Additive Manufacturing of Silicon Carbide-Based Ceramic Matrix Composites:

Technical Challenges and Opportunities

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Outline

- Introduction and Background
- Technical Challenges
- Additive Manufacturing of SiC based Materials
    - Laminated Object Manufacturing
    - Binder Jet Printing
    - Wood Containing Filaments for Preforms
    - Powder Loaded Filaments/Paste Extrusion
  - New Efforts
    - NScrypt Machine
    - Polymer composites for multi-functional applications
- Summary and Conclusions

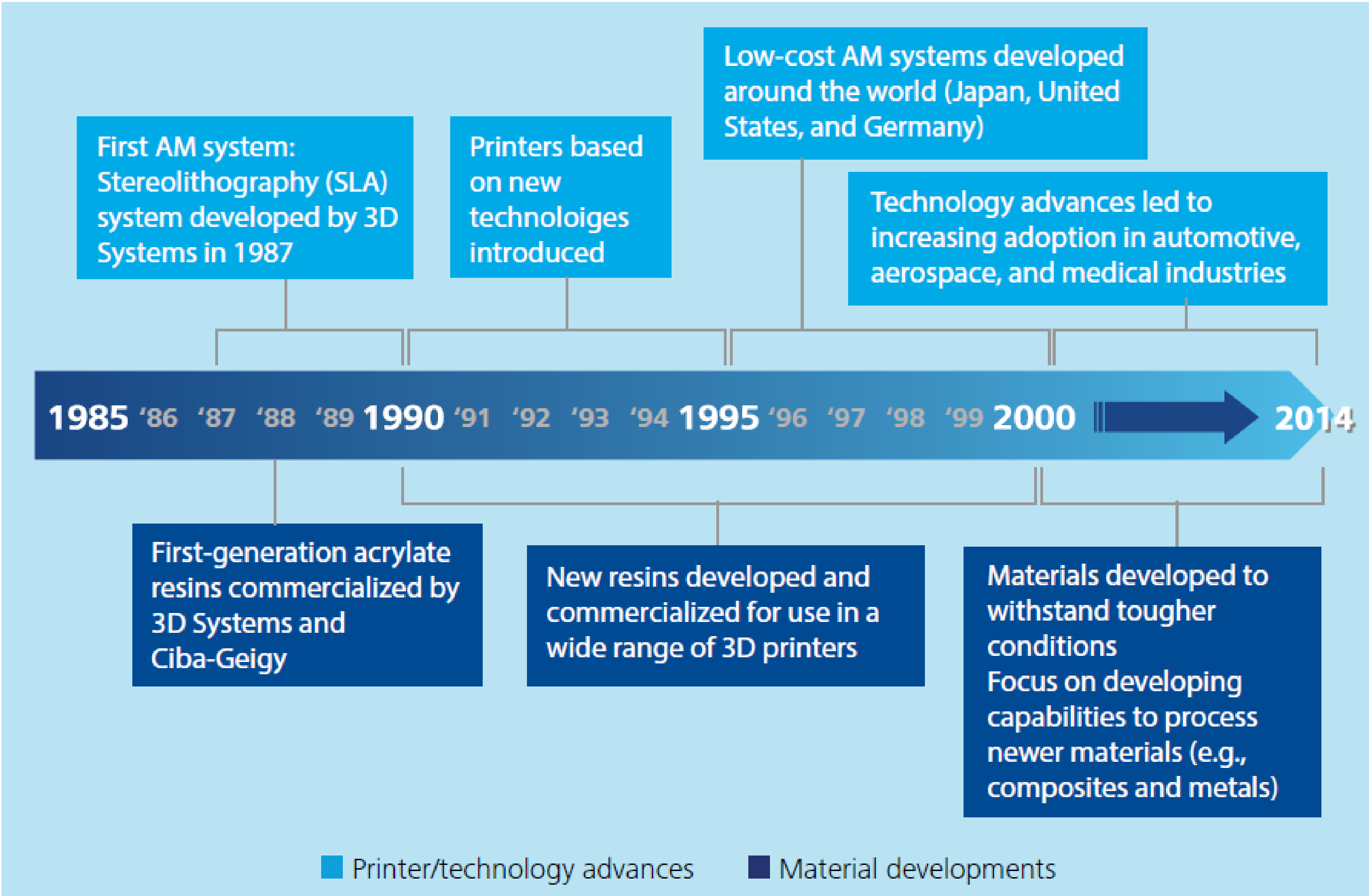
National Manufacturing Initiative and Role of Additive Manufacturing Technologies

Major Policy Milestones

Frank Gayle, AMNPO, NIST

Additive Manufacturing Technologies

Major Milestones



Source: Deloitte analysis; Wohlers Associates, *Additive manufacturing and 3D printing state of the industry*, 2012; The University of Texas at Austin, "Selective laser sintering, birth of an industry," December 7, 2012, http://www.me.utexas.edu/news/2012/0712_sls_history.php, accessed January 25, 2014.

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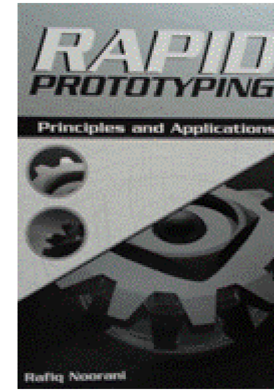
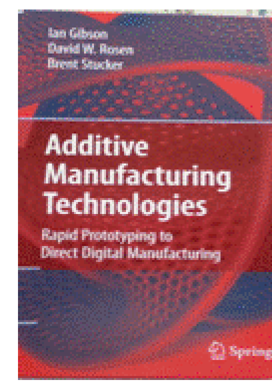


2006

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



2010

Layers Have Been Used Differently Through Cultures and Times…

- **Subtractive**
  - Material is successively removed from a solid block until the desired shape is reached (2.5M BC – Hominids)
- **Fabricative**
  - Elements or physical material are combined and joined (6,000 BC – Western Asia)
- **Formative**
  - Mechanical forces and, or heat are applied to material to form it into the desired shape such as bending, casting and molding (3,000 BC – Egyptians)
- **Additive**
  - Material is manipulated so that successive pieces of it combine to make the desired object (1984 – Californians)

Dr Phil Reeves – lead consultant, Econolyst

Potential Benefits of Additive Manufacturing

- Ease of Fabrication and Manufacturing

- Simplified formation matrix materials.
- Custom-made and complex geometries are possible which were previously limited by traditional CMC processing methods.
- Complex shapes involving the formation of curvatures and sharp part transitions can be fabricated.

- Tailorable Composition and Properties

- Hybrid composites can be fabricated by the manipulation of ceramic fiber preforms. Manual layer by layer assembly is time consuming and expensive.
- Fabrication of composites with multifunctional properties.

- Lower Cost

- Reduced cost through fewer processing steps and short production time from utilization of additive manufacturing.

Additive Manufacturing of CMCs

Conventional Manufacturing

- Customized parts in small volumes are time consuming and expensive to produce.
- Complex shape fabrication issues: mold design, dimensional tolerances, etc..
- Manufacturing of multifunctional parts are challenging.

Efforts in the last >30 years have now resulted in commercialized turbine engine applications.

Additive Manufacturing

- Small series of ceramic parts can be manufactured rapidly and cost-effectively.
- Specific molds are not required.
- Different designs can be optimized (no major cost of changes)
- Parts with significant geometric complexity.

Efforts in this very promising field are just now underway.

Material and Process Challenges

- Property and behavior of starting materials
- Sintering and densification challenges
- Process modeling
- Mechanical behavior
- NDE and in-situ damage characterization
- Material and property databases

Materials and processing challenges are quite similar

Largest barrier to CMC insertion has been high acquisition cost

For AM, the starting materials are very low cost (powders and fibers)

Overview of Additive Manufacturing Technologies

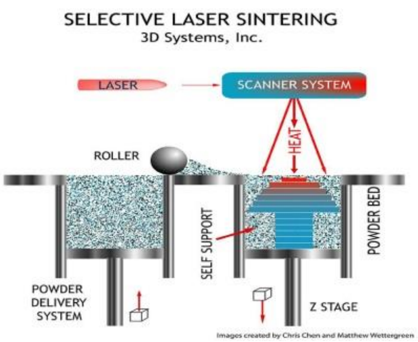
(many variants and combinations)

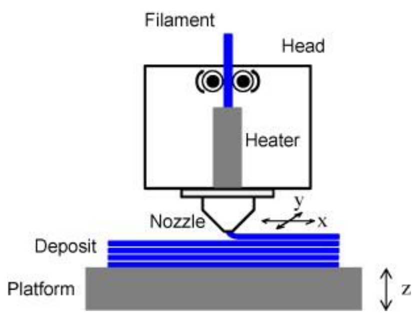
Selective Laser Sintering

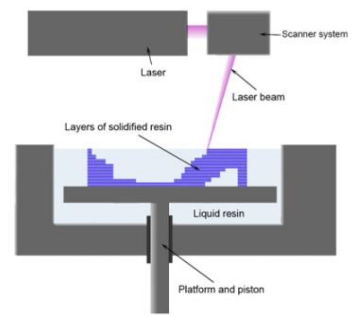
High powered laser fuses plastic, metal, or ceramic powders by moving along cross-sections repeating the process upon the addition of powder.

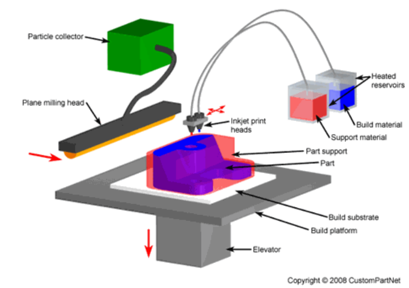
Stereolithography

A beam of ultraviolet light is directed onto a vat filled with a liquid ultraviolet curable photopolymer and moves along cross-sections of the object.









