FORMATION KINETICS OF REACTION BONDED 
SILICON CARBIDE BASED MATERIALS 

by 

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Abstract:

Reaction Bonded Silicon Carbide (RBSC) is produced by infiltrating porous carbon bodies with molten silicon. Alloying the silicon melt with a refractory metal has been shown to result in SiC-metal silicide bodies free of residual silicon. Both bulk samples and surface coatings have been produced using alloyed-melts. The relationship between the microscopic reaction kinetics and fluid flow in the C(s)-Si(l) system has been investigated, including the effect of alloying the silicon melt with molybdenum, boron, and aluminium.

Models describing the flow of reactive fluids into porous media have been developed based on Darcy's Law. The finite infiltration velocity and volume expansive nature of the melt:preform reaction result in a permeability that varies both in time and space. Numerical and analytical solutions describing the system permeability have been developed. These solutions have been used to calculate infiltration rates and to qualitatively predict the effect of various processing parameters on the resultant material.

Micro-porous carbon preforms have been infiltrated, and the dependence of the infiltrated length on the preform pore structure and melt temperature predicted by the models has been verified. The microstructure of the reacted body was found to scale with the microstructure of the preform. The precipitation of the silicide was seen to inhibit fluid flow, and, to a lesser degree, the extent of reaction. Stresses induced by gradients in the distribution of the silicide, residual porosity, and heat generated by reaction were proposed to create flaws in the reacted materials. Reduction of these gradients, and the resultant flaws, should be achieved by increasing the infiltration velocity through increasing the pore size, decreasing the reaction rate, or applying an external infiltration pressure.

The kinetics of the silicon:carbon reaction have also been investigated. Carbon fibers were reacted with silicon melts for times up to ten minutes, and temperatures between 1700 K and 1800 K. This reaction was seen to proceed through two regimes: an initial one of little observed reaction, and a second regime of rapid SiC growth from solution. A SiC reaction layer was seen to form during the initial regime, and growth from solution was suppressed. This suppression was proposed to be due to a lack of defect sites on the SiC layer, which are necessary to sustain SiC growth from solution. The second regime of this reaction was seen to be dominated by the solution and reprecipitation of the sub-micron SiC reaction product into coarser SiC crystals. The rate of the process was limited by carbon diffusion through the melt. At longer times, the SiC physically inhibited further reaction, leading to a decrease in the observed rates. Small additions of molybdenum and boron were found to have little effect on the observed rates, while aluminum additions were seen to reduce it through creation of an aluminum rich layer, presumably Al₄C₃, at the melt:carbon interface.

The implications of this work on the processing of RBSC based materials are as follows: The infiltration temperature should be minimized in order to reduce the reaction rate, thereby increasing the infiltrated length and reducing the resultant flaw population. The pore structure of the preform has to be optimized for the particular application desired,
as the scale of the resultant microstructure, the uniformity of the second phase distribution, 
the extent of reaction through the pore walls, and the macroscopic dimension of the
resultant body all depend on the pore structure of the preform.

Thesis Supervisor: Professor Yet-Ming Chiang
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# Table of Contents

Title Page 1  
Abstract 2  
Table of Contents 4  
Table of Figures 7  
Table of Tables 11  
Acknowledgements 12  

## Chapter 1 Introduction 13  
1.0 Introduction 13  
1.1 Processing Background 13  
1.2 Alloyed-Melt Infiltration 16  
Figures - Chapter 1 18  

## Chapter 2 Reactive-Infiltration Processing 19  
2.0 Introduction 19  
2.1 Model of Flow of Reactive Fluids 20  
2.1.1 Non-Reactive Fluid Flow 20  
2.1.2 Numerical Solution to the Flow of Reactive Fluids 23  
2.1.3 Analytical Solution to the Flow of Reactive Fluids 26  
2.1.4 Reducing Residual Porosity 27  
2.2 Reactive-Infiltration Experiments 28  
2.3 Results 31  
2.3.1 Particulate Preforms 31  
2.3.2 Micro-Porous Preforms 32  
2.4 Discussion 37  
2.4.1 Particulate Preform Infiltrations 37  
2.4.2 Micro-Porous Preforms 38  
2.4.3 Defects in Reacted Materials 45  
2.5 Conclusions 46  
2.6 Implications 47  
Figures - Chapter 2 49  

## Chapter 3 Carbon-Silicon Reaction Kinetics 73  
3.0 Introduction 73  
3.1 Literature Review 73
3.1.1 Si and C Self-Diffusion in β-SiC 73
3.1.2 C$_{(s)}$ and Si$_{(l)}$ Reaction Kinetics 73
3.2 Theory of SiC Growth 77
  3.2.1 Heterogeneous Growth 77
  3.2.2 Solution Growth 78
    3.2.2.1 Normal Growth 78
    3.2.2.2 Surface Nucleated Solution Growth 80
    3.2.2.3 Defect Site Growth 81
  3.2.3 Summary 82
3.3 Reaction Experiments 82
3.4 Results 86
  3.4.1 Extent of Reaction versus Time 86
  3.4.2 Microstructures of Reacted Fibers 87
3.5 Discussion 90
  3.5.1 Mechanism of the Initial Regime 90
  3.5.2 Mechanism of the Rapid Reaction Regime 92
    3.5.2.1 Evolution of SiC 92
    3.5.2.2 Absence of SiC Coarsening 94
  3.5.3 Final Reaction Regime 96
  3.5.4 Non-Graphitic Carbons 96
  3.5.5 Summary of the Growth Mechanism 97
3.5.6 Rate Limiting Process in the Rapid Reaction Regime 98
  3.5.6.1 Rate of Diffusion Controlled Growth 101
  3.5.6.2 Rate of Surface Reaction Controlled Growth 103
  3.5.6.3 Summary-Rate Limiting Process 104
3.5.7 Dopant Effects 104
3.6 Conclusions: Carbon-Silicon Reaction Kinetics 106

Figures - Chapter 3 108

Chapter 4 Conclusions 125
  4.1 Summary of Thesis Results 125
  4.2 Application to Other Alloying Systems 127
  4.3 Future Work 128

Appendix 1 Increase in Deposition Rate at Liquidus 131

Appendix 2 Coarsening Rate Estimation 133
Appendix 3  Dislocations in SiC  134
Appendix 4  Temperature of Reaction  136
Appendix 5  Reynolds Number Estimation  137
References  138
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>Schematic melt trajectories during alloyed-melt reactive-infiltration of a carbonaceous preform with a silicon-molybdenum melt.</td>
<td>18</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>Flow chart for the numerical solution of reactive-infiltration.</td>
<td>49</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Numerical Solution to reactive-infiltration as a function of time for SiC:C preforms.</td>
<td>50</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Analytical Solution to reactive-infiltration as a function of time for SiC:C preforms.</td>
<td>51</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>Calculated porosity gradients in a preform of half-thickness 0.3L, 0.5L, 0.7L, and 0.9L, with initial porosity P=0.3, using the analytical solution to system permeability.</td>
<td>52</td>
</tr>
<tr>
<td>Figure 2.5</td>
<td>Microstructures of microporous glassy carbon preforms supplied by D. R. Behrendt, NASA Lewis. Note the uniformity across each sample, and the variation between the two.</td>
<td>53</td>
</tr>
<tr>
<td>Figure 2.6</td>
<td>A SiC:C preform infiltrated with a single phase melt. Scale is in centimeters.</td>
<td>54</td>
</tr>
<tr>
<td>Figure 2.7</td>
<td>Microstructure of reactively infiltrated sample. The light phase is a molybdenum silicide, and the dark phase is silicon carbide.</td>
<td>54</td>
</tr>
<tr>
<td>Figure 2.8</td>
<td>X-ray spectra of a fully infiltrated SiC:C preform showing α and β SiC, MoSi₂, Mo₅Si₃, but no detectable free silicon. An unidentified phase is present, and may be a ternary Mo-Si-C compound.</td>
<td>55</td>
</tr>
<tr>
<td>Figure 2.9</td>
<td>A SiC:C preform typical of those infiltrated at or below the melt liquidus.</td>
<td>56</td>
</tr>
<tr>
<td>Figure 2.10</td>
<td>SEM micrograph of the coating seen in Figure 2.9</td>
<td>56</td>
</tr>
<tr>
<td>Figure 2.11</td>
<td>XRD pattern of a ground portion of the coating showing no detectable free silicon.</td>
<td>57</td>
</tr>
<tr>
<td>Figure 2.12</td>
<td>Annular dark field STEM micrograph of a MoSi₂ precipitate showing a dihedral angle with the SiC grain boundary of approximately 120°.</td>
<td>58</td>
</tr>
<tr>
<td>Figure 2.13</td>
<td>Si-Mo phase diagram showing melt compositions and infiltration temperatures used in experiments M16 - M33.</td>
<td>59</td>
</tr>
<tr>
<td>Figure 2.14</td>
<td>Infiltration experiment M20, infiltrated at 1703 K with a 3.2%Mo-Si melt. Solidified residual melt can be seen at the bottom.</td>
<td>60</td>
</tr>
</tbody>
</table>
of the preform. Scale is in centimeters.

Figure 2.15 Infiltration experiment M26, infiltrated at 1838 K with a 3.2% Mo-Si melt. Note the uniform but limited infiltration distance. Scale is in centimeters.

Figure 2.16 Relative composition of samples M24, M26, M27, M29, M30, and M31 plotted against distance from the edge of the sample.

Figure 2.17 Optical micrograph of the infiltrated portion of M26, with normalized compositional data plotted at the same scale.

Figure 2.18 Higher magnification optical micrograph of the initial, uniform region of M26 (Figure 2.17). The phases are: Si / MoSi₂ (lightest), SiC, and residual carbon (darkest).

Figure 2.19 Mo:Si ratio plotted against distance into the sample for infiltration experiment M24.

Figure 2.20 Infiltration fronts of samples M30 (0% Mo), M26 (3.2% Mo), and M29 (6.4% Mo). These experiments were done at 1838 K, with infiltration occurring from right to left.

Figure 2.21 The Mo:Si ratio for samples M26 (3.2% Mo), and M29 (6.4% Mo). Note the sharp increase at the infiltration front of the Mo rich sample.

Figure 2.22 The standard deviation of the average Mo:Si ratio of samples M20 and M17, as a function of magnification. M20 had an initial pore diameter of 2.6 µm, while that of M17 was 1 µm.

Figure 2.23 A scanning electron micrograph of a defect from a sample infiltrated at 1883 K (melt-filled vein).

Figure 2.24 Ultimate Infiltrated Length L plotted against the Initial Permeability of samples infiltrated at 1703 K with Si-3.2% Mo melts.

Figure 2.25 Standard deviation of the average Mo/Si ratio obtained with EDX on the SEM plotted against the linear dimension of the scanned area. The effective pore diameters of the preforms used are shown for reference.

Figure 3.1 Si and C Diffusion Coefficients in β-SiC (from Hon and Davis, Refr. 1 and 2).

Figure 3.2 X-ray diffraction spectra of P55 and AS4 fibers. The P55 spectra is indicative of graphite, while that of the AS4 indicates a glassy carbon.

Figure 3.3 Extent of Reaction plotted against Time of Reaction for P55
fibers in silicon melts, for varied reaction temperatures (1703 K, 1733 K, 1763 K, 1803 K).

Figure 3.4 Extent of Reaction plotted against Time of Reaction for P55 fibers reacted at 1803 K with a pure silicon melt, a Si-3.2%Mo melt, and a Si-3.2% B melt.

Figure 3.5 Extent of Reaction plotted against Time of Reaction for P55 fibers reacted at 1703 K and 1803 K with pure silicon melts.

Figure 3.6 Extent of Reaction plotted against Time of Reaction for AS4 fibers reacted at 1703 K and 1803 K with pure silicon melts.

Figure 3.7 P55 fiber surface prior to reaction. The striations are a result of the drawing process used in fiber production.

Figure 3.8 Cross-section of P55 fibers in silicon after reaction for 40 seconds at 1703 K with a silicon melt. Little reaction product or erosion of the fiber is visible.

Figure 3.9 SiC reaction layer seen on P55 fibers after reaction for 5 seconds at 1703 K. Melt removed by acid etch.

Figure 3.10 SiC reaction layer seen on P55 fibers after reaction for 60 seconds at 1703 K. Melt removed by acid etch.

Figure 3.11 Cross-section of P55 fiber coated with Betarundum SiC powder prior to reaction with a silicon melt for 50 seconds at 1703 K. Note the decrease in the fiber diameter, indicating reaction occurred.

Figure 3.12 Cross-section of P55 fiber typical of second stage of reaction (Rapid Reaction Regime). Notable features include SiC crystals forming in the silicon melt, and an eroding carbon fiber.

Figure 3.13 SEM micrograph of a P55 fiber during the second stage of reaction (silicon melt removed by acid etchant).

Figure 3.14 TEM bright field micrograph of particles seen in Figure 3.13. Selected Area Diffraction identified them to be fine grained β-SiC.

Figure 3.15 SEM micrograph of SiC crystal growing in the silicon melt from the original fiber surface. Melt removed by acid etch.

Figure 3.16 TEM bright field micrograph of SiC crystal similar to that in Figure 3.15, showing both planar (P) and line (l) defects, as indicated by the arrows.

Figure 3.17 Cross-section of P55 fibers at later stages of reaction (575 seconds in a silicon melt at 1703 K).

Figure 3.18 TEM of SiC particles found in samples at longer time of
reaction. Note the similarity between these particles and those found in samples reacted for much shorter times (Figure 3.14).

Figure 3.19 Cross-section of AS4 fibers after reaction in silicon melts for a) 40 seconds, b) 145 seconds, and c) 375 seconds, all at 1703 K.

Figure 3.20 Cross-section of a flat plate of Siggradur G glassy carbon exposed to a silicon melt for 40 seconds at 1703 K.

Figure 3.21 Backscattered electron image of cross-section of P55 fibers reacted with a Si-3.2\% Al melt for 40 seconds at 1803 K, with the corresponding elemental Al EDX map.

Figure 3.22 SiC growing inside the original melt:fiber interface, possibly indicating coarsening of the fine SiC particles.

Figure 3.23 Linear rate from Figure 3.3 showing a linear dependence on the equilibrium carbon solubility in silicon at the respective temperatures.
**Table of Tables**

<table>
<thead>
<tr>
<th>Table 2.1</th>
<th>Preform Characterization and Infiltration Conditions</th>
<th>33</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.2</td>
<td>Infiltration Results</td>
<td>34</td>
</tr>
<tr>
<td>Table 2.3</td>
<td>Infiltration Temperature Effects</td>
<td>42</td>
</tr>
<tr>
<td>Table 2.4</td>
<td>Molybdenum Concentration Effects</td>
<td>43</td>
</tr>
</tbody>
</table>
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Chapter 1 Introduction

1.0 Introduction

Ceramic materials must have improved fracture resistance if they are to be used as high temperature structural materials. Several processes have been developed to increase their toughness, most of which involve a composite system of matrix and reinforcement. Evans\(^1\) has reviewed these processes and found that substantial increases in toughness can be achieved in the following classes of ceramic composites: fiber-reinforced systems, systems incorporating a ductile second phase, and systems based on the stress induced crystallographic transformation of included particles. Of these, only the first two are currently considered for use at high temperatures, i.e. \( T > 1800 \) K. Fiber-reinforced systems and systems containing ductile inclusions can be optimized to produce materials with high toughness at the laboratory scale; however, processing often limits the size and shape of the bodies produced. Other limitations that must be overcome before toughened ceramic materials are widely used include poor oxidation resistance, eventual degradation of the reinforcement, and the inherently anisotropic properties of composite materials. Processing considerations are fundamental, however, and must be addressed if structural ceramic materials are to be feasibly produced.

1.1 Processing Background

In the production of refractory fiber-reinforced systems with high fracture toughness, it has been found that densification of a fiber-reinforced crystalline green body is often difficult. The presence of non-shrinking inclusions in a sintering matrix have been shown to exert a tensile force on the matrix, inhibiting densification.\(^2\) This effect can be countered by the application of hydrostatic compressive stresses\(^3\), which explains the predominance of hot pressing techniques in the fabrication of fiber/whisker reinforced materials. At higher volume percent reinforcement, however, impingement of the
reinforcement phase presents the ultimate limitation to densification. Hot pressing has obvious limitations, primarily that the geometry of the part must be fairly simple, and that it is a batch operation.

Fiber reinforced ceramics have also been fabricated using fluid deposition techniques. Matrices can be deposited into fibrous preforms from both liquid and vapor precursors. Chemical vapor infiltration (CVI) techniques have been used to produce SiC:SiC composite materials with fracture toughness values greater than 25 MPa√m, as determined with notched-beam bend tests.\(^4\) The primary attribute of the CVI technique is the ability to deposit refractory crystalline matrices uniformly throughout a fibrous preform. The components of the matrix are contained in the precursor gas, which decomposes to form the matrix phase \textit{in situ}. Gas phase reaction bonding is a similar technique, in which the gas phase reacts with the porous matrix to form the desired compound. The prototypic system is reaction bonded Si\(_3\)N\(_4\) (RBSN), in which silicon is nitried \textit{in situ} to form a refractory crystalline matrix.

Infiltration of fibrous preforms with liquid precursors has also been done, notably in the production of high temperature carbon:carbon composites. This technique generally involves the decomposition of organic liquids into the matrix phase and another, usually volatile, product phase. SiC and Si\(_3\)N\(_4\) matrices have been deposited with this technique using polycarbosilanes as the liquid precursors.\(^5\)

The primary limitation of these fluid deposition techniques is the length of time required to achieve a dense matrix. In the absence of induced temperature gradients, CVI processes typically require times on the order of hundreds of hours at elevated temperatures. Recent developments at MIT have decreased the times required for complete reaction of RBSN matrices to tens of minutes.\(^6\) However, producing a fiber reinforced RBSN requires impregnating the fibrous preform with silicon, thereby creating an additional processing step. The infiltration and subsequent decomposition of liquid organic
precursors requires repeated infiltration/heating cycles, as the yield of these precursors is generally low. Additional problems arise in the removal of the other decomposition products, which are primarily gases.

While processing fiber-reinforced ceramics is difficult, the need for tough, lightweight, refractory materials for use at extreme temperatures in air has provided the impetus for their development. Alternative processing routes to this class of materials would be desirable.

Ductile inclusions have been shown to increase the fracture toughness of ceramics substantially. These inclusions can be isolated particles, continuous in one direction (metal fibers), or continuous in all directions. The latter case is found in a novel class of materials produced from the controlled oxidation of metal melts to create a porous oxide matrix. The metal wets its oxide, thereby filling the pore structure, and resulting in an isotropic ceramic:metal composite. Fibrous preforms have been used in conjunction with this technique and materials with very high fracture resistance have been developed. Systems produced by this technique include Al₂O₃/Al, AlN/Al, and ZrN/Zr. These materials have excellent room temperature properties, can be easily fabricated, and recent advances have improved their elevated temperature properties.

Reaction bonded SiC (RBSC) was developed in the 1950's as a method of densifying SiC, based on the infiltration of a porous SiC:C preform with molten silicon. The silicon and carbon react to form SiC, which bonds the "seed" SiC grains together. The reaction is volume-expansive with respect to the solid phases, resulting in potentially dense, refractory materials. Infiltration and reaction does not greatly affect the bulk dimensions of the preform, providing near-net shape, near-net dimension processing capabilities. Thus, a low temperature, ambient pressure processing route to dense Si:SiC bodies had been developed, however, the presence of residual silicon in these bodies limited their application to temperatures below ≈1600 K. Conventional RBSC may be
easily processed but has neither the toughness imparted by a ductile second phase (since silicon is brittle), nor the refractory properties of hot pressed or sintered SiC.

The limitations of RBSC, then, are primarily due to the presence of residual silicon, as it limits the ultimate use temperature and imparts little increase in toughness. Ideally, RBSC could be produced with no residual silicon (100% SiC); however, the toughness of such a body would be on the order of that of sintered or hot pressed SiC, i.e., lower than that required for many structural applications. Optimally, RBSC could be improved by replacing the residual silicon with a more ductile and refractory phase, while maintaining the processing simplicity necessary for economic production.

1.2 Alloved-Melt Infiltration

The alloyed melt approach to reaction formed SiC may remove these limitations. In this process the melt to be infiltrated is alloyed with a refractory silicide-forming metal. As the preform is infiltrated, the silicon reacts with the carbon to form SiC. This depletion of silicon increases the concentration of the alloying metal in the melt within the preform. As this enrichment process continues, the silicide phase eventually precipitates out of the melt. This process is shown schematically for the Mo-Si system\textsuperscript{11} in Figure 1.1. The Si-C reaction is exothermic, so the proposed melt trajectory increases in temperature as well as in metal concentration. Alloyed-melt reactive-infiltration, therefore, replaces the residual silicon with a residual silicide.

