**DEPARTMENT OF ENERGY
NUCLEAR ENERGY RESEARCH INITIATIVE (NERI)**

**2.2 Next Generation Nuclear Plant
2.2.2 Materials Related to the NGNP Project**

**FINAL REPORT
Silicon Carbide Ceramics for Compact Heat Exchangers
Project Number: 05-032**

PRINCIPAL INVESTIGATORS
Dennis C. Nagle, PhD
Dajie Zhang, PhD
Advanced Technology Laboratory
Johns Hopkins University
810 Wyman Park Drive / Suite G010
Baltimore, Maryland 21211
dnagle@jhu.edu
410 516 8970

**SUBMITTED ON
March 26, 2009**

EXECUTIVE SUMMARY

Silicon carbide (SiC) materials are prime candidates for high temperature heat exchangers for next generation nuclear reactors due to their refractory nature and high thermal conductivity at elevated temperatures. This research has focused on demonstrating the potential of liquid silicon infiltration (LSI) for making SiC to achieve this goal. The major advantage of this method over other ceramic processing techniques is the enhanced capability of making high dense, high purity SiC materials in complex net shapes.

For successful formation of net shape SiC using LSI techniques, the carbon preform reactivity and pore structure must be controlled to allow the complete infiltration of the porous carbon structure which allows complete conversion of the carbon to SiC. We have established a procedure for achieving desirable carbon properties by using carbon precursors consisting of two readily available high purity organic materials, crystalline cellulose and phenolic resin. Phenolic resin yields a glassy carbon with low chemical reactivity and porosity while the cellulose carbon is highly reactive and porous. By adjusting the ratio of these two materials in the precursor mixtures, the properties of the carbons produced can be controlled.

We have identified the most favorable carbon precursor composition to be a cellulose resin mass ratio of 6:4 for LSI formation of SiC. The optimum reaction conditions are a temperature of 1800°C, a pressure of 0.5 Torr of argon, and a time of 120 minutes. The fully dense net shape SiC material produced has a density of 2.96 g cm⁻³ (about 92% of pure SiC) and a SiC volume fraction of over 0.82.

Kinetics of the LSI SiC formation process was studied by optical microscopy and quantitative digital image analysis. This study identified six reaction stages and provided important understanding of the process.

Although the thermal conductivity of pure SiC at elevated temperatures is very high, thermal conductivities of most commercial SiC materials are much lower due to phonon scattering by impurities (e.g., sintering aids located at the grain boundaries of these materials). The thermal conductivity of our SiC was determined using the laser flash method and it is 214 W/mK at 373 K and 64 W/mK at 1273 K. These values are very close to those of pure SiC and are much higher than those of SiC materials made by industrial processes. This SiC made by our LSI process meets the thermal properties required for use in high temperature heat exchanger.

Cellulose and phenolic resin carbons lack the well-defined atomic structures associated with common carbon allotropes. Atomic-scale structure was studied using high resolution transmission electron microscopy (HRTEM), nitrogen gas adsorption and helium gas pycnometry. These studies revealed that cellulose carbon exhibits a very high degree of atomic disorder and angstrom-scale porosity. It has a density of only 93% of that of pure graphite, with primarily sp² bonding character and a low concentration of graphene clusters. Phenolic resin carbon shows more structural order and substantially less angstrom-scale porosity. Its density is 98% of that of pure graphite, and Fourier transform analysis of its TEM micrographs has revealed high concentrations of sp³ diamond and sp² graphene nano-clusters. This is the first time that diamond nano-clusters have been observed in carbons produced from phenolic resin.

AC and DC electrical measurements were made to follow the thermal conversion of microcrystalline cellulose to carbon. This study identifies five regions of electrical conductivity that can be directly correlated to the chemical decomposition and microstructural evolution during carbonization. In Region I, a decrease in overall AC conductivity occurs due to the initial loss of the polar groups from cellulose molecules. In Region II, the AC conductivity starts to increase with heat treatment temperature due to the formation and growth of conducting carbon clusters. In Region III, a further increase of AC conductivity with increasing heat treatment temperature is observed. In addition, the AC conductivity demonstrates a non-linear frequency dependency due to electron hopping, interfacial polarization, and onset of a percolation threshold. In Region IV, the DC conductivity continues to increase with heat treatment due to the growth and percolation of carbon clusters. Finally in Region V, the DC conductivity reaches a plateau with increasing heat treatment temperature as the system reaches a fully percolated state.

Thermophysical properties of carbon materials derived from microcrystalline cellulose have been measured under vacuum and compared with earlier measurements conducted under nitrogen to better understand the influence of porosity, composition, and atmosphere effects. The effective thermal conductivity in vacuum is lower than that observed in nitrogen primarily due to the conductivity of nitrogen gas. Radiation effects in both atmospheres were determined to be negligible. Reduction of diffusivity in nitrogen was attributed to the effects of nitrogen gas phonon scattering. The trends for electrical and thermal property changes with structure are similar but not identical due to the differences in electron and phonon transport mechanisms.

TABLE OF CONTENTS

EXECUTIVE SUMMARY.....	ii
TABLE OF CONTENTS.....	vi
CHAPTER 1. INTRODUCTION.....	1
1.1 High-temperature solid-liquid reactions.....	1
1.2 Carbonization process.....	3
1.3 Theoretical models for LSI reactions.....	3
1.4 Reaction between liquid silicon and glassy carbon at the silicon-carbon interface.....	9
1.5 Reactive wetting of glassy carbon surfaces by liquid silicon droplets.....	12
1.6 Reaction between liquid silicon and graphite fibers.....	13
1.7 Research objectives.....	16
1.8 References.....	16
CHAPTER 2. POROUS CARBON SUBSTRATES FOR LIQUID SILICON INFILTRATION REACTIONS.....	23
2.1 Requirements for successful liquid silicon infiltration of porous carbons.....	23
2.2 Processing of porous carbon monoliths.....	29
2.3 SEM analysis of carbon preforms.....	38
2.4 Bulk density and mass yields of carbons produced from various precursor blend.....	40
2.5 Tuning carbon preform micron-scale porosity.....	42
2.6 Tuning carbon preform reactivity.....	46
2.7 Changes in electrical properties of microcrystalline cellulose as function of carbonization temperature.....	72
2.8 Changes in the thermophysical properties of cellulosic materials as a function of microstructural changes occurring during carbonization.....	90
2.9 Summary and conclusions.....	106
2.10 References.....	107
CHAPTER 3. FULLY DENSE, NET SHAPE SILICON CARBIDE HEAT EXCHANGER MATERIALS.....	117
3.1 Formation of silicon carbide by liquid silicon infiltration of carbon with engineered structure.....	117
3.2 Kinetics of the LSI process.....	133
3.3 Thermophysical properties of using the laser flash method.....	144
3.4 Chemical analysis.....	151
3.5 Description of steps involved in the formation of silicon carbide.....	166
3.6 Summary.....	168
3.7 References.....	170
CHAPTER 4 CONCLUSIONS.....	177

CHAPTER 1. INTRODUCTION

1.1 High-temperature solid-liquid reactions

High-temperature solid-liquid reactions are of great interest in the field of materials science and engineering¹⁻¹⁷. These reactions are used to grow an interfacial phase on the surface of the solid component¹⁸⁻²⁰, and to form bulk near net shape structural materials from mixtures of high melting and low melting components²¹⁻²⁷ as depicted in Figure 1.1a and b. This allows the production of engineering ceramics at temperatures much lower than the highest melting point of its precursor components. Examples include refractory carbides and borides. In this dissertation, high-temperature solid-liquid reactions between liquid silicon and porous carbon were studied. Carbon has a sublimation temperature greater than 3000°C, and silicon has a melting point of 1414°C. These reactions were carried out at temperatures between 1450 and 1900°C to yield silicon carbide with a melting point greater than 2800°C^{28,29}.

Figure 1.1. Illustrations of solid-liquid reactions: (a) microelectronics interconnects fabricated by melting a Sn-Ag-Cu alloy on the solid Cu conductor to grow a solid Cu-Ag interfacial layer¹⁸⁻²⁰; (b) near net shape M_2AX -phase compounds produced by heating Ti, Si and C fine powder mixtures above the Si melting point^{21,22}.

Previous studies by Nagle, Byrne and Kercher^{9,30-34} have shown that near net shape silicon carbide can be produced by reactions between liquid silicon and carbonized wood (Figure 1.2). However, the silicon carbides produced from these carbons have low densities due to high porosity of the carbons. Liquid silicon infiltration (LSI) has also been performed using high density glassy carbon preforms created from furfuryl alcohol resin, diethylene and triethylene glycols, and *p*-toluene sulfonic acid precursors^{7,8,10,35-43}. Due to the low reactivity of glassy carbons, these reactions resulted in heterogeneous products with high volume fractions of unreacted silicon and carbon. These materials also exhibited microstructural cracks.

Figure 1.2. LSI products. (a) A metal bolt inside a SiC nut. The SiC nut was prepared by LSI of a tapped carbon preform made by the carbonization of medium density fiberboard. (b) A SEM image of SiC prepared from carbonized redwood showing the original cellular structure of the wood³².

This research primarily focused on engineering the pore size of carbon monolithic structures that will allow liquid silicon to infiltrate the carbon and convert all of the carbon to silicon carbide⁴⁴. To accomplish this goal, a two-component precursor system consisting of crystalline cellulose and phenolic resin was engineered to generate carbon preforms with controllable porosity and reactivity.

1.2 Carbonization process

Carbonization is the conversion of hydrocarbons and carbohydrates, such as crystalline cellulose and phenolic resin, to pure carbon. During carbonization, these organic compounds are thermally decomposed in an inert atmosphere resulting in the increase in carbon content to nearly 100% through the volatilization of all non-carbon elements^{31,45-51}. The carbonization of crystalline cellulose and phenolic resin produces two types of high purity amorphous carbon materials with very different structures and reactivities. By using these two components in different mass ratios, it is possible to form carbon preforms with controllable pore structure and reactivity that will yield silicon carbide materials with controlled properties.

1.3 Theoretical models for LSI reactions

Mathematical models for LSI of porous carbon structures have been developed^{6,40,41,52-55} by applying capillary flow theories to the flow of liquid silicon in carbon preforms with variable porosities. These models simulate one-dimensional liquid silicon flow in a porous carbon preform in contact with an infinite liquid silicon source as illustrated in Figure 1.3a. They also account for liquid silicon-carbon reactions in the pores, as shown in Figure 1.3b. These reactions are time-dependent and at any given time have occurred to a greater extent in the bottom of the carbon preform than at the tip of the infiltration front. Reaction within the pores is described by using a variable carbon preform permeability value, $\kappa(h,t)$, which can be dependent on both infiltration height, h , and time, t . This temporal and spatial dependence was created by introducing a variable pore radius into the permeability relation, $r(t)$, and by keeping an updated account of the

pore radius at each height along the porous carbon preform. The most significant prediction made in these simulations is the time dependence of the depth of LSI into porous carbon. It is generally believed that both silicon infiltration and the reaction occur over the same time-scale, and that the rate of infiltration decreases over time due to a reduction in pore diameter caused by the formation of silicon carbide at the liquid silicon-carbon interface.

Figure 1.3. (a) Schematic of 1-D LSI of a carbon preform with an infinite liquid silicon source. (b) Schematics of the progression of liquid silicon-solid carbon reactions. (1) The original carbon pore. (2) Silicon infiltration of the pore. (3) SiC formation at the interfacial region. (4) The reaction at completion with the pore being filled with SiC.

Messner and Chiang⁶ developed a model based on a time-dependent liquid silicon permeability of porous carbon. Viscous incompressible flow of liquid silicon through porous carbon preforms was described by the one-dimensional volume flow rate given by Darcy's law. An augmented Young-Laplace equation was used to determine the capillary pressure of liquid silicon. By assuming a homogeneous permeability across the entire carbon preform at any given reaction time, the permeability was described as a function of pore radius at the initial infiltration surface of the carbon preform. This pore radius was a function of reaction time and reaction rate constant. The rate of reaction between liquid silicon and solid carbon was assumed to be either linear or parabolic. For the linear

reaction, the function describing the time-dependent pore size was $r(t)=r_o-kt$, and for the parabolic reaction the time-dependent pore size was $r(t)=r_o-k't^{1/2}$, where t is reaction time, r_o is the initial pore radius, and k and k' are linear and parabolic reaction rate constants. Two equations for permeability were provided with one describing the linear reaction and the other describing the parabolic reaction. A simplified Hagen-Poiseuille model of parallel capillaries of identical diameters was considered for the porous carbon to determine the time-dependent permeability. A time-dependent Darcy's law then could be developed. Time-dependent infiltration height, $h(t)$, for both the linear and parabolic reactions was derived from the Darcy equations as

$$h^2(t) = \frac{P_o \Delta P}{4\eta r_o^2} \left(r_o^4 t - 2r_o^3 k t^2 + 2r_o^2 k^2 t^3 - r_o k^3 t^4 + \frac{1}{5} k^4 t^5 \right) \text{ and}$$

$$h^2(t) = \frac{P_o \Delta P}{4\eta r_o^2} \left(r_o^4 t - \frac{8}{3} r_o^3 k' t^{3/2} + 3r_o^2 k'^2 t^2 - \frac{8}{5} r_o k'^3 t^{5/2} + \frac{1}{3} k'^4 t^3 \right).$$

The first equation describes the linear reaction and the second equation describes the parabolic reaction. P_o is the initial porosity of the carbon preform, ΔP is the pressure differential, and η is the fluid viscosity.

Time-dependent infiltration heights were calculated for both linear reaction and parabolic reactions and Figure 1.4 shows recreation of the original plots⁶. The linear reaction reached a maximum infiltration height of about 1.5 cm after 5 seconds, and the parabolic reaction reached a maximum infiltration height of about 0.5 cm after less than 1 second. LSI experiments were conducted with a carbon preform with 200 nm diameter pores to compare with the calculations. A maximum infiltration height of about 1.5 cm was achieved. This experimentally obtained value was close to the value of the simulated

linear reaction, indicating that the reaction between liquid silicon and solid carbon was most likely a linear reaction.

Figure 1.4. Illustrative recreation of the results of simulations of LSI reactions from the original plots presented by Messner and Chiang⁶.

Gern and Kochendörfer⁵² developed a numerical simulation for LSI by using a diffusion model to describe silicon carbide layer growth and pore diameter reduction. The authors took into account an empirically determined statistical distribution function of pore diameter with the assumption that each pore had a uniform diameter. The pore size range was assumed to be between 10 and 50 μm for the simulation. An extension of the Hagen-Poiseuille viscous fluid flow model was adopted⁵⁶ which introduced a pore tortuosity term, ϕ . Integration of the extended Hagen-Poiseuille equation yielded,

$$\rho \phi^2 h \frac{du}{dt} + 1.16 \rho \phi^2 u^2 + 8 \eta \phi^2 h u d^{-2} + \rho g h - 2 \rho \cos \theta d^{-1} = 0,$$

where ρ is the fluid density, u is the infiltration velocity, d is pore diameter, g is the gravitational acceleration, σ is liquid silicon surface tension, θ is liquid silicon-carbon contact angle, and d is the time-dependent capillary diameter. The above equation was solved to obtain the time dependence of the infiltration height. The main results from these calculations include the relations of infiltration height vs. time, and infiltration height vs. pore diameter. Recreations of the original plots⁵² depicting these relations are illustrated in Figure 1.5. The simulations predicted a maximum infiltration height of 30

cm after 100 seconds of infiltration in 20 μm pores. The increase of infiltration height with reaction temperature resembles the same trend obtained theoretically by Chiang and Messner⁶. However, Chiang and Messner predicted a significantly lower maximum infiltration height in carbons with much smaller pores (200 nm).

Figure 1.5. Illustrative recreation of simulations of LSI reactions from the original plots presented by Gern and Kockendörfer⁵².

Nelson and Colella⁵³ used Darcy's law to describe the velocity of the infiltration front

$$u = -\frac{\kappa}{\mu} \frac{dP}{dh} ,$$

where u is the velocity of the infiltration front, κ is the liquid silicon permeability of the porous carbon preform, μ is the viscosity of the liquid, P is the capillary pressure at the infiltration front, and h is the height of the infiltration front. They adopted the linear reaction model and the linear reaction pore size equation developed by Messner and Chiang⁶ and assumed a constant reaction rate for each calculation within a rate range of 10^{-9} to 10^{-7} m s^{-1} . Both capillary pressure P and permeability κ are functions of pore radius, which in turn become functions of reaction time. Pore radii were varied between 0.1 and 0.2 μm , and initial porosity values were between 0.4 and 0.6. The time-dependent

Nelson and Colella Darcy equation for the linear reaction was solved to obtain the time dependence of the infiltration height while the permeability field $\kappa(h,t)$ and pressure field $P(h,t)$ were continually updated with reaction time. The effects of reaction rate, initial porosity, and initial pore radius were analyzed by varying these parameters independently during calculation. The results of these simulations show a general trend of increasing infiltration height over reaction time. This trend is shown by the plot in Figure 1.6. Three regions of the reaction front were identified with reaction time. The first region of the curve represents the initial non-reactive infiltration where Laplace forces dominated, and in the second region the competition between Laplace forces and chemical forces occurred. Finally, in the third region, chemical forces began to dominate.

Figure 1.6. Illustrative recreation showing the general trend of the relation between infiltration height and reaction time as described by the results obtained by Nelson and Colella⁵³.

The simulation efforts described above provide great insight into the events involved in the liquid silicon-solid carbon reactions. These results can aid in the selection of carbons with appropriate properties for liquid silicon-carbon reactions and can help to determine optimum conditions for these experiments. Numerous experimental results^{6,40,41,52-55} have been obtained showing general agreement with these theoretical

predictions. Additionally, experimental results can also be used to further improve the quality of these simulations.

1.4 Reaction between liquid silicon and glassy carbon at the silicon-carbon interface

While mathematical models focus mostly on the overall capillary flow of liquid silicon in porous carbon, little consideration is given to the localized physical changes and chemical reactions at the liquid silicon-solid carbon interface. Properly designed experiments can help to reveal more details of these events and their evolution throughout the entire process. By reacting liquid silicon with flat dense glassy carbon plates^{16,17}, direct observations of interfacial phenomena between liquid silicon and carbon were made without the need to take liquid silicon capillary flow into consideration. These experiments demonstrated that silicon carbide is formed instantly at the interface between liquid silicon and glassy carbon. Due to the difficulties of quenching this high-temperature reaction ($T > T_{M,Si} = 1414^{\circ}\text{C}$) at the early stages (< 1 min), little information regarding the mechanisms and kinetics of the instant formation of silicon carbide at the interface has been extracted. Measurements of the time-dependent silicon carbide layer thickness revealed that the interfacial reaction occurred in two sequential stages as illustrated in Figure 1.7:

1. Rapid growth of a continuous silicon carbide layer to a thickness of approximately $10\text{ }\mu\text{m}$ due to direct contact,
2. Very little additional growth of the silicon carbide due to the very slow diffusion of carbon atoms across the silicon carbide barrier layer.

Figure 1.7. Reaction at the interface between liquid silicon and carbon. (1) rapid growth of a SiC interfacial layer, and (2) slow additional SiC growth by carbon diffusion^{16,17}.

Zhou and Singh¹⁶ fitted the silicon carbide layer thickness data to reaction time using least square regressions and showed that the silicon carbide layer average thickness obeyed a fourth-power rate law as $\delta = kt^{1/4}$, where δ is the average thickness of the continuous silicon carbide layer, k is a temperature-independent kinetic constant (≈ 3), and t is the reaction time. Thus, after the initial formation of a 10 μm layer of silicon carbide, the reaction essentially stopped.

Additionally, Zhou and Singh¹⁶ adopted an oxidation model that was originally developed for oxide layer formation on metal surfaces^{57,58}, theorizing that the diffusion of carbon through silicon carbide is analogous to diffusion of oxygen through oxide layers formed at the interface between metals and air at elevated temperatures. This model was applied to determine the kinetics of the diffusion limited silicon carbide formation reactions. The initial reaction at the liquid silicon-carbon interface was assumed to occur very rapidly and it stopped when a continuous dense silicon carbide layer separating liquid silicon and solid carbon was formed. As shown in Figure 1.8, further reaction must be facilitated by the diffusion of carbon and/or silicon through the silicon carbide layer. An assumption was made that there exists a “considerable concentration of lattice and/or electronic defects” in silicon carbide at the high temperatures. These defects enhance the

diffusion of carbon and silicon atoms through silicon carbide. The diffusion of carbon was believed to be driven by an electric field across the silicon carbide barrier layer. This electric field is due to the positive charge at the Si-SiC interface caused by electron donation from silicon to silicon carbide, and the negative charge at the SiC-C interface caused by electron donation from silicon carbide to carbon.

Figure 1.8. Illustration of SiC growth at the liquid silicon-glassy carbon interface through carbon diffusion driven by an electric field¹⁶.

Hon, et. al.⁵⁹ measured the diffusion rates of carbon and silicon in silicon carbide at high temperatures using ^{14}C and ^{30}Si isotopes to trace carbon and silicon diffusion. The diffusion of silicon and carbon in β -silicon carbide was attributed to a vacancy mechanism. The major lattice defects within silicon carbide were assumed to be carbon and silicon Schottky defects. The diffusivity of carbon in silicon carbide was found to be $2.90 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 1800°C ⁶⁰, which is three orders of magnitude greater than the diffusivity of silicon, $9.5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, at the same temperature⁵⁹. Therefore, the contribution of silicon diffusion to silicon carbide formation can be ignored and the diffusion of carbon is assumed to control silicon carbide growth, as shown in Figure 1.8.

From this model three important equations that govern carbon ion vacancy diffusion and silicon carbide layer growth were derived. These equations describe carbon vacancy concentration, $n_{VC}(x)$, the vacancy diffusion flux, $J(\delta)$ and the reaction layer thickness $\delta(t)$. They predict that the carbon ion vacancy concentration decreases with distance across the silicon carbide layer away from silicon as $n_{VC}(x) \propto x^{-0.5}$, where x is distance across the silicon carbide from silicon to carbon. The carbon ion vacancy flux decays with silicon carbide layer thickness as $J(\delta) \propto \delta^{-3}$. The silicon carbide layer thickness increases with time as $\delta(t) \propto t^{1/4}$. The calculated $\delta(t)$ values were plotted together with the time-dependent experimental silicon carbide thickness values and these two curves showed similar trends with increasing reaction time. However, the calculated $\delta(t)$ values were only about one fourth of the experimental values.

1.5 Reactive wetting of glassy carbon surfaces by liquid silicon droplets

By introducing millimeter-sized droplets of liquid silicon to carbon surfaces, wetting and spreading behavior of the droplets were studied⁶¹⁻⁶⁴. Two important parameters that define this wetting behavior are degree of wetting, and rate of wetting⁶⁵. Degree of wetting is determined by the contact angle, and rate of wetting is the velocity of the vapor-liquid-solid triple line. The overall solid-liquid reaction process has been described as occurring in three sequential stages as illustrated in Figure 1.9⁶². These stages are:

1. Non-reactive wetting with an initial contact angle of 180° that decreases to approximately 150° . This stage is very short because silicon carbide quickly forms at the interface.
2. Reactive wetting occurs as silicon carbide is formed over the entire contact area⁶³. The contact angle further decreases to approximately 50° and the spreading rate of liquid silicon is very high.
3. During the terminal stage, the contact angle decreases at a much smaller rate, reaching a final value of approximately 35° . This corresponds to the wetting angle of liquid silicon on silicon carbide.

Figure 1.9 Illustration of the wetting of liquid silicon droplets on glassy carbon surfaces. (1) non-reactive wetting, (2) reactive wetting, and (3) the terminal stage⁶¹⁻⁶⁴.

1.6 Reaction between liquid silicon and graphite fibers

Chiang, et al.⁷ carried out reactions between liquid silicon and graphite fibers at various temperatures in order to reveal the reaction kinetics and possible reaction mechanisms for the formation of silicon carbide. Polished cross sections of reacted fibers were examined by optical and scanning electron microscopy, and thin sections of the product cross sections were studied with a TEM. The progress of the reaction was determined by measuring the area fraction of silicon carbide in the images of the cross

sections by quantitative digital image analysis and the results are illustrated in Figure 1.10. The plot in Figure 1.10a shows the amount of silicon carbide formed with reaction time, and three reaction stages are marked. These reaction stages correspond directly to the images in Figure 1.10b-d. The reaction between liquid silicon and graphite fiber begins with an ‘initial incubation period’ (Figure 1.10b) during which carbon is dissolved into liquid silicon and the entire surface of the fiber becomes covered by a very thin (submicron) polycrystalline silicon carbide layer. The second stage (Figure 1.10c) arrives when the critical carbon concentration is reached to allow rapid silicon carbide formation. During this intermediate rapid reaction stage, the amount of silicon carbide was linearly dependent on time. In the third stage (Figure 1.10d), more and more carbon is isolated from liquid silicon by the silicon carbide formed and the reaction slows and eventually ends. The researchers mainly focused on reaction stage II.

Figure 1.10. High temperature reaction between liquid silicon and a graphite fiber. (a) SiC formation vs. reaction time (Chiang, et. al.⁷). (b-d) Cross section of the graphite fiber in liquid silicon, (b) incubation stage, (c) intermediate stage, and (d) terminal stage.

Amounts of silicon carbide were collected for reactions performed at 1430 (T_1), 1460 (T_2), 1490 (T_3), and 1530°C (T_4) and are illustrated in Figure 1.11a. An Arrhenius relation⁶⁶ was used to calculate the equilibrium carbon concentration in the liquid silicon, $X_{C \text{ in } Si}$, for these temperatures, and the results are illustrated in Figure 1.11b. From Figure

1.11a, the rates of silicon carbide layer growth were determined as the derivative of the temperature-dependent amount of silicon carbide with reaction time. These rates were plotted against the temperature-dependent equilibrium carbon solubility in liquid silicon, $X_{C \text{ in Si}}$, as illustrated in Figure 1.11c. This figure indicates that the rate of silicon carbide layer growth is linearly proportional to the carbon solubility in liquid silicon.

Figure 1.11. Analysis of silicon carbide growth by reaction between liquid silicon and a graphite fiber (Chiang, et. al.⁷). (a) Amount of silicon carbide vs. reaction time, (b) equilibrium carbon concentration in liquid silicon vs. temperature, and (c) reaction rate vs. equilibrium carbon concentration in liquid silicon.

The studies on the reactions between liquid silicon and dense carbons, such as glassy carbon and graphite fibers, have shown that the direct reaction between liquid silicon and solid carbon is a fast process that can be completed within seconds⁶⁴. Additional reaction between liquid silicon and carbon can only be achieved by the diffusion of carbon atoms through the dense silicon carbide barrier. The reaction rate is controlled by carbon diffusion through silicon carbide, which is a very slow process. Therefore, in order to achieve a high degree of conversion of a carbon into silicon carbide, direct contact between liquid silicon and the overall structure of the carbon must be achieved in a very short period of time. This can only be possible for a carbon with a high degree of porosity to allow rapid infiltration of liquid silicon through the entire

structure before significant formation of silicon carbide occurs. The reactivity of carbon towards liquid silicon also affects the outcome of the reaction since it determines the rate of silicon carbide formation.

1.7 Research objectives

Numerous efforts have been made to make net shape silicon carbide by LSI techniques^{6-13,30-43,52-55,67,68} with the intention of producing fully dense net shape silicon carbide based ceramics and understanding the mechanisms and kinetics associated with these reactions. Several theoretical models have been proposed to describe this process. In addition, experimental studies have been carried out with various carbon materials, including graphite fibers, powder mixtures of graphite and silicon carbide, and carbons derived from phenolic resin and from lignocellulosic materials. For the LSI process, the important issues are the carbon preform properties and the reaction conditions which are temperature, time and atmosphere.

This research effort has been undertaken to:

1. Define the important characteristics of porous carbon monoliths that allow the making of silicon carbide materials with predictable physical properties by LSI.
2. Identify optimum conditions, including temperature, time and pressure/atmosphere, for the LSI reaction with any porous carbon.
3. Examine the silicon carbide formation reactions and characterize the silicon carbide produced.

1.8 References

1. L.J. Gauckler, T. Graule and F. Baader. Ceramic forming using enzyme catalyzed reactions, *Materials Chemistry and Physics*, 61, 78-102 (1999).
2. W.E. Lee, D.D. Jayaseelan and S. Zhang. Solid–liquid interactions: The key to microstructural evolution in ceramics, *Journal of the European Ceramic Society*, 28, 1517-25 (2008).
3. P. Boch and J.P. Giry. Preparation and properties of reaction-sintered mullite-ZrO₂ ceramics, *Materials Science and Engineering*, 71, 39-48 (1985).
4. A.J. Moulson, Reaction-Bonded Silicon-Nitride - its Formation and Properties, *J. Mater. Sci.*, 14, 1017-51 (1979).
5. W.G. Fahrenholtz, Reactive processing in ceramic-based systems, *International Journal of Applied Ceramic Technology*, 3, 1-12 (2006).
6. R.P. Messner and Y.M. Chiang. Liquid-Phase Reaction-Bonding of Silicon-Carbide using Alloyed Silicon Molybdenum Melts, *J Am Ceram Soc*, 73, 1193-200 (1990).
7. Y.M. Chiang, R.P. Messner, C.D. Terwilliger and D.R. Behrendt. Reaction-Formed Silicon-Carbide, *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing*, 144, 63-74 (1991).
8. M. Singh and D.R. Behrendt. Reactive Melt Infiltration of Silicon-Molybdenum Alloys into Microporous Carbon Preforms, *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing*, 194, 193-200 (1995).
9. C.E. Byrne and D.C. Nagle. Cellulose derived composites - A new method for materials processing, *Materials Research Innovations*, 1, 137-44 (1997).
10. Y. Wang, S. Tan and D. Jiang. The fabrication of reaction-formed silicon carbide with controlled microstructure by infiltrating a pure carbon preform with molten Si, *Ceramics International*, 30, 435-9 (2004).
11. T. Ota, M. Takahashi, T. Hibi, et al. Biomimetic process for producing SiC "wood", *J Am Ceram Soc*, 78, 3409-11 (1995).

12. P. Greil, T. Lifka and A. Kaindl. Biomorphic cellular silicon carbide ceramics from wood: I. Processing and microstructure, *Journal of the European Ceramic Society*, 18, 1961-73 (1998).
13. H. Sieber, C. Hoffmann, A. Kaindl and P. Greil. Biomorphic cellular ceramics, *Advanced Engineering Materials*, 2, 105-9 (2000).
14. D. Chen, G. Chen, S. Ni, G. Chen, H. Yan and Z. Chen. Phase formation regularities of ultrafine TiAl, NiAl and FeAl intermetallic compound powders during solid-liquid reaction milling, *Journal of Alloys and Compounds*, 457, 292-5 (2008).
15. S. Bodoardo, C. Portesi, P. Fino, et al. Production by solid/liquid reaction and characterization of high purity MgB₂ powders and thick films for superconducting application, *Journal of the European Ceramic Society*, 24, 1837-40 (2004).
16. H. Zhou and R.N. Singh. Kinetics Model for the Growth of Silicon-Carbide by the Reaction of Liquid Silicon with Carbon, *J Am Ceram Soc*, 78, 2456-62 (1995).
17. A. Favre, H. Fuzellier and J. Suptil. An original way to investigate the siliconizing of carbon materials, *Ceram. Int.*, 29, 235-43 (2003).
18. D.R. Frear, J.W. Jang, J.K. Lin and C. Zhang. Pb-free solders for flip-chip interconnects, *Jom-Journal of the Minerals Metals & Materials Society*, 53, 28,+ (2001).
19. H.Y. Lu, H. Balkan and K.Y.S. Ng. Solid-liquid reactions: The effect of Cu content on Sn-Ag-Cu interconnects, *JOM*, 57, 30-5 (2005).
20. L.H. Su, Y.W. Yen, C.C. Lin and S.W. Chen. Interfacial reactions in molten Sn/Cu and molten In, *Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science*, 28, 927-34 (1997).
21. M.W. Barsoum and T. ElRaghy. Synthesis and characterization of a remarkable ceramic: Ti₃SiC₂, *J Am Ceram Soc*, 79, 1953-6 (1996).
22. Y.C. Zhou, Z.M. Sun, S.Q. Chen and Y. Zhang. In-situ hot pressing solid-liquid reaction synthesis of dense titanium silicon carbide bulk ceramics, *Materials Research Innovations*, 2, 142-6 (1998).

