Additive Manufacturing of Ceramic Matrix Composites for Propulsion Applications

NASA Aeronautics Research Institute

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NASA Aeronautics Research Mission Directorate (ARMD)
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Outline

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- **Introduction and Background**
  - ***Benefits of CMCs in Aerospace Systems***
  - ***Current Manufacturing Approaches and Challenges***
  - ***Additive Manufacturing Technologies***
- **Objectives**
- **Technical Approach**
- **Impact of the Innovation**
- **Results of the LEARN Phase I effort to date**
- **Distribution/Dissemination of Results**
- **Future Plans**

Benefits of Ceramic Matrix Composites in Propulsion Systems

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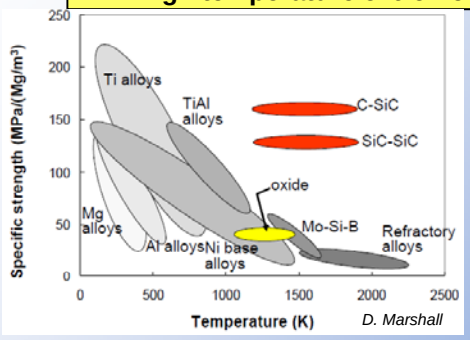
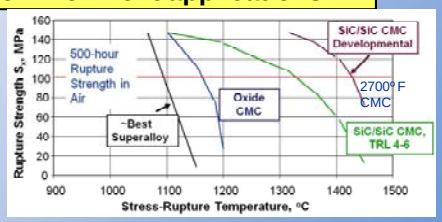
CMCs are enabling materials for aero-propulsion and other high temperature extreme environment applications



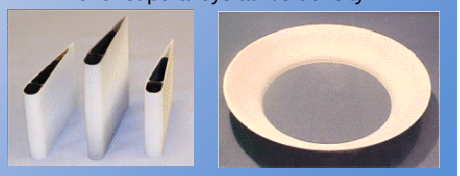
D. Marshall



Jim DiCarlo

SiC/SiC CMCs offer significant advantage over superalloys at 1/3 density

From GE



Coated CMC Components from NASA Programs

Current Approaches for Manufacturing of Ceramic Matrix Composites

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Preforming and Interface

Hand lay-up and tooling of ceramic fibers or woven shapes

Chemical Vapor Infiltration (CVI) Process

A gas mixture is infiltrated and SiC is deposited into a fiber preform.

- Slow; large objects can take weeks to months.

Polymer Infiltration/ Pyrolysis (PIP) Process

Preceramic polymer infiltration and pyrolysis to create a SiC based matrix.

- Multiple steps to achieve matrix density

Melt Infiltration (MI) Process

Slurry coated prepregs or infiltration of slurry/ resins into a fiber preform.

- Infiltration of liquid silicon to react with carbon to form SiC.

Hybrid Process

Combination of CVI/PIP, CVI/MI, or PIP/MI to create a SiC based matrix.

- Several steps to make a matrix

Post Processing and Nondestructive Evaluation

Machining (grinding, milling, drilling) → **Joining (brazing and attachments)** → **Coating and Finishing NDE**

National Manufacturing Initiative and Role of Additive Manufacturing Technologies

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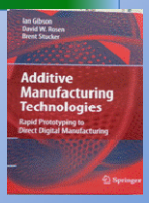
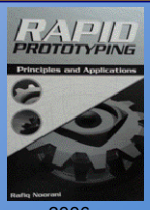
Major Policy Milestones



2010

Various AM or RP technologies were developed in late 80's and 90's.



2006

Frank Gayle, AMNPO, NIST

Selective Laser Curing (SLC) of Preceramic Polymers and 3D-Printing of SiSiC Ceramics

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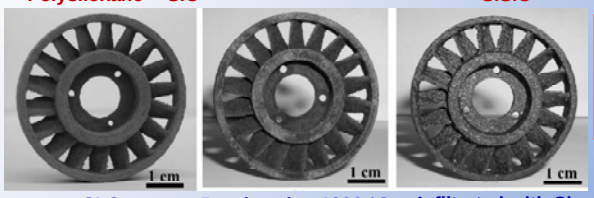
Starting Material: 50 vol.% Polysiloxane / 50 vol.% SiC

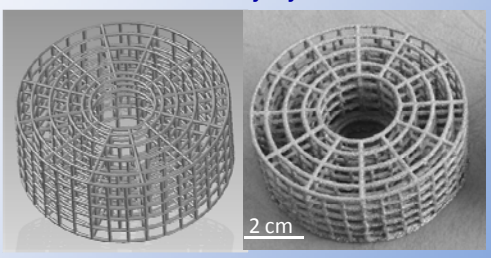
Polysiloxane + SiC **SiSiC**



SLC **Pyrolyzed at 1200 °C** **Infiltrated with Si**

No Fiber Reinforcements in SLC and 3D Printing Process

T. Friedel, et al, J. Eur. Ceramic Soc., 25, 2005, 193-197



CAD design of macro-cellular lattice reactor structure (left) and SiSiC component fabricated by 3D printing (right)

L. Schlier, et al, Int. J. Appl. Ceram. Techn., 8 [5], 2011, 1237-1245

Typical Properties of Commercially Available Silicon Carbide Fibers

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: *Nearly stoichiometric SiC fiber*