Fused Deposition Modeling

Plastic or metal is heated and supplied through an extrusion nozzle and deposited in a path determined by a CAD model.

Binder Jet 3D Printing

An inkjet-like printing head moves across a bed of powder and deposits a liquid binding material in the shape of the object's cross section

Material choices are limited by the machine's manufacturers
Fabrication of continuous fiber composites is not possible

Current Approaches for Manufacturing of Ceramic Matrix Composites

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)

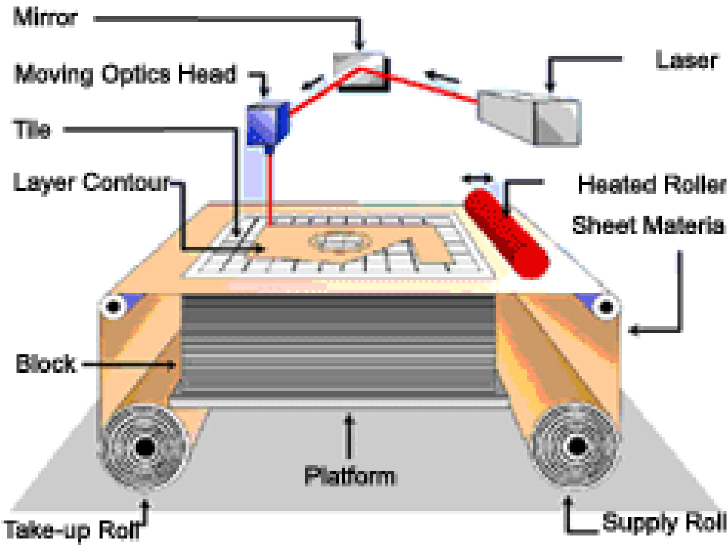
→ **Coating and Finishing**
NDE

Laminated Object Manufacturing of Ceramic Matrix Composites (NASA LEARN Project by OAI)

- **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 adhered 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

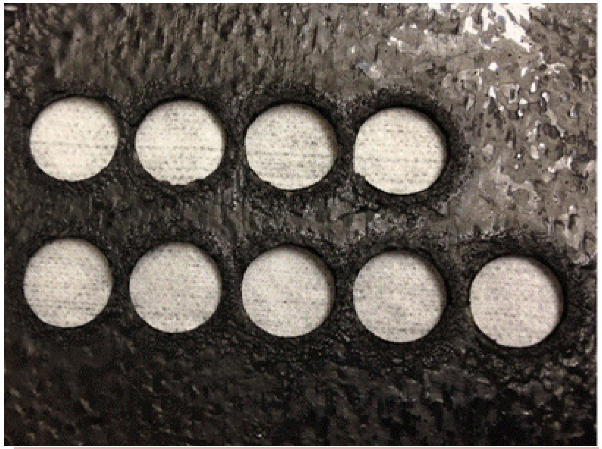
New CMC prepreg material development and characterization is a critical step

Evaluation of Laser Cutting Parameters for Silicon Carbide Fabrics and Prepregs

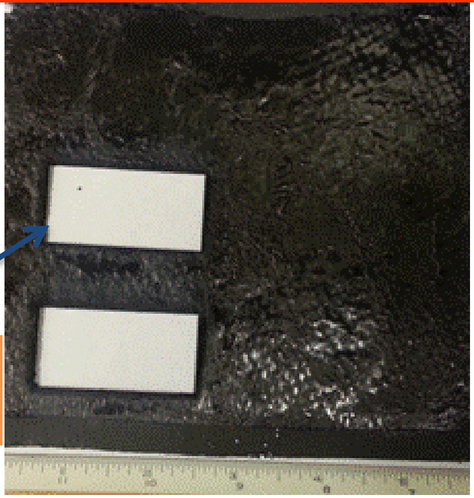
Prepregs for Composite Processing

- 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")



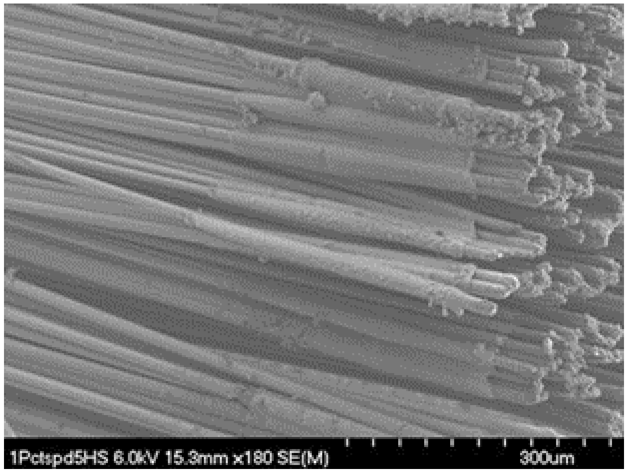
SEM specimens cut with different laser power/speeds



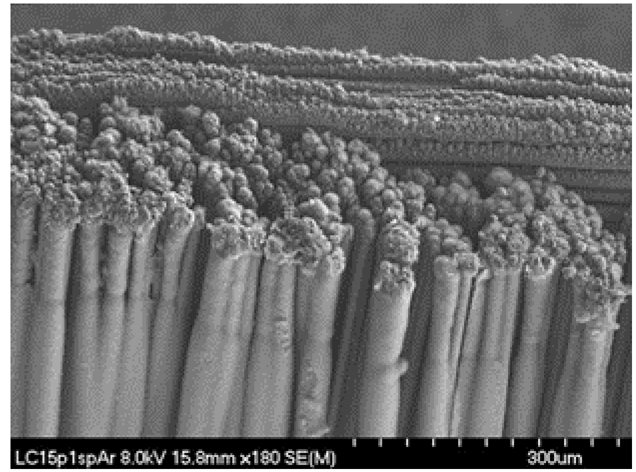
Laser cut prepregs used for composite processing

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

Fabrics

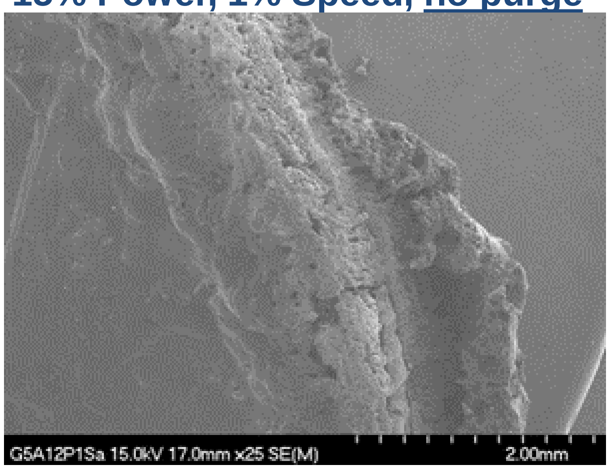


15% Power, 1% Speed, no purge

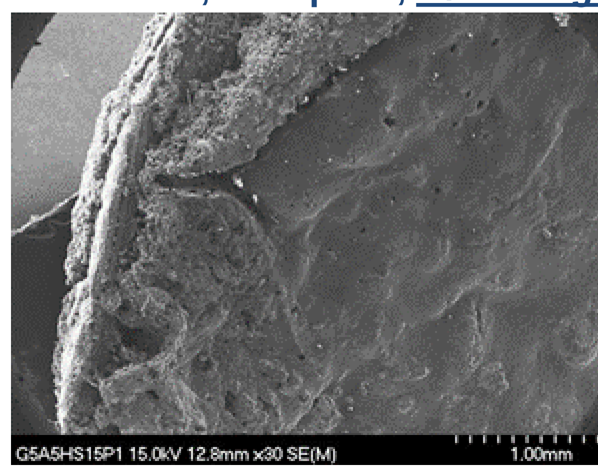


15% Power, 1% Speed, w/Ar Purge

Prepregs



12% Power, 1% Speed, no purge

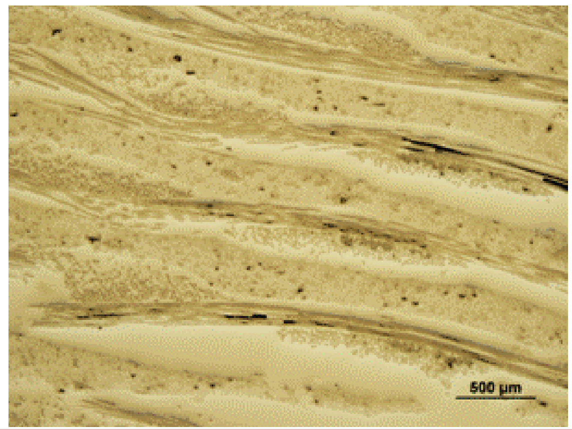


15% Power, 1% Speed, no purge

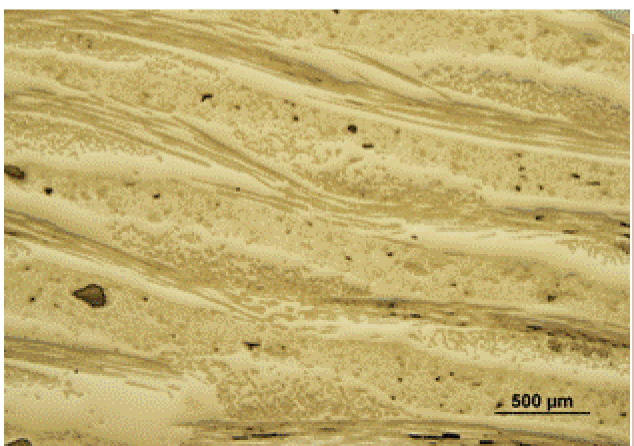
Microstructure of SiC/SiC Composites Fabricated Using Silicon Infiltration

