero boron addition.](image)

The decrease in interfacial area follows the trend of increasing calcium in the metal phase. As the concentration of Ca approaches equilibrium, the interfacial area approaches a minimum. Thusly it is evident that it is the transfer of calcium to the silicon phase that gives rise to the observed transient interfacial phenomena.

### 7.2.2 Gibbs Energy of Calcium Oxide Reduction

Calcium oxide is reduced at the interface and transfers to the metal phase. It is most likely that calcium oxide is reduced by silicon. In Raoultian standard states:

\[
\text{CaO(s)} + \frac{1}{2}\text{Si(l)} = \frac{1}{2}\text{SiO}_2(s) + \text{Ca(l)} \quad \text{(Eq. 7.13)}
\]

\[
\Delta G^\circ_{\text{Eq. 7.13}} = 156000 - 20.07T \text{ J/mol} \quad \text{(Eq. 7.14)}
\]
where the value of Eq. 7.14 is taken from Kume et al. [63]. At 1823 K, then

\[ \Delta G_{\text{Eq. 7.13, 1823 K}}^\circ = 119540 \text{ J/mol} \quad (\text{Eq. 7.15}) \]

Although Eq. 7.13 is not spontaneous at the given standard states, when the system has not attained chemical equilibrium then:

\[ \Delta G_{\text{Eq. 7.13}} = \Delta G_{\text{Eq. 7.13}}^\circ + RT \ln Q_{\text{Eq. 7.13}} \quad (\text{Eq. 7.16}) \]

where \( Q \) is the activity quotient. From Eq. 7.13 the activity quotient is written:

\[ Q_{\text{Eq. 7.13}} = \frac{a_{\text{SiO}_2(s)}^{1/2} \cdot \gamma_{\text{Ca(l) in Si(l)}} \cdot \chi_{\text{Ca}}}{a_{\text{CaO(s)}} \cdot a_{\text{Si(l)}}^{1/2}} \quad (\text{Eq. 7.17}) \]

Using the appropriate values in Eq. 7.17, the activity quotient \( Q \) with increasing time can be calculated. The values for the mass percent of calcium in the silicon as a function of reaction time are taken from the curve fit shown in Figure 6-5 (100 rpm speed) and converted to mole fractions of calcium using the relationship Eq. 3.11, which is valid for dilute Ca in Si:

\[ \chi_{\text{Ca}} = \frac{[\% \text{ Ca}] \cdot M_{\text{Si}}}{100 \cdot M_{\text{Ca}}} \quad (\text{Eq. 7.18}) \]

where \( M_{\text{Ca}} \) and \( M_{\text{Si}} \) are the molecular weights of Ca and Si. Only a small amount of calcium is transferred to the silicon phase, so the slag composition is assumed constant. The activity values for the binary CaO-SiO\(_2\) slag of 54 mass % CaO are \( a_{\text{CaO(s)}} = 9 \times 10^{-3} \) and \( a_{\text{SiO}_2(s)} = 0.249 \), which are extrapolated values from data provided by Kume et al. [63]. For self-consistency, the value of the activity coefficient for Ca(l) in Si at infinite dilution used in the calculations is from Miki et al. [26] (the value used in the calculations by Kume et al.). From Table 4-1:

\[ \ln \gamma_{\text{Ca(l) in Si}}^\circ = -17664 \div T + 3.52 \quad (\text{Eq. 7.19}) \]

Which is valid for the temperature interval 1723 to 1823 K. At 1823 K, then

\[ \gamma_{\text{Ca(l) in Si, 1823 K}}^\circ = 2.10 \times 10^{-3} \quad (\text{Eq. 7.20}) \]

For simplicity, the value of the activity of Si(l) is taken as unity. Figure 7-8 is a plot of \( \Delta G_{\text{Eq. 7.13}} \) as a function of reaction time.
To make calculations more convenient, the standard state for calcium can be changed from Raoultian (pure liquid) to 1 mass %. Rewriting Eq. 7.13 with the changed standard state for calcium:

$$\text{CaO(s)} + \frac{1}{2}\text{Si(l)} = \frac{1}{2}\text{SiO}_2(s) + [\text{Ca}]$$  \hspace{1cm} (Eq. 7.21)

where the brackets [ ] denote that Ca is in the 1 mass % standard state in liquid silicon. From Eq. 3.12 and Eq. 7.19:

$$\Delta G^\circ_{\text{Ca(l) \rightarrow 1 mass\% in Si}} = -146900 - 12.0T \text{ J/mol}$$  \hspace{1cm} (Eq. 7.22)

Combining Eq. 7.14 and Eq. 7.22 gives:

$$\Delta G^\circ_{\text{Eq. 7.21}} = -9100 - 32.0T \text{ J/mol}$$  \hspace{1cm} (Eq. 7.23)

