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Applied Solvent-based slurry stereolithography process to fabricate high-performance ceramic earrings with exquisite details

Jia–Chang Wang[1] Ph.D., Hitesh Dommati[2]

[1] Department of Mechanical Engineering, National Taipei University of Technology; jcw@mail.ntut.edu.tw
[2] College of Mechanical & Electrical Engineering, National Taipei University of Technology; iamhitesh89@gmail.com

Abstract: This paper discusses the application of Slurry based Stereolithography additive manufacturing process in the fabrication of complex earring models without any support structures requirement, using High-Performance Ceramic (HPC) materials. The earring model chosen in this study is a Rose flower with blossomed petals. The petals have edge thickness in microns and extreme overhangs with a custom text and logo on the bottom. Using any other ceramic additive manufacturing process, it requires support structures to build this model. The support removal in such minute structures is not easy and not always successful. Using Solvent based Slurry Stereolithography (3S) process, models with the micron details and overhangs can be easily built. This is enabling the neat and clean post-processing procedure to maintain the exquisite details and also gain high surface quality. The ceramic material used in this application is alumina. With some additives, it will show in different colors like sapphire. The resultant flowers are vividly shown in white, pink, green, and blue. In this study, it is also discussed about the slurry process, Stereolithography system, and proven applications of the 3S process.

Keywords: *Slurry based Stereolithography, High Performance Ceramics, non-self-supporting structures, earrings*

I. INTRODUCTION

Additive manufacturing (AM) is a class of technologies that use Computer Aided Design (CAD) based layer-by-layer manufacturing process to construct the parts. Unlike conventional material removing process, AM works in complete contrary by adding layer upon layer. AM is considered as a driving force of "Third Industrial Revolution" since it has revolutionized the way we manufacture almost everything. There are multiple AM technologies that can shape High Performance Ceramics (HPC) to net-shaped parts by the resin consisting of structural materials and binders. Most common AM technologies that are used to for shaping ceramics are Material Extrusion (ME), Vat Photopolymerization (VP), and Powder Bed Fusion process (PBF) [1, 2, 3]. The ceramic AM process is classified into direct fabrication process and indirect fabrication process. In the direct fabrication process, the structure particles are fused when exposed to powerful laser beams and doesn't require further thermal sintering process. The obtained surfaces of the parts through this process are rough because of the local thermal stresses due to temperature gradients. The Selective Laser Sintering (SLS), Selective Laser Melting (SLM) function as direction fabrication process. Whereas, indirect fabrication techniques such as Stereolithography (SL), Fused Deposition Modeling (FDM) requires a three-step process, consisting of three dimensional printing, thermal debinding and Sintering. Having less internal stresses in this process, it is possible to fabricate complex geometries with sufficient structural strength and adequate mechanical properties. In photopolymerization process, the formation of the three dimensional parts happens on the layer-by-layer basis on a ceramic suspension in a photopolymer resin. The SL process uses a light source such as a projector which projects the light mask dynamically through a Digital Micromirror Device (DMD). The intensity of the light and exposure time are completely adjustable by the user depending upon the characteristics possessed by the resin. Repeating this step until the last layer, a green part is obtained. The green parts are cured ceramic parts but very soft in nature due to the presence of the binder within them. To remove the binder and strengthen the green parts, it is necessary to follow the thermal debinding and sintering processes. During debinding, the binder inside the green parts will evaporate and escapes through the surfaces incurring internal voids. While sintering, the structure particles bond with each other filling the void and causes shrinkage. The property of shrinkage of ceramics green parts during sintering is inevitable but, it can be controlled to a certain amount by altering the volume of binder. The occurrence of cracks in the green parts during the debinding and sintering process is a common phenomenon which is important to be avoided. It can be optimized by adjusting the rates of rising and fall of temperatures during debinding and sintering process.

