

Investigating Thermally Induced Phase Separation as a Composite Powder Synthesis Technique for Indirect Selective Laser Sintering

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Abstract

The nuclear energy and nuclear defense industries have long relied on traditional manufacturing techniques for fabrication of reactor and weapon components. With the recent growth of additive manufacturing (AM), the nuclear industry is now asking the question of how AM could be used to manufacture components found in the nuclear fuel cycle. Many important components in the nuclear fuel cycle are made from ceramics, including the popular fuel, uranium oxide. This research investigates an indirect selective laser sintering technique (iSLS) that can be used to fabricate complex ceramic components. Thermally induced phase separation (TIPS) was explored as a technique to coat ceramic particles with a polymer, which can then be employed in an indirect SLS method. Two process variables of TIPS were studied, and the resulting powder characterized.

Keywords: Indirect selective laser sintering, thermally induced phase separation

Introduction

Additive manufacturing (AM) is a family of techniques capable of fabricating complex 3-dimensional objects by consolidating many 2-dimensional cross sections on top of one another in a layered process. There are robust AM processes to produce high density polymer and metal structures, but AM processes for such ceramic structures are not as robust. Selective laser sintering (SLS) is a powder bed fusion AM process that can be used to produce fully dense polymer components. In this process, a laser is used to selectively melt a 2-dimensional cross section of a polymer powder bed. The powder bed is then lowered, and a new layer of powder spread. The laser will then selectively melt the next 2-dimensional cross section. When repeated many times over, a 3-dimensional polymer part is formed [1]. A similar powder bed fusion process to SLS, selective laser melting (SLM), can be used to fabricate fully dense metal components [2]. Unfortunately, if a similar direct laser method is applied with ceramic powder, fully dense parts are not obtainable. Bertrand et al. researched a direct laser process where yttria-stabilized zirconia parts were fabricated with 56% theoretical density [3]. Other work has shown that cracks are present in final ceramic structures fabricated using direct laser processes [4]. This is due to the large thermal gradients induced in the structure during powder melting and re-solidification. Several groups have tried to increase density and remove crack formation by preheating the powder bed. Deckers et al. were able to produce 85% dense ceramic structures by preheating the powder bed to 800 °C [5]. Fully dense alumina/zirconia composite parts were formed by preheating the powder bed to over 1800 °C, but with poor geometric resolution [6].

As it became clear that direct laser AM processes were not capable of fabricating crack-free and geometrically accurate ceramic structures, research groups began developing other AM methods to produce these structures. One such method is indirect selective laser sintering (iSLS).

In this process, a polymer/ceramic composite powder is used for processing in an SLS machine. The polymer portion is sacrificial and used to 'glue' together the ceramic particles into a net shape, known as the green part. The polymer can then be burnt out and the remaining ceramic sintered together in an oven. The success of iSLS is largely dependent on the input polymer/ceramic powder. The powder must exhibit properties that can be processed in an SLS machine to be viable. It is for this reason that the produced powder in this research is compared to standard polymer powder that is known to process very well in SLS. Two of the methods that have been used to create the polymer/ceramic composite powder for iSLS is dry mixing, and thermally induced phase separation (TIPS). Gill et al. used a special mixing unit to mechanically mix silicon carbide grit and polyamide powder for use in iSLS [7]. This method is prone to powder agglomeration leading to a non-homogeneous powder mixture and poor spreading in the SLS machine. To combat these issues, a polyamide 12 (PA12)/dimethyl sulfoxide (DMSO) TIPS system was explored by Shazhad et al. as a method to coat ceramic powder with a polymer phase [8]. This provided motivation for the work outlined in this manuscript. The hypothesis is that the TIPS method produces a more homogeneous composite powder than dry mixed powders. The research outlined in this paper investigates several variables of the TIPS process and their effect on the obtained polymer/ceramic powder.

Thermally Induced Phase Separation

Thermally induced phase separation is a process that can be utilized to coat ceramic powders with a polymer. This is achieved by employing a polymer and solvent that are insoluble at room temperature, but soluble at an elevated temperature. First, the solution is heated above the solubility temperature. Next, the solution is cooled back to room temperature, where the polymer begins to precipitate out of the solvent when it crosses below the solubility temperature. If ceramic powder is present during the precipitation it will act as a nucleation site for the polymer precipitation and the polymer will therefore coat the ceramic. In this work, the polymer used was polyamide 12 (nylon 12), and the solvent was dimethyl sulfoxide (DMSO).

