

## Three-Dimensional Slurry Printing Technology in Ceramic and Metal Application

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**Abstract.** Vat photopolymerization is one of additive manufacturing and also known as photo-curable three-dimensional printing technology. It uses light energy with the proper wavelength to expose on the liquid photo-curable resin inducing the photopolymerization process and resulting in solidification layer-by-layer. The building method is classified into two ways: free-surface and constrained-surface. The advantage and disadvantage of both methods are described and analysed according to the different material property and requirement. The basic composition for photo-curable resin consists of photo-initiator and monomer. Adding powder into photo-curable resin makes the photo-curable slurry. Literatures report that high density powder such as zirconia oxide or Inconel 718 is suitable for free-surface building method because of poor suspension. However, the volume percentage in the slurry is less than 50% causing the higher shrinkage ratio and inaccuracy after sintering process. The coupling agent may increase the suspension of powder in slurry but experimental result shows that it still cannot improve the success rate in the constrained-surface building method. Therefore, this study proposes a combination method to overcome the difficulty of making high density ceramic or metal part. In addition, the sintering process is a key factor to obtain the high dense part with no crack occurrence and desirable microstructure. The optimized sintering parameters for zirconia oxide and Inconel 718 are also introduced.

### Introduction

Additive manufacturing (AM), also known as the three-dimensional printing, has widely promoted and applied in varying fields because it offers high fabrication efficiency, lower material waste and flexible integration with subtractive manufacturing. It also provides the customize product fabrication without the mold investment. Although the ASTM classified the AM into 7 categories consisting of the most common and affordable machine is the fused deposition modeling (FDM) and stereolithography apparatus (SLA). However, both fabrication methods cannot make metal part easily. Therefore, few researches have tried to develop new materials such as metal filament for FDM [1] and metal slurry for SLA [2]. The difficulties need to be overcome are fragility of metal filament for FDM and poor suspension of metal slurry for SLA. Furthermore, traditional SLA uses single laser to scan the photo-curable resin to form a layer. The fabrication speed is slow and comparable to the FDM. The digital light projection (DLP) [3-4] and liquid crystal display (LCD) [5] have used in SL system as the light engine to instead of single laser scan for forming a layer, also known as the layer-curing type, in a few seconds. The fabrication speed becomes faster than the FDM. Hence, it becomes the major AM system to make ceramic or metal part with affordable price as a consumer machine.

Layer-curing type SL can be classified into top-down and bottom-up methods [4] as shown in Figure 1. Slurry in vat needs to have good suspension and uniform distribution of particles. The density of particle and viscosity of resin is a balance of weight gravity and surface mass. Zirconia has high density (5.68 g/cm<sup>3</sup>) resulting in poor suspension. In addition, the density of Inconel 718 is 8.19 g/cm<sup>3</sup> that is higher than zirconia. Both materials are not suitable for using in bottom-up method SL. Therefore, using top-down method can avoid the problem of poor suspension.

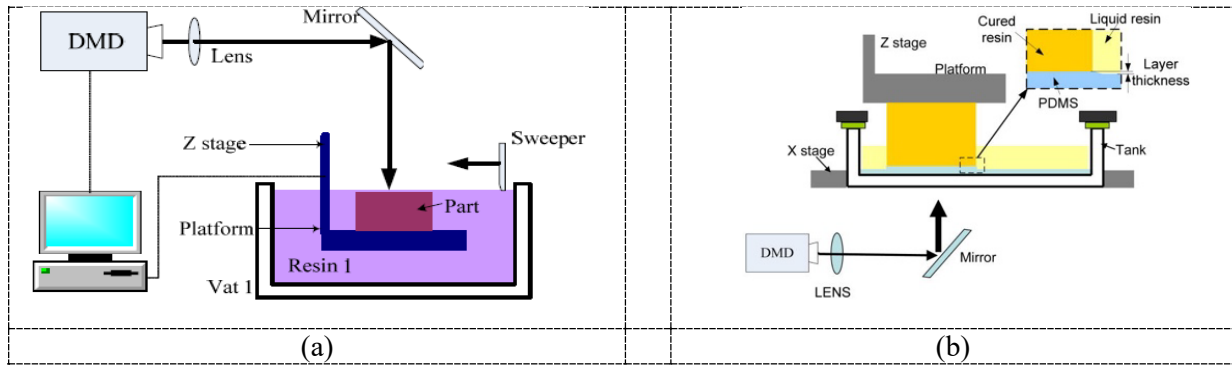


Fig. 1 The top-down (a) and bottom-up method of SL system [4]

The basic compositions of slurry are monomer, photo-initiator and powder. The powder can be ceramic or metal. In this study, we use zirconia and Inconel 718 to print to the green body of dental restoration device and spur gear, respectively. The principle of three-dimensional slurry printing (3DSP) is briefly introduced and proposed a novel near-field 3DSP.