Conventional ceramic manufacturing methods can produce parts with high mechanical properties but they are not cost efficient for unit production or small scale production. They cannot produce high resolution objects due to the limitations of high tool wear during the grinding process [4]. Using AM technologies, it is possible to manufacture any high complexity geometrical structures in small scale at reduced costs and high resolutions. Yet, there is a limitation for topology optimization where it is difficult to fabricate ceramic objects which consist of non-self-supporting details. For parts having details which are facing downwards to the surface called overhangs, they can be fabricated efficiently using AM techniques only if they persist above a critical value with respect to the build platform. Any part having details which do not meet the critical values, they are non-self-supporting parts and requires sacrificial support structures added to the overhangs in order to fabricate in an AM system. Langelaar.M proposed a Topology Optimization (TO) method that overcomes the limitations of the design process by implementing layer wise filtering and avoiding the unprintable objects from the design space resulting in fully self-supporting design [5]. It is not a common aspect for every part to be a self-supporting structure and falls within the critical value of overhangs. Parts with overhangs can be arranged in specific orientations to avoid sacrificial support structures following the TO techniques but, it is uncertain for every similar case. The critical angle of the overhangs that are typically found to be in the order of 45^0 [6]. Any part that has geometrical details which fall less than the critical angle, can be adjusted by changing the orientation or providing sacrificial support structures. The addition of sacrificial support structures have clear disadvantages in terms of modifying the CAD file that may affect the mechanical properties, and consequently, it requires manual machining to remove them during post fabrication which increases the material and machining costs.

No studies had supported fabrication of HPC's using AM process without the requirement of sacrificial supports until Solvent based Slurry Stereolithography (3S) process was implemented by

Wang J.C [7]. The 3S process can produce HPC parts by using a light source of a projector exposing photo masks on to the slurry layers from the top. This process attributes the novelty of conciliating any ceramic materials such as Alumina or Zirconia as structure materials with a recommended proportions of photopolymer agents and solvents. Also, the unmasked portion of slurry on the build surface acts as sacrificial support structures to the curing portion of the next layer where overhangs are present. Thus it doesn't require any sacrificial support structures design for the overhangs. In this paper, the 3S process has been implemented and discussed in depth about its novelty of manufacturing complex geometrical structures which is an earring in this case.

II. Materials and Methods

2.1. Solvent based Slurry Stereolithography system

The 3S system comprises of a DLP projector above a build platform making this a Top-Down system. The build platform moves downwards for every processed layer until the last layer. The layer coating is enabled by a scraping mechanism where a scarping blade distributes the deposited slurry evenly onto the platform and pushing out the unwanted portion of slurry off the platform. Once the solvent vaporizes, the DLP system exposes a masked light onto the surface of the slurry layer. The masked portion of the light over the slurry photopolymerizes and links to the previous layer.