7.2.3 Interfacial Area Related to the Gibbs Energy

To explain the observation that this system rapidly generates a very large interfacial area that decreases with reaction time, the overall driving force, viz. the total change in the Gibbs energy of the system between the initial and the final states is considered:

$$\Delta G_{\text{TOT}} = \Delta G_{\text{Eq. 7.21}} + \gamma \cdot A$$  \hspace{1cm} (Eq. 7.24)
with \( \Delta G_{\text{TOT}} \) being the change in total Gibbs energy of the system (in total joules), and where \( \gamma \) is the interfacial tension and \( A \) is the interfacial area. The change in Gibbs energy, \( \Delta G_{\text{Eq.7.21}} \), of the reaction of calcium reduction occurring at the interface (in joules), was described above. A number of studies have been published reporting the variation of the interface with time in non-equilibrium systems. The observed interfacial tension has a defined value only when the system has reached equilibrium. The apparent interfacial tension that is observed indeed depends not just on \( \gamma \) but actually on \( \Delta G_{\text{TOT}} \).

At the initial stages of the process, the two phases are far from equilibrium with respect to calcium, i.e. \( \Delta G_{\text{Eq.7.21}} \) is very negative, and therefore it is the dominating term in Eq. 7.24. The extremely low apparent interfacial tension would result in a large interfacial area between slag and silicon, facilitating emulsion formation. As the two phases approach chemical equilibrium (as \( \Delta G_{\text{Eq.7.21}} \) approaches zero), the second term, \( \gamma \cdot A \) in Eq. 7.24 becomes increasingly significant. To reach a minimum total Gibbs energy level, the system would prefer a minimum interfacial area at the latter stage of the process, which explains the drastic decrease in the interfacial area as equilibrium is approached.

Mechanical agitation facilitates the break-up and dispersion of metal droplets into the slag phase. As the reaction (Eq. 7.21) attenuates, the apparent interfacial tension increases. At this point, with 100 rpm mixing speed, there is not enough energy imparted to the melt to maintain the slag–metal emulsion, and the metal phase re-coalesces.

7.2.4 Mass Transfer of Calcium

It is very difficult to describe the reaction process in a simple mathematical manner. Hence, the following discussion should only be considered qualitative. As is common practice, assuming first-order behavior, one could write a rate equation for the transfer of calcium to the silicon phase as follows:

\[
\frac{d[\% \text{ Ca}]}{dt} = \frac{\tau \cdot A}{V_{\text{M}}} \left( [\% \text{ Ca}]_{\text{eq}} - [\% \text{ Ca}] \right) \quad \text{(Eq. 7.25)}
\]

where the rate of change is unit concentration per second. The bulk concentration of calcium in the metal phase is \([\% \text{ Ca}]\). The concentration of calcium in silicon at the interface can reasonably be assumed to be at thermodynamic equilibrium, \([\% \text{ Ca}]_{\text{eq}}\). The difference in these two terms, the concentration gradient (\( \Delta C \)), is the chemical driving force for mass transport. An apparent rate constant is designated as \( \tau \), and the interfacial area is \( A \). The volume of the metal phase is \( V_{\text{M}} \).

The decrease in the reaction rate of Eq. 7.21 shown in Figure 6-5 is due to three factors as indicated by Eq. 7.25: (1) the decrease in \( \tau \), (2) the decrease in \( A \), and finally (3) the decrease in the chemical driving force \([\% \text{ Ca}]_{\text{eq}} - [\% \text{ Ca}]\). Note that both \( \tau \) and \( A \) also depend on the chemical driving force. The significance of these three factors on the decrease of the reaction rate would vary with time. Nevertheless, the experimental results suggest that the variation of the interfacial area plays a very important role. It is expected that the large interfacial area and the large chemical driving force are the main reasons for the rapid reaction rate observed at the initial stages of the reaction.
7.2.5 Mass Transfer of Boron

The equilibrium of boron between the metal and slag phases can be represented by the equation, in Raoultian standard states:

\[
\text{B(l)} + \frac{3}{4} \text{O}_2(g) = \text{BO}_{1.5}(l)
\]  
(Eq. 7.26)

Comparison of Figure 6-5 and Figure 6-6 reveals that the rate of boron transfer follows very closely the rate of calcium transfer: by 300 seconds it appears that both the boron and the calcium concentrations have achieved equilibrium. The calculated boron partition ratio at 300 seconds is about 2.4, and this agrees reasonably well with the results presented in Section 6.1. The transfer of calcium to the metal phase during slag refining is incidental. Nonetheless, it is very likely that calcium transfer enhances the boron mass transfer rate by increasing the available interfacial area. This perhaps unintended benefit is worthy of further study.