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

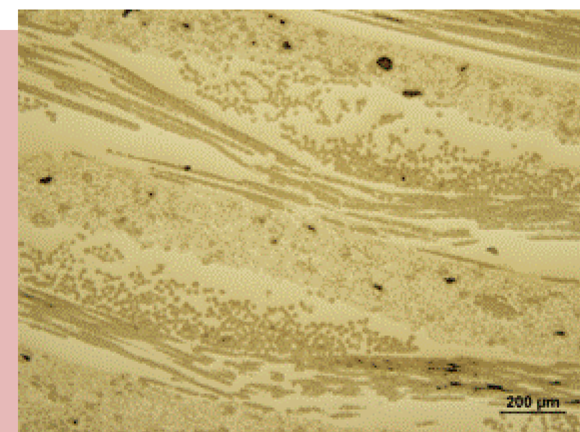
Green Preforms:
8 layers of prepregs; warm pressed @75-85°C



Silicon Infiltration:
1475 C, 30 minutes in vacuum



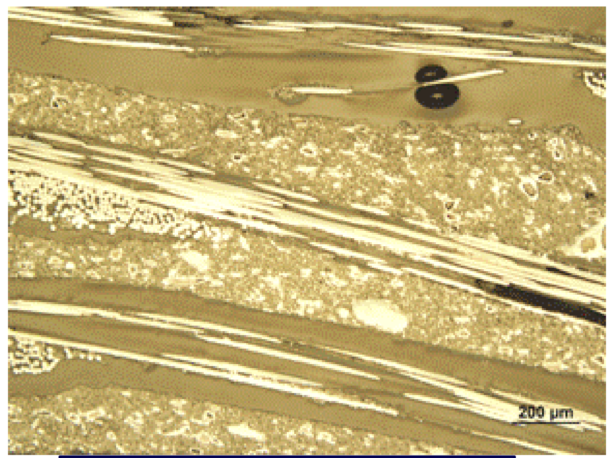
- Dense matrix after silicon infiltration. However, uncoated fibers are damaged due to exothermic Si+C reaction.
- Fiber coatings needed to prevent silicon reaction and provide weak interface for debonding and composite toughness.



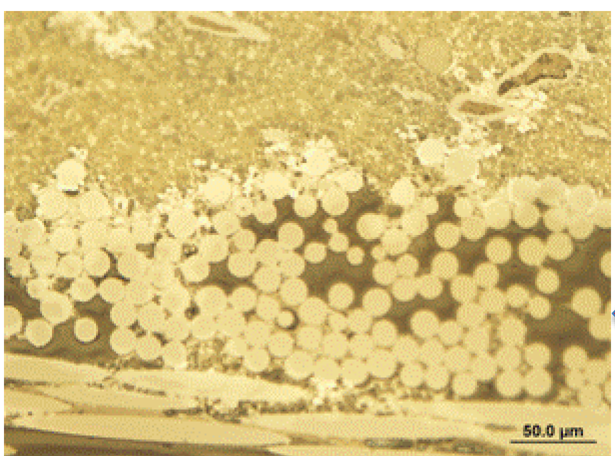
Microstructure of SiC/SiC Composites Fabricated Using Single Step Reaction Forming Process

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

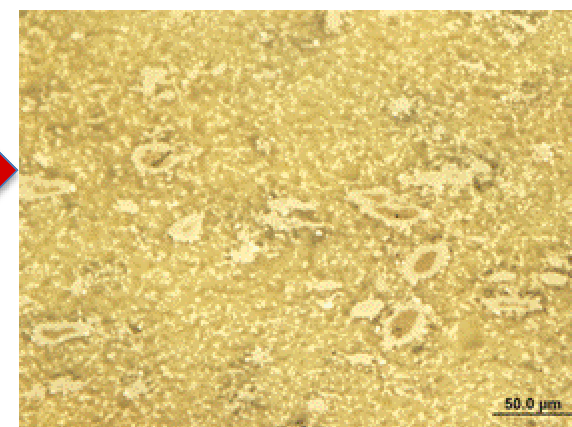
Green Preforms:
8 layers of prepregs; warm pressed @75-85°C



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.

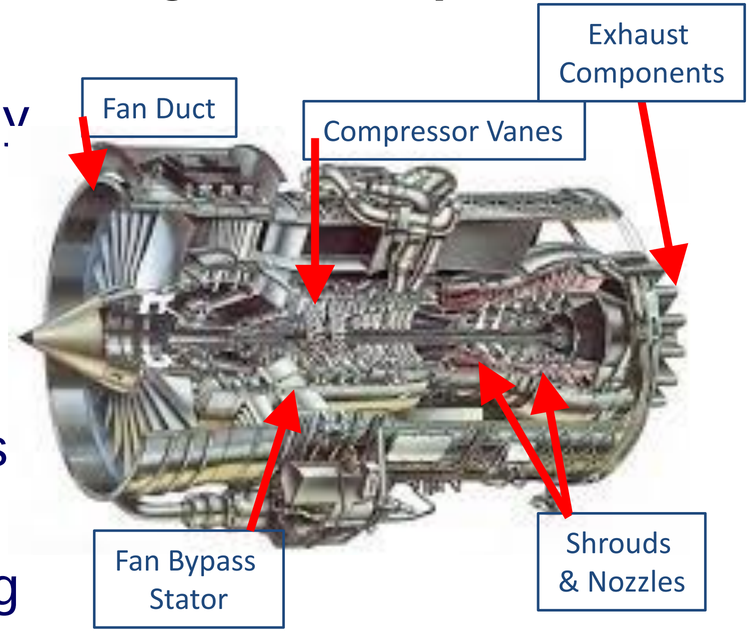
Non-Metallic Turbine Engine Project

TEAM: NASA GRC, OAI, Honeywell Aerospace, RP+M, NASA LaRC

Objective: Conduct the first comprehensive evaluation of emerging materials and manufacturing technologies that will enable fully non-metallic gas turbine engines.

- Assess the feasibility of using additive manufacturing technologies to fabricate gas turbine engine components from polymer and ceramic matrix composites
    - Fabricate and test prototype components in engine operating conditions
- Conduct engine system studies to estimate the benefits of a fully non-metallic gas turbine engine design in terms of reduced emissions, fuel burn and cost

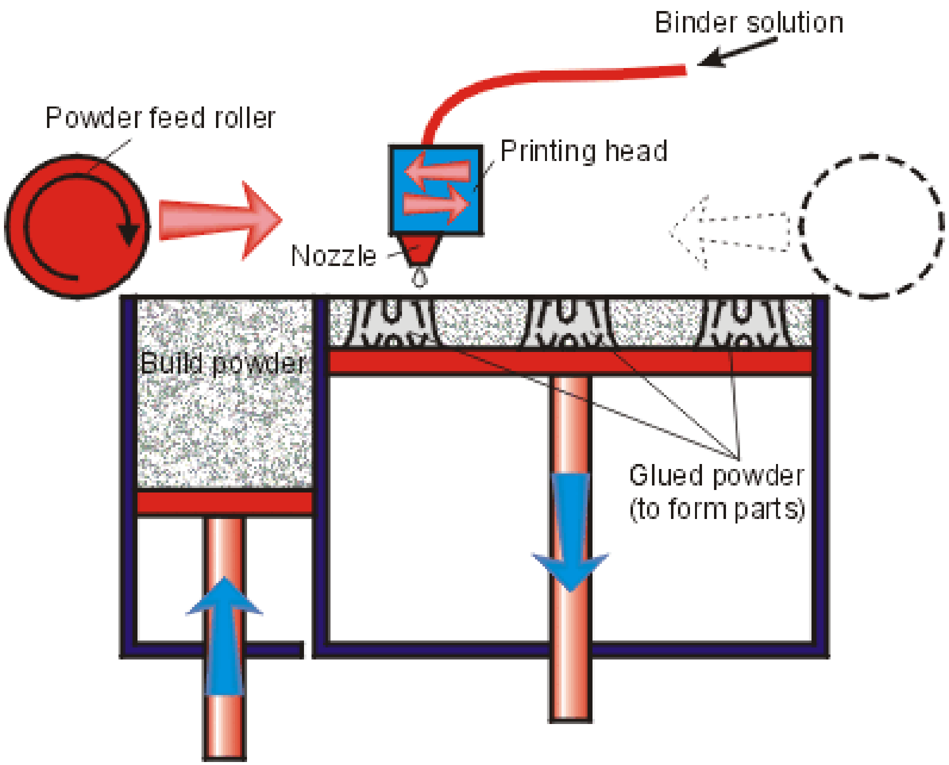
Targeted Components

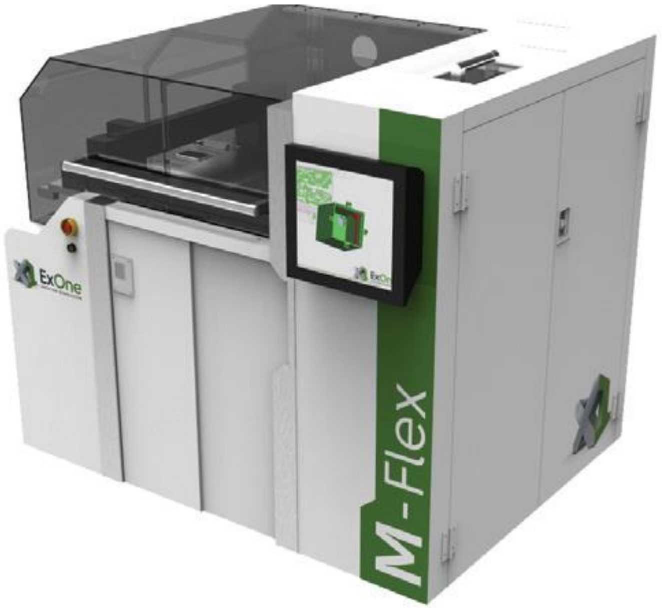


Business Jet size turbofan

Additive Manufacturing of Ceramics using Binder Jet Printing Technologies

In Collaboration with rp+m





ExOne's M-Flex print machine

Binder Jet printing

An inkjet-like printing head moves across a bed of powder and deposits a liquid binding material in the shape of the object's cross section

Binder jet printing capability will allow for powder bed processing with tailored binders and chopped fiber reinforcements for advanced ceramics.

