

EFFECTS OF LASER PROCESSING ON NICKEL OXIDE – YTTRIA STABILIZED ZIRCONIA

TAN HONG YI KENNETH, SU PEI-CHEN

*Singapore Centre for 3D Printing,
SIMTech-NTU Joint Laboratory (3D Additive Manufacturing),
School of Mechanical and Aerospace Engineering, Nanyang Technological University,
50 Nanyang Avenue, Singapore 639798*

SUN CHEN-NAN, WEI JUN

*SIMTech-NTU Joint Laboratory (3D Additive Manufacturing),
Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798
Singapore Institute of Manufacturing Technology
71 Nanyang Drive, Singapore 638075*

ABSTRACT: Laser based additive manufacturing techniques such as selective laser melting (SLM) and selective laser sintering (SLS) have been gaining much attention in recent years due to their ability to create complex shapes and designs from layers of powdered materials. These two technologies although similar in mechanisms, vary in their use of laser systems due to the difference in materials used. A material's absorptivity at different wavelengths will affect the amount of energy transferred by the laser to that material. In this study, a ceramic composite material, Nickel Oxide – Yttria Stabilized Zirconia (NiO-YSZ), which is commonly used as an electrode in solid oxide fuel cell applications was analyzed using two different laser systems. Carbon dioxide laser (10.6 μm) was found to be better absorbed by NiO-YSZ as compared to fiber laser (1.06 μm) through observation of the microstructure after laser processing. Due to poor absorptivity of NiO-YSZ at 1.06 μm , only liquid state sintering between the particles was observed, while at 10.6 μm , eutectic microstructures was evident after laser processing demonstrating that melting of NiO-YSZ had occurred. With increasing laser power used, amount of eutectic microstructure within the processed region was also increased and becomes more aligned. This paves the way of using laser parameters to control the microstructure of a desired structure at each layer.

KEYWORDS: Additive manufacturing, NiO-YSZ, SOFC

INTRODUCTION

Additive manufacturing or 3D printing is rapidly gaining interest due to its ability to manufacture complex and customized structures that were traditionally difficult to fabricate. This new form of manufacturing technique utilizes the addition of material layer upon layer to construct the desired form. From its initial usage as a rapid prototyping tool, Kruth, Leu, and Nakagawa (1998) discussed how additive manufacturing would evolve from rapid prototyping to direct manufacturing, increasing its appeal to manufacturers. As compared to subtractive manufacturing technologies such as milling and drilling, it allows for greater freedom of design for product designers, while maintaining similar material properties. Currently, there are several different types of additive manufacturing techniques available which can be classified into 7 different categories according to ASTM F2792 as shown in Table 1.

Table 1. Classification of additive manufacturing techniques based on ASTM F2792.

Process	Explanation	Machines
Binder Jetting	A liquid bonding agent is selectively deposited to join powder materials	3D Printing (3DP)
Directed Energy Deposition	A focused thermal energy is used to fuse materials by melting as they are being deposited	Laser Engineered Net Shaping (LENS)
Material Extrusion	The material is selectively dispensed through a nozzle or orifice	Fused Deposition Modelling (FDM)
Material Jetting	Droplets of build material are selectively deposited	Polyjet
Powder Bed Fusion	Thermal energy selectively fuses regions of a powder bed	Selective Laser Melting (SLM) Selective Laser Sintering (SLS) Electron Beam Melting (EBM)
Sheet Lamination	Sheets of material are bonded to form an object	Laminated Object Manufacturing (LOM)
Vat Photo-polymerization	Liquid photo-polymer in a vat is selectively cured by light-activated polymerization	Stereolithography Apparatus (SLA)

Laser based additive manufacturing is a combination of directed energy deposition and powder bed fusion process. This technique utilizes a high energy laser beam to selectively scan the powder bed thereby transferring enough heat energy to melt or sinter the powdered material, bonding them together. Selective laser melting (SLM) and selective laser sintering (SLS) are two examples of the most commonly used laser based additive manufacturing processes. Although these two processes are similar in mechanisms, they vary in their laser systems used due to the differences in materials used. Tolochko et al. (2000) showed that metallic and carbide demonstrated higher absorbance when interacting with laser of 1.06 μm wavelength, having around twice the absorbance value than at 10.6 μm wavelength. However, for oxides and polymers, the reverse behavior was observed, with 10.6 μm wavelength laser being better absorbed by the materials. The difference in absorptivity between the materials led to the development of SLM machines equipped with fiber laser which focused on the development of metallic materials, while SLS machines equipped with CO₂ laser concentrated on polymeric materials.