23. X.H. Wang and Y.C. Zhou. Solid-liquid reaction synthesis of layered machinable Ti_3AlC_2 ceramic, *Journal of Materials Chemistry*, 12, 455-60 (2002).
24. H.Y. Dong, C.K. Yan, S.Q. Chen and Y.C. Zhou. Solid-liquid reaction synthesis and thermal stability of Ti_2SnC powders, *Journal of Materials Chemistry*, 11, 1402-7 (2001).
25. Y.C. Zhou, F.L. Meng and J. Zhang. New MAX-Phase compounds in the v-cr-al-c system, *J Am Ceram Soc*, 91, 1357-60 (2008).
26. W. Tian, P. Wang, G. Zhang, Y. Kan, Y. Li and D. Yan. Synthesis and thermal and electrical properties of bulk Cr_2AlC , *Scripta Materialia*, 54, 841-6 (2006).
27. J.C. Viala, N. Peillon, F. Bosselet and J. Bouix. Phase equilibria at 1000°C in the AlCSiTi quaternary system: An experimental approach, *Materials Science and Engineering A*, 229, 95-113 (1997).
28. H.J. Seifert and F. Aldinger. Phase equilibria in the Si-B-C-N system, pp. 1 in *High performance non-oxide ceramic*. Edited by M. Jansen. Springer, Berlin; New York, 2002.
29. H.O. Pierson, *Covalent Carbides: Structure and Composition*, pp. 118 in *Handbook of Refractory Carbides and Nitrides*. Noyes Publications, Westwood, NJ, 1996.
30. C.E. Byrne and D.C. Nagle. Carbonized wood monoliths - Characterization, *Carbon*, 35, 267-73 (1997).
31. C.E. Byrne and D.C. Nagle. Carbonization of wood for advanced materials applications, *Carbon*, 35, 259-66 (1997).
32. C. E. Byrne. Polymer, ceramic and carbon composites derived from wood. PhD dissertation. (1995) Johns Hopkins University, Baltimore, MD.
33. A. K. Kercher. Processing and characterization of monolithic carbon structures based on wood fiberboards. PhD dissertation. (2002) Johns Hopkins University, Baltimore, MD.
34. A.K. Kercher and D.C. Nagle. Monolithic activated carbon sheets from carbonized medium-density fiberboard, *Carbon*, 41, 3-13 (2003).

35. D.R. Behrendt and M. Singh. Effect of carbon preform pore volume and infiltrants on the composition of reaction-formed silicon carbide materials , J. Mater. Synth. Process., 2, 117-123 (1994).
36. M. Singh and D.R. Behrendt. Microstructure and Mechanical-Properties of Reaction-Formed Silicon-Carbide (Rfsc) Ceramics, Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing, 187, 183-7 (1994).
37. M. Singh and T.A. Leonhardt. Microstructural characterization of reaction-formed silicon carbide ceramics, Mater Charact, 35, 221-8 (1995).
38. A. Munoz, J. Martinez-Fernandez, A. Dominguez-Rodriguez and M. Singh. High-temperature compressive strength of reaction-formed silicon carbide (RFSC) ceramics, Journal of the European Ceramic Society, 18, 65-8 (1998).
39. M. Singh and S.C. Farmer. Morphological characterization of microporous carbon materials, J. Mater. Sci. Lett., 16, 946-9 (1997).
40. P. Sangsuwan, S.N. Tewari, J.E. Gatica, M. Singh and R. Dickerson. Reactive infiltration of silicon melt through microporous amorphous carbon preforms, Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science, 30, 933-44 (1999).
41. P. Sangsuwan, J.A. Orejas, J.E. Gatica, S.N. Tewari and M. Singh. Reaction-bonded silicon carbide by reactive infiltration, Ind Eng Chem Res, 40, 5191-8 (2001).
42. Y.X. Wang, S.H. Tan, D.L. Jiang and X.Y. Zhang. Preparation of porous carbon derived from mixtures of furfuryl resin and glycol with controlled pore size distribution, Carbon, 41, 2065-72 (2003).
43. Y.X. Wang, S.H. Tan and D.L. Jiang. The effect of porous carbon preform and the infiltration process on the properties of reaction-formed SiC, Carbon, 42, 1833-9 (2004).
44. J. Narayan, R. Raghunathan, R. Chowdhury and K. Jagannadham. Mechanism of Combustion Synthesis of Silicon-Carbide, J. Appl. Phys., 75, 7252-7 (1994).
45. I.C. Lewis, Chemistry of carbonization, Carbon, 20, 519-29 (1982).

46. E. Fitzer, K. Mueller and W. Schaffer. The chemistry of the pyrolytic conversion of organic compounds to carbon, in Vol. 7, Chemistry and physics of carbon. Edited by P.L. Walker. M. Dekker, New York, 1965.
47. A. Oberlin, Carbonization and graphitization, Carbon, 22, 521-41 (1984).
48. M.M. Tang and R. Bacon. Carbonization of cellulose fibers—I. Low temperature pyrolysis, Carbon, 2, 211,214, IN1, 215-220 (1964).
49. R. Bacon and M.M. Tang. Carbonization of cellulose fibers—II. Physical property study, Carbon, 2, 221,222, IN3-IN4, 223-225 (1964).
50. F. Shafizadeh, Pyrolysis and Combustion of Cellulosic Materials, pp. 419-74 in Vol. 23, Advances in Carbohydrate Chemistry. Academic Press, New York, 1968.
51. I.A.S. Edwards and H. Marsh. Introduction to carbon science; pp. 321. Butterworths, London ;Boston, 1989.
52. F.H. Gern and R. Kochendorfer. Liquid silicon infiltration: Description of infiltration dynamics and silicon carbide formation, Composites Part A-Applied Science and Manufacturing, 28, 355-64 (1997).
53. E.S. Nelson and P. Colella. Parametric Study of Reactive Melt Infiltration," NASA TM-2000-209802, (2000).
54. E.O. Einset, Analysis of Reactive Melt Infiltration: I. Derivation of the Governing Equations," 96CRD028, April 1996 Class 1, (1996).
55. E.O. Einset, Analysis of reactive melt infiltration in the processing of ceramics and ceramic composites, Chemical Engineering Science, 53, 1027-39 (1998).
56. O. Tietjens, Stromungslehre, Band I; Springer-Verlag, Berlin, 1960.
57. K. Hauffe, Oxidation of Metals; Plenum Press, New York, 1965.
58. K.R. Lawless, Oxidation of Metals, Reports on Progress in Physics, 37, 231,& (1974).
59. M.H. Hon, R.F. Davis and D.E. Newbury. Self-Diffusion of Si-30 in Polycrystalline Beta-Sic, J. Mater. Sci., 15, 2073-80 (1980).

60. M.H. Hon and R.F. Davis. Self-Diffusion of C-14 in Polycrystalline Beta-Sic, J. Mater. Sci., 14, 2411-21 (1979).
61. N. Eustathopoulos, Dynamics of wetting in reactive metal ceramic systems, Acta Materialia, 46, 2319-27 (1998).
62. O. Dezellus, F. Hodaj and N. Eustathopoulos. Chemical reaction-limited spreading: the triple line velocity versus contact angle relation, Acta Materialia, 50, 4741-53 (2002).
63. O. Dezellus, F. Hodaj and N. Eustathopoulos. Progress in modelling of chemical-reaction limited wetting, Journal of the European Ceramic Society, 23, 2797-803 (2003).
64. O. Dezellus, S. Jacques, F. Hodaj and N. Eustathopoulos. Wetting and infiltration of carbon by liquid silicon, J. Mater. Sci., 40, 2307-11 (2005).
65. G. Kumar and K.N. Prabhu. Review of non-reactive and reactive wetting of liquids on surfaces, Adv. Colloid Interface Sci., 133, 61-89 (2007).
66. R.I. Scace and G.A. Slack. Solubility of Carbon in Silicon and Germanium, J. Chem. Phys., 30, 1551-5 (1959).
67. C. Zollfrank and H. Sieber. Microstructure evolution and reaction mechanism of biomorphous SiSiC ceramics, J Am Ceram Soc, 88, 51-8 (2005).
68. K.E. Pappacena, K.T. Faber, H. Wang and W.D. Porter. Thermal conductivity of porous silicon carbide derived from wood precursors, J Am Ceram Soc, 90, 2855-62 (2007).

CHAPTER 2. POROUS CARBON SUBSTRATES FOR LIQUID SILICON INFILTRATION REACTIONS

2.1 Requirements for successful liquid silicon infiltration of porous carbons

The important properties of the carbon preform that determine the success of formation of silicon carbide by liquid silicon infiltration (LSI) are bulk density, porosity, and reactivity. These physical and chemical properties will be optimized utilizing a two-component composite precursors consisting of crystalline cellulose and phenolic resin.

For a porous material, the bulk density is defined as the mass divided by the sum of the actual solid volume and pore volume¹. Formation of silicon carbide by conversion of a porous carbon preform to porosity-free silicon carbide requires an equivalent number of carbon atoms per unit volume in the bulk carbon preform and in the silicon carbide product. Therefore, the ideal carbon bulk density, P_{Carbon}^{Ideal} , of 0.964 g cm^{-3} ² can be calculated by dividing the molar mass of carbon, $M_C = 12 \text{ g mol}^{-1}$, by the molar volume of silicon carbide, $V_{SiC} = 12.45 \text{ cm}^3 \text{ mol}^{-1}$, and $P_{Carbon}^{Ideal} = M_C / V_{SiC} = 0.964 \text{ g cm}^{-3}$. Some of the carbon preforms in this study are bimodal in pore structure; they have large *micron-scale* porosity which can be filled with liquid silicon during infiltration reactions, and they also have small *angstrom-scale* porosity that is too small to allow infiltration but affects reactivity.

The bulk density of a porous carbon preform is dependent on its actual density and porosity. The carbon actual density, ρ_C , is defined as the mass of the carbon material divided by the actual volume of the carbon, which is the volume excluding all porosity

(of micron, nano and/or angstrom-scale). The actual densities of carbon substances with sp^2 -bonding and high crystallinity can be assumed to be near the theoretical value of graphite, approximately 2.26 g cm^{-3} , while sp^2 -bonded carbons with low crystallinity can have an actual density slightly lower than that of graphite due to the high level of atomic disordering. Porosity, V_P , is the fractional volume occupied by pores. The relation among carbon preform bulk density, actual density and porosity is $P_{Carbon} = (1 - V_P)\rho_C$.

The skeletal density, $\rho_{Carbon}^{skeletal}$, is the density of the carbon skeleton in microporous carbons (the carbon skeleton can have angstrom-scale porosity within it) and is defined as the mass divided by the volume of the carbon preform excluding micron-scale pores but including nano-scale and angstrom-scale pores. Carbons with a high concentration of submicron-scale pores can have skeletal densities as low as 1.4 g cm^{-3} , and nonporous carbons with highly graphitic character can have skeletal densities up to the density of graphite, 2.26 g cm^{-3} . In this text, micron-scale porosity, $V_P^{\mu m}$, is defined as the fractional volume occupied by pores approximately $0.1 \mu\text{m}$ or greater. The bulk density of the carbon preforms can be calculated from the micron-scale porosity and carbon preform skeletal density as $P_{Carbon} = (1 - V_P^{\mu m})\rho_{Carbon}^{skeletal}$. Calculated bulk density values of pure graphite and of carbons with a skeletal density of 1.4 g cm^{-3} are plotted in Figure 2.1. The ideal bulk density, P_{Carbon}^{ideal} , of 0.96 g cm^{-3} is plotted as the gray dotted line as a reference. This plot shows that a carbon preform made from pure graphite with a skeletal density of 2.26 g cm^{-3} requires a porosity of near 0.6 to reach the ideal bulk density while a carbon with a skeletal density of 1.4 g cm^{-3} requires a porosity of approximately 0.35.

Figure 2.1. Carbon bulk density, P_{Carbon} , vs. micron scale porosity, $V_p^{\mu m}$, for low skeletal density carbon ($\rho_{Carbon}^{skeletal} = 1.4 \text{ g cm}^{-3}$) and high skeletal density carbon ($\rho_{graphite}^{skeletal} = 2.26 \text{ g cm}^{-3}$).

Figure 2.2. Schematic of the LSI process. (a) porous carbon preform, (b) liquid silicon infiltration, (c) initial silicon carbide formation, and (d) pore closure.

It has been shown that in order to achieve successful LSI of porous carbon, the pore diameters must be above a critical value of approximately $1\text{ }\mu\text{m}$ ^{2,4-7}. If pore diameters are far below $1\text{ }\mu\text{m}$, the volume expansion associated with carbon to silicon carbide conversion can lead to pore closure during infiltration as depicted in Figure 2.2.

The fractional volume change of the carbon skeleton, $\Delta V/V_C$, upon conversion to porosity-free silicon carbide can be expressed as

$$\frac{\Delta V}{V_C} = \frac{V_{SiC} - V_C}{V_C} = \frac{V_{SiC}}{V_C} - 1 = \frac{M_{SiC}}{\rho_{SiC}} \frac{\rho_C^{skeletal}}{M_C} - 1,$$

where V_{SiC} and V_C are the molar volumes of silicon carbide and carbon, M_C is carbon molar mass, and $\rho_C^{skeletal}$ is the carbon skeletal density. As described in Section 2.1.1, carbon skeletal density can vary from approximately 1.4 to 2.26 g cm^{-3} . A plot depicting the volume increase of the carbon skeleton during silicon carbide formation is presented in Figure 2.3; the volume increase can range from about 45 to 140%.

It has been empirically proven² that when carbon micron-scale pore diameters are below approximately $1\text{ }\mu\text{m}$, the volume increase caused by silicon carbide formation within pores near the carbon preform outer surface can lead to “pore choking.” This process restricts further liquid silicon flow into the carbon preform, resulting in early termination of the reaction as depicted in Figure 2.4.

Figure 2.3. Calculated fractional volume increase of a carbon skeleton during conversion to silicon carbide.

Schematic of early reaction termination near the carbon preform outer surface

Optical micrograph showing pore choking near the carbon preform outer surface

Figure 2.4. Illustration of early stage termination of the LSI reaction near the surface of the carbon.

Carbon reactivity towards liquid silicon plays an important role in determining the outcome of the silicon carbide formation reaction⁸. The reactivity of carbon controls the rate of carbon dissolution by liquid silicon; and thus, the rate of silicon carbide formation at the carbon-silicon interface. Carbon reactivity is dependent on the degree of atomic ordering and angstrom-scale porosity. When carbon atomic ordering decreases, and when angstrom-scale porosity increases, the concentration of available carbon ‘active sites’ rises. As a result, carbon atoms can be more readily dissolved by liquid Si. Carbons produced from various organic materials can have different levels of atomic disordering and atomic-scale porosity. By using precursors consisting of mixtures of organic materials, the reactivity of the carbons can be controlled.

The structural properties of carbon control the effectiveness of silicon carbide formation using the LSI process. Figure 2.5 illustrates the outcomes of liquid silicon reactions with three types of carbon preforms. Figure 2.5a shows the outcome of reacting liquid silicon with a highly porous and reactive carbon. Rapid dissolution of carbon leads to the loss of bulk structure and the precipitation of dispersed silicon carbide crystals in liquid silicon. Figure 2.5b depicts the reaction between liquid silicon and a low porosity low reactivity carbon preform. Pore choking at the surface leads to early termination of the reaction. In Figure 2.5c, full conversion is observed. Liquid silicon completely infiltrates the carbon preform as the reaction proceeds to completion.

Figure 2.5. Illustration of the effects of carbon bulk density, porosity and reactivity on the liquid silicon-carbon reaction. (a) A highly porous and highly reactive carbon preform, (b) a low porosity and low reactivity carbon preform, and (c) a carbon preform with ideal bulk density and reactivity.

2.2 Processing of porous carbon preform monoliths

To make carbon preforms with tunable bulk density, micron-scale porosity, and reactivity, particulate crystalline cellulose and phenolic resin were selected for this study. Crystalline cellulose produces carbons with high reactivity⁹⁻¹¹ and high micron-scale porosity, while phenolic resin yields carbons with low reactivity and high skeletal density.

The precursors were thoroughly mixed and then uniaxially cold-pressed under a 35 MPa pressure into monolithic discs of about 57 mm in diameter. The thermal processing and carbonization conditions were determined by chemical and thermal analysis of the precursor materials using TGA and DTA techniques. Samples were first oxidized in air at temperatures below 300°C to thermoset the phenolic component and to

partially decompose the cellulose component. This low temperature oxidative pretreatment helps maintain the shape of the discs during carbonization, and it also produces higher angstrom-scale porosity in the final carbon products due to the partial oxidation of the cellulose phase. During this heat treatment process, the phenolic resin was sufficiently cured so that machining into desirable geometries was possible. The pretreated and machined discs were then carbonized in argon at temperatures up to 1000°C to form the final carbon preforms.

Crystalline cellulose

Cellulose molecules (1,4-β-D-linked polyanhydro glucopyranose) are comprised of repeat units of $(C_6H_{10}O_5)_n$ with relatively large molecular weights ($500 \leq n \leq 7500$)^{12,13}. The chemical structure is illustrated in Figure 2.6.

Figure 2.6. Chemical structure of the cellulose molecule.

Pure crystalline cellulose is isolated from plant matter by acid hydrolysis reactions. The disordered regions of natural cellulose fibers are readily accessible and susceptible to chemical attack. Acid hydrolysis reactions depolymerize these less ordered regions, leaving only the crystalline portions of the microfibrils¹⁴⁻¹⁶. Decanting this solution removes the solvent and the suspended amorphous species resulting in nanocrystalline cellulose fibers. If these fibers are dried, aggregates of very porous one

hundred percent crystalline cellulose are formed. Purified crystalline cellulose is an excellent precursor for the production of high purity carbons.

Due to the lack of aromatic carbon rings in the cellulose molecular structure, thermal treatment of crystalline cellulose yields a highly amorphous carbon with angstrom-scale porosity. Further heating to graphitization temperatures ($>2600^{\circ}\text{C}$) still results in an essentially non-crystalline sp^2 -bonded carbon due to the inability to break carbon-carbon bonds to form the six membered carbon ring structure that is characteristic of graphite.

The Avicel PH-105 crystalline cellulose used in this research was produced by FMC Biopolymer (Philadelphia, Pennsylvania, USA) and is particulate in nature with a relatively uniform particle size of approximately 20 μm . These particles are aggregates of long (about 0.1 to 1 μm) and thin (about 1 to 30 nm) crystalline cellulose microfibrils aligned parallel to one another¹⁶.

Low temperature oxidation of crystalline cellulose

The conditions for thermal oxidation pretreatment of the carbon preforms were determined by using thermogravimetric analysis (TGA) and differential thermal analysis (DTA)¹⁷⁻²⁵. The SDT 2960 Simultaneous DTA/TGA instrument produced by TA Instruments (New Castle, DE 19720 USA) was used to perform these oxidation measurements. Figure 2.7a shows the TGA/DTA data for the oxidation of 52.5 mg of crystalline cellulose in flowing air with a thermal profile of $0.5^{\circ}\text{C min}^{-1}$ and a temperature range of 50-290 $^{\circ}\text{C}$. Figure 2.7a reveals two thermo-oxidation reaction zones, with Zone I occurring at approximately 240 $^{\circ}\text{C}$ and Zone II, a highly exothermic reaction, occurring at approximately 275 $^{\circ}\text{C}$.

Figure 2.7. TGA and DTA curves of the thermo-oxidation of crystalline cellulose for the temperature range of (a) 50-290°C, and (b) an expanded region showing the onset of reaction Zone II.

Zone I marks the onset of mass loss due to decomposition associated with cellulose depolymerization and the evolution of CO, CO₂, H₂O, carbonyl and carboxyl groups²⁶⁻²⁹. When the temperature reaches 276°C, combusive Zone II reactions become dominant resulting in the large jump of ΔT and the sharp increase in mass loss as shown in Figure 2.7b. This analysis indicates that Zone II reactions can be avoided by staying below the onset temperature of these reactions.

To further illustrate the onset temperature for Zone II reactions, DTA studies were performed by exposing crystalline cellulose to air at dwell temperatures ranging from 250 to 280°C for long periods of time. The DTA data in Figure 2.8 agree with Figure 2.7 in that a critical temperature exists for the occurrence of Zone II reactions. This critical temperature is between 260 and 280°C. Therefore, Zone II reactions for crystalline cellulose can be avoided by staying below 260°C. Since the onset temperature for Zone I reactions is just below 250°C, it was chosen as the maximum temperature to perform the thermo-oxidative pretreatments.

Figure 2.8. DTA data of the thermo-oxidation of crystalline cellulose with various dwell temperatures.

Phenolic resin

Phenolic (phenol-formaldehyde) resins are widely used by carbon-carbon composite producers as the matrix phase in the composite because they produce a very homogeneous glassy carbon with a carbon yield of over 50%. These resins are produced by combining phenol and formaldehyde with the aid of a catalyst, as shown in Figure 2.9. They have an idealized chemical formula of $(-C_6H_4O_2-)_n$. However, the actual reaction products contain many isomers of the phenolic molecular structure shown in Figure 2.9³⁰.

Figure 2.9. Synthesis and chemical structure of the phenolic resin molecule.

There are various types of phenolic resins, and they have relatively low molecular weights prior to curing. They can be cured at temperatures between 100 and 140°C. The curing leads to the formation of highly crosslinked three dimensional macromolecules

with high molecular weight³⁰. The curing cycle of the phenolic resin begins by first reaching the glass transition temperature of about 100°C. Once the temperature reaches about 140°C³⁰, the curing process is complete.

The Durite AD-5614 phenolic resin used in this study was produced by Hexion Specialty Chemicals (Columbus, Ohio, USA). This product is in particulate form with particle sizes less than 70 µm.

Curing of phenolic resin

In contrast to crystalline cellulose, phenolic resin is not significantly oxidized at temperatures below 300°C. However, it does go through crosslinking reactions that increase the strength and hardness of the composite. Phenolic resin in the precursor discs produces a carbon phase with high density and low reactivity upon carbonization. The low reactivity is directly due to a higher degree of atomic ordering and the lack of open porosity. In order to determine the appropriate thermal processing conditions for the phenolic component, TGA/DTA analyses similar to those performed on crystalline cellulose were carried out. This TGA and DTA experiment was performed with 35 mg of phenolic resin in air with a thermal profile of 1°C min⁻¹ over a temperature range of 60 to 160°C, and the data are plotted in Figure 2.10. Examination of these data shows evidence of exothermic curing reactions that begin at approximately 131°C.

Figure 2.10. TGA and DTA data for air curing of phenolic resin

In addition to the exothermic curing reactions that occur near this temperature, literature suggests that there are numerous other curing reactions beginning at approximately 80°C. These reactions are difficult to describe precisely. In Figure 2.10, the normalized mass and ΔT curves are far from being linear within the temperature range of 80 to 130°C due to the various reactions over this temperature range. These reactions can only be allowed to reach completion by raising the temperature very slowly from 80 to 130°C.

Carbon preform processing technique

Crystalline cellulose and phenolic resin particulates were blended into mixtures with various mass ratios without the aid of any solvent. Samples weighing 12 to 30 g were uniaxially cold-pressed to 35 MPa using a 57 mm diameter cylindrical die. These discs were pretreated in air at temperatures below 300°C following a thermal oxidation and curing procedure determined by the TGA/DTA studies. The temperature profile of this thermo-oxidation and curing procedure is given in Table 2.1.

Table 2.1. Temperature profile of the thermo-oxidation and curing procedure

Action	Rate/Time	T (°C)
Ramp	5°C/day	80-115
Ramp	115°C/day	230
Dwell	24 hr	230
Ramp	20°C/day	250
Dwell	5 day	250
Ramp	25°C/hr	RT

The sample discs pretreated with this thermal oxidative procedure were stronger and harder than the as-pressed discs. The as-pressed discs are too fragile and the fully carbonized discs are too hard and brittle to be machined. Thus, all machining operations in this study were performed after the oxidative pretreatment process. The final carbonization step was carried out in a 1218 Rapid Temp Retort Furnace from CM Furnaces, Inc. (Bloomfield, NJ, USA) under argon at temperatures up to 1000°C following the thermal schedule given in Table 2.2. This thermal schedule is a modified version of the profiles established in previous studies on the carbonization of various organic precursors^{9,10,31-33}. The various ramping and dwell steps in this schedule correspond to the temperature-dependent physical and chemical changes involved in the carbonization process including degassing, dehydration, and chemical decomposition at higher temperatures. Figure 2.11 presents a photograph of carbon monoliths created from 18 g discs made of 60:40 precursor material heated to 1000°C using the thermal schedule in Table 2.2. Figure 2.12 is a flowchart that describes the overall carbon preform production process with crystalline cellulose and phenolic resin as raw materials.

Table 2.2. Thermal profile for carbonization

Action	Rate/Time	T (°C)
Ramp	100°C/hr	RT-250
Dwell	0.5hr	250
Ramp	5°C/hr	275
Dwell	2hr	275
Ramp	5°C/hr	325
Dwell	2hr	325
Ramp	50°C/hr	450
Ramp	100°C/hr	1000
Dwell	1hr	1000
Ramp	100°C/hr	RT

Figure 2.11. Photograph of machined 1.45 inch micron-porous carbon preforms.

Figure 2.12. Flow chart of the process for making porous carbon monoliths.

2.3 SEM analysis of carbon preforms

The key to formation of silicon carbide by liquid silicon infiltration (LSI) of carbon monoliths is controlling pore structure and reactivity of the carbon. The chemical nature and porosity of the carbon has been characterized using scanning electron microscopy, mercury intrusion porosimetry, helium gas pycnometry, nitrogen gas adsorption surface analysis, and transmission electron microscopy.

Fracture surfaces of the monoliths after cold-pressing, after thermal oxidation, and after carbonization 1000°C are shown in Figure 2.13. These images were collected using a JEOL (Tokyo, Japan) JSM-6700F scanning electron microscope. The images of carbonized crystalline cellulose and phenolic resin show that carbons produced from these two materials have very different microstructures. The pure cellulose particles shrink in volume but retain their original morphologies through carbonization. This material retains the high open porosity originated from the initial packing of the cellulose particles. In addition, new nano-scale porosity is generated from the loss of volatiles. Phenolic resin particles melt during the early thermal oxidation stage, resulting in densification of the pressed disc. This results in the formation of closed pores due to entrapment of evolved gases as the phenolic resin crosslinks. The microstructure of the phenolic resin disc formed by melting is maintained during the final carbonization, leading to the formation of a highly dense glassy carbon with large closed pores. The 60:40 wt% cellulose and phenolic resin mixture yields a carbon with moderate open micron-scale porosity and nano-scale porosity. The effect of blending crystalline cellulose and phenolic resin into a mixture precursor is also illustrated in Figure 2.14.

Figure 2.13. SEM images of fracture surfaces of (1) crystalline cellulose, (2) phenolic resin, and (3) 6:4 precursor blend after pressing, after thermo-oxidation and after carbonization to 1000°C (scale bar = 20 μm).

Figure 2.14. SEM images of carbon preforms created from (a) crystalline cellulose, (b) phenolic resin, and (c) a 60:40 mixture. Scale bar is 10 μm .

2.4 Bulk density and mass yields of carbons produced from various precursor blends

The carbon yields of cellulose and phenolic resin mixtures with various ratios are shown in Figure 2.15a. The cellulose has a carbon yield of 9% and the phenolic resin has a yield of 64%. It was expected that the mass yields for the blends would follow the linear ‘rule of mixture’ relationship as the cellulose concentration was increased. However, this did not occur. During the carbonization of pure phenolic resin, some evolved gases are trapped within the microstructure and they are decomposed to produce additional carbon. This also occurs for the mixtures with low cellulose concentrations.

However, as the concentration of cellulose reaches about 50 wt%, a percolated pore network is achieved to allow gases evolved from the phenolic resin to escape before they decompose. This leads to a lower carbon yield for the phenolic resin.

Figure 2.15. (a) Carbon yields and (b) bulk densities of carbons made from precursor mixtures.

The bulk densities of the carbon monoliths are plotted in Figure 2.15b and they also show a deviation from linear behavior similar to Figure 2.15a. The bulk density of cellulose carbon is 0.82 g cm^{-3} and the value of phenolic resin carbon is 1.45 g cm^{-3} . As the concentration of cellulose is reduced, the carbon bulk density slowly decreases until a concentration of 50 wt% is reached. Upon carbonization, pure cellulose precursor discs shrink 49% in comparison with 18% for pure phenolic resin discs³⁴. The addition of a small amount of phenolic resin to cellulose reduces the shrinkage of the overall structure during carbonization and decreases the bulk density, even when the overall carbon mass yield is increased. The carbon yield of phenolic resin is much higher than that of cellulose, but the cellulose carbon phase still dominates the overall carbon structural evolution until the phenolic resin concentration reaches 50 wt%. Beyond this point, the overall carbon structure becomes dominated by the phenolic resin carbon phase.

Although the carbon dimensional yield continues to increase with increasing phenolic resin concentration, the decrease in percolation pathways and the much higher phenolic resin mass yield leads to a rapid increase in bulk density. As discussed earlier, the ideal bulk density of carbon preforms for LSI is theoretically determined to be 0.96 g cm^{-3} . This ideal value corresponds to a cellulose mass fraction of about 0.35. However, the true ideal bulk density of the carbon preforms must be determined through experiments.

2.5 Tuning carbon preform micron-scale porosity

As stated in earlier sections, carbon preforms need to have pores with diameters larger than $1 \text{ }\mu\text{m}$ ³⁵⁻³⁹ to allow successful silicon carbide formation by LSI. However, pores much larger than $1 \text{ }\mu\text{m}$ can result in residual porosity in the final product since large pores cannot be fully eliminated by the reaction. Based on literature reviews and our own observations, we have determined that the preferred pore diameter of the carbon preforms should be within an approximate range of 1 to $10 \text{ }\mu\text{m}$. The overall porosity of the carbon preforms produced from cellulose and phenolic resin precursor mixtures is defined by the composite carbon structure containing both cellulose carbon and phenolic resin carbon as shown in Figure 2.14. Carbon precursor mixtures with different mass ratios will produce carbon preforms with different porosity. The micron-scale porosity of these carbon preforms was analyzed with mercury intrusion porosimetry.

Mercury intrusion porosimetry is a technique that uses liquid mercury as a probing material to determine the micron-scale pore characteristics of a solid material. The specimen is placed in a specimen chamber that is filled with liquid mercury as shown in Figure 2.16. Mercury is then forced into the pores of the specimen under an increasing

chamber pressure from vacuum to 30,000 psi. As the pressure increases, liquid mercury is forced into smaller pores. The cumulative volume of mercury forced into the specimen pores as a function of the applied chamber pressure is recorded as the original data. The Micromeritics (Norcross, GA, USA) Poresizer 9320 was used to perform this study.

Figure 2.16. Illustration of mercury porosimetry.

According to general principles of capillary theory, the size of pores that can be forcibly filled by liquid mercury under a particular applied pressure is a function of this pressure, the surface tension and advancing contact angle of liquid mercury, and the geometry of the pores. For cylindrical pores, such function can be described by the Washburn equation, $D = -4\gamma \cos\theta P^{-1}$ ⁴⁰⁻⁴², where D is the pore diameter, γ is the surface tension, θ is the advancing contact angle, and P is the applied pressure. Since γ is 485 dyne cm⁻¹ at 20°C and if θ is assumed to be 130 degrees at 20°C⁴², the Washburn equation becomes $D = 181P^{-1}$ with μm as the unit for D and psi as the unit for P . The pore diameters of various carbon preforms produced from various cellulose and phenolic resin precursor mixtures were calculated with the simplified Washburn equation. The cumulative intrusion volume for these carbon preforms were then plotted as functions of both the applied pressure and the calculated pore diameter in Figure 2.17a. Pore size

distributions can be extracted from the cumulative intrusion plot by differentiating with respect to the logarithm of pore diameter in Figure 2.17b. By plotting the derivative function, $dV/d\log D$, against the logarithmically scaled pore diameter D , the specific volume of pores as a function of pore size is obtained. When plotted this way, the cumulative volume of pores in any range is equivalent to the area under the pore size distribution function in that range. The apparent volume of a carbon specimen can be measured by subtracting the volume of mercury needed to fill the pressure chamber containing the specimen under a vacuum from the volume of the empty specimen chamber. This apparent volume can be used to calculate the carbon bulk density. The median pore diameter of a specimen is determined from the cumulative intrusion plot (Figure 2.17a), and it is defined as the pore diameter at which 50% of total intrusion is reached⁴². Median pore diameters and bulk densities for carbon preforms are given in Table 2.3.

The cumulative intrusion curve with pressure is shown in Figure 2.17a. The curve of finely ground pure phenolic resin carbon shows low pressure intrusion. This is only a result of intrusion into void spaces between the finely ground specimen particles and is not due to intrusion into pores because phenolic resin carbon has no open micron-scale porosity. The lack of open micron-scale porosity in the pure phenolic resin carbon preforms prevents any infiltration, and reaction can only occur at the surface. The carbon preform produced from pure cellulose is also not suitable for LSI reactions since it has a median pore diameter of 0.6 μm that is below the critical pore diameter of 1 μm , which was discussed earlier. The 40:60 carbon preform has a pore size distribution between 0.5 and 5 μm and a median pore diameter of 1.3 μm . It also has a bulk density value of 0.93

Figure 2.17. Mercury porosimetry measurements of carbons made from cellulose and phenolic resin mixtures. (a) Cumulative intrusion data, and (b) pore-size distributions.

