

REACTION BONDED SILICON CARBIDE: SFF, PROCESS REFINEMENT AND APPLICATIONS

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Abstract

Reaction bonded silicon carbide (RBSiC) has a wide variety of industrial applications and a manufacturing process based on Selective Laser Sintering (SLS) has been demonstrated in previous research at the University of Texas. That study was directed toward semiconductor manufacturing applications and was based on prior indirect SLS methods. Several key research questions were addressed for three main manufacturing phases: preform SLS, binder burnout and reactive infiltration. The current research is focused on development of material systems and manufacturing capability and is directed toward a broader set of potential applications. Preform formation utilizes SiC powder of an appropriate average particle size mixed with a multi-component binder. The preform or green part is then placed in a vacuum furnace to carbonize the binder. The details of the binder chemistry must support accurate SFF shapes and acceptable surface roughness, a strong green part and maintenance of the part shape during the first furnace operation. Finally, the physics and chemistry of the infiltration process, based on the microstructure of the initial green preform, determine the viability of the manufacturing process and the characteristics of the final composite material.

The functionality of metal, polymer and ceramic matrix composites can support the growing SFF industry desire to move beyond functional prototyping and into manufacturing arenas. This project is being explored for more general application to matrix composite materials, especially highly functional systems tailored specifically for SLS. The goal is to establish the governing principles of binder function, carbonization and infiltration as well as to understand the interdependence of these phases in terms of manufacturing application. With this understanding new applications and special SLS composites can support the development of new products and a greater SFF manufacturing presence.

This paper provides an introduction to the material, a look at basic rapid manufacturing trends, an overview of the previous work, a review of relevant RBSiC material science issues, and an outline of the current study.

Why Silicon Carbide?

Material Properties

SiC is an extremely hard, heat resistant, abrasion resistant, chemical resistant, and thermally conductive material. However, it is very difficult to manufacture. Fully dense, sintered varieties of SiC can cost \$400 per cubic inch just for raw material. The powdered variety, however, may be purchased by the boxcar for around \$2.00/pound. Discovered over a century ago, SiC has been the subject of extensive materials research for many decades [Taylor and Laidler]. Over 140 microstructural variations of the material have been identified, each

associated with certain formation parameters and subtle property differences [Babula]. For this paper, two main variations are important; high temperature α -SiC, formed above 2000°C and relatively low temperature β -SiC with synthesis at temperatures as low as 1150°C, probably as a precipitate or gas-phase deposition. Table 1, compiled from several standard sources, illustrates several advantages of SiC material and puts it in context with aluminum and steel. As with all ceramics, SiC is brittle. However, some fiber-reinforced SiC composites have shown promising impact strength.

Material	Density	Tensile Modulus	Flexural Strength	Thermal Cond.	Melt/ Soft Temp.
Silicon Carbide	3.1 kg/m ³	>400 GPa	550 MPa	120 W/m/K	2800°C
RBSiC	2.9 kg/m ³	200-375 GPa	40-450 MPa	110 W/m/K	1375°C
Aluminum	2.7 kg/m ³	62-70 GPa	240 MPa	150-210 W/m/K	550-650°C
Steel	7.8 kg/m ³	~195 GPa	750-2500 MPa	15-35 W/m/K	300-650°C

Table 1 : Material Properties (for basic comparison only)