By proper selection of the silicide, additional benefits may be expected. MoSi\textsubscript{2} becomes increasingly ductile at temperatures above 1300 K\textsuperscript{10} and does not melt until 2280 K\textsuperscript{11}. It is oxidation resistant\textsuperscript{10} and thermodynamically stable with SiC at temperatures up to its melting point.\textsuperscript{12} Consequently, infiltrating carbonaceous preforms with silicon melts alloyed with molybdenum can result in a refractory, oxidation resistant ceramic composite material. Eventually, the infiltration of a fibrous preform with an carbon-forming
precursor, followed by alloyed-melt reactive-infiltration to form a refractory, tough material should be feasible. It should be noted that the development of such a composite will require optimizing the fiber:matrix interface, ensuring that the fibers are not degraded during infiltration, while providing the weak interfacial bond necessary for toughness increases.

This thesis examines the kinetics of the formation of alloyed-melt reaction-bonded silicon carbide. The concept is demonstrated in the next chapter, along with the results of a processing study. The third chapter investigates the kinetics of the silicon-carbon reaction, including the effect of alloying elements. Implications for improved processing of RBSC will be given in the final chapter, as well as recommendations for future work.
Figure 1.1  Schematic melt trajectory during alloyed-melt reactive-infiltration of a carbonaceous preform with a Si-Mo melt.
Chapter 2 Reactive-Infiltration Processing

2.0 Introduction

This chapter focuses on the processing of reactivity-infiltrated materials, and starts with the development of fluid flow models to describe the simultaneous infiltration and reaction of porous preforms. These models are then used to interpret the results of a series of controlled infiltration experiments, performed using highly uniform micro-porous glassy carbon preforms. The feasibility of alloyed-melt reactive-infiltration is demonstrated with two examples: a fully infiltrated bulk sample and a reactively-formed surface coating.

Micro-porous glassy carbon preforms similar to those used in this work were initially developed and infiltrated with silicon melts by E. E. Hucke.¹ Hucke and co-workers undertook an extensive program of preform development and infiltration, as well as the evaluation of mechanical properties and identification of critical flaws in the resultant RBSC.¹ The micro-porous carbons made excellent preforms, with the resultant RBSC having bend strengths as high as 1 GPa, with 600 MPa being typical¹ (commercial RBSC has strengths on the order of 200-300 MPa). Critical flaws in these materials were identified as unreacted carbon, residual silicon in large pockets and cracks, and coarsened SiC surface grains. Direction for the elimination of these flaws was given, including infiltrating at temperatures below 1450°C and optimizing the carbon preforms, i.e., the carbon particles should be no greater than 10 μm, while the average pore size should be less than 2 μm.¹

For the present study, D. R. Behrendt of NASA Lewis Research Center has provided micro-porous glassy-carbons similar to those developed by Hucke. The uniform pore structure of these materials allowed the effects of infiltration temperature and melt composition to be readily determined. These preforms also allowed investigation of the
effect of the scale of the porosity and pore morphology on the infiltrated length and molybdenum distribution.

2.1 Model of Flow of Reactive Fluids

Fluid flow in a porous medium has been successfully described using Darcy's Law when the Reynolds number is less than one. As is shown in Appendix 5, the Reynolds number in the present system is expected to be less than 0.1, validating the use of Darcy's Law in the models developed below. In general, the pore structure of a porous medium undergoing reactive-infiltration will change; and this change in pore structure is reflected in a change in the preform permeability. The models assume the reaction produces no heat, nor any change in system volume. Incorporation of these effects will be discussed in the final chapter of this thesis. Non-reactive infiltration is first discussed as an introduction to fluid flow.

2.1.1 Non-reactive Fluid Flow

Darcy's Law of flow through isotropic porous media is given as: \[ Q = -(K/\eta)V_P \] (2.1)
in which Q is the volumetric flow rate vector of the fluid through the porous medium, and \( V_P \) is the pressure gradient across this fluid. The solid permeability tensor, K, and the fluid viscosity, \( \eta \), describe the system's resistance to fluid flow. A porous medium with an isotropic pore structure, such as the preforms used in present work, will have an isotropic permeability tensor.

Darcy's Law for one dimensional flow (\( V_P = \Delta P/\eta \)) is:

\[ Q = -K\Delta P/\eta l \] (2.2)

where \( \Delta P \) is the pressure drop across the fluid, and l is the bulk dimension of the porous medium. Equation 2.2 describes the macroscopic flow of fluid through a porous medium.
viewed from the laboratory reference frame. However, the local volumetric flow rate within the pore structure is greater than this macroscopic flow rate, and can be obtained by amending Darcy's Law with the Dupuit-Forchheimer relation.\textsuperscript{2} This relation states that the cross-sectional area available for fluid flow inside a porous body is the cross-sectional area of the pore space ($P_o$), not that of the bulk. Therefore, the bulk flow rate, $Q$, should be increased by a factor of $1/P_o$, where $P_o$ is the initial porosity of the body. The volumetric flow rate within the pore structure, $Q'$, (cm$^3$/cm$^2$/sec) is thus given by:

$$Q' = Q/P_o = -K\Delta P / \eta P_o$$  \hspace{1cm} (2.3)

Most expressions of $K$ attempt to relate the permeability of a porous body to its microstructure, which is often characterized by the porosity, pore surface area (or pore dimension), and the size of the solid phase. The majority of these expressions, however, also incorporate empirical corrections, i.e. tortuosity, in their descriptions.\textsuperscript{2} Kozeny\textsuperscript{3} derived an expression that is relatively free of these empirical corrections, and is instead dependent on the specific surface area of the porosity ($S$), the amount of porosity ($P$), and a constant determined by pore geometry ($c$)\textsuperscript{3}:

$$K = cP^3/S^2$$  \hspace{1cm} (2.4)

Based on theoretical considerations, Kozeny found that $c$ varied between $1/2$ to $2/3$ for pores of either circular or rectangular cross-section.\textsuperscript{3} The Kozeny expression describes capillary flow if the constant $c$ is set equal to $1/2$, and the volume to surface area ratio $P/S$ to $d/4$, where $d$ is the effective pore diameter of the porous medium.

The permeability and pore structure (pore volume and surface area) of the particulate preforms developed in the initial stage of this work were measured. The permeability was determined to be $5.8 \times 10^{-11}$ cm$^2$ using helium gas flow measurements, the pore volume was $0.48$ cm$^3$/cm$^3$, and the specific pore surface area was $3.7 \times 10^4$ cm$^2$/cm$^3$, both measured with mercury intrusion porosimetry. This results in $P^3/S^2 = 8.1 \times 10^{-11}$, or $c = K/ (P^3/S^2) = 0.7$, which is in good agreement with Kozeny's original value of $2/3$. 

21
Thus, Kozeny’s expression for permeability appears to describe the materials used in this study.

The pressure gradient in the present system is induced by capillary wetting, as may be expected in general for reactively-infiltrating systems.\textsuperscript{4} Scherer\textsuperscript{5} has expressed the capillary pressure in terms of the pore structure, the surface energy of the fluid ($\gamma$), and wetting angle ($\theta$) as:

\[
\Delta P = -(S/P)\gamma \cos \theta
\]  

(2.5)

Combining equations 2.3, 2.4, and 2.5 results in an expression for fluid flow in a porous material of constant permeability with infiltration driven by capillary pressure:

\[
Q' = \frac{((cP^3/S^2)(S/P)\gamma \cos \theta)/(P\eta l)}{(\gamma \cos \theta/\eta)(cP/S)(l)^{-1}} \]

(2.6a)

(2.6b)

Thus, the volumetric flow rate of fluid inside a porous material ($Q'$) is related to the physical properties and interfacial energies of the fluid ($\gamma$, $\theta$, $\eta$), the characteristics of the pore structure ($c$, $P$, $S$), and the infiltration distance ($l$). The volumetric flow rate ($Q'$) is the velocity ($\partial l/\partial t$) of the infiltration front within the pore structure. Integration of equation 2.6b, therefore, shows that the infiltration distance inside the porous medium varies with the square root of time:

\[
Q' = \frac{\partial l}{\partial t} = -K\Delta P/\eta l P_o
= (\gamma \cos \theta/\eta)(cP/S)(l)^{-1}
\]

(2.6b)

\[
\int \partial l = (\gamma \cos \theta/\eta)(cP/S) \int \partial t
\]

(2.7)

\[
l^2 = (2\gamma \cos \theta/\eta)(cP/S)(t)
\]

(2.8)

This result applies to capillary driven non-reactive fluid infiltration of porous materials of constant permeability.

The separation of the length and time dependences, and subsequent integration performed in going from equations 2.6 to 2.8 entails the implicit assumption that none of the terms in right side of equation 2.7 vary in time or space. This is clearly not an
appropriate description of reactive-infiltration. A reaction between the fluid and the solid will affect each parameter in equation 2.7 to some extent. A first-order correction for these effects would allow for a change in the pore structure of the infiltrated body. The \( \text{C}_s + \text{Si}_l \rightarrow \text{SiC}_s \) reaction is volume expansive with respect to the solid phase, resulting in a decrease in the porosity. Furthermore, the time of reaction is a spatially varying entity, making the porosity a complex function of time and space for which an analytical solution may not exist. Numerical techniques can then be employed, as described in the next section.

2.1.2 Numerical Solution to the Flow of Reactive Fluids

Reducing the reactive infiltration problem to one of discrete infiltration and reaction steps allows these dependences to be separated, and the permeability to be determined numerically. Such an approach requires that the separate dependences of the system permeability on length and time be known.

The dependence of the permeability \( K \) on distance \( l \) may be determined by considering a closed system of \( n \) slabs of porous media, each with a different thickness \( (l_i) \) and permeability \( (K_i) \). The flow through each slab obeys Darcy's Law, and the volumetric flow rate \( Q \) is the same through any cross section of the system. The pressure drop across any slab \( i \) may be expressed as:

\[
Q = Q_i = K_i \Delta P_i / \eta l_i \tag{2.2a}
\]

or,

\[
\Delta P_i = -Q \eta (l_i / K_i) \tag{2.9}
\]

The total pressure drop across the system \( (\Delta P) \) is the sum of the incremental \( \Delta P_i \)'s:

\[
\Delta P = \sum \Delta P_i = -Q \eta \sum (l_i / K_i) \tag{2.10}
\]

or,

\[
Q = (-\Delta P / \eta) (\sum (l_i / K_i))^{-1} = (-\Delta P / \eta) (K_{\text{eff}} / l) \tag{2.11}
\]
Thus, the system permeability \( K_{\text{eff}} \) is related to the individual permeabilities \( K_i \) in the same way that the system resistance is related to a parallel array of resistors; that is, it is the inverse of the sum of the length weighted inverse permeabilities.

The change in the permeability with time is dependent on the fluid:solid reaction mechanism and rate. The Si-C reaction proceeds through different mechanistic regimes (see Chapter 3), but the porosity is expected to change fastest during the solution-reprecipitation regime. The observed rate during this regime is linear in time, resulting in a pore volume that will also decrease linearly with time. The measured permeability of the particulate preforms is consistent with that predicted by Kozeny (Eq. 2.4) for a model pore geometry of rectangular slits \( \mathfrak{c}=2/3 \). Reaction in such a pore volume by a solution-reprecipitation mechanism is likely to result in ever narrower slits, thereby decreasing the volume without greatly affecting the pore surface area. Assuming that the pore surface area remains constant and that the pore volume decreases linearly in time, \( K(t) \) may be expressed for the Kozeny permeability as:

\[
K(t) = \left( \frac{c}{S^2} \right) P(t)^3 = \left( \frac{c}{S^2} \right) (P_0 - kt)^3
\] (2.12)

where \( P_0 \) is the initial porosity of the body, and \( k \) is the reaction rate constant. The assumption of a constant pore surface area during reaction will be less appropriate for cylindrical pore morphologies and as the reaction goes to completion for any morphology.

However, a qualitative understanding of the kinetics of reactive-infiltration, including identification of the controlling physical parameters, can be obtained with the present model.

Using the separate \( K(t) \) and \( K(l) \) relations, the infiltrated length can be obtained through numerical solution of Eq. 2.11. The approach used is explicit, i.e., the unknown length \( (\Delta l_{i+1}) \) is determined from the known \( (\Sigma \Delta l_i) \), rather than an iterative process as could be used in integrating a complex but known \( K(l,t) \) expression. Discrete infiltration and reaction steps are assumed, all of equivalent time interval \( \Delta t \). Conceptually, the
preform is infiltrated by the fluid for a time $\Delta t$ with no change in permeability. Reaction is then allowed to occur, changing the local permeability by an amount $K(t+\Delta t)$. The system permeability is re-calculated, infiltration is again allowed for time $\Delta t$, and the process repeated. The error in this type of explicit calculation has been shown to be proportional to the step size $\Delta t$. The flow-chart for the computer code written to solve this system of equations is given in Figure 2.1.

The infiltrated length vs. time curve generated by such a solution is shown in Figure 2.2. The input for this calculation was either measured using the particulate preforms ($K$) or obtained from the literature (refr. 7 - 10). Five hundred time steps were used in this simulation.

As can be seen in Figure 2.2, at short times, infiltration is predicted to occur much faster than reaction, with half the ultimate length being infiltrated in approximately one fifteenth of the available time. Furthermore, the distances predicted are on the order of centimeters, which is in agreement with the experimental observation of complete infiltration through the 0.5 cm radius of these preforms.

The shape of the infiltrated length vs. time curve is dependent only on $K(t)$, since the functional dependence of infiltrated length on time will be the same for a given $K(t)$. Thus, the relative rates seen here are specific to $K(t) = (c/S^2)(P_0 - kt)^3$. The time dependence of the infiltration length inferred from these results appears to be a power law relation.

Thus, with a numerical approach an acceptable solution to the reactive infiltration problem can be obtained for any specified form of $K(t)$. An analytical solution of the reactive infiltration problem would provide more insight into the physical processes involved, however such a solution would require an explicit expression for the permeability as a function of length and time, and that the integral with respect to time of this expression

25
be known. One such expression follows from the entry pore argument, which will be discussed in the next section.

2.1.3 Analytical Solution to the Flow of Reactive Fluids

It has been proposed that the permeability of a body is accurately represented by the lowest local permeability in the body (the entry pore argument).\(^1\) This approximation to \(K(l,t)\) sets the permeability of a reactively-infiltrated body equal to that at its surface, removing the spatial dependence of the time of reaction. An analytic expression for the reactively-infiltrated length can then be obtained from Darcy's Law (Equation 2.6a), combined with the expression for the time dependence of the permeability (Equation 2.12):

\[
Q' = \frac{dl}{dt} = \frac{[K(t)(S/P_o)\gamma \cos \theta]}{(P_o \eta l)} \\
K(t) = (c/S^2)P(t)^3 = (c/S^2)(P_o - kt)^3
\]

(2.6a)

(2.12)

multiplying by 1 and integrating yields:

\[
l^2 = [c\gamma \cos \theta/(2SP_o^2 \eta k)](P_o^4 - (P_o - kt)^4)
\]

(2.13)

The porosity in the capillary pressure term is not a function of time, as it refers to the porosity at the infiltration front, which is constant and equal to \(P_o\). Equation 2.13 expresses the infiltrated length \(l\) solely in terms of known constants and the time of infiltration, \(t\). This expression has been plotted using the same data used in the numerical solution, and can be seen in Figure 2.3. As expected, this lower limit on the system permeability predicts shorter infiltrated lengths than the more detailed numerical solution. The initial rate of infiltration is again seen to be much faster than the rate of reaction.

The total time of reaction \(T\) is the time required to close off the porosity \(P_o\) at the surface (\(T \equiv P_o/k\)). Defining a dimensionless time of reaction \(\tau\) as \(\tau \equiv t/T\) allows Equation 2.13 to be rewritten as:

\[
l^2 = c\gamma P_o^2 \cos \theta/(2Snk)[1 - (1 - \tau)^4]
\]

(2.14)
The ultimate infiltrated length \( L \) is the length infiltrated before reaction closes the porosity at the surface of the preform, preventing further fluid flow into the body. \( L \) may be obtained by setting \( t = T \) (\( \tau = 1 \)):

\[
L^2 = c \gamma P_0^2 \cos \theta / (2S \eta k)
\]  
(2.15)

Thus, \( L \) is dependent on the pore structure (\( P_o \) and \( S \)), the fluid constants (\( \gamma, \theta, \) and \( \eta \)), and the reaction rate (\( k \)). Maximizing \( L \), then, can be achieved through control of the pore structure (increasing \( P_o \) and decreasing \( S \)) and the temperature (decreasing \( k \)). The relation between the infiltrated length (\( l \)), the ultimate infiltratable length (\( L \)), and the time dependence of the infiltration is then:

\[
l^2 = L^2 [1 - (1 - \tau)^4]
\]  
(2.16)

Equation 2.16 shows that the functional dependence of infiltrated length on infiltration time is a power law, which is determined solely by the form of \( K(t) \).

Both the shape of the infiltration curves, and the predicted infiltrated lengths of the analytical expression (Figure 2.3) and the numerical calculation (Figure 2.2) are very similar (within 15%). Given the error that arises from the assumptions of isothermal reaction, and a constant volume system, the simplified analytical expression provides a reasonable description of the reactive-infiltration process.

2.1.4 Reducing Residual Porosity

While the \( C(s) + Si(l) \rightarrow SiC(s) \) reaction is volume expansive with respect to the solid phase, it is volume contractive overall. Once reaction closes the pore structure at the surface of the sample, therefore, porosity is expected to form in the interior. The amount of porosity will decrease with increasing extent of reaction, which varies across the sample due to finite infiltration velocities. The infiltration curves shown in Figures 2.2 and 2.3 show that the velocity decreases with increasing infiltrated length, indicating that the
gradient in time of reaction, and therefore, porosity will increase with increasing sample thickness.

Figure 2.4 shows calculated porosity gradients for preforms of half-thickness 0.3L, 0.5L, 0.7L, and 0.9L immediately after the closure of surface porosity (reaction choking). These curves are plotted as porosity vs. relative length, where relative length = 1 identifies the center of the preform. The curves shown in Figure 2.4 were calculated assuming full reaction of the melt left in the pores when reaction choking closes the surface porosity. Using typical values for the micro-porous preforms, the initial porosity, $P_o$, is 0.30, and the preform bulk density, $\rho_{\text{bulk}}$, is 0.96 gm/cm$^3$. As can be seen, reducing the half thickness of the preform to 0.5L results in residual porosity of less than 7% of $P_o$ (2% absolute porosity in the present example). Similar gradients are also expected in the distribution of the silicide phase, as that is also a product of this reaction.

As will be discussed in section 2.4.3, most of the flaws in these materials are thought to be caused by gradients in one or more of these reaction products. Thus, minimizing these flaws can be accomplished by decreasing the time required to infiltrate the sample. This can be achieved by decreasing the thickness of the preform relative to the L of that preform, decreasing the reaction rate, or by applying additional infiltration pressure to the melt.

2.2 Reactive-Infiltration Experiments

A series of controlled infiltrations was performed to experimentally investigate the kinetics of reactive-infiltration. The effect of the molybdenum concentration, its distribution in the reacted body, and qualitative verification of the model were sought.

Bulk infiltration experiments were carried out with two different types of preforms. Particulate preforms of pressed synthetic graphite and SiC powders were developed, and
micro-porous glassy carbon preforms similar to those used by Hucke\textsuperscript{1} were obtained from D. R. Behrendt of the NASA Lewis Research Center.

The particulate preforms were produced from commercially available synthetic graphite [Desulco 9039, Superior Graphite Co.] and \( \alpha \)-SiC [39 Crystolon, Norton Co.] powders. A 1:1 volume ratio of the powders was dispersed in an aqueous solution (NH\(_4\)OH-H\(_2\)O) of pH=10. This slurry was approximately 2% solids by volume, allowing uniform mixing of the two powders with a mechanical stirring apparatus. The liquid content was reduced to approximately 30% by volume through evaporation. The resultant mixture was uniaxially pressed at 5000 psi into 1/2 inch diameter preforms.

The micro-porous glassy carbon preforms were produced at NASA Lewis, after the process developed by Hucke.\textsuperscript{1} Briefly, the process involves mixing the resin with a liquid pore former (triethylene glycol or 2-hydroxy ethyl ether), catalyzing the polymerization with an organic acid, with continued polymerization occurring during a low temperature curing cycle (65°C to 90°C). The pore former and resin separate during the curing cycle, and the pore former evaporates. Pyrolysis of the polymerized resin yields a glassy carbon material with the dimensions of the polymerized body. A dense surface layer forms when resin monomers are deposited on the surface by the evaporating pore former, are polymerized, and subsequently pyrolyzed. The pore volume and size can be controlled through adjusting the amount of pore former added and by controlling the rate of the polymerization of the resin. Solid carbon particulate can also be incorporated into the resins. Typical microstructures are shown in Figure 2.5. Note the uniformity of the solid dimension and pore size within each preform, and the variation in the carbon morphology between the two. These preforms were cast as cylindrical rods approximately 1.3 cm in diameter and 4 cm in length.

The glassy carbon preforms were lightly sand-blasted to remove the dense surface layer. Mercury Intrusion Porosimetry was used to obtain the pore size distribution and
total pore volume of both the SiC:C and glassy carbon preforms. Selected glassy carbon
preforms also underwent nitrogen adsorption measurements to determine pore surface area
using the technique developed by Brunauer, Emmett, and Teller (BET).

