Laser 3D Printing of SOFCs

Project ID: FE069-p

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Laser 3D Printing of SOFCs

DoE SBIR Phase II DE-SC0015199 (04/10/2017 - 04/09/2019)

14b. Additive Manufacturing for Solid Oxide Fuel Cell (SOFC) Components

Timeline and Budget

Direct 3D Femtosecond Laser Manufacturing of SOFC

• Project Start Date: 04/10/2017
• Project End Date: 04/09/2019
• Total Project Budget: $999K
  • Total DOE Funds Spent*: $426K as of 3/31/2018

Barriers

• Limited R&D on 3D printing of SOFC
• Challenge in multi-material AM
• Challenge in thickness control and interface quality

Partners

• Funded by DOE NETL
• Engaging with public companies for collaboration and potential investment, M&A.

Innovating 3D Manufacturing
SOFC AM Phase II Objectives

**Ni-YSZ**

**YSZ** (8 mol% \( \text{Y}_2\text{O}_3 \))

**LSM**: La0.8Sr0.2MnO3, (La0.8Sr0.2)0.98 MnO3, La0.85Sr0.15MnO3, (La0.85Sr0.15)0.98 MnO3, (LaxSr1-x)yMnO3

Key Objectives in Phase II:
- Multi-layer and multi-material additive manufacturing
- Subtractive manufacturing
- SOFC fabrication and test

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>Thickness</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Ni/YSZ</td>
<td>0.3-0.6 mm</td>
<td>~ 40%</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>YSZ</td>
<td>5-10 µm</td>
<td>&lt; 5%</td>
</tr>
<tr>
<td>Cathode</td>
<td>Conducting ceramic</td>
<td>10-50 µm</td>
<td>~ 30%</td>
</tr>
</tbody>
</table>
fs Fiber Laser Based AM Setup

Electrical control schematic

Innovating 3D Manufacturing
Phase II Major Milestones

<table>
<thead>
<tr>
<th>Item</th>
<th>Delivery Month</th>
<th>Major milestones</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>Experiment setup of AM for Ni-YSZ anode</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>Experiment results &amp; optimization of Ni-YSZ anode</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>Optimization of AM for YSZ-electrolyte</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>Optimization of Multi-layer anode and electrolyte</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>Make small fuel cell. Continuation application</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>Experiment results of SOFC fabrication, packaging, and thermal management. SM process optimization. Make small cells and do optimization</td>
</tr>
<tr>
<td>7</td>
<td>18</td>
<td>SOFC testing results and design scaling and optimization</td>
</tr>
<tr>
<td>8</td>
<td>21</td>
<td>Optimization of SOFC AM system and stabilizing the process</td>
</tr>
<tr>
<td>9</td>
<td>24</td>
<td>Prototype and marketing report</td>
</tr>
<tr>
<td>10</td>
<td>24</td>
<td>Publications</td>
</tr>
<tr>
<td>11</td>
<td>24</td>
<td>Final patent report on Phase II project</td>
</tr>
<tr>
<td>12</td>
<td>24</td>
<td>Wrap up all the deliverables</td>
</tr>
</tbody>
</table>
## Multi-layer YSZ AM Process

<table>
<thead>
<tr>
<th>Scanning Speed (mm/s)</th>
<th>Laser Power (W)</th>
<th>Image 1</th>
<th>Image 2</th>
<th>Image 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60 W</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td></td>
<td>90 W</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td></td>
<td>110 W</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

**Two layers YSZ AM**

**18 um thick YSZ on YSZ**

**After optimization**

**Innovating 3D Manufacturing**
Multi-layer Ni-YSZ AM and Optimization

<table>
<thead>
<tr>
<th>Layer</th>
<th>Power</th>
<th>Type</th>
<th>Tile Size</th>
<th>Spacing</th>
<th>Speed</th>
<th>Overlap</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>200W</td>
<td>Line</td>
<td>1</td>
<td>0.03</td>
<td>2000mm/s</td>
<td>0.5</td>
</tr>
<tr>
<td>2nd</td>
<td>200W</td>
<td>Line</td>
<td>2</td>
<td>0.03</td>
<td>4000mm/s</td>
<td>0.5</td>
</tr>
<tr>
<td>3rd</td>
<td>200W</td>
<td>Stripe</td>
<td>3</td>
<td>0.03</td>
<td>2000mm/s</td>
<td>0.5</td>
</tr>
<tr>
<td>4th</td>
<td>200W</td>
<td>Line</td>
<td>4</td>
<td>0.03</td>
<td>4000mm/s</td>
<td>0.5</td>
</tr>
<tr>
<td>5th</td>
<td>200W</td>
<td>Line</td>
<td>5</td>
<td>0.03</td>
<td>4000mm/s</td>
<td>0.5</td>
</tr>
</tbody>
</table>

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6/13/2018
Optimized Ni-YSZ AM Process

1st Layer
- Power: 230w
- Type: Line
- Speed: 400mm/s

2nd Layer
- Power: 230w
- Type: Chess
- Tile Size: 2
- Spacing: 0.03
- Speed: 70mm/s
- Overlap: 0.5
- AOM: 4

Uniform and smooth surface is made with good repeatability.

Ni-YSZ AM is very sensitive to process parameters (power, speed, hatch, scan pattern, powder, substrate, etc.). Only small process window works.
Crystal structure of ZrO₂ is different between commercial sample and PolarOnyx sample. Tetragonal for commercial, and cubic for PolarOnyx. This is because of processing temperature is different. The tetragonal is formed at 2370 °C, and cubic is formed at 2690 °C.

Will cubic phase be good for SOFC?
Ni-YSZ Anode Substrate

Substrate made

Selected for next step
YSZ on Ni-YSZ

Scan pattern 1

Scan pattern 2

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10x10 mm SOFC Samples

Succeeded in making a few complete cells with controlled thickness.

- Ni-YSZ Layer Thickness (After Remove Bottom Powder): ~280 µm
- YSZ Layer Thickness: 10µm – 25µm
- LSM Layer Thickness: 10µm -40µm

10 µm thick YSZ (electrolyte) can be processed on Ni-YSZ (Anode)
- Chess pattern works the best to mitigate residual stress induced by thermal gradience
- 12x12 mm area is achieved
Subtractive Manufacturing (SM) is used to drill holes to enhance performance.

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SOFC Test Results

It is working and improvement is needed.
Next Steps

• Optimize process to get uniform thickness and interface control
• Optimize subtractive manufacturing (SM) to control porosity.
• Strengthen the Ni-YSZ anode substrate
• Scale the dimension

Priority: Performance improvement
Summary-Phase II Accomplishments

- Designed, developed, and assembled an AM system with fs fiber laser
- Developed YSZ AM with high repeatability and multi-layer process
- Developed Ni-YSZ as anode layer with 12x12 mm area and high repeatability and uniformity
- Developed triple-layer AM of YSZ (electrolyte), Ni-YSZ (Anode) and LSM (Cathode) with 10x10 mm area. World’s first demonstration of a working SOFC using fs Laser AM.
- Modeled the AM process on thermal stress
- One publication
Thank You Very Much!

The future is in our hand!