Table 2.3. Median pore diameters and bulk densities of carbon preforms.

precursor (cellulose : resin)	median μm-scale pore diameter (μm)	bulk density (g mL ⁻¹)	Comments
cellulose	0.64	0.82	pore diameters below the critical value
60:40 mass ratio	1.52	0.79	bulk density slightly below ideal value and pore diameters above critical value
40:60 mass ratio	1.29	0.93	ideal bulk density but low chemical reactivity
resin	-	1.45	no open porosity

g cm³ which is very close to the theoretically determined value. However, bulk silicon carbide formation reactions with this carbon preform were unsuccessful due to its low reactivity and low micron-scale porosity. The 60:40 carbon has a narrow pore size distribution of 0.5 to 2 μm with a median pore diameter of 1.5 μm. It gives the best results for the reaction, although it only has a bulk density value of 0.8 g cm³.

2.6 Tuning carbon preform reactivity

At atomic scale, the liquid silicon-carbon reaction begins with the dissolution of carbon by liquid silicon, followed by the precipitation of silicon carbide crystals out of the saturated silicon-carbon liquid phase. Therefore, the rate of the silicon carbide formation reaction is controlled by the rate of carbon dissolution. The rate of carbon dissolution in liquid silicon is defined by the carbon reactivity towards liquid silicon. Carbon reactivity is determined by its atomic structure which includes the nature of its chemical bonding and the concentration of ‘active sites’ due to bonding imperfection such as unsatisfied bonds, irregular bond angles, and angstrom-scale porosity. If carbon reactivity is too high, the dissolution of carbon proceeds too quickly to allow retention of the original geometry of the carbon preform. If the carbon reactivity is too low, only partial conversion occurs. The effect of undesirable carbon reactivity on the liquid silicon-carbon reaction is illustrated in Figure 2.18.

Figure 2.18. Illustrations for liquid silicon-carbon reactions with nonporous carbons with high and low reactivities

The above discussion illustrates the importance of carbon reactivity. Compared to the common allotropes of carbon including diamond, graphite, nanotube, nanorod, and fullerene, carbons formed from the carbonization of organic precursors are often more reactive because they have much lower degrees of atomic ordering and higher nano-scale and angstrom-scale porosity. The precursor materials used in this study, cellulose and phenolic resin, yield carbons that are believed to have mostly sp^2 C-C bonds as found in graphitic carbons. However, cellulose carbon has a much higher reactivity than the phenolic resin carbon due to the much higher degree of bonding imperfections.

Earlier experiments showed that the reactivity of cellulose carbon is too high for the formation of net shape silicon carbide. The reaction resulted in total disintegration of the carbon preform during the reaction yielding instead only coarse silicon carbide particles. We have also observed that the reactivity of pure phenolic resin carbon is too low, resulting in a partial reaction at the carbon preform outer surface. The use of homogeneous mixtures of cellulose and phenolic resin can produce carbon preforms with

reactivities between those of the cellulose and phenolic resin carbons. The desired mixture can be found by examining the atomic structure of carbon preforms from different mixtures and by analyzing their reaction products.

These carbon atomic structures have been studied with analytical techniques that include helium gas pycnometry, nitrogen gas adsorption and transmission electron microscopy. Helium gas pycnometry determines the actual densities of the carbons. Nitrogen gas adsorption techniques measure specific surface area and provide information on size distribution and volume fraction of fine pores. Transmission electron microscopy allows direct observation of lattice structure and imperfections.

Carbon actual density measured by helium gas pycnometry

The presence of high levels of atomic disordering and angstrom-scale porosity in cellulose carbons leads to its high reactivity. Atomic disordering in the carbon preforms also causes lower carbon actual density as compared with the theoretical actual density of graphite, 2.26 g cm^{-3} . Actual density of a solid is defined as its weight divided by its actual volume, and the actual volume is the overall volume minus *all* voids. Therefore, carbon actual density can be used as a measure for the level of atomic disordering, which is an indication of carbon reactivity. By comparing carbon preform actual density with that of graphite, the level of atomic disordering (i.e., lattice imperfections) can be qualitatively estimated and this can reveal the reactivity of the carbon preform. A Micromeritics (Norcross, GA, USA) Accupyc 1330 helium gas pycnometer was used to measure carbon actual density because the helium gas molecules can easily penetrate *all* open porosity to obtain the actual volume of the solid. Samples were prepared by

outgassing at temperatures between 200 and 350°C. Due to high levels of angstrom-scale porosity in the samples, pycnometry measurements took many hours to equilibrate.

The actual density values of carbons derived from cellulose, phenolic resin and a 60:40 mixture are given in Table 2.4. These values are all lower than the actual density of pure graphite due to the presence of atomic disordering in the carbon preforms.

Table 2.4. Actual densities of carbon preforms measured by helium gas pycnometry.

precursor (cellulose : resin)	density (g cm⁻³)	fraction of graphite density (g cm⁻³)
cellulose	2.098	0.928
60:40 mixture	2.191	0.969
phenolic resin	2.027	0.897
	2.212*	0.978
<i>graphite</i>	<i>2.261</i>	<i>1.000</i>

* calculated value

The presence of aromatic rings in the phenolic resin molecules results in the formation of small graphene clusters during heat treatment³⁴. These clusters increase the overall atomic ordering of the phenolic resin carbon and also lead to higher actual density. Cellulose molecules have no aromatic rings and thus form amorphous carbon with virtually no graphene character. This carbon should have a lower actual density and a higher reactivity than a phenolic resin carbon. The actual density of the 60:40 carbon should fall between those of the cellulose and phenolic carbons. However, as shown in Table 2.4 the measured actual density of phenolic resin carbon is lower than those of the 60:40 carbon and the pure cellulose carbon. The lower measured actual density value of phenolic resin carbon compared with the expected value is due to the presence of a large volume of nano-scale and angstrom-scale closed pores that cannot be reached by helium

gas. This leads to a higher measured actual volume than the true actual volume of the phenolic resin carbon. The cellulose carbon phase in the 60:40 carbon preform prevents the formation of closed pores in the phenolic resin carbon phase during carbonization, and this allows the accurate measurement of the actual volume of this carbon and provides a dependable actual density value.

The actual density of the phenolic resin carbon can be calculated from the measured actual density values of the pure cellulose carbon and the 60:40 carbon. As shown in Figure 2.15a, the carbon yield of cellulose is about 10%, and the carbon yield of phenolic resin is up to 65%. Based on these carbon yield values, the mass fraction of the cellulose carbon phase in the 60:40 carbon can be calculated to be about 18% and the phenolic resin carbon phase accounts for 82% of the total weight. This allows the actual density of the phenolic resin carbon phase in the 60:40 carbon to be calculated as 2.212 g cm^{-3} as shown in Table 2.4. The calculated actual density of the phenolic resin carbon can be used to compare with that of the cellulose carbon (2.098 g cm^{-3}) to show the difference in the level of atomic disordering and reactivity. It is apparent that cellulose carbon has a much higher level of atomic disorder and higher reactivity compared to phenolic resin carbon.

Specific surface area measurements by nitrogen gas adsorption

Carbons produced from cellulose and phenolic resin have nano-scale and angstrom-scale pores due to the difficulty of rearranging covalently bonded carbon atoms during carbonization⁴³⁻⁴⁶. The amount of this very fine porosity is a measure of carbon atomic disorder and is an indirect indication of carbon reactivity^{47,48}. A high level of nano-scale and angstrom-scale porosity results in a high concentration of active sites that

readily promote carbon dissolution in liquid silicon. This porosity was analyzed using a Coulter (Fullerton, CA, USA) SA 3100 nitrogen gas adsorption analyzer.

Nitrogen gas adsorption analyzes very fine porosity in solids by measuring the amount of surface-adsorbed N_2 gas molecules as the pressure is varied from very low to near saturation⁴⁹⁻⁵³. The measurement begins with placing an outgassed specimen into a sealed sorption chamber and the chamber is evacuated. The chamber is then cooled with liquid nitrogen and nitrogen gas is slowly introduced to the chamber with incremental doses to be adsorbed. The experimental setup of this measurement is shown in Figure 2.19. The nitrogen gas pressure is recorded as each of the small doses of nitrogen is incrementally injected into the chamber. Initially, nitrogen molecules are adsorbed onto any surfaces within the chamber without raising the gas pressure, and the pressure stays very low until a nitrogen monolayer is formed on all surfaces as shown in Figure 2.19. Then the gas pressure rises as nitrogen begins to form multilayers and/or a vapor phase. Continued nitrogen dosing culminates in a saturated vapor phase when the pressure approaches the nitrogen vapor pressure.

Figure 2.19. Illustration of the nitrogen gas adsorption technique.

The fundamental dataset measured by nitrogen gas adsorption is known as the adsorption isotherm. It is a measure of the specific volume of nitrogen gas at standard

temperature and pressure (20°C, 1 atm), V_{ads} , adsorbed by a specimen inside the measurement chamber at 77 K versus the relative nitrogen gas pressure P/P_o inside the chamber. Nitrogen adsorption isotherms for carbons made from cellulose, phenolic resin, and a 60:40 wt% cellulose and phenolic resin mixture are plotted in Figure 2.20. The shape of an isotherm can be used to determine carbon surface characteristics (e.g., being non-porous, porous with pore diameters greater than 2 nm, porous with pore diameters below 2 nm, non-adsorbing, etc.)^{51,53,54}. In order to better examine the shapes of the isotherms obtained, they are plotted against normalized V_{ads} scales in Figure 2.21.

Many nitrogen gas adsorption theories have been developed, and when applied to adsorption isotherms, they can be used to determine the specific quantity of gas that is required to form a monolayer, V_{mono} . Once V_{mono} is determined, the specific surface area (SSA) of the solid can be calculated as $SSA = V_{mono}\sigma N_A V_o^{-1}$, where σ is the surface area occupied by a single adsorbed N₂ gas molecule, N_A is Avogadro's number, and V_o is the molar volume of nitrogen gas^{53,55}. Since V_o is 22414 cm³ mol⁻¹, and σ is estimated to be 16.2 Å²⁵¹, the specific surface area equation becomes, $SSA = 4.35V_{mono}$. Carbon specific surface area can be used as an indicator for carbon reactivity because it is directly related to the degree of nano-scale and angstrom-scale porosity.

It is generally believed that under relatively low pressures nitrogen adsorption can only occur as sub-monolayer and up to monolayer adsorption^{49,50,55}. Since a N₂ molecule has a width of about 2 – 3 Å and a length of about 5 Å, the size of any adsorbing pore has to be greater than 2 – 3 Å and only sub-monolayer adsorption can occur in pores smaller than twice the N₂ molecular length, about 2 nm. Sub-monolayer, monolayer and multilayer adsorption can all occur in pores greater than 2 nm. The overall specific

Figure 2.20. Nitrogen adsorption isotherms for carbon specimens made from pure cellulose, pure phenolic resin, and a 60:40 wt% mixture.

Figure 2.21. Normalized nitrogen adsorption isotherms for carbon specimens made from (a) cellulose, (b) phenolic resin, and (a) a 60:40 wt% mixture.

surface area of a solid with pores smaller than 2 nm can only be measured by analyzing its sub-monolayer and monolayer adsorption. Langmuir's adsorption isotherm model was specifically developed to describe sub-monolayer and monolayer gas adsorption, and it can be used to measure the overall specific surface area, SSA_{total} , of the carbon preforms whose isotherms, as shown in Figure 2.20, are dominated by this sub-monolayer and monolayer adsorption. The direct value derived from Langmuir theory is the specific volume of gas required to form a monolayer, i.e., monolayer capacity V_{mono} . The Langmuir equation for gas adsorption under equilibrium is⁴⁹

$$\frac{P/P_o}{V_{ads}} = \frac{1}{V_{mono}b} + \frac{P/P_o}{V_{mono}}$$

where V_{ads} is the quantity of gas adsorbed at pressure P , and b is an empirical Arrhenius constant. The Langmuir model is most accurate at very low relative pressures well before monolayer saturation occurs⁵⁶, and the linear Langmuir equation only applies to adsorption in very low relative pressure regions that are generally between 0.005 and 0.05^{52,53}. A Langmuir plot is obtained when the term $(P/P_o)/V_{ads}$ is plotted against (P/P_o) over the relative pressure interval of 0.005 to 0.05, and the value of $1/V_{mono}$ is the slope of the linear Langmuir plot. Langmuir plots from the adsorption isotherms of carbon preforms are shown in Figure 2.22, and the values of the monolayer capacity V_{mono} and Langmuir specific surface area SSA_{total} are given in Table 2.5.

Figure 2.22. Langmuir plots over the relative pressure interval of 0.005 to 0.05 for carbons produced from pure cellulose, pure phenolic resin and a 60:40 wt% mixture.

Figure 2.23. Harkins-Jura t-plots for carbons produced from cellulose, phenolic resin and a 60:40 wt% mixture.

Table 2.5. Summary of specific surface area and monolayer capacity data

	Carbon preform		
	cellulose	60:40 mixture	phenolic resin
SSA_{total} ($m^2 g^{-1}$)	653	643	62
$SSA_{d>2nm}$ ($m^2 g^{-1}$)	32	26	20
SSA_A ($m^2 g^{-1}$)	621	617	42
% SSA_A	95	96	68
V_{mono} ($cm^3 g^{-1}$)	150	148	14

The Harkins-Jura t-plot model developed by Harkins and Jura in 1944 and deBoer and Lippens in 1966 allows the determination of specific surface areas for pores with discrete diameter ranges^{52,53,55,57-59}. This model provides a universal equation for the thickness t of an adsorbed nitrogen layer as a function of relative pressure P/P_o ^{57,58}

$$t = \left[\frac{13.99}{0.024 - \log_{10} \frac{P}{P_o}} \right]^{1/2}$$

When V_{ads} is plotted against t rather than the relative pressure, as shown in Figure 2.23, the V_{ads} value at the thickness interval of 5 – 7 Å corresponds to the overall volume of nitrogen adsorbed when pores smaller than 2 nm have been fully saturated, and the slope of V_{ads} over this thickness interval can be used to calculate the specific surface area of pores with diameters greater than 2 nm, $SSA_{d>2nm} = 1.547 \times (\text{t-plot slope})$ ⁵⁹. The specific surface area of pores with diameters less and 2 nm $SSA_{\text{\AA}}$ can be determined by subtracting $SSA_{d>2nm}$ from the total Langmuir specific surface area, SSA_{total} , $SSA_{angstrom} = SSA_{total} - SSA_{d>2\text{\AA}}$. These values are given in Table 2.5.

In general, nitrogen adsorption isotherms can be categorized into six standard isotherm curves according to IUPAC as illustrated by Donohue, et. al.⁵⁴, with each isotherm representing a distinct type of adsorption by a material with a specific type of surface and porosity^{51,53,54}. A Type I isotherm describes adsorption on microporous adsorbents and it approaches a limiting value as relative pressure is increased. Type II and III isotherms describe adsorption on macroporous adsorbents. Type IV and V describe mono- and multilayer adsorption combined with capillary condensation, and Type VI describes multimodal adsorption on materials with pores of different sizes⁵⁴. The

IUPAC classification on adsorption isotherms can be used to identify the surface characteristics of the carbon preforms by examining and comparing their adsorption isotherms with the standards^{55,60}. The normalized nitrogen adsorption isotherms of cellulose carbon and a 60:40 carbon are shown in Figure 2.21a and they exhibit Type I character. These Type I isotherms are characterized by their steep initial rise (*a*), a sharp knee (*b*), a leveling out to a long and nearly horizontal intermediate region (*c*) and a final rise, or a tail, to saturation and bulk condensation (*d*)^{51,53,54}. Type I isotherms are indicative of solids that contain pores with diameters about 2 nm and below⁵², and these very fine pores exhibit extraordinary adsorption capacity due to their high specific surface areas⁵³. Adsorption of nitrogen molecules on Type I materials occurs by progressively filling angstrom-scale pores in the order of increasing size. Once all angstrom-scale pores are completely filled with nitrogen molecules, very little subsequent adsorption occurs because there is essentially no surface area remaining⁵³.

Pure phenolic resin carbon was very difficult to outgas and its nitrogen adsorption results showed erratic adsorption behavior that cannot be well understood. This is because the as-prepared pure phenolic resin carbon has a high concentration of nano-scale (≤ 2 nm) and angstrom-scale closed pores. This makes outgassing almost impossible and nitrogen molecules cannot reach inside these pores to be adsorbed. To overcome this problem, it was necessary to grind the glassy carbon into very fine particles. This was accomplished by grinding with a ball mill, followed by sieving to obtain fine particles smaller than 50 μm . The nitrogen adsorption study on this fine powder sample was successful. The adsorption isotherm is shown in Figure 2.20 and is normalized in Figure 2.21. This isotherm exhibits a combined behavior of Type I and

Type II isotherms⁵². The Type I isotherm portion has a steep initial rise (*a*) with a sharp knee (*b*) due to the high concentration of angstrom-scale pores^{53,55,61}. Type I behavior occurs at low relative pressure and Type II adsorption dominates in higher relative pressure regions⁵⁵. The Type II isotherm portion indicates the presence of appreciable adsorption in pores larger than 2 nm that can accommodate N₂ multilayers. The Type II adsorption rises moderately at intermediate relative pressures (*c*)⁵⁵ and culminates in an abrupt rise in V_{ads} as relative pressure approaches unity (*d*).

In the Harkins-Jura thickness plots in Figure 2.23, the specific volume value of adsorbed nitrogen gas, V_{ads} , at a certain thickness value, *t*, indicates the overall quantity of N₂ molecules needed to achieve such adsorption thickness. However, it must be emphasized that the surface area available for nitrogen adsorption decreases with increasing pressure and nitrogen adsorption. The decrease in specific surface area available for additional nitrogen adsorption upon the increase in pressure is much more significant for materials with high concentrations of nano-scale and angstrom-scale pores. Inside these tiny pores, nitrogen adsorption can only achieve sub-monolayer to monolayer before these pores are totally filled. After these pores are totally filled, additional nitrogen adsorption can no longer occur inside these pores and this essentially leads to the decrease of the effective surface area. The further increase of pressure will no longer have an effect on the adsorbed nitrogen molecules inside the small filled pores, and there is no distinction between the material itself and these trapped molecules. Further nitrogen adsorption leading to thicker multilayers is very low because it can only occur on open surface. Therefore, only very small amounts of nitrogen are needed to build up these thick multilayers. By examining the shape of a t-plot, especially for the

lower thickness region, the contribution to nitrogen adsorption by the nano-scale and angstrom-scale pores can be determined. The t-plots for the cellulose and 60:40 carbons reveal that very high specific volumes of N₂ molecules (V_{ads} of about 150 cm³ g⁻¹) were required to achieve adsorption layers up to about 5 Å in thickness, and these are sub-monolayers and monolayers. After these thin layers are formed, much less nitrogen is needed to further increase the film thickness t . This indicates high concentrations of nano-scale (≤ 2 nm) and angstrom-scale porosity in these two carbons. The t-plot of the pure phenolic resin carbon shows that adsorption up to a complete monolayer requires a nitrogen gas specific volume of about 15 cm³ g⁻¹, also indicating a significant degree of nano-scale (≤ 2 nm) and angstrom-scale porosity. However, this t-plot also shows a large amount of multilayer adsorption as V_{ads} increases by about 10 cm³ g⁻¹ for thicknesses ranging from 5 to 18 Å. This is due to the presence of a large quantity of nano-scale pores larger than 2 nm within which multilayer adsorption can occur at higher pressures. These larger pores do not make a significant contribution to the reactivity of the carbon since the reaction between liquid silicon and carbon occurs at atomic scale.

Although the cellulose, phenolic resin, and 60:40 carbons all have similar levels of nano-scale (> 2 nm) pores as shown by $SSA_{d>2nm}$ values in Table 2.5, the cellulose and the 60:40 carbons have much higher nano-scale (≤ 2 nm) and angstrom-scale porosity than the phenolic resin carbon. This means the phenolic resin carbon has much lower reactivity than the cellulose and 60:40 carbons. In addition, due to the lack of micron-scale porosity, most of the angstrom-scale pores in the phenolic resin carbon are not accessible to liquid silicon. This makes the effective reactivity of the phenolic resin

carbon towards liquid silicon even lower and reaction can only occur on the phenolic resin carbon surface.

Diamond and graphene structures revealed by bright field TEM imaging

Helium gas pycnometry and nitrogen gas adsorption studies have demonstrated that the cellulose carbon possesses a much higher level of atomic-scale disordering than the phenolic resin carbon. The higher level of structural disorder in cellulose carbon indicates a higher concentration of active sites due to lattice imperfections that leads to a higher reactivity with liquid silicon. Additional information on the atomic-scale structure of the carbons was obtained by using a Phillips (FEI Company, Hillsboro, OR, USA) CM300 FEG energy filtered high-resolution scanning transmission electron microscope (TEM). All images were collected at a magnification of 600kx with an electron beam acceleration voltage of 300 kV. Specimens were prepared into 100 to 200 nm sized particles using a Netzsch (Exton, PA, USA) MiniCer type 993-04 fine-bead attrition mill in water with spherical zirconium oxide particles with diameters of 200 μm as grinding media. Specimen particle sizes were measured with a Horiba (Kyoto, Japan) Partica LA-950 laser scattering particle size distribution analyzer. Bright field TEM images were collected at thin near-uniform thickness edges⁶²⁻⁶⁴ of numerous thin specimens of cellulose and phenolic resin carbons to allow high quality imaging. Two examples of such images are shown in Figure 2.24.

a
cellulose carbon

b
phenolic resin carbon

Figure 2.24. Bright field TEM images of (a) cellulose carbon and (b) phenolic resin carbon.

TEM images can contain information on atomic and/or crystallographic lattice structure⁶⁵. An open-sourced image analysis software developed and maintained by NIST, ImageJ⁶⁶, was used to quantitatively analyze the TEM images of cellulose carbon (Figure 2.25a) and phenolic resin carbon (Figure 2.26a). Several regions exhibiting periodic structures were identified for each specimen. *3-D contour plots* and *vertically averaged pixel intensity profiles* for each region were constructed. Examples of the 3-D contour plots are shown for cellulose carbon in Figure 2.25b and for phenolic resin carbon in 2.26b. In these plots, the original TEM pixel intensity values (0-256) are represented by the vertical axis and the image area forms the basal plane. Examples of the vertically averaged pixel intensity profiles are shown for cellulose carbon in Figure 2.25c and for phenolic resin carbon in Figure 2.26c. These profiles can provide the periodicities of the visible layered structures in the TEM images.

a

b

c

Figure 2.25. (a) TEM image of cellulose carbon. (b) A 3-D contour plot and (c) a vertically averaged pixel intensity profile of a region with periodic structure.

a

b

c

Figure 2.26. (a) TEM image of phenolic resin carbon. (b) A 3-D contour plot and (c) a vertically averaged pixel intensity profile of a region with periodic structure.

Electron beam diffraction patterns showing crystallographic structure can be obtained from small volumes of materials during TEM imaging. However, the high doses of electron energy needed for electron beam diffraction can damage the original atomic-scale structures of the highly disordered cellulose and phenolic resin carbons⁶⁷. Therefore, electron beam diffraction was not performed on these samples. Instead, Fourier transform image processing⁶⁸⁻⁷⁹ was applied to analyze randomly selected regions within the TEM images to obtain crystallographic information. 2-D fast Fourier transform treatment of TEM images converts discrete digital data to the frequency domain⁸⁰⁻⁸³. This treatment can reveal the frequency of periodic patterns within the images that directly correspond to periodic structures within the specimen. 2-D fast Fourier transform treatments of TEM images of the carbons were performed by using the computer program, Gatan DigitalMicrograph⁸⁴. Examples of the 2-D Fourier transform power spectra are shown in the insets within the TEM images in Figure 2.27a and Figure 2.27c. These 2-D power spectra are radial plots with frequency values increasing from zero at the plot's central point to higher values as radial distance is increased, with the frequency values having units of inverse distance ($\text{\AA}^{-1}$). Bright spots or rings in the 2-D power spectra indicate structure within the original image⁶⁸⁻⁷⁹. The region of small inverse distance in a 2-D power spectrum represents low frequency coarse periodic structures within the original TEM image, and the region of large inverse distance represents high frequency fine periodic structures⁶⁹.

The 2-D power spectra show data in the form of reciprocal space values. Real space values can be obtained by radially averaging these intensity values to obtain a 1-D plot, followed by inversion of the x-axis values. Structural periodicities appear as peaks

CELLULOSE CARBON

RESIN CARBON

Figure 2.27. TEM images of (a) cellulose carbon and (c) phenolic resin carbon with insets showing 2-D fast Fourier transform power spectra of the TEM images, and 1-D real space power spectra for (b) cellulose carbon and (d) phenolic resin carbon obtained from the 2-D power spectra.

in the 1-D plot⁷²⁻⁷⁸. Any structural peaks within the 1-D plot have distance values that correspond directly to the periodicities in the original TEM image⁶⁸⁻⁷⁹. Therefore, 1-D plots provide a more convenient approach to observe the periodic structure within the original image. 1-D plots were made by using the NIST created and maintained image processing program, Lispix⁸⁵. Examples of 1-D spectra are shown for cellulose carbon in Figure 2.27b and for phenolic resin carbon in Figure 2.27d.

The d-spacing values, d_{hkl} , of graphite and diamond standards determined by x-ray diffraction for each family of diffracting planes and the relative intensity values for each diffracting plane, I/I_1 , were obtained from the JCPDS database⁸⁶ and are tabulated in Table 2.6 and Table 2.7 for easy comparison with structural information of the cellulose and phenolic resin carbons. For graphite, the {002} family of crystallographic planes have a relative intensity of 1, which is roughly one order of magnitude greater than the relative intensity of any other crystallographic planes. As a result, if there is graphitic structure within the TEM images, they are most likely to be observed as {002} planes. For diamond, the {111} family of crystallographic planes have a relative intensity of 1, and the {220} planes have a relative intensity roughly one quarter of that of the {111} planes.

The TEM images of cellulose and phenolic resin carbons in Figure 2.24 show some periodic near-linear structures that are consistent with structures observed in other carbonized organic materials^{43,87-91}, and these linear structures are expected to be graphene⁹²⁻⁹⁴ in nature. However, the overall degree of atomic-scale ordering in both images is quite low, with the phenolic resin carbon image showing a higher degree of ordering than the cellulose carbon image. The carbonization of phenolic resin produces

**Table 2.6. Graphite
powder diffraction data**

JCPDS card no.	12-212	
a_0 (Å)	2.464	
c_0 (Å)	6.736	
d_{hkl} (Å)	I/I_1	{hkl}
3.37	100	002
2.132	2	100
2.036	3	101
1.80	1	102
1.682	8	004
1.541	2	103
1.232	6	110
1.155	6	112
1.12	2	006, 105
1.05	2	201
0.994	4	106, 114
0.842	1	008
0.827	2	116

from JCPDS Powder diffraction database⁸⁶

**Table 2.7. Diamond
powder diffraction data**

JCPDS card no.	6-0675	
a_0 (Å)	3.5667	
d_{hkl} (Å)	I/I_1	{hkl}
2.060	100	111
1.261	27	220
1.0754	16	311
0.8916	7	400
0.8182	15	331

from JCPDS Powder diffraction database⁸⁶

**Table 2.8. The interlayer spacings of cellulose and phenolic resin
carbons compared to standard graphite and diamond.**

TEM material	observed interlayer spacing (Å)	carbon crystal	{hkl}	lattice spacing (Å)
cellulose carbon	3.5 - 3.7	graphite	{002}	3.37
phenolic resin carbon	3.5			
cellulose carbon	2.1	graphite	{110}	2.132
phenolic resin carbon	2.05	diamond	{111}	2.06
phenolic resin carbon	1.2	diamond	{220}	1.261

brittle glassy carbons that form sharp jagged edges when broken. Nanoscale sharp jagged edges are also observed in the TEM images of the phenolic resin carbon (Figure 2.24b). Regions with linear structural periodicity are often found along these nano-scale edges in the TEM images, and they can be as long as 20 nm. The frequent appearance of these regions along the sharp jagged edges can be explained as the preferential fracture of the phenolic resin carbon parallel to the graphene planes. In addition to these coarse linear structures, phenolic resin carbon clearly exhibits regions with very fine periodic structure, as shown in the higher magnification inset image in Figure 2.24, and such fine structure is not observed in the cellulose carbon images (inset in Figure 2.24). The periodicity of this fine phenolic resin carbon structure is very close to the d-spacing of diamond {100} planes. This indicates that the phenolic resin carbon exhibits sp^2 -bonded graphene structures in some regions and it also exhibits highly ordered nano-scale volumes of sp^3 -bonded diamond crystals in other regions.

In Figure 2.25, a small area cropped from a cellulose carbon TEM image shows a periodic near-linear structure over a square area of about 1.8 by 1.8 nm. The vertically averaged pixel intensity profile compiled from this region shown in Figure 2.25c exhibits a sinuous appearance with interlayer periods of 3.6, 3.5, 3.7 and 4.6 Å. These interlayer spacing values are comparable to the d-spacing value of the {002} family of graphite crystal planes, $d_{002} = 3.37 \text{ Å}$ ^{43,87-91} as shown in Table 2.6, but are about 7% larger than the graphite value. The larger d-spacing values for the nano-scale graphene clusters in the cellulose carbon are due to their high energy state as compared with that of bulk graphite. Figure 2.26a shows a small region of a phenolic resin carbon TEM image exhibiting a highly ordered structure. In Figure 2.26c, the vertically averaged pixel intensity plot for

this region shows nearly identical interlayer spacing values of $3.5 \pm 0.1 \text{ \AA}$. Compared to the layered structure in the cellulose carbon (Figure 2.25), this phenolic resin carbon layered region has a much higher level of periodic ordering over a much larger area of about 5 by 10 nm. The interlayer spacing values of this phenolic resin carbon region are also higher than the standard graphite d-spacing value. Since these phenolic resin carbon graphite-like nano-clusters are larger and more ordered than those found in cellulose carbon, their energy state is lower. This explains the fact that the interplanar spacing values of the phenolic resin clusters are only about 4% larger than the standard graphite d-spacing value.

Figure 2.27 shows examples of digitally magnified small regions cropped from the original TEM images of cellulose carbon and phenolic resin carbon for Fourier transform image processing. These small regions were selected to represent the common features found in the TEM images. The image of cellulose carbon (Figure 2.27a) shows structure that is neither linear nor periodic, and the phenolic resin carbon image (Figure 2.27c) shows a high degree of linear periodicity that cannot be visually identified under the original magnification. 1-D real space power spectra can be used to identify periodic patterns within the TEM image representing lattice ordering and to obtain spacing values for these structures. The strongest feature found in both of the 1-D power spectra of cellulose carbon (Figure 2.27b) and of phenolic resin carbon (Figure 2.27d) is a broad peak with a maximum near $5.5 \text{ \AA}$ for cellulose carbon and $7 \text{ \AA}$ for phenolic resin carbon. As suggested by Oshida, Endo, et. al.⁷²⁻⁷⁶, and others^{77,78}, these broad peaks are due to the angstrom-scale porosity in the carbons and the ranges of the peaks represent the size distribution of these pores. Due to the presence of these broad peaks, the sp^2 -bonded

graphene interlayer spacing value of about 3.6 Å for both the cellulose and phenolic resin carbons cannot be seen in the 1-D plots since the graphene clusters observed in the original TEM images only account for small fractions of the overall imaging area.

For the phenolic resin carbon, two additional peaks with maxima at about 2.05 and 1.2 Å can be identified. The 2.05 Å peak is very close to the d-spacing of diamond, $d_{111} = 2.06$ Å (Table 2.8), which has an XRD relative intensity of 100%. This strongly suggests that there is a large volume fraction of highly ordered diamond in the phenolic resin carbon. The 2.05 Å peak is also close to the spacing of graphite, $d_{100} = 2.13$ Å, but this crystallographic plane only exhibits an XRD relative intensity of 2%, thus it is not very likely to be observed during TEM phase contrast imaging. Further support for this assumption lies in the fact that the d-spacing for nano-scale graphene structures should be larger than that of graphite. The 1.2 Å peak in phenolic resin carbon is very close to the d-spacing for diamond, $d_{220} = 1.26$ Å, which has an XRD relative intensity of 27%. The cellulose carbon has one small diffuse peak at about 2.1 Å corresponding to the {111} diamond planes, but the amount of this structure appears to be much lower than in phenolic resin carbon.