7.2.6 Effect of Stirring Rate on Mass Transfer

The rate of calcium transfer is seen to increase with increasing mixing speed up to a point, so it is evident that the rate-limiting step is the mass transfer of calcium either in the slag or metal phase. It is evident from Figure 6-5 and Figure 6-6 that increasing the mixing speed up to 100 rpm indeed increases the rates of mass transfer of Ca and B. Mixing speeds greater than 100 rpm have a diminishing effect.

Classical theory describes a boundary layer at the interface with stagnant fluid flow where mass transfer across this thin film takes place by diffusion. The apparent rate constant, \( \tau \), is thusly defined in terms of:

\[
\tau = \frac{D}{\delta}
\]  
(Eq. 7.27)

with \( D \) being the diffusion coefficient for the solute, and \( \delta \) is an “effective film thickness”. Such a system as the one described here, however, is not a static system in any way. Complex fluid flow due to the rapidly fluctuating interfacial area render impracticable the concept of a constant effective film thickness; and therefore neither should \( \tau \) be truly constant.

The overall mass flux could be considered to be influenced by three resistance terms, namely the resistance of convective mass transfer in the bulk phases, \( R_1 \), the resistance of mass transfer at the interface, \( R_2 \), and the resistance due to limitations in the rate of chemical reaction, \( R_3 \). In a system exhibiting transient interfacial turbulence, \( R_2 \), should be time-dependent. These resistances are in series, so the mass flux of a solute, \( J \), would be described mathematically as:

\[
J = \frac{\Delta C}{R_1 + R_2 + R_3}
\]  
(Eq. 7.28)

Mixing speeds greater than 100 rpm have a diminishing effect on the mass transfer rates, and this can be explained with the aid of Eq. 7.28 in that by increasing the mixing speed, the bulk phase mass transfer improves due to increased convection. In other words, the \( R_1 \) resistance term attenuates with increased convention. Above a certain threshold, either the interfacial resistance term, \( R_2 \) dominates, the chemical reaction resistance term, \( R_3 \), dominates, or it is
joint resistance due to both $R_2$ and $R_3$. Hence, the complexity of the interface and fluid dynamics would limit the usefulness of the conventional concept of the global mass transfer coefficient; Brooks et al. brought attention to this in an earlier publication [64]. It is expected that as the two phases are reaching equilibrium, $\tau$ decreases to a constant value due to the decrease in interfacial turbulence. The results of the present study further emphasize that use of a laboratory-derived mass transfer coefficient in industrial practice must be used with serious caution.

7.2.7 Effect of Slag Composition on Rate of Ca Transfer

Turning to Figure 6-7, it can be seen that decreasing the CaO content in the slag from 54 to 46 mass % CaO significantly reduces the rate of calcium transfer. A further reduction to 37 mass % CaO in the slag produces only a modest reduction in the Ca transfer rate. It is expected that the reduction in the chemical driving force should play a large role in this reduction in rate. However, the slag viscosity and the interfacial area must also impact the mass transfer rates. An increase in slag viscosity negatively impacts convection in the bulk slag phase and thereby reduces the apparent rate constant (i.e. bulk resistance term $R_1$ in Eq. 7.28). However, as already pointed out, inspection of Table 5-1 shows that the viscosity difference between Slag A and B is not significant in contrast to Slag C, which has much higher viscosity due to its very high silica content.

At 1823 K, the value of Eq. 7.23 is:

$$\Delta G^{\circ}_{\text{Eq. 7.21, 1823 K}} = -49187 \text{ J/mol} \quad \text{(Eq. 7.29)}$$

It follows that the activity quotient for Eq. 7.21 is now:

$$Q_{\text{Eq. 7.21}} = \frac{a_{1/2}^{SiO_2(s)} \times [\% \text{Ca}]}{a_{CaO(s)}^{1/2} \times a_{Si(l)}^{1/2}} \quad \text{(Eq. 7.30)}$$

Like in Section 7.2.2, using the appropriate values in Eq. 7.30, the reaction quotient $Q$ at $t = 90$ s can be calculated for each of the three slag compositions, and thus the Gibbs energy of Eq. 7.21 (in joules) in each instance. The values for the mass percent of calcium in the silicon at $t = 90$ s were taken from the curve fits shown in Figure 6-7. Using the $Q$ values, the values of $\Delta G_{\text{Eq. 7.21}}$ were calculated at $t = 90$ s. The resulting calculations are listed in Table 7-1. As can be seen in Table 7-1, the Gibbs energy change due to Eq. 7.21 is much more negative for Slag A than for Slags B and C; for these latter slags, their values are nearly the same.

