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A Novel Fabrication Method of High Strength Alumina Ceramic Parts Based on Solvent-based Slurry Stereolithography and Sintering

Jia-Chang Wang[1,#]

1 Department of Mechanical Engineering, National Taipei University of Technology, No. 1, Chung Hsiao East Road, Sec. 3, Taipei, Taiwan, 10608
Corresponding Author / E-mail: jcw@ntut.edu.tw, TEL: +886-2-27712171, FAX: +886-2-27317191

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The aim of this paper is to develop a novel Solvent-based Slurry Stereolithography and Sintering (4S) process which can fabricate high strength ceramic parts. High performance solvent-based slurry, which was composed of alumina powder as a structure material, visible light curable resin as an organic binder and methanol as a solvent and a dispersant, could be prepared with colloidal processing. During layer casting, the diaphanous slurry can penetrate into pores of the subjacent layers. After drying, the binder in the penetrated liquid could connect the fresh layer and subjacent layers. Eventually, a gel-like green block could be built layer by layer. In the exposed region, the resin contained in the green block was cured to connect the alumina powders to be a part of the rigid green part. However, the un-exposed region remained gel-like and is methanol-soluble. Afterward, the green block was immersed in a methanol solution. Due to dissolving of the resin, the un-exposed region could completely collapse to obtain the rigid green part. The obtained rigid green part was then heated up to 600ºC for binder burnout, and then sintered at 1600ºC to obtain a dense alumina ceramic part. The results show an average tensile and flexural strength are 327 and 472 MPa, respectively, and a relative density of 98% was achieved. The proposed method of solvent-based slurry was briefly described and it was proved that the good capacity of solidifying thin layer. The results also show that the developed system can fabricate complicated rigid green parts quickly with high accuracy (less than 5 μm).

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1. Introduction

Ceramic materials are characterized with high hardness, brittleness and heat resistance; therefore, the ceramic parts can hardly be produced with conventional machining processes. If parts are small and complex they will be more difficult to be manufactured. Traditionally, ceramic parts are formed by molds and are densified by sintering. Today, a variety of rapid prototyping methods, which fabricate three-dimensional (3D) ceramic parts from computer aided design (CAD) models without molds, have been developed over decades, such as Stereolithography (SL) (Griffith et al., 1996; Hinczewski et al., 1998; Chartier et al., 2002), Microsterelithography (In-Baek Park et al., 2009; Young-Myoung Ha et al., 2010), Selective Laser Sintering (SLS) (Subramanian et al., 1995; Liu et al., 2007), Fused Deposition of Ceramics (FDC) (Agarwala et al., 1996), Laminated Object Manufacturing (LOM) (Klosterman et al., 1998), Computer-aided manufacturing of laminated engineering materials (CAM-LEM) (Cawley et al., 1996), and slurry-based three dimensional printing (S-3DP) (Grau et al., 1997). Most of these processes can make ceramic parts but only limited processes can build parts with high strength.

The objects directly fabricated with conventional powder-based selective laser sintering (SLS) are not fully dense and the strength of the objects is low. Subramanian utilized a mixture composed of polymer binder and alumina particles (average size of 15 μm and 2 μm) to improve the density of the parts made by SLS (Subramanian et al., 1995); however, the relative density and flexural strength of the sintered part were only 50% and 8 Mpa respectively. A mixture composed of calcium stearate and alumina particles with particle size of 0.26 μm to fabricate alumina ceramic bars which have 255 MPa in flexural strength and 88% in relative density (Liu et al., 2007). Tang brought up a slurry-based selective laser sintering process, which also named as Ceramic Laser Sintering (CLS). CLS employs the slurry

composed of ceramic powder, inorganic binder, and water to fabricate ceramic parts (Tang et al., 2006). However, sintering at high temperature, the ceramic parts produced by this process cannot achieve high density; their flexural strengths are only 10 ~ 20 MPa. The high strength ceramic parts cannot be achieved. Tang also proposed a most successful slurry-based approach recently in which a slurry was composed of alumina coated with water-resoluble semi-crystalline polyvinyl alcohol as structure material, water-soluble PVA as an organic binder, ammonium polymethacrylate as a dispersant, and de-ionized water as a solution (Tang et al., 2011). The process using laser as the energy source to heat up the scanning area and the polymer contained in the scanned region were melted to connect the alumina powders and transformed to be water-insoluble. The un-scanned region could collapse to obtain the green part because the un-cured polymers can be dissolved in water. Followed by sintering process, an average flexural strength of 363.5 MPa and relative density of 98% were achieved.