The above analysis indicates that cellulose and phenolic resin carbons have high degrees of crystalline and amorphous sp^2 -bonded structures. The phenolic resin carbon also exhibits significant amounts of diamond-like sp^3 -bonded carbon. Small concentrations of diamond-like carbons have been observed by Rhim, et. al⁹⁵, and diamond structures have been observed in lignocellulosic carbons by Hata, Bronsveld, et. al^{67,96,97}. Future studies on the phenolic resin and cellulose carbons should include analysis with bright field TEM and Fourier image processing, dark field TEM, XRD,

Raman spectroscopy, EELS, XPS and FTIR to identify the true bonding character (i.e., sp^2 or sp^3).

In summary, both phenolic resin and cellulose carbons show periodic near-linear graphene structures with interlayer spacing values within the approximate range of 3.5 to 3.7 Å. The higher atomic-scale ordering in phenolic resin carbon explains its low reactivity with liquid silicon as compared with cellulose carbon. These two carbons also exhibit periodic ordering with spacing values of about 2.05 Å that correspond to the diamond {111} crystallographic planes, but this feature is more significant in phenolic resin carbon.

2.7 Changes in electrical properties of microcrystalline cellulose as function of carbonization temperature

Electrical properties of various forms of carbons, including graphite, anthracite carbons, carbon nanotubes, and graphene materials are of great interest in many areas. The electrical properties of carbon materials derived from organic precursors have been studied extensively over the years and have been shown to vary widely depending on the nature of the precursor and the heat treatment temperature (HTT) [98-105]. Microcrystalline cellulose is a basic component of wood that has been highly refined to remove all the inorganic ash. By using this high purity precursor material, it is believed that more definitive observations could be made on the carbonization mechanisms of organic compounds as they are converted to non-graphitizing hard carbons. Since cellulose molecules do not contain any aromatic structures and does not exhibit an intermediate mesophase, they yield a highly amorphous carbon even when heated to extremely high HTTs. This study focuses on measuring changes in AC and DC electrical

conductivities of microcrystalline cellulose during its transformation into carbon over the temperature range from 250°C to 2000°C. By carefully observing electrical conductivity changes caused by different final HTTs, the structural evolution of microcrystalline cellulose carbon could be followed.

Earlier studies of electronic properties of soft carbons described by Pinnick HT [98] and Seldin EJ [106] have shown that electrical resistivity decreased by nine orders of magnitude as HTT increased from 600°C to 3000°C, resulting in a non-metal to metal transition. In an attempt to describe such observations, a band model was proposed [98] in which resistivity varied as a function of an energy gap. As the thermal energy (kT) increased with increasing testing temperatures (T), resistivities of soft carbons were shown to decrease as the number of electrons lifted to the conduction band increased for samples heat treated below 1200°C. Later work (Giuntini and Jullien [99], Guintini and Zanchetta [107]) described electron hopping between localized states as the main mechanism for electric conduction for samples heat treated to 600°C and between localized states near the Fermi level for samples heat treated to 650°C. Such studies were attempted to better describe the non-metal-metal transition observed between HTT of 600°C and 650°C for anthracene carbons. By calculating the number of density of states as a function of HTT, the authors have shown that the number of localized states increases as HTT is increased within the range of 600°C to 700°C, thus explaining the non-metal to metal transition observed.

More recent studies by Kercher and Nagle [101] showed a change of DC electrical conductivity of carbonized medium-density fiberboard heat treated to temperatures of 600°C and above. A percolation model based on the nucleation and

growth of highly conducting turbostratic sites embedded within a dielectric was used to explain the varying conductivities [108]. AC studies by Sugimoto and Norimoto [102, 109] of carbonized wood materials heat treated to temperatures lower than 600°C showed frequency dependent conductivity values. Dipole polarization and Maxwell-Wagner interfacial polarization were used to explain such results. Furthermore, a heterogeneous structure exhibiting interfacial polarization that seemed to occur at the interface of isolated conductive regions was described to support both percolation and interfacial polarization by Kercher and Nagle [108].

Two models of two-phase composites consisting of conductive regions embedded within an insulating matrix have been proposed by McLachlan et al [110-115]. Systems composed of conductive regions separated interstitially by an insulating medium with separation distances large enough to limit electron hopping and tunneling are best described by the Maxwell-Wagner model:

$$\frac{\sigma_m - \sigma_c}{\sigma_m + 2\sigma_c} = \frac{(1 - \phi)(\sigma_i - \sigma_c)}{\sigma_i + 2\sigma_c} \quad (1)$$

where σ_m , σ_c , and σ_i denote the mean conductivity of the system, the conductivity of conductive clusters, and the conductivity of the insulating matrix, respectively, and ϕ denotes the volume fraction of the conductive phase.

Electrical properties of binary composites have also been well described by the effective media and percolation theories [110, 112, 115]. In such systems the conductivity is shown to increase sharply when the volume fraction of the conductive phase reaches a critical volume fraction, ϕ_c . At this point the percolation threshold is reached and the conductivity of the composite changes from that of an insulator to

conductor. Systems with the conducting phase surrounded by a mixture with an effective conductivity of the medium are well characterized by the general effective media (GEM) equation:

$$\frac{(1-\phi)(\sigma_i^{1/s} - \sigma_m^{1/s})}{(\sigma_i^{1/s} + A\sigma_m^{1/s})} + \frac{\phi(\sigma_c^{1/t} - \sigma_m^{1/t})}{(\sigma_c^{1/t} + A\sigma_m^{1/t})} = 0 \quad (2)$$

where $A = \frac{(1-\phi_c)}{\phi_c}$, s and t are exponents that dependent on the dimensionality and geometry of the system, and the conductivity of the composite, σ_m , is characterized by finite values of conductivity for the conductive phase and insulating phase, σ_c , and σ_i , respectively. The GEM equation above yields two limits below and above the critical volume fraction:

$$\sigma_m = \sigma_i \left(\frac{\phi_c}{\phi_c - \phi} \right)^s \text{ for } \phi < \phi_c \quad (3a)$$

$$\sigma_m = \sigma_c \left(\frac{\phi - \phi_c}{1 - \phi_c} \right)^t \text{ for } \phi > \phi_c \quad (3b)$$

Above the critical volume fraction, ϕ_c , Equation (2) reduces to Equation (3b) and has the same form as the percolation equation:

$$\sigma_m = \sigma_c (\phi - \phi_c)^t \text{ for } \phi > \phi_c \quad (4)$$

A two-phase system of conductive regions in contact within an insulating matrix, where an increasing volume fraction, ϕ , of the conductive phase facilitates hopping and tunneling of electrons, may best described by the percolation model.

Percolation of many two-phase composites varying in conductive and insulating volume fractions has been extensively studied [110-118]. The reported AC conductivities followed the general relationship:

$$\sigma = \sigma_0 + \sigma(\omega) \quad (5)$$

where the total AC conductivity observed, σ , displayed a frequency independent term at low frequencies ($\omega \rightarrow 0$ Hz) or DC conductivity, σ_{dc} , and a frequency dependent term, $\sigma(\omega)$, whose real term followed a power law relationship of $A\omega^s$ [117, 119]:

$$\sigma = \sigma_{dc} + A\omega^s \quad (6)$$

For low fractions of conductive material below the percolation threshold, the system behaved as an insulator; and for high fractions above the percolation threshold, the system behaved as a conductor. The conductivity of the overall system was observed to increase dramatically as the fraction of conductive material reached the percolation threshold. Percolation of conductive sites was shown to assist electron hopping and tunneling [104, 118, 120-122], therefore increasing the overall conductivity of the system.

This study was undertaken to fully characterize the electrical property changes that take place during the carbonization process involving both compositional and structural changes. By using a high purity homogeneous carbon precursor such as microcrystalline cellulose, more definitive observations can be made regarding the organic matter to carbon conversion process.

Experimental methods

Avicel microcrystalline cellulose powder was mechanically pressed and compacted into 2 inch diameter disks at 10 Tons. Pressed disk samples were placed between flat graphite sheets to ensure uniform temperature distribution during heating. Samples were then heat treated in an argon filled inconel-lined retort furnace to final HTTs using the following heating schedule: 100°C /hr to 250°C, 3 hr dwell; 5°C /hr to 275°C, 2 hr dwell; 5°C /hr to 325°C, 2 hr dwell; 50°C /hr to 450°C, 1 hr dwell; 100°C /hr to final HTT, 12 hr dwell; 100°C /hr to 25°C.

Samples for electrical conductivity studies made in the retort furnace have final HTTs of 250°C, 300°C, 350°C, 400°C, 450°C, 500°C, 550°C, 600°C, 650°C, 700°C, 750°C, 800°C, 900°C and 1000°C. Samples of higher HTTs of 1200°C, 1500°C, 1800°C, and 2000°C were prepared by further heating the 1000°C retort furnace samples in a high-temperature graphite furnace. Before the high-temperature treatments, these samples were first outgassed in vacuum at 1300°C for 12 hours (except for 1200°C samples, which were outgassed at 1000°C instead).

AC conductivity measurements were performed using an HP4194A impedance/gain analyzer with the HP16451B dielectric test fixture. Samples were placed in between two 38-mm electrodes (guarded/unguarded). Samples for AC measurements included those heat treated at final temperatures of 250°C to 650°C. Parallel conductance was recorded as a function of frequency (ranging from 1000Hz to 1MHz) at room temperature.

DC conductivity was measured for samples heat treated from 650°C to 2000°C at several temperatures between -50°C to 150°C using a four-point probe apparatus

following the standard procedure for measuring electrical resistivity as described by ASTM C 611-98, ASTM 2003 [123]. Samples were machined and polished to fit specimen dimensions and to reduce errors from surface imperfections. A Lodestart 8300 variable power supply was used as the current source and two HP 34401A multimeters were used for current and voltage measurements.

Skeletal density measurements were conducted using the Accupyc 1330 helium pycnometer for all samples heat treated from 250°C to 2000°C. Since the effect of closed micropores becomes significant for samples heat treated at 650°C to 2000°C, these samples were first activated in a convection furnace at 290°C for 24 hours before skeletal density measurements to minimize the effects such closed pores and adsorption.

Results and Discussion

Microcrystalline cellulose was used as a carbonization precursor to produce a series of materials with final heat treatment temperatures (HTTs) ranging from 250°C to 2000°C. The AC and DC electrical conductivities of these materials have been measured and are summarized in Figure 2.28. As shown in Figure 2.28, five distinct regions of electrical conductivity can be identified. These five regions of electrical properties are interpreted to be in direct correlation with the microstructural changes during carbonization. By closely examining the effect of final HTTs on the AC and DC electrical conductivities of the carbonization products, it is possible to identify and interpret stages of microstructural evolution during carbonization.

Region I (Figure 2.28a) comprises samples heat treated to final HTTs of 250°C, 300°C, and 350°C. The electrical conductivity of this region increases with increase in

frequency of applied electric field. As indicated by Sugimoto and Norimoto [102, 109], at this HTT range, the hydrocarbon is not fully depolymerized and still possesses high concentrations of hydroxyl and carboxyl functional groups that dominate the overall electrical conductivity in this region. These organic groups have dipole moments that respond to an applied AC field and such dipole interaction increases as the frequency of the AC field becomes stronger. The overall AC conductivity of this group of materials decreases as a function of increasing HTTs since the increase of HTTs leads to the removal of more and more hydroxyl and carboxyl groups from the original precursor as gaseous by-products.

Figure 2.28. Five regions of electrical conductivity measurements and microstructure evolution originated from microcrystalline cellulose carbonization at final HTTs of 250°C to 2000°C; (a) Region I – dipole polarization (HTT 250°C-300°C); (b) Region II – linear AC conductivity, carbon cluster formation & growth (HTT 400°C-500°C) ; (c) Region III – non-linear AC conductivity, electron hopping (HTT 550°C-600°C); (d) Region IV - DC conductivity, percolation (HTT 650°C-1000°C); and (e) Region V – DC conductivity, percolation threshold (HTT 1200°C-2000°C).

In Region II (Figure 2.28b) the HTT is progressively increased to 400°C, 450°C, and 500°C, and the electrical conductivity of the materials is dominated by the formation

and onset growth of conducting carbon clusters. Hydroxyl and carboxyl groups, which are responsible for the electrical conductivity of the Region I materials through dipole polarization, are now almost fully driven off due to the higher HTTs. Highly conductive carbon nano-clusters begin to form at HTT of 400°C and the concentration and size of these conductive clusters grow with the increase of HTT from 400°C to 500°C, explaining the overall rising trend of conductivity with increasing HTTs.

Region III (Figure 2.28c) includes samples heat treated to final temperatures of 550°C and 600°C. In this region, non-linear electrical conductivity as a function of applied frequency is clearly observed. Continuous growth of conductive carbon nano-clusters within the dielectric matrix of disordered hydro-carbon groups gives rise to interfacial polarization under an applied AC electric field and a quasi-percolated system aiding electron hopping. Sugimoto and Norimoto [102] observed similar results with carbonized wood specimens with HTTs of 500°C, 550°C, and 600°C, proposing that the non-linear increase in conductivity with frequency was due to the existence of interfacial polarization. At HTT higher than 550°C, no more polar functional groups or permanent dipoles are left; and instead, polarization is caused by the localized movement of free electrons and ions causing dipole moments. An applied AC field induces polarization across this interfacial phase when the polarization energy barrier is overcome at higher frequencies. Interfacial polarization is a result of the localized movement of free electrons of the carbon clusters as suggested by [102, 108, 124-126], and such frequency dependent polarization across the interfacial phase causes a dipole moment. Maxwell Wagner relaxation observed due to interfacial polarization is caused by a heterogeneous nature of the material.

As suggested by Barrau et al [116], electron hopping between conducting nano-clusters is aided by the continuous development of a percolated system reaching a percolation threshold. Simultaneous growth of both conducting carbon clusters and shrinkage of carbon monolithic structure with increasing HTTs reduces inter-particle distance of the carbon clusters. At this stage these carbon clusters become close enough for electron hopping and quasi-percolation of conducting sites to occur, as predicted by Kercher and Nagle [101, 108].

AC electrical conductivities of samples with HTTs ranging from 600°C to 650°C were closely analyzed to further study the insulator to semi-conductor transition and the results are shown in Figure 2.29. As Figure 2.29 shows, the electrical conductivity becomes frequency independent at HTT of 610°C. However, these results differed from the gradual transition from frequency dependent to frequency independent AC conductivities observed before and after the percolation threshold for carbon nanotube polyepoxy [116], carbon anthracites [99], and carbon-insulator composite systems described [111, 113, 114]. The influence of interfacial polarization deterred our results from following the power law stated in Equation (6). AC conductivity of our materials begins to become independent of frequency abruptly between HTTs of 600°C to 610°C, suggesting that the percolation threshold volume, ϕ_c , of conducting carbon nano-clusters has been reached between these two very close HTTs. In traditional two-component conducting filler/insulating matrix composite systems [111, 112, 118], the arrival at the percolation threshold is achieved by increasing the concentration of conductive fillers. In our system, the arrival at percolation threshold is also achieved by the increase of carbon nano-cluster concentration by the increase of HTTs. The increase of HTTs also leads to

the increase of intrinsic electric conductivities of the conducting phase; while in traditional two-component systems the intrinsic electrical conductivities of the conductive phase remains constant.

Figure 2.29. Electrical conductivity measurements near the percolation threshold, HTT 600°C, 610°C, and 650°C.

As HTT increases from 600°C to 1000°C (Region IV shown in Figure 2.28d), the overall DC conductivity increases by about 5 orders of magnitude as the result of further percolation and rising intrinsic conductivity with HTT increase. As shown in Figure 2.30, the greatest increase of bulk conductivity occurs at HTT 600°C-610°C, signaling the arrival at percolation threshold and onset of DC conductivity due to electron hopping between conductive carbon nano-clusters. The increase in conductivity due to the growth and interconnectivity of the carbon clusters can be described by percolation theory. Similar results of increasing ϕ with HTT and a sharp increase in conductivity at ϕ_c have been observed for anthracite carbons by Giuntini et al. [99] and Celzard et al [100]. In addition to anthracite carbons, composites consisting of wood-based carbons [127],

carbon blacks [111, 128], and graphite flakes [129, 130] within a polymer matrix also showed such conductivity behaviors and these systems were well described by percolation theory. However, it is important to note that for our materials, the conductive carbon clusters grow and intrinsically become more organized with higher HTTs, thus leading to the increase of the intrinsic conductivity of the conductive phase.

Figure 2.28e and Figure 2.30 show that the overall conductivity of our materials becomes constant with further increase HTTs from 1200°C to 2000°C. This indicates that the system has reached full percolation with the intrinsic conductivity of the carbon clusters being constant in this HTT region. Although we can firmly propose the arrival of full percolation at the HTT of 1200°C, we cannot determine the exact HTT range (below 1200°C) where the intrinsic conductivity of the carbon nano-clusters becomes constant.

Figure 2.30. Extrapolated frequency independent electrical conductivity ($\sigma_{0,dc}$) of heat treated microcrystalline cellulose samples as a function of HTT from AC and direct DC conductivity measurements, ● (as shown in Figure 2.28); and calculated skeletal electrical conductivities, ▲.

In our carbon materials the connectivity path of carbon conducting nano-clusters among the insulating matrix and the porosity within the matrix are equally important in determining the overall conductivity. In Figure 2.31, electrical conductivity is shown to increase with increasing skeletal density (decreasing porosity) as expected. As HTT is increased, samples shrink in volume while conductive carbon nano-clusters form and grow.

Figure 2.31. Electrical conductivity dependence on skeletal He density.

In order to analyze the net contribution to overall electrical conductivity by the carbon conducting nano-clusters and insulating matrix, skeletal conductivity is chosen over bulk conductivity in order to neglect the effects of porosity. Skeletal conductivity can be calculated based on skeletal and bulk densities as indicated by Ashby et al [101, 131]:

$$\left(\frac{\sigma}{\sigma_s}\right) = \frac{1}{3}\left(\frac{\rho}{\rho_s}\right) + \frac{2}{3}\left(\frac{\rho}{\rho_s}\right)^{1.5} \quad (7)$$

where σ is the measured bulk conductivity, σ_s is the skeletal conductivity, ρ is the bulk density, and ρ_s is the skeletal conductivity. Bulk and calculated skeletal conductivities as a function of HTT are shown in Figure 2.30. The skeletal density, ρ_s , is solely dependent upon the densities and volumes of conductive carbon clusters, ρ_c and V_c , and those of the non-conductive amorphous phase, ρ_i and V_i . The total volume of the skeletal phase, V_{total} , is sum of the volumes of conductive and insulating phases, V_c , V_i . The volume fraction of the conductive phase, ϕ , can be derived from:

$$V_{total} = V_c + V_i \quad (8a)$$

$$\rho_s = \frac{\rho_c V_c + \rho_i V_i}{V_{total}} \quad (8b)$$

With $\phi = \frac{V_c}{V_{total}}$, Equation (8b) reduces to:

$$\phi = \frac{\rho_s - \rho_i}{\rho_c - \rho_i} \quad (8c)$$

To implement Equation (8) several assumptions should be taken into account:

- (1) The skeletal density of our materials only depends on the volume fraction and density of conductive and non-conductive phases. Since we used a purified form of cellulose as a precursor, our materials do not have ashes as found in other forms of carbons such as anthracites [100].
- (2) The density of the amorphous phase, ρ_i , is assumed to be that of the measured skeletal density of HTT 400°C sample, 1.37 g/cm³, based on the assumption that at the of HTT of 400°C, most of the non-carbon elements have been volatilized and a high purity amorphous carbon has been formed.
- (3) The density of the conductive phase, ρ_c , is assumed to be that of the measured skeletal density of the HTT 2000°C sample, 2.16 g/cm³, based on the assumption that at the HTT of 2000°C, the only existent phase is the conductive phase and the amorphous phase has been eliminated.

Taking all these assumptions into account, the calculated skeletal conductivity, σ_s , as a function of ϕ is shown in Figure 2.32. A sharp increase in conductivity occurs when

ϕ equals 0.39, corresponding to the HTT of 600°C sample and to the critical volume fraction, ϕ_c . Above this ϕ_c value, σ_s continues to increase with increasing ϕ , eventually reaching a plateau. For our system, the increase in conductivity at ϕ_c , is not as sharp as it has been observed for materials in previous studies [100, 127-130], where the exponent, t , is reported to have had values of about 2. The GEM and percolation equations have been fitted to the skeletal conductivity σ_s vs. volume fraction ϕ data and a value of 3.94 resulted for t and these results are summarized in Figure 2.32. A high value of t greater than 2 is the result of the lacking of connectivity between some conductive phases [110, 115] and may also be attributed to the changing intrinsic conductivity of the conductive carbon clusters. The calculated value for t exponent agrees with those observed for carbon composites by Deramn et al [132]. The observed value for ϕ_c of 0.39 also indicates that the shape of the conductive phase is approximately spherical [110, 115].

Figure 2.32. Skeletal electrical conductivity (σ_s) as a function of volume fraction of conductive phase (ϕ), with GEM equation regression.

The electrical conductivity for samples with HTTs above 600°C is related to the energy gap associated with electron hopping between conductive sites [98, 103, 104, 120-122] and can be described by the Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_{HTT}}{kT}\right) \quad (9)$$

where the conductivity, σ , is a function of an activation energy associated with each HTT (E_{HTT}), k is the Boltzman constant, and T is the testing temperature. kT must surpass the energy gap E_{HTT} to observe DC conduction. Electrical conductivities, σ , as a function of testing temperatures, T , are shown in Figure 2.33a. Samples heat treated to 800°C and 900°C exhibit increasing conductivities with T , showing behaviors typical for semi-conductors. For samples heat treated to 1200°C and higher, electrical conductivities exhibit little variation with testing temperatures, T .

Figure 2.33. (a) DC electrical conductivity as a function of inverse testing temperatures for samples with HTTs of 800°C, 900°C, 1000°C, 1200°C, 1500°C, and 2000°C; and (b) Calculated activation energies from slopes as a function of HTT.

The activation energy (E_{HTT}) values are calculated from the slopes of linear regressions of the σ vs. T data and are shown in Figure 2.33b. As HTT increases from

800°C to 1200°C, the energy gap decreases from 0.015 eV to 0.002 eV (agreeing with previous results observed [98, 105] for carbons) as the degree of percolation of conductive carbon clusters increases. For samples heat treated to temperatures of 1200°C to 2000°C the calculated energy gap becomes constant as the system reaches a fully percolated state and as the effects of thermal scattering increases. Therefore, as shown in Figure 2.30, the conductivities reach a plateau for samples with HTTs of 1200°C to 2000°C due to a constant energy gap and a fully percolated state.

Conclusions

AC and DC electrical conductivity measurements have provided new insights to the decomposition and conversion of cellulosic materials to carbon. A model is presented that describes the depolymerization of microcrystalline cellulose and the evolution of the carbon structure with thermal treatment. Five distinct electrical conductivity regions were identified that could be directly linked to the microstructure changes during the cellulose-to-carbon conversion process. In Region I (HTTs of 250°C to 350°C), AC electrical conductivity is the result of polarization of organic functional groups and is observed to decrease with increase in HTT as the cellulose starts to decompose and lose the polar organic functional groups.

Region II (HTTs of 400°C, 450°C, and 500°C) samples show increasing AC electrical conductivities with rising HTTs due to the homogenous formation and further growth of highly conducting carbon nano-clusters. Also observed is a linear frequency response that is attributed to the carbon clusters being sufficiently separated from each other so that inter-particle interaction may not occur. In this stage, the material is

described as a system consisting of well dispersed and highly conducting nano-clusters embedded in a matrix of low conducting amorphous carbon.

In region III (HTTs of 550°C and 600°C), a non-linear frequency dependence of AC conductivity is observed as the conductive nano-clusters grow in size and move sufficiently close to each other. In this region, electron hopping and interfacial polarization between the conductive carbon clusters lead to an order of magnitude increase in the AC conductivity.

The growth of the conductive carbon clusters continues to increase the volume fraction of the conductive phase and the system reaches a percolation threshold at HTT between 600°C and 610°C with a critical conductive phase volume fraction of 0.39, where frequency independent AC conductivity (DC conductivity) is observed. For samples heat treated to temperatures of 610°C to 1000°C (Region IV), a five order magnitude increase of DC conductivity with rising HTTs is observed due to percolation and the rise of intrinsic conductivity of the carbon clusters. Finally, in Region V (HTTs from 1200°C to 2000°C), a constant electrical conductivity with rising HTTs is observed due to a fully percolated state and constant intrinsic carbon nano-cluster conductivities.

This research has shown that by using highly pure carbon precursors such as microcrystalline cellulose and by carefully controlling the carbonization conditions, a more comprehensive and definitive description can be made for the decomposition and carbonization mechanism of hydrocarbon and carbohydrate carbon precursors.

2.8 Changes in the thermophysical properties of cellulosic materials as a function of microstructural changes occurring during carbonization

Previous electrical studies and thermal studies of carbon materials derived from microcrystalline cellulose performed under nitrogen atmosphere have demonstrated that the evolution of microstructure during carbonization can be divided into four distinctive stages. The wide range of applicability of carbon materials arises from the many macro and microstructures that are possible. By controlling these structural morphologies, the physical properties can be tailored to specific applications. Specifically, the thermal properties of porous carbons have always been a very important topic in the field of materials engineering. Pitch-derived graphitic foams have high thermal conductivity, low coefficient of thermal expansion, and good mechanical strength. These properties have made them a popular choice for heat sinks, heat exchangers, and electronic packaging [133, 134]. Conversely, porous carbons are also used for thermal insulating materials [135]. Chars [136-138] and wood based carbons [139-141] have low effective thermal conductivities due to the presence of macroporosity and low conducting nature of the ligands.

Earlier studies of graphite, polycrystalline carbons, baked carbons, glassy carbons, pitch-based carbons, and amorphous carbon films [142-151] showed that thermal transport in these materials is dominated by phonon transport. Porosity, crystal boundaries, and impurities increase heat resistance by acting as centers for phonon scattering which interrupt phonon transport through the structure. Mrozowski et al [143, 144], Castle [142], and Kelly [149, 152] et al have shown that thermal conductivity is highly dependent on crystallite size. They showed that heat travels easily through

graphite and other highly ordered carbons due to the low concentration of grain boundaries.

The conversions of organic materials to carbon under controlled thermal and atmospheric conditions have been extensively studied. Studies by Kelly and Gilchrist [149] on charcoals in the temperature range from 1500°C to 2500°C demonstrated a significant increase in the thermal conductivity as macrostructural and microstructural evolved into a more ordered graphitic structures. However, their studies did not include carbons heat treated at lower temperatures where organic compounds are decomposing and the early carbon structure is formed. In our previous studies, the electrical conductivity of heat treated microcrystalline cellulose from 250°C to 1000°C indicate four distinct stages of compositional and structural evolution during carbonization [153]. Rhim et al [154] have also studied thermal property changes for the carbonization of cellulosic materials a nitrogen atmosphere. In this study, thermal diffusivity, specific heat, and thermal conductivity of these materials were analyzed under vacuum for comparison with previous values obtained under nitrogen in order to better understand the influence of porosity, composition, and measurement atmosphere.

Experimental Methods

This study used the identical samples prepared previously [153, 154]. The techniques used to prepared microcrystalline cellulose carbons samples for both electrical and thermal evaluations can be found there.

Thermal diffusivity, specific heat, and thermal conductivity were measured as a function of testing temperature, T , for samples with various final heat treatment temperature, HTT , using the laser flash technique described by Parker et al [155].

Anter's Flashline 3000 was used to record thermal diffusivity values and to qualitatively measure specific heat using thermographite as the reference. Tests were conducted first in nitrogen and then in vacuum with testing temperatures kept below the samples' final *HTTs*.

Total porosity includes macroporosity and microporosity. It was deduced from measured bulk and skeletal density values for all samples. The total porosity, ε_{total} , can be calculated from bulk, ρ , and skeletal densities, ρ_s as:

$$\varepsilon_{total} = 1 - \left(\frac{\rho}{\rho_s} \right) \quad (1)$$

Bulk density was calculated by dividing the sample weight with apparent volume and skeletal density (density of material comprising the physical support structure) was measured by using the Accupyc 1330 helium pycnometer. Samples heat treated to *HTTs* of 650°C to 1000°C were activated at 290°C for 24 hours before skeletal density measurements to minimize the effects of closed pores. Mercury porosimetry was used to determine median macropore diameter and macroporosity, ε_{macro} . Microporosity, ε_{micro} , may then be estimated [136] as:

$$\varepsilon_{total} = \varepsilon_{macro} + \varepsilon_{micro} \quad (2)$$

Results and Discussion

Thermal diffusivity is a measure of the rate of heat flow through the material. Kishimoto et. al have shown that for non-metallic solids such as mesophase carbons, diffusivity initially decreases as the measurement temperature, T increases then plateau at higher temperatures [156, 157]. Rhim et al studied thermal diffusivities for microcrystalline cellulose samples heat treated in the range of 250°C to 1000°C were

measured as a function of the testing temperatures, T , under nitrogen [154]. These values decreased as testing temperature, T , was raised from room temperature to 600°C. Above 600°C, thermal diffusivities increased slightly with rising temperature, exhibiting an unexpected behavior for non-metallic materials. This increase may be attributed to the higher contribution of (a) gas-surface conduction or (b) increase in thermal radiation [158] at higher temperatures.

In this study, diffusivity was measured under vacuum for samples heat treated to from 750°C to 1000°C. These results are presented in Figure 2.34 along with the previously reported data collected in nitrogen. Diffusivities collected in nitrogen are generally lower than those observed in vacuum at measurement temperatures up to 750°C. This is due to phonon scattering by the nitrogen molecules. While the thermal diffusivity in vacuum stays almost constant at testing temperatures of 600°C to 1000°C, the thermal diffusivity in nitrogen begins to rise in this testing temperature range and eventually equals or becomes higher than the vacuum values. This increase of thermal diffusivity in nitrogen cannot be explained by the thermal radiation effects as suggested by others [158] because identical samples were used for tests under nitrogen and vacuum, and thus the contribution from thermal radiation must be the same for these two data sets. A better explanation for the increase in diffusivity observed in nitrogen is the increase in thermal conductivity of nitrogen itself [159].

Figure 2.34. Comparison of measured thermal diffusivity under nitrogen gas flow (●) and in vacuum (▲) for *HTTs* from 750°C to 1000°C, as a function of testing temperature, *T*.

Normalized diffusivity values at various testing temperatures as a function of *HTT* are shown in Figure 2.35. All normalized diffusivity values fall on a single curve, showing that the increase of diffusivity is directly related to the increase of *HTTs*. Four linear regions can be identified for this data with R-values ranging from 0.90 to 0.95. The main causes for the variation in diffusivity with rising *HTTs* are the compositional and structural changes that take place as a result of thermal treatment. Such evolution is also responsible for the change in electrical conductivity as observed in our previous studies [153].

Figure 2.35. Normalized thermal diffusivity as a function of HTT at testing temperatures of 100°C, 200°C, 350°C, 450°C, 550°C, 650°C, 750°C, and 800°C, delineating the four regions of thermal diffusivity.

Region I, which contains samples with heat treated from HTT of 250°C to 400°C, shows a slow increase in diffusivity. The carbon concentration increases with rising $HTTs$ in this region with the loss of organic residues. Region II and III include samples heat treated from 400°C to 750°C. This region exhibits a faster increase in diffusivity with rising $HTTs$. By 400°C, the decomposition of organic phase is completed and leaving essentially amorphous carbon with discrete semi-crystalline carbon nano-clusters. Further increase in HTT in this region causes the growth of semi-crystalline carbon nano-clusters out of the amorphous carbon matrix. This leads to the increase of overall

structural ordering that enhances phonon transport. Percolation of our heat treated microcrystalline cellulose is defined as the state at which phonons or electrons can move easily from one carbon nano-cluster to neighboring clusters [153]. Previous electrical studies have shown that the percolation threshold is reached at about HTT 610°C, where electrical conductivity switches from AC to DC conductivity. Further increase of HTTs leads to higher degree of percolation and higher DC conductivity. Similarly, as the thermal treatment is increased beyond 610°C, diffusivity rise with the increase degree in percolation. As the heat treatment is increased to 1000°C (Region IV) carbon nano-cluster growth continues resulting in more percolation which further reduces phonon boundary scattering. This causes a sharp increase in diffusivity with *HTTs* from 750°C to 1000°C. A similar sharp increase in diffusivity was also observed for diamond-carbon composites as the sp^2/sp^3 carbon ratio increased from 0.4 to 0.5 [160]. At temperatures above 750°C, amorphous sp^2 carbons are converted into a crystalline sp^2 carbon phase, resulting in an increase of diffusivity in Region IV. The relation between the increase of thermal diffusivity and the crystallinity will be discussed in a future publication.

Thermal diffusivity can be reduced by porosity. Pores interrupt heat transport path by increasing phonon-imperfection scattering. For microcrystalline cellulose derived carbons, sample volume shrinks and the degree of particle packing increases with rising *HTTs*. This leads to the reduction of porosity and the increase of thermal diffusivity. Figure 2.36 shows that thermal diffusivity decreases as skeletal density decreases, or, conversely, as macroporosity increases.