Approach for Additive Manufacturing of CMCs

Processing

- Constituents
  - <u>SiC powders</u>: Carborex 220, 240, 360, and 600 powders (median grain sizes of 53, 45, 23, and 9 microns respectively). Used solely and in powder blends
  - <u>Infiltrants</u>: SMP-10 (polycarbosilane), SiC powder loaded SMP-10, phenolic (C, Si, SiC powder loaded), pure silicon
  - <u>Fiber reinforcement</u>: Si-TUFF SiC fiber; 7 micron mean diameter x 65-70 micron mean length, 350 GPa Modulus
  - Optimization of powder spreading and bimodal distributions of powders is critical

Microstructure

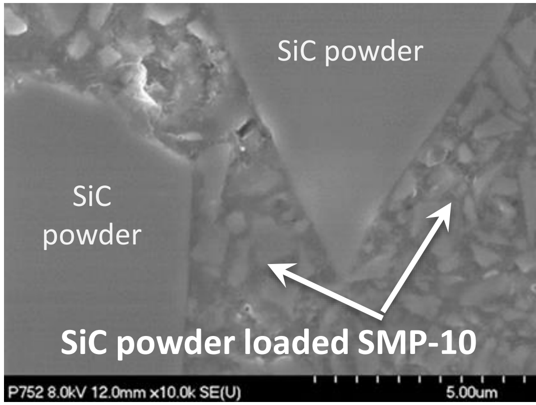
- Optical microscopy
- Scanning electron microscopy

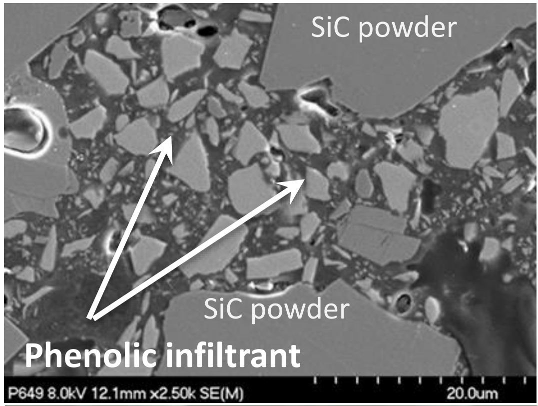
Properties

- Material density (as-manufactured and after infiltration steps)
- Mechanical properties: 4-point bend tests

Processing, microstructure, and property correlations provide an iterative process for improving the CMC materials.

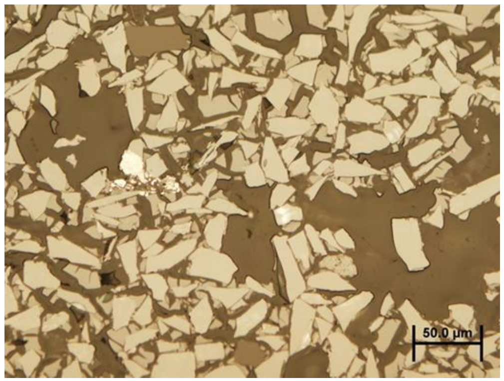
Constituents

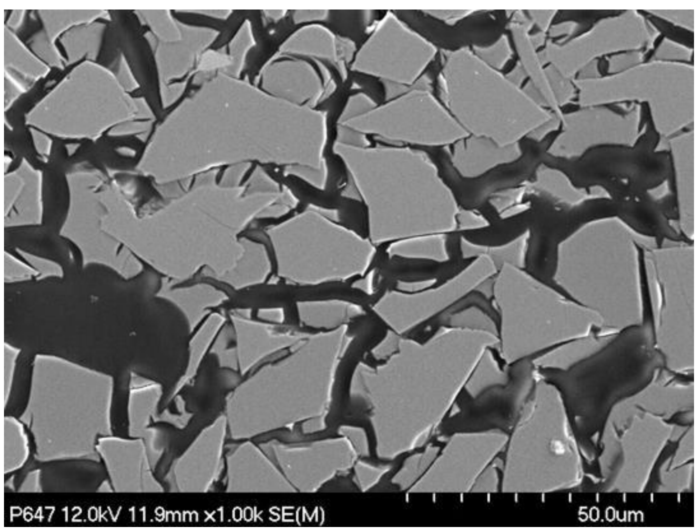




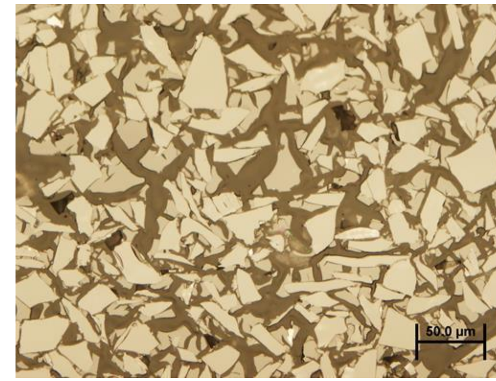
Microstructure of Silicon Carbide Preforms

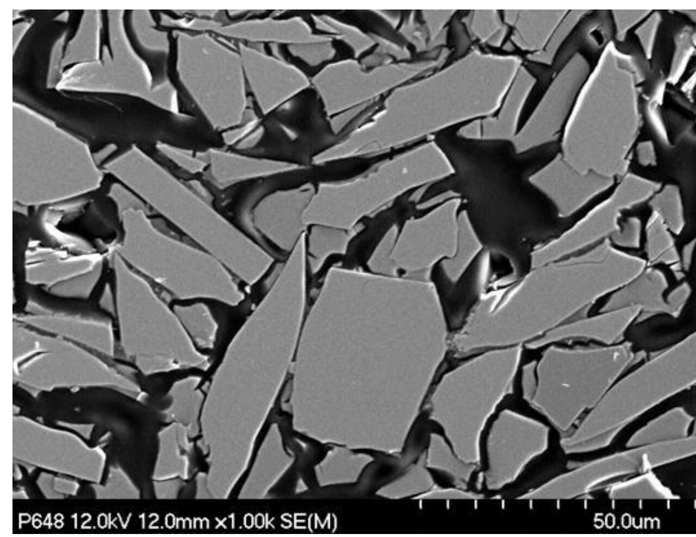
Carborex 240 SiC Powders with SMP-10 Infiltration



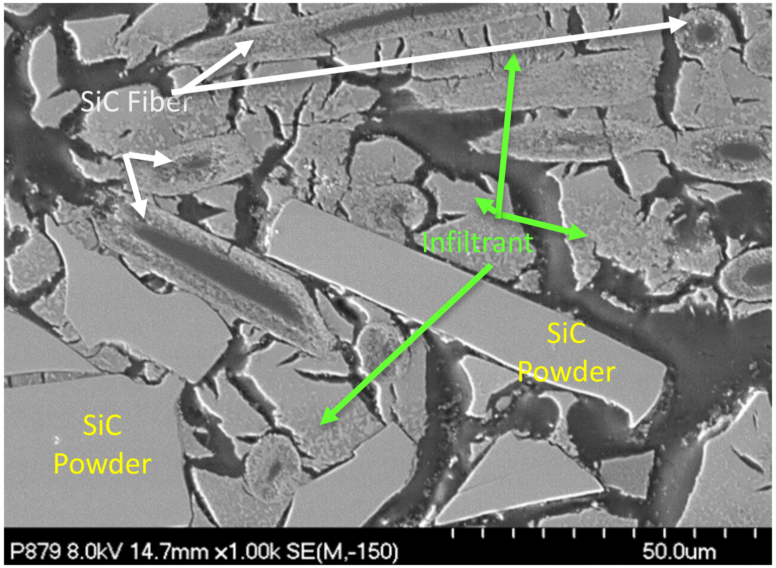


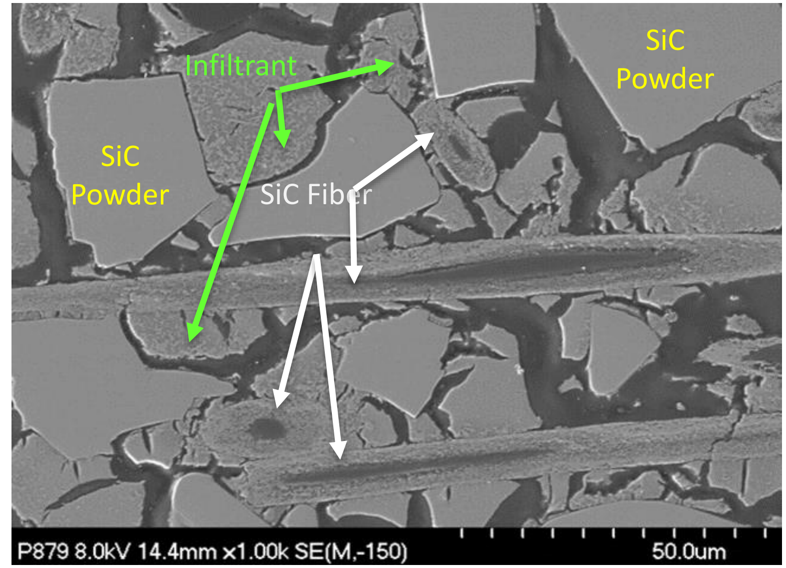
Carborex 360 SiC Powders with SMP-10 Infiltration