In general, applying laser beam to selective sintering the powder is difficult to shorten fabrication time and obtain high accuracy and surface finished. This is because the total fabrication time of the rigid green part is a function of the total scanning area. The larger scanning area is, the longer total fabrication time needs. Moreover, the high resolution of the final parts needs a highly definition laser beam to scan a tiny features, which will also increase the scanning path and scanning time.

Instead of laser scanning, this paper proposes a novel fabrication method based on solvent-based slurry stereolithography and sintering process. It uses a dynamic mask exposing for accelerating the fabrication time of green parts with high accuracy and bring high strength after sintering. The slurry preparation, the principle of solvent-based slurry stereolithography and mechanical properties of sintered part are briefly presented.

2. Material and Methods

2.1 Principle of solvent-based slurry stereolithography and sintering process

There are four sections of the proposed method: (1) making solvent-based slurry, (2) building up sacrificed layers, (3) building up parts by layer additive process, and (4) post-process to get the final ceramic parts. The whole process is named as Solvent-based Slurry Stereolithograph and Sintering (4S).

Figure 1 illustrated the making solvent-based slurry section in which alumina powder as a structure material, methanol as a solvent and a dispersant, and visible light curable resin as an organic binder. By adding all ingredients into a bottle and milling for fully mixing and wait for bubble escaping, the resulting slurry can be made.

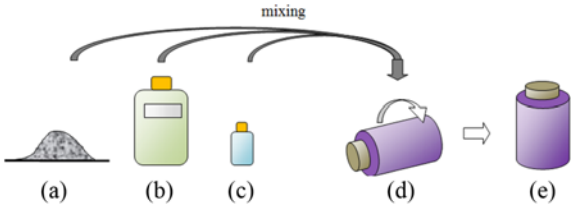


Fig. 1 Slurry mixing (a) alumina powder, (b) methanol, (c) visible light curable resin, (d) slurry milling, (e) bubble escaping

Figure 2 illustrated the building up sacrificed layers section in which (a) descending platform for one layer thickness and casting a thin slurry layer by a moving scraper, (b) drying the slurry layer with a fan to form a fresh gel-like green layer, (c) repeat (a) and (b) until there are stable substrate layers. For example, the thickness is 50 μm, once slurry is casting to the plate, it will dry out and the thickness will be thinner. If the thickness shrinkage rate is 50%, the resulting thickness will be 25 μm. When the platform descends another layer thickness, there will be 75 μm gap in between and the slurry is casting the 75 μm thickness to the substrate. Again, the thickness will shrink to 37.5 μm and remain 37.5 μm gap. When the platform descends another layer thickness, there will be 87.5 μm gap. Layer by layer, the gap will reach to 100 μm and the thickness will shrink to 50 μm and continue to be 50 μm. This is the process to stabilizing the substrate.

Figure 3 illustrated the building up parts by layer additive process section in which (a) descending platform for one layer thickness and casting a thin slurry layer by a moving scraper, (b) drying the slurry layer with a fan to form a fresh gel-like green layer, (c) mask is generated by a digital light processing (DLP) projector (named mask generator) and exposing the green layer. Particles in exposed area are consolidated and become a rigid portion; on the contrary, the un-exposed portion forms an inherent support, (d) repeating steps from step (a) to step (c) until the slicing files is executed completely to form

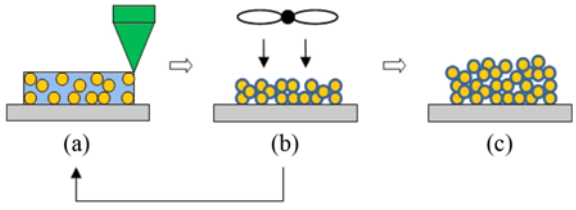


Fig. 2 Building up sacrificed layers (a) descending one layer thickness and casting slurry, (b) drying the slurry layer with a fan, (c) stable substrate layers