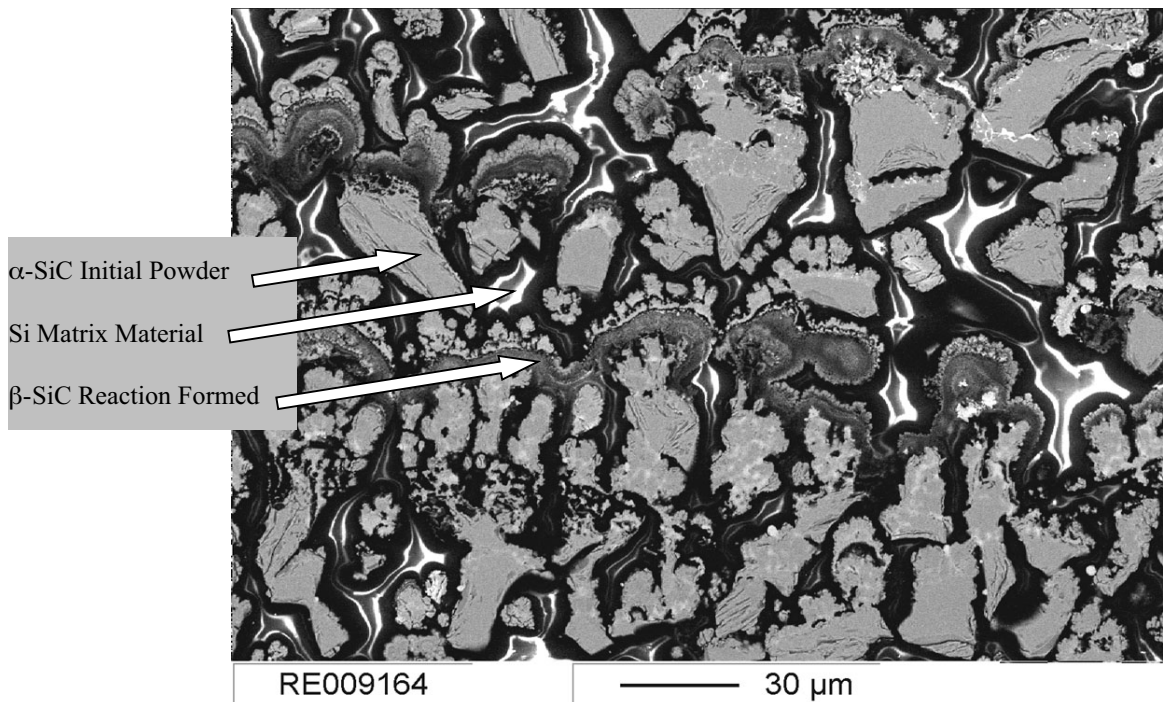


Figure 1 : RBSiC from Laser Sintered Preform
http://www.fraunhofer.de/english/press/md-e/md1998/f_1298-f5e.html

Typical manufacturing processes for SiC are pressureless sintering, gas pressure sintering, hot pressing, hot isostatic pressing, chemical vapor deposition, recrystallization and reaction sintering

-Suyama et al., p.1201

The temperatures, pressures and material preparation of these processes make them costly and impractical for large scale operations. Reaction sintering (pursuing fully dense SiC) and its close relative, reaction bonding (creating a matrix composite) as seen in Figure 1, are considered

the most promising fabrication strategies for SiC materials due to their net-shape capabilities, speed and low cost [Suyama et al., Rajesh and Bhagat]. Suyama, et al., add that the process imparts almost negligible dimensional changes. Figure 1 shows the main elements of RBSiC; α -SiC from the starting powder, β -SiC formed during the infiltration process and remaining Si. Additional details about reactive infiltration are discussed below. Several variations on these processes are found in industry. The process employed by Poco Graphite (www.poco.com) involves machining graphite to final part dimensions and a chemical vapor infiltration process to convert the carbon structure to SiC. Rohm and Haas (www.cvdmaterials.com/silicon.htm) employs a chemical vapor deposition process directly into SiC. Other companies create SiC/carbon powder slurries which are molded into part shapes and directly sintered or reaction infiltrated.

Product Applications

A wide variety of SiC products exist today, as seen in Table 2, but not all of them represent potential for SLS manufacturing. Many have simple shapes due to the difficulty involved in making complex shapes with SiC. Others require fully dense SiC, rather than RBSiC. Finally, those made using certain molding operations are mass produced, which leaves SLS at a disadvantage. However, the ability of SLS to make nearly any shape could put SiC into service for entirely new applications.