	SiC fibers							
	Nicalon			Tyranno				Sylramic
	NL-200	Hi-Nicalon	Hi-Nicalon-S	Lox M	ZMI	ZE	SA	
Atomic Composition	$SiC_{1.34}O_{0.36}$	$SiC_{1.39}O_{0.01}$	$SiC_{1.05}$	$SiTi_{0.02}C_{1.37}O_{0.32}$	$SiZr_{<0.01}C_{1.44}O_{0.24}$	$SiZr_{<0.01}C_{1.52}O_{0.05}$	$SiC_{O,Al<0.008}$	$SiCTi_{0.02}B_{0.09}O_{0.02}$
Tensile Strength (GPa)	3.0	2.8	2.6	3.3	3.4	3.5	2.8	3.0
Tensile Modulus (GPa)	220	270	410	187	200	233	410	420
Elongation(%)	1.4	1.0	0.6	1.8	1.7	1.5	0.7	0.7
Density($g \cdot cm^{-3}$)	2.55	2.74	3.10	2.48	2.48	2.55	3.02	>3.1
Diameter(μm)	14	14	12	8 & 11	8 & 11	11	8 & 10	10
Specific Resistivity (Ω・cm)	10^3-10^4	1.4	0.1	30	2.0	0.3	—	—
Thermal Expansion coeff.(10^{-6}/K)	3.2 (25-500°C)	3.5 (25-500°C)	—	3.1	4.0	—	4.5 (20-1320°C)	—
Thermal Conductivity (W/mK)	2.97(25°C) 2.20(500°C)	7.77(25°C) 10.1(500°C)	18.4(25°C) 16.3(500°C)	—	2.52	—	64.6	40-45

Laminated Object Manufacturing of Ceramic Matrix Composites

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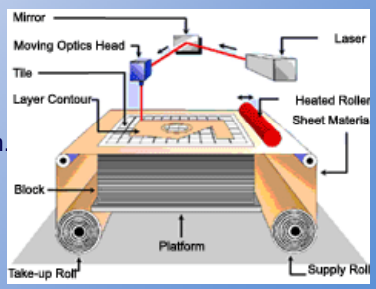
- **LOM is a viable option for manufacturing fiber reinforced CMCs with modification to the machine.**
- **Issues with LOM machines manufacturing base.**

Typical Process:

1. CAD design is turned into computer generated cross sections.
2. Layers of adhesive coated materials to substrate with heated roller.
3. Laser cuts cross-section of part.
4. Laser cross hatches non-part area.
5. Platform with completed layer moves down.
6. Fresh sheet moves over and platform moves up. Layers are stacked to form the shape with the desired thickness.



http://www.rpc.msoe.edu

New CMC prepreg material development and characterization is a critical step

Laminated Object Manufacturing of SiC Based Composites

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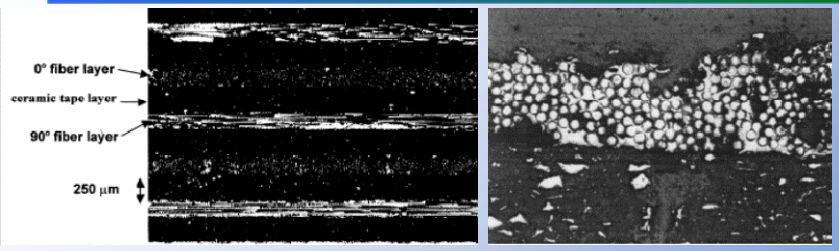

Cross section of reaction bonded SiC/SiC composite showing alternating prepreg and ceramic tape layers. Fibers are carbon-coated CG-Nicalon SiC.

Donald Klosterman, et al, Composites Part A, 29A (1998) 1165–1174

Gear wheel (diameter 50 mm) manufactured from SiC-filled preceramic paper

N. Travitzky, et al, J. Am. Ceram. Soc., 91 [11], 2008, 3477–3492.

Objectives and Technical Approach

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Objectives:

To establish the feasibility of fabricating SiC-based ceramic matrix composites (CMCs) with desired properties by Laminated Object Manufacturing (LOM).

Technical Approach:

- Develop carbonaceous prepreg compositions with appropriate properties (viscosity, curing behavior, high char yield, etc.).
- Detailed study of prepreg material properties.
- Establish laser cutting parameters for fabrics and prepregs and optimize lay-up schemes.
- Devise high temperature treatments for conversion to ceramic matrix composites and process optimization.
- Characterize thermomechanical properties of CMCs.

Additive Manufacturing of Ceramic Matrix Composites: Technical Approach

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- Development of compositions and efficient mixing technologies for highly loaded polymer mixtures
- Study of viscosity and curing behavior

Pyrolysis of Prepreg Materials under various conditions

Characteristic decomposition patterns	Environmental Effects	Phase identification

Laser cut SiC woven fabrics and prepregs using various parameters

Severity and phase composition of the heat affected region

Composite Processing

Lay-up of prepregged fibers	Reduce processing steps	Evaluation of Properties

Additive Manufacturing of Ceramic Matrix Composites: Technical Approach

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Overview of Prepreg Material System Design and Optimization

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Carbon
- Carbon Sources
  - Solid (micro and nano), liquid

SiC
- Particle Size Effect
  - Micron size
  - Nanopowders (two sizes, Nano 1 and Nano 2)

