Additive Manufacturing of Multifunctional Ceramic Matrix Composites (CMCs) for Propulsion Systems

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Purpose

The objective of the current project was to establish the feasibility of fabricating silicon carbide (SiC)-based ceramic matrix composites (CMCs) by laminated object manufacturing approach. In order to demonstrate the feasibility of this concept, essential parameters were developed and optimized to prepare carbonaceous prepreg compositions with appropriate properties (viscosity, curing behavior, high char yield, etc.) and material properties were studied. In addition, laser cutting parameters for fabrics and prepregs were established and the microstructure of laser-fiber interaction zone was studied by scanning electron microscopy. Effect of laser power, cutting speed, and argon purge during cutting was also evaluated. Fiber lay-up and high temperature treatments for conversion to ceramic matrix composites were devised. In addition, optimization of processing and microstructures has been carried out.

Background

Ceramic matrix composites (CMCs) are being developed and tested for numerous aerospace and energy applications. Advanced silicon carbide (SiC)-based CMCs are expected to make significant contributions toward reducing fuel burn and emissions by enabling high overall pressure ratio (OPR) of gas turbine engines and reducing or eliminating cooling air in the hot-section components, such as shrouds, combustor liners, vanes, and blades. The first generation CMCs are projected to be used in commercial gas turbine engines starting in 2016-17. Current generation of SiC-based composites are typically fabricated by multiple steps, which include fabrication of SiC fiber performs, chemical vapor infiltration (CVI), melt infiltration (MI), polymer infiltration and pyrolysis (PIP), or hybrid processing approaches combining CVI, MI, and PIP [1]. All these processes require extensive manual labor in various manufacturing steps (cutting and hand lay-up of preforms, composite fabrication, machining, etc.) leading to high cost and scatter in properties.

Additive manufacturing, which allows high value, custom designed parts layer by layer, has been demonstrated for metals and polymer matrix composites. However, there has not been much research and development activity on additive manufacturing of ceramic matrix composites (CMCs) and very limited data has been reported in the literature. An alternate approach for the fabrication of SiC based CMCs using laminated object manufacturing (LOM) can overcome cost, time, and complex geometry formation issues due to the automation of additive manufacturing processes. LOM is a rapid prototyping process in which laser-cut layers of green or adhesive-coated laminates are successively stacked and bonded together to form the part. Limited research appears in the literature for the additive and laminated manufacturing of SiC-based ceramics and composites. Klosterman et al [2] have reported on the use of ceramic grade Nicalon (CG-Nicalon) fiber prepregs with alternating layers of monolithic ceramic tapes. A number of issues related to weak interlayer bonding were encountered. In addition, weak composite flexural strength was exhibited due to inadequate fiber coating and poor high temperature stability of SiC (CG-Nicalon) fibers. For the fabrication of a non-fiber reinforced material, Windsheimer and Travitzky et al [3-4] have reported the fabrication of Si-SiC material using preceramic paper derived performs. Also, Weisensel et al [5] fabricated biomorphous SiSiC composites using LOM in which pyrolyzed paper sheets and phenolic resin were used to make biocarbon preforms. The preforms were subsequently pyrolyzed which result in a 34% reduction in weight and a liquid silicon infiltration step was used to densify the porous perform, which had a porosity of 69.4%. Analysis revealed 16 vol. % unreacted carbon and 23 vol. % residual silicon which filled in pores and the gaps in-between laminates. Residual silicon in the material is undesirable for high temperature applications since it would limit the use temperature to below 1300°C.

For the additive manufacturing of SiC/SiC composites using laminated object manufacturing (LOM) approach, high temperature silicon carbide fiber prepregs with desirable materials and properties have to be developed and optimized.