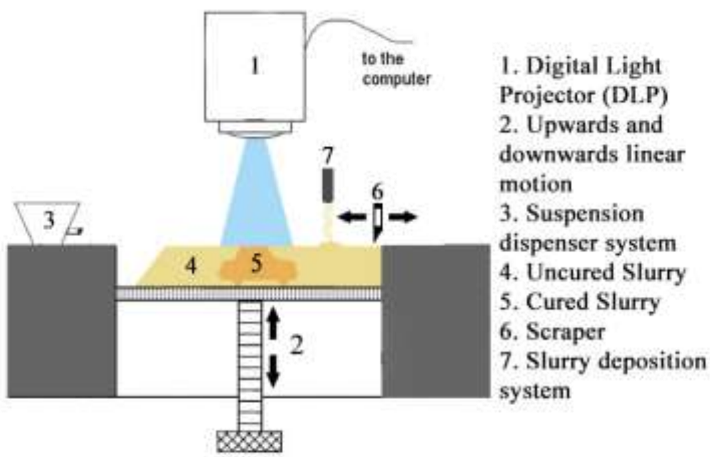


Figure 1: Solvent based Slurry SLA (3S) system

2.2. Slurry with Ceramic suspension

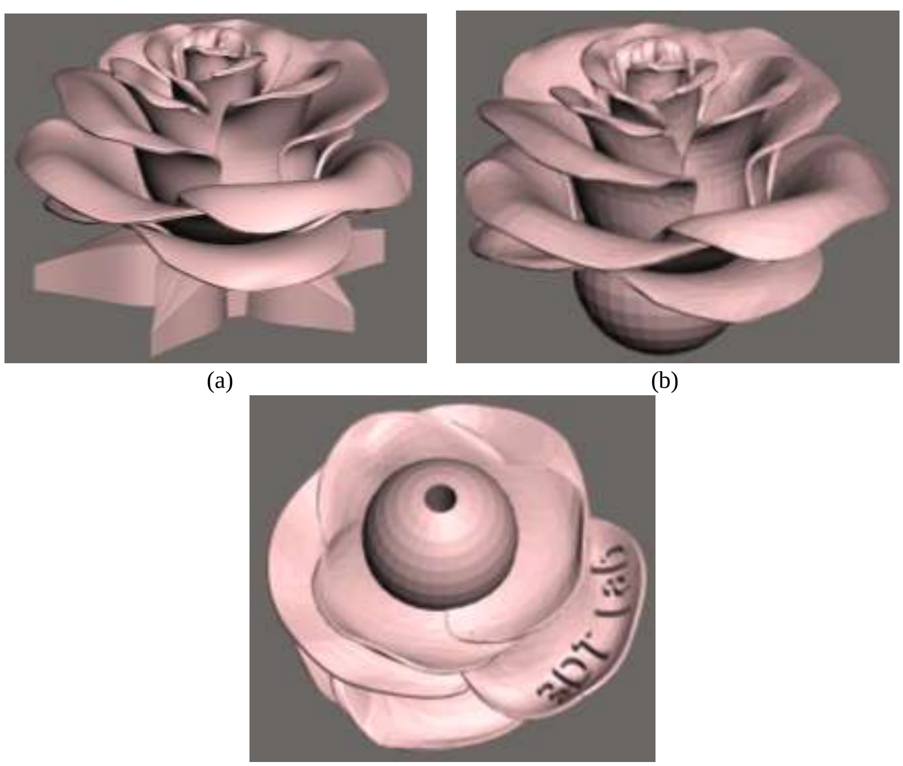
The slurry in this process is prepared by blending the main structural elements with a highly reactive photopolymer resin, methanol as a solvent and a dispersant. The structure element used in this study is Alumina (Al_2O_3). This forms a homogenous mixture by subjecting it to ball milling for one day using Alumina balls as grinding media. The target viscosity of the slurry should be in the range of 2800Mpa - 3200Mpa or capable of spreading uniformly on the platform covering the build area evenly. An inorganic pigment of orange color is mixed in the slurry. It aids to absorb the blue light from the projector and suppress the light scattering over the slurry layers caused due to diffraction in order to control the overgrowth.

2.3.Manufacturing of non-self-supported structures HPC earrings using 3S process:

To manufacture non-self-supported structures HPC earrings using 3S process, the following steps are involved:

1. STL file orientation and slicing
2. Green parts formation
3. Post processing
4. Post curing
5. Sintering

STL file orientation and Slicing: The CAD file format commonly used in the AM technologies is STL which is a globally recognized format and recognized by every CAD software. The STL file of a Rose model (Opensource model, Thingiverse.com) considered in this study. The original model of the Rose is having a flat bottom as a base without any provision for the stud. It is as shown in figure 2(a). It is modified to by removing its base and applied a hole at the center. This hole is not a pass through but it can accommodate a stud. The modified rose model is as shown in figure 2(b). The structure also has a custom text '3DT Lab' written on the bottom of a petal as shown in figure 2(c). This model has extreme overhangs with critical angle measured in negative values. The model is scaled to 13.44mm*13.36mm*10.10mm in length, width, and height such that the bottom hole can accommodate a stud. The edge thickness of the model's petals are very minute and it is very difficult to fabricate by using any other AM system.

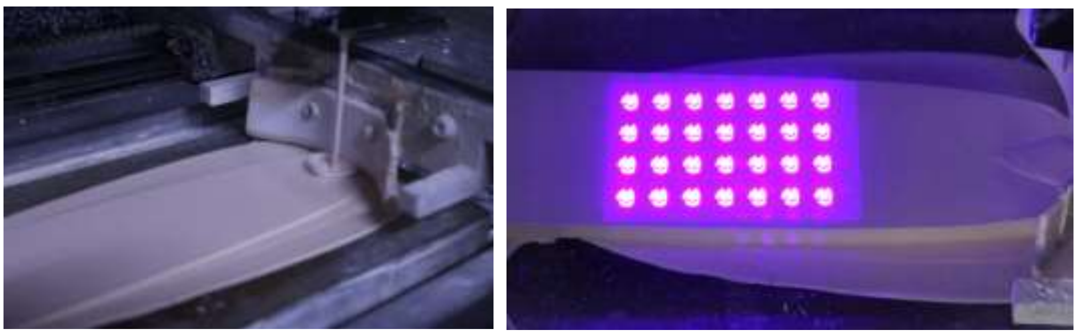


(a) (b)