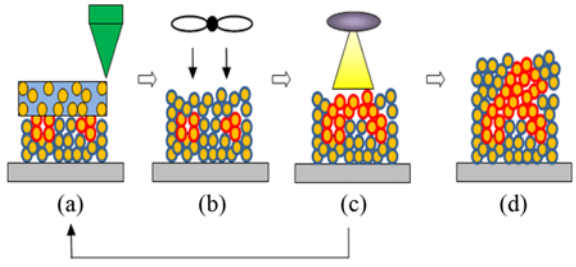


Fig. 3 Building up parts by layer additive process, (a) descending one layer thickness and casting slurry, (b) drying the slurry layer with a fan, (c) mask exposing, (d) complete a 3D rigid green part

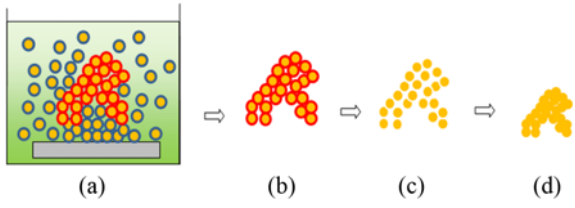


Fig. 4 Post-process to get the final ceramic parts, (a) immersing the green block, (b) the resulting green part, (c) binder burnout, and (d) the sintered ceramic part

a 3D rigid green part. In this section, particles in exposed area are consolidated as a rigid portion; on the contrary, the un-exposed portion forms an inherent support.

Figure 4 illustrated the post-process in which (a) immersing the green block in methanol to remove the un-exposed green portion with the assistance of an ultrasonic vibration, (b) taking the green part out from the ultrasonic cleaner and wait for dry out, (c) binder burnout, and (d) part sintering in a furnace to obtaining a ceramic part.

2.2 Preparation of solvent-based slurry

The reason why the ceramic parts fabricated by existing slurry-based selective laser sintering cannot achieve high strength is that because clay is used in the slurry as a binder, so that the resulted green parts are not uniform and contain large pores. Consequently, theses green parts cannot be densified fully by sintering. To obtain a high density part with such process, an organic binder should take the place of the clay. This viewpoint has been proved by many processes which utilize polymer as a binder and fabricates sintered ceramic parts with high strength, such as SL, FDC, LOM, and CAM-LEM. Instead of clay, photopolymer resin (Accura SI 10, 3D Systems Co.) mixed with visible photo-initiator (3DV1, double bond Chemicaline Co.) as a binder was used in this paper to prepare the solvent-based slurry. The solvent and ceramic particle used was methanol with dielectric constant of 33.1 and Al2O3 with average size of 0.3 μm.

The solvent-based slurry preparation process was illustrated in Figure 5. The slurry composed of 5 g of Accura SI 10, 50 g of methanol, 0.6 g of 3DV1 and 55 g of $Al2O_3$ powder. The slurry was milled for 24 hours and average size of particle became to 150 nm. After all, the solvent-based slurry stayed still under ambient conditions for 24 hours, and then the residual bubble could continuously escape from the slurry.

2.3 Layer casting

The holding plate is a plaster plate. During the layer casting stage, the plate will decent a layer thickness, which is 30 μm in this paper, and followed by the paving. The solvent-based slurry is paved on the top of the plaster. This diaphanous slurry will penetrate into the pores of the plaster plate to bring strong mechanical holding force between the working plate and the building part. After the paving, a fan is used to aid the solvent to vaporize rapidly, resulting in shrinkage of the slurry volume of the current layer. Although the thickness is abbreviated, ceramic powders are connected by the resin and a dense gel-like substrate can be established as a green layer by the capillary effect during the vaporization. This dense gel-like substrate can be exposed to cure as a rigid portion (step c in Fig. 3) and unexposed region can be treated as a solid support to avoid damaging caused by the force generated during the next layer paving.