It is also possible to calculate the equilibrium calcium concentration in the silicon phase, $[\% \text{Ca}]_{eq}$, for each of the different slag compositions. Since at chemical equilibrium, $\Delta G_{\text{Eq. 7.21}} = 0$, and therefore:

$$\Delta G^{\circ}_{\text{Eq. 7.21}} = -RT \ln Q_{eq} \quad \text{(Eq. 7.31)}$$

and from Eq. 7.29 and Eq. 7.31, the equilibrium constant of Eq. 7.21 at 1823 K is calculated:

$$K_{\text{Eq. 7.21, 1823 K}} = Q_{eq} = 25.69 \quad \text{(Eq. 7.32)}$$
and thereby the equilibrium calcium concentration in the silicon phase, $[\% \text{Ca}]_{eq}$, can be calculated for each slag compositions (these values are also listed in Table 7-1). The calculations of $[\% \text{Ca}]_{eq}$ are in very close agreement with the measured data in the present study (see Figure 6-5 and Figure 6-7). This confirms that for Slag A, the equilibrium calcium concentration in the silicon, which is 0.46 mass % Ca, is already reached by 300 seconds of reaction time.

Table 7-1. Calculation of the Gibbs energy of Eq. 7.21 at $t = 90$ s.

<table>
<thead>
<tr>
<th>Slag</th>
<th>(% CaO)</th>
<th>$x_{(\text{CaO})}$</th>
<th>$a_{\text{CaO}(s)}$</th>
<th>$a_{\text{SiO}_2(s)}$</th>
<th>$[% \text{Ca}]_{eq}$</th>
<th>$\Delta G_{7.21,1823 K}$</th>
<th>$[% \text{Ca}]_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>54</td>
<td>0.52</td>
<td>$9.00 \times 10^{-3}$</td>
<td>0.249</td>
<td>0.33</td>
<td>44052</td>
<td>-1657</td>
</tr>
<tr>
<td>B</td>
<td>46</td>
<td>0.44</td>
<td>$2.60 \times 10^{-3}$</td>
<td>0.614</td>
<td>0.069</td>
<td>45989</td>
<td>-213</td>
</tr>
<tr>
<td>C</td>
<td>37</td>
<td>0.35</td>
<td>$1.70 \times 10^{-3}$</td>
<td>1</td>
<td>0.031</td>
<td>44005</td>
<td>-157</td>
</tr>
</tbody>
</table>

From Figure 6-8, it is evident that the degree of emulsification is very high with Slag A, and much lower for Slags B and C; i.e. interfacial phenomena are not playing a role in the mass transfer in these heats as evidenced by the low amount of entrained silicon in the slag phase.

Thus, it is established that it is indeed the large reduction in chemical driving force that accounts for the precipitous drop in Ca transfer rate from 54 to 46 mass % CaO in the slag. It is somewhat challenging to delineate the individual effects of these factors since in fact they are interdependent: the chemical driving force influences the overall rate of mass transfer, but at sufficient concentration of CaO in the slag, interfacial turbulence comes into play and therefore the interfacial area becomes transient. In the end, it is the difference in chemical potential between the silicon and slag phases that is the ultimate driving force for mass transfer.

From an engineering perspective, mechanical stirring appears to be an extremely efficacious means to increase the reaction rate in slag refining of silicon to extract boron. The ability to use graphite as a refractory material in this system offers great flexibility in the design of both the reactor vessel and the impeller, making it quite feasible to implement this technique on an industrial scale.

### 7.3 Silicon–Graphite Interactions

As shown previously, the initial apparent contact angle between liquid silicon and graphite and the rate of spreading is shown to depend on the heating history as well as the type of graphite substrate, and this observation needs to be addressed. There are many past studies that have quantified the rate of change in the apparent contact angle of liquid silicon on graphite and carbon with time [44,45,46,47,48], and similar dynamic observations have also been reported for many other high-temperature systems [65,66,67]. It is, however, essential to have an in-depth understanding of the dynamic nature of wetting behavior in order to make this type of measurement useful for the development and optimization of any materials process.
To begin the discussion, the classic schematic illustrating Young’s law is provided in Figure 7-9, depicting a force balance between the surface tension between molten silicon and the gas phase, the surface tension between graphite and the gas phase, and the interfacial tension between liquid silicon and graphite. Note that this situation is only valid for systems in thermodynamic equilibrium. It should be questioned whether Figure 7-9 is also applicable to a system under non-equilibrium conditions. A value for the interfacial tension between liquid silicon and graphite, $\gamma_{\text{Si/C}}$, is required in order to apply the force balance shown in Figure 7-9.