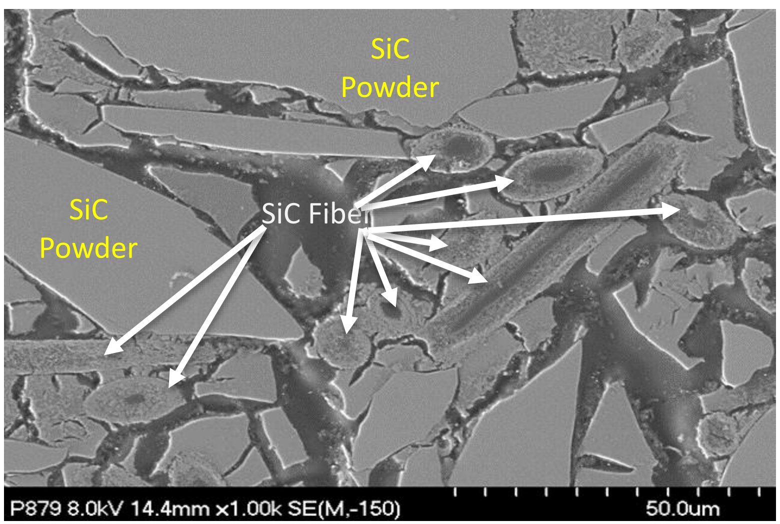




Fabrication and Microstructure of SiC Fiber Reinforced CMCs



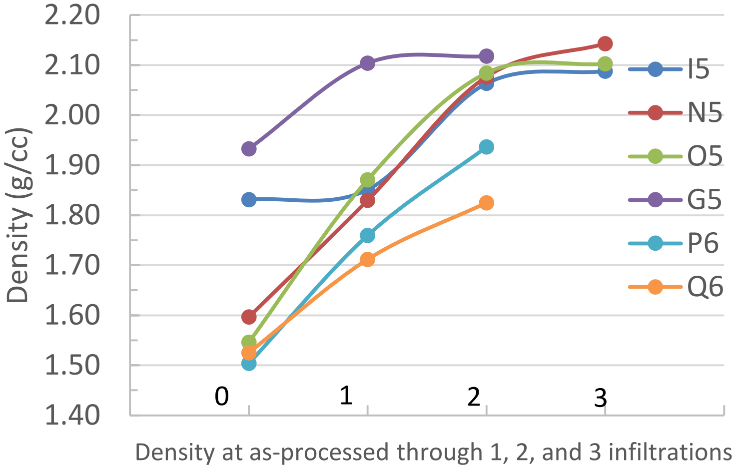




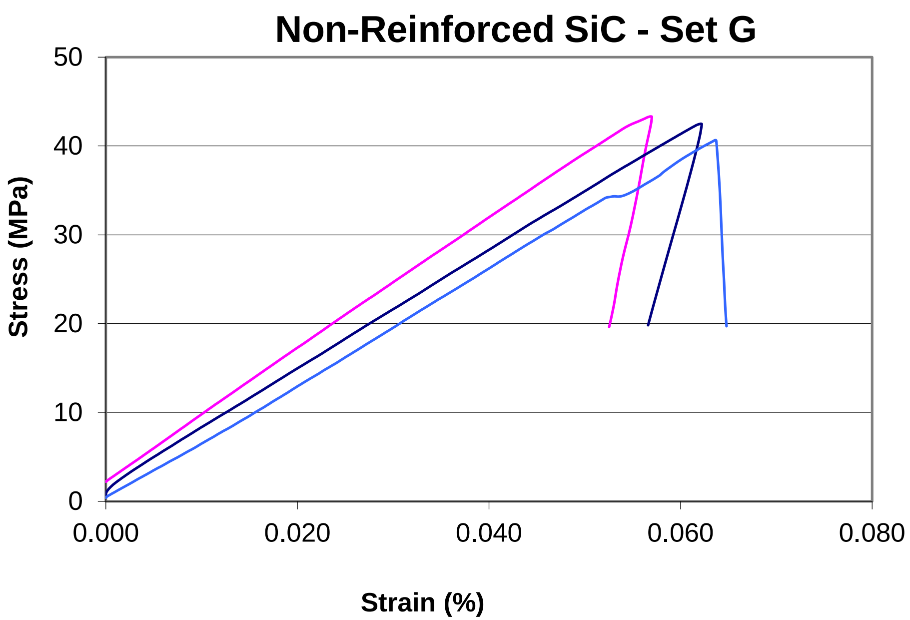
Different views of are shown of a CMC coupon with 35 vol% SiC fiber loading and infiltrant with smaller SiC powders.

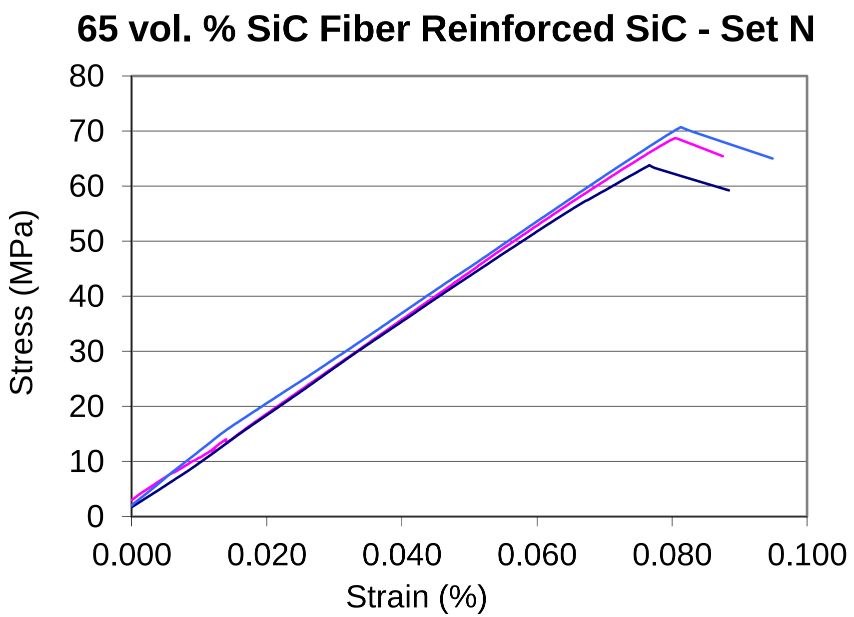
- ***Higher density observed due to powder loaded infiltrant***
- ***Good distribution and non-preferred orientation of SiC fibers is observed.***

Mechanical Properties of SiC and CMC Materials at RT and 1200°C

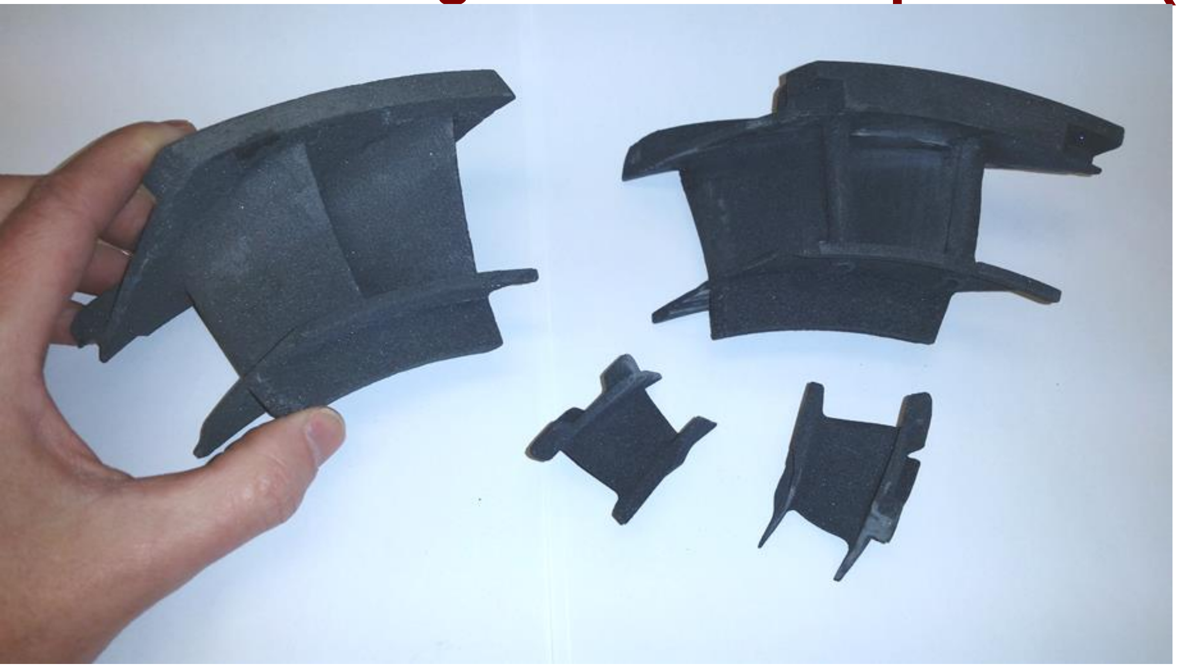


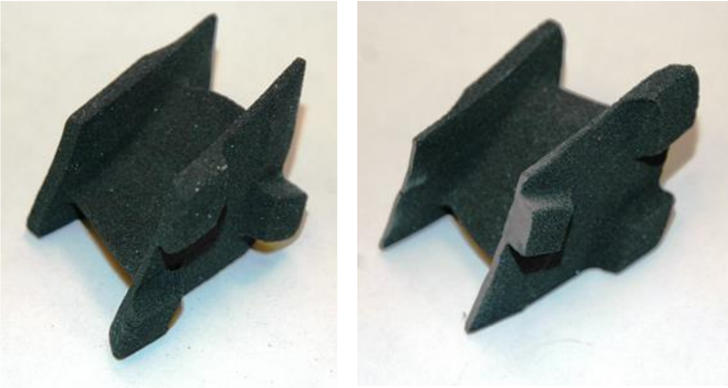
The fiber loaded SiC materials had significantly higher stresses and higher strains to failure.





Demonstration of the Additive Manufacturing of Turbine Engine CMC Components (20 vol.% SiC Fiber)





First stage nozzle segments.

High pressure turbine nozzle segments: cooled doublet vane sections.

