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# A new slurry-based shaping process for fabricating ceramic green part by selective laser scanning the gelled layer

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**Abstract**

This paper proposes a new slurry-based shaping process for fabricating ceramic green parts. Slurry was composed of $SiO_2$ powders (without polymer coating) as a structural element, silica sol and polyvinyl alcohol (PVA) as binders. The new process derived gelling effect from vaporization to generate a uniform gelled layer. By selective laser scanning, an alkali-insoluble 2D pattern was formed on the gelled layer. A green part was built by sequentially layer casting, drying, selective scanning and self-supporting removing. Because gelling occurs uniformly in the whole fresh layer, distortion is minimized. Therefore, this process not only can cast thinner layers to improve the staircase effect but also achieve a better surface by preventing surface pitting induced by laser ablation. No additional design for supports is required since overhangs and undercuts are supported by an inherent gelled support. Compared to other slurry-based processes, the process possesses time-efficiency in slurry preparation and support removal.


*Keywords:* Sintering; Shaping; $SiO_2$; Gelled layer

## 1. Introduction

Rapid prototyping (RP) is a novel technology for directly producing complex components without tooling. Rapid the demands for functional materials lead researches to work on ceramic applications. Several RP processes have been developed to manufacture ceramic components, such as stereolithography (SL),[1] slurry-based three-dimensional printing (S-3DP),[2] laminated object manufacturing (LOM),[3] fused deposition of ceramics (FDC),[4] computer-aided manufacturing of laminated engineering materials (CAM-LEM).[5] A variety of laser-based processes holds a distinctive position within rapid prototyping techniques. It offers two basic choices. One can be described as powder-based process, such as selective laser sintering (SLS)[6] and selective laser melting (SLM).[7] The powder-based process uses a ceramic and polymer powder mixture or polymer-coated ceramic particles. The polymer plays a role as a sacrificial binder, which is removed by a secondary operation. Compared to ceramic and polymer powder mixture, structural ceramic particles coated with polymer have a more effective bonding since the binder already surrounds all structural particles. However, ceramic particle coated with polymer leads to enlargement of particle size, which causes increasing the finite thickness of the layers and the porosity of the green part. The other one is slurry-based process, such as ceramic laser fusion (CLF),[8,9] ceramic laser sintering (CLS),[10,11] ceramic laser gelling (CLG),[12,13] and layer-wise slurry deposition (LSD).[14,15] The consolidation mechanism of CLF is somewhat similar to the mechanism of SLM. Slurry-based SLS allows the use of smaller ceramic particles which leads to a higher green density in every single layer and in final green part. Subsequently, a higher green part density is available.[16] Tang et al.[11] reported the slurry-based process of CLS can fabricate high-density and high-strength alumina parts. In practical, coating particle and removing self-supporting in a secondary operation require considerable effort and time. The process of CLG is worked by selective gelation of a 2D pattern on each slurry layer by a $CO_2$ laser exposure.

The aim of this paper is to develop a new shaping process with a systematical experimental analysis. The new process employed slurry consisting of ceramic powder without binder-coating. Instead of selective gelation of a slurry layer in CLG, the

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Table 1
Slurry composition.

| | $SiO_2$ powder (g) | Silica sol (g) | PVA solution (g) |
|---|---|---|---|
| Slurry A | 100 | 17.5 | 0 |
| Slurry B | 100 | 0 | 90 |
| Slurry C | 100 | 17.5 | 90 |

new process was use of selective scanning to form a 2D image on a solid gelled layer. A ceramic part was built by sequential layer manufacturing and self-supporting removing. This research can provide an alternative to rapidly fabricate the ceramic green parts with better surface.

## 2. Experiments

This study included two steps. Initially, an experiment of heat treatment for investigating the transformation of collapsibility of the gelling green block was executed. Based on the experiment of heat treatment, the next was an experiment of layer manufacturing for originating a shaping process. To create thin slurry layers, a conventional tape casting was used. Eventually, a green block was built in a layer-by-layer sequence to verify the feasibility of the new shaping process.

### 2.1. Experiment of heat treatment

This experiment was to observe the variations in collapsibility of the gelled green blocks which were heated in a furnace at various temperatures.

