Frozen Slurry-based Selective Laser Gasification to Fabricate Ceramic Parts with Foam Structure

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Abstract: This paper presents a rapid prototyping (RP) method of frozen slurry-based selective laser gasification for fabricating ceramic parts with foam structure. The slurry is composed of ceramic powder and water glass. The processing of a layer of green part involves casting, freezing and scanning. After accumulation and moulding, the sample is placed into water to melt and remove the excess materials. In the process of laser scanning, the gasified ice crystals make water glass foam and form the foam structure. The freezing method helps to improve the stability and strength of the paved layer. The foam structure of different sizes can be obtained by adjusting the laser processing parameters.

1. Introduction

Ceramics have the properties of thermal stability, corrosion resistance, high chemical stability and dimensional stability, and they are widely used in aviation, aerospace, energy, bio-engineering and other fields. However, ceramic materials are hard and brittle, and it is difficult to process complex ceramic parts by using traditional processing methods [1,2]. Therefore, it is important to study the ceramic rapid prototyping (RP) technology.

Compared to the polymer and metal materials, ceramics have higher melting points and smaller thermal conductivities. The question of how to combine ceramic particles together and fix the shape of the parts is a key issue in ceramic RP technology research. Melting ceramic methods, such as SLM [3], and CLF [4], use high-power lasers to melt ceramic particles together. Melting binder methods, such as SLS [5], LSD [6], 3DP [7], FDM [8], and CLS [9], use low-power lasers or other heat sources to locally melt an adhesive and make ceramic particles stick together. The binder used in these methods may be an inorganic binder, an organic binder, a metal or a ceramic material with a relatively low melting point. In the stereolithography method [10], light (ultraviolet or visible light) or electron beam is used as energy, causing the liquid binder with chemical reactivity to quickly change into the solid state, binding and fixing the ceramic particles together. In the water-loss bonding method [11], the ceramic slurry is taken as the processing materials; based on the principle that some of binder solution may have cohesive action in the loss of moisture, lasers or other heat sources are adopted to evaporate the moisture in the slurry. Such binders include silica sol, aluminium sol, sodium silicate and other materials. In the freeze-drying method [12,13], a three-dimensional extrusion process is used to stack and form the ceramic slurry with freeze-drying characteristics, and the rapid freezing method is used to fix the shape of the green parts. The solvent used in this ceramic slurry may be water or camphene. In addition, there are also several RP methods for fabricating ceramic parts through the chemical
reaction, such as SLC (Selective Laser Curing) [14], SLG (Selective Laser Gelation) [15], and SALD (Selective Area Laser Deposition) [16].

Foamed structure ceramics has the characteristics of low density and low thermal conductivity. Unfortunately, there are less reports on the RP methods for processing foamed structure ceramics. This paper explored a frozen slurry-based selective laser gasification (FSLG) method to process ceramic parts with foam structure. The slurry is made of ceramic powder and water glass, using the laser to scan over the frozen materials, then the water glass is heated and foamed. By using the method of freezing, the strength of the blank during the process is improved and the deformation of the body in the curing process is reduced.

2. Materials and methods

2.1 Materials
Using water glass as the binder, we prepared a water glass aqueous solution with the modules of 3.1-3.4, with alumina powder (D₅₀=0.3 µm, Baqian Chemical, China) used as the structural material. The ceramic powder and the water glass are mixed thoroughly to prepare water-based ceramic slurry with 50 wt % solid content.

2.2 Experimental apparatus
The experimental platform used in this paper consists of a casting device, a freezing device and a CO₂ laser scanning device. The casting device is used to control the paving thickness of the slurry. The freezing device is used for the rapid freezing of the material layer. CO₂ laser scanning is used to locally gasify the frozen material layer.

The FSLG processing includes casting, freezing, scanning and cleaning, as shown in Fig. 1. (a) Pave a layer of ceramic slurry on the working table; (b) use the cryopanel to contact the material layer for rapid freezing; (c) use the CO₂ laser to locally gasify the frozen slurry layer, thus building the 2D-shape of green parts; and (d) the working table goes down by a layer. After layers of accumulation, the 3D green part wrapped by frozen slurry can be obtained. Finally, the entire sample is placed in water, and the frozen slurry used as the supporting material is rapidly melted and removed.