2.4 Part solidification

Accura SI 10, an ultraviolet (UV light) sensitive photopolymer, is widely used in Stereolithography system. The visible photo-initiator was added in Accura SI 10 for expanding photo-sensitive range from UV to visible light as a regular organic binder so that the white light layer pattern from mask generator can be used to cure the resin. After irradiating by white light, the binder was fully solidified, which is not dissolved in methanol at room temperature. Furthermore, the ceramic particles in the exposed region were connected by the fully solidified binder and show a rigid property. The other portion of the region is remaining as a gel-like substrate which can be dissolved in methanol at room temperature. Layer by layer, green layers will stack into a green block and the rigid green part inside the gel-like green block can be fabricated.

Figure 6 illustrates the states of the green layer before and after white light irradiation. In Figure 6(a), the methanol-soluble binder in the un-exposed region connects the ceramic particles which are in a round shape. There are also few void pores in this region. The binder will be dissolved and the ceramic particles will be dispersed if this region is immersed in methanol. In Figure 6(b), the methanol-soluble binder in the exposed region solidifies and connects ceramic particles to form a methanol-insoluble composite.

2.5 Post-processing and sintering

The un-cured portion of green block will be dissolved when it is immersed in methanol, and an intact green part can be obtained. Because of using organic binder, the principle of colloidal science can be applied for making sufficiently dispersed slurry. Afterward, the photopolymer-coated ceramic particles could undergo re-crystallization with heat treatment to further reduce the methanol solubility of the binder.

The finished green parts were placed in an electric furnace (LHT-04/17, Nabertherm GmbH, Lilienthal/Bremen, Germany). Furnace temperature was raised at a rate of 5°C /min to 600°C and was kept for 30 minutes to burn out the organic binder. Afterwards, these parts were placed in the furnace, in which the temperature was raised to 1600°C at a rate of 5°C /min and was retained for 2 hours.

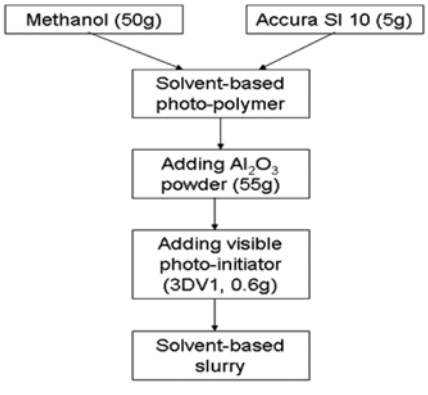


Fig. 5 Solvent-based slurry preparation process

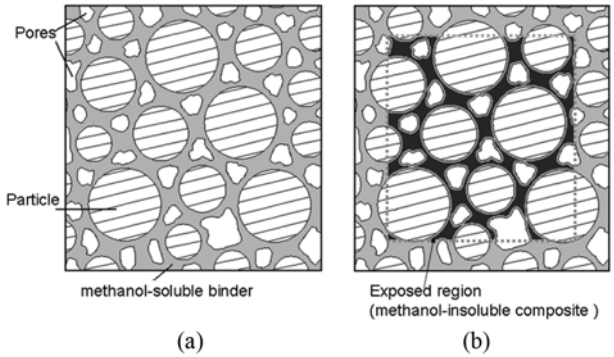


Fig. 6 Schematic of the property transformation of used binder (a) before and (b) after white light irradiating

2.6 Mechanical property measurement

According to ASTM-E112 and ASTM C1161-02 standard tests, six specimens of each test were fabricated for tensile and flexural strength tests, respectively. The tensile and flexural strength of the sintered parts was measured in tensile tester (Insight, 5 kN, MTS Co., Ltd.) and three-point bend configuration by a strength tester (HT-8116, Hung Ta Instrument Co., Ltd.). Finally, we also used aforementioned process parameters to fabricate 3D ceramic parts for demonstration of the ability of manufacturing complex ceramic parts with this process. The topography of the fracture, upper and lateral surfaces of the green parts and the sintered parts were observed by a scanning electron microscopy (SEM) as shown in Fig. 7. The density of the green parts and the sintered parts were measured with Archimedean principle by an electronic densimeter (SD-120L, ALFA Mirage Co., Ltd., Osaka, Japan).