Silicon
- Particle Size Effect
  - Micron size (two types)

Surface Modifiers
- Surfactants
- Dispersants
- Coupling agents

Prepreg composition design is critical since it will convert to matrix filling the voids in the fiber tows/cloth

Curing Behavior of Prepreg Materials

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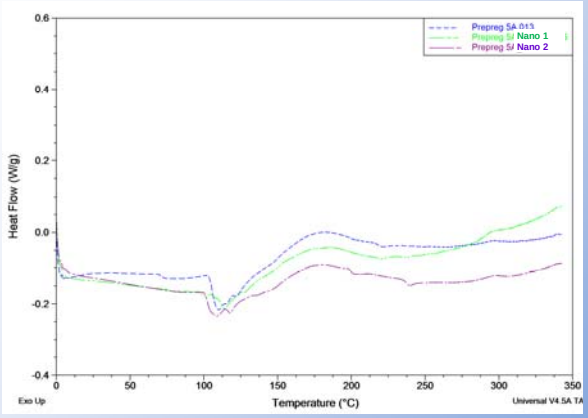
DSC Curves of mixtures with different SiC particle sizes in Nitrogen



Observations:
- No evidence of partial curing from the mixing process.
- These temperatures can be used as guidance for the warm pressing and curing steps of composite fabrication.
- Fine particle size of silicon carbide and silicon has an influence on the curing behavior.

Characterization of Prepreg Materials

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Analysis of characteristic decomposition patterns corresponding with varying SiC, Si, and Carbon powder particle sizes in polymer mixtures and pyrolysis conditions.

Prepreg Materials

- 5A
- 5A+Nano1
- 5A+Nano2
- 5A + Si
- 5A+Nano1 + Si
- 5A+Nano2 + Si

Cure at 60°C for 30 min, 90°C for 1 hr, then 160°C for 2 hrs

- 700°C Pyrolysis in Argon
- 1000°C Pyrolysis in Argon
- 1200°C Pyrolysis in vacuum
- 1350°C Pyrolysis in vacuum
- 1450°C Pyrolysis in vacuum

Weight Loss Measurements

Comparison with TGA Analysis

TGA Results from Prepreg Materials Pyrolysis in N_2 and Air up to 1000° C

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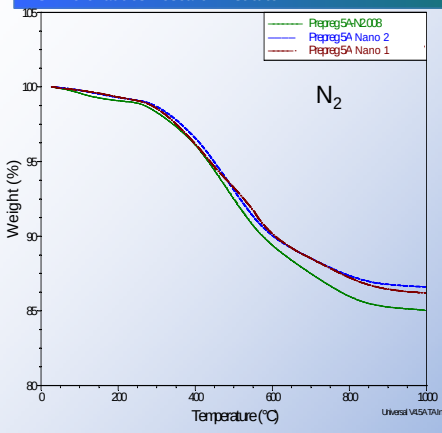

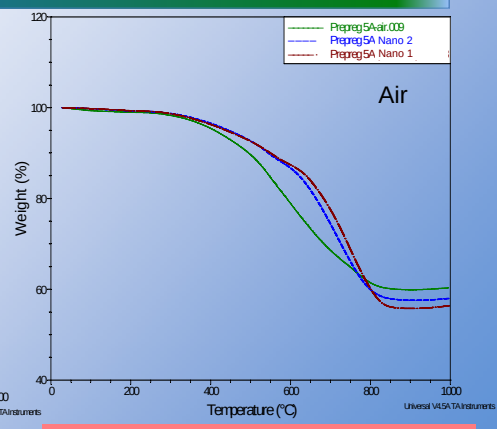

Higher weight retention from exposure in Nitrogen. Similar weight retention trends in nanoparticle prepregs.

Lower weight retention in air overall. Some weight gain near 1000° C due to oxidation. Nanoparticle prepregs had greater weight retention weight until roughly 675° C.

TGA Results from Prepreg Materials + Si Pyrolysis in N_2 and Air up to 1000 ° C

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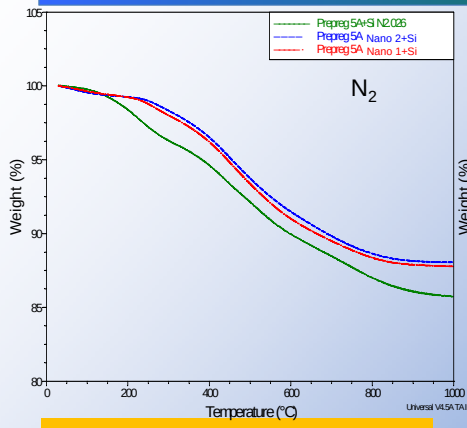

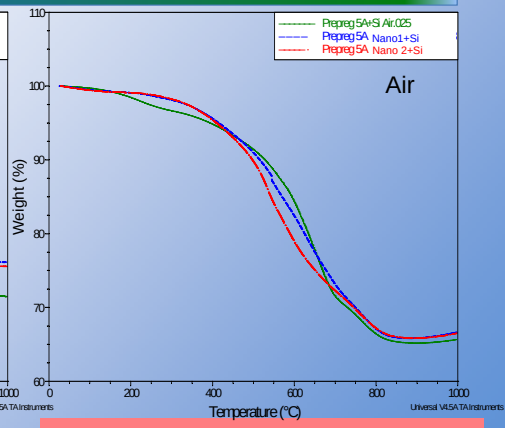

Similar trend to 5A prepregs in N2. Nanoparticle prepregs have higher weight retention than the microparticle.