Turbine components	Semiconductor	Beams
Automotive	Wear & Corrosion Resistant	Batts
Armor	Components	Posts and Rollers
Burner Nozzles	Heat Exchanger Tubing	Ball valve parts
Metal working equipment	Valve & Valve Trim	Wear plates
Bearings	Hydrocyclones	Kiln furniture
DC Magnetron Sputtering	High Temperature /	Brakes
Faucet Washers	Thermal Components	Foundry equipment
Mechanical Seal Faces	Thermocouple Tubes/Prices	Heat exchangers
Pulp and Paper	Kiln Systems	

Table 2 : Current Applications of SiC Components

Rapid Manufacturing

Rapid manufacturing (RM) may not soon replace mass production, but the economic model advanced by Hopkinson and Dickens, as an example, indicates SLS is a viable alternative to injection molding at product runs up to 14,000 units and with some lower cost RM materials that number would increase significantly. The fit with foundries has been one of integration into previously existing manufacturing standards [McDonald, et al., p.87]. The opportunity for parallel fabrication in SFF also tends to favor smaller parts. Yet, complex parts even now are more cost effectively produced via RM methods [Pham and Dimov]. As an example, the heat exchanger assembly for the Pratt and Whitney PW6000 engine is manufactured using SLS to create the shape of each part before casting in aluminum. The reduced costs of tooling, design freedom and flexibility have been addressed widely in SFF literature, but what may be more critical is the importance of materials research for realizing the anticipated impact of RM [Kai & Fai. p.201, Hague et al.].

Rapid manufacturing will become more of a reality when the properties of the materials that are produced become more acceptable and consistent. This materials research is one of the main stumbling blocks to (RM)...

-Hague, et al., p.30

Even though SLS has the largest material set among SFF techniques [Ryder, et al.] there is a long way to go before designers have the range of materials necessary to address a critical mass of manufacturing tasks [McDonald, et al., p.240]. During this material development a move from low-volume applications toward higher volumes could proceed with improved RM processes, increasing the design of products to be made specifically by SFF techniques.

Previous Project Overview

The previous work was driven by a desire to leverage the capabilities of SFF to develop a new fabrication scheme for RBSiC, particularly for the manufacture of wafer carrier boats. The resistance of SiC materials to thermal shock and corrosion fits well with the challenging constraints of high-temperature semiconductor processing. The coefficient of thermal expansion (CTE) matches well with Si, reducing the particulate contamination and wafer defects when compared to the more traditional quartz fixtures, and contributes to the estimated 20x service life over quartz. Wang's focus was on the physics and chemistry of pressureless liquid Si infiltration of the porous preforms. She established the basic indirect process used to make SiC from SLS preforms; laser sintering a SiC powder mixed with binder compounds (green part), carbonization of the binder (brown part) and reactive infiltration of liquid silicon. The novelty of this research was the use of SLS for the creation of SiC preforms for reaction bonding. The main developments during Wang's work were an examination of wicking mechanisms in porous media, an analysis of the SiC forming reactions present and ultimately a fabrication process that produced viable parts. Figure 2 shows a part made during the previous study.

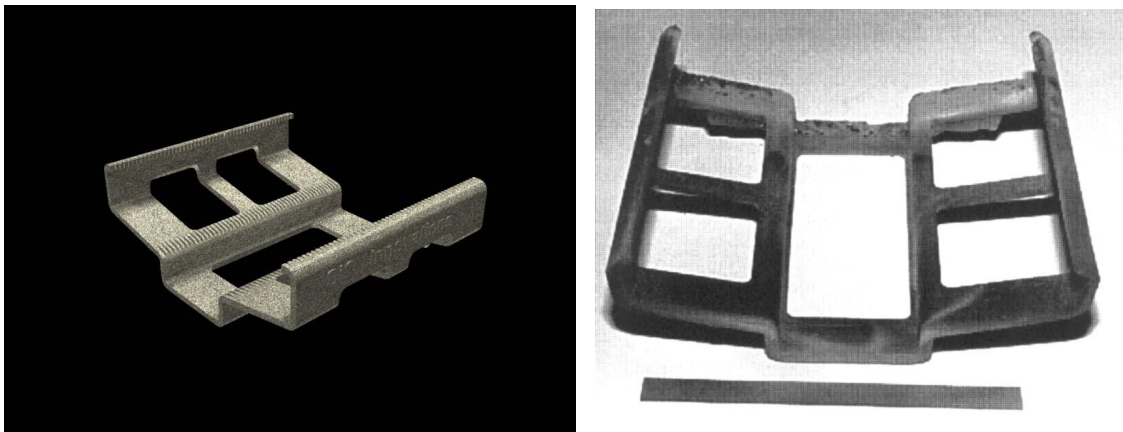


Figure 2 : (a) A Rendering of a Slotted Horizontal Boat. (b) A Silicon Carbide/Silicon Composite Boat Produced by Selective Laser Sintering and Silicon Infiltration. Also shown is a 6-Inch Scale.

