Direct Laser 3D Printing of Refractory Materials
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Abstract: Direct laser 3D printing of refractory materials such as silicon carbide (SiC), tungsten (W), and tantalum hafnium carbide (TaHfC) have been systematically investigated. High relative density has been achieved for SiC, SiC/Al, W, and W/TaHfC. High density SiC structures and W thin wall were also fabricated. By mixing the metal powders (e.g. Al or W) with ceramic powder such as SiC or TaHfC, a metal/ceramic matrix is formed during the direct laser melting process to tailor the mechanical properties.

Keywords: additive manufacturing, laser 3D printing, silicon carbide, tungsten, refractory materials.

1. Introduction

Hot structure or high temperature structure/component is essential to next generation industries of steel, energy, semiconductor, and aerospace. However, at high temperature above 2000°C, the structures experience severe recrystallization and grain growth, which creates cracks and fatigue. Therefore, breakthrough approaches on both material and manufacturing must address not only the current need in high temperature operation capability, toughness, durability, reusability, and cost, but also the near future need for space and nuclear operation against high neutron and radiation flux.

Refractory ceramic materials such as silicon carbide (SiC) and tantalum hafnium carbide (TaHfC) are potential candidates for future high temperature and high radiation environment (Pierson, 1996). SiC has a melting temperature of 2,830°C, thermal conductivity of 120 W/(m·K), and thermal expansion coefficient of 4x10^{-6}/K. TaHfC has a melting temperature of 3990°C and thermal conductivity of 21 W/(m·K). However, these ceramic materials are too brittle to be used directly for fabricating high temperature structures without appropriate binders or enhancement matrix, which is a very complicated and costly process (Cedillos, et al. 2015). Refractory metal materials such as tungsten (W) and its alloys are also being considered promising candidates for high temperature structures due to its high melting temperature of 3422°C and high thermal conductivity of 173 W/(m·K).

Additive manufacturing (AM) or 3D printing, especially laser based AM, becomes a powerful tool to replace conventional methods such as casting and hot spray, due to its cost effectiveness and capability of making complex structures and compositions such as SiC (Du, et al. 2020), Iron (Nie, et al. 2015), tungsten [5], YSZ [6], YSZ fuel cell device [7], boron carbide [8], mixed boron carbide and Aluminum [9], Ti alloys [10], steels [11], etc. However, direct laser 3D printing (direct melting, instead of sintering plus post annealing) of high temperature ceramics such as SiC and TaHfC has not been reported, though direct laser 3D printing of zirconia [6], boron carbide [8], and tungsten[5] have been demonstrated and intensively studied.
In this paper, direct laser 3D printing of SiC, TaHfC, and W were demonstrated by using powder bed fusion (PBF) approach. The process parameters were optimized to obtain high density through direct melting of refractory materials without binders and post heat treatment. Direct melting and synthesis process of mixed ceramic powders with aluminum (Al) or W were also investigated.

2. Materials and Methods

The SiC-6H SiC powder (American Elements, Los Angeles, CA) used in the experiment have an average size of 40 μm in diameter and with irregular shape. The histogram of size distribution (Figure 1), analyzed by ImageJ, shows that most of the particles are within 20 - 60 μm. In our experiments, it is found that the shape is not necessary to be a perfect round shape to obtain a good density. However, a good size distribution plays an important role [12]. The composition of SiC, provided by the vendor, has 99.99% purity. Since the SiC has high absorption (i.e., 17%) at the laser wavelength of 1064 nm and highly temperature dependent thermal conductivity, it makes the SiC AM very challenging to deal with the brittleness, residual thermal stress, cracks, and defects.

The TaHfC powder (Diversified Advanced Technologies, Reno, NV) has similar powder size distribution with that of SiC. Figure 2(Left) shows a scanning electron microscope (SEM) photo. The powder has an irregular shape as well. Ta and Hf have a weight ratio of 4:1.

Al alloy (AlSi10Mg) powder (Figure 2(Right)) and tungsten powder are commercial products readily available and the detailed information can be found in our previous publications [6], [9]. Al alloy has a Gaussian distribution of powder size from 10-50 mm. Tungsten powder has a Gaussian distribution of powder size from 10-25 mm, with near spherical shape. A summary of material properties of these four materials is given in Table 1. However, TaHfC has very limited searchable data.