Similar trend to 5A prepregs without silicon but higher weight retention even in air. Nanoparticle particle prepregs have similar weight retention pattern to microparticle.

TGA Results from Prepreg Materials with and without Si Pyrolysis in N_2 up to 1000° C

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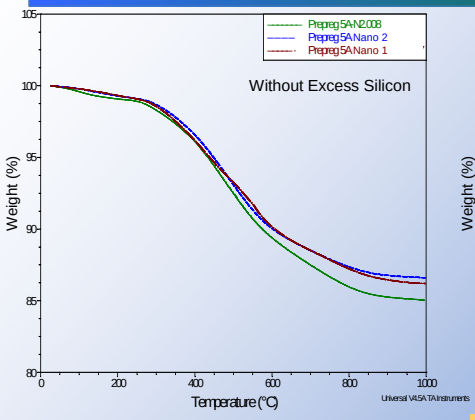

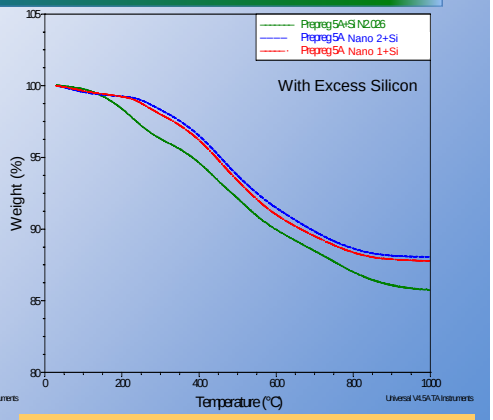

More drastic decline in weight from 300° C -600° C. Nano and microparticle performance is similar up until 600° C.

Higher weight retention overall for samples with additional Silicon powder. Defined higher weight retention of nanoparticle prepregs with Si throughout temperature regime. ~5% increase of weight retention due to Si.

Furnace Pyrolysis of Prepreg Materials up to 1450° C

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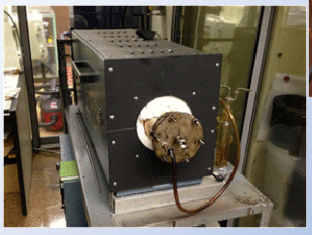

700° C & 1000° C in Argon

1200° C, 1350° C, 1450° C in low vacuum

1450° C in high vacuum

Effect of SiC Particle Size and Temperature/Environment on the Pyrolysis of Prepreg Materials

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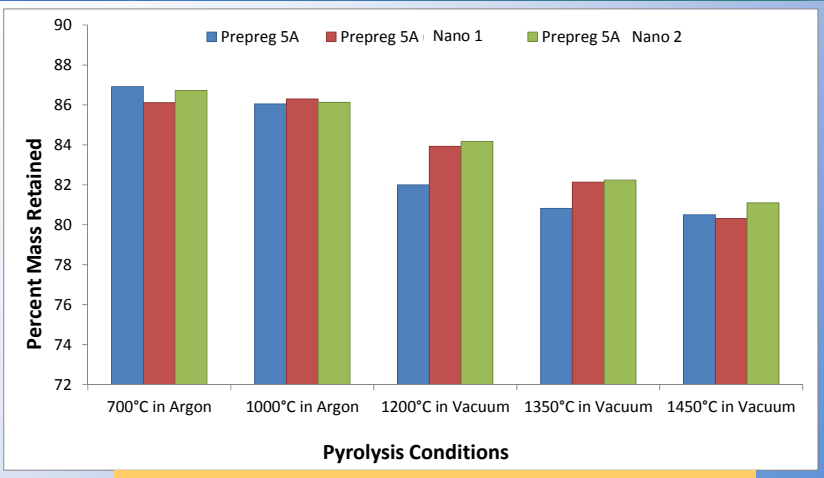

High mass retention indicates that secondary infiltration process may not be required to get dense composites.

Effect of SiC Particle Size, SiC Powder Addition, and Temperature/Environment on the Pyrolysis of Prepreg Materials

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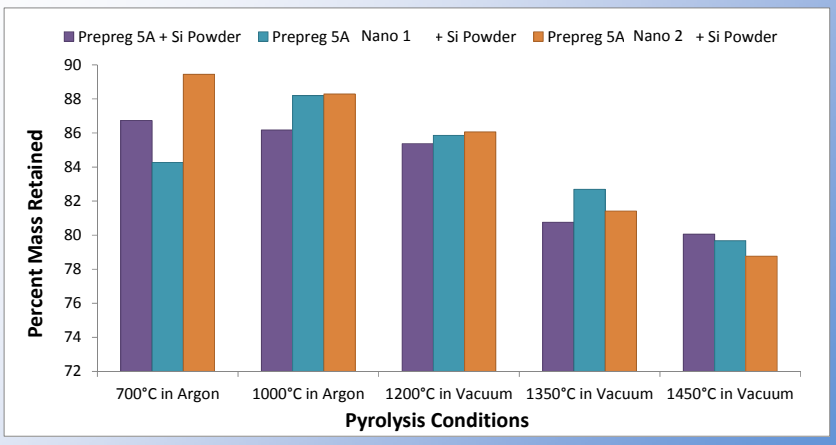

The weight loss in vacuum at high temperature can be influenced by vaporization of silicon.

