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<th>Porosity formation in selective laser melting of spodumene</th>
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ABSTRACT: Additive manufacturing of spodumene was carried out using selective laser melting to study the porosity formed in the printed parts. Parts were printed with similar power, scan velocity, and hatch spacing but with different layer thicknesses. To study the porosities formed in the parts, micro-computerised tomography was utilise to obtain x-ray images of the printed parts. The results showed that the pores formed randomly in the core throughout the samples printed with layer thickness of 50 μm. However, as the layer thickness increases, pores were seen to form along the edges near the surfaces of the parts. In addition, the size of the pores reduced and heat-treatment has negligible effect of reducing the porosity.

KEYWORDS: Additive Manufacturing; selective laser melting; glass-ceramic; spodumene; lithium aluminosilicate

INTRODUCTION
Additive manufacturing (AM) has proven to be an advantageous and valuable technology due to its rapid establishment into both commercial and non-commercial industries (Bandyopadhyay et al. 2015). Improvement in each of the different AM techniques has now enable users to manufacture practical end parts rapidly (Wong et al. 2016). Furthermore, the layerwise fabrication process of AM eliminates the need for special tooling required for producing geometrically complex parts such as interconnecting parts (Chua et al. 2017). The AM method used in this study is the selective laser melting (SLM) technique which produces dense metal parts from a bed of powder particles through full melting and liquid phase fusion. Due to the ability to melt high melting point metals and print parts at very thin layer thicknesses, it is one of the many AM technique used to manufacture complex metal components (Bremen et al. 2012).

Currently, most of the research work on SLM involved metals but rarely on ceramics. Parameter optimisation through these studies has enabled users to manufacture metal parts with a relative density of more than 99% (Kruth et al. 2010, Attar et al. 2014). However, this was not the case for nonmetallic-based materials such as ceramics and glass-ceramics. Despite the advantages this method has presented, the challenges to produce a ceramic part still persist. For instance, selective laser melting (SLM) of ceramics such as alumina has been proved to be extremely challenging due to its poor absorptivity and susceptibility to develop internal microcracks (Sing et al. 2017). Alumina by itself is a very useful and popular material. Despite the
appropriate aesthetical properties such as chemical and biological inertness and high wear resistance suitable for dental implants, it has low fracture toughness due to structural defects such as pores and flaws. Furthermore, its thermal instability has limit its usage at high temperatures.

Nevertheless, by incorporating a glassy phase of lower viscosity, pores can be eliminated. Moreover, the glassy phase will eventually crystallise between the alumina particles, giving it a fine-grained structure and better mechanical properties (Guedes et al, 2013). Other suitable areas of applications are replacing existing ceramic parts requiring high thermal shock resistance such as mold for high melting temperature metals and diesel particulate filters.

As shown in several studies, introducing the lithium aluminosilicate phase into alumina reduces the thermal expansion, thereby improving its high temperature stability preventing failure due to thermal fluctuations. For instance, García-Moreno et al. (2013) found a favourable solid-state compatibility between Al₂O₃ and one of the phases of LAS (β-eucryptite) for designing of such new ultrastable material. The compositions (Al₂O₃/LAS) being studied on were 50/50, 75/25, and 25/75 in mol%. According to this study, β-eucryptite (Li₂O:Al₂O₃:3SiO₂) was found to be the most stable phase with negative thermal expansion amongst the others such as Li₂O:Al₂O₃:2SiO₂ and Li₂O:5Al₂O₃.

A second study showed that Al₂O₃/LAS (85/15 weight %) put under thermal shock conditions exhibited minimal strength deterioration as compared to their alumina counterpart although the overall strength was one-third lower (Bayuseno et al. 1999). From the results of this study, spodumene was found to have softening effects, reducing the composite’s hardness and young’s modulus. In addition, the density and strength of the composite was relatively lower than pure alumina. Nevertheless, this composite has comparable fracture toughness to pure alumina. Most importantly, the thermal shock resistance improved due to the addition of low thermal expansion β-spodumene. In addition, coarse grain microstructure is preferred over fine grain microstructure as it retained most the strength after thermal quenching.

Latella et al. (1995) also showed that liquid-phase sintered (LPS) Al₂O₃ containing 15 weight % of spodumene had properties similar to commercially available debased Al₂O₃ ceramics used for wear applications. Addition of spodumene reduces the bulk density, porosity, shrinkage, grain size, young’s modulus, and hardness of the composite. Similar to the above study, the fracture toughness of the composite is similar to pure alumina of approximately 4.0 MPa m¹/².

Last but not least, García-Moreno et al. (2011) demonstrated that spark plasma sintering (SPS) of LAS–Al₂O₃ (84.35/15.65 weight %) improved the mechanical properties as compared to furnace sintered parts and can be used in oxidising conditions. Through pressureless sintering, the density of the sample is very low when the alumina content is more than 50%. On the other hand, when the LAS content is more than 80 %, the density obtained is more than 90%. In addition, residual porosity can also be observed after sintering. Fabrication by SPS was able to increase the density of the composite, and hence reduced the required post-sintering temperature to achieve a 100% dense part.