## Development of Three-Dimensional Slurry Printing

### Top-down Three-dimensional Slurry Printing

Figure 2 represents the fabrication principle of three-dimensional slurry printing (3DSP) using the top-down method. The fabrication procedure sequence is to descend the platform by a layer thickness as step (a), cast a thin slurry layer on the platform as step (b), and expose the layer pattern as step (c). The exposed part cured and becomes solid part. The un-expose part remains slurry state and becomes the support. To repeat the step (a) to (c) until all layers are fabricated as step (d). The cured part embedded in slurry block as green block after the fabrication is completed. Then the green block is removed from platform and immersed in solvent (methanol) as step (e). The obtained green part, step (f), can be sintered in the oven, step (g), as high dense zirconia sintered part in the step (h). This process has advantage of avoiding support creation but the major drawback is the waste of material.

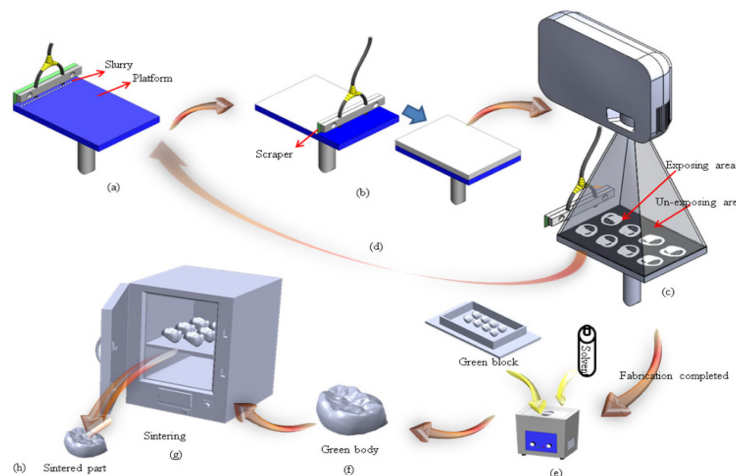


Fig. 2 The workflow of top-down 3DSP

### Near-focused Three-dimensional Slurry Printing

Figure 3 shows a novel method, near-focused solidification, using the top-down method in SL system to save the material and control the thickness of solidifying layer. It uses the liquid crystal display (LCD) to generate the sliced pattern and dip into the slurry to keep a distance of layer thickness. The LED array emits the light with a wavelength of 405 nm to solidified the slurry between the platform and the surface of LCD. This design has advantage that the building green body is bonded on the platform with its weight gravity aided. In addition, it also saves the slurry comparing with the top-down 3DSP.

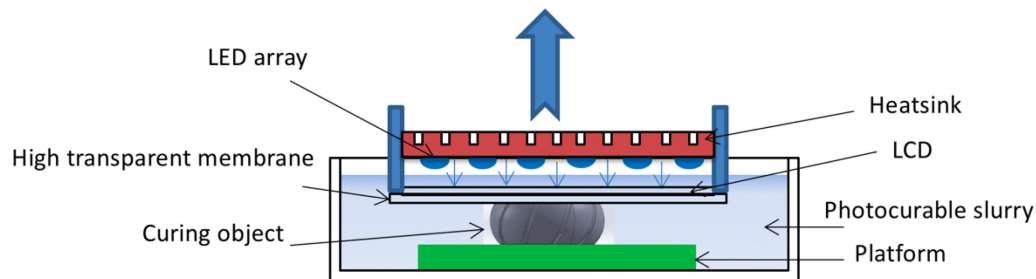


Fig. 3 The principle of near field three-dimensional slurry printing

### Zirconia Oxide for Dental Application

Industrial polycrystalline ceramics consisting of alumina, zirconia and alumina-zirconia have been applied in dental application for making the restoration device. The material is yttrium stabilized tetragonal zirconia polycrystalline (YTZP) due to it has advantage of good aesthetic, high fracture toughness and biocompatibility [6-7].