Unfortunately, $\gamma_{\text{Si/C}}$ is not a measureable quantity in reality. Exactly as in the case that the activity of a component cannot be defined and measured in a non-equilibrium system, the interfacial tension $\gamma_{\text{Si/C}}$ term cannot be defined and measured in this system since molten silicon and carbon cannot exist in thermodynamic equilibrium. Actually, the variation of the apparent contact angle is not only a result of the change in $\gamma_{\text{Si/C}}$, but also due to the change in the total Gibbs energy between the two states:

$$\Delta G_{\text{TOT}} = \Delta G_{\text{Eq. 4.5}} + \gamma \cdot A$$

(Eq. 7.33)

where in this case $\Delta G_{\text{Eq. 4.5}}$ is the Gibbs energy of the reaction to form silicon carbide (Eq. 4.5), and $\gamma \cdot A$ is the interfacial energy term. Hence, a scientific consideration of the dynamic variation in this system (see Figure 6-10 and Figure 6-11) should, again, really be based on Eq. 7.33. For this reason, the observed contact angle should strictly be called an “apparent contact angle”.

It is expected that the mechanism and rate of the reaction are directly related to the experimental conditions, e.g. in the present case, the type of substrate and the heating history. The variation of the apparent contact angle is in fact a measure of the reaction rate. In order to properly utilize this type of measurement in a proper scientific manner for process optimization, a good understanding of the reaction mechanism including the effects of the substrate properties and the heating history is required. Hence, the following discussion is based on this premise.

7.3.1 Wetting & Infiltration

As shown in the micrographs Figure 6-12(a), no silicon carbide phase is found on the graphite surface ahead of the three-phase interface, nor is there any infiltration ahead of this point. This is evidence that the Gibbs energy of Eq. 4.5 is the primary driving force for the outward spreading of the droplet; the ongoing reaction forms silicon carbide at the interface, and the droplet changes form and expands in area as the reactants are consumed. The fine layer of carbide product at the silicon-graphite interface would act as a diffusion barrier that limits
further reaction and growth of this layer. It is most probable that the liquid silicon dissolves a significant amount of carbon, and leads to surface tension gradients and Marangoni flow on the surface of the droplet near the three-phase interface, which would also contribute to facilitate the spreading of the droplet. It could be said that what is actually being observed is the wetting of SiC by a carbon-saturated Si–C alloy. The fact that infiltration only occurs directly under the silicon droplet suggests that the molten silicon penetrates the open pores in the graphite due to hydrostatic pressure from the droplet, with the rate and extent of infiltration being dependent on the graphite properties.

7.3.2 Effect of Heating History

As shown in Figure 6-11, the heating history has a profound impact on the melting behavior of silicon on graphite. As seen in this figure, the results are reproducible as evidenced by the close results of the replicate experiments SD1 and SD8; the variation observed by altering the heating rate was not random behavior, but was indeed dependent on the chosen experimental conditions.

Longer holding times at the sub-liquidus temperature of 1573 K led to smaller initial apparent contact angles. This leads to the conclusion that the graphite surface was being modified below the liquidus temperature of silicon. One could reason that the longer the heating history, the more complete is the carbidization of the graphite surface. It appears that silicon carbide forms on the surface, either by a solid–solid reaction or a gas–solid reaction.

To elucidate which mechanism is responsible, Test SD16 was performed. A piece of silicon on Grade C graphite was heated for 12 hours at a temperature of 1573 K under pure argon, and the results are shown in Figure 7-10. There was a gap between the irregularly shaped piece of silicon and the graphite substrate, so the two materials were in contact at only a few points as shown in (a). The next photograph, taken after cooling and seen in (b), shows the piece of silicon and the graphite substrate side by side in the same orientation as (a). Clearly visible in the photograph is a distinct discoloration of the graphite in the region that was directly under the gap between silicon and the substrate. Indeed, SEM and EDS analyses of this discolored region, shown in (c) and (d), reveal the localized depositing of silicon on the top surface of the graphite. This is strong evidence that it is indeed a gas-solid reaction that occurs to modify the surface properties of the graphite. This explains the much lower initial apparent contact angle of silicon with longer heating intervals. This supports the observation that the heating rate is truly an important test parameter, and also implies that the initial apparent contact angle and spreading rate of liquid silicon on graphite is system-dependent.

A gas-solid reaction to form SiC has already been alluded to in the literature by Israel et al. [51] where they provided evidence to support their claim that Si(g) reacts with graphite substrates below the liquidus temperature. The situation, however, may be even more complex than their analysis shows. It is well known that in the silicon-oxygen system, several vapor species can co-exist at elevated temperatures, with the partial pressures of these species being dependent on both temperature and the partial pressure of oxygen. Although the predominant silicon-bearing vapor species is silicon monoxide vapor, SiO(g), other vapor species are also present at significant partial pressures (see Section 3.1).
Figure 7-10. Results of Test SD16 after treatment below the liquidus temperature of Si at 1573 K with pure Ar gas, where the silicon reacts with the graphite substrate.