Figure 2.36. Thermal diffusivity, α , as a function of measured skeletal density, ρ .

Specific heat is the energy needed to raise a unit mass of a substance by one degree. It depends highly on the chemical nature and microstructure of the material. Specific heats are highest for polymers (~ 2000 J/kgK), intermediate for ceramics and glasses (~ 750 J/kgK), and lowest for metals (~ 30 J/kgK). For two-phase composites, the total specific heat is the sum of the weighted specific heats of each of the phases. Since the weight fraction of gas is very small, the total specific heat is essentially equal to that of the solid [158].

Figure 2.37. Specific heat, C_p , measured under nitrogen gas flow for samples with (a) $HTTs$ of 250°C, 350°C, 400°C, 450°C, and 500°C showing a linear relationship with testing temperature, T ; (b) $HTTs$ of 550°C, 600°C, and 650°C showing an overall decrease with HTT and a second-order polynomial relationship with T ; and (c) $HTTs$ of 700°C, 750°C, 800°C, 900°C, 1000°C showing first an overall decrease with increasing $HTTs$ and later an increase with $HTTs$, and a second-order polynomial increase with T .

Table 2.9. Specific heat

Heat Treatment Temperature, HTT [°C]	Specific Heat, C_p [J/kgK]	R-Value
250	$6.296T - 964.808$	0.95815
350	$7.5545T - 1489.0785$	0.9948
400	$5.3594T - 688.2162$	0.99975
450	$4.67583T - 688.88647$	0.95265
500	$3.84927T - 494.93805$	0.99279
550	$-0.00682T^2 + 10.41124T - 1623.96712$	0.9945
600	$-0.000464T^2 + 3.34511T - 153.90108$	0.99259
650	$-0.00188T^2 + 4.78962T - 585.73846$	0.99151
700	$-0.0033T^2 + 6.77048T - 939.46641$	0.99685
750	$-0.00113T^2 + 3.68938T - 248.99533$	0.99139
800	$-0.00201T^2 + 4.96503T - 483.50168$	0.98566
900	$-0.00123T^2 + 3.6051T - 240.33471$	0.98765
1000	$-0.00157T^2 + 4.4006T - 271.41051$	0.98776

As shown in Figures 2.37a-c and Table 2.9, a decrease of specific heat with rising $HTTs$ is observed for these samples until HTT of 800°C. This decrease is due to the degradation of organic phases. Organic materials such as wood have higher specific heats than carbon [161, 162] and the loss of organic phase during decomposition decreases the overall specific heat. For samples with $HTTs$ of 900°C and 1000°C,

specific heats start to increase. Although at these HTTs the organic phases have been completely eliminated, the increase of specific heat is due to the enhanced percolation of sp^2 carbon nano-clusters and the continuous formations of these clusters at the expense of the amorphous sp^2 carbon phase. As reported by Manocha et al [163, 164], higher specific heats were observed for long-range ordered mesophase pitch because of the reduced scattering at crystalline boundaries. This is analogous to polymer-carbon fiber systems [164] where specific heat increases with increasing fiber percolation.

For all samples, specific heat increased with rising testing temperature, T . The increase of specific heat with T is linear between HTTs of 250°C to 500°C, similar to the results observed for wood [162]. For HTTs between 550°C to 1000°C, specific heat increases as second-order functions of testing temperatures agreeing with the results of charcoals reported by Lardfeldt et al [136] and Gupta et al [162].

Thermal conductivity, k , is the thermophysical property indicating a material's ability to conduct heat when subjected to a temperature gradient, ∇T :

$$q = -k\nabla T \quad (3)$$

It is also related to thermal diffusivity, α , specific heat, C_p , and bulk density, ρ as:

$$k = \alpha\rho C_p \quad (4)$$

Effective thermal conductivity of a material is reduced by introducing void spaces that act as imperfections for phonon scattering. For porous materials, the total effective thermal conductivity k_{eff} , may depend on four main factors: conduction through the solid material k_{solid} , convection inside the pores k_{conv} , conduction through the gas in pores k_{gas} , and radiation through pore walls and across pores k_{rad} [158].

$$k_{eff} = k_{solid} + k_{conv} + k_{gas} + k_{rad} \quad (5)$$

Conduction through the solid phase, k_{solid} , is expressed as a product of solid volume fraction, $(1-\varepsilon_{total})$, and the skeletal conductivity, k_s . Convection within pores only become important for large pores in the order of 10mm [136, 158]. Since the macropores were estimated to be from 0.51 μm to 1.23 μm for heat treated microcrystalline cellulose samples, the convection within pores can be ignored. Radiation absorbed within and reflected by the pores may greatly affect the effective thermal conductivity, especially at high testing temperatures and for large pores. Radiation heat transfer can be described as a function of macropore diameter, d_{macro} , testing temperature, T , and emissivity, ψ :

$$k_{rad} = 4\varepsilon_{macro}\sigma\psi d_{macro}T^3 \quad (6)$$

where σ is Stefan-Boltzmann's constant and ψ equals 0.9 for carbons [136, 138, 165]. The contribution from conduction through gas can be expressed as product of the total porosity, ε_{total} , and thermal conductivity of the gas, k_g .

Effective thermal conductivity for heat treated microcrystalline cellulose samples were measured in nitrogen and vacuum as a function of testing temperature, T . These values are summarized in Figure 2.38 for samples with HTTs of (a) 250°C to 400°C – Region I; (b) 450°C to 600°C – Region II; (c) 650°C to 700°C – Region III; and (d) 800°C to 1000°C – Region IV. Thermal conductivity increases with rising HTTs and linearly with testing temperatures. Due to the contribution of nitrogen, the thermal conductivity measured under nitrogen is higher than the value measured in vacuum for all samples. In vacuum, conduction through gas is ignored, and the effective thermal conductivity becomes the result of conduction through the solid phase and radiation within pores:

$$k_{vac} = k_{solid} + k_{rad} = (1 - \varepsilon_{total})k_s + 4\varepsilon_{macro}\sigma\psi d_{macro}T^3 \quad (7)$$

The ratio $\frac{k_{solid}}{k_{vac}}$ for each sample is shown to decrease with rising testing temperatures as radiation heat transfer increases at higher temperatures. $\frac{k_{solid}}{k_{vac}}$ increases with rising HTTs as macropore diameters decrease.

Figure 2.38. Four regions of measured effective thermal conductivity, k_{eff} , in nitrogen (●, solid line regression) and in vacuum (▲, dashed line regression), as a function of testing temperatures, T .

Figure 2.39 shows $\frac{k_{solid}}{k_{vac}}$ decreasing very slightly from 1 to 0.9995 with rising testing temperatures, T , and with increasing HTTs, and these results agree well with those for coke [165]. Based on this observation, we can conclude that the contribution of

radiation to the overall vacuum thermal conductivity from radiation is far less than 1% and thus can be neglected.

Figure 2.39. k_{solid}/k_{vac} as a function of testing temperature, T .

Thermal conductivity of nitrogen gas varies with temperature as [159]:

$$k_{g,N_2} = 2.27497 \times 10^{-11} T^3 - 6.04034 \times 10^{-8} T^2 + 1.02 \times 10^{-4} T - 6.21122 \times 10^{-5} \quad (8)$$

Effective thermal conductivities of samples in nitrogen can be calculated from vacuum measurement data by adding the contribution of nitrogen conduction within the pores:

$$k_{calc,N_2} = k_{rad} + k_{gas} = (1 - \varepsilon_{total})k_s + (\varepsilon_{total})k_{gas} \quad (9)$$

As shown in Figure 2.40, these calculated values agree well with the measured values.

Figure 2.40. Four regions of effective thermal conductivity, k_{eff} , measured in nitrogen (N_2) and calculated (N_2 calculated) from Equation (9), as a function of testing temperatures, T .

Kantorovich and Bar-Ziv [138] have indicated that the effective thermal conductivity of porous char is affected by both porosity and microstructural development that includes changes in dimension, orientation, and connectivity of microcrystals. In order to examine the change in thermal conductivity of the solid phase with rising HTTs, skeletal thermal conductivities were calculated to negate the effects of porosity and are shown in Figure 2.41. Skeletal thermal conductivity is almost constant during the depolymerization stage from $HTTs$ 250°C to 400°C. As $HTTs$ rise from 450°C to 600°C, thermal conductivity increases due to the onset of carbon cluster formation. After the percolation threshold for carbon nano-clusters is reached at the HTT of 610°C, thermal conductivity increases faster due to the further percolation until HTT of 750°C. From

HTT s of 750°C to 1000°C, a sharp increase of skeletal thermal conductivity occurs due to the conversion of amorphous sp^2 carbons to crystalline sp^2 carbons.

Figure 2.41. Calculated skeletal thermal conductivity, k_s , as a function of heat treatment temperatures, HTT .

This observation agrees well with the thermal properties of two-phase composites where increase in volume fraction of the conductive phase leads to percolation resulting in the rise of thermal conductivity [166-168]. The variation in thermal conductivity of microcrystalline cellulose carbons with rising HTT s correlates well with the change in electrical conductivity. Electrical studies have shown a transition from frequency dependent AC electrical conductivity to a frequency independent DC electrical conductivity when percolation threshold for the electrically conductive carbon nano-

clusters is reached. Electrical conductivity increases by several orders of magnitude as the conductive phase continues to grow and percolate.

Conclusions

Thermophysical properties of microcrystalline cellulose as a function of testing temperatures and final heat treatment temperatures have been measured under vacuum for comparison with studies under nitrogen. The effects of composition change and structural evolution on the thermophysical properties of hard carbons have been discussed. Specific heat was shown to be independent of porosity but highly dependent upon the development of structural and chemical composition. Porosity decreases diffusivity and effective thermal conductivity by phonon scattering. Effective thermal conductivities in nitrogen were calculated and they agree well with the measured data. Conduction through gas within pores is significant, but radiation heat transfer within pores was determined to be negligible. The thermal conductivity in nitrogen was observed to be higher than those observed in vacuum due to conductivity of nitrogen gas. The effects on nitrogen on diffusivity at low temperatures were shown to be dominated by phonon scattering by nitrogen molecules. At temperatures above 750°C, diffusivity is observed to increase due to nitrogen diffusivity increasing with temperature.

Both vacuum and nitrogen diffusivities and skeletal thermal conductivities increased with rising heat treatment temperatures. They are grouped into four regions corresponding to the stages of microstructural evolution during carbonization. The first region shows a slow increase in diffusivity and constant skeletal thermal conductivity and it correlates with the initial degradation of organic materials at low heat treatment temperatures. In the second region, diffusivity and skeletal thermal conductivity rise

faster with the formation of amorphous carbon and the onset of carbon nano-cluster formation. With further heat treatment, the continuous growth of the carbon nano-clusters leads to percolation. This results in a much faster increase in diffusivity and skeletal thermal conductivity, especially in Region IV. The structure evolution indicated by thermophysical property changes has also been observed in our previous electrical studies. However, compared with electrical property change, there is a less dramatic change in thermophysical properties in regions II and III. This is due to the different phonon and electron transport mechanisms.

2.9 Summary and conclusions

Porous carbon preforms produced from carbonization of cellulose and phenolic resin mixture precursors were studied. SEM images of these carbons clearly show the effectiveness of using these precursors in providing a method for controlling the pore characteristics and reactivity of the final carbon preform. This approach also produced carbon preforms with bulk densities near the ideal value of 0.96 g cm^{-3} and over a range of 0.7 to 1.4 g cm^{-3} by varying the mass ratio of the precursors. These carbon preforms can have considerable porosity with median pore diameters just above $1 \text{ }\mu\text{m}$ to satisfy the pore diameter requirement for the silicon carbide formation reaction. Helium gas pycnometry, nitrogen gas adsorption and TEM studies indicate that atomic-scale ordering varies considerably among the carbon preforms produced from precursors with different compositions, and this provides a method to control carbon reactivity. Information obtained through the analysis of the carbon preform microstructures can help provide a general approach for designing and controlling the properties of the carbon preforms.

However, carbon preforms with the optimum properties for the LSI reactions must be further identified through experimentation.

2.10 References

1. P.A. Webb and C. Orr. Pore Structure by Mercury Intrusion Porosimetry (MIP), pp. 154 in Analytical Methods in Fine Particle Technology. Micromeritics Instrument Corporation, Norcross, GA, 1997.
2. Y.M. Chiang, R.P. Messner, C.D. Terwilliger and D.R. Behrendt. Reaction-Formed Silicon-Carbide, Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing, 144, 63-74 (1991).
3. J.J. Kipling, J.N. Sherwood, P.V. Shooter and N.R. Thompson. The pore structure and surface area of high-temperature polymer carbons, Carbon, 1, 321-8 (1964).
4. R.P. Messner and Y.M. Chiang. Liquid-Phase Reaction-Bonding of Silicon-Carbide using Alloyed Silicon Molybdenum Melts, J Am Ceram Soc, 73, 1193-200 (1990).
5. D.R. Behrendt and M. Singh. Effect of carbon preform pore volume and infiltrants on the composition of reaction-formed silicon carbide materials, J. Mater. Synth. Process., 2, 117-123 (1994).
6. M. Singh and D.R. Behrendt. Microstructure and Mechanical-Properties of Reaction-Formed Silicon-Carbide (Rfsc) Ceramics, Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing, 187, 183-7 (1994).
7. M. Singh and S.C. Farmer. Morphological characterization of microporous carbon materials, J. Mater. Sci. Lett., 16, 946-9 (1997).
8. J.C. Margiotta, D. Zhang, D.C. Nagle and C.E. Feeser. Formation of dense silicon carbide by liquid silicon infiltration of carbon with engineered structure, J. Mater. Res., 23, 1237-48 (2008).
9. C. E. Byrne. Polymer, ceramic and carbon composites derived from wood. PhD dissertation. (1995) Johns Hopkins University, Baltimore, MD.
10. C.E. Byrne and D.C. Nagle. Cellulose derived composites - A new method for materials processing, Materials Research Innovations, 1, 137-44 (1997).
11. A. K. Kercher. Processing and characterization of monolithic carbon structures based on wood fiberboards. PhD dissertation. (2002) Johns Hopkins University, Baltimore, MD.
12. A.C. OSullivan, Cellulose: the structure slowly unravels, Cellulose, 4, 173-207 (1997).
13. J.F. Kennedy, Structure of cellulose and its relation to properties of cellulose fibers, pp. 2-27 in Cellulose and its derivatives: chemistry, biochemistry, and applications. Editor E. Horwood; Halsted Press, Chichester West Sussex; New York, 1985.
14. R.A. Young and R.M. Rowell. Cellulose: structure, modification, and hydrolysis; pp. 379. Wiley, New York, 1986.
15. J. W. Kimball. Carbohydrates: Kimball's Biology Pages-Online biology textbook. <http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/C/Carbohydrates.html> . accessed Feb/15, 2007.
16. M. Drechsler. Microcrystalline cellulose. <http://www.mardre.com/> . accessed Feb/15, 2007.

17. T. Hatakeyama and F.X. Quinn. Thermal analysis: fundamentals and applications to polymer science; pp. 180. Wiley, Chichester ;New York, 1999.
18. W.W. Wendlandt and W.W. Wendtlandt. Thermal analysis; pp. 814. Wiley, New York, 1986.
19. P. Budrugaec, Differential non-linear isoconversional procedure for evaluating the activation energy of non-isothermal reactions, *Journal of Thermal Analysis and Calorimetry*, 68, 131-9 (2002).
20. J.H. Flynn and L.A. Wall. General Treatment of Thermogravimetry of Polymers, *Journal of Research of the National Bureau of Standards Section A-Physics and Chemistry*, A 70, 487 (1966).
21. L. Katsikas and I.G. Popovic. Improvement to the Flynn-Wall Method of Determining Apparent Activation Energies of the Thermal Degradation of Polymers, *J. Phys. Chem. B*, 107, 7522-5 (2003).
22. H.E. Kissinger, Reaction Kinetics in Differential Thermal Analysis, *Anal. Chem.*, 29, 1702-6 (1957).
23. V. Mamleev, S. Bourbigot, M.L. Bras and J. Lefebvre. Three model-Free methods for calculation of activation energy in TG, *Journal of Thermal Analysis & Calorimetry*, 78, 1009-27 (2004).
24. T. Ozawa, A New Method of Analyzing Thermogravimetric Data, *Bull. Chem. Soc. Jpn.*, 38, 1881,& (1965).
25. T. Ozawa, Temperature control modes in thermal analysis, *Journal of Thermal Analysis and Calorimetry*, 64, 109-26 (2001).
26. F. Shafizadeh, Pyrolysis and Combustion of Cellulosic Materials, pp. 419-74 in Vol. 23, *Advances in Carbohydrate Chemistry*. Academic Press, New York, 1968.
27. J.F. Kennedy, Degradation reactions of cellulose and lignocellulose, pp. 97-118 in *Cellulose and its derivatives: chemistry, biochemistry, and applications*. Editor E. Horwood; Halsted Press, Chichester West Sussex; New York, 1985.
28. J.F. Kennedy, Combustion of cigarette paper under conditions similar to those during smoking, pp. 401-10 in *Cellulose and its derivatives: chemistry, biochemistry, and applications*. Editor E. Horwood; Halsted Press, Chichester West Sussex; New York, 1985.
29. J.L. Banyasz, S. Li, J. Lyons-Hart and K.H. Shafer. Gas evolution and the mechanism of cellulose pyrolysis, *Fuel*, 80, 1757-63 (2001).
30. A. Gardziella, L. Pilato and A. Knop. Phenolic resins: chemistry, applications, standardization, safety, and ecology; pp. 560. Springer, Berlin ;New York, 2000.
31. C.E. Byrne and D.C. Nagle. Carbonized wood monoliths - Characterization, *Carbon*, 35, 267-73 (1997).
32. C.E. Byrne and D.C. Nagle. Carbonization of wood for advanced materials applications, *Carbon*, 35, 259-66 (1997).
33. A.K. Kercher and D.C. Nagle. Monolithic activated carbon sheets from carbonized medium-density fiberboard, *Carbon*, 41, 3-13 (2003).
34. J.C. Margiotta, D. Zhang, D.C. Nagle and C.E. Feeser. Formation of dense silicon carbide by liquid silicon infiltration of carbon with engineered structure, *J. Mater. Res.*, 23, 1237-48 (2008).

35. Y.M. Chiang, R.P. Messner, C.D. Terwilliger and D.R. Behrendt. Reaction-Formed Silicon-Carbide, *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing*, 144, 63-74 (1991).
36. R.P. Messner and Y.M. Chiang. Liquid-Phase Reaction-Bonding of Silicon-Carbide using Alloyed Silicon Molybdenum Melts, *J Am Ceram Soc*, 73, 1193-200 (1990).
37. D.R. Behrendt and M. Singh. Effect of carbon preform pore volume and infiltrants on the composition of reaction-formed silicon carbide materials, *J. Mater. Synth. Process.*, 2, 117-123 (1994).
38. M. Singh and D.R. Behrendt. Microstructure and Mechanical-Properties of Reaction-Formed Silicon-Carbide (Rfsc) Ceramics, *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing*, 187, 183-7 (1994).
39. M. Singh and S.C. Farmer. Morphological characterization of microporous carbon materials, *J. Mater. Sci. Lett.*, 16, 946-9 (1997).
40. E.W. Washburn, The dynamics of capillary flow. *Physical Review*, 17, 273-83 (1921).
41. E.W. Washburn, Note on a Method of Determining the Distribution of Pore Sizes in a Porous Material, *Proc. Natl. Acad. Sci. U. S. A.*, 7, 115-6 (1921).
42. P.A. Webb and C. Orr. Pore Structure by Mercury Intrusion Porosimetry (MIP), pp. 154 in *Analytical Methods in Fine Particle Technology*. Micromeritics Instrument Corporation, Norcross, GA, 1997.
43. I.A.S. Edwards and H. Marsh. Introduction to carbon science; pp. 321. Butterworths, London ;Boston, 1989.
44. P.L. Walker, Chemistry and physics of carbon; M. Dekker, New York, 1965.
45. E. Raymundo-Piñero, D. Cazorla-Amorós, A. Linares-Solano, et al. High surface area carbon nanotubes prepared by chemical activation, *Carbon*, 40, 1614-7 (2002).
46. H. Tamai, M. Kouzu and H. Yasuda. Preparation of highly mesoporous and high surface area activated carbons from vinylidene chloride copolymer containing yttrium acetylacetonate, *Carbon*, 41, 1678-81 (2003).
47. S.B. Tong, P. Pareja and M.H. Back. Correlation of the Reactivity, the Active Surface-Area and the Total Surface-Area of Thin-Films of Pyrolytic Carbon, *Carbon*, 20, 191-4 (1982).
48. Q.G. Feng, Q.Y. Lin, Z.F. Tong and S. Sugita. Study on preparation of rice husk ash with high specific surface area and its chemical reactivity, *Chin. J. Chem. Eng.*, 12, 711-5 (2004).
49. I. Langmuir, THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM. *J. Am. Chem. Soc.*, 40, 1361-403 (1918).
50. S. Brunauer, P.H. Emmett and E. Teller. Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.*, 60, 309-19 (1938).
51. S.J. Gregg and K.S.W. Sing. Introduction, pp. 1-40 in *Adsorption, Surface Area and Porosity*. Academic Press, New York, NY, 1982.
52. S.J. Gregg and K.S.W. Sing. The Physical Adsorption of Gases by Microporous Solids: The Type I Isotherm, pp. 195-247 in *Adsorption, Surface Area and Porosity*. Academic Press, New York, NY, 1982.

53. P.A. Webb and C. Orr. Surface Area and Pore Structure by Gas Adsorption, pp. 53 in Analytical Methods in Fine Particle Technology. Micromeritics Instrument Corporation, Norcross, GA, 1997.
54. M.D. Donohue and G.L. Aranovich. Classification of Gibbs adsorption isotherms, *Advances in Colloid and Interface Science*, 76-77, 137-52 (1998).
55. S.J. Gregg and K.S.W. Sing. The Physical Adsorption of Gases by Nonporous Solids: The Type II Isotherm, pp. 41-110 in *Adsorption, Surface Area and Porosity*. Academic Press, New York, NY, 1982.
56. J.B. Hudson, *Surface science: an introduction*; pp. 321. Butterworth-Heinemann, Boston, 1992.
57. W.D. Harkins and G. Jura. Surfaces of solids XIII A vapor adsorption method for the determination of the area of a solid without the assumption of a molecular area, and the areas occupied by nitrogen and other molecules on the surface of a solid, *J. Am. Chem. Soc.*, 66, 1366-73 (1944).
58. J.H. de Boer, B.C. Lippens, B.G. Linsen, J.C.P. Broekhoff, A. van den Heuvel and T.J. Osinga. The t-curve of multimolecular N₂-adsorption, *Journal of Colloid and Interface Science*, 21, 405-14 (1966).
59. B.C. Lippens, B.G. Linsen and J.H.d. Boer. Studies on pore systems in catalysts I. The adsorption of nitrogen; apparatus and calculation, *Journal of Catalysis*, 3, 32-7 (1964).
60. J. Rouquerol, D. Avnir, C.W. Fairbridge, et al. Recommendations for the Characterization of Porous Solids, *Pure and Applied Chemistry*, 66, 1739-58 (1994).
61. S.J. Gregg and K.S.W. Sing. The Physical Adsorption of Gases by Mesoporous Solids: The Type IV Isotherm, pp. 111-94 in *Adsorption, Surface Area and Porosity*. Academic Press, New York, NY, 1982.
62. D.B. Williams and C.B. Carter. High-Resolution TEM, pp. 457-84 in *Transmission electron microscopy: a textbook for materials science*. Plenum Press, New York, 1996.
63. D.B. Williams and C.B. Carter. Imaging in the TEM, pp. 349-68 in *Transmission electron microscopy: a textbook for materials science*. Plenum Press, New York, 1996.
64. D.B. Williams and C.B. Carter. Specimen preparation, pp. 155-76 in *Transmission electron microscopy: a textbook for materials science*. Plenum Press, New York, 1996.
65. D.B. Williams and C.B. Carter. Phase-Contrast Images, pp. 439-56 in *Transmission electron microscopy: a textbook for materials science*. Plenum Press, New York, 1996.
66. ImageJ, Computer Program. W. S. Rasband. (1997-2006) Bethesda, MD.
67. T. Hata, T. Vystavel, P. Bronsveld, et al. Catalytic carbonization of wood charcoal: graphite or diamond? *Carbon*, 42, 961-4 (2004).
68. J.C.H. Spence, *Image Processing and Superresolution Schemes*, in *Experimental high-resolution electron microscopy*. Oxford University Press, New York, 2003.
69. Y. Yoo. Tutorial on Fourier Theory. http://www.cs.otago.ac.nz/cosc453/student_tutorials/fourier_analysis.pdf . accessed June/13, 2008.

70. K.R. Castleman, The Fourier transform, pp. 171-206 in Digital image processing. Prentice Hall, Englewood Cliffs, N.J., 1996.
71. G.P. Tolstov and R.A. Silverman. Fourier series; pp. 336. Prentice-Hall, Englewood Cliffs, N.J., 1962.
72. K. Oshida, K. Kogiso, K. Matsubayashi, et al. Analysis of Pore Structure of Activated Carbon-Fibers using High-Resolution Transmission Electron-Microscopy and Image-Processing, J. Mater. Res., 10, 2507-17 (1995).
73. K. Oshida, M. Endo, T. Nakajima, S.L. Divittorio, M.S. Dresselhaus and G. Dresselhaus. Image-Analysis of Tem Pictures of Fluorine-Intercalated Graphite Fibers, J. Mater. Res., 8, 512-22 (1993).
74. M. Endo, K. Oshida, K. Kobori, K. Takeuchi, K. Takahashi and M.S. Dresselhaus. Evidence for Glide and Rotation Defects Observed in Well-Ordered Graphite Fibers, J. Mater. Res., 10, 1461-8 (1995).
75. M. Endo, T. Furuta, F. Minoura, et al. Visualized observation of pores in activated carbon fibers by HRTEM and combined image processor, Supramolecular Science, 5, 261-6 (1998).
76. T. Miyazaki, T. Oshida, T. Nakatsuka, H. Yamamoto, M. Okamoto and M. Endo. Analysis of pore structure of activated carbon by using image processing of TEM images, Molecular Crystals and Liquid Crystals, 388, 499-504 (2002).
77. Z.H. Huang, F.Y. Kang, W.L. Huang, et al. Pore structure and fractal characteristics of activated carbon fibers characterized by using HRTEM, J. Colloid Interface Sci., 249, 453-7 (2002).
78. D. Lozano-Castello, D. Cazorla-Amoros, A. Linares-Solano, et al. Comparative characterization study of microporous carbons by HRTEM image analysis and gas adsorption, J Phys Chem B, 109, 15032-6 (2005).
79. D.B. Williams and C.B. Carter. Quantifying and Processing HRTEM Images, pp. 499-528 in Transmission electron microscopy: a textbook for materials science. Plenum Press, New York, 1996.
80. K.R. Castleman, Discrete Image Transforms, pp. 281-302 in Digital image processing. Prentice Hall, Englewood Cliffs, N.J., 1996.
81. W. S. Rasband. ImageJ: 3-D Fast Hartley Transform. <http://www.optinav.com/FHT3D.htm> . accessed June/13, 2008.
82. Anonymous Discrete Hartley transform - Wikipedia, the free encyclopedia. http://en.wikipedia.org/wiki/Discrete_Hartley_transform . accessed 2008, June 26, 2008.
83. W. S. Rasband. ImageJ: Documentation. <http://rsb.info.nih.gov/ij/docs/index.html> .
84. Gatan DigitalMicrograph, Computer Program. Gatan Software Team. (2003) Pleasanton, CA, USA.
85. LispixLx92P for PC, Computer Program. D. S. Bright. (2006) National Institute of Standards and Technology (NIST).
86. JCPDS--International Centre for Diffraction Data and 20 American Society for Testing and Materials. Selected powder diffraction data for metals and alloys: data book; The Centre, Swarthmore, Pa., 1978.
87. P.J.F. Harris and S.C. Tsang. High-resolution electron microscopy studies of non-graphitizing carbons, Philosophical Magazine A-Physics of Condensed Matter Structure Defects and Mechanical Properties, 76, 667-77 (1997).

88. P.J.F. Harris, A. Burian and S. Duber. High-resolution electron microscopy of a microporous carbon, *Philosophical Magazine Letters*, 80, 381-6 (2000).
89. L.L. Ban, D. Crawford and H. Marsh. Lattice-Resolution Electron-Microscopy in Structural Studies of Non-Graphitizing Carbons from Polyvinylidene Chloride (Pvdc), *Journal of Applied Crystallography*, 8, 415-20 (1975).
90. R.E. Franklin, Crystallite Growth in Graphitizing and Non-Graphitizing Carbons, *Proceedings of the Royal Society of London Series A-Mathematical and Physical Sciences*, 209, 196,& (1951).
91. G.M. Jenkins and K. Kawamura. Structure of Glassy Carbon, *Nature*, 231, 175,& (1971).
92. D.J. Palmer, Conducting on the graphene orchestra, *Materials Today*, 11, 9- (2008).
93. M.I. Katsnelson, Graphene: carbon in two dimensions, *Materials Today*, 10, 20-7 (2006).
94. D. Li and R.B. Kaner. Materials science - Graphene-based materials, *Science*, 320, 1170-1 (2008).
95. Y. R. Rhim. Crystalline cellulose carbons. Ph.D. dissertation. (to be published in 2009) The Johns Hopkins University, Baltimore, MD, USA.
96. K. Ishimaru, T. Vystavel, P. Bronsveld, T. Hata, Y. Imamura and J. De Hosson. Diamond and pore structure observed in wood charcoal, *Journal of Wood Science*, 47, 414-6 (2001).
97. K. Ishimaru, T. Hata, P. Bronsveld, T. Nishizawa and Y. Imamura. Characterization of sp(2)- and sp(3)-bonded carbon in wood charcoal, *Journal of Wood Science*, 53, 442-8 (2007).
98. Pinnick HT. Electronic properties of carbons and graphites. *Proceedings of the First Conference on Carbon*. Buffalo (New York, USA): American Carbon Society, 1956; 3-11.
99. Giuntini JC, Julien D, Zanchetta JV, Carmona F, Delhaes A. Electrical conductivity of low-temperature carbons as a function of frequency. *Journal of Non-Crystalline Solids* 1978; 30 (1): 87-98.
100. Celzard A, Mareche JF, Payot F, Begin D, Furdin G. Electrical conductivity of anthracites as a function of heat treatment temperature. *Carbon* 2000; 38 (8): 1207-1215.
101. Kercher AK, Nagle DC. Evaluation of carbonized medium-density fiberboard for electrical applications. *Carbon* 2002; 40 (8): 1321-1330.
102. Sugimoto H, Norimoto M. Dielectric relaxation due to interfacial polarization for heat-treated wood. *Carbon* 2004; 42 (1): 211-218.
103. Fung AWP, Dresselhaus MS, Endo M. Transport properties near the metal-insulator transition in heat-treated activated carbon fibers. *Physical Review B* 1993; 48(20): 14953-14962.
104. Godet C, Kumar S, Chu V. Field-enhanced electrical transport mechanisms in amorphous carbon films. *Philosophical Magazine* 2003; 83(29): 3351-3365.
105. Kennedy LJ, Vijaya JJ, and Sekaran G. Electrical conductivity study of porous carbon composite derived from rice husk. *Materials Chemistry and Physics* 2005; 91(2-3): 471-476.