The desired mole fraction metal in the melt may be determined from the carbon
density and the amount of porosity in the preform, since the silicide is expected to fill the
excess porosity, i.e. that which would be present after full reaction of the carbon to form
SiC. An expression for the metal concentration ($C^M$ in mole percent) is given below in
terms of the bulk carbon density of the preform ($B$), the volume fraction of any non-
reactive phase ($V_{NR}$), the density of carbon in SiC ($\rho_{C^1}=0.961$ gm/cm$^3$), the molar volume
($V_{MS}$) of the silicide $M_ySi_x$, and the molecular weight of carbon ($MW_c=12$).

$$C^M = \frac{y(1-V_{NR}-B/\rho_{C^1})}{(x+y)(1-V_{NR}-B/\rho_{C^1})+(BV_{MS}/MW_c)} \quad (2.17)$$

The above relationship assumes a dense body of SiC and a metal silicide $M_ySi_x$, while
allowing for the presence of a non-reactive phase.

The desired melt compositions were calculated using equation 2.19 and were
formulated from commercially available silicon and molybdenum disilicide powders [Alfa
Products Division of Johnson Matthey Co.]. The powders were placed in a BN crucible,
which was covered with a flexible graphite [Grafoil, Union Carbide Corp.] rupture
membrane to minimize vapor transport prior to infiltration. The preform was positioned 2
to 3 inches above the crucible, both being in the hot zone of a graphite resistance heated hot
press [Astro Industries model HP20]. The system was heated under vacuum and back-
filled with He at 1673 K. The temperature was measured using an optical pyrometer
[Leeds and Northrup model 8622-C] calibrated by observing the change in reflectance of
silicon upon solidification, resulting in an estimated accuracy of $\pm 5$ K. The alloyed melts
were taken through a homogenization step consisting of a one hour soak at temperatures 75
K to 100 K above the infiltration temperature. These melts were then cooled and held at the
infiltration temperature for 15 minutes, allowing the temperature in both the melt and preform to re-equilibrate prior to infiltration. The non-alloyed silicon melts did not undergo a homogenization step, but instead were taken directly to the infiltration temperature and held for approximately 30 minutes. (Non-alloyed infiltrations done close to the silicon melting point, 1685 K, underwent a one hour soak at 1723 K, to ensure a liquid melt.) Infiltration was initiated by raising the Grafoil-covered crucible, rupturing the membrane with the preform, and immersing the preform in the melt. The preforms were left in contact with the melt for 30 minutes. The amount of melt in the crucible was typically 150% of that required to fully react the preform.

Cooled, reacted samples were sliced axially and sequentially polished, ending with 1 μm diamond paste. The microstructures were examined using optical [Olympus VANOX-T] and scanning electron microscopy (SEM) [Cambridge Stereoscan 250 MK3]. Energy Dispersive X-Ray (EDX) [Tracer Northern TN-5500] analysis in the SEM was used to obtain the relative amounts of silicon and molybdenum in fully infiltrated samples. X-Ray diffraction [Rigaku RU 300 diffractometer] was used to identify the phases in bulk samples. Relative amounts of silicon, molybdenum, and carbon were obtained using wavelength dispersive X-ray spectrometry (WDS) [Tracer Northern TN-1310] in an electron microprobe [Cameca MBX]. The carbon standard used was SiC, the silicon and molybdenum standards were the pure metals. Scanning transmission electron microscopy was also performed using a Vacuum Generator HB5 system.

2.3 Results

2.3.1 Particulate Preforms

A reacted α-SiC:C preform typical of those infiltrated at temperatures above the melt liquidus is shown in Figure 2.6. A higher resolution view of the microstructure of such a sample is shown in Figure 2.7. EDX identified the bright phase in Figure 2.7 as
containing molybdenum and silicon, while the dark phase was found to contain silicon and carbon using the WDS in the electron microprobe. The x-ray spectra of a sample infiltrated with a single phase melt (8 \% Mo, 1898 K) is shown in Figure 2.8, with the arrow indicating the position of the (111) silicon peak. Phases present include $\alpha$-SiC, $\beta$-SiC, MoSi$_2$, Mo$_5$Si$_3$, and an unidentified phase.

Reactive-infiltration of a particulate preform at the liquidus temperature of the melt results in the formation of a dense surface layer, as is shown in Figure 2.9. Only one end of the preform was in contact with the melt, although the entire surface was wet and reacted. In SEM (Figure 2.10) the uniformity and density of the surface coating are more apparent. Figure 2.11 shows the X-ray diffraction pattern of a portion of this coating ground into a powder, which indicates no detectable residual silicon. The morphology of the MoSi$_2$ phase in the bulk samples was observed using the STEM, (Figure 2.12). Note that the MoSi$_2$ does not penetrate the SiC grain boundaries.

2.3.2 Micro-Porous Preforms

The results of the characterization of the micro-porous preforms using mercury porosimetry and nitrogen adsorption (BET) are shown in Table 2.1. The infiltration conditions used in each experiment are summarized in Table 2.1, and plotted on the phase diagram in Figure 2.13. The results of these experiments are summarized in Table 2.2.
<table>
<thead>
<tr>
<th>ID</th>
<th>Preform</th>
<th>$\rho_{\text{bulk}}$</th>
<th>$K$ (Kozeny)*</th>
<th>$K$ (H-P)$^\dagger$</th>
<th>$[\text{Mol}]$ (ideal)$^\ddagger$</th>
<th>Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>M16</td>
<td>1119-C</td>
<td>0.80</td>
<td>$2.8 \times 10^{-10}$</td>
<td>$1.6 \times 10^{-10}$</td>
<td>7.9 (7.9)</td>
<td>1933 K</td>
</tr>
<tr>
<td>M17</td>
<td>1119-C</td>
<td>0.80</td>
<td>$2.8 \times 10^{-10}$</td>
<td>$1.6 \times 10^{-10}$</td>
<td>3.5 (7.9)</td>
<td>1703 K</td>
</tr>
<tr>
<td>M18</td>
<td>90788</td>
<td>0.96</td>
<td>$2.2 \times 10^{-9}$</td>
<td>$1.1 \times 10^{-9}$</td>
<td>5.0 (0)</td>
<td>1753 K</td>
</tr>
<tr>
<td>M19</td>
<td>90788</td>
<td>0.96</td>
<td>$2.2 \times 10^{-9}$</td>
<td>$1.1 \times 10^{-9}$</td>
<td>0 (0)</td>
<td>1753 K</td>
</tr>
<tr>
<td>M20</td>
<td>90788</td>
<td>0.96</td>
<td>$2.2 \times 10^{-9}$</td>
<td>$1.1 \times 10^{-9}$</td>
<td>3.2 (0)</td>
<td>1703 K</td>
</tr>
<tr>
<td>M21</td>
<td>90788</td>
<td>0.96</td>
<td>$2.2 \times 10^{-9}$</td>
<td>$1.1 \times 10^{-9}$</td>
<td>0 (0)</td>
<td>1703 K</td>
</tr>
<tr>
<td>M22</td>
<td>120188</td>
<td>0.91</td>
<td>N/A</td>
<td>N/A</td>
<td>0 (2.7)</td>
<td>1703 K</td>
</tr>
<tr>
<td>M23</td>
<td>121588*</td>
<td>0.90</td>
<td>$5.2 \times 10^{-10}$</td>
<td>$5.1 \times 10^{-10}$</td>
<td>0 (3.2)</td>
<td>1703 K</td>
</tr>
<tr>
<td>M24</td>
<td>121588*</td>
<td>0.90</td>
<td>$5.2 \times 10^{-10}$</td>
<td>$5.1 \times 10^{-10}$</td>
<td>3.2 (3.2)</td>
<td>1703 K</td>
</tr>
<tr>
<td>M25</td>
<td>121588*</td>
<td>0.90</td>
<td>$5.2 \times 10^{-10}$</td>
<td>$5.1 \times 10^{-10}$</td>
<td>3.2 (3.2)</td>
<td>1773 K</td>
</tr>
<tr>
<td>M26</td>
<td>121588*</td>
<td>0.90</td>
<td>$5.2 \times 10^{-10}$</td>
<td>$5.1 \times 10^{-10}$</td>
<td>3.2 (3.2)</td>
<td>1838 K</td>
</tr>
<tr>
<td>M27</td>
<td>121588*</td>
<td>0.90</td>
<td>$5.2 \times 10^{-10}$</td>
<td>$5.1 \times 10^{-10}$</td>
<td>3.2 (3.2)</td>
<td>1883 K</td>
</tr>
<tr>
<td>M28</td>
<td>121588*</td>
<td>0.90</td>
<td>$5.2 \times 10^{-10}$</td>
<td>$5.1 \times 10^{-10}$</td>
<td>0 (3.2)</td>
<td>1883 K</td>
</tr>
<tr>
<td>M29</td>
<td>121588*</td>
<td>0.90</td>
<td>$5.2 \times 10^{-10}$</td>
<td>$5.1 \times 10^{-10}$</td>
<td>6.7 (3.2)</td>
<td>1838 K</td>
</tr>
<tr>
<td>M30</td>
<td>121588*</td>
<td>0.90</td>
<td>$5.2 \times 10^{-10}$</td>
<td>$5.1 \times 10^{-10}$</td>
<td>0 (3.2)</td>
<td>1838 K</td>
</tr>
<tr>
<td>M31</td>
<td>121588*</td>
<td>0.90</td>
<td>$5.2 \times 10^{-10}$</td>
<td>$5.1 \times 10^{-10}$</td>
<td>3.2 (3.2)</td>
<td>1773 K</td>
</tr>
<tr>
<td>M32</td>
<td>M-9*</td>
<td>0.90</td>
<td>$1.9 \times 10^{-10}$</td>
<td>$1.3 \times 10^{-10}$</td>
<td>3.2 (3.2)</td>
<td>1703 K</td>
</tr>
<tr>
<td>M33</td>
<td>M-5*</td>
<td>0.90</td>
<td>$1.9 \times 10^{-9}$</td>
<td>$3.7 \times 10^{-10}$</td>
<td>3.2 (3.2)</td>
<td>1703 K</td>
</tr>
</tbody>
</table>

# density is given in gm/cm³

*Kozeny permeability $K = cP^3/S^2$ in cm², where $P$=porosity, $S$=surface area, and $c$ = a constant (dependent on pore geometry).

†Hagen-Poiseuille permeability $K = Pd^2/32$ in cm², where $P$=porosity, and $d$=effective pore diameter.

* molybdenum concentration is in atomic percent

* Surface Area from nitrogen adsorption for Kozeny permeability
<table>
<thead>
<tr>
<th>ID</th>
<th>FI*</th>
<th>Phases Present†</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>M16</td>
<td>y</td>
<td>SC, MS, S</td>
<td>poor-macroscopic phase separation</td>
</tr>
<tr>
<td>M17</td>
<td>y</td>
<td>SC, MS, S</td>
<td>cracks and veins/pockets of silicon</td>
</tr>
<tr>
<td>M18</td>
<td>y</td>
<td>SC, MS, C, S</td>
<td>very uniform, dense</td>
</tr>
<tr>
<td>M19</td>
<td>y</td>
<td>SC, C, S</td>
<td>little silicon, extensive porosity</td>
</tr>
<tr>
<td>M20</td>
<td>y</td>
<td>SC, MS, C, S</td>
<td>little melt, extensive porosity</td>
</tr>
<tr>
<td>M21</td>
<td>-</td>
<td></td>
<td>infiltration obstructed by grafoil</td>
</tr>
<tr>
<td>M22</td>
<td>y</td>
<td>SC, C, S</td>
<td>poor-veins, pores, residual carbon</td>
</tr>
<tr>
<td>M23</td>
<td>y</td>
<td>SC, C, S</td>
<td>good- almost fully reacted, uniform</td>
</tr>
<tr>
<td>M24</td>
<td>n, l=6</td>
<td>SC, MS, C, S</td>
<td>good, primary front visible</td>
</tr>
<tr>
<td>M25</td>
<td>n, l=3</td>
<td>SC, MS, C, S</td>
<td>uniform, carbon not continuous</td>
</tr>
<tr>
<td>M26</td>
<td>n, l=3</td>
<td>SC, MS, C, S</td>
<td>uniform, carbon not continuous</td>
</tr>
<tr>
<td>M27</td>
<td>n, l=3</td>
<td>SC, MS, C, S</td>
<td>dense, uniform</td>
</tr>
<tr>
<td>M28</td>
<td>y</td>
<td>SC, C, S</td>
<td>≈full rxn at edges, porous center</td>
</tr>
<tr>
<td>M29</td>
<td>n, l=3</td>
<td>SC, MS, C, S</td>
<td>uniform, continuous carbon phase</td>
</tr>
<tr>
<td>M30</td>
<td>y</td>
<td>SC, C, S</td>
<td>large gradient in porosity/carbon</td>
</tr>
<tr>
<td>M31</td>
<td>n, l=3</td>
<td>SC, MS, C, S</td>
<td>uniform infiltration, see M25</td>
</tr>
<tr>
<td>M32</td>
<td>n, l=1</td>
<td>SC, MS, C, S</td>
<td>carbon continuous and porous</td>
</tr>
<tr>
<td>M33</td>
<td>n, l=3</td>
<td>SC, MS, C, S</td>
<td>relatively little reaction</td>
</tr>
</tbody>
</table>

* FI = Fully Infiltrated. If no, the observed length l is given in mm

† SC=SiC, MS=MoSi₂, S=Si, C=C
The Kozeny permeability (cP³/S², with c=2/3) of the starred preforms was calculated using porosimetry data for the porosity (P) and nitrogen adsorption results for the surface area (S). The surface area of the remaining preforms was obtained with the porosimeter. The Hagen-Poiseuille (H-P) permeability is based on a model system of parallel capillary tubes, thus the actual pore structure of a material is described with an effective cylindrical pore diameter and the relative pore volume. The permeability expression is defined as \( K = Pd^2/32 \), where \( P \) is the porosity, and \( d \) is the effective pore diameter. Porosimetry data were used to calculate the values of this expression presented in Table 2.1. The ideal molybdenum concentration determined by the bulk carbon density of the preform was not necessarily that used to infiltrate the preforms. The actual infiltration conditions used are reported in Table 2.1, and displayed in Figure 2.13.

The term "fully infiltrated" in Table 2.2 refers to infiltration through the radial dimension of the preform. Photographs of typical fully- and partially-infiltrated samples can be seen in Figures 2.14 (M20) and 2.15 (M26). X-ray diffraction identified \( \beta \)-SiC, MoSi₂, and Si in the bulk samples. Carbon was observed in optical microscopy. The relative molar amounts of carbon, silicon, and molybdenum were obtained with the WDS in the electron microprobe.

A preform that is not fully-infiltrated necessarily has gradients in residual porosity and composition. The relative compositions of samples M24, M26, M27, M29, M30, and M31 have been plotted against the distance from the edge of the sample in Figure 2.16. Note the similarity in these curves; all show an initial uniform region, followed by a region of decreasing amounts of silicon. These microprobe data were obtained by sampling 16µm x 16µm areas every 200 µm across the sample. The preforms used have a uniform carbon density, making the carbon composition across the sample constant. By normalizing the relative composition given by the microprobe to the absolute carbon composition obtained from the preform density, the absolute composition may be obtained.
These data have been plotted against distance into the sample for M26 in Figure 2.17, along with an optical micrograph of the sampled area. Note that decreasing amounts of silicon correspond to increasing amounts of porosity. An ideally infiltrated and reacted preform of initial carbon density of 0.9 gm/cm³ would contain 47.53 % carbon, 50.82 % silicon, and 1.65 % molybdenum.

A higher magnification view of the microstructure of the uniform region close to the surface of sample M26 is shown in Figure 2.18. Ordered from brightest to darkest, the phases are: residual melt (the optical reflectance of silicon and MoSi₂ are very similar), SiC, carbon, and porosity. As can be seen in Figure 2.18, the initial, uniform region is dense and of a fine scale (10 μm between carbon centers).

Figure 2.19 shows the Mo:Si ratio across sample M24. Again, two regions may be identified: an initial one of constant composition, and an interior region of increasing molybdenum concentration.

The infiltration front of three samples infiltrated at identical temperatures but differing molybdenum concentrations can be seen in Figure 2.20. Sample M30 was infiltrated with a pure silicon melt, M26 had 3.2 % Mo, while M29 had 6.4 % Mo. The light phases in Figure 2.20 are infiltration products (SiC, Si, MoSi₂, or C), while the dark phase is porosity. The Mo:Si ratio obtained from the microprobe are plotted against distance into the sample in Figure 2.21 for M26 and M29.

The standard deviation in the average Mo/Si ratio over a sample is an indication of the uniformity of the molybdenum distribution in that sample. The size of the sampled area is dependent on the magnification of the instrument used. The standard deviation as a percentage of the average composition is displayed as a function of magnification in Figure 2.22 for two samples of differing preform pore diameter, M17 (d=1μm) and M20 (d=2.6μm). These data were obtained from random locations on each sample with the EDX spectrometer in the SEM.
Figure 2.23 shows a scanning electron micrograph of a flaw in these materials (a melt-filled crack or vein). The bright phase in the vein is MoSi₂, while the light phase is residual silicon. Unfilled cracks can also be seen in most partially infiltrated samples, for example that shown in Figure 2.15.

2.4 Discussion

2.4.1 Particulate Preform Infiltrations

Infiltrating a particulate preform at temperatures above the melt liquidus can result in a fully-infiltrated body, as shown Figure 2.6. Infiltrating at or below the liquidus temperature for a given composition results in reduced infiltrated lengths, as shown in Figure 2.9. Initially, a molybdenum alloyed silicon melt that is above its liquidus temperature will react with a carbonaceous preform to form SiC. One at the melt liquidus temperature will form SiC, and immediately supersaturate the melt in molybdenum, resulting in the precipitation of MoSi₂. This precipitation will increase the rate of product deposition and pore closure, thereby decreasing the infiltrated lengths. Appendix 1 shows that this rate increase is constant for a constant Si-C reaction rate, and that the expected increase in product deposition rate is approximately 27% by volume for a 10% Mo - Si melt at its liquidus temperature (1913 K).

The x-ray spectra shown in Figures 2.8 and 2.11 indicated that both the α and β phases of SiC are present in these materials. The SiC that forms when carbon is immersed in molten silicon is the cubic (β) polytype.¹² The preforms infiltrated in this work were ≈50% α-SiC. Ogbuji et al.¹³ have shown that the reaction-formed β phase deposits on the α "seed". The α grows into the β along stacking faults, eventually resulting in fully single phase α-SiC. The presence of both α and β SiC in these samples suggests that this regrowth process was not completed in the times and at the temperatures involved in formation. MoSi₂ is shown to be the primary second phase in Figures 2.8 and 2.11, with
small amounts of Mo₅Si₃ also detectable. Free silicon is not seen in these x-ray spectra, indicating that, if present, it constitutes less than ≈5 % of the sample.

The microstructure typical of a fully infiltrated sample is shown in Figure 2.7. Note the uniform distribution of the silicide phase, and the lack of porosity. Figure 2.10 indicates that the surface coating seen on sample M5 (Figure 1.5) is dense and uniform.

MoSi₂ becomes increasingly ductile at temperatures above 1300 K.¹⁴ The presence of a ductile phase at grain boundaries could have detrimental effects on high temperature strength and creep resistance. However, Figure 2.12 shows that MoSi₂ does not penetrate SiC:SiC grain boundaries in bulk materials. This suggests that for small volume fractions of MoSi₂, little decrease in creep resistance is expected at elevated temperatures, while the toughness may improve relative to that of monolithic SiC, as was discussed in Chapter 1.

2.4.2 Micro-Porous Preform Infiltrations

The discussion of the infiltration experiments performed with the micro-porous glassy carbon preforms will begin with a brief explanation of the data interpretation, followed by a discussion of the effects of the initial preform permeability, and the melt temperature, and the melt composition on the resultant body.

The two values of the calculated permeability presented in Table 2.1 agree well in all but the last case, M33 for which the values differ by only a factor of three. The agreement seen in the first three preforms is not unexpected, since both values were calculated using porosimeter data. The pore surface area of the last three preforms, however, was determined by nitrogen adsorption. The agreement in these permeabilities supports the accuracy of the porosimeter values for the pore surface area and effective diameter. The difference seen in M33 may be due to the error involved in nitrogen adsorption measurements of relatively low surface area materials (the increased error is primarily due to the difficulty in identifying the end of the adsorption-desorption cycle).
The porosimeter measures the pore volume directly, while it calculates the pore surface area and effective pore diameter. The software relates the applied pressure \( P \) to the effective pore radius \( r \) through the Washburn equation, \( P = 2\gamma \cos \theta / r \) where \( \gamma \) is the mercury surface tension and \( \theta \) the contact angle. This implicitly assumes pores of a circular cross-section. Since the Hagen-Poiseuille permeability is based on a model pore structure of aligned circular tubes of equivalent diameter, the effective diameter given by the porosimeter is just that required by the Hagen-Poiseuille model. The porosimeter data was obtained from all the preforms with the same equipment, making it a consistent descriptor of the pore structures. Therefore, the Hagen-Poiseuille permeability is seen to provide a good, relative indication of preform permeability, and will be used in discussing the results of this work.