3. Results

3.1 Optimization of exposing time

The relationship between the exposing time and the solidifying thickness has to be analyzed. In accordance with the steps from (a) to (c) in Figure 3, the green parts were fabricated by the developed rapid prototyping apparatus as shown in Figure 8. Layer pattern was 12 pieces of green part with dimension of 20 mm × 10 mm. The number in the center of mask patterns indicates the exposure duration in seconds. After a formability analysis, the optimized exposure duration can be obtained to fabricate green parts for tensile test and flexural test.

The layer thickness used in this testing is 30 μm. Using suitable exposure duration can fabricate a green part layer by layer. The principle of part forming is the organic binder solidifies in a very short time and binds the adjacent ceramic particles when the gel-like green layer is exposed selectively with a light uniform-intensity projected pattern. The property of exposed region will be transformed to be methanol-insoluble, and the depth of this transformation region must be near 45 μm, which is one and half times of the layer thickness, to ensure the adjacent at least two layers can connect each other. According to the experimental results of the exposure duration optimization as shown in Figure 9, a thin layer about 10 μm can be solidified when the exposing duration exceeds 5 seconds but each corner breaks. This reveals that the binding force between particle and photopolymer do not have enough strength. As a result, 12 seconds of exposing duration creates a solidifying depth greater than 40 μm which is enough to bind the 30m adjacent two layers together.

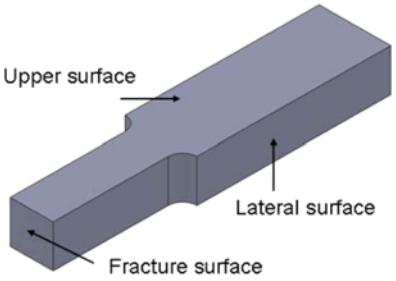


Fig. 7 Illustration of observed surface

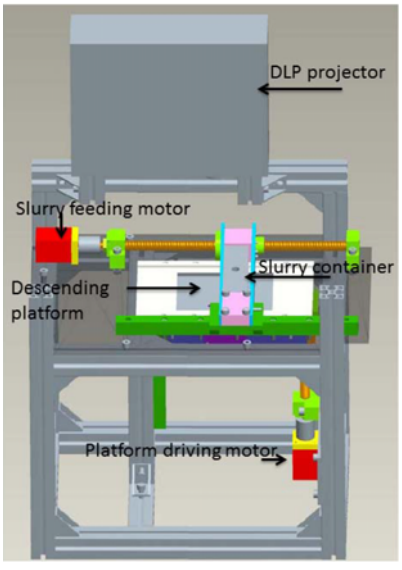
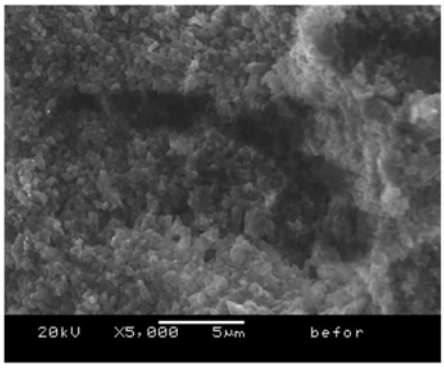
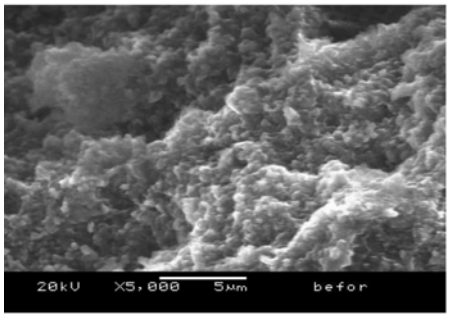


Fig. 8 The photo of the developed 4S rapid prototyping apparatus


Fig. 9 Experimental results of different exposure duration



(a) The exposed region



(b) The un-exposed region

Fig. 10 The fracture surface micrograph of tensile test specimen

3.2 Specimen fabrication

Figure 10(a) and (b) show the fracture surface micrograph of tensile test specimen of the exposed region formed with exposing duration of 12 seconds and the un-exposed region respectively. The microstructures were almost identical. This result indicated that the selective exposing only brought about minor variation in the microstructure of the material.