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting temperature (°C)</th>
<th>Thermal conductivity [W/(m K)]</th>
<th>Thermal expansion coefficient (10^-6/K)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>2800</td>
<td>120-140</td>
<td>4</td>
<td>3.2</td>
</tr>
<tr>
<td>Al</td>
<td>660</td>
<td>237</td>
<td>23</td>
<td>2.7</td>
</tr>
<tr>
<td>W</td>
<td>3422</td>
<td>173</td>
<td>4.5</td>
<td>19.3</td>
</tr>
<tr>
<td>TaHfC</td>
<td>3990</td>
<td>NA</td>
<td>NA</td>
<td>14.5</td>
</tr>
</tbody>
</table>
The PBF system for direct melting of ceramic powders was modified from our commercial system (Tungsten AM). A 200 W fiber laser operating at 1064 nm with pulse repetition rate of 200 MHz and pulse width of 1 ns was used as an energy deposition source. The focal spot size is about 60 mm on the target (powder). The PBF system has a printing surface area of 100 mm x 100 mm and a printing height of 150 mm. The powders were stored in an aluminum container (100 mm x 100 mm x 200 mm). In the case of mixed powders of SiC and Al, 80 wt% SiC powder was mixed with 20 wt% of AlSi10Mg alloy powder before the AM process, by using a jar mill machine to run 24 hours. In the case of mixed powders of W and TaHfC, 80 wt% W powder was mixed with 20 wt% of TaHfC powder before the AM process, by running in a jar mill machine for 24 hours. The powder container was placed in a processing chamber filled with industrial standard argon (Ar) gas to prevent oxidation. It is noted here that this type of mechanical mixing method does not incur chemical reaction. We also found the powder size distribution in gaussian shape helps flowability during AM process.

*Figure 1.* SiC powder image and size distribution

*Figure 2.* (Left) TaHfC powder image. (Right) AlSi10Mg powder image
During fabrication, the laser executes a scanning pattern or strategy. The strategies associated with the laser path are characterized by the length, direction, and separation (hatching space) of neighboring scan vectors. Scanning strategies can affect density, mechanical properties, and residual stress of printed parts. The residual stress is one of the most important parameters that must be optimized for laser-based additively manufactured ceramic parts. It can cause disconnection of the part to its supporting structure, or peel off after printing certain layers, surface deformations that may damage the powder spreading blade or inhibit the blade’s motion. Figure 3 gives some examples of scanning patterns used in the PBF system to optimize the direct laser melting process for ceramic powders. The pattern of “polaronyxchess” works the best for ceramic powders. The scan sequence is selected to be “random” and jump diagonally to avoid adjacent pattern printing.
Figure 4 illustrates the flow chart for parts design and fabrication. Usually, a part is designed with Solidworks and then sent to a 3D printing software (such as Materialise Magics) for editing, slicing, addition of support structures, generation of .STL files. The AM machine will then use the .STL file to print the parts. The AM system is able to adjust laser power, scan speed, scan pattern strategy, powder layer thickness, hatching space, etc. Geometrical calibration data is stored in the computer for control of the precision to +/- 0.05 mm. After printing, the part will be tested on geometry, density and mechanical properties.

3. Results and Discussion

3.1. Direct Laser 3D Printing of SiC and mixed SiC/Al

Process parameters of selective laser melting are listed as follows:
- Laser power (on-target): 50, 100, 150, and 200W
- Scanning speed: 100, 200, 300, 400, 500 mm/s
- Hatching space: 0.150, 0.125, 0.1, 0.075 mm
- Adjacent layer thickness: 50 μm

![Figure 5. SiC 10x10x10 mm³ cubic printing](image)

Unlike metal 3D printing, ceramic materials are brittle and only have a small process window to melt to form shapes. Figure 5 shows the printed cubic shapes with a size of 10x10x10 mm³. It indicates that only a small region in combination of power (150W) and speed can make the parts melt to form solid shapes without any peeloff or delamination. Beyond those specific parameters,
layers of the cubic structure can be easily separated. As the laser power goes as high as 200 W, all samples were broken into pieces.

Figure 6 and Figure 7 show the relative density measurement of a selected sample fabricated with 150 W and 300 mm/s. The sample was diamond-polished to check uniformity across the surface and vertical cross-section. Five points were used to measure the surface area and ten points for the cross-section area. Microscopic image processing (software Image-J) is used to test relative density, while 1mm x 1mm area is used for each measurement. As high as 99% relative density was achieved. Over 90% density was achieved for all checking points. The x-ray powder diffraction (XRD) result indicates that the sample has SiC-6H (hexagonal).