The preform permeability was varied in infiltration experiments M20, M24, M32, and M33. These infiltrations were done using 3.2\% Mo-Si melts at 1703 K. The ultimate infiltrated length (L) scales with the Hagen-Poiseuille permeability in these samples, as can be seen in Figure 2.24. M20 was completely and uniformly infiltrated, making the observed L a lower limit for this preform. These results indicate that the ultimate infiltrated length obtained in a reactively-infiltrated system depends on the initial permeability of the porous solid.

A method for depicting the degree of uniformity of a two phase microstructure has been presented by Lange and Miller. EDX analysis is used to obtain the relative composition of the material at a given magnification. The standard deviation of the average composition is then an indication of the uniformity of the microstructure at that magnification. At lower magnifications, the analyzed area is sufficiently large that the sample appears homogeneous. As the magnification is increased, the sampled area is eventually no longer representative of the bulk, and the standard deviation is expected to rise.
This technique has been applied to two fully infiltrated samples (M17 and M20), with the results shown previously in Figure 2.22. Figure 2.25 recasts these data as the percent standard deviation vs. the length of the scanned area, providing an indication of the absolute scales involved. The preforms were infiltrated under identical conditions (1703 K, 3.2% Mo), but the scale of the porosity differed. The preform used in M17 had an effective pore diameter ($d_{eff}$) of 1.0 μm, while that used in M20 had a $d_{eff}$ of 2.6 μm. Figure 2.25 shows a "break" in the standard deviation curve at approximately 100 μm for M20 and 30 μm for M17, indicating that below these levels the microstructure becomes increasingly less homogeneous. These lengths are roughly 30x the effective pore diameters of the preforms used. Thus, while there is a relative dependence of the scale of the second phase distribution on the scale of the initial preform microstructure, the absolute scales differ by roughly an order of magnitude. This may be due to differences in the actual scale of the preform pore structure versus that assumed by the porosimeter, infiltrating with a inhomogeneous melt, or a non-uniform initial preform pore structure.

The gradient in the molybdenum distribution shown in Figure 2.19 is consistent with simultaneous infiltration and reaction, since reaction will increase the molybdenum concentration of the melt. This gradient is not dissimilar to those calculated for porosity in Figure 2.4, where it was suggested that a decrease in reaction product gradients would result from a decrease in the preform half-thickness:L ratio.

Thus, larger pores result in larger infiltrated distances and decreased gradients, while smaller pores increase the uniformity of the distribution of the silicide. Therefore, the optimum preform pore structure is a balance between the half-dimension of the part and its bulk uniformity, and the scale of the resultant microstructure.

The relative amounts of carbon, silicon and molybdenum obtained from the microprobe (Figure 2.16) show two regions: one of uniform composition, and one of decreasing amounts of silicon and increasing amounts of carbon and molybdenum.
Physically, the decreasing amount of silicon corresponds to the increasing amounts of porosity, as was shown in Figure 2.17. Figure 2.18 shows the uniform region to be dense, while X-ray spectra identify Si, β-SiC, and MoSi₂ in these materials. The relative amounts of SiC, Si, C, and MoSi₂ in the uniform region can be calculated from the absolute compositions and the molar volumes of these phases. This analysis assumes that the molybdenum is present only as MoSi₂, and that there is no porosity. MoSi₂ was the only molybdenum compound observed in the bulk XRD spectra of the infiltrated microporous preforms. Figure 2.18 supports the second assumption.

The infiltration temperature was varied in experiments M24, M25/31, M26, and M27, being done at 1703 K, 1773 K, 1838 K, and 1883 K respectively. Identical preforms and melt compositions (3.24% Mo-Si) were used. The relative microprobe data obtained from the uniform regions of these samples is presented in Table 2.3, along with the results of the calculated phase composition. The percent carbon reacted is defined to be the calculated molar amount of SiC divided by the total measured amount of carbon present.
Table 2.3

Infiltration Temperature Effects

<table>
<thead>
<tr>
<th>ID</th>
<th>Temp(K)</th>
<th>C</th>
<th>Si</th>
<th>Mo</th>
<th>%C Reacted</th>
<th>Length</th>
<th>Mo/Si(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M24v</td>
<td>1703</td>
<td>59.0</td>
<td>40.6</td>
<td>0.4</td>
<td>41.6</td>
<td>5.0 mm</td>
<td>1.42</td>
</tr>
<tr>
<td>M31v</td>
<td>1773</td>
<td>60.1</td>
<td>39.3</td>
<td>0.6</td>
<td>40.6</td>
<td>3.8 mm</td>
<td>1.61</td>
</tr>
<tr>
<td>M26v</td>
<td>1838</td>
<td>55.9</td>
<td>43.4</td>
<td>0.7</td>
<td>58.2</td>
<td>2.2 mm</td>
<td>1.78</td>
</tr>
<tr>
<td>M26h</td>
<td>1838</td>
<td>55.6</td>
<td>43.8</td>
<td>0.6</td>
<td>60.0</td>
<td>1.8 mm</td>
<td>1.39</td>
</tr>
<tr>
<td>M27v</td>
<td>1883</td>
<td>54.2</td>
<td>45.2</td>
<td>0.6</td>
<td>66.5</td>
<td>2.1 mm</td>
<td>1.42</td>
</tr>
</tbody>
</table>

v indicates a vertical scan (along the preform axis), and h a horizontal (i.e. radial) scan.

The errors in the calculated results are: ±5% for the percent carbon reacted, ±0.2% for the Mo:Si ratio, and ±0.3 mm in the length of the uniform region.

The length of the uniform region was obtained from microprobe data. Table 2.3 shows that the extent of reaction increases with increasing temperature, while the length of the uniform region decreases. This is consistent with a reaction rate that increases with temperature.

The results presented in Table 2.3 also show that the average Mo:Si ratio in the uniform region of these samples is approximately half the melt composition at all temperatures. Figure 2.19 indicates that the molybdenum concentration in the preform increases as the infiltration front is approached. This increase occurs beyond the uniform region in these materials, and thus is not reflected in the Mo/Si values given in Table 2.3. Averaging the molybdenum concentration over the entire infiltrated region results in this ratio approaching the melt composition (M26 had an overall average Mo/Si ratio of 3.86%). This is consistent with simultaneous infiltration and Si - C reaction, resulting in a molybdenum enriched melt infiltrating further into the sample.
The molybdenum concentration was varied in experiments M30 (0 \% Mo), M26 (3.2 \% Mo), and M29 (6.4 \% Mo), all of which were infiltrated at 1838 K using identical preforms. The microprobe data and calculated extent of reaction in the uniform regions of these samples are presented in Table 2.4. The molybdenum concentration of each melt is also given for reference.

Table 2.4

<table>
<thead>
<tr>
<th>Microprobe Data (atomic %)</th>
<th>Uniform Region</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo]*</td>
<td>C</td>
</tr>
<tr>
<td>M30h</td>
<td>0</td>
</tr>
<tr>
<td>M26h</td>
<td>3.2</td>
</tr>
<tr>
<td>M26v</td>
<td>3.2</td>
</tr>
<tr>
<td>M29h</td>
<td>6.4</td>
</tr>
<tr>
<td>M29v</td>
<td>6.4</td>
</tr>
</tbody>
</table>

v indicates a vertical scan (along the preform axis), and h a horizontal (i.e. radial) scan

* melt concentration

There is a substantial difference between the vertical and horizontal scans in sample M29. The reasons for this difference are not known, but it is most likely due to bulk melt inhomogeneities.

The effect of solute concentration can be addressed by comparing the compositions of the uniform regions of M29v with M26 and M30. As can be seen in Table 2.4, the extent of reaction remains approximately constant at 58\% to 60\% when the molybdenum concentration in the preform is less than 1.8\%, but decreases to 40\% at higher molybdenum concentrations. This suggests that molybdenum can affect the extent of reaction inside the preform when present in excessive amounts, perhaps through the
precipitation of MoSi$_2$ from the melt during reaction. (Small amounts of a precipitate would not be expected to noticeably affect the reaction, while larger amounts may impede flow of the melt to the unreacted carbon.)

Increasing the molybdenum concentration of the melt also affects the infiltration kinetics through changing the location of the minimum permeability in the reactivity-infiltrated body. The models presented in Section 2.1 assumed that the permeability decreased with time of reaction, and therefore the surface of the sample would have the lowest permeability at any given time. Precipitating a second phase will increase the pore closure rate, thereby accelerating the decrease in the permeability. The location of the silicide precipitation, therefore, may determine the minimum in the system permeability. Two limiting cases can be envisioned: flow being restricted either at the preform surface (reaction choking), or at the infiltration front (plug flow). The porosity gradient expected from reaction choking was shown in Figure 2.4 and discussed in section 2.1.4. Again, it was proposed that this gradient in porosity is caused by the decrease in system volume upon reaction, the gradient in time of reaction, and the closing of surface porosity. Flow stopped at the infiltration front (plug flow), on the other hand, should result in very little porosity across the sample, as melt continues to flow into the sample to be consumed by reaction instead of advancing the infiltration front. The reaction in the plug flow case is not limited by the flow of silicon, and should continue to completion. Thus, the amount of expected porosity behind the front is small, and the infiltration front should be abrupt.

Figure 2.20 shows optical micrographs of the infiltration fronts of samples M30, M26, and M29, while the Mo:Si ratio is plotted against distance into the sample in Figure 2.21. These compositional data were obtained from the microprobe, and were presented in Figure 2.16. These samples were infiltrated at 1838 K with increasing amounts of molybdenum. The ideal melt composition for these preforms was 3.2 wt% Mo-Si.
M30 was infiltrated with a pure silicon melt. No distinct infiltration front is observed, merely increased porosity as the center of the preform is approached. This is indicative of reaction choking, as was predicted in the calculated porosity gradients in Figure 2.4. The infiltration front in the molybdenum rich sample (M29v) is very sharp, with little observed porosity behind the front. Figure 2.21 shows a similarly sharp increase in the molybdenum concentration at the infiltration front. The molybdenum concentration of the melt used in M29 was higher than the ideal for the preform used. This is consistent with flow being stopped at the infiltration front due to MoSi$_2$ precipitating there, effectively decreasing the local permeability. M26 was infiltrated with the ideal melt composition and shows intermediate behavior in Figure 2.20, resulting in no clear indication of the location of minimum permeability during infiltration. Figure 2.21 indicates that the molybdenum concentration increases as the reaction front is approached in M26, which suggests plug flow. The decrease in the extent of reaction seen at higher molybdenum concentrations, coupled with these results, indicate that excess solute can physically inhibit both flow and reaction in these materials.

2.4.3 Defects in Reacted Materials

Defects in these materials are primarily of three types: residual carbon, cracks, and melt-filled veins. Residual carbon is observed as large (10 µm) nodules in all samples, as well as a continuous phase in the samples infiltrated at lower temperatures. The cracks and veins are thought to occur as a result of the thermal stresses generated during reaction or upon cooling. Melt filled veins similar to those seen in Figure 2.23 clearly result from preform cracks that fill during infiltration. These cracks can either be formed during infiltration if the heat generated during reaction induces thermal shock, or they may have been present in the unreacted preform. Unfilled cracks presumably form after infiltration and are attributed to differential thermal expansion stresses induced by the non-uniform
distribution of phases across the sample. Correcting these problems would involve modifying the preform (smaller solids dimension), and moderating the reaction. The latter could be achieved by lowering the temperature and/or adding a non-reactive phase to the preform, effectively diluting the amount of heat generated per unit volume. As discussed in section 2.1.4, uniformly infiltrating a preform should minimize the gradients in heat, porosity, and precipitate phase, resulting in higher quality material. Those preforms infiltrated at lower temperatures were in general more fully infiltrated and had fewer flaws than those infiltrated at higher temperatures. However, the amount of residual carbon was found to increase in the low temperature infiltrations, indicating a trade-off in the optimal preform characteristics between the dimension of the solid carbon and the dimensions of the bulk part.

2.5 Conclusions

Alloyed-melt reactive infiltration has been shown to be a viable process for the production of refractory bodies at relatively low temperatures. X-ray spectra of both bulk and surface reacted samples showed no residual silicon, indeed, the identified phases should remain stable up to 2100 K. The bodies produced were dense and showed a uniform distribution of the second phase.

Two models describing reactive infiltration by a liquid into a porous solid were presented. In the first, the permeability was allowed to vary over space and time, and a numerical solution was obtained. In the second, it was assumed that the permeability of the system was controlled by that at the surface, and the system permeability became a function of time alone, allowing an analytical solution to be obtained. Both of these solutions predicted that infiltration was much more rapid than reaction, and that infiltrated lengths on the order of centimeters should be obtainable with the available preforms. It was predicted that higher quality materials (i.e., of lower residual porosity with a more uniformly
distributed second phase) should result when the half thickness of the preform is much less than the maximum infiltratable length (L). Maximizing L was seen to be achieved through increasing the amount of porosity and the pore dimension, and decreasing the reaction rate. The effects of changes in the system volume and the heat generated during reaction were not included in these models.

A series of systematic infiltration experiments were performed using uniform micro-porous glassy carbon preforms. The effects of infiltration temperature, pore structure, and solute concentration were examined. The extent of reaction was seen to increase with increasing temperature. Raising the infiltration temperature decreased the length of the uniform region, as predicted by the model, given a reaction rate that decreases with increasing temperature. The ultimate infiltrated length L increased with increasing pore dimension, again consistent with the predictions made in the model. The scale of the molybdenum distribution was found to be dependent on the scale of the preform pore structure. Excessive amounts of molybdenum inhibited both the extent of reaction, and the advancement of the infiltration front, resulting in diminished porosity behind the front. Processing flaws in the reacted bodies included residual carbon, cracks, and melt-filled veins. Infiltrating at the minimum temperature with high permeability materials minimized the presence of these processing flaws, but left residual carbon.

2.6 Implications

The modeling work predicted that increasing the pore volume and decreasing the pore surface area and the reaction rate would improve the quality of the resultant material. These predictions are supported by the infiltration studies. Increasing the pore volume while maintaining a constant bulk carbon density can be achieved by increasing the specific density of the solid carbon. In going from the glassy carbons used in this study to graphite, an increase in pore volume of 67% is achieved for a bulk preform density of 0.90
gm/cm³. Decreasing the surface area of the porosity implies coarser preforms should be used. However, consideration must also be given to the scale of the resultant solute distribution, and to the necessity of avoiding unreacted carbon. Decreasing the reaction rate can be achieved by infiltrating at lower temperatures, as will be shown in Chapter 3. Thus, the pore structure of the preform must be optimized for the specific application, while the infiltration temperature should be minimized, and the ideal amount of solute used if high quality materials are to be produced.
read $\Delta P$, $K_o$, $k$, $\eta$, $\Delta t$, $P_o$, $c/S^2$

$\Delta l_1 = l = [\Delta P K_o \Delta t / \eta P_o]^{1/2}$

$m = 2$
$i = 1$

$mK = 0$

$K_{mi} = c/S^2[P_o - k(m - i)\Delta t]$

if $K_{mi} = 0$, then end

$mK_i = \Delta l_i / K_{mi}$

$mK = mK + mK_i$

$i = i + 1$

if $i \neq m$, then

$i = i - 1$

$mK = mK + \Delta l_i / K_o$

$K_m = (1 + \Delta l_i)mK$

$i = i + 1$

$\Delta l_i = [\Delta P K_m \Delta t / \eta l P_o]$

$l = l + \Delta l_i$

write $l$

$t = m \Delta t$

write $t$

$m = m + 1$

Initialise Parameters
Infiltrate with no reaction for $\Delta t$
Set dummy variables for time ($m$) and distance ($i$)
Initialise summation
Calculate incremental permeability
Signals Reaction Choking
Calculate system permeability at $m$
Check for completion of the distance loop
Add permeability ahead of the infiltration front into the system permeability
Update $i$
Calculate new $\Delta l$
Update $l$
Update $t$
Update $m$

Figure 2.1  Flow chart for the numerical solution of reactive-infiltration.
Figure 2.2  Numerical Solution to reactive-infiltration as a function of time for SiC:C preforms.
Figure 2.3 Analytical Solution to reactive-infiltration as a function of time for SiC:C preforms.
Figure 2.4 Calculated porosity gradients in a preform of half-thickness 0.3L, 0.5L, 0.7L, and 0.9L, with initial porosity $P_0=0.3$, using the analytical solution to system permeability.
Figure 2.5  Microstructures of microporous glassy carbon preforms supplied by D. R. Behrendt, NASA Lewis. Note the uniformity across each sample, and the variation between the two.
Figure 2.6  A SiC:C preform infiltrated with a single phase melt. Scale is in centimeters.

Figure 2.7  Microstructure of reactively infiltrated sample. The light phase is a molybdenum silicide, and the dark phase is silicon carbide.
Figure 2.8  X-ray spectra of a fully infiltrated SiC:C preform showing α and β SiC, MoSi$_2$, Mo$_5$Si$_3$, but no detectable free silicon. An unidentified phase is present, and may be a ternary Mo-Si-C compound.
Figure 2.9  A SiC:C preform typical of those infiltrated at or below the melt liquidus.

Figure 2.10  SEM micrograph of the coating seen in Figure 2.9
Figure 2.11  XRD pattern of a ground portion of the coating showing no detectable free silicon.
Figure 2.12  Annular dark field STEM micrograph of a MoSi$_2$ precipitate showing a dihedral angle with the SiC grain boundary of approximately 120°.
Figure 2.13  Si-Mo phase diagram showing melt compositions and infiltration temperatures used in experiments M16 - M33.
Figure 2.14 Infiltration experiment M20, infiltrated at 1703 K with a 3.2% Mo-Si melt. Solidified residual melt can be seen at the bottom of the preform. Scale is in centimeters.

Figure 2.15 Infiltration experiment M26, infiltrated at 1838 K with a 3.2% Mo-Si melt. Note the uniform but limited infiltration distance. Scale is in centimeters.
Figure 2.16a  Relative composition of sample M24 plotted against distance from the edge of the sample. Infiltrated with a 3.2% Mo-Si melt at 1703 K.

Figure 2.16b  Relative composition of sample M31 plotted against distance from the edge of the sample. Infiltrated with a 3.2% Mo-Si melt at 1773 K.
Figure 2.16c  Relative composition of sample M26 (vertical scan) plotted against distance from the edge of the sample. Infiltrated with a 3.2% Mo-Si melt at 1838 K.

Figure 2.16d  Relative composition of sample M26 (horizontal scan) plotted against distance from the edge of the sample. Infiltrated with a 3.2% Mo-Si melt at 1838 K.
Figure 2.16e  Relative composition of sample M27 plotted against distance from the edge of the sample. Infiltrated with a 3.2% Mo-Si melt at 1883 K.

Figure 2.16f  Relative composition of sample M30 plotted against distance from the edge of the sample. Infiltrated with a pure Si melt at 1838 K.
Figure 2.16g Relative composition of sample M29 (vertical scan) plotted against distance from the edge of the sample. Infiltrated with a 6.4% Mo-Si melt at 1838 K.

Figure 2.16h Relative composition of sample M29 (horizontal scan) plotted against distance from the edge of the sample. Infiltrated with a 6.4% Mo-Si melt at 1838 K.
Figure 2.17  Optical micrograph of the infiltrated portion of M26, with normalized compositional data plotted at the same scale.
Figure 2.18  Higher magnification optical micrograph of the initial, uniform region of M26 (Figure 2.17). The phases are: Si / MoSi$_2$ (lightest), SiC, and residual carbon (darkest).
Figure 2.19  Mo:Si ratio plotted against distance into the sample for infiltration experiment M24.
Figure 2.20  Infiltration fronts of samples M30 (0% Mo), M26 (3.2% Mo), and M29 (6.4% Mo). These experiments were done at 1838 K, with infiltration occurring from right to left.
Figure 2.21  The Mo:Si ratio for samples M26 (3.2% Mo), and M29 (6.4% Mo). Note the sharp increase at the infiltration front of the Mo rich sample.

Figure 2.22  The standard deviation of the average Mo:Si ratio of samples M20 and M17, as a function of magnification. M20 had an initial pore diameter of 2.6μm, while that of M17 was 1μm.
Figure 2.23  A scanning electron micrograph of a defect from a sample infiltrated at 1883 K (melt-filled vein).
Figure 2.24  Ultimate Infiltrated Length $L$ plotted against the Initial Permeability of samples infiltrated at 1703 K with Si-3.2% Mo melts.
Figure 2.25  Standard deviation of the average Mo/Si ratio obtained with EDX on the SEM plotted against the linear dimension of the scanned area. The effective pore diameters of the preforms used are shown for reference.
Chapter 3  Carbon - Silicon Reaction Kinetics

3.0 Introduction

The reactive-infiltration models developed in Chapter 2 depend on an assumed mechanism and rate of reaction between carbon and molten silicon. Correct interpretation of the bulk infiltration experiments described in Chapter 2 also require an understanding of this reaction. The objective of the study reported in the present Chapter is to determine the rate and mechanism of the $\text{C}_3(\alpha) + \text{Si}_(\ell) \rightarrow \text{SiC}_3(\alpha)$ reaction. The variables of interest include the density, orientation and degree of crystallinity of the carbon, the effect of alloying the melt, and the temperature of the system. The results of the Si-C study are presented first, followed by the observations made on alloyed melts.