Comparison of Prepreg Materials Mass Retention after Pyrolysis

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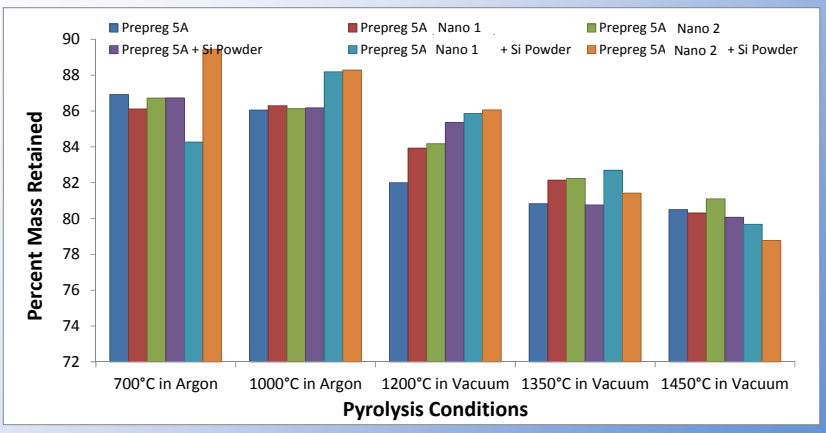

Average weight retention is quite good in all systems after pyrolysis under different conditions. These systems provide many options for process optimization.

Effect of Furnace Vacuum on the Weight Loss Behavior of Prepreg Materials at 1450° C

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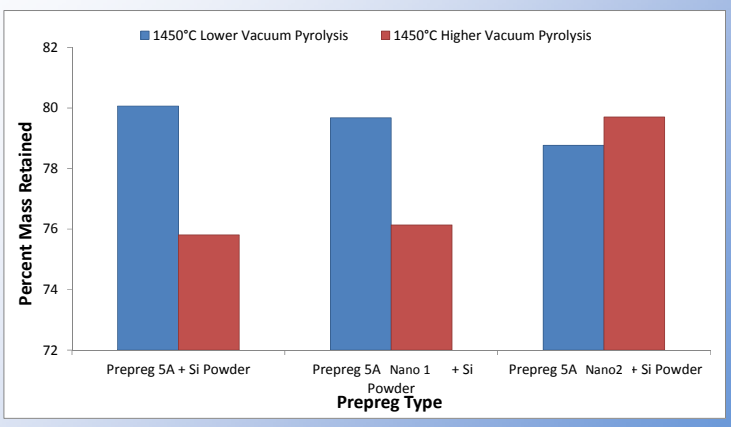

The weight loss in vacuum at high temperature can be influenced by vaporization of silicon. Uniform mixing of nanopowders could also play a role (better mixing of Nano-2 powders were observed than Nano-1).

Comparison of Weight Loss in TGA and Furnace Pyrolysis of Prepreg Materials

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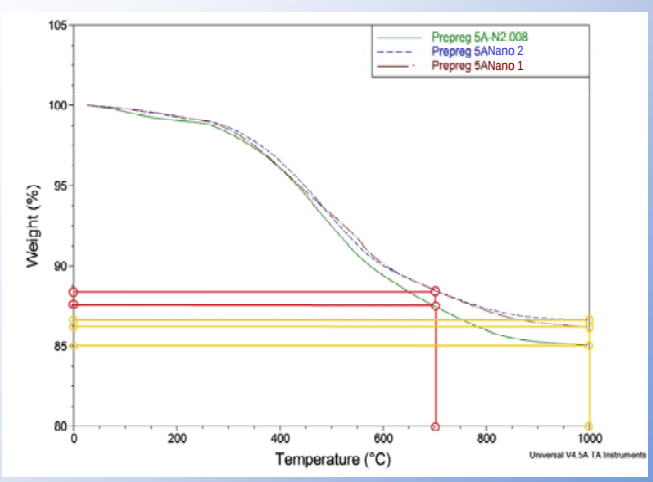

700 °C Pyrolysis		
Prepreg	Weight % in Argon	Weight % in Nitrogen
5A	86.92	87.50
5A Nano 1	86.11	88.50
5A Nano 2	86.72	88.50

1000°C Pyrolysis		
Prepreg	Weight % in Argon	Weight % in Nitrogen
5A	86.05	85.00
5A Nano 1	86.30	86.25
5A Nano 2	86.13	86.50

- Good correlation between furnace and TGA weight loss data

Comparison of Weight Loss in TGA and Furnace Pyrolysis of Prepreg Materials + Silicon Powders

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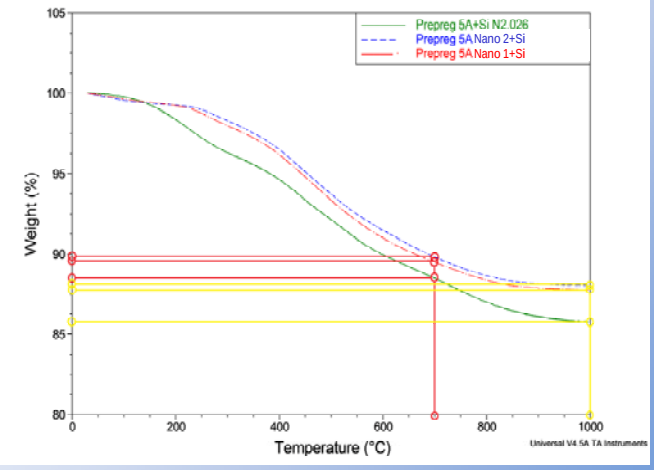