Vapor pressure / phase stability diagrams for the Si–O system were constructed, and are presented in Figure 3-1 and Figure 3-2. The vapor pressure of SiO(g) in the system, even at 1573 K (1300 °C), is significant and highest at an oxygen partial pressure value corresponding to the equilibrium between the condensed phases. The total effective vapor pressure of silicon is highly dependent on the system temperature and oxygen potential. As can be seen in Figure 3-2, at 1573 K the greatest total effective vapor pressure of silicon ($P_{\text{Si,eff}}$) is $7.0 \times 10^{-2}$ atm, which is a significant value considering that this temperature is well below the liquidus temperature of silicon. At 1687 K (1414 °C), the liquidus temperature of silicon at 1 atm, the maximum total effective vapor pressure of silicon is 0.15 atm.

7.3.3 Effect of Atmosphere on Melting Behavior

Another interesting observation from this study is that the presence of carbon monoxide in the furnace gas at concentrations of greater than 5 % (0.05 atm) leads to a thin layer of reactant that is formed very rapidly (in a matter of a few seconds) on the surface of the silicon as seen in Figure 7-11; this happened in Test SD3 where the specimen was pushed rapidly into the hot zone. Even after heating up the silicon sample above its liquidus temperature to 1703 K (1430 K).
°C), the piece of silicon maintained nearly the same morphology as in the original state – only the surface color had changed to black, as seen in (a) and (b). This is evidence that a quite different gas–solid reaction took place on the surface of the silicon. Infiltration was insignificant as seen in the SEM micrographs shown in (c) and (d). SEM analysis and elemental mapping of the top surface of the silicon are shown in (e) and (f), and only a very tenuous silicon carbide shell is formed. It seems this is enough to prevent the spreading of the silicon on the graphite substrate. One can also see in (a) that a few small droplets of Si managed to squeeze out of the shell, yet they did not wet the graphite substrate.

It is thermodynamically possible for CO(g) to react directly with solid silicon according to the reaction:

\[
\text{Si}(s) + \text{CO}(g) = \text{SiC}(\beta) + \frac{1}{2} \text{O}_2(g) \quad \text{(Eq. 7.34)}
\]

Figure 7-12 is a phase stability diagram of the Si–O–C system at 1687 K, (the liquidus temperature of silicon), as already shown in Section 3.2. Calculating from Eq. 5.2 and the law of mass action at 1703 K (the prevailing furnace temperature), the oxygen partial pressure is \(2.63 \times 10^{-19}\) atm at 0.05 atm CO; at 0.10 atm CO the partial pressure of \(\text{O}_2\) is \(1.05 \times 10^{-18}\) atm. These coordinates are marked “*”, and “+” in the figure, respectively. In the figure it can be seen that these operating points are clearly in the SiC phase field. These are not unreasonable partial pressures of CO(g) by industrial standards, so it has practical implications for silicon melting since leakage or ingress of oxygen (air) leads to CO(g) formation in the furnace atmosphere, which at significant partial pressures can lead to severe problems during heating of silicon. This phenomenon may even be more pronounced when melting fine-grained silicon granulate or secondary materials such as silicon fines due to a much higher available surface area for a gas-solid reaction.
(a) Photograph of specimen after heating, showing discoloration and partial melting.

(b) Cross-section of silicon/graphite substrate.

(c) SEM micrograph at 50× magnification of a gap between Si and graphite.

(d) 50× micrograph showing extent of infiltration where silicon was in direct contact with graphite.

(e) SEM micrograph of top surface of silicon at 470× magnification.

(f) Elemental mapping of SEM micrograph in (e) showing distribution of C on top surface of silicon.

Figure 7-11. Results of Test SD3 after heating above the liquidus temperature of Si (1703 K) with 5 % CO in furnace gas, where the specimen does not wet the graphite substrate.
8 SUMMARY AND CONCLUSIONS

8.1 Thermodynamics of Slag Refining

The $L_B$ values from this study are in fair agreement with the industrial process norms. Stabilization of the oxygen potential in the furnace atmosphere is also important for a consistent industrial process. The results of this study could impact how the industrial slag treatment process is operated. Several salient conclusions can be drawn:

1. Both the slag composition and the oxygen potential have an influence on the distribution of boron between the silicon and oxide phases.

2. The presence of nitrogen in the reaction gas positively enhances the partition ratio of boron. This could help to explain why observed industrial partition ratio values are considerably higher than in previously published works where only the effects of slag composition and oxygen potential were studied.