The morphology of the polymer after precipitation is directly related to the concentration of polymer and solvent in the solution. Figure 1 shows the binary phase diagram of the polymer/solvent system of interest [9]. The phase diagram has two curves of interest, the spinodal and binodal curves. Above the binodal curve the system is a homogenous liquid mixture where the polymer-solvent interactions trump the polymer-polymer interactions. In simpler terms, when above the binodal curve a single-phase system is obtained and when below the binodal curve a two-phase system is obtained. The spinodal curve separates the unstable region from the stable regions. Below the spinodal curve is an unstable region (region B) where the phase separation is controlled by spinodal decomposition resulting in an unwanted bi-continuous membrane structure. The desired process happens in the regions between the binodal and spinodal curves, deemed the stable area (both A regions). It is in this region where two distinct phases can exist. When the polymer concentration is below the critical point and the system reaches the stable region, a polymer rich phase will nucleate and grow. If ceramic particles are present in the solution, the ceramic particles will act as nucleation sites for the described polymer precipitation. The ceramic particles are coated with polymer consequently. This is the region

explored throughout the presented work in this paper. When the polymer concentration is above the critical point and brought into the stable region, a polymer rich cellular membrane structure will be formed [8].

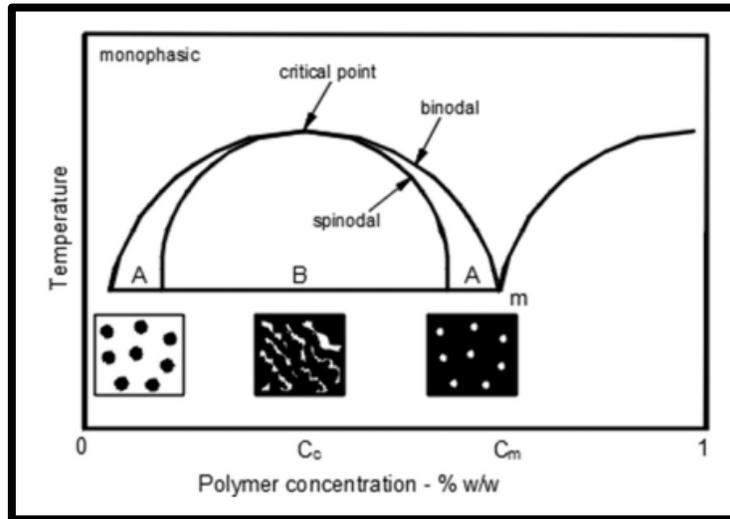


Figure 1: Binary phase diagram for polymer/solvent system used in TIPS

Experimental Setup and Procedure

Experiments were performed to see how two process variables affect the output composite powder of the TIPS process. The two variables that were investigated were the input ceramic powder characteristics and the cooling rate through the solubility point. These two variables were chosen to be investigated because it was hypothesized that these were the most important process variables in TIPS. Other variables that could have been investigated include the polymer to solvent ratio, polymer to ceramic ratio, mechanical stirrer velocity, temperature the solution is raised to, and pressure of the reaction kettle. The produced powder is compared to ALM PA650, a commercially available polyamide-12 (PA12) SLS powder. This is also the polyamide-12 input powder that was used in the TIPS process. The reason this powder is the comparison metric is because it processes very well in SLS machines. If the produced TIPS powder has similar characteristics to PA650 it should process well in an SLS machine to make composite green parts. Three batches of composite polymer/ceramic powder were made for investigation. The first powder batch had input ceramic that was not de-agglomerated, and the cooling rate through the solubility point was ‘fast’ (‘Fast’ non-milled). The second batch consisted of de-agglomerated ceramic and ‘slow’ cooling (‘Slow’ milled). The third batch had de-agglomerated ceramic and a ‘fast’ cooling rate (‘Fast’ milled). Due to limited resources, a ‘slow’ non-milled powder was not produced. For the same reason, each powder batch was produced only one time. To gain further statistical significance, future work should repeat powder production and characterization.