![Relative Density Measurements](image)

**Figure 6.** Cross-section microscope images and relative density measurements of cubic sample printed with 150 W power and 300 mm/s sanning speed. Total 10 positions were taken. Relative density are higher than 90%.
Figure 7. Surface section microscope images and relative density measurements of cubic sample printed with 150 W power and 300mm/s scanning speed. Total 5 positions were taken. Relative density are higher than 90%.

Figure 8. SiC cylinder structured with thin walls. Top: Solidworks design. Bottom: direct 3D printed parts on substrates.

Several types of structured architectures were designed to show the capability of direct 3D printing of SiC. 150 W and 300 mm/s were selected for the part printing. Figure 8 shows an example of the cylinder structure design using Solid works and its printed part. The cylinder has a diameter of 50 mm and height of 50 mm. The thin wall structure has a thickness of 1 mm. Another example of square shape cylinders (50x50x50 mm³) was printed and shown in Figure 9. These as-built SiC parts are robust and have a very good control on uniformity and thickness of the thin wall structures.
The sample shows very strong support and excellent control on thickness and uniformity. It was found that mixed powders of 80wt% SiC and 20wt% Al can further eliminate cracks and delamination during the direct melting process. Density as high as 99% was achieved with high uniformity and repeatability. Various types of solid shapes and structured shapes were designed and fabricated. Figure 10 gives an example of fabricating both solid and structured architecture in one single piece with the mixed SiC/Al powder. It shows that the process is repeatable and provides high accuracy in geometric control. The solid surface was diamond-polished to show the mirror effect. There are no severe cracks or defects observed.

3D printed part with mixed SiC/Al powders. The structured architecture and solid base are printed in a single process. The solid base is diamond-polished to show the mirror effect. The Al forms an excellent bonding matrix with SiC.

Figure 11 shows the hardness test for one of the cubic samples of mixed SiC/Al powder. 1.2 GPa hardness (Vickers hardness 116) and 64 GPa Young’s module were achieved, which is a very encouraging result. As references only, with conventional casting methods, the hardness for Al is 160MPa and 2.8GPa for SiC.
3.2. Direct Laser 3D Printing of W and mixed W/TaHfC

Figure 12 and Figure 13 show the density tests for a variety of cubic samples with different hatching spaces under on-target power of 200W and scanning speed of 200 mm/s while other parameters (pulse width, pulse repetition rate, and focal spot size) remain the same as described in section 2. During etching, those unmelt or weak bonded portion is taken out and the resulting relative density becomes degraded (Figure 13). It indicates that the hatching space plays an important role in obtaining excellent density with a good tolerance in process variation. The developed process is very robust against etching (corrosion) and has a broad process window to obtain >96% relative density.

<table>
<thead>
<tr>
<th>Test</th>
<th>Hardness (Vickers)</th>
<th>Hardness (Mpa)</th>
<th>Young’s Modulus (Mpa)</th>
<th>Max Depth (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>98.57</td>
<td>1043.1</td>
<td>73530</td>
<td>25.29</td>
</tr>
<tr>
<td>2</td>
<td>126.89</td>
<td>1342.8</td>
<td>50458</td>
<td>20.10</td>
</tr>
<tr>
<td>3</td>
<td>129.49</td>
<td>1370.3</td>
<td>75278</td>
<td>22.34</td>
</tr>
<tr>
<td>4</td>
<td>110.89</td>
<td>1172.3</td>
<td>58344</td>
<td>24.26</td>
</tr>
<tr>
<td>5</td>
<td>114.96</td>
<td>1216.6</td>
<td>63655</td>
<td>23.75</td>
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<tr>
<td>Average</td>
<td>116.16</td>
<td>1229.3</td>
<td>64333</td>
<td>23.75</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>11.24</td>
<td>118.9</td>
<td>9389</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Figure 12. Cross-section of W cubic samples after etched for 15 seconds. The relative density in relation with each hatching space: (a) 50 µm, 97.61%; (b) 80 µm, 99.61%; (c) 100 µm, 98.73%; (d) 150 µm, 98.27%.

Figure 13. Summary of density as a function of etching time with various hatching spaces.

Figure 14 shows the latest study on fabrication of W thin wall structures in one dimension and two dimensions. It shows that as thin as 130 µm wall was fabricated with less than 10% non-uniformity of width. It also shows that the relative density of the thin walls can reach as high as 99%. This provides a good foundation for making complex high temperature structures.
Figure 14. (Top) Tungsten thin wall structures in one dimension and two dimensions. (Bottom) Microscopic images for measurement of wall thickness and relative density.