3. The highest boron partition ratios were achieved at 0.4 atm N$_2$ and 0.6 atm CO, and at the lowest SiO$_2$ concentrations in the slags. Further investigation is necessary to determine the optimum ratio of CO to N$_2$ in the reaction gas.

4. A concentration of MgO of up to 15 mass % in the slag does not have a deleterious effect on the partition ratio of boron, which could be advantageous for the industrial process.

5. Stabilization of the oxygen and nitrogen potentials in the furnace atmosphere is important for a consistent industrial process.
8.2 Kinetics of Slag Refining

Experiments carried out to study the mass transfer between liquid silicon and CaO–SiO$_2$ slag during mechanical stirring have revealed the occurrence of transient interfacial phenomena. The apparent interfacial tension appears to become very low, as is evident in the development of an irregular phase boundary and a surge in interfacial area. This rapid change in interfacial area follows the progress calcium oxide reduction at the interface. During this period of low apparent interfacial tension, the agitation of the melt facilitates emulsification in the slag phase, further enhancing the rate of mass transfer rate. As the rate of the interfacial reaction attenuates, the apparent interfacial tension increases, and the interfacial area returns to a much lower level.

The rates of mass transfer of both Ca and B are seen to increase with the implementation of impeller mixing, which shows that overall rates are limited by mass transfer and not the rate of the reaction at the interface. However, at mixing speeds greater than 100 rpm, the rates of mass transfer do not improve significantly, since above this threshold interfacial resistance dominates or there is chemical reaction control (or these two jointly). In this system, mass transfer rates are impacted by a complex interplay of many factors.

These results have many practical implications. Firstly, mechanical mixing was confirmed to be an extremely potent means to increase the mass transfer rates of B and Ca in slag refining of silicon. With a high content of CaO in the slag, interfacial turbulence aids mass transfer by facilitating emulsification. From a reactor design perspective, this is welcome news since it should be simpler to achieve optimal mixing conditions with less kinetic energy input into the melt. Perhaps the amount of Ca in the system can even be manipulated in such a manner to facilitate emulsification and maximize mass transfer rates. Ideally, a continuous, counter-current slag–metal reactor would combine a maximized chemical driving force with a high efficacy of mixing achieved by inducing emulsification.

In general, this experimental effort has revealed that mass transfer in this system is far more complex than previously known. It is untenable to construct a simple global, analytical model that can accurately describe the mass transfer in this case. Perhaps a more promising approach for reactor design would be to develop a computer mass-transfer “micro-model” that employs finite element methods to incorporate complex fluid flow caused by forced convection and transient interfacial conditions.

8.3 Silicon–Graphite Interactions

There are several conclusions from this study that could have potential industrial significance:

1. The infiltration of silicon is highly material-dependent, i.e. related to the internal structure of the graphite. The choice of graphite grade should be tailored to the particular application. High-density, isostatically-pressed graphite grades such as Grade A are most suitable for direct melting of silicon.

2. The heating rate influences the melting behavior of silicon on graphite – the rate of infiltration and rate of wetting are therefore also system-dependent and should vary in different industrial unit operations. Silicon-bearing vapor species can react with graphite to form SiC even below the liquidus temperature of silicon and alter the surface properties of the graphite.
3. A significant concentration of CO(g) in the furnace atmosphere has a deleterious effect on the melting behavior of silicon. This finding may influence how silicon is melted in graphite-lined vessels in industrial processes. Proper control of the furnace atmosphere composition is paramount.

8.4 Suggestions for Continued Research

During the course of this research study, it became increasingly clear that there are still many gaps in our knowledge base where very critical data is sparse. Below are some proposed fundamental research subjects that would have great potential for direct application in high temperature processing of silicon:

*Activity of Ca in liquid silicon.* Data for this particular system is sparse. This is understandable since there are many experimental challenges: calcium is very easily oxidized, and the enthalpy of mixing is very exothermic. As explained in this thesis, this is an important system for silicon refining. Not only would the measurement of the activity of Ca in Si over the entire compositional range be beneficial, but also accurate data for the activity of Ca at infinite dilution would be most useful.

*Integral molar enthalpy of mixing for Ca in Si.* In some processes, silicon is alloyed with calcium. Better data for the enthalpy of mixing could improve process control of alloying.

*Henrian activity coefficient of B in Si.* Data for this system is also difficult to gather, but considering the industrial significance, efforts should be made to find better ways to determine this experimentally.

*Solubilities of N and C in slags.* Carbon and nitrogen are omnipresent in the melting and slag refining of silicon, and affect inclusion and accretion formation. A more accurate picture of how carbon and nitrogen behave in slags would be very beneficial and could improve many areas of the refining process and lead to a cleaner silicon product.