There are three inputs into the TIPS process to form a polymer/ceramic composite powder, a polymer, a solvent, and the desired ceramic. Polyamide-12 (ALM PA650, $d_{50} = 55 \mu\text{m}$) was used as the polymer, dimethyl sulfoxide (DMSO, reagent grade, Millipore Sigma) was

used as the solvent, and alumina (AKP-50, Sumitomo, $d_{50} = 0.2 \mu\text{m}$) was the ceramic of choice. For all powder batches, the ratio of polymer to solvent by weight was 95% DMSO – 5% PA12. The ceramic to polymer ratio by weight was 60% alumina – 40% PA12 for all powder batches. The exact quantities used were 1000 mL DMSO, 57.89 g PA12, and 86.84 g alumina. The three inputs are put into a 2-liter round bottom reaction kettle. The kettle is housed inside a heating mantle to allow for heating above the solubility temperature of the polymer and solvent system. The solution is continuously stirred throughout the entire process. A k-type thermocouple was dipped into the liquid to allow for PID control of the temperature of the fluid. The process is performed in an inert nitrogen atmosphere to discourage any reactions. Figure 2 shows the experimental equipment used to create the powder batches via TIPS. After the TIPS process has been complete and the solution allowed to cool to room temperature, vacuum filtration is used to separate the newly formed composite powder from the DMSO solvent. The powder is then washed with ethanol and dried for 48 hours at 65 °C. In the two cases where the powder was de-agglomerated prior to the TIPS process, the alumina and DMSO were put into a ball mill jar and placed on a ball mill for 48 hours to de-agglomerate the alumina.



Figure 2: TIPS equipment overview (left) and close-up of fittings (right)

The detailed TIPS procedure followed is outlined below:

1. If ceramic de-agglomeration is desired, put the input alumina and DMSO into a milling jar. Place the jar on a ball mill for 48 hrs. Skip this step if de-agglomeration is not being performed.
2. Insert the polymer, ceramic, and solvent into reaction kettle. Secure lid, attach the nitrogen ports, thermocouple, and stirring rod.
3. Begin stirring at 300 RPM. Stir throughout entire heating and cooling.

4. Heat the solution up to 140 °C and keep at this temperature for 15 minutes.
5. Cool solution to room temperature. Drop heating mantle for ‘fast’ cooling, leave heating mantle covering kettle for ‘slow’ cooling.
6. Separate composite powder from DMSO via vacuum filtration
7. Wash composite powder with ethanol 3 times.
8. Dry composite powder in an oven for 48 hrs. at 65 °C.

One thing to note in the setup is the ability to drop the heating mantle off the reaction kettle. This was designed to be able to control and study the cooling rate of the solution. The term ‘slow’ cooling is used when the heating mantle is left over the kettle during cooling. When the heating mantle is dropped off the kettle to induce more heat transfer, it has been named ‘fast’ cooling. Figure 3 shows the cooling curves for each scenario, starting at 143° C and ending at a room temperature of 22 °C. The cooling follows Newton’s law of cooling, and it can be seen that lowering the mantle significantly increases the cooling rate of the solution [10].