700 °C Pyrolysis		
Prepreg	Weight % in Argon	Weight % in Nitrogen
5A +Si	86.17	88.75
5A Nano 1 +Si	84.26	90.00
5A Nano 2 +Si	89.44	88.90

1000°C Pyrolysis		
Prepreg	Weight % in Argon	Weight % in Nitrogen
5A +Si	86.17	85.10
5A Nano 1 +Si	88.19	87.30
5A Nano 2 +Si	88.28	87.37

- Good correlation between furnace and TGA weight loss data

Phase Identification through X-Ray Diffraction

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XRD Results - 1450° With and Without Extra Si

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Si C	Silicon Carbide	Hexagonal	01-074-1302	96
C	Carbon	Hexagonal	00-023-0064	4

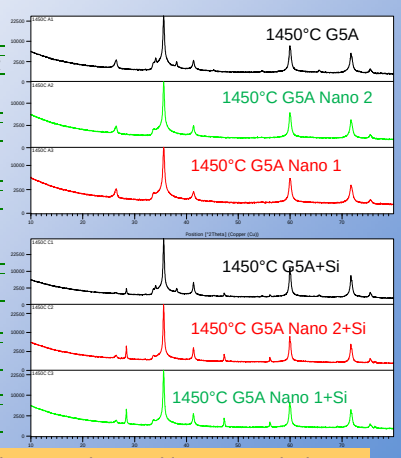
Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Si C	Silicon Carbon	Cubic	04-008-4949	91
C	Carbon	Hexagonal	04-016-4291	9

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Si C	Silicon Carbon	Cubic	04-009-1655	96
C	Carbon	Hexagonal	00-041-1487	4

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Si C	Silicon Carbon	Hexagonal	04-002-9069	99
Si	Silicon	Cubic	04-001-7247	1
C	Carbon	Hexagonal	00-041-1487	1

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
C	Carbon	Hexagonal	00-041-1487	1
Si	Silicon	Cubic	04-001-7247	7
Si C	Silicon Carbide	Cubic	01-074-2307	92

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
C	Carbon	Hexagonal	00-041-1487	1
Si	Silicon	Cubic	04-001-7247	9
Si C	Silicon Carbide	Cubic	01-074-2307	91



- Desired high amounts of SiC were observed in XRD analysis.
- Critical for eliminating a expensive processing step.

Phase Identification through X-Ray Diffraction

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XRD Results - 1450° With Extra Si Under Low and High Vacuum

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Si C	Silicon Carbon	Hexagonal	04-002-9069	99
Si	Silicon	Cubic	04-001-7247	1
C	Carbon	Hexagonal	00-041-1487	-

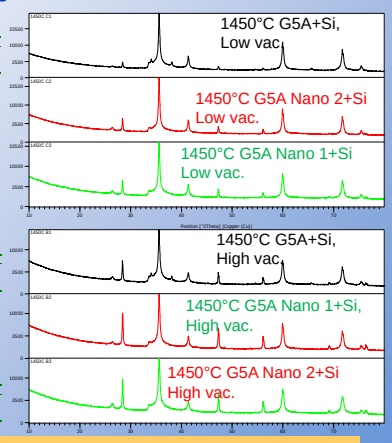
Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
C	Carbon	Hexagonal	00-041-1487	1
Si	Silicon	Cubic	04-001-7247	7
Si C	Silicon Carbide	Cubic	01-074-2307	92

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
C	Carbon	Hexagonal	00-041-1487	1
Si	Silicon	Cubic	04-001-7247	9
Si C	Silicon Carbide	Cubic	01-074-2307	91

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Si	Silicon	Cubic	00-026-1481	6
Si C	Silicon Carbide	Hexagonal	04-010-5698	94
C	Carbon	Hexagonal	00-041-1487	-

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Si	Silicon	Cubic	00-026-1481	35
C	Carbon	Hexagonal	00-041-1487	1
Si C	Silicon Carbide	Cubic	01-073-1708	65

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Si	Silicon	Cubic	00-026-1481	24
C	Carbon	Hexagonal	00-041-1487	1
Si C	Silicon Carbide	Cubic	01-074-2307	75



- Silicon carbide particle size and vacuum play a critical role.