Approach

In this project, a number of prepreg materials with different amounts of fillers (SiC, C, and Si) were developed and their curing behavior was characterized. The solid loading in these compositions helps to reduce the shrinkage during the pyrolysis and high temperature treatments. In addition, the effect of environment on the pyrolysis and characteristic decomposition behavior was evaluated. The effect of SiC and Si powder size in prepreg materials were investigated using Thermogravimetric Analysis (TGA) and weight loss measurements taken after furnace pyrolysis. The furnace pyrolysis data under different conditions has been compared with TGA data. Phase identification was also conducted in the pyrolyzed samples using x-ray diffraction (XRD). The goal is to develop a matrix material that has minimal shrinkage and is compatible (chemically, mechanically, and thermally) to SiC fiber. The ability to fabricate a dense matrix will avoid the extra processing steps which are typically used to further densify the composite and are quite time consuming and costly.

The technical scope of the work includes the (1) development and characterization of prepreg compositions; (2) preparation of silicon carbide fabric prepregs with optimum properties; (3) optimization of laser cutting and

lamination process; (4) development and optimization of composite fabrication process; and (5) characterization of composite microstructures. For the development of prepreg compositions various amounts of phenolic and furan resins (solids and liquids), carbon powders, nano and micro size silicon carbide powders, fine silicon powders, active refractory ceramics fillers, silane coupling agents, dispersants, and surfactants were used. The solid loading in these compositions is very high (more than 65%) to reduce the shrinkage during the pyrolysis and high temperature treatment at 1450-1475°C.

In addition, high solid loaded phenolic and furan resin mixtures need to be mixed carefully since the heat generated during the mixing process could start the curing of prepreg mixtures. We have utilized 3-roll mill with water cooled rollers to mix these compositions. The differential scanning calorimetric (DSC) analysis data showed no evidence of partial curing during the mixing process. The curing and pyrolysis behavior of more than fifteen mixtures developed for this work have been studied in detail. These mixtures were thinned with appropriate amounts of silane coupling agents and triethylene glycol and used for b-staging of prepregs. The b-staged prepregs can be stored for a period of time, without sacrificing performance, in between application, assembly, and curing. These polymeric mixtures were used to prepreg silicon carbide (Hi Nicalon-S, 5-HS weave) fabrics and b-staged prepregs were prepared after heating in oven at 70°C. The uniformly distributed fine carbon and silicon powders are expected to aid the fabrication process and formation of silicon carbide ceramics in the matrix.

In order to optimize the laser power and cutting speed, a number of 1" diameter discs were cut from the as received SiC (Hi-Nicalon S) fabric and prepregs. The Universal Laser System utilized in this project has two 60 watt laser heads and a work area of 32"x18". Different cutting speeds and laser powers were utilized to evaluate the laser-material interaction, heat affected zone, and the resultant microstructures. Different types of prepregs were laser cut to make six to eight layer composites. These laminates were stacked, warm pressed, and pyrolyzed to convert resin to carbon. These multilayer composite specimens have been heat treated and silicon infiltrated in the furnace up to 1475°C to fabricate net-shaped silicon carbide matrix composites. It is well known that the bonding in between different interlayers is quite critical for the development of successful materials and products by additive manufacturing processes. Special attention was paid to develop the fiber prepregs which will yield well bonded interlayers without any voids or porosity.

Summary of Accomplishments

A summary of various technical accomplishments, publications and presentations and other outreach activities have been provided below. These accomplishments will be discussed in detail in the next section.

(1) **Design and Development of Prepreg Compositions:** Various types of silicon carbide, carbon, silicon powders (nano and micro sizes) and different types of dispersants and surfactants were utilized for developing prepreg compositions. Effect of silicon powder addition was evaluated. The efficient mixing methodologies for high solid loaded prepreg compositions have been developed.

(2) **Characterization of Prepreg Materials:** The differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) have been carried out in air and in nitrogen environment to study the curing and weight loss behavior. In addition, these specimens were also evaluated in furnace pyrolysis from 700-1450°C in vacuum and in nitrogen. X-Ray diffraction analysis of powders was carried out to characterize different phases after the heat treatments.