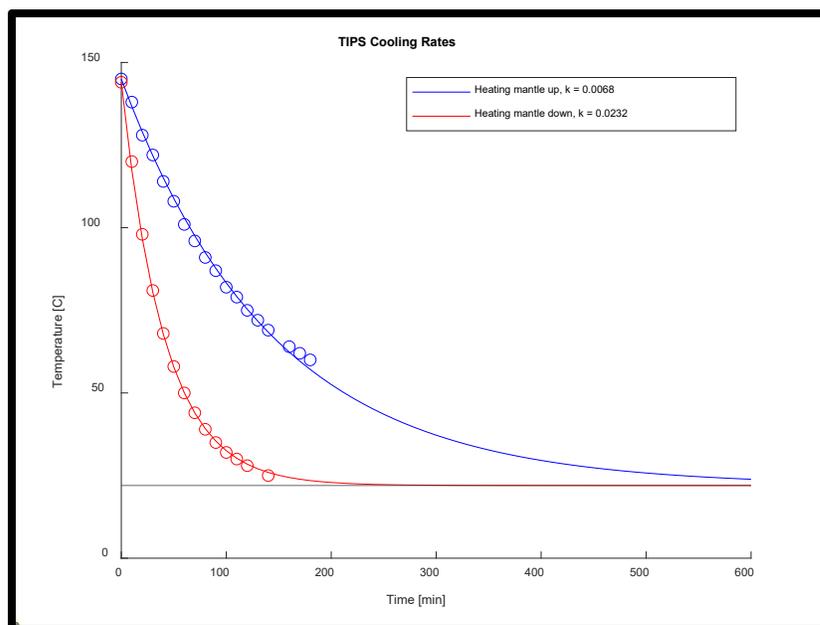


Figure 3: Solution cooling curves for ‘fast’ and ‘slow’ cooling

Several tests were performed to evaluate the characteristics of the synthesized composite powder. The first test was thermogravimetric analysis (TGA) to prove a polymer/ceramic powder was obtained. SEM images were taken of all powder batches to get an idea of the morphology as well as confirm only one phase is visible. The TIPS process coats ceramic particles with a polymer shell, so you should not be able to see both ceramic and polymer particles when viewed under a SEM. The bulk density and tapped density were evaluated to obtain the Hausner ratio (HR), which is defined as the tapped density divided by bulk density. The HR can shed light into how well a powder flows. The lower the HR the better the powder will theoretically flow, with a ratio of 1 being perfectly flowing powder. Lastly, the particle size distribution (PSD) and sphericity of the powder were analyzed. These are key metrics that can

help determine whether a powder can be processed in an SLS machine. The powder must be within a certain size range and shape to spread easily in the machine with adequate powder bed packing density. Once again, these metrics are compared to commercially available PA12 powder as this is known to process well in an SLS machine.

Results and Discussion

TGA was performed up to 600 °C to verify that the TIPS process was outputting PA12/alumina composite powder. PA12 is known to begin decomposing at approximately 420 °C in an air atmosphere [11]. If the powder is brought above the 420 °C degradation temperature of PA12, then it will begin to be removed and remaining weight would have to be alumina. Figure 4 shows the results from the performed TGA analysis. From Figure 4 it is shown that 55% of the initial weight is remaining at 600 °C. This verifies that a composite powder was created. Ideally, the remaining weight percent would be 60%, as this is the alumina weight percent that was inserted into the process. One reason for this discrepancy could be due to the very small sample sizes used in TGA (500 mg). Another reason for this error could be a non-homogenous coating of alumina particles. All particles may not have the same PA12-alumina weight ratio.

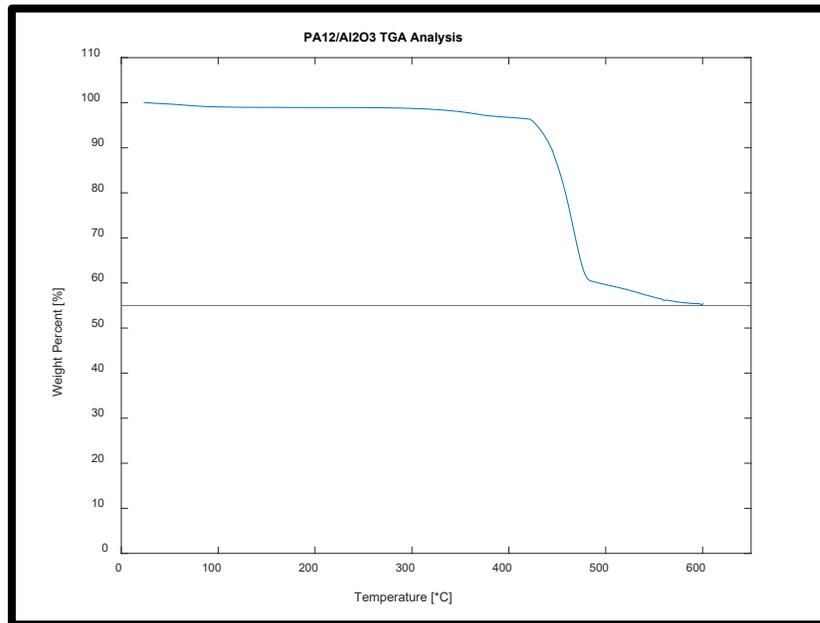


Figure 4: TGA analysis of TIPS powder

To get a glimpse of the morphology of the created powder, SEM images were taken of each batch. SEM images of the pure PA12 input material was taken as well for reference. Figures 5 and 6 house 500x images of the three trial batches and the input PA12. There are several conclusions that can be drawn directly from the SEM images. The first is that de-agglomerating the input ceramic powder prior to TIPS produces powder that is much more spherical. This makes sense as the ceramic powder acts as a nucleation site for the PA12 when precipitation out of the solvent begins. If the ceramic is agglomerated, it will have random shaping leading to

random shaping of the TIPS powder. Also, it seems from the SEM images that all 3 TIPS powder batches are slightly smaller than the pure PA12. This could be due to the input alumina powder being much smaller than the input PA12 powder. Lastly, only one phase can be seen in all SEMs of the TIPS powder batches. This further proves that the TIPS process was successful in coating the alumina powder with PA12.