106. Seldin EJ. Recent work on electronic properties of carbons at the University of Buffalo. Proceedings of the second conference on carbon. Buffalo (New York, USA): American Carbon Society, 1956; 117-124.
107. Giuntini JC, Zanchetta JV. Use of conduction models in the study of "low temperature" carbons. *Journal of Non-Crystalline Solids* 1979; 34: 419-424.
108. Kercher AK, Nagle DC. AC electrical measurements support microstructure model for carbonization: a comment on 'Dielectric relaxation due to interfacial polarization for heat-treated wood'. *Carbon* 2004; 42(1): 219-221.
109. Sugimoto H, Norimoto M. Dielectric relaxation due to interfacial polarization for heat-treated wood. *Journal of Wood Science* 2005; 51: 554-558.
110. McLachlan DS, Blaszkiewicz M, Newnham RE. Electrical resistivity of composites. *Journal of American Ceramic Society* 1990; 73(8): 2187-2203.
111. McLachlan DS, Heaney MB. Complex ac conductivity of a carbon black composite as a function of frequency, composition, and temperature. *Physical Review B* 1999; 60(18): 12746-12751.
112. McLachlan DS. Analytical functions for the dc and ac conductivity of conductor-insulator composites. *Journal of Electroceramics* 2000; 5(2): 93-110.
113. McLachlan DS, Chitame C, Heiss WD, Wu J. Fitting the DC conductivity and first order AC conductivity results for continuum percolation media, using percolation theory and a single phenomenological equation. *Physica B* 2003; 338: 261-265.
114. McLachlan DS, Chitame C, Park C, Wise KE, Lowther SE, Lillehei PT, Siochi EJ, Harrison JS. AC and DC percolative conductivity of single wall carbon nanotube polymer composites. *Journal of Polymer Science: Part B: Polymer Physics* 2005. 43: 3273-3287.
115. McLachlan DS, Sauti G. The AC and DC conductivity of nanocomposites. *Journal of Nanomaterials* 2007: Article ID 30389.
116. Barrau S, Demont P, Peigney A, Laurent C, Lacabanne C. DC and AC conductivity of carbon nanotubes-polyepoxy composites. *Macromolecules* 2003; 36: 5187-5194.
117. Belin R, Taillades G, Pradel A, Ribes M. Ion dynamics in superionic chalcogenide glasses: complete conductivity spectra. *Solid State Ionics* 2000. 136-137: 1025-1029.
118. Hussain S, Barbariol I, Roitti S, Sbaizero O. Electrical conductivity of an insulator matrix (alumina) and conductor particle (molybdenum) composites. *Journal of the European Ceramic Society* 2002; 23: 315-321.
119. Papathanassiou AN. The power law dependence of the ac conductivity on frequency in amorphous solids. *Journal of Physics D: Applied Physics* 2002; 35: L88-L89.
120. Sullivan JP, Friedmann TA. Electronic transport in amorphous carbon. 1997, Sandia National Labs, Albuquerque, NM.
121. Shimakawa K, Miyake K. Hopping transport of localized pi electrons in amorphous carbon films. *Physical Review B* 1989; 39(11): 7578-7584.
122. Godet C. Physics of bandtail hopping in disordered carbons. *Diamond and Related Materials* 2003; 12: 159-165.
123. American Society for Testing and Materials. 2003 Annual Book of ASTM Standards 2003; 15.01: 239-244.

124. Bayot V, Piriaux L, Michenaud JP, Issi JP. Weak localization in pregraphitic carbon fibers. *Physical Review B* 1989. 40(6): 3514-3523.
125. Von-Bardeleben HJ, Cantin JL, Zellama K, Zeinert A. Spins and microstructure of amorphous carbon. *Diamond and Related Materials* 2003; 12: 124-129.
126. Delhaes P, Carmona F. Physical properties of noncrystalline carbons. In: Walker PL, editor. *Chemistry and physics of carbon*, 1965, New York; Marcel Dekker: 89-174.
127. Celzard A, Treusch O, Mareche JF, Wegener G. Electrical and elastic properties of new monolithic wood-based carbon materials. *Journal of Materials Science* 2005. 40: 63-70.
128. Jager KM, McQueen DH. Fractal agglomerates and electrical conductivity in carbon black polymer composites. *Polymer* 2001; 42: 9575-9581.
129. Celzard A, McRae E, Furdin G, Mareche JF. Conduction mechanisms in some graphite-polymer composites: the effect of a direct-current electric field. *Journal of Physics: Condensed Matter* 1997; 9: 2225-2237.
130. Celzard A, McRae E, Deleuze C, Dufort M, Furdin G, Mareche JF. Critical concentration in percolating systems containing a high-aspect-ratio filler. *Physical Review B* 1996; 53(10): 6209-6214.
131. Ashby MF, Evans A, Fleck NA, Gibson LJ, Hutchinson JW, Wadley HNG. *Metal foams: a design guide*. Boston MA: Butterworth-Heinemann. 2000.
132. Deraman M, Zakaria S, Ramli O, Aziz AA. Electrical conductivity of carbon pellets from mixtures of pyropolymer from oil palm bunch and cotton cellulose. *Japanese Journal of Applied Physics* 2000. 39: 1236-1238.
133. Klett J, Rommie H, Romine E, Walls C, Burchell T. High-thermal-conductivity, mesophase-pitch-derived carbon foams: effect of precursor on structure and properties. *Carbon*, 2000. 38: 953-973.
134. Gallego NC, Klett JW. Carbon foams for thermal management. *Carbon*, 2003. 41: 1461-1466.
135. Leong CK, Chung DDL. Carbon black dispersions and carbon-silver combinations as thermal pastes that surpass commercial silver and ceramic pastes in providing high thermal contact conductance. *Carbon*, 2004. 42: 2323-2327.
136. Larfeldt J, Leckner B, Melaaen MC. Modeling and measurements of heat transfer in charcoal from pyrolysis of large wood particles. *Biomass and Bioenergy*, 2000. 18: 507-514.
137. Staggs J. Estimating the thermal conductivity of chars and porous residues using thermal resistor networks. *Fire Safety Journal*, 2002. 37: 107-119.
138. Kantorovich I, Barz-Ziv E. Heat transfer within highly porous chars: a review. *Fuel*, 1999. 78: 279-299.
139. Thunman H, Leckner B. Thermal conductivity of wood-models for different stages of combustion. *Biomass and Bioenergy*, 2002. 23: 47-54.
140. Gronli M, Melaaen M. Mathematical model for wood pyrolysis - comparison of experimental measurements with model predictions. *Energy and Fuels*, 2000. 14: 791-800.
141. Larfeldt J, Leckner B, Melaaen M. Modeling and measurements of the pyrolysis of large wood particles. *Fuel*, 2000. 79: 1637-1643.

142. Castle JG. Heat conduction in carbon materials. Proceedings of the First and Second Conferences on Carbon, Buffalo. (Buffalo, New York): Pergamon Press, 1953, 1956; 13-19.
143. Jamieson CP, Mrozowski S. Thermal conductivities of polycrystalline carbons and graphites. Proceedings of the First and Second Conferences on Carbon. (Buffalo, New York): Pergamon Press, 1953, 1955; 155-166.
144. Mrozowski S. Thermal conductivity of carbons and graphite. Physical Review, 1952. 86(2): 251.
145. Powell RW, Schofield FH. The thermal and electrical conductivities of carbon and graphite to high temperatures. Proceedings of the Physical Society, 1939. (1): 153.
146. Null M, Lozier W, Moore A. Thermal diffusivity and thermal conductivity of pyrolytic graphite from 300 to 2700K. Carbon, 1973. 11(2): 81-87.
147. Mizushima S. Thermal and electrical conductivities of carbon materials. Physical Review, 1952. 36(6): 1040.
148. Mizushima S, Okada J. Notes on the electrical and thermal conductivities of graphite and amorphous carbon. Physical Review, 1950. 82(1): 94-95.
149. Kelly BT, Gilchrist KE. The basal thermal conductivity of highly oriented pyrolytic graphite as a function of degree of graphitisation. Carbon, 1969. 7: 355-358.
150. Lutcov AI, Volga VI, Dymov BK. Thermal conductivity, electric resistivity and specific heat of dense graphites. Carbon, 1970. 8: 753-760.
151. Bullen AJ, O'Hara KE, Cahill DG, Monteiro O, Keudell Av. Thermal conductivity of amorphous carbon thin films. Journal of Applied Physics, 2000. 88(11): 6317-6320.
152. Kelly BT. Chemistry and Physics of Carbon. Series Chemistry and Physics of Carbon. Vol. 5. 1956, New York: Marcel Dekker. 119-215.
153. Rhim YR, Zhang D, Nagle DC, Herman C. Modeling the carbonization process using AC and DC conductivity methods. 2007 Carbon Conference. (Seattle, Washington), 2007.
154. Rhim YR, Zhang D, Nagle DC, Rooney M, Herman C. Thermal properties of microcrystalline derived carbons. ASME-JSME Thermal Engineering Summer Heat Transfer Conference. (Vancouver, B.C.), 2007; 32348.
155. Parker WJ, Jenkins RJ, Butler CP, Abbott GL. Flash method of determining thermal diffusivity, heat capacity, and thermal conductivity. Journal of Applied Physics, 1961. 32(9): 1679-1685.
156. Kishimoto I, Baba T, Ono A. Relationship between thermal diffusivity and microscopic structure in graphitic carbon I: mesophase carbon. Proceedings of the 24th International Thermal Conductivity Conference, 1998. 24: 265-276.
157. Siebeneck HJ, Urick PA, Hasselman DPH, Minford EJ, Bradt RC. Thermal diffusivity gradients in thick glassy carbons. Carbon, 1977. 15: 187-188.
158. Gibson LJ, Ashby MF, Thermal, electrical and acoustic properties of foams, in Cellular solids. 1999, Cambridge University Press: Cambridge ; New York. 283-295.
159. Incropera FP, DeWitt DP, Thermophysical Properties of Matter, in Fundamentals of Heat and Mass Transfer. 2001, John Wiley & Sons, Inc.: New York. 903-932.

160. Vlasov A, Ralchenko V, Gordeev S, Zakharov D, Vlasov I, Karabutov A, Belobrov P. Thermal properties of diamond/carbon composites. *Diamond and Related Materials*, 2000. 9: 1104-1109.
161. Kano M, Momota M, Okabe T, Saito K. Specific heat capacity of new porous carbon materials: woodceramics. *Thermochimica Acta*, 1997. 292: 175-177.
162. Gupta M, Yang J, Roy C. Specific heat and thermal conductivity of softwood bark and softwood char particles. *Fuel*, 2003. 82: 919-927.
163. Manocha LM, Warriar A, Manocha S, Sathiyamoorthy D, Banerjee S. Thermophysical properties of densified pitch based carbon/carbon materials - I. Unidirectional composites. *Carbon*, 2006. 44: 480-487.
164. Manocha LM, Warriar A, Manocha S, Sathiyamoorthy D, Banerjee S. Thermophysical properties of densified pitch based carbon/carbon materials - II. Bidirectional composites. *Carbon*, 2006. 44: 488-495.
165. Kasai A, Murayama T, Ono Y. Measurement of effective thermal conductivity of coke. *ISIJ International*, 1993. 33(6): 697-702.
166. Devpura A, Phelan P, Prasher R. Percolation theory applied to the analysis of thermal interface materials in flip-chip technology. *Inter Society Conference on Thermal Phenomena*, 2000. 21-28.
167. Devpura A, Phelan P, Prasher R. Size effects on the thermal conductivity of polymers laden with highly conductive filler particles. *Microscale Thermophysical Engineering*, 2001. 5: 177-189.
168. Tian W, Yang R. Effect of interface scattering on phonon thermal conductivity percolation in random nanowire composites. *Applied Physics Letters*, 2007. 90: 263105-1-263105-3.

CHAPTER 3. FULLY DENSE, NET SHAPE SILICON CARBIDE HEAT EXCHANGER MATERIALS

3.1 Formation of fully dense, net shape silicon carbide by liquid silicon infiltration of carbon with engineered structure

Formation of net shaped silicon carbide using liquid silicon infiltration (LSI) involves packing porous carbon monoliths in a bed of silicon particles and heating the mixture above the silicon melting point. The driving forces for this process are capillary effects and reactive wetting¹⁻⁵. The combination of these forces leads to the infiltration of liquid silicon into the pores of the carbon followed by reaction of the carbon with the liquid silicon. Silicon carbide formation begins with the dissolution of carbon atoms into liquid silicon. Silicon carbide formation begins with the dissolution of carbon atoms into liquid silicon⁶ followed by the precipitation of silicon carbide crystals. The chemical reaction between liquid silicon and carbon,

has a negative free energy ΔG_f° that is a function of reaction temperature T as

$$\Delta G_f^\circ = (-27100 - 2.73T \log T + 18.1T) \text{ cal mol}^{-1} \text{ }^7,$$

and this relation is plotted in Figure 3.1.

Figure 3.1. Temperature-dependent free energy of the silicon carbide formation reaction.

The success of this process depends on several important factors including carbon preform porosity and reactivity, and reaction conditions including temperature, atmosphere/pressure and time. Carbon preform porosity dictates the flow of liquid silicon, and carbon reactivity controls the rate at which the silicon-carbon reaction proceeds for any given set of reaction parameters. In Chapter 2, methods for the production of carbon preforms with controllable properties were described in detail. In this Chapter, the effects of carbon preform properties and reaction conditions were studied. Other factors and phenomena associated with the liquid silicon-carbon reaction include the temperature dependence of contact angle^{1,2,4}, surface tension¹, reaction rate constant^{6,8}, reaction mechanisms^{6,8,9}, and silicon viscosity¹⁰.

The ideal carbon preform for the liquid silicon-carbon reaction should have sufficient porosity to allow effective infiltration of liquid silicon. However, overabundance of porosity will lead to a low density reaction product. Proper pore sizes and a narrow pore size distribution are also important for LSI. The pores must be large enough to allow capillary force to overcome liquid silicon viscosity to achieve total pore filling. However, if the pores are too large, the silicon carbide formed cannot fully eliminate the pores leaving unreacted silicon in the residual voids. If the pores are too small, pore choking by the carbide occurs early in the reaction process at outer regions of the carbon preform. This pore choking blocks the further flow of liquid silicon into the main body of the carbon preform, thus terminating the reaction inside the preform. Therefore, pores in the carbon preform must be large enough for the silicon to react with the interior of the preform to allow complete conversion to silicon carbide.

The reactivity of the carbon preforms towards liquid silicon must be tailored to allow substantial liquid silicon-carbon reaction without leading to disintegration of the carbon preform. We have demonstrated that carbon preforms with variable reactivities can be produced by using cellulose and phenolic resin precursor mixtures with different mass ratios.

Although theoretical calculations and information from literature on similar reactions can assist in choosing the right carbon preforms and deciding the appropriate reaction conditions, experimentation is needed to determine the optimum parameters to carry out the conversion reaction. Thus, LSI reactions with different carbon preforms were performed under various reaction conditions.

LSI reactions were performed in an Astro Industries, Inc. (Thermal Technology LLC, Santa Rosa, CA, USA) 1000A water-cooled high-temperature graphite element furnace equipped with a type C thermocouple and a Eurotherm (Leesburg, VA, USA) 2404 PID temperature controller. A photograph of this furnace is presented in Figure 3.2. Round carbon preform discs were prepared by core drilling to the desired diameter, followed by ultrasonication in ethanol for 1 minute to remove loose debris, and drying at low pressure. The carbon discs were packed in a bed of silicon powder (Alfa Aesar, Si powder, crystalline, -325 mesh, 99.5%) inside a high purity and high density graphite crucible with a lid. This custom machined crucible, shown in Figure 3.3, has an outside diameter of 6 cm, an inside diameter of 2.2 cm, a height of 6 cm and a cavity depth of 4 cm.

Figure 3.2. Astro 1000A water-cooled graphite element vacuum furnace.

Figure 3.3. Graphite crucible and lid used for performing LSI reactions.

The amount of silicon used was 150% of the theoretically required mass for the full conversion of carbon into silicon carbide. The thermal profile for LSI is presented in Table 3.1. This schedule ensures sufficient outgassing of graphite parts and the carbon preform at temperatures below the silicon melting point. In order to melt silicon as swiftly as possible, the furnace was programmed to heat at 100% output from 1300°C to the reaction temperatures. When the desired reaction time was reached, the power to the furnace was turned off and it was allowed to cool to room temperature quickly with the aid of circulating chilled water. The cooling rate was very high, especially at higher temperatures. As measured by the thermocouple, it took less than 1 minute to cool from the reaction temperature of 1800°C to below the melting point of silicon, 1414°C. After being cooled to room temperature, the crucible containing the specimen was removed from the furnace, and the rough silicon-rich surface layers (no more than 1 mm in thickness) of the specimen were removed by grinding.

Table 3.1. Thermal profile for SiC formation by LSI.

Action	Rate/Time	T (°C)
Ramp	25°C/min	RT-1000
Step	NA	1300
Dwell	30 min	1300
Step	NA	1414-1900
Dwell	10-300 min	1414-1900
Step	NA	25

The carbon preforms studied were produced from pure cellulose, pure phenolic resin, and their precursor mixtures with cellulose:resin mass ratios of 90:10, 80:20, 75:25, 70:30, 65:35, 60:40, 55:45, 50:50, 45:55, 40:60, and 20:80. The silicon carbide formation conditions are: temperatures between 1414 and 1900°C; reaction chamber pressures of 1550, 760, and 0.5 Torr of argon; and reaction periods of 10, 15, 30, 60, 120, and 300 minutes.

The outcome of each reaction was evaluated by the following studies:

1. Visual examination of the crucible content and the silicon carbide formed
2. Measurement of the density of the silicon carbide disc and comparison with pure silicon carbide (3.220 g cm^{-3})
3. Analyzing porosity and impurities (Si, C) by microscopic imaging of silicon carbide cross sections

Samples were sectioned vertically in half, and the cross sections were ground and polished according to the procedure developed by R. E. Chinn¹¹ for observation. Analytical tools used in the study of the silicon carbide include optical microscopy, scanning electron microscopy (SEM), electron probe microanalysis (EPMA), Auger electron microscopy (AES), and x-ray diffraction (XRD).

During initial LSI experiments, the reaction temperature ranged from 1450 to 1900°C, reaction time was limited to 30 and 60 minutes, and the reaction chamber argon pressure was kept at 1550, 760, or 0.5 Torr of argon. Samples were analyzed in detail and the best reaction conditions were identified.

Analysis of temperature effects on the silicon carbide reaction showed that infiltration temperatures only slightly above the silicon melting point (1414°C) resulted in significant erosion of the carbon preform surfaces without silicon carbide formation. The reaction results obtained from this analysis lacked reproducibility. Reactions at higher temperatures were more successful. However, when the reaction temperature was increased to 1900°C, significant silicon vaporization took place. This resulted in depletion of the silicon source and incomplete silicon carbide conversion. The optimum reaction temperature was identified to be 1800°C. High quality silicon carbide was formed and silicon loss due to vaporization was minimized.

The effect of furnace chamber pressure was studied by carrying out the reactions in argon under three different pressures of 1550, 760 and 0.5 Torr. Under a lower pressure of 0.5 Torr, infiltration depth increased and this allowed a higher degree of silicon carbide conversion. This is interpreted to be a result of the enhanced reactive wetting and infiltration flux caused by the reduction of argon pressure at the Ar-Si-C triple line^{1,2,4}.

Earlier studies on LSI reaction models¹²⁻¹⁶ indicated that the reaction rate decreases as reaction time evolves. To fully examine the effect of reaction time, the 1800°C LSI reactions were varied from 10 to 300 minutes. The 120 minute reaction time produced the highest volume fraction of silicon carbide. Longer reaction times generated silicon carbide monoliths with extensive cracking. This cracking slowly grew with time until they formed a network that resembled a spider web.

The 1800°C reaction was also used to identify the ideal carbon preform. Carbon preforms examined included those created from cellulose, phenolic resin, and precursor mixtures with mass ratios varying from 9:1 to 1:9. Helium gas pycnometry was used to determine the densities of the reaction products. The products with the highest densities and their precursor compositions are given in Table 3.2.

Table 3.2. Density of silicon carbide reaction products

precursor ratio (cellulose : resin)	density (g cm ⁻³)	fraction of pure SiC density (g cm ⁻³)
65:35	2.85	0.88
60:40	2.96	0.92
55:45	2.76	0.86
50:50	2.76	0.86
<i>pure SiC</i>	3.22	<i>1</i>

Bulk silicon carbide formation from cellulose carbon was unsuccessful. The contents inside the crucibles after the reactions included small unreacted carbon preform fragments and a powdery substance loosely encasing these fragments. The severe erosion of the cellulose carbon preform is attributed to the high reactivity of cellulose carbon, allowing it to be readily dissolved by liquid silicon at a rate that is higher than the rates of nucleation and growth of silicon carbide. The liquid silicon becomes supersaturated with carbon resulting in homogeneous precipitation of silicon carbide from the liquid silicon-carbon phase. This results in formation of a silicon carbide material that does not maintain the shape of the carbon preform.

Bulk silicon carbide formation from phenolic resin carbon was also unsuccessful. Due to the lack of micron-scale porosity in this carbon and its low reactivity, the reaction with liquid silicon can only occur at the carbon preform surface creating a silicon carbide layer thickness of only $10\text{ }\mu\text{m}^{8,9}$. The lack of a network of pores of critical size in this glass carbon prevents full conversion to silicon carbide.

The high reactivity of the cellulose carbon and the low reactivity of the phenolic resin carbon prevent them from being good carbon preforms for the liquid silicon-carbon reaction. By using homogeneous mixtures of cellulose and phenolic resin as precursors, carbons with moderate reactivities suitable for these reactions were made. The overall reactivity of the carbons produced from these precursors is determined by the cellulose:resin mass ratios. These different mass ratios also influence the bulk density and micron-scale porosity of the carbon preforms.

Micron-scale porosity in carbon preforms produced from precursor mixtures originated from the initial packing density of the cellulose particles. If the cellulose:resin

ratio is too low, then during thermal processing most of the cellulose particles are fully coated by the phenolic resin. This results in the cellulose carbon being coated with a dense glassy carbon. This effect is observed in the 40:60 carbon preform where the liquid silicon cannot penetrate the carbon preform pore structure to form silicon carbide. Although the ideal carbon bulk density is approached at this precursor mass ratio and the median pore diameter is above 1 μm , the total fractional volume of open micron-scale pores (32%) is still too low to allow effective silicon carbide formation through the entire carbon preform¹⁷. As a result, pore choking occurs terminating the reaction near the preform surface as shown in Figure 3.4. In this optical micrograph, the region to the far right is the silicon phase with silicon carbide crystals precipitated from the silicon-carbon solution. The middle region of the micrograph is the reaction region where some LSI has occurred. This region is approximately 150 μm in depth with silicon, silicon carbide and carbon phases present. The region at the far left of the micrograph is an un-infiltrated and unreacted region of the micron-porous carbon preform. In this region, large pores (~ 20 -50 μm) can be observed as black areas. However, no such large pores were detected by mercury intrusion porosimetry. This indicates that these large pores are either fully closed or 'bottleneck' pores with openings too small for mercury intrusion. These pores cannot be infiltrated by liquid silicon.

Figure 3.4. Optical micrograph showing pore choking and early termination of the LSI reaction near the outer surface of the carbon preform.

Liquid silicon penetrated deeply into the 75:25 carbon preform but the infiltration was heterogeneous and only partial conversion of the carbon preform structure to silicon carbide occurred, leaving some regions with unreacted carbon and unfilled pores. Figure 3.5a shows the entire cross section of this reaction product disc. The surface regions of the product are much more porous than the inner regions, indicating that a significant amount of carbon was removed by the liquid silicon from the surfaces of the carbon preform during the reaction. The removal of the surface carbon by liquid silicon without forming silicon carbide at the surfaces is due to the higher than ideal reactivity of the carbon preform. Carbon at the surfaces was dissolved too quickly by liquid silicon to allow the complete in-situ formation of silicon carbide crystals by precipitation at these regions. The liquid silicon solution of carbon continued infiltrating the inner regions of the carbon preform and left the surface regions with a high degree of porosity. Figure 3.5b is a high magnification image of the central region of the reaction product. Although

this image shows that the central region has a high volume fraction of silicon carbide, unfilled pores and unreacted carbon and silicon can also be clearly seen.

Figure 3.5. Optical micrographs of the 75:25 silicon carbide reaction product. (a) A low magnification image of the entire specimen cross section, and (b) a high magnification image of the central region.

Reaction product density values given in Table 3.2 indicate that near complete LSI and high degrees of silicon carbide formation occurred during the reactions between liquid silicon and porous carbon preforms produced from cellulose:resin mixture precursors with mass ratios between 65:35 and 50:50. Microscopic images of these reaction products show that silicon carbide was formed throughout the entire sample cross sections and unfilled pores were not observed. The results of these reactions reveal that the reactivity of these carbons was sufficiently high for effective silicon carbide formation without being too high, as was for the case of pure cellulose carbon. LSI of the 60:40 carbon yielded a product with the highest density of 2.95 g cm^{-3} , which is over 91% of that of pure silicon carbide. Figure 3.6 presents photographic images of the polished surface of the 60:40 product, and the high reflectivity of the polished surface indicates that this product is non-porous and has a fine grain texture. The 60:40 carbon

preform has a median micron-scale pore diameter of 1.52 μm , large enough to prevent pore choking. The micron-scale porosity of this carbon is 43% and the bulk density is 0.79 g cm^{-3} . This bulk density is lower than the calculated ideal bulk density value of 0.96 g cm^{-3} and this suggests that this carbon preform is still not perfect. Further improvement on the carbon preform density can be made by using a lower cellulose:resin mass ratio and cellulose particles with a slightly larger size or a higher aspect ratio.

Figure 3.7 shows one of the 60:40 product optical micrographs. Quantitative digital image analysis of a collection of such optical micrographs shows zero residual micron-scale porosity after 15 minutes of reaction. By 120 minutes of reaction time, nearly 82.5 vol% of the product microstructure was β -SiC with the remaining volume fractions being un-reacted silicon (~16.5 vol%) and carbon (~1 vol%). The unreacted silicon in the reaction product is due to the lower than ideal bulk density of the carbon preform, and the low concentration of residual carbon indicates that carbon reactivity has been optimized. The density of this product can be calculated based on the fractional volumes of silicon, silicon carbide and carbon as $\rho_{\text{Calculated}} = \rho_{\text{SiC}}\phi_{\text{SiC}} + \rho_{\text{Si}}\phi_{\text{Si}} + \rho_{\text{C}}\phi_{\text{C}}$, where ϕ_x is the volume fraction of phase x. The value of $\rho_{\text{Calculated}}$ is 3.06 g cm^{-3} , which is slightly above the density value determined by helium gas pycnometry. This is due to the high residual silicon content at the surfaces of the reaction product disc. If more of the surface regions were removed by grinding, then the measured density value should increase towards the calculated value. Figure 3.8 is the x-ray diffraction pattern of the polished cross section of the 60:40 product. It shows strong β -SiC diffraction peaks and weak silicon diffraction peaks, confirming that the substantial portion of the reaction product is β -SiC.

Figure 3.6. Photographs of the highly reflective polished surface of a 35 mm 60:40 silicon carbide disc.

Figure 3.7. Optical micrograph of the 60:40 silicon carbide. The white regions are silicon, the gray regions are silicon carbide, and the black regions are carbon.

Figure 3.8. X-ray diffraction pattern of the 60:40 silicon carbide.

In summary, the ideal conditions for silicon carbide formation by LSI of porous carbon preforms were determined to be a reaction temperature of 1800°C, a chamber argon gas pressure of 0.5 Torr and a time of 120 minutes. The best carbon preforms for this technique were produced from a cellulose:resin mixture precursor with a 60:40 mass ratio. These carbon preforms have a bulk density of 0.79 g cm⁻³, a median micron-scale pore diameter of 1.5 μm, a skeletal density of 1.4 g cm⁻³, a micron-scale porosity of 43%, an actual density of 2.19 g cm⁻³, and a Langmuir total specific surface area of 645 m² g⁻¹. Silicon carbide formed by liquid silicon reaction with these carbon preforms have a density of 2.97 g cm⁻³, which is about 92% of that of pure β-SiC, with a silicon carbide volume fraction of over 0.82. At this point, the technique for the production of net shape silicon carbide by LSI of porous carbon preforms has been established and it is illustrated in the flow chart in Figure 3.9.

Figure 3.10 shows a photograph of an original 60:40 carbon preform and the silicon carbide formed, a SEM image of the carbon preform, and an optical micrograph of the silicon carbide. The photograph of the original carbon and the product demonstrates the retention of geometry during the reaction. The SEM image illustrates the porous morphology of the carbon preform. The optical micrograph shows the non-porous and fine-textured three phase (SiC, Si, C) microstructure of the reaction product. Figure 3.11a shows 60:40 carbon preforms with machined grooves and Figure 3.11b shows the net shape reaction products maintaining the original geometries at the right. Silicon carbide structures with channels for liquid or gas flow for high temperature applications, such as high temperature heat exchangers for nuclear reactors, can be formed by stacking the grooved silicon carbide discs together. These discs can be bonded with high temperature

corrosion resistant sealants such as borosilicate glass to form liquid or solid seals. In-situ bonding of the reaction products during silicon carbide formation can also be achieved by placing mixtures of fine silicon and carbon powders in between stacked carbon preforms.

Figure 3.9. Flow chart showing the process for making net shape silicon carbide.

Figure 3.10. (a) A photograph of the original 60:40 carbon preform and the silicon carbide formed from it, (b) a SEM image of the carbon preform, and (c) an optical micrograph of the silicon carbide.

Figure 3.11. (a) 35 mm 60:40 carbon preforms with machined grooves, and (b) net shape silicon carbide that maintained the original geometry.

3.2 Kinetics of the LSI process

Kinetic processes involved in liquid silicon infiltration (LSI) of porous carbon preforms were studied by performing reactions with the 60:40 carbon preforms for time periods ranging from 10 to 300 minutes. The reaction temperature and chamber argon pressure were held constant at of 1800°C and 0.5 Torr. The densities of products with different reaction times were obtained by using a Micromeritics (Norcross, GA, USA) Accupyc 1330 helium gas pycnometer and are plotted in Figure 3.12. The density vs. reaction time curve exhibits an initial steep rise until about 30 minutes followed by a leveling off to a nearly constant value at 300 minutes. After just 10 minutes a density of 2.71 g cm^{-3} was reached. This value is already over 82% of that of pure silicon carbide, 3.22 g cm^{-3} . The rapid increase in density during the early stage of reaction is a direct result of liquid silicon pore filling and a significant degree of silicon carbide formation. The plot approaches a maximum value of just under 3 g cm^{-3} with a final recorded value of 2.96 g cm^{-3} for the reaction time of 300 minutes, which is about 92% of that of pure silicon carbide.

Figure 3.12. The density of silicon carbide reaction products vs. reaction time.

Optical microscopy and quantitative digital image analysis was employed to determine the volume fractions occupied by silicon carbide, carbon, silicon and porosity

in the 60:40 products. This analysis was based on the unique grayscale values of each phase in optical micrographs, as shown in Figure 3.13. Digital optical imaging (32-bit RGB) of the polished cross sections of the products were collected with a digital camera (Diagnostic Instruments, Inc., Insight 2 (2MP) (1600x1200), 11.2 Color Mosaic) mounted on a Zeiss (Thornwood, NY 10594 USA) ICM 405 metallographic optical microscope with a x16 objective and x10 eyepiece. Digital image processing and analysis were performed using the open-source java-based image analysis program, ImageJ¹⁸. Figure 3.14 is a flowchart that illustrates the processes involved in gathering, processing, and analyzing images of the product cross section, and a silver mirror reference.

For each sample, five separate viewfield locations near the center of the product cross section were imaged. In order to reduce the effect of noise within the imaging system, ten raw images were collected at each viewfield location to derive an averaged image². To remove the effects of uneven illumination in the sample images and to increase photometric accuracy^{19,20}, flat-field correction was performed by dividing each averaged raw image by a flat-field reference image¹⁹. This flat-field reference image was obtained by averaging ten raw flat-field images of a broadband silver mirror surface (Newport Corporation, Silver coated, Round, Zerodur substrate, product # 10Z20ER.2) at ten adjacent viewfield locations. In order to further process the images with ImageJ, the flat-field corrected product images were converted from 32-bit RGB to 8-bit grayscale type images¹⁹. These images were then processed by intensity histogram saturation^{19,20} with 0.5% pixel saturation in order to take advantage of the full dynamic brightness range. Phase discrimination was made more accurate by enhancing edges within the image by unsharp filtering²¹. In some instances, grayscale intensity values in pore regions

Figure 3.13. An example of image segmentation achieved by grayscale thresholding. (a) A processed optical image of a 60:40 silicon carbide. (b)–(e) Segmented images with black pixels representing the phase of interest: (b) pores, (c) carbon, (d) silicon carbide (e) silicon.

Figure 3.14. Schematic of the steps involved in digital processing and analysis of images of the 60:40 silicon carbide with a silver mirror as a reference.

were misleading due to light reflection, so these pores were manually filled to eliminate the distorted brightness. At this stage, the optical images show four distinct phases, each having a unique and relatively uniform grayscale value. The chemical identities of these four phases were determined by using EPMA and the black, dark gray, light gray, and white regions in the images were identified as pores, carbon, silicon carbide, and silicon, respectively. For each processed image the exact grayscale value for each phase was determined. As shown in Figure 3.13, a thresholding^{19,20} tool was used to segment the final processed image (Figure 3.13a) into four images (Figure 3.13b-e) with each representing a single phase. In these segmented images, black pixels represent the phase of interest while white pixels represent all of the other phases. The fraction of the image area occupied by the phase of interest then could be measured by dividing the number of black pixels by the total number of pixels. According to stereological theory, averaged area fractions of a set of flat images are considered equivalent to the averaged volume fractions of the same specimen²². Volume fractions for each phase were determined in five separate viewfields for each reaction product. The volume fraction of each phase was averaged over the five separate viewfields and the standard deviation of each volume fraction was calculated. The results of these analyses are presented in Figure 3.15.