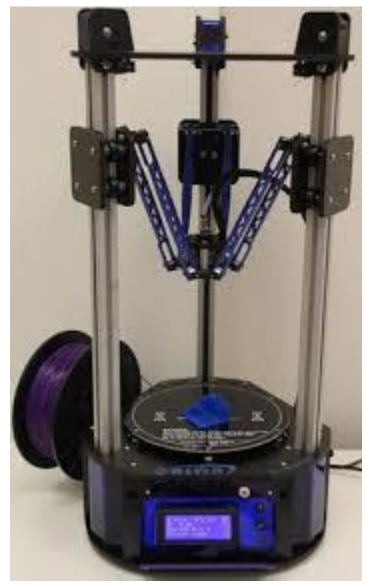
Additive Manufacturing of Ceramics using 3-D Printing Technologies

Develop and characterize feed materials for 3-D printing of silicon carbide (SiC)-based ceramics.

3-D Printing Efforts

- Powder Loaded Filament - direct printing of ceramic parts
- Wood Containing Filament - provide preforms for densification
- Slurry Dispensing of Pastes - evaluate pastes for full conversion to dense SiC

MakerBot Replicator 2X



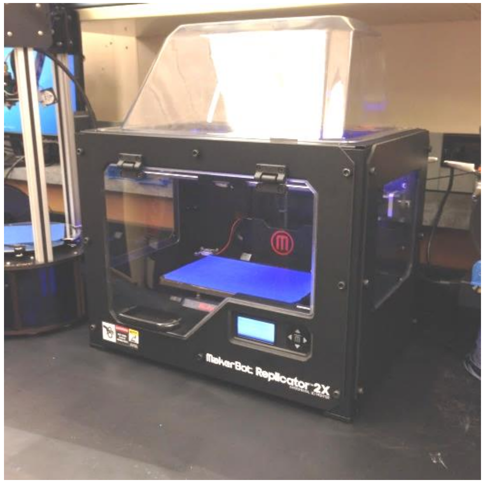
Orion Delta 3D Printer

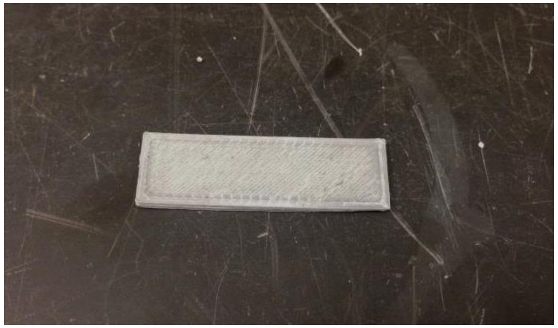
Rostock 3D Printer

These printers can print polymers with specific filaments
Ability to fabricate ceramics is being investigated

3-D Printing: Powder Loaded Filament

- **Green SiC ceramic filament was extruded for the 3-D printing.**





3-D Printed Sample

3-D Printing: Wood Containing Filament Parts for Ceramic Preforms and Conversion

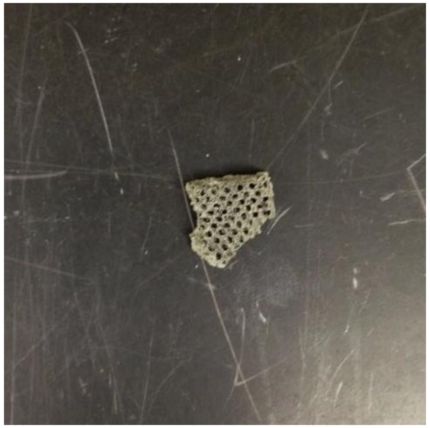
A 3-d printed disc is made using a commercially available wood filament. Printed part is pyrolyzed to serve as a preform.

Procedure:

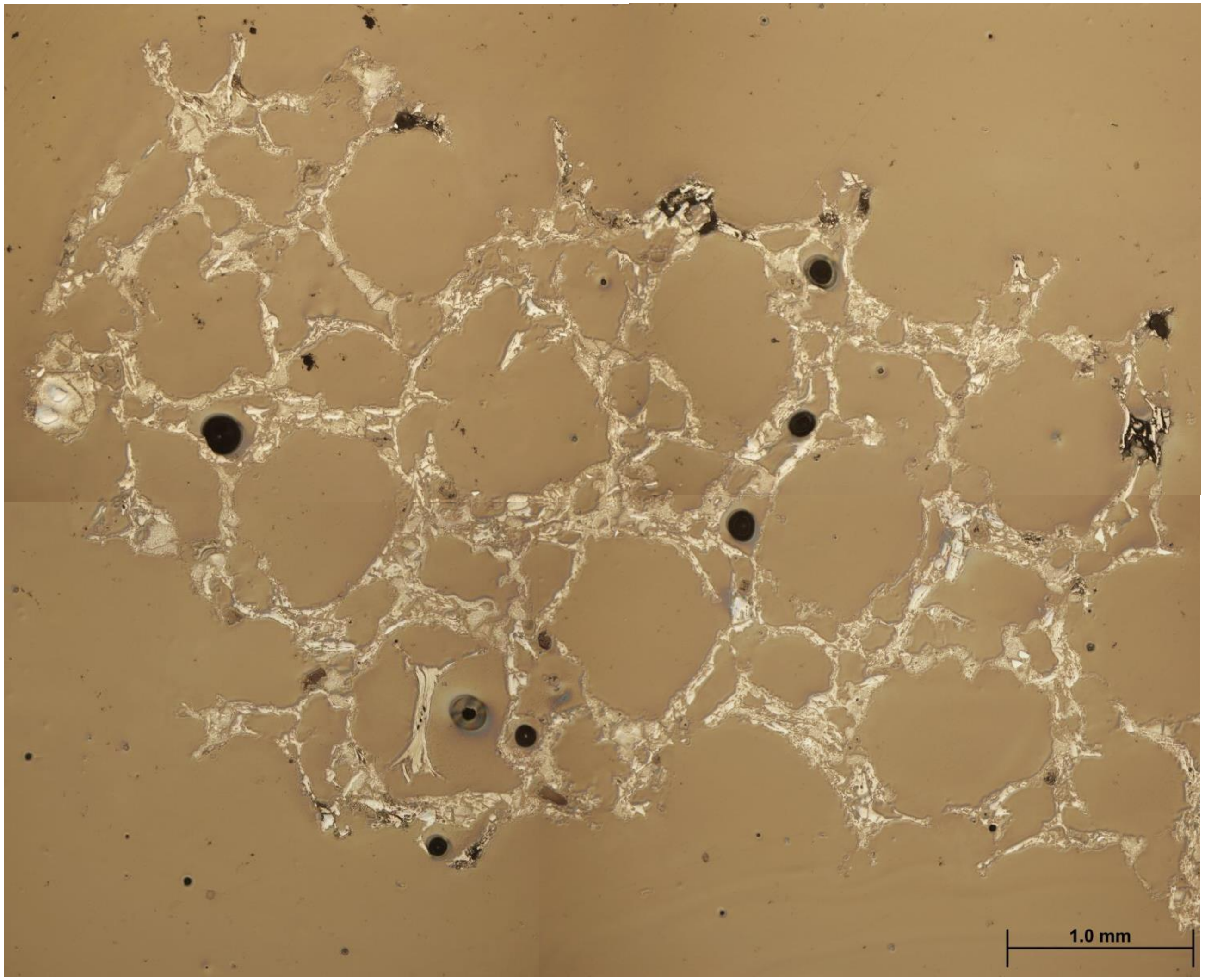
3-D printed porous disc → Dip-coated in Polycarbosilane (PCS) solution → Heat treated at 400°C in argon → Dip-coated in PCS solution → Exposed to 1000°C in argon → Pyrolyzed at 1450°C in vacuum

35%
wt. Retention

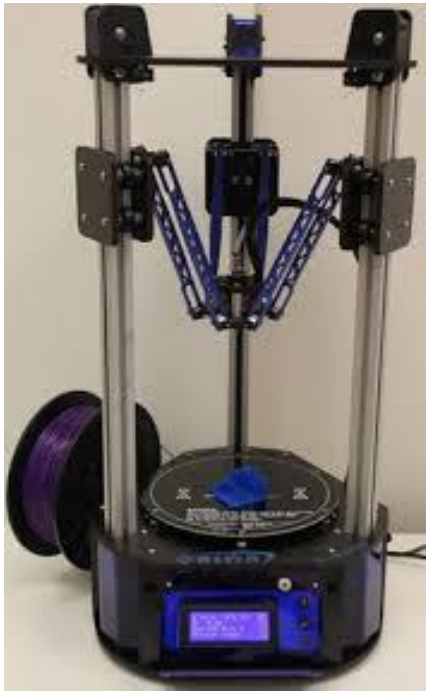
50%
wt. Retention



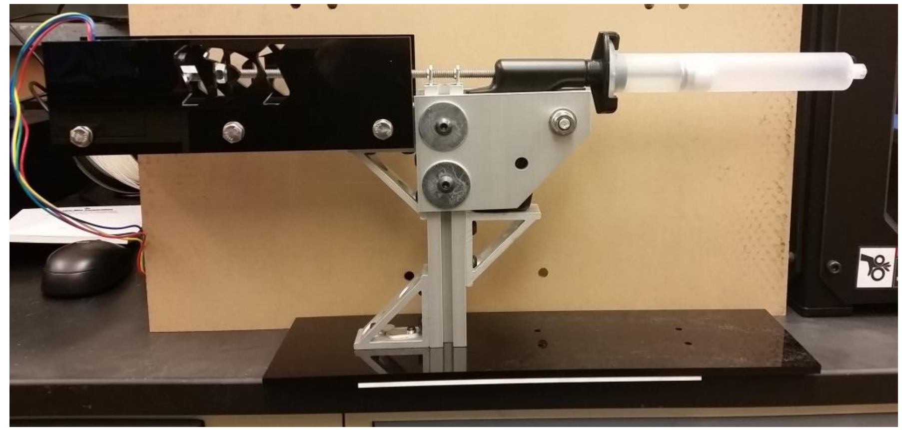
Wood Containing Filament – PCS/SiC then PCS –1450°C