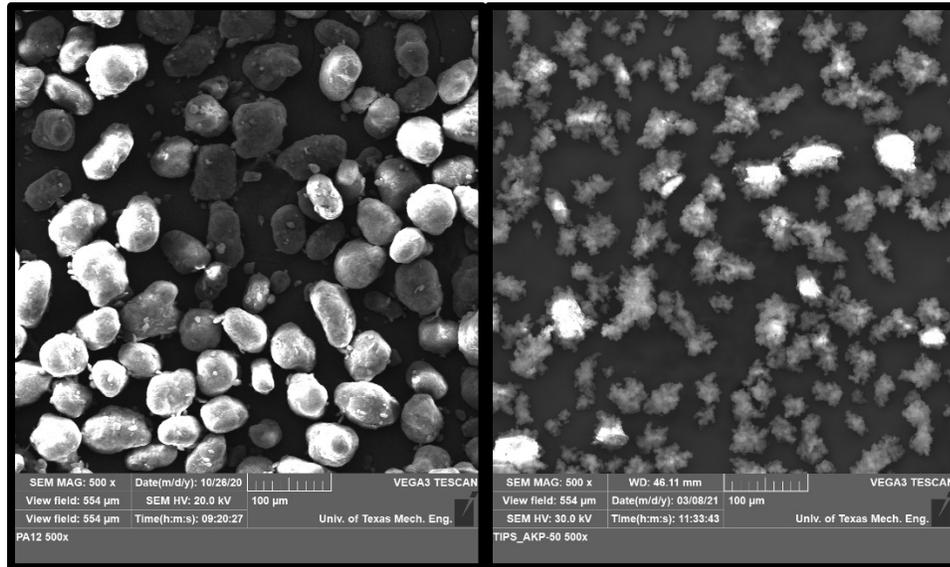


Figure 5: 500x SEM of input PA12 (left) and ‘Slow’ agglomerated ceramic TIPS (right)

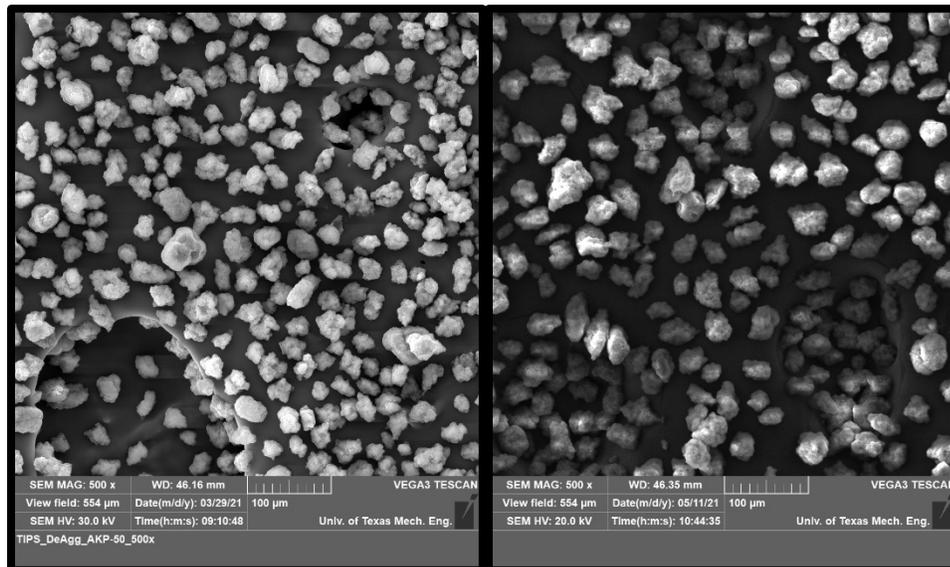


Figure 6: 500x SEM of de-agglomerated ceramic ‘fast’ (right) and de-agglomerated ceramic ‘slow’ (left)

To further prove the details the SEM images revealed, the bulk density, tapped density, particle size distribution characteristics, and sphericity of each TIPS powder batch was found.