(3) **Development of SiC Fiber Prepregs:** Six sets of 6"x6" high temperature silicon carbide fabrics (Hi-Nicalon-S, 5 HS weave) were prepregged and b-staged. In addition to fibrous prepregs, five types of tapes were also fabricated with prepreg compositions. These tacky prepregs have been used to investigate the optimal parameters for laser power and cutting speed.

(4) **Optimization of Laser Cutting Process:** A number of circular pieces (1"dia) from the SiC fabric and prepregs were cut at different power and speed. Cut surfaces were evaluated in scanning electron microscope to evaluate the surface roughness, morphology, and heat affected zone. In addition, large size pieces were also cut to fabricate the composites and evaluate the heat affected zones during the laser cutting.

(5) **Fabrication and Characterization of Composites:** Composites were fabricated with eight layers of prepregs and heat treated and silicon infiltrated to compare the microstructure. Microstructural analysis of these specimens was carried out.

(6) **Publications, Presentations, and Outreach Activities:** Two presentations (one invited and one regular) were made in international conference in Florida. One summer student was also co-mentored. In addition, a talk was given in a regional workshop at OAI and NARI LEARN seminar. One paper has been accepted in Ceramic Engineering and Science Proceeding and other paper is being prepared for submission to a journal.

Details of Accomplishments

This section provides a detailed overview of significant technical progress made in different technical areas which includes (a) design and development of novel prepreg compositions; (b) characterization of prepreg materials; (c) optimization of laser cutting parameters and evaluation of heat affected zones; and (d) fabrication and characterization of composites.

Design and Development of Prepreg Materials

The prepreg design and development scheme is presented in Figure 1. For the development of novel prepregs, more than fifteen prepreg compositions with various amounts of phenolic and furan resins (solids and liquids), carbon powders, silicon carbide powders of different sizes (micron

and nano size: Nano1 and Nano2), fine silicon powders (micron sizes), silane coupling agents, dispersants, and surfactants were used.

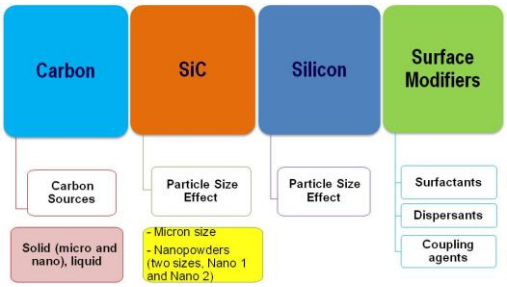


Figure 1: Novel prepreg design and development philosophy.

The solid loading in these compositions is very high (more than 65%) to reduce the shrinkage during the pyrolysis up to 1000°C and high temperature treatment at 1450-1475°C. In addition, fine particles in the prepreg compositions could also facilitate the infiltration and uniform distribution of silicon carbide and carbon into fiber tows. However, high solid loaded resin mixtures need to be mixed carefully since the heat generated during the mixing process could start the curing of prepreg mixtures. The challenge of mixing highly loaded solid mixture was alleviated using the three roll milling approach with water cooled rollers since the heat generation during the mixing could start the curing process. After the mixing, all the prepreg mixtures were shown to have uniform consistency. The differential scanning calorimetric (DSC) analysis of the mixtures was carried out in nitrogen and air. In-house developed compositions were given the names of 5A, 5A Nano1, and 5A Nano2 which consist of differing powder sizes. The three compositions were also modified with an additional 20 weight % of silicon powder. The differential scanning calorimetric (DSC) analysis data of three prepreg mixtures showed no evidence of partial curing during the mixing process (provided in previous reports). The exotherm and its onset temperature can be used as guidance for the warm pressing and curing steps of composite fabrication. In addition, it seems that fine particle size of silicon carbide and silicon also has an influence on the curing behavior of these materials. Detailed analysis of all the heat flows and related factors has been carried out. Similar behavior was observed in other prepreg specimens in air and in nitrogen.