3-D Printing: Slurry Dispensing of Pastes



Orion Delta 3D Printer

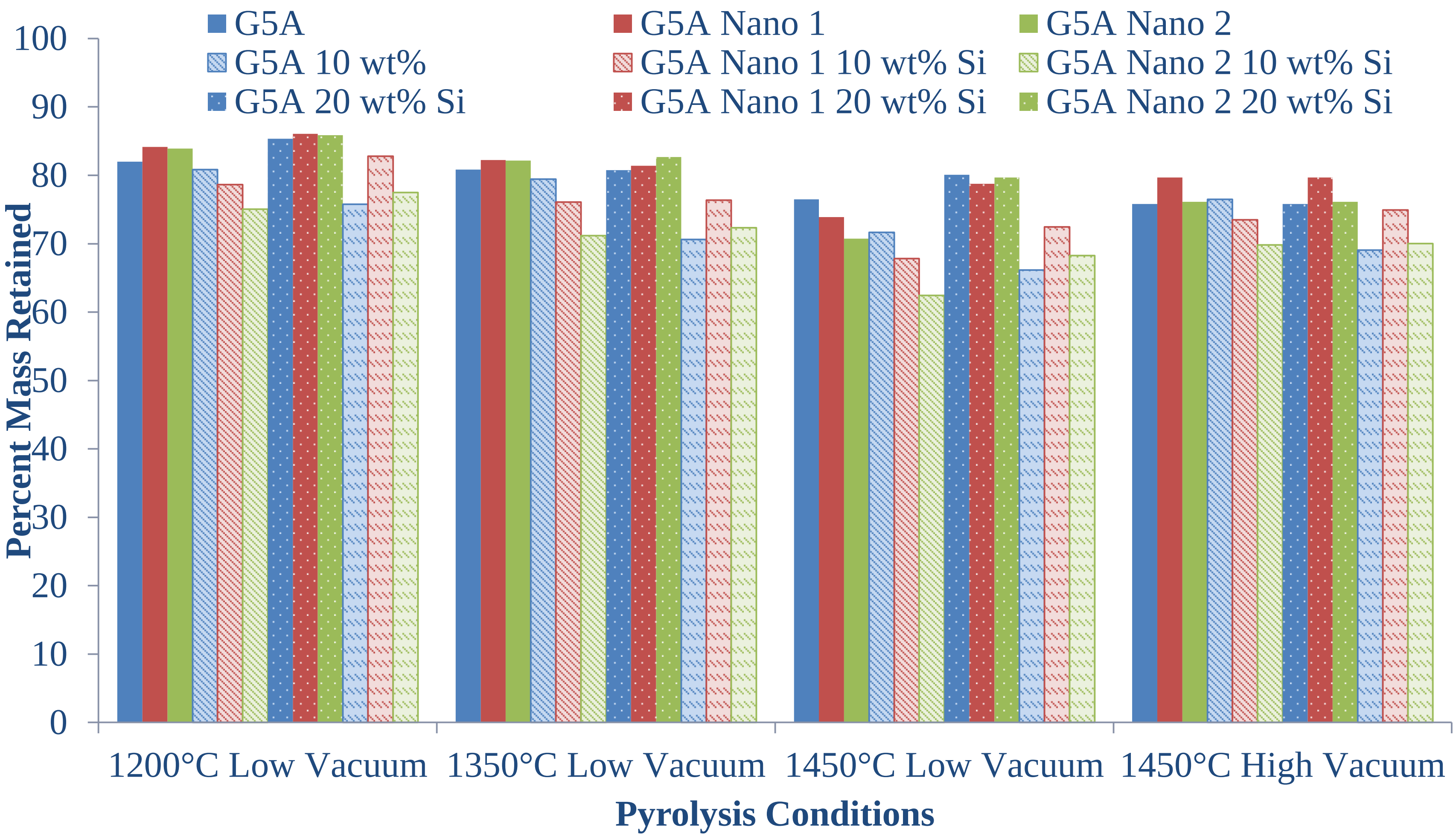


Design of Silicon Carbide Based Material System for Additive Manufacturing

G5A, G5A Nano 1, G5A Nano 2 - in descending order of SiC particle size

- **Carbon**
  - Carbon Sources
    - Solid, liquid
- **SiC**
  - Particle Size Effect
    - Micro and Nano sizes (Nano 1 and Nano 2)
- **Silicon**
  - Particle Size Effect
  - Weight Percent Effect
- **Surface Modifiers**
  - Surfactants
  - Dispersants
  - Coupling agents

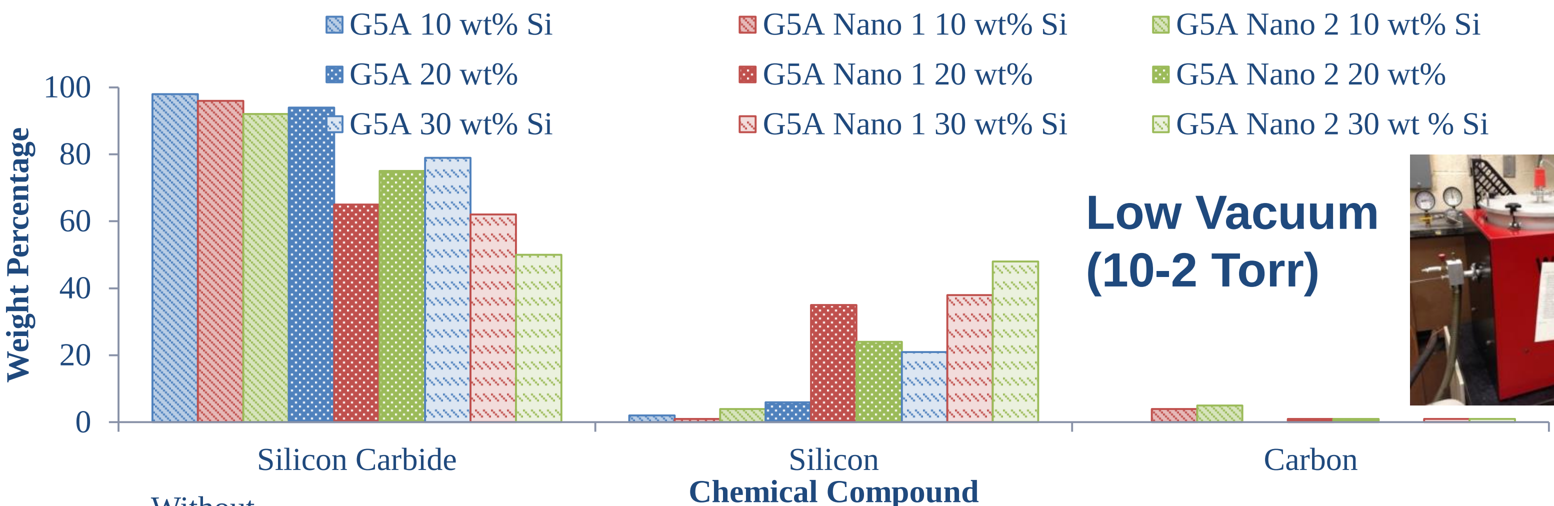
Weight Retention of Pre-Ceramic Pastes



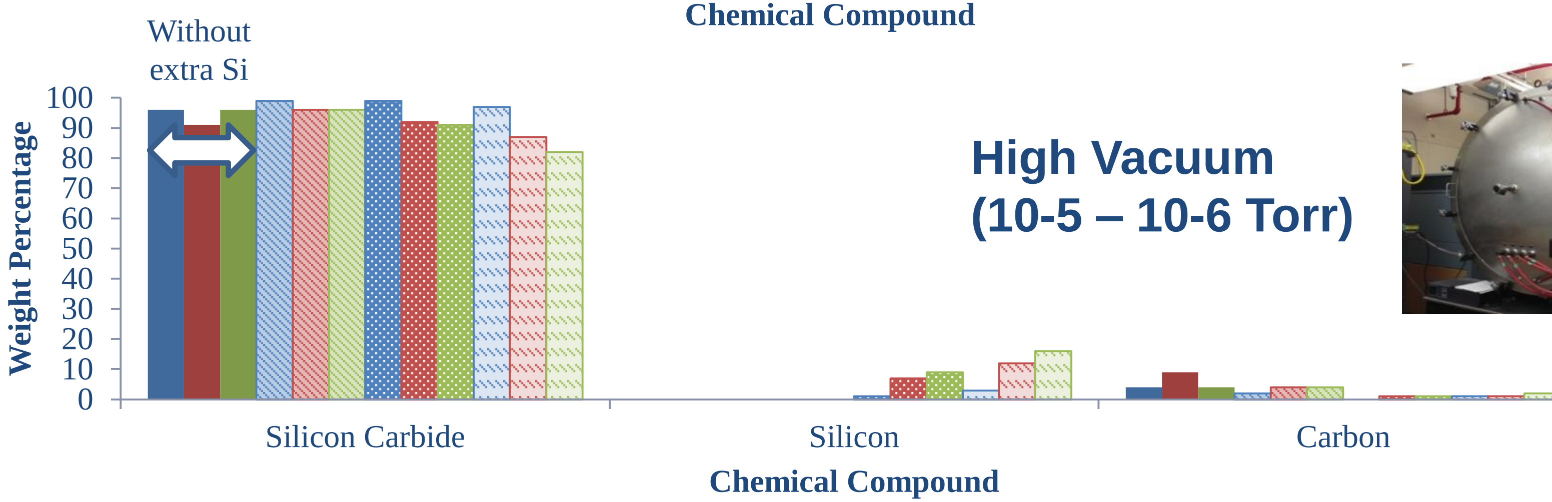
Weight retention values are promising for all samples → secondary infiltration steps may not be necessary