Figure 3.15a illustrates the change in pore volume fraction with increasing reaction time, and it reveals that by 15 minutes pore filling by liquid silicon was almost complete, and by 30 minutes zero porosity remained. Figure 3.15b shows that silicon volume fraction increased rapidly to a maximum of approximately 23% in 15 minutes as liquid silicon infiltrated and filled the voids within the carbon. As the liquid silicon filled the pores, it immediately began reacting with the carbon to form silicon carbide.

Figure 3.15. Volume fraction of (a) pores, (b) silicon, (c) carbon, and (d) silicon carbide in the time-controlled reactions.

After 15 minutes of reaction, the silicon volume fraction decreased gradually until it reached a minimum value of about 16.5% after 120 minutes. The decrease in silicon volume fraction after initial infiltration was due to the consumption of silicon by silicon carbide formation. At 15 minutes, Figure 3.15c shows that most of the carbon had reacted to form silicon carbide. This is because after initial reaction, the remaining carbon regions became isolated from liquid silicon by silicon carbide, thus preventing further reaction. As discussed in literature²³⁻²⁵, once a continuous silicon carbide layer of approximately 10 μm is formed between the liquid silicon and carbon, all further growth of this layer occurs slowly by carbon diffusion through the silicon carbide barrier.

Careful examination of the silicon volume fraction (Figure 3.15b) reveals a slightly higher value of 17.9% for 300 minutes than the minimum value of 16.5% reached at 120 minutes. This observation was accompanied by optical micrographs showing long silicon-filled cracks in the main silicon carbide phase in the 300 minute product (Figure 3.16b). Such cracks were not observed for reaction times of or below 120 minutes (Figure 3.16a). We believe the mechanism for crack formation to be the wicking of excess liquid silicon into the reaction product over time. The high capillary pressures at the sharp crack tips led to high localized stress fields which induced crack formation and propagation that allowed further wicking of the liquid silicon. As this action progressed, long and thin silicon-filled regions were established and the silicon volume fraction increased. An alternate explanation of such cracking is carbon diffusion through the silicon carbide phase to silicon forming silicon carbide. The volume expansion during silicon carbide growth at sharp crack tips results in stress cracking, and eventually crack networks form.

Figure 3.16. Optical micrographs of silicon carbide after reacting for (a) 2 hours and (b) 5 hours.

In Figure 3.15c, the carbon volume fraction quickly drops to less than 3% in 60 minutes and remains nearly constant for longer reaction times. The presence of unreacted silicon (between 16 to 18% for reaction times of 60, 120 and 300 minutes) and residual carbon indicates that the reaction did not achieve completion.

The silicon carbide volume fraction plot in Figure 3.15d indicates rapid formation during the first ten minutes of reaction as its volume fraction jumps from 0 to over 70%. Then the silicon carbide volume fraction levels off to a plateau reaching a maximum value of over 82% at 120 minutes. For the reaction time of 300 minutes, the silicon carbide volume fraction is 81%, which is slightly lower than the 120 minute value. This is believed to be caused by the wicking of excess liquid silicon into the reaction product over time as discussed earlier.

During the reaction, pores are filled with unreacted liquid silicon and silicon carbide forms at the pore walls. By plotting the pore volume fraction values and silicon volume fraction values with reaction time in one plot, as shown in Figure 3.17, easy comparison can be made on these two sets of values. This reveals the fractions of the

original pore space occupied by silicon and silicon carbide during the reaction after all the pores are filled. As Figure 3.17 shows, the volume fraction of the original pore is 43% and they are fully filled after 30 minutes. The silicon volume fraction curve reaches a near constant value of about 17% after 120 minutes, indicating that the fractions of the original pore volume occupied by silicon and silicon carbide becomes constant at this moment. The fraction of the pore volume in the original carbon preform occupied by silicon in the reaction product can be calculated by dividing the silicon volume fraction value of 17% by the original pore volume fraction value of 43%. This gives a value of about 40% for the fraction of the original pore space occupied by silicon in the reaction product, and the rest is occupied by silicon carbide.

Figure 3.17. A comparison of the volume fraction of pores and silicon with reaction time.

By combining literature²⁴⁻⁵⁸ and our own results²³, six events that occur during the overall LSI and silicon carbide formation process can be identified as:

- I.** Rapid liquid silicon infiltration
- II.** Rapid carbon dissolution in liquid silicon
- III.** Rapid silicon carbide formation
- IV.** Formation of a continuous silicon carbide layer at all silicon-carbon interfaces
- V.** Carbon diffusion through the continuous silicon carbide layer to react with liquid silicon
- VI.** Formation of cracks within the silicon carbide structure that are filled with liquid silicon

The occurrences of these events with volume fraction changes are marked by Roman numerals in the plots in Figure 3.15. Events I-III take place simultaneously and culminate in Event IV. Events I-III are transient, dynamic, and non-equilibrium processes which are not precisely described in this study. A more in-depth study of the reaction over the period of 0 to 15 minutes is necessary to fully explore the chemical kinetics and reaction mechanisms involved. However, in practice, such experiments are extremely difficult to design and conduct. The continuous silicon carbide layer formed in Event IV isolates the residual carbon from liquid silicon so further reaction can only occur through Event V. At 1800°C the diffusivity of carbon in silicon carbide is $2.90 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which is three orders of magnitude greater than the diffusivity of silicon, $9.5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ ²⁴. Therefore, Event V proceeds by carbon diffusion to liquid silicon from isolated solid carbon across the silicon carbide layer^{23,24}. This is a very slow process that is limited by the high temperature diffusivity of carbon in silicon carbide; therefore, further reaction due to silicon diffusion can be neglected. Further evidence supporting the occurrence of Event V includes a small increase in silicon carbide volume fraction and a slight decrease in carbon volume fraction after Event IV. At some time after the beginning of Event V, Event VI accompanies the diffusion limited reaction. Event VI has also been noticed by others³³ and it was attributed to thermal stresses during the highly exothermic reaction. This assumption is different from our interpretation for Event VI as a result of the wicking of excess liquid silicon into the reaction product over long reaction times.

To support our interpretation for Event VI, an experiment was designed to determine if the wicking of excess liquid silicon into the reaction product was the cause for the formation of silicon carbide cracks over long times. First, a carbon preform was

allowed to react with liquid silicon for 30 minutes and the surfaces of the product were ground to remove excess silicon. This cleaned product was put back into the reaction chamber and treated at the same reaction temperature of 1800°C for 4.5 hours under flowing argon gas ($P \sim 1$ atm) without using any silicon. The total thermal treatment time of this product is 300 minutes and its optical micrographs are shown in Figure 3.18. The high magnification optical micrograph in Figure 3.18b does not show any cracks or other major structural defects. However, as shown by the low magnification optical micrograph in Figure 3.18a, the surfaces of this sample are highly porous. This surface porosity is due to the vaporization of unreacted silicon trapped in the pores. Although silicon vapor can be captured by the residual carbon to form silicon carbide, some of it can escape the product resulting in a porous SiC-C composite, and this is most significant at the surfaces. It can be assumed if this product is heated for enough time at the reaction temperature, it will no longer have any excess silicon.

Figure 3.18. Optical micrographs of a polished cross section of silicon carbide reacted for 300 minutes with excess silicon removed after the first 30 minutes. (a) Image of the entire cross section, and (b) higher magnification image of the central region.

3.3 Thermophysical properties using the laser flash method

High temperature thermophysical properties of the 60:40 silicon carbide product were studied using the laser flash method⁵⁹⁻⁶¹. To measure the temperature-dependent thermal diffusivity and specific heat, one side of a thin sample disc was heated with a fast laser pulse and the thermal response of the other side was monitored with time by an infrared detector⁶². Measurements were made at temperatures between 100 and 1000°C. The laser flash instrument determines thermal diffusivity based on the thickness of the specimen and the time required for the thermal response at the back side to reach half of its maximum temperature increase⁵⁹⁻⁶¹. The specific heat was determined by comparing this thermal response with that of a reference sample of known heat capacity. The thermal conductivity, κ , was calculated from the values of thermal diffusivity, α , specific heat, C , and density, ρ , according to the equation $\kappa = \rho C \alpha$ ⁵⁹.

Thermal diffusivity and specific heat measurements were performed with an Anter Flashline instrument (Pittsburgh, PA 15235 USA). The specimen disc had a diameter of 1.25 inches, a thickness of 0.197 cm, and its density was determined to be 2.9 g cm⁻³ by helium gas pycnometry. A pyrolytic graphite disc was used as the reference. Thermal diffusivity was recorded in argon three times and averaged at each measurement temperature during both heating to the maximum temperature of 1000°C and cooling back to 100°C. The heating and cooling curves in Figure 3.19 show good agreement, indicating the stability of the sample during measurement and the reproducibility of the data.

Specific heat was measured three times at each testing temperature during both heating and cooling. The data were averaged for each temperature and are plotted as

points in Figure 3.20. Except the value measured at 1000°C, the temperature-dependent specific heat obeys the Debye model^{65,66} well and they were fitted to a logistic sigmoidal growth function, $C = 0.18/(1 + 26.46 \exp(-0.01034T))$ as the solid curve in Figure 3.20.

Thermal diffusivity of the 60:40 product is shown in Figure 3.21a. This curve decays with increasing measurement temperature, exhibiting a value of $0.64 \text{ cm}^2 \text{ s}^{-1}$ at 373 K and a value of $0.12 \text{ cm}^2 \text{ s}^{-1}$ at 1273 K. These values are higher than those measured for most sintered silicon carbide materials^{48,62-64}. The specific heat values of the 60:40 product are presented with temperature in Figure 3.21b. The high temperature specific heat values are slightly higher than the values of other silicon carbide based materials in literature^{64,65,67}. The specific heat curve exhibits values of $1.15 \text{ Jg}^{-1}\text{K}^{-1}$ at the lowest measurement temperature of 373 K and $1.8 \text{ Jg}^{-1}\text{K}^{-1}$ at the highest measurement temperature of 1273 K. Thermal conductivity data are presented in Figure 3.21c, and they are comparable to values measured for other silicon carbide materials^{48,62,64,65,67}. The thermal conductivity decays with increasing temperature, exhibiting values of $214 \text{ Wm}^{-1}\text{K}^{-1}$ at 373 K and $64 \text{ Wm}^{-1}\text{K}^{-1}$ at 1273 K.

Figure 3.19. Diffusivity data obtained during heating and cooling.

Figure 3.20. Specific heat data that has been fitted to approximate Debye behavior.

Figure 3.21. Thermophysical properties of the 60:40 silicon carbide product determined by the laser flash method. (a) Thermal diffusivity, (b) specific heat and (c) thermal conductivity.

Thermal conductivity is an important property for consideration during the selection of materials for high temperature heat exchangers⁶⁸. The thermal conductivity of high purity silicon carbide is very high^{69,70}, with a value of $490 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature. However, most silicon carbide materials exhibit much lower conductivities due to impurities, secondary phases, grain boundaries and other defects⁶⁹. The thermal conductivity of the 60:40 reaction product is compared with two groups of silicon carbide materials: (1) silicon carbide thin films, wafers and boules grown from the gas phase, and (2) silicon carbide prepared by sintering techniques. Typically, thermal conductivities of silicon carbide grown from gas phase are much higher than those of silicon carbides produced by sintering techniques. This is because sintering techniques often utilize sintering aids (i.e., secondary phases), and the products usually contain porosity, high grain boundary concentrations, and high impurity concentrations. In contrast, gas phase growth techniques are capable of eliminating porosity, controlling crystal orientation, increasing grain size, and decreasing the concentration of defects and impurities in the products.

The temperature-dependent thermal conductivity of the 60:40 product is compared to the thermal conductivities of silicon carbides from literature as shown in Figure 3.22. The silicon carbides from literature include electronic grade CVD silicon carbide⁶⁵, sintered β -silicon carbide particles⁶⁷, biomorphic silicon carbide⁴⁸, CVD silicon carbide composite⁶², and silicon carbide particles sintered with BeO ⁶⁴. The thermal conductivity of the silicon carbide made in this study is nearly one order higher than the values exhibited by the silicon carbides made by other processing techniques. The temperature-dependent thermal conductivity of our silicon carbide is slightly lower than

that of the electronic grade CVD silicon carbide⁶⁵ at low temperature and they are nearly equivalent at higher temperatures. The high thermal conductivity of electronic grade CVD silicon carbide is due to its high purity. Silicon carbide made by LSI exhibits similar high thermal conductivities because carbon and silicon are isolated secondary components that do not adversely affect the ability to transfer heat energy.

Figure 3.22. Comparison of measured thermal conductivities of (a) electronic grade CVD SiC, (b) the 60:40 SiC, and (c-f) various other SiC materials.

Heat transfer in dielectric solids such as silicon carbide is mostly driven by phonon transport⁷⁰ that can be hindered by phonon scattering. This scattering can occur in phonon-phonon, phonon-boundary and phonon-defect modes. Thermal conductivity is reduced as phonon scattering increases. Phonon-phonon scattering is enhanced as temperature is increased because of the higher concentration and energy of phonons at higher temperatures. At room temperature or above, phonon-phonon scattering modes dominate in silicon carbides with low levels of impurities/defects⁷⁰. For ceramics sintered with sintering aids and surface oxides, phonon scattering at these highly insulating

secondary layers at every grain boundary will substantially reduce the overall thermal conductivity.

To illustrate the effects of sintering aids and impurities on the thermal conductivity⁶⁹ of silicon carbides, Figure 3.23 was made to compare the thermal conductivities of electronic grade silicon carbide, silicon, various types of carbons, sintering aids, and surface oxides. These values were compiled from literature⁷⁰⁻⁷⁹. This figure clearly shows that diamond⁷² and graphite⁷¹ have higher thermal conductivities than silicon carbide⁷⁰. The thermal conductivity of sintering aid BeO⁷³ is similar to that of electronic grade silicon carbide, and the thermal conductivity of silicon⁷⁴ is slightly lower than that of the pure silicon carbide. Other impurities including the sintering aids La₂O₃⁷⁹ and Y₂O₃^{76,77}, and surface SiO₂^{75,78} all have much lower thermal conductivities.

Figure 3.23. Thermal conductivity of various substances including SiC.

Due to its high thermal conductivity, BeO in sintered silicon carbides⁸⁰ is not likely to reduce the overall thermal conductivity. However, since BeO is highly toxic⁸¹, safer sintering aids with much lower thermal conductivities, such as La₂O₃ and Y₂O₃^{76,77}, are frequently used and their concentrations in the final products can be higher than 1 mol%. The silicon carbide powders used to prepare sintered silicon carbides most likely have SiO₂ surface coatings. The sintering aids and SiO₂ impurities are localized at the silicon carbide grain boundaries during sintering. In addition to the presence of impurities at the grain boundaries, the random crystallographic orientation of the silicon carbide particles during sintering can lead to misorientation at the grain boundaries. Misoriented grain boundaries are highly insulating since the lattice mismatch at these boundaries enhances phonon scattering. The high concentration of such grain boundaries in sintered silicon carbides and the insulating materials at or near the grain boundaries are the main reasons for the reduction of the overall thermal conductivity.

The only impurities in our silicon carbide product are unreacted carbon and silicon. The residual carbon is highly amorphous. The thermal conductivities of different types of amorphous carbons can vary greatly, and they are all much lower than the values of highly crystalline carbons such as graphite⁷¹ and diamond⁷². Although the thermal conductivity of the residual carbon in our product has not yet been determined, we believe it should be lower than the thermal conductivity of pure silicon carbide based on work by Rhim, et. al⁸². However, since amorphous carbon only accounts for about 2 vol% in this material and is only present as isolated islands, its effect on the overall thermal conductivity is small. Our product has a high silicon content of about 16 vol%, but the effect of silicon on the reduction of the overall thermal conductivity is also not

significant because the thermal conductivity of silicon is only slightly lower than that of pure silicon carbide. The only other factor that can reduce the overall thermal conductivity of our silicon carbide is porosity⁶⁴. Our silicon carbide has shown no measurable porosity therefore its effect can be ignored.

The higher thermal conductivity of our silicon carbide may also be due to its different grain characteristics in comparison to silicon carbides made by sintering techniques. Our material has a percolated silicon carbide structure that was grown from a liquid silicon-carbon solution which leads to a highly percolated structure with a lower concentration of grain boundaries.

3.4 Chemical analysis

Electron probe microanalysis (EPMA)

Electron probe microanalysis (EPMA) performs quantitative elemental analysis by detecting x-rays generated from a specimen by electron bombardment^{83,84} and analyzing the relative strengths of the characteristic x-rays of elements to reveal chemical composition. It is typically performed in a scanning electron microscope (SEM) or a transmission electron microscope (TEM) so that chemical composition data can be accompanied by direct specimen imaging. EPMA was used to study the chemical compositions of the individual phases (SiC, Si, C) within the 60:40 reaction products and the interfaces between these phases. A SEM (JEOL JSM-6700F, Tokyo, Japan) was used to perform EPMA by energy dispersive spectroscopy (Silicon SUTW-Sapphire detector, EDAX, Mahwah, NJ, USA). Atomic percent quantification was performed by EDAX Genesis v.5.1 software using the standardless analysis technique⁸⁵ where x-ray spectra

were subjected to automatic smooth-fit background subtraction, ZAF matrix corrections⁸³ and normalization.

Initial EPMA of a 60:40 reaction product indicated a strongly non-stoichiometric⁸⁶ carbon-rich silicon carbide phase. EPMA conditions were a probe current of 3×10^{-10} A and a working distance of ~ 15 mm. Figure 3.24 presents a backscattered SEM image of a polished reaction product cross section. The chemical compositions of each of the three phases (SiC, Si, C) are given to the right of the image. The measurement locations are marked by crosshairs and the phases are specified. The results indicate that the silicon carbide phase has a carbon concentration of approximately 59 at% and a silicon concentration of about 41 at%. This deviates sharply from the 1:1 silicon carbide atomic stoichiometry at thermodynamic equilibrium^{87,88}. Large deviations from equilibrium silicon carbide stoichiometry have not been well-documented, and the small amount of available literature describing such large deviations⁸⁹⁻⁹² all suggest elevated silicon concentrations.

Figure 3.24. Backscattered SEM image and EPMA data of a 60:40 silicon carbide.

Figure 3.25. Chemical composition of a three phase C-SiC-Si region obtained by EPMA.

To study the effects of neighboring carbon and silicon on the composition distribution of a silicon carbide phase, an EPMA line scan was performed on a polished reaction product cross section. This scan was performed across a three phase C-SiC-Si region as shown in Figure 3.25. The distance between each measurement was 0.8 μm because the width of the specimen-electron beam interaction volume in this study was about 0.8 μm as calculated by a Monte Carlo simulation (Electron Flight Simulation, Version 3.1, copyright 1998, EDAX, Inc.) for the beam conditions and material. This inter-probe distance is too large for resolving the exact thickness of the phase transition regions that are estimated to be between 1 and 2 μm . Therefore, the exact compositions of the phase transition regions could not be precisely resolved. The concentrations of carbon and silicon in the silicon carbide phase are almost constant through most of the region with an average carbon concentration of 58 at% and an average silicon concentration of 42 at%. We initially developed two explanations for this strongly non-stoichiometric silicon carbide. First, during reaction, liquid silicon instantly became supersaturated with carbon upon contact due to the high reactivity of the carbon preform²³, and carbon-rich silicon carbide was formed out of this solution. Second, if stoichiometric silicon carbide was initially formed, it can be further enriched with carbon by carbon diffusion from the pure carbon phase at the reaction temperature of 1800°C. At this temperature, there is a high vacancy concentration within silicon carbide²⁴, and these vacancies provide a means for carbon and silicon to diffuse through silicon carbide^{24,93,94}. Silicon diffusion can be ignored because at 1800°C the diffusivity of carbon in silicon carbide⁹³ is three orders of magnitude higher than that of silicon⁹⁴.

The composition of the carbon region indicated that it is pure carbon. The silicon region has a carbon concentration just below 10 at%, which is much higher than the equilibrium concentration of carbon in liquid silicon at 1800°C (about 1 to 5 at%) indicated by the C-Si phase diagram^{87,88}.

Although the above results were obtained by following the standard EPMA procedures, the highly non-stoichiometric compositions of the silicon carbide and silicon phases cast doubt on the reliability of the measurements. In order to validate this technique, silicon carbide reference materials were studied for comparison with our products. A silicon carbide gemstone⁹⁵, shown in Figure 3.26a, was obtained from Charles and Colvard, Ltd / Cree Research (Durham, North Carolina, USA). This gemstone is transparent and colorless, indicating its high purity. A particulate silicon carbide standard reference material (NIST SRM 112) was obtained from the National Institute of Standards and Technology [(NIST), (Gaithersburg, Maryland, USA)]. This powder has small amounts of carbon, iron, aluminum, titanium, zirconium, calcium and magnesium impurities⁹⁶. A backscattered SEM image of this silicon carbide standard is shown in Figure 3.26b. A high purity n-type silicon carbide wafer grown from vapor phase, shown in Figure 3.26c, was obtained from Technologies & Devices International, Inc. (TDII, Silver Spring, MD, USA). The SEM image of this material shows a striped pattern. This may be due to orientational or compositional variations within this material. The n-type dopant concentration was too low to be detected by EPMA.

Figure 3.26. Silicon carbide reference materials for comparison with our silicon carbide. (a) Optical image of a silicon carbide gemstone from Charles and Colvard. (b) SEM image of the NIST SRM 112 silicon carbide particles. (c) SEM image of a n-type silicon carbide wafer from Technologies & Devices International, Inc.

Characteristic x-rays are radiation emitted by atoms in the specimen upon excitation by the electron beam, and the energy and wavelength of these x-rays are constant for atoms of a particular element^{97,98}. These x-rays are detected during EPMA and this allows the determination of specimen composition. Caution must be taken when analyzing silicon carbides with EPMA because silicon atoms strongly absorb⁹⁷ carbon characteristic x-rays. To ensure the accuracy of analysis, optimum EPMA conditions must first be determined by theoretical analysis of the electron beam-specimen interactions and the relative emissions of carbon and silicon characteristic x-rays from a silicon carbide matrix.

When an electron beam strikes a specimen, an electron interaction volume is generated and characteristic x-rays are emitted from within. The depth of the x-ray generation volume is called the *x-ray range*⁹⁹, R_x , and it is different for each element in the specimen, as shown in Figure 3.27a. R_x can be calculated as $R_x = (0.064/\rho) \left(E_o^{1.68} - E_c^{1.68} \right)^{100}$, where ρ is the density of the material, E_o is the electron beam acceleration voltage, and E_c is the electron critical excitation energy. The x-ray ranges of silicon and carbon atoms in silicon carbide are plotted as a function of EPMA acceleration voltage in Figure 3.27b. The plot indicates that the x-ray range of carbon in silicon carbide is only approximately 50 nm greater than that of silicon.

Figure 3.27. (a) Illustration and (b) plots of x-ray ranges for silicon and carbon in silicon carbide.

X-rays must be able to exit the specimen surface to be detected, and absorption by the specimen reduces their strength. High levels of carbon characteristic x-rays are absorbed by silicon L shell electrons in silicon carbide because the energy of carbon $K\alpha_1$ x-rays (0.277 keV^{101}) lies in the range of the silicon L shell absorption edge region (0.150 keV^{101}). The absorption of x-radiation as it passes through matter is described by

$1 - I(x)/I_o$ where I_o is the intensity of the original x-ray, $I(x)$ is the intensity of the x-rays emitted from the specimen, and x is the x-ray path length. The x-ray path length, x , is the depth of the specimen at which an x-ray is generated. $I(x)/I_o$ describes the fractional emission of the original x-rays and is $I(x)/I_o = \exp(-\mu_{absorber}^{emitter} \rho_{SiC} x)$ ⁹⁹, where μ is the empirical mass absorption coefficient with units of $\text{cm}^2 \text{g}^{-1}$, and ρ is the specimen density. The fractional emission of the original x-rays decreases with the x-ray path length. The mass absorption coefficient is a property of the material under study and is a measure of the degree that x-rays are absorbed by this material. The mass absorption coefficient for a multicomponent solid is a weighted average of the mass absorption coefficients of the individual components. The mass absorption coefficient of carbon $K\alpha_1$ x-rays in silicon carbide is $\mu_{SiC}^{CK\alpha_1} = \mu_{Si}^{CK\alpha_1} X_{Si} + \mu_C^{CK\alpha_1} X_C$ ⁹⁷ and the mass absorption coefficient of silicon $K\alpha_1$ x-rays in silicon carbide is $\mu_{SiC}^{SiK\alpha_1} = \mu_{Si}^{SiK\alpha_1} X_{Si} + \mu_C^{SiK\alpha_1} X_C$, where X_j is the mass fraction of element j in silicon carbide, $\mu_C^{CK\alpha_1}$ is $2147 \text{ cm}^2 \text{g}^{-1}$, $\mu_C^{SiK\alpha_1}$ is $445 \text{ cm}^2 \text{g}^{-1}$, $\mu_{Si}^{CK\alpha_1}$ is $34881 \text{ cm}^2 \text{g}^{-1}$, and $\mu_{Si}^{SiK\alpha_1}$ is $347 \text{ cm}^2 \text{g}^{-1}$ ¹⁰². The mass fractions of silicon and carbon in stoichiometric silicon carbide are $X_{Si} \approx 0.7$ and $X_C \approx 0.3$. The mass absorption coefficients calculated for silicon carbide are given in Table 3.3 and they indicate that (1) carbon $K\alpha_1$ x-rays are heavily absorbed by silicon carbide and (2) absorption of silicon $K\alpha_1$ x-rays in silicon carbide is much lower. The empirical equations for the fractional emission of generated x-rays, $I(x)/I_o$, for carbon $K\alpha_1$ x-rays and silicon $K\alpha_1$ x-rays in silicon carbide, can be determined by inserting the mass absorption coefficients and silicon carbide density of 3.22 g cm^{-3} . The equation for carbon $K\alpha_1$ x-

rays becomes $I(x)/I_o = \exp(-80693x)$ and the equation for silicon $K\alpha_1$ x-rays in silicon carbide is $I(x)/I_o = \exp(-1212x)$; both equations are plotted in Figure 3.28. This plot shows that carbon $K\alpha_1$ x-rays are heavily absorbed in silicon carbide and the escape of this radiation is improbable at all but the smallest of x-ray generation depths.

Table 3.3. Mass absorption coefficients for $K\alpha_1$ x-rays of carbon and silicon in silicon carbide.

$\mu_{\text{absorber}}^{\text{emitter}}$	$\mu \text{ (cm}^2 \text{ g}^{-1}\text{)}$
$\mu_{\text{SiC}}^{\text{CK}\alpha_1}$	25061
$\mu_{\text{SiC}}^{\text{SiK}\alpha_1}$	377

¹⁰²
calculated from values obtained from Heinrich

Figure 3.28. Depth-dependent fractional emission for $K\alpha_1$ x-rays of silicon and carbon in silicon carbide.

In order to generate x-rays only at small depths, a low electron beam acceleration voltage should be used¹⁰³⁻¹⁰⁵. The effect of low acceleration voltage on the x-ray range is shown in Figure 3.29a. In this figure, the x-ray range in Figure 3.27b is re-plotted with a different scale to emphasize lower acceleration voltage values. Overvoltage is defined as the ratio of the electron beam energy to the characteristic excitation energy, $U = E/E_C$ ¹⁰³. For characteristic x-ray production to occur, the overvoltage must be greater than

unity ($U \geq 1$). Ideal overvoltage depends on the critical excitation energy⁹⁷ and the specimen composition. EPMA operators usually use an acceleration voltage between two and three times of the highest critical ionization energy of the individual elements¹⁰³. Since silicon has a higher critical ionization energy (1.84 keV¹⁰¹) than that of carbon (0.284 keV¹⁰¹), the ideal acceleration voltage for silicon carbide must be at least 3.68 kV. It provides energy of 3.68 keV to each beam electron. As shown in Figure 3.29a, this acceleration voltage results in an x-ray range of 125 nm for silicon in silicon carbide and an x-ray range of 175 nm for carbon in silicon carbide. The fractional emission of carbon and silicon $K\alpha_1$ x-rays in silicon carbide in Figure 3.28 are re-plotted between the x-ray path length range of 0 to 125 nm for silicon and 0 to 175 nm for carbon in Figure 3.29b to demonstrate the effect of lower acceleration voltage on the reduction of carbon $K\alpha_1$ x-ray absorption. For the ideal acceleration voltage of 3.68 keV and the corresponding maximum silicon x-ray path length of 125 nm, silicon $K\alpha_1$ x-rays experience virtually no absorption over the entire electron interaction volume ($0 < x < 125$ nm). Within the carbon x-ray generation region with an x-ray range of 175 nm, about 25% of the carbon $K\alpha_1$ x-rays are able to escape from the deepest depth, and the overall fractional emission of the carbon x-rays is over 50%. Therefore, low voltage microanalysis¹⁰³⁻¹⁰⁵ reduces the disparity in degree of absorption of carbon and silicon x-rays, and it allows more accurate quantitative elemental analysis during EPMA.

Figure 3.29. (a) Relations between x-ray range and electron acceleration voltage of silicon and carbon in silicon carbide. (b) Relations between fractional x-ray emission and x-ray path length of silicon and carbon in silicon carbide.

Low voltage microanalysis on our silicon carbide products and the references was accomplished by using an acceleration voltage of 5 kV to achieve a silicon overvoltage slightly above 2. A probe current of 3×10^{-9} A was used to generate x-ray signals of sufficient intensity for detection. A working distance of 20 mm was used to reduce x-ray absorption by maximizing take-off angle⁹⁹. To reduce surface contamination, specimens were ultrasonicated in ethanol for 1 minute, outgassed overnight under vacuum in a sealed glass tube at temperatures from 100 to 350°C, and treated with reactive ion etching (RIE) in oxygen for 20 minutes. Samples were repeatedly measured and the values were averaged to increase accuracy. A sample x-ray spectrum collected from EPMA of silicon carbide is shown in Figure 3.30.

Figure 3.30. Sample x-ray spectrum recorded by the energy dispersive spectrometer inside of a SEM during EPMA of silicon carbide.

The results of low voltage microanalysis of the 60:40 reaction products and the silicon carbide reference materials are given in Table 3.4. Unexpectedly, the low voltage EPMA measurements showed that all the silicon carbide references had carbon-rich compositions, and their values are very close to those of our products. This is very abnormal since the reference materials are highly pure silicon carbides.

Table 3.4. Chemical compositions of SiC reaction products and SiC reference materials collected by low voltage microanalysis.

	reaction time	C at%	
		measured	calibrated
SiC reaction products	10 min	57.0 $\pm$ 0.7	50.7
	15 min	54.7 $\pm$ 0.5	48.5
	30 min	56.8 $\pm$ 0.5	50.6
	60 min	56.5 $\pm$ 2.2	50.3
	120 min	56.3 $\pm$ 1.3	50.1
	300 min	58.8 $\pm$ 0.3	52.6
SiC references	reference	C at%	
	NIST SRM 112	57.4 $\pm$ 4.6	51.2
	C&C gem	56.2 $\pm$ 0.9	49.9
	TDII wafer	56.3 $\pm$ 0.3	50.1

The silicon carbide gem and wafer should be nearly stoichiometric with a silicon to carbon ratio of 50:50, and the NIST standard may be only slightly carbon-rich. The large deviation of the data may be either due to carbon contamination in the specimen

chamber or the fact that the program used for analysis needs to be further calibrated for silicon carbide. The EPMA carbon concentrations of the gem and the wafer were averaged (56.25 at%) as the standard to calibrate the experimental results, and the calibrated values are listed in Table 3.4. Among these corrected values, only the 300 minute product shows a significant carbon-rich composition. This supports our previous assumption that carbon diffusion can increase carbon content in silicon carbide. Since carbon diffusion is a very slow process, a significant level of carbon concentration can only be achieved over a long period of time.

Carbon contamination has been observed by others during electron imaging^{106,107}. To examine its occurrence in our study, x-ray spectra were collected twice at each of four locations of the 60 minute reaction product and the results are plotted in Figure 3.31. This bar graph shows that for each location, the measured carbon concentration from the second probe is always higher than the first, thus indicating that carbon contamination is present and increases with analysis time. SEM images recorded on areas after electron beam scanning display distinctive features that resemble the paths of the electron beam as shown in Figure 3.32. We believe these features are carbon films deposited on the specimen surface at the electron beam interaction area.

Figure 3.31. Carbon concentrations measured twice at four separate locations on the 60:40 SiC.

Figure 3.32. SEM images showing deposited carbon films at the electron beam interaction area of the specimen surface.

Deposition of carbon films at the electron beam interaction area of the specimen surface is a result of hydrocarbon contamination originated from the specimen, stage, and/or instrument chamber. These hydrocarbons can be oil molecules from the vacuum pump^{108,109} or other organic contaminants in the specimen chamber. Hydrocarbon molecules have been observed to diffuse along the surface of the specimen towards the electron probe¹⁰⁷. Bombardment by the electron beam decomposes these molecules^{103,110}, resulting in carbon-rich deposits on the specimen surface in the area of beam

interaction¹⁰⁷. The amount of deposition depends on the duration that the beam is focused at a particular location^{106,107}.