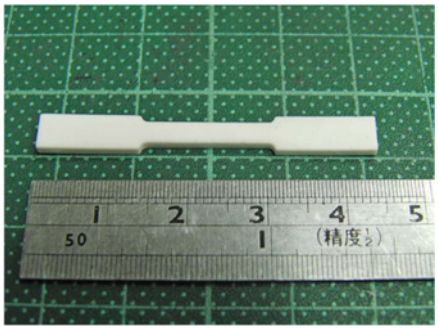
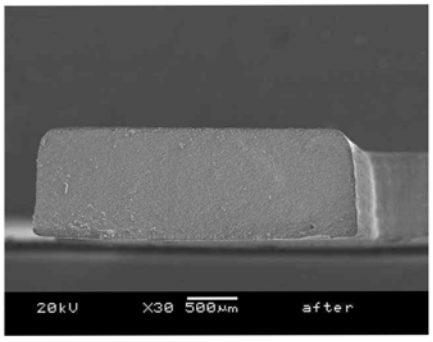
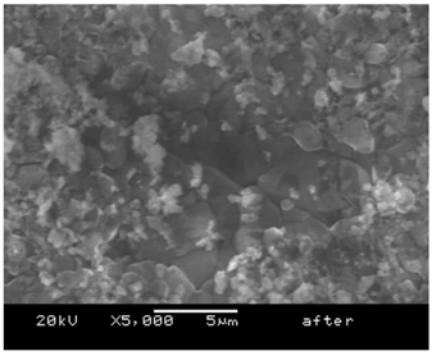


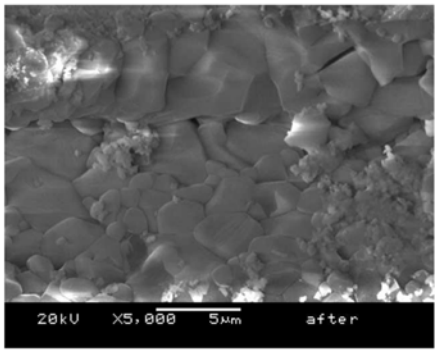
Fig. 11 Sintered test specimen (sintered at 1600°C for 2 hours)



(a) The facture surface



(b) The upper surface micrograph



(c) The lateral surface micrograph

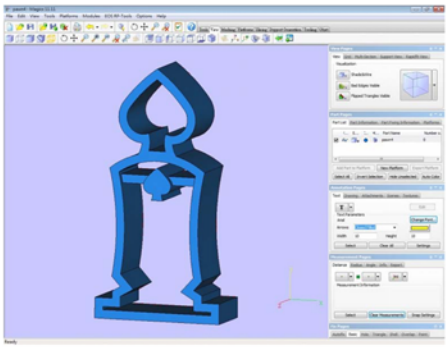
Fig. 12 The surface micrograph of an alumina test specimen (sintered at 1600°C for 2 hours)

3.3 Mechanical property measurement

The sintered ceramic test specimen is shown in Figure 11. The relative density of the sintered ceramic parts was increased to 98%. The average tensile and flexural strength was 327 MPa with a standard deviation of 20.4 MPa and 476 MPa with a standard deviation of 54.4 MPa, respectively. The surface micrographs of the fracture surface, upper surface and lateral surface of the sintered part of sintered tensile test specimen is shown in Figure 12, which still contained a few closed pores.

3.4 Results of complex shape with fine features

Rapid prototyping (RP) technology is the technology to build up parts in additive process instead of traditional subtractive process. The most advantage of this additive process is the ability to build up parts with no geometrically constraint. According to the proposed 4S RP process, a fine featured object has been designed and fabricated to show the ability to build up parts traditional methods cannot perform. The CAD of the testing spacemen is shown in Figure 13(a) and the final part after sintering is shown in Figure 13(b). The resolution of the



(a)

(b)

(c)

Fig. 13 Results of fine featured objects, (a) the CAD drawing, (b) the final part, and (c) the single batch of parts

dynamic mask setup is 77 μm/pixel and the layer thickness is 30 μm in the developed 4S rapid prototyping apparatus. The resulting part show fine features down to 60 μm due to the shrinkage during the sintering. Furthermore, this 4S process can produce a batch of many different parts in one time as shown in Figure 13(c).