Table 2 Process parameters and results of mixed W and TaHfC

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power: 200W</td>
<td>Size: 18.22mm * 7.16mm * 3.92mm ~ 4.25mm</td>
</tr>
<tr>
<td>Speed: 100mm/s</td>
<td>(72 layers)</td>
</tr>
<tr>
<td>Hatching: 0.20mm</td>
<td>Roughness: 21.38μm (top); 24.96μm (sides)</td>
</tr>
<tr>
<td>Thickness: 0.05mm</td>
<td>Broken while removing the support away</td>
</tr>
<tr>
<td>Power: 200W</td>
<td>Size: 18.25mm * 7.14mm * 3.85mm (72 layers)</td>
</tr>
<tr>
<td>Speed: 100mm/s</td>
<td>Roughness: 22.59μm (top); 25.02μm (sides)</td>
</tr>
<tr>
<td>Hatching: 0.18mm</td>
<td></td>
</tr>
<tr>
<td>Thickness: 0.05mm</td>
<td></td>
</tr>
<tr>
<td>Power: 200W</td>
<td>Size: 18.18mm * 7.10mm * 3.39mm ~ 3.70mm</td>
</tr>
<tr>
<td>Speed: 100mm/s</td>
<td>(72 layers)</td>
</tr>
<tr>
<td>Hatching: 0.16mm</td>
<td>Roughness: 14.64μm (top); 26.08μm (sides)</td>
</tr>
<tr>
<td>Thickness: 0.05mm</td>
<td></td>
</tr>
</tbody>
</table>

20 wt% of TaHfC was added to W powder and printed under 200W on-target laser power and 100 mm/s scanning speed. Table 2 lists the process parameters, photos of the fabricated parts, and description of the test results. As we learned from the W 3D printing, hatching space plays an important role in fabrication of high density and robust W/TaHfC parts. It is noticed that the sample printed with 0.20mm hatching space was broken when it was removed from the
support structure, suggesting that this hatching space is too large to have a reasonable density. The sample with 0.16 mm hatching space was evaluated after being polished and etched. Figure 15 shows the relative density as a function of etching time and SEM and EDS test results. It shows a good relative density (>97%) for the cross-section and about 80% relative density for the top surface. The relationship between relative density and etching time is a good indicator for the stability of the ceramic/metal composite parts. The averaged grain size is measured to be 152µm. After etching 120 seconds, the metal matrix becomes more visible. Figure 16 and Figure 17 show optical images for the top surface and cross-section under different etching times, respectively. Tungsten and TaHfC form a uniform matrix composite during direct laser melting process.

Figure 15. Relative density as a function of etching time for mixed W/TaHfC samples with hatching space of 0.16 mm; SEM/EDX test results. The ratio of Ta and Hf is 4:1.
Figure 16. Optical microscopic images for the top surface of W-TaHfC sample etched after 15 seconds (Left) and 120 seconds (Right)

Figure 17. Optical microscopic images for the cross-section of W-TaHfC sample etched after (a) 0 second; (b) 15 seconds; (c) 30 seconds; (d) 45 seconds; (e) 90 seconds; (f) 120 seconds.
Figure 18. XRD result of the W/TaHfC sample.

Figure 18 shows XRD results of a sample made with mixed W/TaHfC. The phase identified with a high degree of percentage is W (cubic); and the phase identified with a low degree of percentage is Ta$_{0.5}$W$_{0.5}$ (cubic, synthesized during laser melting process). Since XRD is sensitive to crystal structure as opposed to chemical composition, the true stoichiometries may be different than the listed. Since the Hf was less than 2 wt%, it is too low to be detected by XRD.

4. Conclusion

Direct laser 3D printing using PBF system was employed to fabricate hot structures or high temperature components with refractory materials such as SiC, W, and TaHfC. It shows that with a careful control of process parameters, high relative density can be achieved for SiC and SiC/Al (99%), W (99%), and W/TaHfC (97%). High density W thin wall, as thin as 130 $\mu$m, is achieved. By mixing the metal powders with ceramic powders, a metal/ceramic matrix is formed during the direct laser melting process for SiC/Al and W/TaHfC. This will further strengthen the mechanical properties of hot structures (i.e. 1.2 GPa hardness and 64 GPa Young’s module were achieved for SiC/Al matrix composite) and provide another dimension to design the matching hot structure for a variety of high temperature applications such as nuclear energy and hypersonic vehicles.

Author Contributions: Shuang Bai did design, experiment and analysis, and manuscript writing; Hyeong Jae Lee did experiment and data process; Jian Liu did design, analysis and manuscript revision.

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Conflicts of Interest: The authors declare no conflict of interest.
References