3.1 Literature Review

3.1.1 Si and C Self-Diffusion in $\beta$-SiC

Hon and Davis measured the diffusion of Si (1) and C (2) in $\beta$-SiC using thin films of $^{30}\text{Si}$ and $^{14}\text{C}$ tracers, and their results are shown in Figure 3.1. Even though the samples were embedded in SiC and there was excess silicon present, sample decomposition prevented the measurement of silicon diffusion along grain boundaries. No other data were found in the literature for silicon diffusion along grain boundaries in $\beta$-SiC. As can be seen in Figure 3.1, the activation energies reported for lattice diffusion of Si $(9.45 \pm 0.05 \text{ eV})$ and C $(8.72 \pm 0.14 \text{ eV})$ are similar. Hon and Davis postulated a vacancy jump mechanism for lattice diffusion of both silicon and carbon in $\beta$-SiC. The activation energy for grain boundary diffusion of carbon in $\beta$-SiC was found to be $5.84 \pm 0.09 \text{ eV}$. (2)

3.1.2 $\text{C}_3(\alpha)$ and $\text{Si}_(\ell)$ Reaction Kinetics

The kinetics of the reaction between molten silicon and solid carbon to form silicon carbide are of interest to both the structural ceramics and semiconductor research
communities. Fitzner and Gadow\textsuperscript{3} reported the formation of a SiC reaction layer at the molten silicon:carbon interface. They assumed that the rate of growth was limited by diffusion of the reactants through this product layer, and classic fluid:solid reaction kinetics for the unreacted core problem applied. Using such a model to fit their data, the "effective" diffusion coefficients, $D_{\text{eff}}$, reported were $4.2 \times 10^{-10}$ cm$^2$/sec and $9.5 \times 10^{-10}$ cm$^2$/sec for Sigradur G vitreous carbon at 1873 K and 2073 K respectively. Carbon fibers were also used as a carbon source, and the resultant effective diffusion coefficients ranged from $10^{-11}$ cm$^2$/sec to $10^{-10}$ cm$^2$/sec. The $D_{\text{eff}}$ was seen to decrease linearly with the SiC layer thickness. The authors attributed this to coarsening of the SiC grains, effectively decreasing the amount of grain boundary area, hence decreasing the effective diffusion coefficients measured.\textsuperscript{3}

These values are not consistent with those reported for carbon or silicon lattice diffusion in $\beta$-SiC as determined by Hon and Davis\textsuperscript{1,2} ($8.8 \times 10^{-16}$ cm$^2$/sec and $1.6 \times 10^{-13}$ cm$^2$/sec for $D_C$ and $3.0 \times 10^{-18}$ cm$^2$/sec and $8.7 \times 10^{-16}$ cm$^2$/sec for $D_{\text{Si}}$ at these temperatures). These authors implied that the reported effective diffusion coefficients may represent grain boundary diffusion once the relative area of the boundaries is considered. Assuming a model of the layer based on 1 $\mu$m square grains with 10 Å grain boundaries, a relative grain boundary area ($A_{gb}/A$) of 0.002 is estimated. The reported carbon diffusion coefficients along grain boundaries at these temperatures are $8.4 \times 10^{-9}$ cm$^2$/sec and $2.8 \times 10^{-7}$ cm$^2$/sec (2), resulting in effective diffusion coefficients [$D_{\text{eff}} = (A_{gb}/A)D$] of $1.7 \times 10^{-11}$ cm$^2$/sec and $5.6 \times 10^{-10}$ cm$^2$/sec. These estimated values agree with Fitzner and Gadow's\textsuperscript{3} data, thereby supporting their hypothesis that growth is limited by diffusion along grain boundaries, given that the area fraction of those boundaries changes with both temperature and time. However, Fitzner and Gadow's\textsuperscript{3} data for Sigradur G also show very high reaction rates at short times, i.e. at times less than 2 minutes. These rates are much higher
than those predicted by the solid state transport model they used to describe their data, possibly indicating a change in mechanism as the reaction proceeds.

Minnear also reported the formation of a SiC layer at the carbon:silicon melt interface, and made the following observations: SiC was reported to form in times as short as $10^{-1}$ seconds, and the SiC layer was found to remain one crystallite thick at times up to $10^5$ seconds. Minnear postulated that layer growth occurs via the outward diffusion of carbon along grain boundaries, based on the observation of cusps at most boundaries.

Pampuch et al. also investigated silicon reactions with carbon fibers, but proposed a solution-reprecipitation mechanism for SiC growth. Large SiC crystals were seen to be growing outside of the original fiber diameter from SiC crystallites inside this surface. The driving force for this process was proposed to be sinusoidal fluctuations in the local melt temperature. The derived rate equation, however, is based on steady-state flow at constant temperature. The reaction is assumed to be adiabatic, with the end-point temperature reached at time $t > 0$. The proposed rate equation does not accurately describe the experimental results. It should be noted that while the mechanism is inconsistent with the data presented, the reported morphologies of reacting fibers are consistent with the present study.

Hase et al. studied the reaction that occurs when carbon powder compacts are infiltrated with molten silicon. They obtained a critical carbon particle size for complete conversion to SiC by taking the difference between the particle size distributions of the initial carbon powders and the carbon left in the samples after reaction. This critical particle size was seen to increase with the crystallite size in the carbonaceous material, an observation explained in terms of the known anisotropy of the reaction between molten silicon and graphite. These authors concluded that diffusion through a product layer was therefore not rate limiting, as this would lead to approximately the same critical particle size for all cases. The conversion mechanism postulated was one of surface reaction control,
with stress-induced spallation (due to the volume expansion of the solid phase that occurs during this reaction) continually creating fresh surface, thus keeping the diffusion distance small.

Ness and Page postulated that solution-reprecipitation was the dominant mechanism in the $C(s) + Si(l) \rightarrow SiC(s)$ reaction in bulk RBSC materials. Their conclusion was based on observations made on partially reacted bulk samples that had been etched with acid to remove the residual silicon. They proposed that the carbon dissolves into the melt at the carbon:melt interface and reprecipitates out as SiC on SiC seed grains, with the process being driven by carbon concentration gradients in the melt.

Ness and Page also examined the boundaries between reaction-formed SiC grains using transmission electron microscopy, and concluded that silicon does not penetrate for any distance along these boundaries. A thin (10.5 Å), amorphous film was found at reaction-formed boundaries and was proposed to be amorphous SiC rather than silicon. This conclusion was based on dark field TEM observations of the boundaries that showed a maximum intensity at reciprocal space positions corresponding to those expected for amorphous SiC. The TEM micrographs presented in Ness and Page's previous paper showed dihedral angles of between 25° and 65° between residual silicon and SiC grain boundaries. A true dihedral angle of less than 60° indicates continuous wetting along grain edges, i.e. triple junctions, while continuous wetting of grain faces requires a dihedral angle of 0°. Furthermore, silicon expands upon freezing, making retraction of the liquid from these reaction-formed boundaries during cooling unlikely. Thus, it appears that silicon does not penetrate reactively-formed SiC grain boundaries, but that it should penetrate down triple grain junctions.

The semiconductor community has demonstrated that solution growth techniques can be used to produce $\beta$-SiC. Shinozaki et al. investigated grain growth in fine $\beta$-SiC particles at 2120 K. They found that substantial growth occurred only in the presence
of liquid silicon. From this they concluded that the dominant process was one of transport through the liquid phase rather than solid state grain boundary motion.

In summary, the mechanism and rate of the RBSC formation reaction have not been conclusively defined by the literature. Fitzner and Gadow\textsuperscript{3} and Minnear\textsuperscript{4} reported seeing a continuous layer of $\beta$-SiC forming at the carbon:silicon interface. Minnear postulated, and Fitzner and Gadow implied, that the growth of this layer is rate limited by solid state diffusion of either carbon or silicon along its grain boundaries. The results of Hase \textit{et al.}\textsuperscript{6} appear to refute this hypothesis. Ness and Page\textsuperscript{7} proposed carbon going into solution at the carbon:silicon interface, not forming SiC until it reprecipitates. Shinozaki \textit{et al.}\textsuperscript{11} demonstrated that grain growth in $\beta$-SiC is a liquid phase process at the temperatures of current interest. The relationship between these observations is not obvious. Thus, after reviewing the current literature, the details of the $C(s) + Si(l) \rightarrow SiC(s)$ reaction remain ambiguous.

3.2 Theory of SiC Growth

3.2.1 Heterogeneous Growth

Heterogeneous reactions that form a product layer between the two reactants proceed by a number of sequential steps. Reactants must be transported to the reacting interface, reaction at that interface must take place, and products of the reaction may have to be removed from the interface. A SiC product layer has been reported to form at the carbon:silicon melt interface\textsuperscript{3,4}, thereby creating two reaction sequences: one in which silicon diffuses to the carbon:carbide interface and reacts, and one of carbon diffusion and subsequent reaction at the carbide:melt interface. The net growth rate of the product layer will be the sum of the rates at each interface, each of which is controlled by the slowest step in the sequence.
It is not uncommon that one series is much faster than the other, resulting in growth occurring predominantly at one interface. However, the only step for which quantitative rates are available for the present system is the diffusion of carbon along grain boundaries in the product layer. Therefore, the kinetics of the growth of the product layer in the present system cannot be accurately estimated.

The growth of a volume expansive reaction layer at either interface is expected to induce compressive lateral stresses in the layer.\textsuperscript{12} The surface oxidation of metals is another example of such a reaction layer, and compressive stresses were directly observed for the first time in FeO and NiO layers\textsuperscript{13}, both of which have larger molar volumes than the base metals. The magnitude of these stresses depends on the location of the growth interface, the distribution of the formation strains in the layer, the elastic moduli of both the layer and the substrate, the difference in their molar volumes, and the geometry of the system.\textsuperscript{14} The formation mechanism of the SiC layer that forms on carbon immersed in molted silicon is not well understood. Thus, while the magnitude of these compressive lateral stresses cannot be accurately estimated, they are expected to form in the SiC reaction layer regardless of the location of the growth interface.

### 3.2.2 Solution Growth

Liquid phase growth of SiC was reported by Shinozaki \textit{et. al.}\textsuperscript{11} and proposed by Ness and Page.\textsuperscript{7} This process involves dissolving carbon in molten silicon at the carbon source, and reprecipitating SiC at the sink. The details of this process will be presented below.

#### 3.2.2.1 Normal Growth

Normal growth kinetics are based on the assumption that any site on the growing interface is equally likely to sustain growth, and are thought to be a valid description of
growth on atomically rough surfaces.\textsuperscript{15} Thus, the morphology of a growing interface suggests the mechanisms involved in advancing that interface.

Jackson\textsuperscript{15} recognized that the growth morphologies of crystalline materials depended on the entropy change at the growth interface. The entropy change in advancing a rough (macroscopically smooth) interface is small, while that of a smooth (macroscopically faceted) interface is large. Using growth from the melt as an example, Jackson expressed the free energy of the interface $\Delta F_s$ as a function of the fraction of sites occupied ($x$) as:\textsuperscript{15}

$$\frac{\Delta F_s}{NkT_e} = \alpha x(1-x) + x \ln x + (1-x) \ln(1-x)$$

(3.1)

where $N$ is the total number of available surface sites, $k$ is Boltzmann's constant, $T_e$ is the equilibrium melting point, and $\alpha$ is defined as:

$$\alpha \equiv \frac{L \xi}{RT_e}$$

(3.2)

where $L$ is the latent heat of melting, and $\xi$ is a crystallographic term that relates the number of bonds formed in the growth plane to the total number of bonds formed. For growth on close-packed planes, $\xi = 2/3$. For small values of $\alpha$, i.e. $\alpha < 2$, the free energy of the interface was seen to be a minimum at $x = 0.5$, which should result in atomically rough (macroscopically smooth) interfaces. This would suggest normal growth kinetics. Conversely, systems with high entropy changes during growth (i.e. $L/RT_e > 4$) were observed to have atomically smooth (macroscopically faceted) interfaces, suggesting growth occurs at step sites.\textsuperscript{15}

Bennema and van der Eerden\textsuperscript{16} expanded Jackson's discussion to describe growth from dilute solutions. They re-defined $\alpha$ for solution growth as:

$$\alpha = \xi (1-x_{eq})^2 (-\ln x_{eq} + \Delta f_s)$$

(3.3)

where $\xi$ has the same meaning as in Jackson's original expression, and $x_{eq}$ is the equilibrium solubility of the solute. $\Delta f_s$ is the difference in free energy of the solute species in solution and in the solid, and ranges in value from 1 to 2.5.\textsuperscript{16}
Using Bennema and van der Eerden's expression, \( \alpha \) is found to range from 7.7\( \xi \) to 9.2\( \xi \) for solution growth of SiC at 1800 K (\( x_{eq} = 1.2 \times 10^{-3} \)).\(^{17} \) These values reflect the large changes in entropy involved in growth from dilute solutions. Thus, the Jackson model predicts atomically smooth, macroscopically faceted surfaces when growing SiC from carbon in solution in moleten silicon. This is suggestive of growth occurring at steps or ledges on the SiC surface, and is inconsistent with the morphologies expected for normal growth.

3.2.2.2 Surface Nucleated Solution Growth

Surface nucleation is one possible formation mechanism for step sites on a growing surface. It involves nucleating a stable cluster of atoms on the surface, thereby creating step sites which enable rapid lateral completion of the layer. The stability of the cluster will be determined by the net free energy change of the system, i.e. the balance between the positive surface energy and the negative volume free energy. The net free energy change for nucleating a disc on a flat surface, assuming isotropic surface energies, is given as:

\[
\Delta G = \pi n^2 a^3 \Delta G_v + 2 \pi n a^2 \gamma
\]  

(3.4)

where \( n \) is the number of atoms in the radius of the disk, \( a \) is the interatomic distance, \( \Delta G_v \) is the free energy per unit volume for growth, and \( \gamma \) is the liquid:solid surface energy. By minimizing \( \Delta G \) with respect to the number of atoms, \( n \), the number of atoms in the critical radius, \( n^* \), of the smallest stable disc on a flat surface is found to be:

\[
n^* = \frac{\gamma a \Delta G_v}{\gamma a^2}
\]  

(3.5)

Using values of \( \gamma = 1400 \) ergs/cm\(^2 \) (see Equation 3.9), \( a = 3 \text{Å} \), and \( \Delta G_v = -9 \times 10^9 \) ergs/cm\(^3 \) (shown to be an upper limit in Section 3.4.2, with Equation 3.13), a critical radius of 15 atoms is obtained. The activation energy for surface nucleation, \( \Delta G^* \), can be obtained from Equation 3.4 by replacing the number of atoms in the radius, \( n \), with the critical number, \( n^* \):
\[ \Delta G^* = \pi(n^*)^2a^3\Delta G_v + 2\pi n^*a^2\gamma \] (3.6)

This results in an activation energy of \(6.4 \times 10^{-11}\) ergs for the present system, which is approximately 260 kT at 1800 K. Since the \(\Delta G_v\) chosen for this estimation was an upper limit, the actual value is likely to be smaller. Decreasing \(\Delta G_v\) will further increase \(n^*\), which will in turn further increase the activation energy. Surface nucleated solution growth of SiC is therefore unlikely.

3.2.2.3 Defect Site Growth

Twin boundaries and stacking faults are common planar defects in SiC\(^{18}\), and their intersection with the crystal surface may create ledges, i.e., growth sites. Barlett and Martin\(^{19}\) grew \(\beta\)-SiC from molten silicon in a graphite crucible. The crystals grew as triangular platelets or lathes (truncated triangles), and were examined using X-ray topography, and optical and electron microscopy. Stacking faults were observed in the topographs on inclined \{111\} planes, while twin boundaries were observed in the \(\langle 111\rangle\) habit plane. Etching these crystals in a molten salt revealed etch-pit rows on the \(\langle 111\rangle\) surface, corresponding to the intersection of the observed stacking faults with that surface. The emergence of these defects from the close-packed habit plane of the platelets suggests that stacking faults do not act as solution growth sites for \(\beta\)-SiC crystals.

Kohn and Eckart\(^{20}\) examined \(\beta\)-SiC crystals prepared in the same way as those studied by Barlett and Martin\(^{19}\) and reported no correlation between twinning and the morphology of the crystal. This further indicates twin boundaries do not act as preferred growth sites.

Van Torne\(^{21}\) reported that \(\beta\)-SiC whiskers grown from the vapor have stacking faults at \(70^\circ\) to the whisker axis. X-ray diffraction identified the whisker axis to be \[111\], indicating that the faults were on inclined \{111\} planes (the angle between \(<111>\) directions is \(70.5^\circ\)). The whisker morphology indicates that growth is not as favorable at
the intersection of these faults with the whisker surface as it is along the axial [111] direction. While the surface energies and kinetics of vapor growth are different from those for growth from solution, these observations are consistent with those reported in solution growth: i.e., that the intersection of stacking faults and twin boundaries with a surface does not create a preferred growth site.

3.2.3 Summary

A SiC reaction layer has been reported to form at the carbon:melt interface. The kinetics of the formation of this layer are not well understood. This reaction is volume expansive, and therefore thought to generate compressive lateral stresses in the SiC layer.

The modified Jackson model predicts faceted morphologies for SiC grown from solution, which is suggestive of growth occurring at steps or ledges on the surface. The energetics of generating these steps through a surface nucleation process were found to be unfavorable. Experimental observation suggests that planar defects intersecting the surface do not create preferred growth sites for β-SiC. Line dislocations intersecting a surface may create the necessary step sites. Thus, these conclusions suggest that the growth of SiC from solution occurs at dislocation sites. Several authors\textsuperscript{22,23} have similarly concluded that dislocation growth is the most likely surface reaction mechanism in the growth of SiC from the vapor phase. Therefore, it may be concluded that there must be preferred surface sites present for SiC to grow from solution, and that these sites are likely to result primarily from line dislocations intersecting the surface.

3.3 Reaction Experiments

A study was performed to define the kinetics of the \( \text{Si}(l) + \text{C}(s) \rightarrow \text{SiC}(s) \) reaction, as they were not clearly defined in the literature. Microstructural observations of partially
reacted carbon provided information on the reaction mechanism, while the amount of SiC formed after a given time allowed determination of the rate.

Fibers were chosen as the carbon source for the majority of the study, with flat plates of glassy carbon used for selected comparisons. Carbon fibers present very uniform and well defined initial shape, are of a comparable scale to the carbons in the bulk preforms, are dense, and are readily available in reproducible structure and chemistry. Two fibers were used: P55 [Union Carbide Corporation] and AS4 [Hercules Aerospace Company]. P55 is a pitch-based fiber and is 70% to 80% microcrystalline graphite.24 AS4 is derived from polyacrylnitrile and may be described as a turbostratic graphite.25 This difference in structure was observed in the X-ray spectra of these two fibers, with the P55 spectrum showing a peak at 26.6° corresponding to the (002) plane of graphite, while the AS4 fiber shows a broad, amorphous peak (Figure 3.2).

Sigradur G glassy carbon plates [SIGRI GmbH] were also used in a few experiments. This material has a density of 1.42 gm/cm³, and is similar in structure to the AS-3 fibers.26 Plate specimens were polished with 1 μm diamond grit on at least two sides prior to reaction.

In a separate experiment, P55 fibers were coated with Betarundum Ultrafine β-SiC powder [Ibiden Company, Ltd.] prior to reaction. This powder has an average grain size of 0.2 μm.27 The coating procedure involved dipping the fiber in an ultrasonicated slurry of Betarundum in water for approximately 10 minutes. The coated fiber was wrapped around a BN plunger while wet.

Two crucible materials were chosen: BN [Sohio Engineered Materials Co.], which was used in the bulk infiltration work reported in Chapter 2; and SiO₂ [Finkenbeiner Scientific Glass], used to reduce boron and nitrogen impurities in the melts.28 The crucible and melt charges were covered with a flexible graphite sheet [Grafoil, Union Carbide Corporation] to prevent vapor transport of silicon to the fibers prior to immersion.
The compounds used to formulate the melts were elemental silicon and aluminium, molybdenum disilicide, and silicon tetraboride (B₄Si), all of which were obtained from the Alfa Products Division of Johnson Matthey, and were nominally 99.9% pure.