However, limited studies have been done with regards to creating a dense structure for ceramic components. Initial fabrication methods involved SLS and a sacrificial binder phase, produced parts with lower density and required much post processing. Shahzad, Deckers, Kruth, and Vleugels (2013) managed to obtain a final density of 89% from polypropylene – alumina composite powder after infiltration with alumina suspension. More recent works on ceramics aim to directly melt or sinter the material with a laser source, eliminating the need for additional post processing. Bertrand, Bayle, Combe, Goeuriot, and Smurov (2007) first successfully demonstrated that YSZ ceramic parts can be fabricated by direct laser sintering, although the density achieved was low at 56%. Juste, Petit, Lardot, and Cambier (2014) further improved the density of alumina parts produced to 90% by adding graphite additives into the powder mixture which improves the material's absorptivity. Near 100% density zirconia – alumina parts was also obtained by Wilkes, Hagedorn, Meiners, and Wissenbach (2013) via preheating the powder bed with an additional laser source during the fabrication process.

Although there have been an increasing effort to fabricate dense ceramic structures by laser based additive manufacturing, most of the researches focused primarily on alumina and zirconia. Few were done to study the effect of different laser systems on the microstructure of ceramics material in particular composite ceramic that consists of 2 or more components. Larrea, Orera, Merino, and Peña (2005) demonstrated that eutectic composition could be obtained in alumina – yttria stabilized zirconia (Al_2O_3 -YSZ) and alumina – yttrium aluminum garnet (Al_2O_3 -YAG) when directionally solidified by laser. In this study, nickel oxide – yttria stabilized zirconia (NiO-YSZ), a commonly used electrode material for solid oxide fuel cells (SOFC) applications was analyzed using both fiber and CO_2 laser systems. Preliminary investigations on the effect both laser processing methods have on the microstructural change of the material was compared and studied.

MATERIALS AND METHODS

Commercial 60wt%NiO-40wt%YSZ powder (FuelCellMaterials, USA) was used in the following experiment.

Figure 1 showed the morphology of NiO-YSZ powder with a Brunauer-Emmett-Teller (BET) surface area of 1-4 m^2/g . In order to test the interaction of the powder with different laser systems, SLM 250HL (SLM Solutions GmbH) and HRPS-VII SLS Machine (Wuhan Binhu Mechanical & Electrical Co., Ltd) equipped with fiber laser having 1.06 μm wavelength and CO_2 laser having 10.6 μm wavelength respectively were used in the experiment.

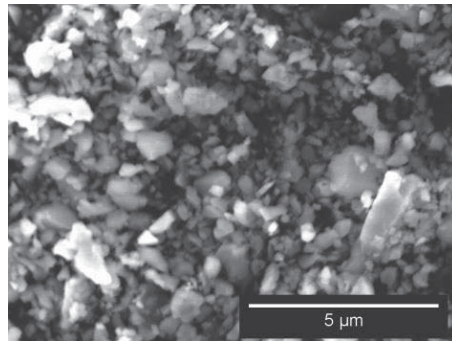


Figure 1. SEM image of NiO-YSZ powder with a BET surface area of 1-4 m^2/g

The experiments were broken into two parts. The first part consisted of comparing the difference in surface morphology and microstructure obtained by the two laser systems. A single layer of NiO-YSZ powder was manually laid onto the platform, followed by scanning of the material with the two laser systems respectively, while maintaining a constant energy vector of 0.4. Energy vector is the amount of energy supplied per millimeter by the laser to the materials as shown in Equation 1.

$$\text{Energy vector } (J/mm) = \frac{\text{Laser Power } (W)}{\text{Scanning Speed } (mm/s)} \quad (1)$$

For the fiber laser, a power of 400 W and scanning speed of 1000 mm/s was used while for the CO₂ laser, scanning strategy with power of 100 W and scanning speed of 250 mm/s was used.

The second experiment focused mainly on the use of the CO₂ laser system. Single layers were scanned using the CO₂ laser system in order to investigate microstructural changes of NiO-YSZ at different powers. The fabrication of a single layer allowed preliminary study to understand the interaction between different scan lines and the effect these would have on the microstructure. For this experiment, the scanning speed and hatch spacing was fixed at 5 mm/s and 0.1 mm respectively, while the laser power varied between 20 W and 80 W.

RESULTS AND DISCUSSIONS

Comparison between laser systems

The first experiment demonstrated that NiO-YSZ powder could be processed using both laser systems with an energy vector of 0.4. At lower magnification as shown in Figure 2(a), fiber laser processed specimen presented melt pools that overlapped over the previous scan track illustrating that NiO-YSZ had obtained sufficient heat energy to behave in a liquid-like behavior during the fabrication process before rapid solidification took place. As compared to processing by fiber laser, specimen produced using CO₂ laser was able to achieve smoother surface area as observed in Figure 2(b), although certain regions within the track did not appear dense due to the low energy vector supplied.