Additive Manufacturing of Ceramic Matrix Composites: Technical Approach

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- Development of compositions and efficient mixing technologies for highly loaded polymer mixtures
- Study of viscosity and curing behavior

Pyrolysis of Prepreg Materials under various conditions

Characteristic decomposition patterns | Environmental Effects | Phase identification

Laser cut SiC woven fabrics and prepregs using various parameters

Severity and phase composition of the heat affected region

Composite Processing

Lay-up of prepregged fibers | Reduce processing steps | Evaluation of Properties

Evaluation of Laser Cutting Parameters for Silicon Carbide Fabrics and Prepregs

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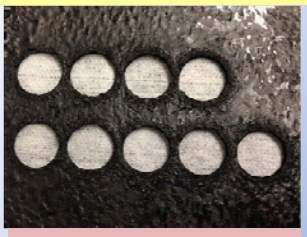
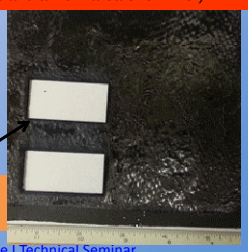
Prepregs for Composite Processing

- A number of SiC (Hi-Nicalon S, uncoated) fabrics (~6”x6”) were prepregged.
- These prepregs were used for optimization of laser cutting process.
- Baseline laser cutting data was also generated for different types of SiC fabrics (CG Nicalon, Hi-Nicalon, and Hi-Nicalon S)

Universal Laser System (Two 60 watt laser heads and a work area of 32”x18”)



SEM specimens cut with different laser power/speeds



Laser cut prepregs used for composite processing

Investigation of Laser Cutting Parameters (Hi-Nicalon S, 5HS Fabric)

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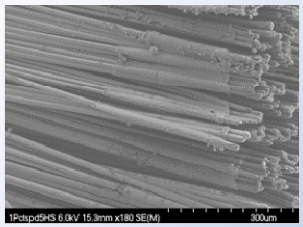
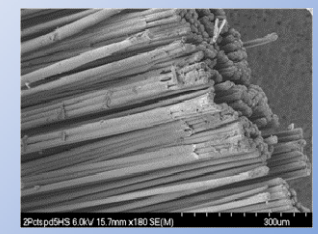
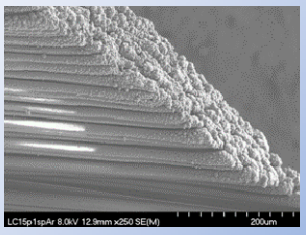


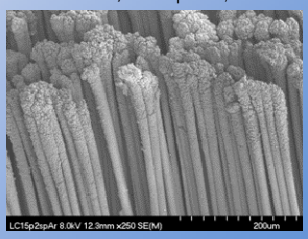
15% power, 1% speed, 1000 PPI



15% Power, 2% speed, 1000 PPI



15% power, 1% speed, 1000 PPI, Ar purge



15% power, 2% speed, 1000 PPI, Ar purge

Investigation of Laser Cutting Parameters (Hi-Nicalon S, 5HS Fabric and Prepreg)

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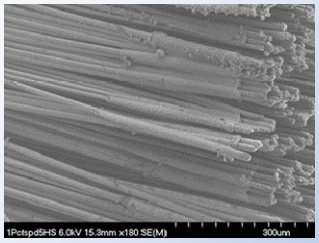
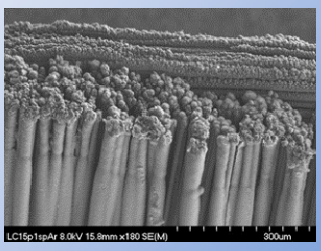
Fabrics

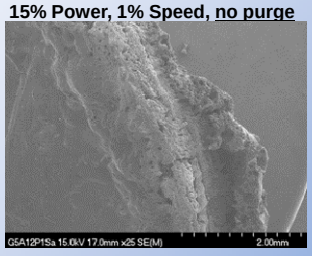


15% Power, 1% Speed, no purge

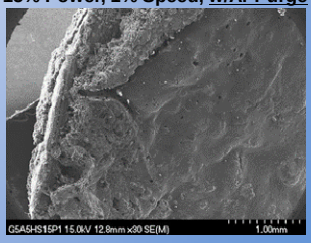


15% Power, 1% Speed, w/Ar Purge

Prepregs



12% Power, 1% Speed, no purge



15% Power, 1% Speed, no purge

Additive Manufacturing of Ceramic Matrix Composites: Technical Approach

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- Development of compositions and efficient mixing technologies for highly loaded polymer mixtures
- Study of viscosity and curing behavior

Pyrolysis of Prepreg Materials under various conditions

Characteristic decomposition patterns | Environmental Effects | Phase identification

Laser cut SiC woven fabrics and prepregs using various parameters

Severity and phase composition of the heat affected region

Composite Processing

Lay-up of prepregged fibers	Reduce processing steps	Evaluation of Properties

Processing of SiC/SiC CMCs Using Prepreg Lay-Up Approach

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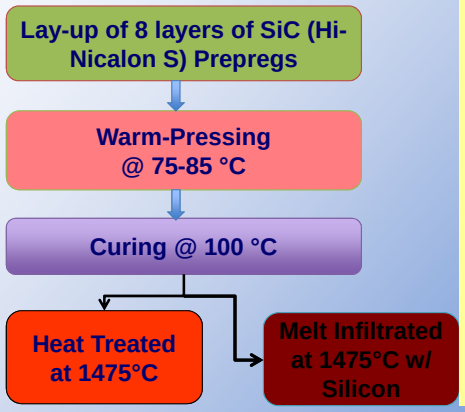
Formation of ceramic matrix composites using similar processing methods to those required for LOM processing using prepreg 5A Nano 2 + Si and Hi-Nicalon S fibers.



Key Observations:

- Carbon and SiC nanophase particles improve the distribution of various phases in the prepregs/ preforms.
- Solid state reaction of silicon and carbon is enhanced by uniform distribution of phases aided by nanosize particles.
- Melt infiltration process is highly exothermic and thick fiber coatings are required to protect fibers.