(c)

Figure 2: The Rose model: (a) Original Rose CAD model (b) Modified Rose CAD model (c) Customized text

Green parts formation: A certain amount of slurry is deposited layer after layer onto the build platform as shown in figure 3(a). The deposited slurry is uniformly distributed onto the previous layer using a scraping tool. For every layer, the DLP system projects the sliced pattern as a mask on to the slurry surface for 1 second. The projected mask is based on a 405nm wavelength LED Full HD projector. The masked portion of the slurry gets solidified once exposed. The unmasked portion of the slurry remains soft and acts as a support structure for the proceeding layer. When the next layer is exposed to the corresponding lighting mask, that portion is linked with the previous layer and forms a three dimensional part. In this study, the objects are printed at the layer resolution of 20µm. Figure 3 depicts the DLP projecting a light mask to cure a layer.



(a) (b)

Figure 3: Green parts formation: (a) Slurry deposition (b) Exposing light mask for curing

Post processing: Once the green parts are fully formed, it is necessary to take the build platform out of the system and clean the uncured slurry off the surface carefully with water. Figure 4 represents the post processing of the cured green parts. In cases of models with complex geometries and soft portions, it is difficult to manually clean the slurry in the complex regions. Hence, the green parts are cleaned thoroughly using an ultrasonic cleaning equipment.

Figure 4: Post processing using water

Post curing: The obtained green parts are the outcome of an incomplete reaction of photopolymerization in the 3S system. They are very soft and deformable in nature. To complete the reaction, they are subjected to 405nm light to post cure for 10 minutes. During post curing, the soft parts lose deforming nature and obtain firmness. Yet, the firm parts do not completely attain the properties of the HPC's. They still carry the binder within them causing to be fragile. The following figure 6 depicts the outcomes after post curing. The dimensions are approximately similar to the values of the CAD model.

Figure 6: Roses after post curing

Debinding and Sintering: The debinding is the step which thermally heats and evaporates the binder present in the post cured green parts. The evaporated binder escapes through the nearest surface of the parts. An abrupt increase in temperature causes non-uniform conduction of heat resulting in cracks due to the non-uniform evaporation of the binder [8]. The rose model has thin features and which helps the binder to exit from the model without causing any cracks. Figure 7 depicts the Thermogravimetric analysis (TGA) test of the binder used in this process. Following the plot, the green parts are subjected to raise in temperature from 40- 350^{0}C for 2 hours. At 350^{0}C, the binder starts to evaporate faster. Hence, the raised temperature is increased to 600^{0}C in next 5 hours in which most of the binder is evaporated and leaves their spaces empty.