For most EPMA studies, carbon contamination is not a significant problem due to short analysis times. Carbon signal is often neglected for compounds whose formulas do not contain carbon. However, this cannot be applied to analysis of silicon carbide; carbon contamination needs to be accounted for and corrected with high purity silicon carbide references.

Auger electron spectroscopy (AES)

An Auger electron spectrometer (AES) (Perkin Elmer PHI 610, Waltham, MA, USA) was used to further analyze the reaction product composition. AES is a surface analysis technique capable of quantitative determination of chemical composition within a depth of less than 20 atomic layers¹¹¹⁻¹¹³. It uses a high energy electron beam to excite characteristic Auger electrons within the specimen for detection. AES was performed on the 60:40 product with a reaction time of 30 minutes at 1800°C. Initial AES indicated an oxygen-rich surface. High-voltage argon sputtering within the UHV AES specimen chamber was performed until the oxygen peak was eliminated. This sputtering process removes organic contamination on the specimen. In addition, UHV is maintained by an oil-free cryogenic pump. Therefore, AES can be free of carbon contamination.

Figure 3.33a and b are two secondary electron images of the sample surface with isolated silicon carbide regions selected for AES. The data collected from these two regions are given in Table 3.5. They indicate a nearly stoichiometric silicon carbide concentration that is only slightly carbon-rich and almost identical to the EPMA data corrected for carbon contamination.

Figure 3.33. Secondary electron images of the 60:40 sample surface with isolated SiC regions selected for Auger electron spectroscopy. Scale bars measure 100 µm.

Table 3.5. Chemical composition of the SiC regions in the 60:40 SiC measured by Auger electron spectroscopy.

Region	C at%	Si at%	O at%
a	50.4	49.4	0.2
b	51.0	48.7	0.4

3.5 Description of steps involved in the formation of silicon carbide

Based on literature data and our analysis of the liquid silicon-carbon reaction products, we were able to produce a schematic illustration of the major events involved in this reaction in Figure 3.34. In the initial stage (Figure 3.34a), liquid silicon makes contact with carbon by rapidly filling the micron-scale carbon pores. In the second stage (Figure 3.34b), the liquid silicon rapidly dissolves the carbon at the interface creating a composition gradient with carbon saturation occurring at the interface. The thickness of the interfacial reaction region is very small. In the third stage (Figure 3.34c), heterogeneous silicon carbide crystallization occurs at the interface. The composition of

Figure 3.34. Schematic of the reaction between liquid silicon and carbon. (a) Initial contact between liquid silicon and solid carbon, (b) dissolution of carbon by liquid silicon forming an interfacial reaction region, (c) heterogeneous silicon carbide nucleation on the carbon, and (d) formation of a continuous silicon carbide layer followed by carbon atomic diffusion through silicon carbide.

the initially formed small silicon carbide crystals may be non-stoichiometric due to Gibbs-Thomson effects¹¹⁴ and/or supersaturation at the interface. In the fourth stage (Figure 3.34d), nucleation and growth of silicon carbide proceeds until a continuous layer is formed. At this stage, liquid silicon is isolated from carbon, thus terminating the direct-contact reaction. Additional reaction may occur through the diffusion of carbon atoms across the silicon carbide layer; however, such diffusion driven reaction is a very slow process and can only make very small contributions to the overall growth^{93,94}. Other possible events may include homogeneous silicon carbide nucleation, coarsening, and variations in local temperatures.

3.6 Summary

To reveal the mechanisms involved in the formation of the silicon carbide materials, the kinetics of the liquid silicon-carbon reaction were examined, and the thermophysical properties and chemical compositions of the silicon carbide products were analyzed.

Reaction kinetics were studied with optical imaging and digital image analysis of the silicon carbide cross sections. The evolution of SiC, Si, C, and porosity in the 60:40 product over reaction times of 0 to 300 minutes were examined to describe the time-dependent reaction process. The initial stages (0 to 15 minutes) of the reaction include simultaneous rapid liquid silicon infiltration of the carbon preform, dissolution of carbon, and formation of silicon carbide at the liquid-solid interfacial regions. These initial stages culminate in the formation of a continuous silicon carbide layer of about 10 μm at every liquid-solid interface. Further reaction can only be achieved by carbon diffusion through

this layer. Evidence of carbon diffusion was observed as a slight increase in silicon carbide volume fraction and a corresponding decrease in carbon volume fraction between the reaction time of 120 and 300 minutes. The reaction is essentially complete after a reaction time of about 120 minutes. Longer reaction times should be avoided because prolonged heating allows the capillary flow of excess silicon into the structure to cause cracking of the silicon carbide.

Thermal properties of the 60:40 silicon carbide reaction product were analyzed and compared with those of other silicon carbides. The temperature-dependent thermal conductivity of our silicon carbide is very high, particularly at heat exchanger operation temperatures of 800 to 1000°C. These thermal conductivity values are double those of silicon carbides prepared by conventional solid-state processing techniques. The high thermal conductivity of our material is due to the percolated character of the silicon carbide phase and the absence of thermally insulating impurities and porosity.

Chemical compositions were examined using electron probe microanalysis (EPMA). Such analysis of silicon carbide deserves special consideration due to the high level of absorption of carbon $K\alpha_1$ x-rays in silicon carbide. To minimize these detrimental absorption effects, electron beam-specimen interactions were studied, resulting in identification of 3.68 kV as the optimum electron microprobe acceleration voltage. EPMA measurements recorded under this condition indicated a carbon-rich silicon carbide phase. The strongly nonstoichiometric composition was determined to be a result of carbon contamination due to backstreaming of diffusion pump oil. High purity silicon carbide reference materials were used to improve measurement accuracy. Results were calibrated with the reference materials and the near-stoichiometric composition of the

silicon carbide phase in our silicon carbide was obtained. Auger electron spectroscopy (AES) was also used to measure chemical composition, and its results agree well with the corrected EPMA data.

3.7 References

1. N. Eustathopoulos, Dynamics of wetting in reactive metal ceramic systems, *Acta Materialia*, 46, 2319-27 (1998).
2. O. Dezellus, F. Hodaj and N. Eustathopoulos. Chemical reaction-limited spreading: the triple line velocity versus contact angle relation, *Acta Materialia*, 50, 4741-53 (2002).
3. O. Dezellus, F. Hodaj and N. Eustathopoulos. Progress in modelling of chemical-reaction limited wetting, *Journal of the European Ceramic Society*, 23, 2797-803 (2003).
4. O. Dezellus, S. Jacques, F. Hodaj and N. Eustathopoulos. Wetting and infiltration of carbon by liquid silicon, *J. Mater. Sci.*, 40, 2307-11 (2005).
5. G. Kumar and K.N. Prabhu. Review of non-reactive and reactive wetting of liquids on surfaces, *Adv. Colloid Interface Sci.*, 133, 61-89 (2007).
6. Y.M. Chiang, R.P. Messner, C.D. Terwilliger and D.R. Behrendt. Reaction-Formed Silicon-Carbide, *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing*, 144, 63-74 (1991).
7. J. Narayan, R. Raghunathan, R. Chowdhury and K. Jagannadham. Mechanism of Combustion Synthesis of Silicon-Carbide, *J. Appl. Phys.*, 75, 7252-7 (1994).
8. H. Zhou and R.N. Singh. Kinetics Model for the Growth of Silicon-Carbide by the Reaction of Liquid Silicon with Carbon, *J Am Ceram Soc*, 78, 2456-62 (1995).
9. A. Favre, H. Fuzellier and J. Suptil. An original way to investigate the siliconizing of carbon materials, *Ceram. Int.*, 29, 235-43 (2003).
10. Y. Sato, Y. Kameda, T. Nagasawa, et al. Viscosity of molten silicon and the factors affecting measurement, *J. Cryst. Growth*, 249, 404-15 (2003).
11. R.E. Chinn, Grinding and Polishing, pp. 35 in *Ceramography: preparation and analysis of ceramic microstructures*. ASM International, Materials Park, OH, 2002.
12. P. Sangsuwan, J.A. Orejas, J.E. Gatica, S.N. Tewari and M. Singh. Reaction-bonded silicon carbide by reactive infiltration, *Ind Eng Chem Res*, 40, 5191-8 (2001).
13. P. Sangsuwan, S.N. Tewari, J.E. Gatica, M. Singh and R. Dickerson. Reactive infiltration of silicon melt through microporous amorphous carbon preforms, *Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science*, 30, 933-44 (1999).
14. E.S. Nelson and P. Colella. Parametric Study of Reactive Melt Infiltration," *NASA TM-2000-209802*, (2000).
15. F.H. Gern and R. Kochendorfer. Liquid silicon infiltration: Description of infiltration dynamics and silicon carbide formation, *Composites Part A-Applied Science and Manufacturing*, 28, 355-64 (1997).

16. E.O. Einset, Analysis of reactive melt infiltration in the processing of ceramics and ceramic composites, *Chemical Engineering Science*, 53, 1027-39 (1998).
17. D.R. Behrendt and M. Singh. Effect of carbon preform pore volume and infiltrants on the composition of reaction-formed silicon carbide materials , *J. Mater. Synth. Process.*, 2, 117-123 (1994).
18. ImageJ, Computer Program. W. S. Rasband. (1997-2006) Bethesda, MD.
19. W. S. Rasband. ImageJ: Documentation. <http://rsb.info.nih.gov/ij/docs/index.html> .
20. K. R. Spring, J. C. Russ and M. W. Davidson. Online Microscopy Resource Center: Basic Concepts in Digital Image Processing. <http://www.olympusmicro.com/primer/digitalimaging/imageprocessingintro.html> .
21. R. Fisher, S. Perkins, A. Walker, et al. Hypermedia Image Processing Reference (HIPR). www.dai.ed.ac.uk/HIPR2/ .
22. R.E. Chinn, Quantitative Ceramography, pp. 145 in *Ceramography: preparation and analysis of ceramic microstructures*. ASM International, Materials Park, OH, 2002.
23. J.C. Margiotta, D. Zhang, D.C. Nagle and C.E. Feeser. Formation of dense silicon carbide by liquid silicon infiltration of carbon with engineered structure, *J. Mater. Res.*, 23, 1237-48 (2008).
24. H. Zhou and R.N. Singh. Kinetics Model for the Growth of Silicon-Carbide by the Reaction of Liquid Silicon with Carbon, *J Am Ceram Soc*, 78, 2456-62 (1995).
25. A. Favre, H. Fuzellier and J. Suptil. An original way to investigate the siliconizing of carbon materials, *Ceram. Int.*, 29, 235-43 (2003).
26. C.E. Byrne and D.C. Nagle. Cellulose derived composites - A new method for materials processing, *Materials Research Innovations*, 1, 137-44 (1997).
27. C.E. Byrne and D.C. Nagle. Carbonized wood monoliths - Characterization, *Carbon*, 35, 267-73 (1997).
28. C.E. Byrne and D.C. Nagle. Carbonization of wood for advanced materials applications, *Carbon*, 35, 259-66 (1997).
29. C. E. Byrne. Polymer, ceramic and carbon composites derived from wood. PhD dissertation. (1995) Johns Hopkins University, Baltimore, MD.
30. A. K. Kercher. Processing and characterization of monolithic carbon structures based on wood fiberboards. PhD dissertation. (2002) Johns Hopkins University, Baltimore, MD.
31. A.K. Kercher and D.C. Nagle. Monolithic activated carbon sheets from carbonized medium-density fiberboard, *Carbon*, 41, 3-13 (2003).
32. D.R. Behrendt and M. Singh. Effect of carbon preform pore volume and infiltrants on the composition of reaction-formed silicon carbide materials , *J. Mater. Synth. Process.*, 2, 117-123 (1994).
33. Y.M. Chiang, R.P. Messner, C.D. Terwilliger and D.R. Behrendt. Reaction-Formed Silicon-Carbide, *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing*, 144, 63-74 (1991).
34. M. Singh and D.R. Behrendt. Microstructure and Mechanical-Properties of Reaction-Formed Silicon-Carbide (Rfsc) Ceramics, *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing*, 187, 183-7 (1994).

35. M. Singh and D.R. Behrendt. Reactive Melt Infiltration of Silicon-Molybdenum Alloys into Microporous Carbon Preforms, *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing*, 194, 193-200 (1995).
36. M. Singh and T.A. Leonhardt. Microstructural characterization of reaction-formed silicon carbide ceramics, *Mater Charact*, 35, 221-8 (1995).
37. A. Munoz, J. Martinez-Fernandez, A. Dominguez-Rodriguez and M. Singh. High-temperature compressive strength of reaction-formed silicon carbide (RFSC) ceramics, *Journal of the European Ceramic Society*, 18, 65-8 (1998).
38. M. Singh and S.C. Farmer. Morphological characterization of microporous carbon materials, *J. Mater. Sci. Lett.*, 16, 946-9 (1997).
39. P. Sangsuwan, S.N. Tewari, J.E. Gatica, M. Singh and R. Dickerson. Reactive infiltration of silicon melt through microporous amorphous carbon preforms, *Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science*, 30, 933-44 (1999).
40. P. Sangsuwan, J.A. Orejas, J.E. Gatica, S.N. Tewari and M. Singh. Reaction-bonded silicon carbide by reactive infiltration, *Ind Eng Chem Res*, 40, 5191-8 (2001).
41. Y. Wang, S. Tan and D. Jiang. The fabrication of reaction-formed silicon carbide with controlled microstructure by infiltrating a pure carbon preform with molten Si, *Ceramics International*, 30, 435-9 (2004).
42. Y.X. Wang, S.H. Tan, D.L. Jiang and X.Y. Zhang. Preparation of porous carbon derived from mixtures of furfuryl resin and glycol with controlled pore size distribution, *Carbon*, 41, 2065-72 (2003).
43. Y.X. Wang, S.H. Tan and D.L. Jiang. The effect of porous carbon preform and the infiltration process on the properties of reaction-formed SiC, *Carbon*, 42, 1833-9 (2004).
44. T. Ota, M. Takahashi, T. Hibi, et al. Biomimetic process for producing SiC "wood", *J Am Ceram Soc*, 78, 3409-11 (1995).
45. P. Greil, T. Lifka and A. Kaindl. Biomimetic cellular silicon carbide ceramics from wood: I. Processing and microstructure, *Journal of the European Ceramic Society*, 18, 1961-73 (1998).
46. H. Sieber, C. Hoffmann, A. Kaindl and P. Greil. Biomimetic cellular ceramics, *Advanced Engineering Materials*, 2, 105-9 (2000).
47. C. Zollfrank and H. Sieber. Microstructure evolution and reaction mechanism of biomimetic SiSiC ceramics, *J Am Ceram Soc*, 88, 51-8 (2005).
48. K.E. Pappacena, K.T. Faber, H. Wang and W.D. Porter. Thermal conductivity of porous silicon carbide derived from wood precursors, *J Am Ceram Soc*, 90, 2855-62 (2007).
49. N. Eustathopoulos, Dynamics of wetting in reactive metal ceramic systems, *Acta Materialia*, 46, 2319-27 (1998).
50. O. Dezellus, F. Hodaj and N. Eustathopoulos. Chemical reaction-limited spreading: the triple line velocity versus contact angle relation, *Acta Materialia*, 50, 4741-53 (2002).
51. O. Dezellus, F. Hodaj and N. Eustathopoulos. Progress in modelling of chemical-reaction limited wetting, *Journal of the European Ceramic Society*, 23, 2797-803 (2003).

52. O. Dezellus, S. Jacques, F. Hodaj and N. Eustathopoulos. Wetting and infiltration of carbon by liquid silicon, *J. Mater. Sci.*, 40, 2307-11 (2005).
53. G. Kumar and K.N. Prabhu. Review of non-reactive and reactive wetting of liquids on surfaces, *Adv. Colloid Interface Sci.*, 133, 61-89 (2007).
54. E.O. Einset, Analysis of Reactive Melt Infiltration: I. Derivation of the Governing Equations," 96CRD028, April 1996 Class 1, (1996).
55. E.O. Einset, Analysis of reactive melt infiltration in the processing of ceramics and ceramic composites, *Chemical Engineering Science*, 53, 1027-39 (1998).
56. F.H. Gern and R. Kochendorfer. Liquid silicon infiltration: Description of infiltration dynamics and silicon carbide formation, *Composites Part A-Applied Science and Manufacturing*, 28, 355-64 (1997).
57. R.P. Messner and Y.M. Chiang. Liquid-Phase Reaction-Bonding of Silicon-Carbide using Alloyed Silicon Molybdenum Melts, *J Am Ceram Soc*, 73, 1193-200 (1990).
58. E.S. Nelson and P. Colella. Parametric Study of Reactive Melt Infiltration," NASA TM-2000-209802, (2000).
59. W.J. Parker, R.J. Jenkins, G.L. Abbott and C.P. Butler. Flash Method of Determining Thermal Diffusivity, Heat Capacity, and Thermal Conductivity, *J. Appl. Phys.*, 32, 1679,& (1961).
60. M.A. Thermitus and P.S. Gaal. Specific heat measurements in a multisample environment with the laser flash method," *Proceedings of the Joint twenty-fourth and twelfth International Thermal Conductivity and Thermal Expansion Conferences*, 219-28 (1997).
61. P.S. Gaal, M.A. Thermitus and D.E. Stroe. Thermal conductivity measurements using the flash method, *Journal of Thermal Analysis and Calorimetry*, 78, 185-9 (2004).
62. H. Tawil, L.D. Bentsen, S. Baskaran and D.P.H. Hasselman. Thermal-Diffusivity of Chemically Vapor-Deposited Silicon-Carbide Reinforced with Silicon-Carbide Or Carbon-Fibers, *J. Mater. Sci.*, 20, 3201-12 (1985).
63. J. Bodzenta, K. Golaszewska, E. Kaminska, et al. Photothermal measurements in determination of the thermal diffusivity of SiC, *European Physical Journal-Special Topics*, 153, 79-82 (2008).
64. B.K. Jang and Y. Sakka. Thermophysical properties of porous SiC ceramics fabricated by pressureless sintering, *Science and Technology of Advanced Materials*, 8, 655-9 (2007).
65. S.G. Muller, R. Eckstein, J. Fricke, et al. Experimental and theoretical analysis of the high temperature thermal conductivity of monocrystalline SiC, *Silicon Carbide, Iii-Nitrides and Related Materials*, Pts 1 and 2, 264-2, 623-6 (1998).
66. Anonymous Specific heat capacity - Wikipedia, the free encyclopedia. http://en.wikipedia.org/wiki/Specific_heat . accessed 2008, Aug 16, 2008.
67. H.O. Pierson, Characteristics and Properties of Silicon Carbide and Boron Carbide, pp. 137-55 in *Handbook of Refractory Carbides and Nitride: Properties, Characteristics, Processing and Applications*. Noyes Publications, Westwood, NJ, 1996.
68. J.W. Klett, A.D. McMillan, N.C. Gallego and C.A. Walls. The role of structure on the thermal properties of graphitic foams, *J. Mater. Sci.*, 39, 3659-76 (2004).

69. Y. Zhou, K. Hirao, K. Watari, Y. Yamauchi and S. Kanzaki. Thermal conductivity of silicon carbide densified with rare-earth oxide additives, *Journal of the European Ceramic Society*, 24, 265-70 (2004).
70. G.A. Slack, Nonmetallic crystals with high thermal conductivity, *Journal of Physics and Chemistry of Solids*, 34, 321-35 (1973).
71. M.R. Null, W.W. Lozier and A.W. Moore. Thermal diffusivity and thermal conductivity of pyrolytic graphite from 300 to 2700° K, *Carbon*, 11, 81-7 (1973).
72. G.A. Slack, Thermal Conductivity of Pure + Impure Silicon Silicon Carbide + Diamond, *J. Appl. Phys.*, 35, 3460,& (1964).
73. G.A. Slack and Austerma.Sb. Thermal Conductivity of Beo Single Crystals, *J. Appl. Phys.*, 42, 4713,& (1971).
74. C.J. Glassbrenner and G.A. Slack. Thermal Conductivity of Silicon + Germanium from 3 Degrees K to Melting Point, *Physical Review A-General Physics*, 134, 1058,& (1964).
75. Y.G. Yoon, R. Car, D.J. Srolovitz and S. Scandolo. Thermal conductivity of crystalline quartz from classical simulations, *Physical Review B*, 70, 012302 (2004).
76. P.H. Klein and W.J. Croft. Thermal Conductivity Diffusivity and Expansion of Y2o3 Y3a15o12 and Laf in Range 77 Degrees-300 Degrees K, *J. Appl. Phys.*, 38, 1603,& (1967).
77. V.Y. Chekhovskoi, G.I. Stavrovskii, A.V. Ivanov, A.I. Pustil'nik and T.S. Sedykh. Thermal conductivity of yttrium oxide, *Refract. & Ind. Cer.*, 10, 323 (1969).
78. A. Sugawara, Precise Determination of Thermal Conductivity of Pure Fused Quartz, *J. Appl. Phys.*, 39, 5994,& (1968).
79. L. Fornarini, J.C. Conde, S.Chiusi, P. Gonzalez, B. Leon and S. Martelli. Analysis of excimer laser annealing of amorphous SiGe on La2O3//Si structures, *Applied Surface Science*, 253, 7957-63 (2007).
80. K. Watari, H. Nakano, K. Sato, et al. Effect of grain boundaries on thermal conductivity of silicon carbide ceramic at 5 to 1300 K, *J Am Ceram Soc*, 86, 1812-4 (2003).
81. L. Richeldi, R. Sorrentino and C. Saltini. HLA-DPB1 Glutamate 69: A Genetic Marker of Beryllium Disease, *Science*, 262, 242-4 (1993).
82. Y. R. Rhim. Crystalline cellulose carbons. Ph.D. dissertation. (to be published in 2009) The Johns Hopkins University, Baltimore, MD, USA.
83. J. Goldstein, Quantitative X-Ray Analysis: The Basics, pp. 391-449 in *Scanning electron microscopy and x-ray microanalysis*. Kluwer Academic/Plenum Publishers, New York, 2003.
84. J. H. Wittke. GLG 510 - Course Overview - Electron Microprobe Techniques. <http://www4.nau.edu/microanalysis/Microprobe/Course%20Overview.html> . accessed 2008, Aug 16, 2008.
85. J. Goldstein, Standardless Analysis, pp. 427 in *Scanning electron microscopy and x-ray microanalysis*. Kluwer Academic/Plenum Publishers, New York, 2003.
86. A.I. Gusev, A.A. Rempel and A.J. Magerl. Disorder and order in strongly nonstoichiometric compounds :transition metal carbides, nitrides, and oxides; pp. 607. Springer, Berlin ;New York, 2001.

87. H.J. Seifert and F. Aldinger. Phase equilibria in the Si-B-C-N system, pp. 1 in High performance non-oxide ceramic. Edited by M. Jansen. Springer, Berlin ;New York, 2002.
88. H.O. Pierson, Covalent Carbides: Structure and Composition, pp. 118 in Handbook of Refractory Carbides and Nitrides. Noyes Publications, Westwood, NJ, 1996.
89. S.M. Bleay, A.R. Chapman, G. Love and V.D. Scott. Electron-Probe Microanalysis of Nicalon Fibers, J. Mater. Sci., 27, 5389-96 (1992).
90. M. Tabellout, A. Kassiba, S. Tkaczyk, L. Laskowski and J. Swiatek. Dielectric and EPR investigations of stoichiometry and interface effects in silicon carbide nanoparticles, Journal of Physics-Condensed Matter, 18, 1143-55 (2006).
91. A. Fissel, B. Schröter, J. Kräußlich and W. Richter. Preparation of SiC films by solid state source evaporation, Thin Solid Films, 258, 64-6 (1995).
92. L.F. Pochet, P. Howard and S. Safaie. Practical aspects of deposition of CVD SiC and boron silicon carbide onto high temperature composites, Surface and Coatings Technology, 86-87, 135-41 (1996).
93. M.H. Hon and R.F. Davis. Self-Diffusion of C-14 in Polycrystalline Beta-Sic, J. Mater. Sci., 14, 2411-21 (1979).
94. M.H. Hon, R.F. Davis and D.E. Newbury. Self-Diffusion of Si-30 in Polycrystalline Beta-Sic, J. Mater. Sci., 15, 2073-80 (1980).
95. S.G. Müller, R.C. Glass, H.M. Hobgood, et al. The status of SiC bulk growth from an industrial point of view, Journal of Crystal Growth, 211, 325-32 (2000).
96. L.J. Briggs, U.S. Department of Commerce, National Bureau of Standards Certificate of Analysis of Standard Sample 112 SILICON CARBIDE," (1937).
97. B.D. Cullity, Properties of X-rays, pp. 3-31 in Elements of x-ray diffraction. Addison-Wesley Pub. Co., Reading, Mass., 1978.
98. J. Goldstein, Qualitative X-Ray Analysis, pp. 355-90 in Scanning electron microscopy and x-ray microanalysis. Kluwer Academic/Plenum Publishers, New York, 2003.
99. J. Goldstein, Generation of X-Rays in the SEM Specimen, pp. 271-96 in Scanning electron microscopy and x-ray microanalysis. Kluwer Academic/Plenum Publishers, New York, 2003.
100. C.A. Andersen and M.F. Hasler. X-ray optics and microanalysis," 310 (1966).
101. J.A. Bearden, X-Ray Wavelengths, Reviews of Modern Physics, 39, 78,& (1967).
102. K.F.J. Heinrich, Mass absorption coefficients for electron probe microanalysis," 67-119 (1986).
103. J. Goldstein, Special Topics in Electron Beam X-Ray Microanalysis, pp. 453-535 in Scanning electron microscopy and x-ray microanalysis. Kluwer Academic/Plenum Publishers, New York, 2003.
104. E.D. Boyes, On low voltage scanning electron microscopy and chemical microanalysis, Microscopy and Microanalysis, 6, 307-16 (2000).
105. D.E. Newbury, Barriers to quantitative electron probe x-ray microanalysis for low voltage scanning electron microscopy, Journal of Research of the National Institute of Standards and Technology, 107, 605-19 (2002).
106. N.J. Zaluzec, Plasma Processing of Specimens for Electron Microscopy & Microanalysis, pp. 343-51 in Transmission Electron Microscopy 1: Concepts and

- Techniques. Edited by X.F. Zhang and Z. Zhang. Springer-Verlag Berlin Heidelberg New York, 2001.
107. S.P. Roberts, S.D. Walck, J.T. Grant and N.J. Zaluzec. Application of Reactive Gas Plasma Cleaning in Mitigating Contamination of Specimens during Transmission and Analytical Electron Microscopy," (1997).
 108. M.H. Hablanian, Vapor Jet (Diffusion) Pumps, pp. 207-68 in Vol. 111, High-vacuum technology: a practical guide. Marcel Dekker, New York, 1997.
 109. M.H. Hablanian, Turbomolecular Pumps, pp. 269-352 in Vol. 111, High-vacuum technology: a practical guide. Marcel Dekker, New York, 1997.
 110. JEOL Ltd. A Guide to Scanning Microscope Observation. <https://imf.ucmerced.edu/downloads/semguide.pdf> . accessed 2008, Aug 16, 2008.
 111. Anonymous Auger electron spectroscopy - Wikipedia, the free encyclopedia. http://en.wikipedia.org/wiki/Auger_electron_spectroscopy . accessed 2008, Aug 16, 2008.
 112. M. Prutton and M.M. El Gomati. Scanning Auger electron microscopy; pp. 368. Wiley, Chichester, England ;Hoboken, NJ, 2006.
 113. J. Venables, Quantification of Auger spectra, pp. 88-95 in Introduction to surface and thin film processes. Cambridge University Press, New York, 2000.
 114. D.A. Porter and K.E. Easterling. Thermodynamics and Phase Diagrams, pp. 1-59 in Phase transformations in metals and alloys. Chapman & Hall, London ;New York, 1992.

CHAPTER 4. CONCLUSIONS

The focus of this research has been on engineering carbon preforms with controlled chemical reactivity and porosity to allow the formation of net shape silicon carbide materials using liquid silicon infiltration (LSI). This was accomplished by using mixtures of phenolic resin and crystalline cellulose. These two materials were chosen due to their high purity, well-known molecular structure and ready availability. In addition, phenolic resin is widely used as a matrix material for carbon/carbon composites and cellulose has been the subject of many carbonization studies. Using mixtures of these materials, we have shown that carbon preforms can be made with a wide range of bulk densities, micron-scale porosities and reactivity. We then demonstrated that LSI techniques can be used to convert these preforms into silicon carbide with exceptional thermal properties that make them prime candidates for high temperature heat exchanger materials for the next generation of nuclear reactors. It is recognized that the procedures used to develop these materials can be used to produce different silicon carbide structures by using mixtures of other readily available hydrocarbon materials to make engineered carbon preforms.

When carbonized, cellulose yields a carbon with low bulk density, high porosity and high reactivity; while phenolic resin yields a carbon with high bulk density, nearly no micron-scale porosity and low reactivity. Several cellulose and phenolic resin mixtures were carbonized at 1000°C. The carbon preforms produced have microstructures varying from fully dense with a bulk density of 1.4 g cm^{-3} to highly porous with pore diameters of approximately $1 \text{ }\mu\text{m}$ and with a bulk density of 0.7 g cm^{-3} . The reactivity of carbon toward liquid silicon is determined by the atomic structure of the carbon. High resolution

transmission electron microscopy (HRTEM), nitrogen gas adsorption and helium gas pycnometry were used to study these atomic structures. The atomic ordering and angstrom-scale pore character were shown to be very different in cellulose carbon than in phenolic resin carbon. Cellulose carbon has a highly amorphous sp^2 -bonded structure with a very high degree of angstrom-scale porosity, and it is highly reactive with liquid silicon. Phenolic resin carbon is also highly disordered, but it has a much lower degree of angstrom-scale porosity and exhibits localized short-range sp^2 -bonded graphene structures and nano-scale volumes of highly crystalline sp^3 -bonded diamond structures. These differences in atomic structure allowed the reactivity of the preform to be controlled.

LSI reactions were performed at temperatures between 1414 and 1900°C and under argon pressures of 1550, 760, and 0.5 Torr for time periods ranging from 10 to 300 minutes. Examination of the results indicated that the ideal carbon preform was produced from the cellulose and phenolic resin mixture of 60:40 mass ratio. It has a bulk density of 0.8 g cm⁻³, an actual density of 2.19 g cm⁻³, median pore diameter of 1.5 μm, and a Langmuir total specific surface area of 645 m² g⁻¹. The ideal reaction conditions were identified as 1800°C, 0.5 Torr, and 120 minutes. The reaction product has a bulk density of 2.96 g cm⁻³, greater than 91% of that of pure β-SiC, with a SiC volume fraction of about 82%.

The temperature-dependent thermal conductivity of our silicon carbide was determined by the laser flash method to be nearly equivalent to that of electronic grade high-purity silicon carbide, and is much higher than those of silicon carbides prepared by conventional solid-state techniques. The low thermal conductivity of the other silicon

carbides is believed to be due to phonon scattering at the grain boundaries of these materials where the oxide sintering aids are concentrated. The thermal conductivity of our material at the operating temperatures of next generation nuclear reactor heat exchangers (about 800 to 1000°C) is very high, ranging from about 60 to 80 W/mK.

The chemical kinetics of the LSI and silicon carbide formation process were studied with optical microscopy and quantitative digital image analysis. This analysis showed that the overall reaction can be divided into six stages: (1) rapid liquid silicon infiltration of the carbon preform, (2) rapid carbon dissolution in liquid silicon, (3) rapid silicon carbide formation through crystallization, (4) complete formation of a continuous silicon carbide layer at all silicon-carbon interfaces, (5) atomic carbon diffusion through this layer and reaction with liquid silicon, and (6) formation of silicon filled silicon carbide cracks. Previous studies involving the LSI process postulate that cracking of the silicon carbide materials is due to CTE stresses developed during cooling. This study shows that cracks are generated by over-reacting. These cracks are caused by diffusion of carbon atoms from the pure carbon phase through silicon carbide to pure silicon. When carbon atoms reach the silicon, silicon carbide is formed. The volume expansion during silicon carbide formation at sharp crack tips generates stress cracks that eventually form extended crack networks. Removing excess silicon can reduce the effects of this detrimental cracking process.

Chemical compositions of our silicon carbide materials were studied using electron probe microanalysis (EPMA) and Auger electron spectroscopy (AES). The optimum EPMA electron beam acceleration voltage was determined to be 3.68 kV by theoretically analyzing the interactions between silicon carbide and an electron beam.

Our EPMA and AES measurements suggest that the silicon carbide phase in our materials is slightly carbon-rich. Carbon contamination due to backstreaming of diffusion pump oil was a possible source of error during EPMA and this error was corrected by using high purity silicon carbide standards.