The experiments were done in a graphite resistance heated hot press [Astro Industries Inc. model HP 20]. The fibers were wrapped around a BN plunger, which was mounted to the upper (fixed) ram of the hot press. The temperature was monitored using an optical pyrometer [Leeds and Northrup model 8622-C] calibrated by observing the decrease in reflectance that occurs when silicon freezes. The accuracy was estimated to be ±5 K. The SiC formation reaction is exothermic. However, the temperature of the system is not expected to increase by more than 5 K, as is discussed in Appendix 4. The hot press was heated to 1670 K under vacuum, while further heating was done under flowing helium. The immersion of fibers into the melt was performed under a slight over-pressure of static helium. Alloyed melts were taken through a homogenization cycle of 60 minutes at 100 K above the infiltration/reaction temperature. After cooling and re-equilibrating the melt to the desired reaction temperature, the experiments were initiated. The crucible was raised into contact with the fiber-wrapped plunger, which broke the graphite foil seal and brought the fibers and melt into contact. After the specified time, the furnace was shut off, the crucible lowered, and the reacted sample allowed to cool within the hot press. The time required for the melt-encased samples to cool below the freezing point of the melt was monitored optically, and was found to be 25 seconds at 1803 K, 18 seconds at 1763 K, 12 seconds at 1733 K, and 5 seconds at 1703 K. These values are depicted as error bars in the time of reaction in Figures 3.4, and 3.6.

After cooling, the reacted specimens were mounted in a castable resin, cut through the cross-section and sequentially polished, ending with 1μm diamond paste.

The reaction rate was determined by measuring the area fractions of SiC and carbon observed in the polished cross-sections of partially reacted fibers. The area fraction data
for the P55 fiber samples were obtained using the point counting method as outlined in ASTM E562. This technique involves superimposing a uniform grid of points over random views of the microstructure of the sample. The area fraction of a given phase is equal to the frequency of occurrence of that phase under a grid point, after a statistically valid number of grid points have been counted. A video display system [Ikegami camera and video screen] mounted on an optical microscope [Olympus Vanox-T] enabled efficient area fraction determination. The grid was fastened to the screen, and the fields of view selected at random. 2025 points were counted over 25 fields for each sample in the present work.

The area fraction measurements of the AS4 fibers were done on a Magiscan 2 Image Analysis System. This technique requires the operator to define the "grey level" of each phase. The Image Analyzer then breaks the micrograph up into points, and counts the number of points of the indicated grey level. Error arises in the definition of the grey level, and from the variation in the grey level of a given phase across a micrograph.

The error was calculated following the description of the 95% Confidence Interval in ASTM E562, and is given as $2\sigma/\sqrt{n}$, where $\sigma$ is the standard deviation of the average, and $n$ is the number of fields examined. The error involved in manual point counting was substantially lower than that from the Image Analyzer (3% vs. >10%), primarily due to the large number of points counted.

The extent-of-reaction for a given experimental condition was then obtained from the area fraction measurements. Extent-of-reaction is defined as the molar amount of SiC present, normalized to the total number of moles of carbon in the system (fiber and SiC), with correction made for the difference in molar volume. That is, the observed amount of silicon carbide ($A_{SiC}$) is multiplied by the ratio of the molar volume of the carbon ($V_c$) to the molar volume of SiC ($V_{SiC}$), thereby obtaining the normalized amount of SiC ($A^{*}_{SiC}$):

$$A^{*}_{SiC} = A_{SiC} \left[ \frac{V_c}{V_{SiC}} \right]$$
The majority of the microstructural analysis was done using optical reflectance microscopy, as the major phases (C, SiC, and Si) can be readily distinguished. Scanning electron microscopy (SEM) was done on a Cambridge Stereoscan 250 MK3 equipped with a Tracer Northern TN-5500 energy dispersive X-ray (EDX) analysis system. A JEOL 200 CX transmission electron microscope (TEM) provided higher-resolution images of the reacted fibers. Selected area diffraction was also done in the TEM, identifying the phases present. The TEM results were obtained by S. L. Furcone. A Tracer Northern model TN-1310 wavelength dispersive spectrometer (WDS) on a Cameca MBX electron microprobe provided compositional analysis. The standards used in the WDS analysis were elemental silicon, molybdenum, and aluminium, and SiC was used for carbon. Bulk X-ray diffraction was performed on a Rigaku RU 300 diffractometer.

3.4 Results

3.4.1 Extent of Reaction versus Time

The reduced data from the reaction rate study using P55 graphite fibers and AS4 carbon fibers can be seen in Figures 3.3, 3.4, 3.5 and 3.6. Figure 3.3 shows the effect of increasing temperature on the extent-of-reaction for P55 graphitic fibers in pure silicon melts contained in silica crucibles, at relatively short times (less than 55% transformed). The temperatures used were 1703 K, 1733 K, 1763 K, and 1803 K. The data point identifies the length of time that the sample was in the melt at the temperature reported. The error in the time-of-reaction indicates the time required to cool the reacted fiber to below the freezing point of the melt, as described in Section 3.3. Figure 3.4 shows the effect on the extent-of-reaction of alloying the silicon melts with 3.2% molybdenum and boron at 1803 K, again using silica crucibles and P55 fibers. Figure 3.5 shows longer time-of-reaction data for P55 fibers at 1703 K and 1803 K. These reactions were carried out in silica crucibles and the results quantified using both image analysis and manual point counting.
techniques. In all cases, these two analysis techniques agreed to within the larger
calculated uncertainty, i.e.that of the Image Analyzer. Figure 3.6 shows the extent-of-
reaction vs. time-of-reaction curves for AS4 fibers at 1703 K and 1803 K for times up to
600 seconds. This work was done in BN crucibles, and the extent-of-reaction data were
obtained using image analysis.

Figures 3.5 and 3.6 show that there are three stages in the $\text{C}_s + \text{Si}_l \rightarrow \text{SiC}_s$
reaction: an initial regime with little observed reaction, a period of rapid reaction and SiC
growth, and a final regime with a decreasing reaction/SiC growth rate.

3.4.2 Microstructures of Reacted Fibers

Figure 3.7 shows the surface of a P55 fiber prior to reaction. Figure 3.2 shows the
X-ray diffraction spectra for P55 and AS4 fibers prior to reaction, and contrasts the
crystalline nature of the P55 fiber with the lack of long range order in the AS4. Figure 3.8
is an optical micrograph showing a polished cross section of P55 fibers held in a silicon
melt for 40 seconds at 1703 K. No evidence of reaction is visually observed, either as a
product phase, or as observable erosion of the carbon fibers. Etching away the silicon
$\text{HF} : \text{HNO}_3 : 2\text{H}_2\text{O}$, however, reveals a continuous layer of reaction product at times
as short as 5 seconds (Figure 3.9), and up to 60 seconds (Figure 3.10). X-ray powder
diffraction identified this layer to be the $3\text{-C} (\beta)$ polytype of SiC. X-ray line broadening
analysis indicated a coherence length in the SiC crystals of approximately 56 nm. Coating
the P55 fibers with a commercial $\beta$-SiC powder (Betarundum) prior to these short-time,
low-temperature, melt exposures resulted in the microstructure shown in Figure 3.11.
Notable features in this micrograph include the eroded fiber cores surrounded by the melt,
with SiC (both reaction formed and the “seed” Betarundum) outlining the original fiber:melt
interface. The reduction in fiber diameter indicates that approximately 30% of the fiber
reacted to form SiC when held in the melt for 50 seconds at 1703 K, in contrast to no
visible reaction in the absence of the seed crystals at the same time and temperature (Figure 3.8).

The second stage of this reaction is initiated at longer reaction times and/or increased reaction temperatures, as seen in Figure 3.3. Cross-sections of reacted fibers typical of this period are shown in Figure 3.12. Three distinct regions can be seen: Region 1 is composed of the melt and of large, faceted, SiC crystals observed outside of the original fiber:melt interface. Region 2 lies between the eroded carbon fiber and the original fiber:melt interface, while the third region is the unreacted carbon fiber core. The extent-of-reaction data presented in Section 3.4.1 were obtained by measuring the area fraction of the large SiC crystals in the first region and the unreacted carbon in the third. Wavelength Dispersive X-Ray Spectrometers (WDS) on an Electron Microprobe provided compositional analysis of the second region, indicating it to be 30\% carbon and 70\% silicon (the solubility limit of carbon in silicon at 1800 K is 1.2x10^{-4}).

Etching the silicon from a similar sample provided a more detailed view of the morphology of reacting fibers during the second regime, as shown in Figure 3.13. The structure revealed in this partially reacted fiber shows a granular interior region surrounded by a dense surface layer of SiC at the original fiber:melt interface. Indication of this surface layer (the ring) is seen in typical micrographs taken at various stages of reaction, e.g., Figure 3.12. The fine particles inside this layer were found to contain silicon and carbon by combining the carbon analysis of the WDS, done prior to etching away the residual melt, with silicon found in these particles with the EDX on the SEM. SiC is the only compound in the Si-C system. The size of these particles was estimated from several micrographs to be ~60 nm, with the reaction layer being between 50 and 80 nm thick. This region was also examined by TEM, and the results clearly showed rounded particles of typically 50-70 nm diameter (Figure 3.14). The Selected Area Diffraction pattern of these particles identify them as \( \beta \)-SiC, confirming the conclusion drawn from the composition
data. Figure 3.15 is an SEM micrograph of a faceted crystal in the region outside ring. The melt was removed by acid etching. Figure 3.16 is a TEM micrograph of a similar crystal. Note the presence of defects in this faceted crystal; both line dislocations and planar defects are seen in Figure 3.16.

Thus, the fiber morphology observed during the second stage of this reaction included faceted SiC crystals outside of the original fiber:melt interface, an observable layer at this interface, rounded SiC particles in the silicon melt inside this layer, and the unreacted carbon fiber core.

Later stages of reaction can be seen in Figure 3.17. Note that an observable amount of SiC is found between the carbon and melt. Extremes of this situation can be observed, where unreacted carbon fibers are embedded in the product SiC phase. Fine, rounded SiC particles were observed in the melt still in contact with the carbon in these samples with the TEM (Figure 3.18).

Figure 3.19 shows the microstructures of AS4 fibers at progressively longer times of reaction. Note the similarity in the morphologies seen in these results and those presented for the P55 fibers in Figures 3.12 and 3.17.

Figure 3.20 shows the result when a flat plate of Siggradur G vitreous carbon is exposed to a silicon melt for 40 seconds at 1703 K. Note that the three regions seen in the partially reacted P55 fiber shown in Figure 3.12 are also present in this sample. Again, these regions are: a region of faceted SiC crystals in the melt, the region between the carbon and the original carbon:melt interface, and the unreacted carbon.

The effect of small additions (3.2%) of aluminium to the silicon melt can be seen in the micrograph shown in Figure 3.21. The P55 fibers shown were reacted for 40 seconds at 1803 K. The backscattered electron image was obtained from the microprobe, while WDS provided the elemental aluminum map. An aluminum rich layer can be seen at the melt:carbon interface.
3.5 Discussion

The discussion will begin by addressing the results of the reaction mechanism study presented above, followed by the reaction rate data given in Section 3.4.1.

Figures 3.5 and 3.6 indicated three stages of this reaction, an initial incubation period, a second regime of rapid reaction, and a final regime of decreasing rate. The discussion of the mechanism will follow this reaction sequence.

3.5.1 Mechanism of the Initial Stage

Figure 3.3 shows that an incubation period of little observable reaction exists at temperatures below 1763 K, and that its duration decreases with increasing temperature. This implies that the onset of the rapid reaction regime is initiated by a temperature-dependent process.

Figure 3.7 is a micrograph of a P55 fiber prior to reaction. No grain structure is visible, only the striations caused by drawing the fiber from the die. Figure 3.9 shows the fine grained layer of SiC (grain size on the order of a few hundred nanometers) that formed on this fiber after very short melt exposures. Figure 3.10 was taken just before the onset of the rapid reaction regime, and demonstrates the extent to which this SiC layer grew/coarsened during the incubation period. Thus, a SiC layer formed and grew on the carbon fiber during the initial regime of this reaction, but at rates much below those observed during the second regime.

Extensive reaction occurs when carbon fibers are coated with β-SiC powder prior to reaction, as is shown in Figure 3.11. These fibers were reacted for 50 seconds at 1703 K, which is within the initial reaction regime for uncoated fibers. The rate of this reaction (30% conversion in 50 seconds) indicates an elimination or a reduction of the incubation period, i.e. the second stage of reaction is initiated immediately. The mechanism of growth...
during the second stage of this reaction will be proposed to be the solution and reprecipitation of carbon as SiC in Section 3.5.1.2. As was discussed in Section 3.2, solution growth of SiC is undoubtedly facilitated by ledges or steps on the growing surface, creating energetically favorable growth sites. Commercial SiC typically has approximately $10^6$ dislocations/cm$^2$ (29), or $2 \times 10^{11}$ dislocations/gm of Betarundum (27). Solution growth would be suppressed without the minimum number of such sites. These observations suggest that a limited number of defect sites are present on the reaction layer during the initial regime, thereby suppressing growth from solution.

The SiC reaction product is observed outside of the original fiber:melt interface in Figure 3.11, indicating that a reaction layer formed on the fiber surface. The observation of a reduced fiber core and an increased amount of SiC outside of the reaction layer indicates carbon transport through this layer occurred in times corresponding to the initial reaction regime in uncoated fibers. Similarly, the observation of melt inside this layer implies that silicon transport through the reaction layer also occurs after very short times. This suggests that the initial regime is controlled by something other than carbon or silicon transport through the reaction layer.

Thus, a reaction layer is seen to form and grow during the initial regime of this reaction. Its growth rate is lower than that observed during the second regime, i.e. lower than the solution growth rate. Introduction of a SiC with a relatively high surface defect site density eliminates the initial regime. For these reasons, it is proposed that the initial regime exists until sufficient defect sites are present on the initial reaction layer to sustain solution growth. Furthermore, growth during the initial regime is not expected to be limited by carbon or silicon transport through the layer. Heterogeneous growth of the SiC reaction layer on the carbon substrate via solid state diffusion is expected to produce lateral compressive stresses in the layer, as was proposed in Section 3.2. These stresses may
generate the surface defects sites necessary to sustain solution growth, i.e. induce the onset of the second stage of this reaction.

3.5.2 Mechanism of the Rapid Reaction Regime

The SiC growth mechanism that dominates the second stage of this reaction is suggested by the morphology of the partially reacted fiber seen in Figure 3.13. The fine grained SiC seen in Figures 3.13 and 3.14 is not faceted, indicating it is dissolving into the melt. The amount of SiC seen outside the original fiber:melt interface increases with time. These crystals are faceted, which is consistent with SiC solution growth, as was discussed in Section 3.2. These observations suggest a mechanism of solution-reprecipitation, in which the fine grained SiC dissolves and reprecipitates out on the larger, faceted crystals.

3.5.2.1 Evolution of SiC

Continued reaction of the fibers does not promote successive rings of SiC layers. Instead, individual SiC particles are observed inside the initial reaction layer. This difference in product morphology merits a more detailed discussion of the evolution of both the initial layer and the individual particles.

The formation of β-SiC on carbon substrates immersed in molten silicon is reported to happen in times as short as 0.1 seconds. In the present study, a thin SiC reaction layer is observed to form at this interface in less than 5 seconds. The strains created by the formation of such a volume-expansive layer will induce a lateral compressive stress, the magnitude of which is dependent, in part, on the elastic modulus of the layer and its geometry. A continuous cylindrical SiC layer should form on a smooth carbon fiber (smooth at the scale of the SiC grains) in contact with molten silicon. Such a layer would remain in a state of lateral compression until the formation strains are relaxed, for example, through deformation or failure of the layer. These layers are observed to remain intact.
throughout the reaction (Figures 3.12, 3.13 and 3.17) implying that failure does not occur. Furthermore, deformation through dislocation motion has not been observed in SiC below 1900°C.34 These observations imply that the continuous cylindrical SiC reaction layer that forms on smooth carbon fiber surfaces should remain in a state of lateral compression.

As the reaction proceeds, diffusion of carbon through the continuous layer along grain boundaries will "pit" the fiber, resulting in a rough carbon surface. Forming SiC on such a surface will locally enhance the formation stress, since changes in the substrate curvature on the scale of the (SiC) grains will generate bending stresses in the SiC. These bending stresses should result in additional stress at the particle:substrate interface, inducing failure along that interface, i.e. the spallation of individual particles. Spallation will relieve the lateral compressive stresses generated by the formation reaction. Spallation of SiC from carbon in contact with molten silicon has also been suggested by other investigators.6,30 Thus, the difference in the morphologies of the SiC that forms at the carbon: melt interface (a continuous layer or individual particles) is proposed to be due to differences in the roughness of the carbon surface.

The spallation process should erode the fiber core quickly as fresh carbon is repeatedly exposed to the silicon melt. These particles may not form as equiaxed grains, but rather as platelets. Their high surface area causes the platelets to dissolve into the melt, and to reprecipitate on the faceted SiC crystals outside the ring. This dissolution process results in the rounded particles observed in the SEM and TEM micrographs presented Figures 3.13 and 3.14. The rate of dissolution should increase as the radius of the particle decreases (Equation 3.7), resulting in very few observations of particles much smaller than average.

Thus, the initial SiC reaction layer forms as a continuous cylindrical layer on a smooth cylindrical surface, and remains in a state of lateral compression. The SiC particles
are proposed to form on a rough carbon surface, spall from that surface due to the additional bending stresses induced by the surface roughness, and dissolve into the melt.

3.5.2.2 Absence of SiC Coarsening

The initial reaction layer appears to provide sites for the solution growth of SiC during the rapid reaction regime, while the fine SiC particles do not. Solution growth of SiC has been argued to occur at steps or ledges on the growing surface. At later stages of this reaction, planar defects were seen in the rounded particles (Figure 3.18), supporting the argument proposed in Section 3.2.3 that such defects do not act as sites for solution growth. SiC coarsening inside the initial reaction layer has, however, been observed in a limited number of cases (Figure 3.22). These coarsening events may have been induced by the presence of a defect site on either the inside surface of the initial reaction layer, or on a SiC particle. Coarsening of the fine particles inside the ring should occur at a rate of greater than 1.6x10⁻⁴ cm/sec at 1800 K (see Appendix 2). The observed rate for coarsening of the large crystals outside the ring is significantly lower, 5.4x10⁻⁶ cm/sec at this temperature. Thus, coarsening of the fine particles must be inhibited, suggesting that a barrier to the solution growth of these particles is present.

A lack of defect sites on the surface of the SiC particles would prevent their growth from solution. Since line dislocations intersecting the surface are a possible source of growth sites, their occurrence in SiC is of interest. Stevens³¹ has suggested that the generation and flow of dislocations in β-SiC at room temperature occurs only under the extreme stresses found close to a crack tip during fracture. He also reported finding very few dislocations in SiC by TEM, which was interpreted as being consistent with the high Peierls Energy of covalent solids ³² (see also Appendix 3). The observations made during the initial regime of this reaction support this view. Recall that there was no evidence of solution growth on the initial reaction layer during the incubation period. This was
proposed in Section 3.5.1.1 to be due to a lack of dislocations in this layer. Thus, SiC is very resistant to the generation and flow of dislocations.

Given that the dislocations in the SiC were generated during its formation, the dislocation density in the particles should be comparable to that in the initial SiC reaction layer, since these morphological differences do not imply differences in the SiC formation mechanism. The rate of erosion of the carbon fiber core, i.e. the slope of the extent-of-reaction curve, is much higher during the second regime than during the first. The mechanism of erosion during the second regime is proposed to be the formation and spallation of SiC particles observed to be approximately 60 nm thick. An average time between spallation events can therefore be calculated from the extent-of-reaction curves. The observed rate for P55 fibers at 1703 K (Figure 3.3) indicates that 1 µm of the fiber eroded in 100 seconds, or 35 SiC particles 60 nm thick spalled from the carbon in that time. This results in an average time between spallation events of 3 seconds for a given increment of fiber surface. There was no evidence of solution growth on the initial layer at this temperature at times up to 60 seconds. Thus, solution growth of the fine SiC particles would be inconsistent with the observations made during the initial regime of this reaction.

The observations indicate a lack of surface defect sites, i.e. dislocations, in the SiC that forms at the carbon:melt interface. Line dislocations, unlike point defects, always increase the free energy of the system, thus a dislocation-free body is stable. Nonetheless, such a crystal would be an anomaly, and this proposed lack of dislocations should be further explained.

Image forces are expected to draw a screw dislocation from SiC only if the dislocation is less than 3 nm from the surface (see Appendix 3). Interfaces between dissimilar materials also exert image forces on dislocations, and that between P55 fibers and β-SiC is expected to produce an image force approximately equivalent in magnitude to a free surface image force (Appendix 3). A dislocation that formed at this interface would
then be drawn into the carbon, and repulsed from the SiC. Thus, while the image force is not sufficient to draw dislocations to the surface of the particles as they spall, the interfacial image force may draw dislocations into the carbon substrate during the growth process.

SiC solution growth was observed on the initial layer, while it was not observed on the fine SiC particles. The difference is proposed to be due to the presence or lack of defect sites on each. The literature reports that the generation of dislocations in SiC requires substantial stresses. The particles are thought to be in a stressed state, i.e., constrained by the carbon substrate, for a much shorter time than the initial layer. These stresses are proposed to generate the dislocations required to sustain solution growth. Thus, dislocations are not expected to form in the fine SiC particles, while their eventual presence in the continuous layer is likely.