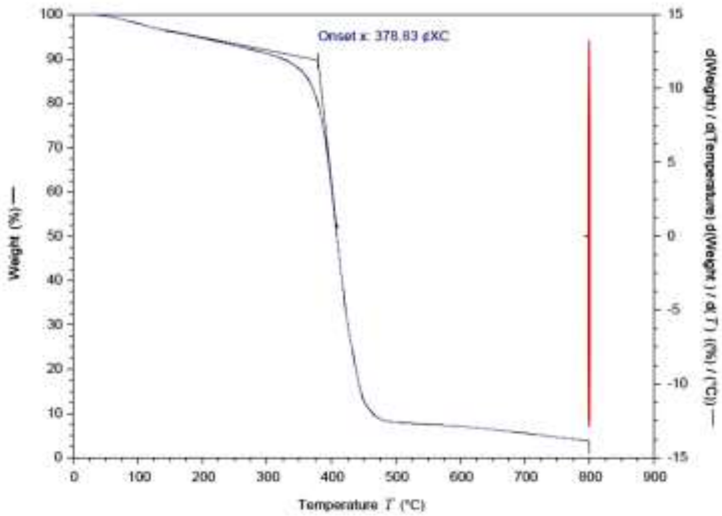


Figure 7: TGA test of the binder used for thermal debinding

The debinding process is then followed by sintering process where the parts are heated from 600^{0}C to 1600^{0}C. The atoms in the green parts diffuse across the boundaries of the particles, fusing the particles together creating one solid piece and fills the voids. The contraction of the particle causes the parts to shrink. The sintering cycle starts heating the parts at 600^{0}C to 1600^{0}C in 3 hours of time and cools down from 1600^{0}C to 45^{0}C in 6 hours. Figure 8 represents the roses obtained after sintering.

Figure 8: Resultant models of the roses after sintering

2.4.3D printing in different colors using 3S process:

The 3S process enables to 3D print the HPC's in various solid colors like blue, green, pink, etc. By adding coloring agents like Nickel Oxide, Cobaltous oxide, Chromium oxide, while preparing the slurry, green, blue and pink colors are obtainable after sintering. Figure 9 depicts the resultant models of the rose which are produced after sintering.

Figure 9: 3D printed Roses with Alumina using 3S process in different solid colors

2.5.Making of Rose earrings:

The bottom hole on the resultant models is used to fix a stud which fits within. Once the stud is fixed in, it is glued to permanently fix. Figure 10 depicts the roses having fixed with the studs to complete as an earring.

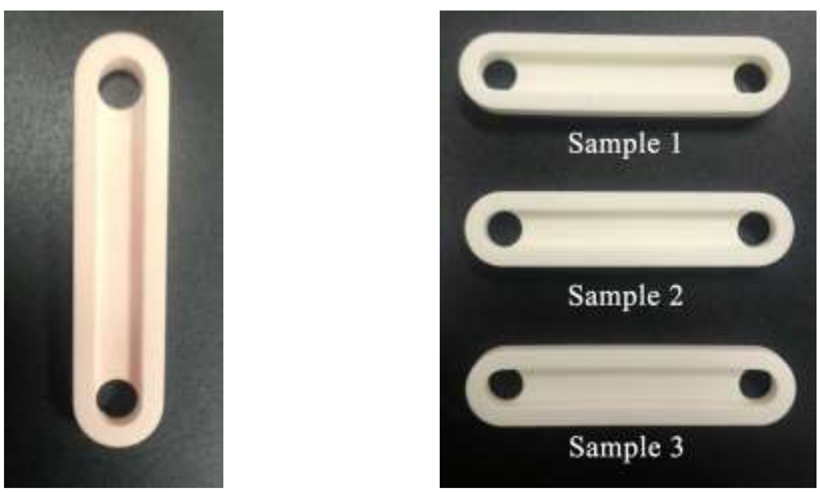
Figure 10: A stud fixed to the bottom hole of the rose

III. Results and Discussion

The resultant parts are now dense ceramic rose earrings which possess complete properties of any ceramic material. These objects are hard but brittle in nature. The overhangs of the structure are strong enough to have no cracks at any portion of the part. The edges are well constructed and maintained firmly even after sintering. The resolution of the parts are analyzed using 3D Macroscope (Keyence VR – 3000 series) and are described in the following.

Shrinkage: The HPC's are unavoidable of shrinkage when sintered at high temperatures. By sintering, they tend to shrink uniformly and become strong and dense components [9]. The 3S process implemented by Wang J.C. shows 20% shrink rate in alumina built parts. To measure the shrinkage, a standard rectangular model with round shaped edges and two holes on both ends is printed using 3S process and its dimensions are measured by a Macroscope equipment.

Three sample models are 3D printed and one of the parts which is post cured is as shown in the figure 12(a). The figure 12 (b) depicts the 3 sintered samples. The before sintered and after sintered samples dimensions are evaluated by the Macroscope equipment and the details are mentioned in the Table 1.