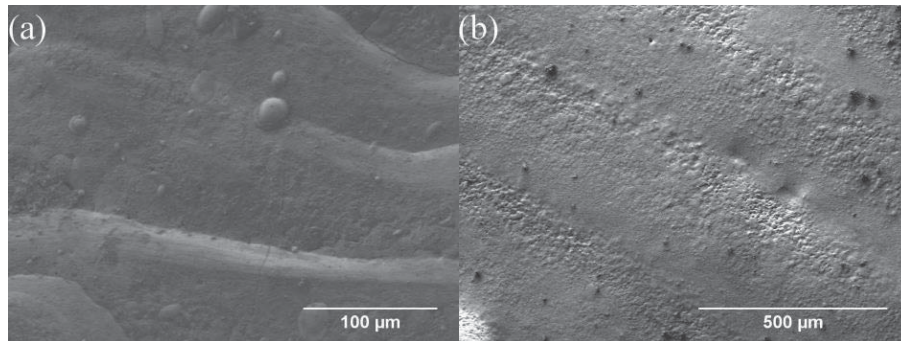


Figure 2. Melt track of (a) fiber laser; (b) CO₂ laser

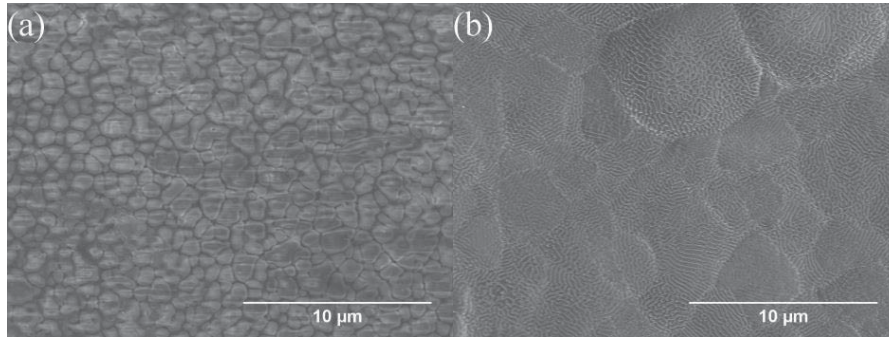
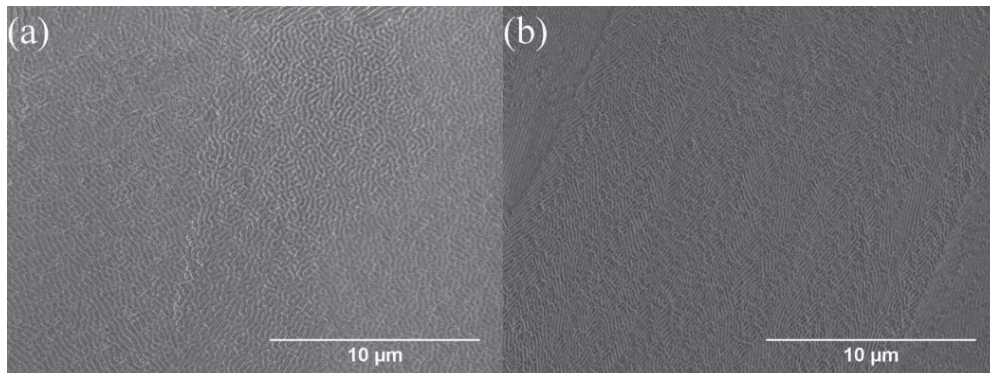


Figure 3. Microstructure of NiO-YSZ processed by (a) fiber laser; (b) CO₂ laser

However, under higher magnification as shown in Figure 3(a), small crystallites were observed to be bonded together between each crystals by liquid state sintering. These microstructures showed that nano-sized gap was present between each crystal, resulting in a less dense structure. This occurred due to insufficient energy absorbed by the material for the particles to reach its melting point coupled by the rapid solidification process when using a laser source. In contrast, for the CO₂ laser processed specimen in Figure 3(b), higher densification between the particles could be observed. Instead of singular crystals bonding together, the microstructure showed that melting had occurred on the surface, with the appearance of grain growth as well as eutectic structures within each grain. From this experiment, it was shown that NiO-YSZ has better absorptivity when processed by the CO₂ laser as compared to fiber laser by comparison of their microstructure. These results are consistent with the results by Tolochko et al. (2000) which showed that oxide materials have a higher absorptivity of approximately 20 times at 10.6 μm wavelength as compared to at 1.06 μm wavelength.