3.5.3 Final Reaction Regime

Figures 3.5 and 3.6 showed a decrease in the observed reaction rate at extent-of-reaction values above 60%. Figure 3.17 indicated that the SiC reaction product is in contact with the remaining unreacted carbon, effectively inhibiting the flow of silicon to it. The majority of the fibers are not completely encased in SiC, however, indicating limited continued reaction. Rounded SiC particles similar to those seen at earlier stages of the reaction were observed in the melt in contact with the carbon surface (Figure 3.18). These observations are consistent with the proposed mechanism for the rapid reaction regime. Therefore, it is suggested that the observed decrease in reaction rate reflects the increase in the amount of the SiC present, and does not indicate a change in the reaction mechanism.

3.5.4 Non-Graphitic Carbons

Partially reacted AS4 fibers have microstructures very similar to those of the P55
fibers, as is shown in Figures 3.19 for the AS4, and 3.12 and 3.18 for the P55. The AS4 and P55 extent of reaction curves presented in Figures 3.6 and 3.3 are also similar.

The microstructure seen in Figure 3.20 shows the result of exposing a polished flat plate of Sigradur G glassy carbon to a silicon melt at 1703 K for 40 seconds. The original carbon:melt interface can be identified, indicating the presence of the initial reaction layer. The morphology observed is very similar to that of partially reacted fibers. Thus, the results of the AS4 fiber study and the Sigradur G flat plate study suggest that the reaction mechanism proposed for P55 fibers is specific neither to graphitic carbons, nor fibers.

While an identical reaction mechanism has been proposed for the P55 and AS4 fibers, the eventual end point of these reactions appears to be different. At both 1703 K and 1803 K, the AS4 reaction stops abruptly at between 80% and 90% of completion, while the P55 fibers eventually reach 90% conversion. Unreacted AS4 fibers had an 8 μm diameter, while the P55 fibers were 10 μm in diameter. Thus, reaction in both fibers stopped when the unreacted fiber core was approximately 3 mm in diameter. This may be an effect of the curvature of the fiber core, a physical effect of increasing product phase, or a chemical effect, due to differences in the reactivity of graphite and glassy carbon as noted by Hase et al. 6

3.5.5 Summary of the Growth Mechanism

The fine SiC particles inside the ring were observed to be rounded, suggesting that they were dissolving over time. The amount of SiC observed outside the initial reaction layer increases with time, implying these faceted crystals were growing. The observation that the particles do not coarsen is proposed to be due to a lack of preferred growth sites, i.e. dislocations, on the particle surfaces. Dislocations were not expected to form in the fine SiC particles, while they are in the initial reaction layer. Instead, the fine SiC particles become the source of carbon going into solution, enabling the large grains outside the ring
to grow. This process continues until the reaction is complete. At longer times, however, the observed rate decreases due to the SiC product phase physically inhibiting continued reaction. The rate limiting transport mechanism of the coarsening of the fine SiC will be discussed in Section 3.5.3.

3.5.6 Rate Limiting Process in the Rapid Reaction Regime

The rate limiting process of the rapid reaction regime is of interest. The individual mechanisms discussed include silicon and carbon transport through the initial reaction layer, and the surface reaction at the growing SiC interface.

If silicon transport through the initial reaction layer were rate limiting, reaction would consume the silicon as it diffused through the layer. Excess silicon (in the form of melt) would not be observed inside the ring, while pores would be expected to form (the molar volume of silicon carbide is lower than the combined molar volumes of molten silicon and carbon). Figure 3.12 showed a carbon:melt interface to be present inside the layer, while porosity was not. Therefore, it is unlikely that silicon transport through the layer is rate limiting.

Carbon transport is the basis of the proposed reaction mechanism, i.e. the dissolution of fine SiC into the silicon melt, and reprecipitation of carbon on growing SiC crystals. The slope of the extent-of-reaction curves may be interpreted as either the SiC growth rate, or as the carbon flux through the ring layer.

Figures 3.13 and 3.14 show small SiC particles, approximately 60 nm in diameter, that were proposed to act as the source of carbon going into solution. The Thompson-Freundlich equation relates the increased solubility of such particles in a medium in which they are limitedly soluble to the radius of curvature of the individual particle. 

\[
RT \ln(c/p/c) = 2\eta_s M/\rho a
\]

(3.8)
where \( cP \) is the increased solubility around the particle, \( c \) is the equilibrium solubility over a flat plate, \( \gamma_s \) is the liquid-solid interfacial energy, \( M \) is the molecular weight of the particle, \( \rho \) is the density of the particle, and \( a \) is the radius of curvature of the particle. The liquid:solid interfacial energy \( \gamma_s \) may be estimated using the Young-Dupree Equation with the appropriate values of the interfacial energies (\( \gamma \) solid:vapor=2030 ergs/cm\(^2\) \( ^{(36)} \), and \( \gamma \) liquid:vapor=800 ergs/cm\(^2\) \( ^{(37)} \)) and the wetting angle \( \theta \) (40\(^o\)) \( ^{(38)} \) as:

\[
\gamma_s = \gamma_{sv} - \gamma_{sv} \cos \theta
\]

\[
= 1400 \text{ ergs/cm}^2
\]

Combining this value with the experimentally observed value for \( a \), and literature values for \( c \) (1.2x10\(^{-3}\)) \( ^{(17)} \), the increase in solubility at 1800 K is found to be:

\[
cP/c = 1.075
\]

or \( \Delta c = cP - c = 0.075c \)

At 1700 K, \( \Delta c \) is 0.079c, or \( \Delta c \) is roughly proportional to \( c \) over the temperature range investigated, while \( cP/c \) should decrease slightly with increasing temperature.

If the observed rate is limited by mass diffusion, the flux of carbon should be proportional to the gradient in its concentration at steady state. For a constant diffusion distance (\( \Delta x \)), and constant diffusion coefficient \( D \), this results in:

\[
J = -D(\Delta c/\Delta x)
\]

Thus, at steady state, diffusion limited growth should occur at a rate proportional to the absolute difference in solute concentration between the source and the sink.

A surface reaction limited growth process must also be considered. The surface reaction process for SiC growth from solution was argued to be one of growth occurring at defect sites, presumably dislocations, in Section 3.2. The expected rate for screw dislocation growth may be estimated with the following expression: \( ^{(35)} \)

\[
U = a v f [1 - \exp(-\Delta G/RT)]
\]
where \( U \) is the growth rate, \( a \) is the average jump distance, \( \nu \) is the average jump frequency, \( f \) is the density of dislocation sites, and \( \Delta G \) is the free energy change for growth. The growth of SiC from a supersaturated solution of carbon ([C]*) in solution in liquid silicon may be expressed as:

\[
[C]^* + Si_l \rightarrow SiC_s + Si_l + [C]^eq
\]  

resulting in an equilibrium constant \( K \) of:

\[
K = a_{SiC} a_{Si} [a_C]^eq / [a_C]^* a_{Si}
\]  

For the present system, the standard state of silicon is liquid and that of silicon carbide is solid, making their activities equal to 1. \( \Delta G \) of this process is therefore dependent on the level of carbon supersaturation in the melt. \( \Delta G = 0 \) when the concentration of carbon in the melt is equal to the equilibrium solubility limit. Increasing the solute concentration beyond the equilibrium limit increases the activity of the solute in solution above that of solute in the solid, creating a driving force for crystallization. The upper bound for the increased activity of carbon in solution is the increase in solubility over small particles, \( c_P \), resulting in the following expression for \( \Delta G \):

\[
\Delta G = -RT\ln(c/c_P)
\]  

Combining this expression for \( \Delta G \) with the expected screw dislocation growth rate (Equation 3.11), the predicted rate is:

\[
U = avf [1-\exp (RT\ln(c/c_P)/RT)]
\]  

\[
= avf [1-(c/c_P)]
\]  

Thus, surface-reaction limited growth is dependent on the relative increase in solute concentration in the melt \( [1-(c/c_P)] \), while diffusion limited processes are dependent on the absolute increase \( (c_P - c) \). The ratio of the solubilities \( c_P/c \) was shown to be approximately constant over the temperature range investigated (1700 K to 1800 K). The resultant surface-reaction limited growth rate should also remain constant (assuming a constant \( \nu \) and \( f \)). In contrast, the absolute difference in concentration \( (c_P-c) \) has a three fold increase over
the same temperature interval. The effect of increasing the reaction temperature on the extent-of-reaction was shown in Figure 3.3. The constant initial slope seen during the rapid reaction regime indicates a constant growth rate of SiC. These rates have been plotted against the carbon solubility in molten silicon at their respective temperatures in Figure 3.23. As can be seen, the observed rate of SiC growth increases linearly with the absolute carbon concentration. This is suggestive of a diffusion controlled process, although control by a surface reaction mechanism that is first order in the carbon concentration would also be consistent with this result.

3.5.6.1 Rate of Diffusion Controlled Growth

Estimation of diffusion controlled growth rates requires definition of the geometry of the system. The SiC particles are the source of carbon going into solution, and the faceted SiC crystals growing outside the ring layer are the sink. The transport mechanism of carbon through the ring layer is therefore of interest. One possible mechanism is the solid state diffusion of carbon along grain boundaries through the β-SiC reaction layer. Taking appropriate values for \( D \) (2 \( \times \) 10\(^{-9}\) at 1800 K\(^{(2)}\), the diffusion distance, \( \Delta x \) (50 nm from Figure 3.13), and the area fraction of grain boundaries, \( A_{gb}/A_t \) (0.075 based on a model of a square array of square, 50 nm columnar grains separated by 2 nm grain boundaries), the expected carbon flux at steady state from the source SiC particles to the sink SiC crystals is found to be:

\[
J = -D(A_{gb}/A_t) \frac{\Delta c}{\Delta x}
\]

\[
= 2.7 \times 10^{-9} \text{ cm}^3/\text{cm}^2\text{sec}
\]

\[
= 9.5 \times 10^{-9} \text{ gm/cm}^2\text{sec}
\]

The actual grain size in the ring is larger and the grain boundary width smaller than these assumed values, making the estimation of the \( A_{gb}/A_t \) term an upper limit, which makes the predicted flux an upper limit as well. The density of diamond (3.52 gm/cm\(^3\)) was used to
convert the dimensions of the predicted flux, since the model describes growth of carbon in a silicon melt. The flux calculated above is three orders of magnitude below that observed \(5.2 \times 10^{-6} \text{ gm/cm}^2\text{sec}\), making it is doubtful that solid state diffusion of carbon along grain boundaries in the ring layer is occurring during the second stage of this reaction.

Alternatively, liquid phase transport through the ring layer would be consistent with the mechanistic observations made. Penetration of the melt at triple grain junctions in the ring layer would provide the necessary path. The microstructures presented by Ness and Page\(^7\) show that the silicon melt partially wets the carbide. Minnear\(^4\) reports that the \(\beta\)-SiC layer that forms on carbon in contact with molten silicon is one crystallite layer thick. This would result in fast transport "pipelines" through this layer at triple junctions. Penetration of the melt along triple junctions in the ring layer is consistent with the available wetting data, the observation of an apparently solid layer, and the necessity of a fast transport path for both carbon and silicon through this layer.

Determination of the expected rates for such a system requires estimation of the geometry of the porous ring layer. Assuming 25 nm square holes at the junctions of 1\(\mu\)m square grains in a square array corresponds to an area fraction of liquid phase to solid phase, \(A_l/A_t\), in the ring layer of 0.06\%. Taking appropriate values of \(D_l\) (2\(\times\)10\(^{-4}\) at 1800K\(^39\)), the diffusion distance \(\Delta x\) (60 nm in Figure 3.13), and \(\Delta c\) (0.075 \(\times\) 1.2\(\times\)10\(^{-3}\))\(^{17}\) the expected rates are:

\[
J = -D_l \frac{A_l}{A_t} \frac{\Delta c}{\Delta x}
\]

\[
= 1.8 \times 10^{-6} \text{ cm}^3/\text{cm}^2\text{sec}
\]

\[
= 6.3 \times 10^{-6} \text{ gm/cm}^2\text{sec}
\]

The experimental value at this temperature is 5.2 \(\times\)10\(^{-6}\) gm/cm\(^2\)sec. Thus, a model system that is rate limited by the diffusion of carbon in molten silicon through a porous initial reaction layer predicts rates that agree with the experimentally obtained values. It is acknowledged that there is considerable freedom in selecting the relative area of the liquid
phase ($A_f/A_i$), making this agreement necessary but not sufficient to prove the proposed model.

3.5.6.2 Rate of Surface Reaction Controlled Growth

Estimation of the bounding growth rates expected in a surface reaction controlled system can be done as follows. The growth rate for a defect site mechanism was given in Equation 3.16 as:

$$ U = \alpha v f \left[ 1 - (c/c_P) \right] $$

A defect-free surface has no ledge sites, resulting in $f$ being zero. Thus, the lower bound on the surface reaction limited growth rate is zero. Estimating the upper bound of the growth rate for a surface reaction controlled process requires quantifying the level of supersaturation ($c_P/c$) at the growth site. This value must be less than that over the source particles ($=1.075$ at 1800 K), making this the upper limit of ($c_P/c$). Thus:

$$(c_P/c)_{\text{max}} = 1.075$$

The jump frequency ($v$) can be estimated from the viscosity of silicon, $\eta$, (0.94 mN sec m$^{-2}$)$^{(40)}$ and the following expression:$^{35}$

$$ v = kT/3\pi a^3\eta $$

$$ = 10^{14} \text{ sec}^{-1} \text{ at 1800 K} $$

Jackson$^{15}$ pointed out that the minimum curvature of a growth spiral of a screw dislocation is the radius of the critical nucleus for surface nucleation growth. The spiral of minimum curvature will have the maximum number of ledge sites. The distance between consecutive ledges on such a growth spiral is therefore of order $a n^*$, where $a$ is the interatomic spacing and $n^*$ is the number of atoms in the critical radius. Thus, for a unit length of spiral, the number of ledge sites is $a$, and the number of total sites on the surface is $a n^*$, making the maximum site density on the surface ($n^*$)$^{-1}$. The $n^*$ for the present
system was calculated to be 15 atoms in Section 3.2.2.3, which corresponds to a maximum value for the site density (f) of 0.06.

Estimating a to be 3Å allows calculation of the limiting growth rate expected from a screw dislocation growth mechanism:

\[ U_{\text{max}} = 7.7 \times 10^3 \, \text{cm/sec} \]
\[ U_{\text{min}} = 0 \, \text{cm/sec} \]

Thus, a wide range of absolute growth rates has been predicted from surface reaction kinetics. This criterion is, therefore, of little use in excluding surface reaction as a possible rate limiting mechanism in the growth process.

3.5.6.3 Summary - Rate Limiting Process

The presence of a melt:carbon interface indicated that silicon transport was not rate limiting in this system. The temperature dependence of the observed rate was correctly predicted by the kinetics describing carbon diffusion through the melt. Models based on carbon diffusion in molten silicon through a porous initial reaction layer predicted absolute rates in agreement with those observed. Surface reaction kinetics predicted a range of rates that was too large to be used as an indicator of the rate controlling mechanism. Thus, the growth of SiC appears to be rate limited by the diffusion of carbon in the melt through the porous reaction layer.

3.5.7 Dopant Effects

The effects of small additions (3.2%) of boron and molybdenum to the melt on the extent-of-reaction were presented in Figure 3.4. As was seen, these additions change the observed rates very little. The effect of adding equal amounts of aluminum to the melt was seen in Figure 3.20. This backscattered electron micrograph and corresponding EDX elemental Al map indicate that an aluminum-rich layer forms around the fibers at short
times. This layer, presumably Al₄C₃, inhibits the formation of SiC. The enthalpy of
formation of Al₄C₃ at 1800 K is -91.6 kJ/gm.atom C⁴¹, while that of SiC is -123
kJ/gm.atom C⁴¹ making SiC thermodynamically favored at this temperature. At longer
times SiC is observed, suggesting that the initial formation of Al₄C₃ was kinetically
favored.

Thus, aluminum additions may be interpreted as effectively extending the
incubation regime of the reaction. The rapid reaction regime was proposed to be rate
limited by the diffusion of carbon through the melt. This process depends on the solubility
of carbon in the melt, the carbon diffusion coefficient in liquid silicon, the SiC layer
thickness and permeability, the particle size of the primary SiC, and the SiC:Si interfacial
energy. Those variables not likely to be affected by small additions to the melt include the
diffusion coefficients and the layer thickness and particle size. The parameters that may be
sensitive to small additions to the melt include the solubility and the SiC:Si interfacial
energy.

The solubility of carbon in silicon is very low in the temperature range examined.
Small additions to a melt are not expected to change its solubility greatly.⁴¹ Thus, doping
to control the reaction rate through the melt solubility is not likely to be effective.

Small amounts of dopants can affect the interfacial energies, however.⁴²
Segregation of a dilute second component to a surface is driven by a decrease in the
interfacial energy. Thus, small additions of dopants can only decrease the interfacial
energies of the system. Such a decrease in the γₛ would result in a decrease in the
observed reaction rate, given that the present interpretation is correct. Therefore, doping
the melt may decrease the observed reaction rate in the second stage of this reaction by
decreasing the melt:SiC interfacial energy.

In short, since the rate of the C - Si reaction is expected to depend on the SiC:melt
interfacial energy. Controlling this property would be one way to control the reaction rate.
A desirable dopant would have a low $\Delta H_f$ for carbide formation and would lower the SiC:melt interfacial energy.

3.6 Conclusions: Carbon - Silicon Reaction Kinetics

The $\text{C(s)} + \text{Si(l)} \rightarrow \text{SiC(s)}$ reaction is seen to occur in two successive regimes. A continuous SiC layer forms on the carbon surface during the first seconds of the initial regime. This layer is observed to grow/coarsen during this regime, but at a lower rate than is observed during the second regime of this reaction. The duration of the initial regime decreased with increasing temperature. This incubation period is not observed if commercial $\beta$-SiC powder is introduced to the system prior to reaction. For these reasons, it is proposed that the incubation period reflects the time required to generate the surface defect sites necessary to maintain growth from solution.

Growth during the second regime was observed to be a two-step process. Primary SiC particles formed at the melt:carbon interface, spalled from the interface and coarsened into faceted crystals outside the initial reaction layer. The formation kinetics of the primary SiC particles ($\text{C(s)} + \text{Si(l)} \rightarrow \text{SiC(s)}$) were not observed to be rate limiting. The pertinent reaction is $\text{SiC(s)} \rightarrow [\text{C}]_{\text{Si}} + \text{Si(l)} \rightarrow \text{SiC(s)}$ and is driven by a decrease in the liquid:solid interfacial area. The defect site growth model was shown to be an appropriate description for SiC growth from solution. Carbon diffusion controlled kinetics correctly predicted the observed temperature dependence of the growth rate during this period. Transport models based on liquid phase diffusion of carbon through a porous initial reaction layer predicted rates that were within an order of magnitude of those experimentally observed. The expected kinetics of a surface reaction controlled system predicted a wide range of absolute rates, making them of questionable use in determining the reaction mechanism. Silicon transport through the ring layer was argued not to be rate limiting.
The reaction continues until it is physically inhibited by the product phase. The reaction mechanism at longer times was seen to be identical to that described for the rapid reaction regime. The observed rate decreased due to SiC product preventing the flow of one reactant to the other.

Observations made on turbostratic carbon fibers are consistent with the mechanism described above. The microstructures of partially reacted flat plates of vitreous carbon are similar to those of graphitic fibers.

Small additions of molybdenum and boron to the melt had little effect on the observed reaction rate. Aluminum additions formed an aluminum rich layer around the fibers at short times that physically impeded the reaction.

Thus, the competing views found in the literature are seen to be appropriate at various stages of this reaction. It is primarily a solution-reprecipitation process, as suggested by Ness and Page;\(^7\) while it also involves the formation of SiC at the melt:carbon interface, as reported by Fitzner and Gadow,\(^3\) and Minnear.\(^4\)
Figure 3.1  Si and C Diffusion Coefficients in $\beta$-SiC (from Hon and Davis, references 1 and 2).
Figure 3.2  X-ray diffraction spectra of P55 and AS4 fibers. The P55 spectra is indicative of graphite, while that of the AS4 indicates a glassy carbon.
Figure 3.3  Extent of Reaction plotted against Time of Reaction for P55 fibers in silicon melts, for varied reaction temperatures (1703 K, 1733 K, 1763 K, and 1803 K).
Figure 3.4  Extent of Reaction plotted against Time of Reaction for P55 fibers reacted at 1803 K with a pure silicon melt, a Si-3.2\% Mo melt, and a Si-3.2\% B melt.
Figure 3.5  Extent of Reaction plotted against Time of Reaction for P55 fibers reacted at 1703 K and 1803 K with pure silicon melts.

Figure 3.6  Extent of Reaction plotted against Time of Reaction for AS4 fibers reacted at 1703 K and 1803 K with pure silicon melts.
Figure 3.7  P55 fiber surface prior to reaction. The striations are a result of the drawing process used in fiber production.

Figure 3.8  Cross-section of P55 fibers in silicon after reaction for 40 seconds at 1703 K with a silicon melt. Little reaction product or erosion of the fiber is visible.
Figure 3.9  SiC reaction layer seen on P55 fibers after reaction for 5 seconds at 1703 K. Melt removed by acid etch.