Table 1 houses the results from these tests. Bulk density, also known as apparent density, refers to the density of the powder when allowed to naturally settle. Tapped density refers to the density of the powder after tapping the powder to maximum consolidation. The HR is calculated from these two quantities. Sphericity is a measurement that quantifies how spherical powder particles are. ISO 9276-6 was followed for this measurement [12]. Three quantities were taken to outline the particle size distribution of the powder batches, d_{10} , d_{50} , and d_{90} . These stand for the diameter of the particles, where the subscript refers to the percentage of particles that have that diameter or lower.

Table 1: Powder characteristics for each TIPS batch and pure PA12

	Bulk Density [g/cm ³]	Tapped Density [g/cm ³]	HR	Sphericity	d_{10} [μ m]	d_{50} [μ m]	d_{90} [μ m]
Pure PA12	0.4529	0.5514	1.22	0.899	41.77	54.59	68.08
'fast' non-milled	0.2042	0.2841	1.39	0.810	33.76	46.19	64.77
'slow' milled	0.2348	0.3026	1.29	0.872	30.90	39.50	53.24
'fast' milled	0.2915	0.3980	1.37	0.862	29.76	38.36	50.14

As the SEM images show, it was verified that the non-milled powder is much less spherical than the milled powder. Because the ceramic powder acts as a nucleation site for the polymer precipitation, it makes sense that a non-spherical ceramic agglomeration would produce less spherical powder. It is worth noting that none of the TIPS powder batches are as spherical as the input PA12, but the de-agglomerated batches are close. All the TIPS produced composite powder was smaller than the input PA12. It is believed this is the case because the input ceramic powder is much smaller than the input PA12. If there are a larger number of input ceramic particles than polymer particles, it makes sense that the output powder will be smaller as the input polymer will be distributed to more particles when precipitating out. To increase the output TIPS particle size, one could increase the polymer content of the solution, or begin with a larger ceramic powder size which will reduce the number of particles needing to be coated.

Like sphericity, the TIPS powder batches that had de-agglomerated (milled) ceramic had better Hausner ratios than the batch with non-milled ceramic powder. This is not a surprise as it is known that more spherical particles flow better. One attention grabbing outcome was that although the 'Fast' milled batch had a much higher tapped density than the 'slow' milled, its HR was much worse. Although the higher HR may mean that the powder does not flow as well, the higher bulk density and tapped density will provide a higher powder bed packing density after being spread. Experiments will need to be performed to determine which property is more important to optimizing the processing of this powder in SLS.

From the experimental results it has been shown when attempting to fabricate composite microspheres using TIPS one should de-agglomerate the ceramic prior to the TIPS process. It has also been shown that the cooling rate of the solution through the solubility point does not have a

profound impact on particle size, but rather the input ceramic size and polymer to ceramic ratio govern that. Future studies need to be performed to ensure that all the DMSO solvent is being removed from the TIPS powder during vacuum filtration, washing, and drying. If this moisture is still present in the powder it is unknown how that will impact the performance in the SLS process

Conclusions and Future Work

Thermally induced phase separation, or TIPS, was used to create three batches of powder. Throughout the three batches of powder, the cooling rate through the solubility point and the input ceramic state was studied. It was found that the input ceramic powder characteristics had the largest impact on the output composite powder size and shape. Specifically, when the input ceramic powder had been de-agglomerated by wet milling the best powder was produced. It was also found that the cooling rate through the solubility point had minimal impact on the size and shape of the output powder.

Future work includes further optimization of the TIPS process to make the output ceramic/polymer composite powder have characteristics closer to pure PA12 powder. This will help the powder be processed in an SLS machine. Ideas to accomplish this is to start with a larger ceramic powder and tailoring the polymer to ceramic input ratio. The next large milestone for this work is to begin printing complex green parts with the optimized TIPS powder in an SLS machine. Many test builds will need to be completed to fine tune the SLS process parameters needed to process this special powder. After the capability for printing green parts is established, the PA12 burnout phase and final ceramic sintering processes will be studied. At the end of this work, the goal is for complex and crack-free ceramic structures to be fabricated.

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