Characterization of Prepreg Materials

In order to characterize prepreg materials, samples with different composition were cured at 60°C for 30 min, 90°C for 1 hr, then 160°C for 2 hrs. Each sample was broken into pieces and one of each type was submitted for TGA studies. Thermogravimetric analysis of prepreg materials was carried out in TA Instrument TGA Q500 in air and in nitrogen environments. The weight loss curves for samples were recorded up to 1000°C in nitrogen and air. The weight loss curves for three samples up to 1000°C in nitrogen and air are shown in Figure 2.

It is clear from the Figure 2 that all the samples at least retained more than 60% of their original weight while the maximum weight retained (more than 85%) was for specimens with Nano2 silicon carbide and fine silicon powders in nitrogen. It appears that fine silicon carbide powders facilitated uniform distribution of carbon particles and there is some reaction already taking place in the system at 1000°C. The weight loss behavior in this system up to 1000°C in air shows different behavior due to oxidation of carbon above 650°C. Another set of specimens were prepared with 20% silicon powder addition. TGA analysis of these specimens was conducted in air and nitrogen as well.

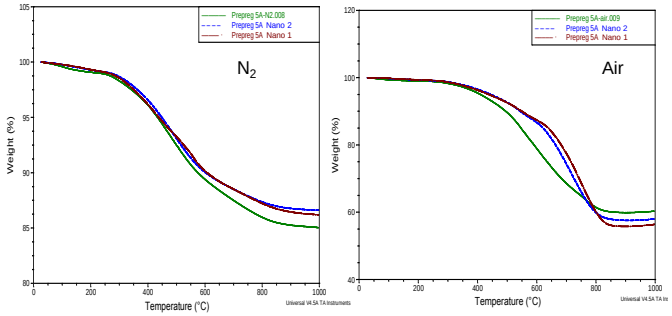


Figure 2: Thermogravimetric Analysis (TGA) of prepreg mixtures in nitrogen and air.

All the silicon powder added samples retained more than 85% of their original weight during the pyrolysis in nitrogen up to 1000°C with the prepregs containing excess silicon, 5A Nano1+Si and 5A Nano2+Si, having weight retentions approaching 90%. In the samples without excess silicon, a more drastic decline in weight from 300-600°C range was observed. In general, the weight loss behavior of nano and micro-particle containing specimens is quite similar up to until 600°C. Specimens with nanosize silicon carbide powders (Nano1 and Nano2) additions have retained higher weights than micron size silicon carbide powders.

In order to compare the weight loss data from TGA analysis to furnace pyrolysis, experiments were carried out in argon (700 and 1000°C) and in vacuum at (1200, 1350, and 1450°C). Baseline and silicon powder added samples were casted into puck size green bodies and small pieces were pyrolyzed at 700°C in Argon, 1000°C in Argon, 1200°C in low vacuum, and 1450°C in low and high vacuum for a 30 min hold. Figure 3 shows the comparison of pyrolysis data of three types of prepreg materials as a function of temperature and environment. High mass retention indicates that secondary infiltration process may not be required to get dense composites.

Figure 4 shows a comparison of the weight retention of prepreg materials with added Si powder after pyrolysis at various temperatures and conditions. It is important to point out that the weight loss in vacuum at high temperature can be influenced by vaporization of silicon. The weight loss obtained in the TGA analysis and furnace pyrolysis compares very well. It is observed that weight retention of all the prepreg materials decreases as temperature increases, but each prepreg material experiences weight loss at differing rates.

X-ray diffraction analysis of pyrolyzed prepreg materials (with and without excess silicon) was carried out to identify

different phases in the final materials. The phase identification results indicate that the high temperature heat treated prepreg mixtures are able to yield quite high concentration of silicon carbide. The highest conversions were observed in G5A, G5A Nano1, and G5A+Si which were 96%, 96%, and 99% SiC, respectively. High yield of silicon carbide will be critical for eliminating an expensive processing step to obtain full composite densification and for the near net-shape fabrication of final parts.