*Development of mass transport models for silicon refining.* In general, this experimental effort has revealed that mass transfer in this system is far more complex than previously known. It is untenable to construct a simple global, analytical model that can accurately describe the mass transfer in this case. A more promising approach for reactor design would be to develop a computer mass-transfer “micro-model” that employs finite element methods to incorporate complex fluid flow caused by forced convection and mass transfer under transient interfacial conditions. COMSOL Multiphysics would be an appropriate tool for such an endeavor.
9 REFERENCES


APPENDIX A

Tabulated Experimental Conditions and Results
Table A-1. Experimental conditions and results of boron distribution experiments with CO–Ar gas mixtures at 1873 K.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Inlet Gas [atm]</th>
<th>Equilibrium Slag Composition</th>
<th>Silicon</th>
<th>Partition Ratio, $L_B$</th>
<th>$Y_{\text{BO}_{3}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{\text{CO}}$</td>
<td>$P_{\text{O}_2}$</td>
<td>SiO$_2$</td>
<td>CaO [mass %]</td>
<td>MgO [mass %]</td>
</tr>
<tr>
<td>B1-2</td>
<td>1.0</td>
<td>$4.6 \times 10^{-16}$</td>
<td>55.2</td>
<td>43.7</td>
<td>1.00</td>
</tr>
<tr>
<td>B1-3</td>
<td>1.0</td>
<td>$4.6 \times 10^{-16}$</td>
<td>55.8</td>
<td>42.9</td>
<td>1.32</td>
</tr>
<tr>
<td>B2-1</td>
<td>1.0</td>
<td>$4.6 \times 10^{-16}$</td>
<td>56.1</td>
<td>41.2</td>
<td>2.72</td>
</tr>
<tr>
<td>B2-2</td>
<td>1.0</td>
<td>$4.6 \times 10^{-16}$</td>
<td>61.6</td>
<td>35.7</td>
<td>2.64</td>
</tr>
<tr>
<td>B2-3</td>
<td>1.0</td>
<td>$4.6 \times 10^{-16}$</td>
<td>64.4</td>
<td>32.8</td>
<td>2.78</td>
</tr>
<tr>
<td>B3-1</td>
<td>1.0</td>
<td>$4.6 \times 10^{-16}$</td>
<td>52.7</td>
<td>45.2</td>
<td>2.08</td>
</tr>
<tr>
<td>B3-2</td>
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<td>56.4</td>
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Table A-2. Experimental conditions and results of boron distribution experiments with CO–N₂ gas mixtures at 1873 K.

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<th>Equilibrium Slag Composition</th>
<th>Silicon Comp.</th>
<th>Partition Ratio, Lᵣ</th>
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<td>Pₜ₀₂</td>
<td>Pₜ₀₁</td>
<td>SiO₂ [mass %]</td>
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<td>0.90</td>
<td>3.7×10⁻⁶</td>
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<tr>
<td>N1-3</td>
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<td>0.90</td>
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<td>55.9</td>
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<td>0.90</td>
<td>3.7×10⁻⁶</td>
<td>61.7</td>
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<tr>
<td>N2-1</td>
<td>0.20</td>
<td>0.80</td>
<td>2.9×10⁻⁶</td>
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<tr>
<td>N2-2</td>
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<td>0.80</td>
<td>2.9×10⁻⁶</td>
<td>49.5</td>
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<tr>
<td>N2-3</td>
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<td>0.80</td>
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</tr>
<tr>
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<td>0.60</td>
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<td>54.5</td>
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<tr>
<td>N3-3</td>
<td>0.40</td>
<td>0.60</td>
<td>1.6×10⁻⁶</td>
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<td>N4-4</td>
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<td>0.60</td>
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Table A-3. Experimental conditions and results of impeller mixing tests.

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<th>Time [s]</th>
<th>Boron doping</th>
<th>Slag</th>
<th>Metal phase [B], ppm</th>
<th>[Ca], %</th>
<th>Slag phase % Si metal</th>
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<td>A</td>
<td>---</td>
<td>*</td>
<td>*</td>
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<tr>
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<td>150</td>
<td>(H₃BO₃)</td>
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<tr>
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<td>(H₃BO₃)</td>
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<tr>
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<td>300</td>
<td>(H₃BO₃)</td>
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*Emulsion formation precluded a clean slag or metal sample.
Table A-4. Experimental matrix and results for sessile drop experiments.

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<td>260 s, complete</td>
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<tr>
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<td>Rapid (6.6 K/s)</td>
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<td>405 s, complete</td>
</tr>
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<td>No wetting</td>
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