Therefore, SLM of spodumene was carried out to establish and develop the process conditions required to additive manufacture Al₂O₃–LAS (lithium aluminosilicate) parts by liquid phase sintering due to its lower melting temperature and viscosity.
METHODOLOGY

The SLM process used in this study is powder bed-based and more commonly associated with metals. In this process, a layer of powder is spread onto a heated substrate plate before the laser radiates the cross-sectional area(s) of the designed part(s) to melt the powder particles and induce liquid phase fusion. The substrate plate is then lowered by an amount equivalent by the layer thickness defined by the user and a fresh layer of powder is deposited. The whole process repeats until a completed part is printed out. In this study, samples were additive manufactured in three groups of different layer thicknesses (LT) — 50 μm, 100 μm, and 150 μm with the same power, hatch spacing, and scan velocity. The samples were built vertically along the z-axis for easy part removal. The SLM-manufactured samples were then heat-treated at 850 °C and 950 °C for 4 hours respectively (Figure 1). The heating and cooling rates for the heat-treatment were 5 °C/min. X-ray images of the internal structure of the printed parts were obtained and analysed with the use of microcomputerised tomography (microCT) scanning.

The materials used is a natural occurring mineral with the chemical composition of the as-received powder as shown in Table 1. Rather than manually producing the glass powder through mixing of raw materials, spodumene mineral was used for this study as it has been shown that it is possible to form LAS glass-ceramic from heat-treating spodumene mineral (A. Nordmann and Y.B. Cheng 1997).

Table 1. Powder composition.

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<th>Compound</th>
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<tr>
<td>Li₂O</td>
<td>7.1</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.25</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>25.4</td>
</tr>
<tr>
<td>SiO₂</td>
<td>65.7</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.13</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.23</td>
</tr>
<tr>
<td>LOI</td>
<td>0.32</td>
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RESULTS AND DISCUSSION

Printing outcome

The direct laser melting of spodumene was successful as shown in Figure 2. Figure 2(a) illustrates the parts as-printed onto a substrate plate. Based on the developed process, the printable height of the LAS part does not have any limit. However, the surface roughness of the printed part remains to be poor due to several reasons such as particle adhesion to surfaces and poor interlayer bonding as the layer thickness increases.

Figures 2(b) to (d) compares the top surfaces of the samples across different layer thicknesses. As shown in the images, the roundedness and colouration increases and darkens with increasing layer thickness. Increasing the layer thickness increases the amount of powder deposited on the next layer. As a result, similar energy density was required to melt more material. Therefore, with an increasing amount of material, the tendency to cause
agglomeration increases. With a lower layer thickness, the laser melts lesser material. In addition, due to the shallower depth the laser had to penetrate, the heat energy deposited was sufficient to overcome the surface tension. As such, preventing the glass bead-forming phenomenon as shown in Fig 2(d).

There is also in-process microstructural changes such as crystallisation induced by laser irradiation as investigated in (Gan and Wong 2017). For instance, the previously solidified surface is nearer to the top surface of the newly deposited powder particle for 50 μm layer thickness. Therefore, given the same amount of laser penetration, the previous layer is likely to experience greater heat input resulting in the differences. X-ray diffraction (XRD) analysis carried out on the white and dark parts (see Fig. 2(d)) revealed and confirmed the microstructural differences as shown in Figure 3. The XRD spectrums obtained show that the dark part consisted of a polycrystalline structure as compared to the white part which was fully crystalline.

![Figure 2: Printed parts (a) on a substrate plate, (b) LT50, (c) LT100, and (d) LT150.](image)

![Figure 3: The differences in XRD spectrum of the white and dark areas as seen in Fig. 2(d).](image)
**MicroCT results**

Figure 3(a) to (c) illustrates the CT images of the LT50 to LT150 samples. As shown in this figure, the pores formed decreases with layer thickness. Furthermore, the location where the pores formed changes from random (at LT50) to surrounding edges (LT150). Through the use of appropriate parameters, the location of pores can be altered to move from being random to the edges near surfaces. The advantage of this development allows users to remove the layer of pores by surface post-processing which results in a denser part. As such, this study provides a potential design rule by determining the boundaries where the pores formed. For instance, users can design the part to be larger such that upon post-processing, obtains the required dimension.

![MicroCT images](image)

**CONCLUSION**

This work shows the potential of AM full ceramic parts without the use of polymeric or metallic binders. The results also show that with appropriate parameters, the amount and location of porosity of the printed parts can be reduced and altered to form near the edges. This allows users to carry out post-processes such as surface polishing to remove the layer of porous surfaces. As such, Nevertheless, future work will consist of investigation to determine the effect of scanning strategies on the pattern and location of the porosities formed.

**ACKNOWLEDGEMENT**

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**REFERENCES**