#### 2.1.1. Materials

Well dispersed slurry with a suitable rheological behavior for casting thin layers (down to 30 μm) was defined. Silica powder (average grain size <10 μm, melting point ~1720 °C, Chin Ching Silica Sand, Taiwan) was a structural material, silica sol (SNOWTEX ST-40, Nissan Chemical, Japan, solid content 40–41 wt%, particle size 10–20 nm, pH 9.0–10.5, melting point ~1700 °C) was an inorganic binder, fully hydrolyzed polyvinyl alcohol (PVA) solution (solid content = 6%, BF-24, Chang Chun Petrochemical, Taiwan) was an organic binder, and deionized water was a solution in all formulations.

#### 2.1.2. Experimental procedure

According to Table 1, three slurries with various compositions were made up. Silica sol was the inorganic binder of Slurry A. PVA solution was the organic binder of slurry B. Silica sol and PVA solution were binders of slurry C. Green specimens (20 mm × 20 mm × 1 mm) were manually fabricated layer by layer on a ceramic substrate, and then were dried at 80 °C.

The green specimens were treated in an electric furnace (LHT-04/17, Nabertherm GmbH, Lilienthal/Bremen, Germany) at various temperatures. Temperature of heat treatment was from 300 °C to 1200 °C at intervals of 300 °C. To observe the collapsibility, each green specimen was individually heated at a specified temperature for 2 h. Afterwards, the specimens were sunk in water and NaOH solution, respectively. The influence of heat treatment on the collapsibility of the green specimen was visually evaluated.

Table 2
Collapsibility of the specimens fabricated with slurry A.

| Slurry A ($SiO_2$ powder + Silica sol) | | | | | |
|---|---|---|---|---|---|
| Solution | Drying (°C) | Temperature of heat treatment (°C) | | | |
| | 80 | 300 | 600 | 900 | 1200 |
| Water | ▲ | ▲ | ▲ | ▲ | ▲ |
| NaOH | ■ | ■ | ■ | ■ | ▲ |

▲: noncollapsible ■: collapsible.

#### 2.1.3. Results and discussion of experiment of heat treatment

Table 2 shows the results of collapsibility of the specimens fabricated with slurry A. Gelling effect occurred during layer drying. After drying at 80 °C, all specimens were noncollapsible in water. Silica sol irreversibly transformed into silica gel which is insoluble in water but is soluble in NaOH solution. The specimens, which were heat-treated at temperature no greater than 900 °C, still collapsed in NaOH solution. However, the specimens treated at 1200 °C were noncollapsible in NaOH solution. The reason is that silica gel crystallizes to be cristobalite at 1200 °C. Cristobalite is insoluble in NaOH solution.

Table 3 shows the results of collapsibility of the specimens fabricated with slurry B. After drying at 80 °C, all specimens were noncollapsible in water and NaOH solution. The specimens heat-treated at 300 °C were noncollapsible in water and NaOH solution. PVA contained in the specimens partially burned out at temperature lower than 300 °C. The melted PVA still could bind the ceramic particles when PVA solidified at low temperature. However, the specimens treated at 600 °C rapidly collapsed in water and NaOH solution. PVA completely burned out when the specimens were treated at 600–1200 °C. Bridges between the ceramic particles disappeared; therefore, the specimens rapidly collapsed in water and NaOH solution.

The results of collapsibility of the specimens fabricated with slurry C is shown in Table 4. The results can be explained by the results listed in Table 2 and 3. The specimens respectively treated at 80 °C and 300 °C were noncollapsible in water and NaOH solution. PVA in the specimen partially burned out and silica gel still retained in the specimens. The specimens respectively treated at 600 °C and 900 °C were collapsible in NaOH solution only. PVA in the specimens was completely burned out, so the

Table 3
Collapsibility of the specimens fabricated with slurry B.

| Slurry B [$SiO_2$ powder + PVA] | | | | | |
|---|---|---|---|---|---|
| Solution | Drying (°C) | Temperature of heat treatment (°C) | | | |
| | 80 | 300 | 600 | 900 | 1200 |
| Water | ▲ | ▲ | ■ | ■ | ■ |
| NaOH | ▲ | ▲ | ■ | ■ | ■ |

▲: noncollapsible ■: collapsible.