![Diagram of machining process](image)

Figure 1 Diagram of machining process: (1) ceramic slurry, (2) scraper, (3) lifting platform, (4) cryopanel, (5) frozen slurry, (6) laser beam, (7) reflector, and (8) scanned material

2.3 Experimental procedure
The slurry is quickly frozen at the temperature T=−50 °C. Different laser parameters (laser power P, scanning speed V) were used on the frozen sample for the scanning experiment. After the samples were naturally melted in water and dried, a scanning electron microscope (model: VEGA-II XMU, TESCAN, Czech Republic) was used to observe the structure of the scanning line. In order to show the processing effect of FSLG, several green parts have been made with the suitable processing parameters.
3. Results and discussion

3.1 The Principle of FSLG

The dehydration procedures of the liquid water glass can be divided into three stages: when temperature is a somewhat low, the free-water of the solution evaporates gradually; when temperature is raised, the bound-water of the solution forms water vapour and begins to foam; and when the temperature reaches a certain value, the water glass stops foaming and forms a Si-O tetrahedron structure in a three-dimensional network, thus obtaining light foam materials [17]. The heat curing reaction is as follows:

\[
\text{Na}_2\text{O} \cdot n\text{SiO}_2 + (2n+1)\text{H}_2\text{O} \rightarrow 2\text{NaOH} + n\text{Si(OH)}_4
\]

\[
n\text{Si(OH)}_4 \rightarrow [\text{Si(OH)}_4]_n \rightarrow \text{Si(OH)}_4^{-2n}\text{H}_2\text{O}
\]

In order to explain the effect of freezing on the processing, laser scanning experiments on liquid water glass and frozen water glass were carried out respectively. The results are shown in Figure 2. When liquid water glass is scanned by laser, spattering, foaming, and shrinkage are produced in the heated region, which seriously affect the shape of the solidified area. In addition, liquid glass can not provide strong support, which can easily make the solidified region deformed by the influence of gravity. The frozen water glass has good stability and mechanical strength, which can effectively support and stabilize the solidified area. By using the method of freezing, the phenomena of spattering, shrinkage and deformation have been greatly improved.

![Figure 2 Laser scanning of liquid water glass and frozen water glass](image)

3.2 Effect of laser parameters

Fig. 3 shows the cross-sectional shape of a single scanning line. Here, \( W \) is the width of the scanning line, \( D \) is the thickness of the scanning line, and \( R \) is the radius of the foaming structure. The energy is rather high when the laser reaches the surface of the material; it can thus directly gasify the ice crystals formed by free-water and bound-water to make the water glass foam. Since the laser energy is distributed according to a Gaussian distribution, the energy of the beam spot centre is the highest, and the excessive high temperature solidified the water glass before it foamed. The farther away it is from
the centre of the beam spot, the smaller the laser energy is. The appropriate temperature promotes the growth and fusion of bubbles, forming a foam structure, as shown in Fig. 3. The laser intensity decays along the incident direction, and the smaller energy is not sufficient to gasify the bound-water, but this energy can make ice crystals of free-water gasify; the dehydrated water glass can then form a three-dimensional mesh structure and bond the ceramic particles together. The overall shape of the section is similar to the Gaussian curve.

![Figure 3 SEM image of the scanning line section](image)

Figure 3 SEM image of the scanning line section

For the laser power $P=30\text{W}$, different laser scanning speed $V$ were used to scan the frozen slurry. Fig. 4 shows the relationship between $V, W, D$ and $R$. $W$ and $D$ decrease as the laser scanning speed increases. Laser energy decreases with the increase of scanning speed, the smaller laser energy can affect the smaller area, causing the decrease of the width and thickness of the scanning lines. The radius of the foaming structure decrease as the laser scanning speed increases. Lower energy decreases the gasification rate of water glass and limits the growth of bubbles.

![Figure 4 Relationship between $V, W, D$ and $R$](image)

Figure 4 Relationship between $V, W, D$ and $R$
For the processing parameters $P=30$ W, $V=100$ mm/s and scanning spacing of 0.3 mm, a single layer green part can be obtained by using the slurry with 50% solid content, as shown in Figure 5.

![Figure 5 SEM images of the surface of the single-layer sample: (a) foam structure on the incident plane of laser, and (b) bottom surface of the sample](image)

Fig. 6 shows the green parts processed by FSLG.

![Figure 6 The green parts processed by FSLG](image)

4. Conclusion

This paper presents and discusses the frozen slurry-based selective laser gasification (FSLG) method for rapid prototyping. FSLG has the potential to process foamed structure ceramics. The result shows that: during the process, the strength of the body is improved and the deformation of the body is reduced by using the method of freezing; Increasing the laser scanning speed can reduce the radius of the bubble.

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