Figure 3.10  SiC reaction layer seen on P55 fibers after reaction for 60 seconds at 1703 K. Melt removed by acid etch.
Figure 3.11  Cross-section of P55 fiber coated with Betarundum SiC powder prior to reaction with a silicon melt for 50 seconds at 1703 K. Note the decrease in the fiber diameter, indicating reaction occurred.

Figure 3.12  Cross-section of P55 fiber typical of second stage of reaction (rapid reaction regime). Notable features include SiC crystals forming in the silicon melt, and an eroding carbon fiber.
Figure 3.13  SEM micrograph of a P55 fiber during the second stage of reaction (silicon melt removed by acid etchant).
Figure 3.14  TEM bright field micrograph of particles seen in Figure 3.13. Selected Area Diffraction identified them to be fine grained $\beta$-SiC.
Figure 3.15  SEM micrograph of SiC crystal growing in the silicon melt from the original fiber surface. Melt removed by acid etch.

Figure 3.16  TEM bright field micrograph of SiC crystal similar to that in Figure 3.15, showing both planar (P) and line (l) defects, as indicated by the arrows.
Figure 3.17  Cross-section of P55 fibers at later stages of reaction (575 second in a silicon melt at 1703 K).

Figure 3.18  TEM of SiC particles found in samples at longer time of reaction. Note the similarity between these particles and those found in samples reacted for much shorter times (Figure 3.14).
Figure 3.19  Cross-section of AS4 fibers after reaction in silicon melts for a) 40 seconds, b) 145 seconds, and c) 375 seconds, all at 1703 K.
Figure 3.20  Cross-section of a flat plate of Sigradur G glassy carbon exposed to a silicon melt for 40 seconds at 1703 K.
Figure 3.21  Backscattered electron image of cross-section of P55 fibers reacted with a Si-3.2% Al melt for 40 seconds at 1803 K, with the corresponding elemental Al EDX map.
Figure 3.22  SiC growing inside the original melt:fiber interface, possibly indicating coarsening of the fine SiC particles.
Figure 3.23  Linear rate from Figure 3.3 showing a linear dependence on the equilibrium carbon solubility in silicon at the respective temperatures.
Chapter 4 Conclusions

This chapter draws together the results of the preceding three chapters, and makes suggestions for improving the processing of RBSC based materials. The conclusions drawn in the previous chapters will be summarized, and future processing direction given. Other alloying systems will be briefly discussed, and suggestions for future work will be made.

4.1 Summary of Thesis Results

The concept of alloyed-melt reactive-infiltration, i.e. the addition of refractory silicide forming metals to the silicon melt, and reactively infiltrating carbonaceous preforms with the alloyed melt thereby replacing the residual silicon with a more refractory silicide, was demonstrated in the initial phase of this work. Both refractory coatings and bulk materials were produced, proving the potential of this process.

The infiltration kinetics of reactive fluid flow were developed and used to interpret experimental results. The models developed assumed a specific rate dependence of the porosity in the preform; however, the general conclusions are independent of these specifics, beyond stating that the porosity decreases with time. These conclusions concern maximizing the ultimate infiltratable length \( L \) of a porous material, and indicate that it can be achieved by increasing the pore size of the material and/or decreasing the reaction rate. The results of the infiltration experiments were consistent these predictions. Furthermore, the effect of the silicide precipitation was observed and proposed to physically impede both the extent of reaction and fluid flow. Thus, these results suggest that RBSC processing can be optimized through minimizing the infiltration temperature, tailoring the pore size for the desired properties (fine scale microstructures and complete reaction are more readily obtainable with smaller preform pore dimensions, while larger macroscopic dimensions
with more uniform phase distributions require larger preform pore structures), and alloying with those elements in amounts that will result in dense, refractory reacted bodies.

The kinetics of the $\text{C}_3(\text{s}) + \text{Si}_4(\text{l}) \rightarrow \text{SiC}_4(\text{s})$ reaction were also investigated. The results of primary interest to improved processing include the following. An incubation period was observed, during which time the SiC growth rate was lower than that observed during the solution growth stage. This period continues until sufficient surface defect sites are present in the system to sustain growth from solution. The length of the incubation period is maximized, and the eventual solution growth rate is minimized when the reaction temperature is minimized. Furthermore, alloying with aluminum suppresses the observed rate through formation of an $\text{Al}_4\text{C}_3$ layer at the melt:carbon interface, while additions of molybdenum and boron have little effect.

Thus, the results of the reaction kinetics study indicate that the temperature should be minimized, and that SiC should not be used as a non-reactive "filler" phase, as commercially available SiC would provide defect sites for solution growth, thereby eliminating the initial regime.

Taken together, the results of this work lead to the following processing directions:

1) Infiltration temperature should be minimized to maximize the sample uniformity.

2) Microcrystalline graphite should be used as the preform carbon source.

3) Non-reactive fillers should not provide sites for the solution growth of SiC.

The minimization of the infiltration temperature is indicated directly by observation of the bulk infiltrations; and indirectly through the coupled results of the temperature dependence of the rate with the model describing an inverse relation between rate and infiltrated length. Graphite is both relatively dense and reactive. This allows the pore size to be maximized and the relatively thick pore walls to be fully reacted. An appropriate non-reactive "filler" for the present system would be MoSi$_2$. It has a high heat capacity, is chemically compatible with the system, and provides high temperature ductility, making it an ideal
candidate for higher volume loading than can be obtained by single phase melt reactive-infiltration done at the minimum temperatures.

4.2 Application to Other Alloy Systems

The alloying element should not form carbides preferentially to silicon, and the anticipated silicide should be more refractory than silicon. These initial considerations eliminate all but a handful of potential alloying elements. The transition metals of group IV A (Ti, Zr, and Hf) and VA (V, Nb, Ta), and boron all form more stable carbides than does silicon.\textsuperscript{1} Refractory silicide formers include B, C, group IV A and V A metals, and Mo, W, Re, Ru, Th, and most likely Os.\textsuperscript{1} Combining these two criteria results in surprisingly few choices - Mo, W, Re, Ru, Th, and Os.

Refractory silicides are not necessarily useful high temperature materials. Oxidation resistance must also be considered, with MoSi\textsubscript{2} being among the most resistant. The oxidation resistance of the disilicides of rhenium and osmium are expected to be comparable to that of molybdenum, since they also have a high silicon content and highly volatile metal oxides.\textsuperscript{1} Tungsten disilicide is also expected to be relatively resistant to oxidation, due to its chemical and structural similarity to MoSi\textsubscript{2}. Thus, those metals which form refractory, oxidation resistant silicides are Mo, W, Re, and Os.

Finally, the cost of the potential silicide former must be considered if this process is to be commercially attractive. Rhenium and osmium are relatively expensive, both being on the order of tens of dollars per gram.\textsuperscript{2} Alternatively, tungsten and molybdenum sell for less than one dollar per gram, based on laboratory quantities.\textsuperscript{2} The density of WSi\textsubscript{2} is higher than that of MoSi\textsubscript{2} (9.3 gm/cm\textsuperscript{3} vs. 6.3 gm/cm\textsuperscript{3}), but WSi\textsubscript{2} is also more refractory than MoSi\textsubscript{2} (melting points of 2433 K and 2303 K respectively).\textsuperscript{3} Thus, tungsten and molybdenum are the most likely candidates for alloying additions to silicon-based melts used in reactive-infiltration of porous carbons.
4.3 Future Work

While each section of this thesis could be expanded and developed further, the following areas show particular promise.

Two important effects were ignored in the models developed: the heat generated during reaction and the decrease in volume upon reaction as it affects the infiltrated lengths. Both are complex problems, and the latter will be discussed first.

The incorporation of an additional "sink" term (R) in Darcy's Law will reflect the reaction and resultant consumption of the melt:

\[ Q' + R = -K\Delta P/\eta IP_0 \]  \hspace{1cm} (4.1)

where \( R = R(l,t) \) and describes the amount of fluid that flows in under the applied pressure \( \Delta P \), but is consumed by reaction and does not advance the infiltration front. Again, \( Q' \) is the volumetric flow rate inside the pores of the material, \( K \) is the preform permeability, \( \eta \) is the melt viscosity, \( l \) is the infiltrated length, and \( P_0 \) is the porosity at the infiltration front, i.e. the initial porosity. The hydrostatic nature of pressure created by the consuming reaction on the fluid in the pores will modify the pressure term as well, making it spatially dependent.

The heat flow problem (and resultant second phase precipitation) is also complex and would result in temperature gradients across the sample. This would lead to a spatially varying reaction rate, since the reaction rate is temperature dependent. The precipitation of the second phase from the melt may not be isothermal, as was assumed, making the heat of reaction dependent on the melt composition as well. The local increase in temperature will be most likely be highest in the center of the sample, since it is farthest from the heat sink (bulk melt). This self-heating will be most severe immediately after infiltration, since the unreacted carbon preform is relatively insulating (thermal diffusivity \( \alpha \) of the glassy carbon preforms infiltrated in Chapter 2 is 0.02 cm\(^2\)/sec\(^4\)), while the SiC reaction product is
relatively conductive ($\alpha = 0.31 \text{ cm}^2/\text{sec}$). Possible outcomes of the resultant temperature gradient include thermal stress cracking, gradients in second phase distribution, and a decrease in the expected porosity gradient, since this gradient is due to differing extent-of-reaction levels across the sample when reaction closes the surface porosity. Minimizing the self-heating problem can be done in a number of ways, including increasing the amount and size of the porosity (molten silicon also has a high thermal diffusivity $\alpha = 0.28 \text{ cm}^2/\text{sec}$), adding a non-reactive second phase to the preform to dilute the heat generated per unit volume, and decreasing the reaction rate through decreasing the infiltration temperature.

Direct measurement of infiltration velocities would also be extremely useful data, as it would provide direct confirmation of the results predicted by the models. This would have to be done prior to any more detailed interpretation of these predicted results.

The continued development of reactively-formed bulk materials is probably the most promising area for future work. Following the direction given earlier, substantial progress toward refractory, high strength materials should be possible. Focussing on preform development, specifically graphite-MoSi$_2$, would be the logical next step. The science of powder processing is quite advanced, making preform development using powder methods entirely feasible.

The kinetics of the $\text{C}_(s) + \text{Si}_(l) \rightarrow \text{SiC}_(s)$ reaction could also be further explored. Particularly, the mechanism of the transition between the incubation period and the rapid reaction regime should be clarified. Suppressing this transition would effectively decrease the reaction rate, thus increasing the uniformity of the materials produced. Also, the generation and flow of dislocations in SiC should be further investigated, in particular of SiC in the presence of molten silicon.
Thus, the kinetics of the reactive-infiltration of silicon based melts into carbonaceous preforms has been explored. The conclusions and suggestions given above are intended to further the development of this promising class of refractory materials.
Appendix 1 Increase in Reaction Rate at the Liquidus Boundary

The rate of product formation in this system is determined by the rate of the controlling chemical reaction: Si + C → SiC. Infiltrating in a single phase melt results in the formation of SiC, and enrichment of the remaining melt in molybdenum. When the melt composition reaches that of the liquidus boundary, MoSi₂ begins to precipitate out, pinning the melt composition at the liquidus. Assuming no solid solution of Mo in SiC, and stoichiometric product phases, the following mole fractions of SiC and MoSi₂ will form at the liquidus:

\[
\begin{align*}
X_{\text{SiC}} &= \frac{1 - 3C_{\text{Mo}}}{1 - 2C_{\text{Mo}}} \quad \text{and} \quad X_{\text{MoSi}_2} = \frac{C_{\text{Mo}}}{1 - 2C_{\text{Mo}}} \\
\end{align*}
\]

where \(C_{\text{Mo}}\) is the molar concentration of molybdenum in the liquid phase. This composition is constant and pinned by the liquidus in an isothermal system.

The rate of product formation at the liquidus is then the sum of the SiC and MoSi₂ rates \((k_{\text{SiC}}, k_{\text{MoSi}_2})\):

\[
k_t = k_{\text{SiC}} + k_{\text{MoSi}_2}
\]

\[
k_{\text{SiC}} \left(1 + \frac{C_{\text{Mo}}}{1 - 3C_{\text{Mo}}} \right)
\]

or,

\[
k_{\text{MoSi}_2} = k_{\text{SiC}} \left(\frac{C_{\text{Mo}}}{1 - 3C_{\text{Mo}}} \right)
\]

Assuming \(k_{\text{SiC}}\) is not affected by the precipitation of MoSi₂, the increase in product formation rate reaching the liquidus is:
\[ \Delta k = k_{\text{liquidus}} - k_{\text{single phase}} \]

\[ = (k_{\text{SiC}} + k_{\text{MoSi2}}) - k_{\text{SiC}} \]

\[ = k_{\text{SiC}} \left( \frac{C_{\text{Mo}}}{1 - 3C_{\text{Mo}}} \right) \]

which is constant, given the above assumptions.

A typical value for \( C_{\text{Mo}} \) in the area of interest in the Si - Mo diagram is 0.1, which results in a 14% rise in the molar rate of deposition upon reaching the liquidus. Correcting for the difference in molar volumes gives a volumetric deposition rate increase of 27.6%.
Appendix 2 Coarsening of SiC

Greenwood\(^1\) expressed the rate of coarsening of a system of highly dispersed particles with a uniform size distribution as:

\[
\frac{da}{dt} = [2DCM\gamma/RT\rho^2a] (1/a_m - 1/a)
\]

where \(D\) is the diffusion coefficient of the solute in the matrix, \(C\) is the solubility over a flat plate of the solute in the matrix, \(M\) is the molecular weight of the particle, \(\gamma\) is the particle:matrix interfacial energy, \(\rho\) is the density of the particle, \(a_m\) is the arithmetic mean particle radius, and \(a\) is the radius of any given particle. This model assumes that the interfacial tension does not vary with particle size, and that the rate is diffusion controlled. Using literature values for \(D \ (2 \times 10^{-4})^2\) and \(C \ (1.2 \times 10^{-3})^3\), estimating \(\gamma \ (1400\ \text{ergs/cm}^2\) in Section 3.5.6), and assuming the largest particles in the system to be 110\% of the average, which is estimated to be 30 nm (Figures 3.13 and 3.14), the coarsening rate of the largest particle is expected to be \(1.6 \times 10^{-4}\ \text{cm/sec}\) at 1800 K. The coarsening rate should increase continuously with particle size for particles in the range \(a_m < a < 2a_m\).\(^1\) Thus, the largest particles in the above example will have the fastest coarsening rate, since they are still less than twice the mean size.

The assumption of highly dispersed particles is troublesome in the present application. The assumption that the rate is diffusion controlled implies a dependence of that rate on the area to length ratio of the diffusion field. Increasing the volume fraction of particles from "highly dispersed" to that indicated by Figure 3.13 will decrease the diffusion distance, thereby increasing the expected rate. Thus, the above rate may be taken as an effective lower limit to the expected coarsening rate of the small SiC particles inside the ring.
Appendix 3  Dislocations in SiC

The presence of dislocations in a material result in severe strains at the dislocation core. The stress required to generate a dislocation will be dependent on the material's resistance to deformation. This resistance is known as the Peierls Stress, and is roughly proportional to the shear modulus for materials of similar bond energies. The Peierls Stress for covalent solids is roughly $10^{-2}$ $\mu$, while that of softer metals is on the order of $10^{-4}$ $\mu$. The shear moduli of $\beta$-SiC and P55 fibers (radial direction) are 233 GPa, and 2.3 GPa respectively.

At temperatures above approximately half the melting point, the Peierls Energy of covalent solids decreases exponentially with temperature. However, this critical temperature has been estimated to be greater than 1900°C for $\beta$-SiC. The temperatures of the present system are therefore not expected to decrease the Peierls Energy below $10^{-2}$ $\mu$ ($\approx$ 2 GPa).

The virtual force known to act on dislocations close to a free surface is referred to as the image force. The image force on a screw dislocation is given as:

$$\sigma = \mu b/4\pi l$$  \hspace{1cm} (A3.1)

where $b$ is the magnitude of the Burgers vector (3.1 Å for $\beta$-SiC), and $l$ is the distance to the surface. Setting this attractive force ($\sigma$ in equation A3.1) equal to the restraining force of the lattice (Peierls Stress), the critical distance $l$ from which a dislocation is pulled to the surface is found to be 2.5 nm for SiC.

Thus, dislocations cannot be supported in $\beta$-SiC if they are within 2.5 nm from the surface. Again, the high Peierls Energy of SiC prevents the flow of dislocations, except under a substantial stress, i.e. $\sigma > 2$ GPa. The fine SiC particles observed in partially reacted fibers are an order of magnitude larger than this critical size, and therefore a line dislocation could be stable if present.
Head has shown that the image force acts on dislocations close to an interface between two materials as well. The magnitude of this interfacial image force is that of the free surface image force reduced by a factor which depends on the shear moduli of the two materials: $(\mu_1 - \mu_2)/(\mu_1 + \mu_2)$ for materials 1 and 2. For a free surface $\mu_2 = 0$, and the reduction factor is unity. Therefore, a dislocation generated in the SiC very close to the graphite:carbide interface would experience an attractive image force drawing it into the graphite, and a repulsive force preventing it from gliding further into the SiC. While the particles in the melt were too large for their presumed lack of dislocations to be explained by image forces, the interfacial image force may have drawn any dislocations out during the growth process, resulting in dislocation-free particles.
Appendix 4 Temperature of Reaction

Reactions of the type solid + fluid -> solid are necessarily exothermic if the reaction is to proceed spontaneously (ΔS < 0). The ΔHf for β-SiC at 1800 K is -32.4 kcal/mole \(^1\), indicating that a substantial amount of heat is generated during reaction. The assumption of a constant temperature during reaction is therefore questionable.

Estimation of the increase in temperature around reacting fibers was done using a model of a continuous, constant line source of heat in an infinite solid.\(^2\) The temperature rise \(v\) a distance \(r\) from the source after a time \(t\) is given as: \(^2\)

\[
v = \frac{-q}{4\pi K} \text{Ei}(-r^2/(4\kappa t)) \tag{A4.1}
\]

where \(q\) is the rate of heat generation, \(K\) is the thermal conductivity of the solid, \(\kappa\) is the thermal diffusivity of the solid, and \(\text{Ei}\) is the exponential integral. The thermal properties of molten silicon were used for the solid (\(K=0.15\) cal/sec cm K, and \(\kappa=0.28\) cm\(^2\)/sec) \(^2\), and an upper bound on the heat flux from the fibers was estimated by doubling the highest observed fiber reaction rate (1803 K in Figure 3.3) and multiplying by the ΔH of reaction. This results in \(q=0.22\) cal/cm sec, and corresponds to complete conversion of the fiber to SiC in 40 seconds. An upper bound for reaction-heating in this system was found to be 2.0 K at a distance of 1 μm from the source after 40 seconds. This ΔT is seen to increase slightly with time, and remain virtually constant over the distances of interest. This indicates that the thermal conductivity of molten silicon is high enough to transport heat away faster than it is generated in the present system. This calculation, coupled with the constant initial rates seen in Figure 3.3, support the assumption of constant reaction temperature.
Appendix 5  Reynolds Number Estimation

Darcy's Law assumes that the pressure drop in the fluid is caused primarily by viscous rather than inertial losses.\(^1\) The Reynolds number may be interpreted as the ratio of viscous to inertial effects, and has been used as an indicator of the validity of Darcy's Law. A Reynolds number of less than one is generally accepted as consistent with the assumptions made by Darcy.\(^2\) The Reynolds number is given as:\(^2\)

\[
Re = \frac{\nu d}{\eta} \tag{A5.1}
\]

where \(\nu\) is the velocity of the fluid with density \(\rho\), and viscosity \(\eta\), flowing in a pore of dimension \(d\).

Estimating the Reynolds number for the reactive-infiltration of silicon into microporous glassy carbon preforms can be done using the results presented in Chapter 2. The infiltration curves presented in Figures 2.2 and 2.3 show a decreasing slope, and therefore a decreasing fluid velocity inside the pore structure. Taking the initial portion of these curves as an upper limit on the expected velocity, a value of 3 cm/sec is obtained. A typical pore dimension for the microporous preforms infiltrated is 1\(\mu\)m. Using literature values for the viscosity (9.4 \(\times\) 10\(^{-3}\) poise)\(^3\) and density (2.5 gm/cm\(^3\))\(^4\), a Reynolds number of 0.08 is obtained. This value will decrease rapidly as the infiltrated length increases, since the fluid velocity decreases. Thus, the Reynolds numbers expected for the present case are within the range assumed by Darcy.
References

Chapter 1


Chapter 2


Chapter 3


24 Personal communications, J. Barr, Union Carbide Corp.


26 Siggradur G Product Literature 02 87/4E, SIGRI GmbH.


Chapter 4


2 Alfa Catalog, Research Chemicals and Accessories 1990/91, Johnson Mathey Company.


4 Unpublished research, R. A. Youngman, B.P. America, Inc.

Appendix 2


Appendix 3