Single layer melting



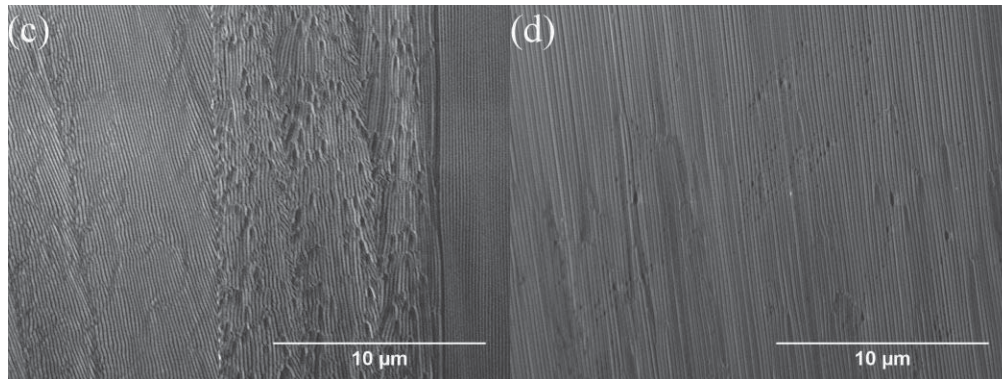


Figure 4. Microstructural change in NiO-YSZ surface layer using CO₂ laser at (a) 20 W; (b) 40 W; (c) 60 W; (d) 80 W

The second experiment looked into the change in microstructure on the specimen surface when processed with CO₂ laser at various laser powers. Eutectic microstructures were evident in all the specimens fabricated. As compared to Figure 3 whereby grains colonies could be easily observed, in Figure 4 it was not observable on the same scale. As the energy supplied and absorbed by the material was increased, grains formed became larger. In addition, with higher laser power, these eutectic microstructures within the grains becomes more aligned as observed from Figure 4(a)-(d), whereby the microstructure evolved from having a random configuration to become more aligned in the same direction as the laser power was increased. As the material received higher heat energy from the laser, the grains would have enough energy to rearrange itself into their preferred orientation. The different microstructure achieved in NiO-YSZ when different parameters were used, would allow for structures with varying properties to be fabricated.

CONCLUSIONS

NiO-YSZ composite ceramic was processed using two different laser systems that are commonly used in laser based additive manufacturing. It was observed that the material has better absorptivity when processed using CO₂ laser, with the appearance of grain growth and eutectic microstructure as compared to liquid state sintering occurring between particles with fiber laser. In addition, the eutectic structure within the grains could be easily controlled at each layer using different parameters, paving the way for structures with different properties to be created.

ACKNOWLEDGEMENT

The authors would like to acknowledge SIMTech-NTU Joint Laboratory for funding this project.

REFERENCES

- Bertrand, P., Bayle, F., Combe, C., Goeriot, P., & Smurov, I. (2007). Ceramic components manufacturing by selective laser sintering. *Applied Surface Science*, 254(4), 989-992.
- Juste, E., Petit, F., Lardot, V., & Cambier, F. (2014). Shaping of ceramic parts by selective laser melting of powder bed. *Journal of Materials Research*, 29(17), 2086-2094.

- Kruth, J. P., Leu, M. C., & Nakagawa, T. (1998). Progress in Additive Manufacturing and Rapid Prototyping. *CIRP Annals - Manufacturing Technology*, 47(2), 525-540.
- Larrea, A., Orera, V. M., Merino, R. I., & Peña, J. I. (2005). Microstructure and mechanical properties of Al₂O₃-YSZ and Al₂O₃-YAG directionally solidified eutectic plates. *Journal of the European Ceramic Society*, 25(8), 1419-1429.
- Shahzad, K., Deckers, J., Kruth, J.-P., & Vleugels, J. (2013). Additive manufacturing of alumina parts by indirect selective laser sintering and post processing. *Journal of Materials Processing Technology*, 213(9), 1484-1494.
- Standard, A. (2012). F2792. 2012. Standard Terminology for Additive Manufacturing Technologies. *ASTM F2792-10e1*.
- Tolochko, N. K., Khlopkov, Y. V., Mozzharov, S. E., Ignatiev, M. B., Laoui, T., & Titov, V. I. (2000). Absorptance of powder materials suitable for laser sintering. *Rapid Prototyping Journal*, 6(3), 155-161.
- Wilkes, J., Hagedorn, Y. C., Meiners, W., & Wissenbach, K. (2013). Additive manufacturing of ZrO₂-Al₂O₃ ceramic components by selective laser melting. *Rapid Prototyping Journal*, 19(1), 51-57.