(a) (b)

Figure 12: (a) Sample before sintering (b) Samples after sintering

Samples	Sample 1	Sample 2	Sample 3
Pre-sintered	27.8	27.87	27.79
Sintered	23	23	22.94
Linear Shrinkage	20.87%	21.17%	21.14%
Results	Average 21.06% sample standard deviation 0.165 %		

Table 1: Length dimensions of 3 samples before and after sintering

The length of the sintered samples of 1,2 and 3 obtained are of 27.8mm, 27.87mm and 27.79mm. The length is measured by considering the midpoint of the part that can be obtained by drawing a line from the center points of both the holes. The same samples after sintered have the length of 23mm, 23mm and 22.94mm. The differences in the lengths gives the linear shrinkage values for which the sample 1 has the shrinkage value of 20.87%, sample 2 has 21.17% and sample 3 has 21.14%. The average linear shrinkage value is 21.06% and the sample standard deviation is of 0.165%.

Resolution: The resolution of the parts can be divided into two categories which are pixel resolution and layer resolution. The pixel resolution gives the quality of the parts in X and Y axis. This is completely dependent on the projector used. The projector used is a Full HD having 1920*1080 pixels in X and Y directions and the setup of the dots size per pixel is 40µm/pixel. This gives the working area size in total length and width of 76.8mm and 43.2mm. Secondly, layer resolution exhibits the parts quality in the Z axis. The layer resolution is dependent on the structure particle size and the minimum displacement and repeatability the Z axis motor can achieve [10]. The d50 of the grain size of alumina particles used in this study is 0.39µm and the Z-axis displacement is 20µm. If calibrated the projector carefully 20µm resolution of the parts can be obtained.

Discussion:

By observing the cross section thickness of the above segment shown in figure 12(a), it is explainable about the 3S process and its system combined are able to build fine features without requiring sacrificial supports. The hardness of the profiles is dependent on the ceramic material which is alumina in this case. The hardness measurement studies of the alumina components fabricated by 3S process conducted by Wang. J.C indicate they are 98% dense and have a tensile strength of 327 MPa, flexural strength of 472 MPa [7]. The strength values vary according to the structure component added in the slurry. The build volume of this system is dependent on the projector's resolution and the pixel size. The build volume can be increased by increasing the pixel size from 40µm to 50µm but, the quality of the parts degrades proportionally. Similarly, by decreasing the pixel size from 40µm to 30µm, the quality of the build parts aggrades but, the build size of the system is decreased proportionally. The shrinkage after sintering accounts in resulting the finest resolution of the parts of 32μm. Due to the thin features in the Rose model and temperature control for the debinding and sintering, no cracks were observed.

During the curing process, one layer of the binder molecules is linked with the previous layer due to the light energy. This energy is directly proportional to the time. The light exposure time is adjusted to its optimum value by performing time to energy experiment where parts are built at different time values starting from 0.1s to 2.0s. The parts exposed for 0.1s to 0.8s resulted in poor curing and very soft which were broken off while post processing. The parts exposed for 0.9s to 1.1s provided good results whereas the parts exposed for greater than 1.1s were shown overgrowth due to over-curing and resulted in protruded structures causing the scraping blade to scrape them off during printing itself. Hence, the optimum and mean exposure value of 1 second is considered to fabricate alumina parts.

IV. CONCLUSION

This work presents the fabrication of non-self-supporting high complex geometrical structures without any requirement of sacrificial support structures using Solvent based Slurry Stereolithography process. A rose model with critical overhangs is considered as the CAD model and modified it to an earring. Using alumina as the structure material, the slurry is prepared with appropriate proportions of photopolymer as a binding agent, dispersant, and methanol as solvent. The 3S system photopolymerizes every layer with lighting mask to cure the layers and forms fully cured ceramic green parts which are later subjected to post processing, post curing and sintering according to the standard procedure. The green parts have pertinent features of dimensions and accuracy of the CAD file. A shrinkage rate of 21.06% with a standard deviation of 0.165% is observed in the post sintering. The resultant sintered parts are fixed with studs to enable to use as earrings. The details and features of the models are steady, strong and aesthetically pleasing. It is conclusive that the 3S process enables to build any non-self-supporting structures without any sacrificial structures at high resolution with accurate dimensions. The shrinking volume has to be considered as a parameter that has to be calculated to scale up the CAD file before printing, such that the final parts meets the desired dimension.

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