This study used a micro-sized zirconia-yttrium (called ZrO<sub>2</sub>) powder with an average particle size of 1  $\mu\text{m}$ . The composition is list in Table 1. The slurry consisted of four components: 70 wt% ZrO<sub>2</sub>, 25 wt% HDDA (1,6-hexandediol diacrylate), 8.5 wt% acrylated monomer and 1.5 wt% photo-initiator (Trimethylbenzoyl diphenylphosphine oxide, TPO). The mixture slurry is then ball milled at 200 rpm for 2 hours. Finally, it is degassed in a vacuum chamber for 10 minutes to remove the air bubble that may be generated during the ball milling process. A viscometer (DV-III, ULTRA) is used to measure the viscosity because the particle size affects the viscosity of slurry and the fluidity during casting a layer. As a result, the viscosity is 3.89 Pa.s.

Table 1 The composition of zirconia-yttrium power (unit: %)

ZrO <sub>2</sub>	Y <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	TiO <sub>2</sub>
>94	5.2±0.2	0.25±0.05	<0.02	<0.002	<0.005	<0.002

### Inconel 718 for Gear Fabrication

Inconel alloy 718 is one of the many nickel-based superalloys. The alloy is made up of 50-55% nickel+cobalt (with cobalt limited to 1% max) and 17-21% chromium. This combination gives the material its corrosion-resistance properties. This includes good resistance to oxidation, high strength in extreme temperature conditions at both ends of the spectrum. It can be used in environments from cryogenic all the way up to 1300°F/704°C. It also shows excellent tensile and impact strength. It is often used within the aviation and aerospace industries. [8]

This study used the monomer, HDDA, with 35 wt%, photo-imitator, 819, with 1 wt% and 64 wt% of Inconel 718 with an average particle size of 20  $\mu\text{m}$  to synthesize the metal slurry. According to the solidifying test, the exposure time of 5 seconds induces 92  $\mu\text{m}$  solidified thickness. Therefore, the slicing layer is determined to be 50  $\mu\text{m}$ .

### Model Preparation for Dental Application

An ideally right maxillary first molar [9] was prepared as a master die from dentoform (Nissin Dental products, Kyoto, Japan) as shown in Figure 3(a). It has a deep chamfer finishing line (0.8) all around with 6 degrees convergence and 2 mm occlusal reduction. A dental scanner was used to digitalize the master die as shown in Figure 3 (b). The restorative model was then designed using CAD software (model builder, 3Shape, Denmark). Figure 4 (c) shows the assembled molar system consisting of digital molar die and designed molar model to show the close-fit of marginal gap. Figure 1(d) presents the designed molar model and will be used to fabricate the zirconia crown by 3DSP.