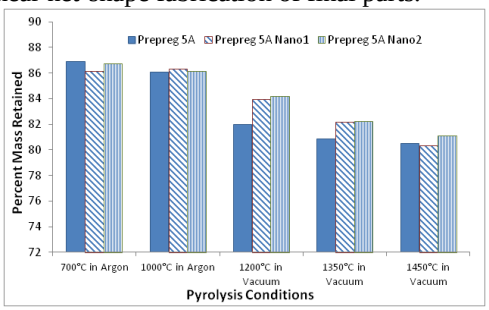


Figure 3: Effect of SiC particle size and temperature/ environment on the pyrolysis of prepreg materials.

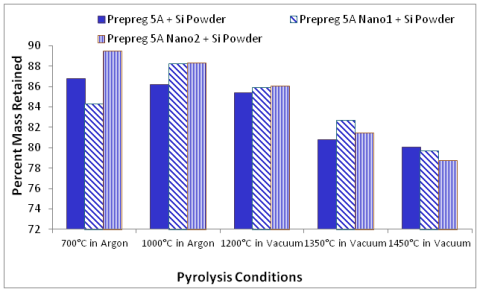


Figure 4: Effect of SiC particle size, Si powder addition, and temperature/environment on the pyrolysis of prepreg materials.

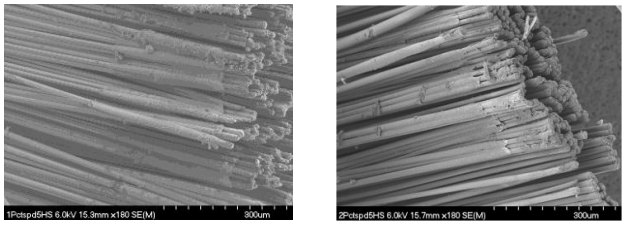
Optimization of Laser Cutting Parameters:

In order to evaluate and optimize the laser cutting parameters for the silicon carbide fabrics and prepregs, various experiments were carried out at different laser power, cutting speed, and argon flow through the laser head. Previous report had a number of micrographs of pure fabrics which were cut with different laser power and speeds. A database of microstructure, laser power, cutting speed, and argon purge/air has been created.

Figure 5 (a-b) shows the micrographs at 1 and 2% speeds with 15% of power. It seems that there is material vaporization at the cut edges and a glassy sheath formation. On the other hand, the argon purge during the laser cutting with similar speeds and power show reduced amount of glassy phase formation away from the cut interface as shown in Figure 6 (a-b).

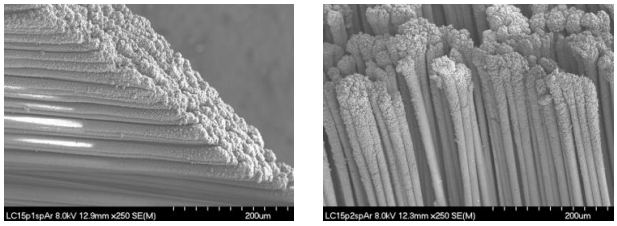
Fabrication and Characterization of Composites

A number of ceramic matrix composites specimens were fabricated using the prepregs in this program. For the fabrication of composites, eight layers of prepregs were utilized. An example of Nano 2 silicon carbide powder containing prepregs with excess silicon powders is shown here. The cut prepregs were used for warm pressing at 75-85°C and heat treated at 1475°C in vacuum. Other pieces were used for infiltration with excess silicon to see the extent of densification and fiber damage. Figure 7 (a) shows the microstructure of carbonaceous prepreg after the warm pressing. It shows good infiltration and distribution of carbonaceous phases, SiC, and Si in and around fiber bundles.