4. Discussion

The proposed material system in this study could be transformed from a methanol-soluble state to a methanol-insoluble state through selective exposing by the visible light of layer pattern generator. The colloidal science was also applied in this process to produce fully dispersed slurry. To obtain high dense alumina ceramic parts, the packing density of the green part before densification by sintering should be no less than 50%. The packing density of the part, which is fabricated with conventional powder-based SLS, is hardly over 50%, so the density of the sintered part cannot be over 90%. The slurry-based CLS was wet process using inorganic binder and no dispersant was used in the slurry, but the pH value of the slurry was not easily adjusted (Tang et al., 2006). This is the reason that agglomeration of the ceramic powders occurs easily. The green part contained many large pores which could not be eliminated by sintering. Consequently, the sintered part could not achieve higher density.

In this study, no dispersant was used to form an absorptive layer on the ceramic particle surface for obtaining a strong steric effect. Furthermore, no pH value needs to be adjusted. As a result, agglomeration of the ceramic powders slurry can not be found. This is the reason why the density of the green part and the sintered part could be 65.5% and 98% individually.

The slurry-based selective laser sintering used slurry containing organic binder to obtain uniform green parts and dense sintered parts. But, having high density cannot ensure the performance of high strength. Strength is also dominated by the ceramic part free from delamination and cracks. In this study, the proposed solvent-based slurry stereolithography and sintering process can fulfill these two demands. The methanol-soluble slurry is helpful for avoiding delamination and cracks. Detail is discussed as following:

In the step (a) of Figure 3, working platform was descended a distance of 30 μm. A fresh slurry layer was overlaid on top of previous dried-layer. The liquid phase in the fresh layer, including methanol and the dissolved binder, penetrated into pores in the previous dried-layers. As a result, a layer contained saturated methanol was formed. The penetrated liquid could locally and partially dissolve the methanol-soluble polymer which was precipitated on the surface of the powder during the step (b) (layer drying), and could connect the individual ceramic particles. After drying, strong connections between adjacent layers were established. Upon light irradiation, one and half layer depth of scanned region was created so that an overlapping ratio of 50% was achieved. The finished green part was free from delamination.

The principle of building ultra-thin layer was reported (Tang et al., 2011) and is briefly discussed here. Casting by a scraper can induce shear stress on the top surface of the previous layer. Such stress is inversely proportional to the layer thickness. If the strength of the previous layer is low and the layer thickness is extremely thin, the shear stress will be greater than the strength of the previous layer. A displacement of the previous layer may occur and result in defects. In this proposed process, the solvent-based slurry has a very low viscosity property which will only bring a small shear stress to the support layer. Moreover, the binder would be precipitated to connect ceramic particles during the layer drying, and then a firm support region was formed to resist the aforementioned shear stress. Therefore, the capability of casting ultra-thin layer was achieved.

Cracking is one of the possible defects during layer drying. Cracking occurs when the layer is thicker than the critical saturation thickness (CST) (Grau et al., 1999). They mentioned that the CST of the 0.5 μm alumina particle is 65 μm. The saturation thickness of the layer in aforementioned experiment was 30 μm which was smaller than the CST, so no cracks were observed during the layer drying. The smaller the particle is, the thinner the CST will be. One of the problems of fabricating monolithic ceramic component with very small particles such as sub-micro powder is the cracking. Because the new process could cast extreme thin layer, using the presented solvent-based slurry stereolithography and sintering process to fabricate monolithic ceramic components from sub-micro particles become possible.

5. Conclusions

In this paper, the photopolymer in the process of solvent-based slurry stereolithography was organic binder. The sintered alumina ceramic parts with a mean density of about 98% were made successfully. Furthermore, because the proposed solvent-based process can produce the parts free from delamination and cracks, a mean tensile and flexural strength of about 327 and 476 MPa were achieved, respectively. This paper shows positive results to build up high mechanical property, complex shape, and fine featured Al_2O_3 ceramic parts. With same process, it is also possible to build up ZrO_2 ceramic parts to bring even higher mechanical property.

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