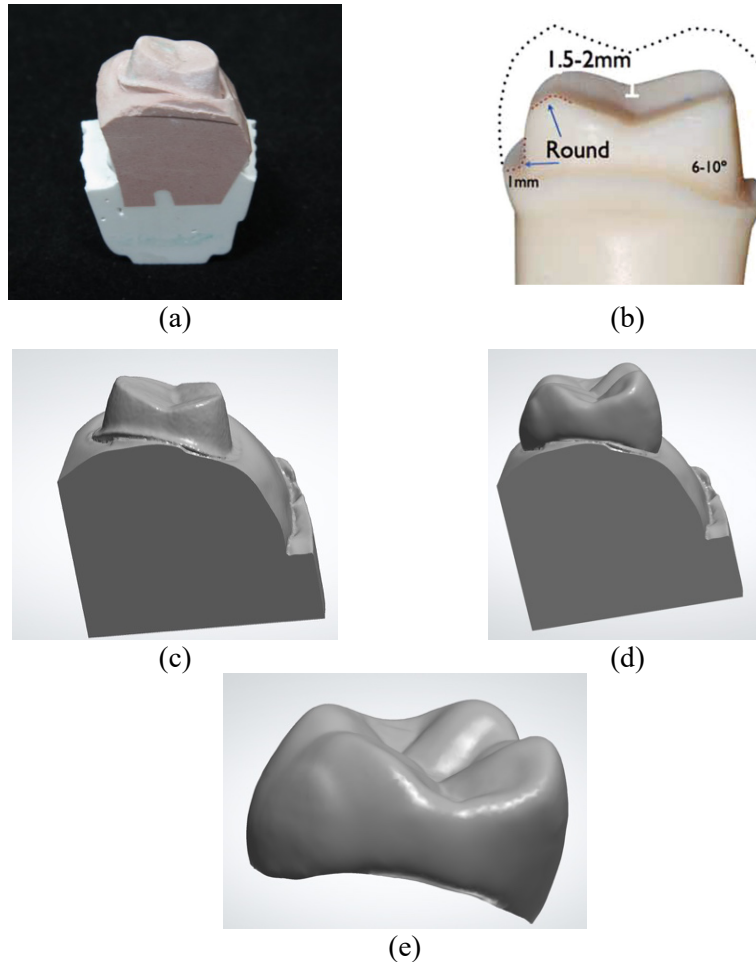


Fig. 4 The prepared molar, reconstructed model and designed fitting molar model

### Model Preparation for Gear Application

The miniature of spur gear is designed to test the printability of metal slurry. The gear thickness is 2 mm. The module and teeth are 1 and 15, respectively. The pressure angle is 20°.



Fig. 5 The model of spur gear

## Result and Discussion

Figure 6 (a) shows the fabricated green body and sintered part of dental crown. The marginal gap is an indicator for clinical use. The acceptable allowance is less than 100  $\mu\text{m}$ . Figure 6(b) shows the maximal marginal gap is about 25  $\mu\text{m}$  and the average marginal gap is about 16.2  $\mu\text{m}$ . This reveals that this fabrication method can obtain high precision dental crown.

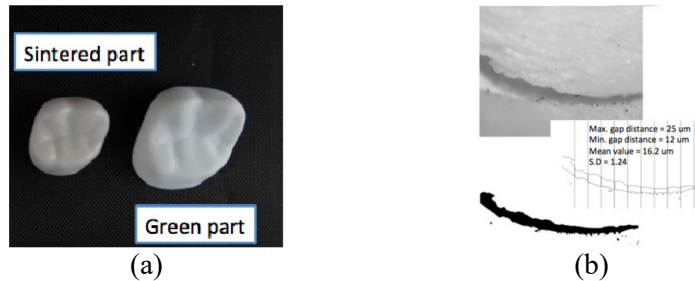


Fig. 6 The printed green body and sintered part of dental crown

Figure 7 (a) shows the printed result of spur gear. It also creates the substrate to support the green body. It made of pure HDDA resulting in good bonding strength. During the sintering procedure, the substrate burnout when heating temperature rises to 400°C. Inconel powders start to fuse together while heating temperature reaches to 1100°C. Figure 7(b) presents the single tooth of sintered part. The debris can be seen on the surface of tooth. This reveals that the green body was not washed clear resulting in few particles adhesive on the surface.

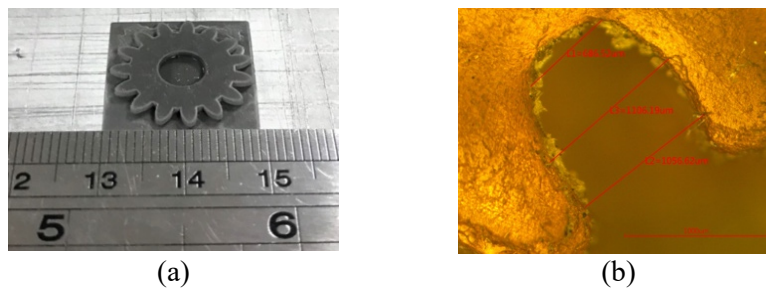


Fig. 7 The printed spur gear (a) and tooth observation (b) of sintered part

## Conclusion

This research mainly focuses on vat photopolymerization with different designs of solidifying method and slurry consisting of ceramic and metal powder, respectively. The advantage and limit of these Lab development systems are briefly introduced. Green bodies of dental crown and spur gear are fabricated successfully but the optimization of slurry content to manage of shrinkage and sintering parameters are the main factors to obtain the high precision high dense part.

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