Weight loss trends found in furnace weight loss studies similar to TGA data

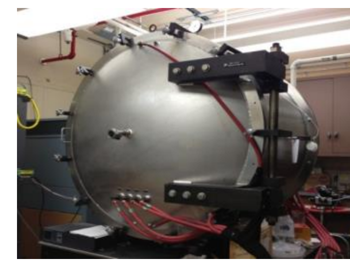
Chemical Composition of Heat-treated Pastes at 1450°C (from X-Ray Diffraction Analysis)



Low Vacuum (10-2 Torr)



High Vacuum (10-5 – 10-6 Torr)



- **All compositions after pyrolysis show a high yield of SiC.**
- **Vaporization of Si occurs in vacuum due to its high vapor pressure.**

Additive Manufacturing of Electric Motors

(Ultra-Efficient Commercial Vehicles and Transition to Low Carbon Propulsion)

NScrypt 3D Printer

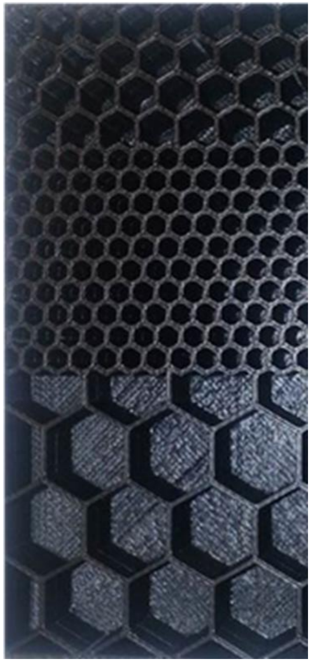
Micro Dispense Pump 3D Direct Printing Systems

- *Ability to host up to four separate materials and print on curved surfaces or print 3D structures.*
- Motion control accuracy of ±5 microns and repeatability of ±2 microns in XY Micro-dispensing pump has volume control of dispensed materials of 100 picoliters.
- Ability to print a wide variety of ceramic pastes (structural and functional), electronic pastes, adhesives, solders, bio-materials.

Additive Manufacturing of Polymer Composites for Multifunctional Applications

Potential Missions/Benefits:

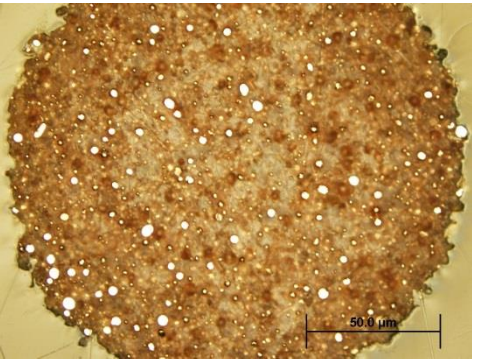
- **On demand fabrication of as needed functional components in space (ISS, in-orbit manufacturing)**
- **Tailored, high strength, lightweight support structures that are reinforced with CNT for lightweight multifunctional aerospace structures (e.g., thermal management with structural capability, solar panels with structural capability, habitat structures)**
- **Tailored facesheets for functional properties, i.e. *wear resistance, vibration dampening, radiation shielding, acoustic attenuation, thermal management***



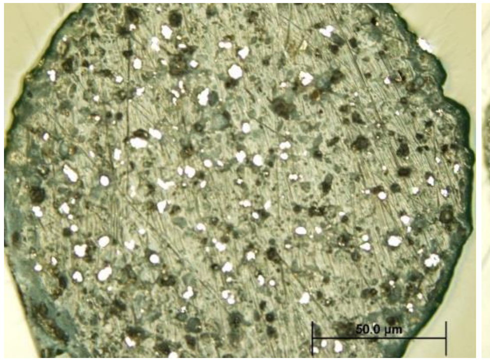
Microstructures and coupon properties being evaluated

- Color Fab, bronze fill metal, PLA
- GMASS, Tungsten, ABS
- Proto Pasta, Magnetic iron, PLA
- 3DXTech, premium red, ABS
- 3DXNano ESD (CNT) black, ABS
- Homemade ABS, (200C)
- SeeMeCNC ABS natural
- Color Fab, copper fill metal, PLA
- GMASS, Bismuth, ABS
- Proto Pasta, Stainless Steel, PLA
- 3DXTech, black, ABS
- Carbon Fiber 5 wt%, ABS
- wood containing filament
- iglidur, I180-PF Tribo Filament

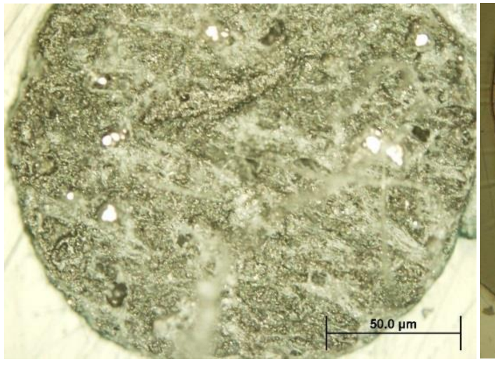
3-D Printing of Multi-Functional Materials



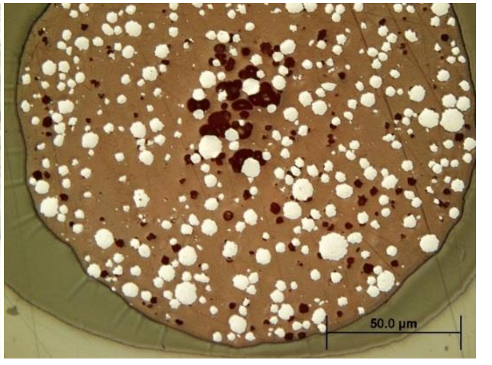
Color Fab, copper fill metal, PLA



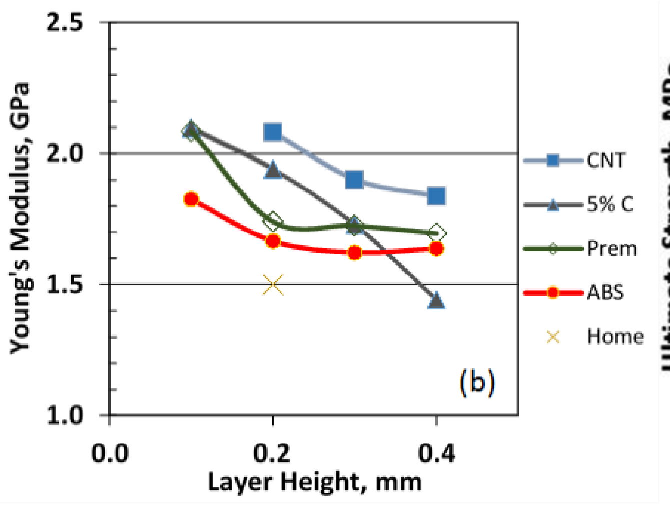
Proto Pasta, Magnetic iron, PLA

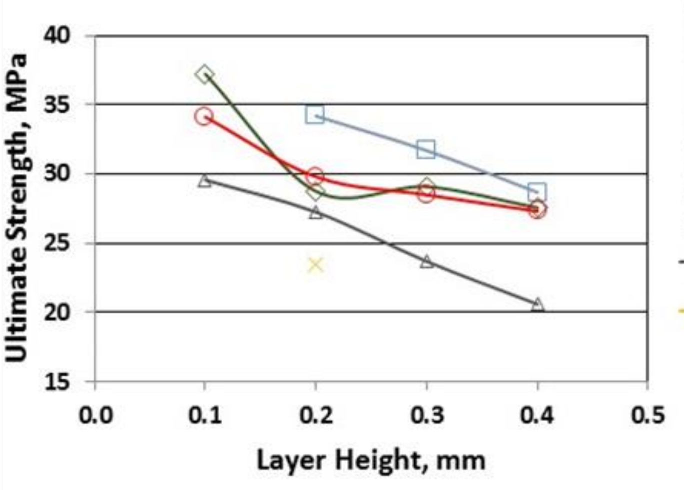


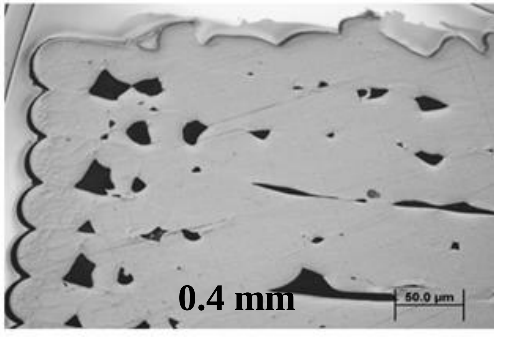
GMASS, Tungsten, ABS

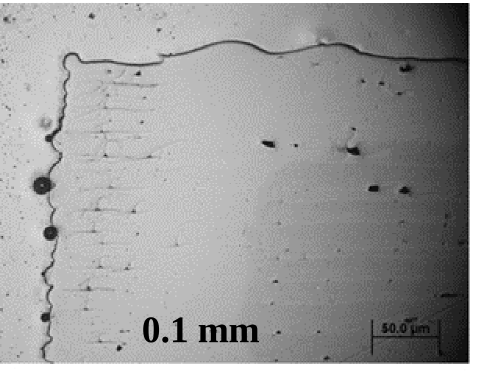


GMASS, Bismuth, ABS









Highest strength and modulus in CNT reinforced coupons
Pure ABS Coupons – less porosity for lower print heights

Summary and Conclusions

- Additive manufacturing can offer significant advantages in fabricating preforms, ceramics and CMCs.
- They will have to be selectively applied to "traditional" components but can also enable new applications.
- Good progress is occurring in binder jet printing and LOM.
- AM and 3-D printing of ceramics has the potential to be game changing.

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