Microstructure of Green (Carbonaceous) Preforms Fabricated Using Prepregs

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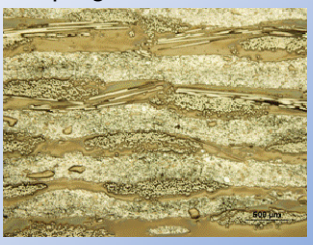
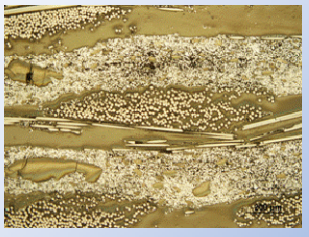
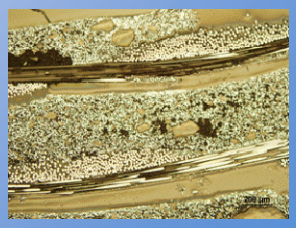
Fibers Used for Prepregs: SiC (Hi-Nicalon S Fibers, 5 HS weave)
Fiber Interface Coating: None
Prepreg Composition: Prepreg 5A Nano 2 + Si

Green Preforms:
8 layers of prepregs; warm pressed @75-85° C







Micrographs show good infiltration and distribution of carbonaceous phases, SiC, and Si in and around fiber bundles.

Microstructure of SiC/SiC Composites Fabricated Using Silicon Infiltration

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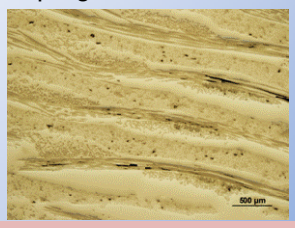
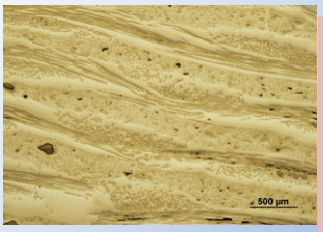
Fibers Used for Prepregs: SiC (Hi-Nicalon S Fibers, 5 HS weave)
Fiber Interface Coating: None
Prepreg Composition: Prepreg 5A Nano 2 + Si

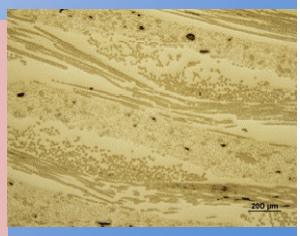
Green Preforms:
8 layers of prepregs;warm pressed @75-85° C



Silicon Infiltration:
1475 C, 30 minutes in vacuum



- Dense matrix after silicon infiltration. However, uncoated fibers are damaged due to exothermic Si+C reaction.
- Fiber coatings needed to prevent silicon reaction and provide weak interface for debonding and composite toughness.



Microstructure of SiC/SiC Composites Fabricated Using Heat Treatment

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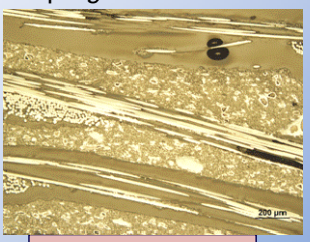
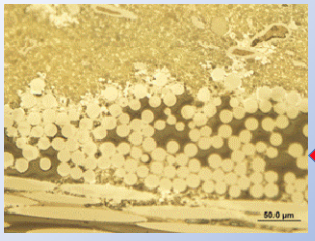
Fibers Used for Prepregs: SiC (Hi-Nicalon S Fibers, 5 HS weave)
Fiber Coating: None
Prepreg Composition: Prepreg 5A Nano 2 + Si

Green Preforms:
8 layers of prepregs;warm pressed @75-85° C

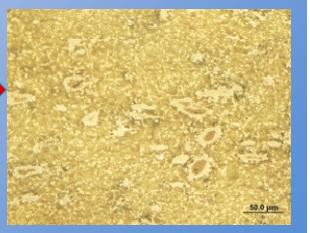


Heat Treatment:
1475° C, 30 minutes in vacuum



Micrographs show good distribution of SiC and Si phases.

Uncoated SiC fibers show no visible damage due to Si exothermic reaction.



Ongoing Activities in Phase 1 of the Project

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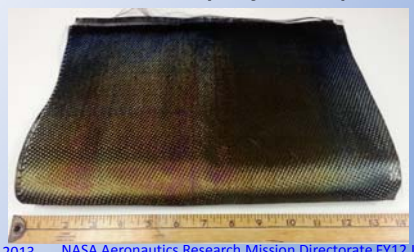
- Fabricate composites with coated Silicon Carbide (Hi-Nicalon S, 5HS weave) fibers and evaluate their mechanical properties (ongoing…).
- Further optimize the prepreg compositions suitable for scale-up, as needed.
- Finish two papers and presentations for the conference as well as the final project report.



Photograph of Mod-1 (BN/Si_3N_4) coated Hi-Nicalon S Fabric

Distribution/Dissemination of Results

NASA Aeronautics Research Institute

- **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" (Xhirley 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:**
  - Two papers in International Conference on Advanced Ceramics and Composites, Daytona Beach, FL (2014), which will be published by Wiley Blackwell and the American Ceramic Society.
  - LEARN final report and Journal paper.

Acknowledgments

NASA Aeronautics Research Institute

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