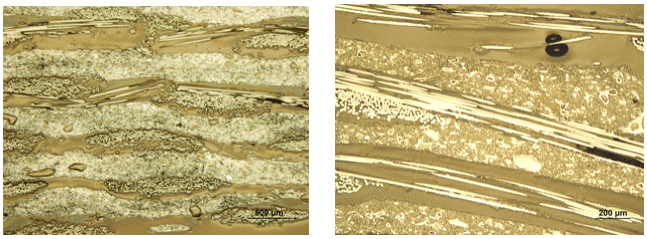
(a) (b)

Figure 5: Effect of laser power and cutting speed on the microstructure of Silicon Carbide (Hi-Nicalon S) fabrics (a) 15% power, 1% speed, 1000 PPI and (b) 15% power, 2% speed, 1000 PPI.



(a) (b)

Figure 6: Effect of argon purge and cutting speed on the microstructure of Silicon Carbide (Hi-Nicalon S) fabrics (a) 15% power, 1% speed, 1000 PPI and (c) 15% power, 2% speed, 1000 PPI.



(a) (b)

Figure 7: Microstructure of SiC/SiC composites (a) green composite; and (b) composites heated at 1475°C.

The microstructure of composites heat treated at 1475°C for 30 minutes in vacuum (Figure 7 b) show good distribution of SiC and Si and uncoated SiC fibers and no visible damage due to Si exothermic reaction. However, fiber coatings will be needed to provide weak interface for debonding and composite toughness. It was observed that carbon and SiC nanophase particles improve the distribution of various phases in the prepregs/ preforms. In addition, solid state reaction of silicon and carbon is enhanced by uniform distribution of phases aided by nanosize particles.

In summary, for the additive manufacturing of silicon based composites, high char yielding compositions were developed and characterized. The process was proven to be a promising method for processing the silicon carbide matrix in a silicon carbide fiber reinforced ceramic matrix composite. High yield of silicon carbide will be critical for

eliminating an expensive processing step and reducing the shrinkage of final parts.

Current TRL:

The current Technology Readiness Level for the completed work is TRL 2.

Applicable Programs/Projects

Additive manufacturing technologies are of critical importance to NASA and the nation. This effort is also aligned with the National Manufacturing Initiative to explore innovative manufacturing technologies, and expands the applicability of additive manufacturing to CMCs.

Presentations

- "Additive Manufacturing of Ceramics: Technical Challenges and Opportunities", National Additive Manufacturing Innovation Institute (NAMII) regional workshop at Ohio Aerospace Institute, May 14, 2013.
- "Characterization of Matrix Materials for Additive Manufacturing of Silicon Carbide-Based Composites" (Shirley Zhu, Michael C. Halbig, and M. Singh) – *Regular Talk,* 38th International Conference on Advanced Ceramics and Composites in Daytona Beach, FL during January 26-31st, 2014.
- "Additive Manufacturing of Ceramic Matrix Composites: Technical Challenges and Opportunities" (M. Singh and Michael C. Halbig) –*Invited Talk,* 38th International Conference on Advanced Ceramics and Composites in Daytona Beach, FL during January 26-31st, 2014.
- *ARMD LEARN Seminar*

Publications

- "Characterization of Matrix Materials for Additive Manufacturing of Silicon Carbide-Based Composites", M. Singh, Michael C. Halbig and Shirley Zhu, Ceramic Science and Engineering Proceedings (2014) published by Wiley and the American Ceramic Society (in press).
- "Materials and processing challenges in laminated object manufacturing of silicon carbide based ceramic composites" M. Singh and Michael Halbig, International Journal of Applied Ceramic Technology (2014) in preparation.
- LEARN reports.

Awards & Honors related to LEARN Research

None

References

[1] R. Naslain, "Design, Preparation and Properties of Non-oxide CMCs for Application in Engines and Nuclear Reactors: An Overview," Composites Science and Technology, Vol. 64, 2 (2004) 155–170.

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