Roughly concurrent to the UT work was a study conducted in Germany [http://ikpindy2.verfahrenstechnik.uni-stuttgart.de/RP_IKP/keramik/SiSiC.html]. The purpose of that work was to create a high-SiC content final part. Although SLS was used to form the

performs several differences existed especially in initial powder and additional resin infiltrations, presumably to enhance the carbon structure after carbonization. Figure 1 was taken from information published about that work.

Several key questions from this previous work provide avenues of exploration for the current research. First, the green strength of the preforms was barely adequate for handling the parts and preparing them for the furnace operations. A viable manufacturing operation would need a significant improvement in this area. The density of parts increased both with infiltration temperature (1450-1600°C) and with dwell time (0.1, 1 and 5hrs). The flexural strength was at a maximum when infiltration was at 1500°C for 1hr and at 1600°C and 0.1hrs. Relatively low strengths were found at all temperatures for the 5 hr dwell time. The greater final density of parts that underwent longer infiltration dwell times suggests more SiC growth; however, this does not necessarily correlate with better final part performance. The differing strength versus temperature [Wang, p.134] indicates the likelihood that the shorter infiltration (0.1h) has not developed significant regions where the β -SiC has established a fragmented structure, a phenomenon discussed below. In other words, although the density of the parts increased, it is possible that the microstructure supports a weaker final part. Although changing the particle size is expected to improve surface roughness, as Wang suggests, it can have greater influence on other parameters such as part strength or infiltration success. Finally, the coefficient of thermal expansion (CTE) was found to be closer to silicon ($\sim 3.5 \times 10^{-6}$ @ 500°C) than pure SiC ($\sim 4.75 \times 10^{-6}$ @ 500°C). The lowest CTE was from samples formed with the 5 hr dwell which paradoxically suggests lower SiC content.

Successful development of the best composite materials will require deeper understanding of the formation of SiC during infiltration. The structure of the “green part” and the “brown part” after binder decomposition need to be improved and correlated to the structure of the final material. Ultimately, the characteristics of the initial binder and SiC powder mixture will need to be optimized for the best system of processing and final part characteristics.

Key Issues in New Research Effort

Binder Development

The polymer chemistry and function of each constituent in the previous binder system is being examined. A new formulation is being developed based on the knowledge from the previous work, a literature review of liquid infiltration and a focused research effort. The specific elements of the binder study, including constituent chemistry, rheology and green and brown part structures are expected to be published separately and are beyond the scope of this paper. It is anticipated that the uniformity and consistency of the finished parts will be greatly supported by this work. There is a correlation between surface conditions, particle sizes and the packing density achievable in the part bed as may be inferred from the work of Paik et al. The final strength of the material is related to this packing density as well as the dispersion of the constituent materials. Further, the microstructure of the green preform is intimately related to the final properties of the infiltrated part. In addition, this work will be a springboard for studying the mechanics of unsupported, pressureless, reactive infiltration as well as the microstructural elements that evolve through the entire SFF-based manufacturing process.

Material Formation

When liquid Si meets carbon it reacts to form SiC. When a porous (<200 μm pore size) SiC preform is placed in contact with liquid silicon, the silicon fills the preform to at least a height of 2m [Wang]. In the following paragraphs a few challenges are discussed that undermine the simplicity of the previous statements.

A rather significant $\sim 116\text{kJ/mol}$ is released when this reaction occurs [Rajesh and Bhagat]. Wang observed a local temperature increase of 400°C . This heat of reaction, which changes based upon the structure of the carbon, influences the formation of SiC and the characteristics of the final parts. This combined with the significant changes in permeability observed by Rajesh and Bhagat indicate an influence on wicking kinetics and therefore final composite microstructure based on temperature at the onset of wicking. It may be possible to tailor preform characteristics for more rapid or more effective infiltration. Enhanced SiC formation from “solution reprecipitation” due to the increased exposure of C to Si melt which is likely due to carbon diffusing from higher temperature regions of the Si melt and supersaturating others. Favre et al., observed significant SiC growth at the liquid atmosphere boundary, away from the interface between carbon and silicon which they attributed mainly to the diffusion of $\text{CO}_{(\text{g})}$ to the SiC grains within the Si melt. The effects of reaction heating, dissolved carbon and other transport phenomena need to be addressed.

A thorough understanding of the wetting characteristics and the driving capillary action from the previous work coupled with a newly available model of transient permeability within preforms for reaction-formed SiC materials [Rajesh and Bhagat] should provide insight into the infiltration mechanics. If the Si is introduced to the preform as a melt, the main SiC formation occurs within the first minute of contact and proceeds to a relatively final thickness of 10-12 μm at carbon surfaces [Favre, et al.]. After this thickness has been reached further growth is inhibited by the extremely low diffusion of carbon or Si through SiC. High compression forces at the grain boundaries cause crystals to break away, causing periodic growth and local breaks [Favre, et al.]. These breaks cause a sudden exposure of carbon to Si and also cracks in the carbon surface itself. In small capillary channels the growth of SiC can choke off the subsequent flow of Si. SiC growth can also occur in other regions where liquid saturation or gas-phase (specifically $\text{Si}_{(\text{G})}$, $\text{SiO}_{(\text{G})}$, CO and CO_2) transport supports growth. The quick initial boundary growth and the liquid surface growth are both promising SiC formation avenues, but must be understood in practice.

Residual silicon has a detrimental effect on the mechanical properties and reliability of the finished parts [Paik et al.] with fracture of RBSiC dominated by the failure of the Si matrix [Fernandez et al.]. This is especially apparent in maximum temperature, acid resistance and fracture toughness. The sintering study by Suyama et al. generated a remarkably strong sintered material by, “controlling the residual Si size under 100 nm.” Fernandez, et al., also observed a significant strength when a continuous SiC structure (from carbonized wood) was a feature of the infiltrated material. This was corroborated by the work of Dyban where larger SiC particles ($\sim 100\mu$) maximized the connection of SiC to SiC within the structure of the infiltrated material. Again, it seems likely that a very capable material may be made, but what is possible within this manufacturing strategy is unclear.

Basic Research Tasks

It is known that the infiltration reaction occurs and that fully dense parts may be created. Yet, we need to explore the transient permeability, the local temperature effects, the reaction kinetics, the kinetics of various chemical reactions, and the evolution of the composite microstructure. These elements must be linked to the nature of the preforms that can be produced via SLS. We want to create a final material system with an interconnected microstructure of SiC that supersedes the limitations of a silicon matrix. One key to this may be in the tailoring of the carbonized brown part which may help to create an interstitial β -SiC structure similar to that formed in RBSiC created from charcoal as discussed by Fernandez et al. and others. This will be challenging due to the complexity of SiC formation coupled with the need for a binder material and initial powder to work within the constraints of SLS processing.

There is a desire to move from proof of concept to a far more refined process and better finished product. Based on this greater understanding of each manufacturing phase we seek methods of part design as well as a deeper understanding of this technology in terms of Rapid Manufacturing. In other words, we want to tie the potential of the microstructure to a system for understanding the tradeoffs across the manufacturing process and incorporating the design of finished parts. More generally, we see the development of new materials as a key driver to the future development of SFF technology in general and expect that this project will generate a template for the more rapid deployment of additional powder-based composite materials in SLS systems.

Conclusion

In this paper we have discussed SiC material, specifically in a reaction bonded form and its applications. The previous work conducted at UT has provided a good foundation for the current effort. The desire within the SFF industry to support more manufacturing presence will require more extensive research into highly functional materials that may be manipulated effectively into useful shapes. This particular material system is complicated but we are confident that it will yield a viable manufacturing alternative for a variety of applications and serve as a basis for additional SFF materials research.

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