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Ceramic laser gelling

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Abstract

This paper presents a novel layered manufacturing method, ceramic laser gelling (CLG), for forming ceramic green part. This process involves mixing ceramic powder with an inorganic binder to form ceramic slurry. Owing to evaporation of water in a portion of slurry layer caused by laser exposure, the ceramic slurry is gelled locally to form 3D ceramic green part layer by layer. A series of experiments was conducted to obtain suitable laser and scanning parameters for layers of 140–440 μm thickness and to obtain the smallest pave-able layer thickness of 80 μm on a self-made experimental rapid prototyping machine. The feasibility of this process was demonstrated by manufacturing an intricate fan blade. In comparison with SLA and SLS, CLG has an advantage of using environmental compatible water-soluble inorganic binder. It needs lower laser power and has faster production rate than ceramic laser fusion (CLF). Futhermore, it can fabricate green parts composed of almost 100% pure silica.

Keywords: Rapid prototyping; Forming; SiO_2; Gelling; Suspensions; Laser gelling

1. Introduction

In the last decade, many researchers have investigated the rapid prototyping technologies for forming ceramic green parts. Most of the processes developed for this purpose are related to bonding ceramic powder with an organic binder. Ceramic resin comprised of ceramic powder and photo-curable resin could be used as a raw material in stereolithography (SL),[1,2] and then exposed under a directed ultraviolet light in order to polymerize the liquid state resin. The solidified resin bonds the ceramic powder to form ceramic green parts. The selective laser sintering (SLS) technology is applied to various materials for fabricating three-dimensional rapid prototyping (RP) work pieces.[3,4] To date, the SLS technology comprises the steps of coating the ceramic powder with resin and then melting the resin by a laser, with the resin acting as a bonding agent of the ceramic powder for forming a ceramic green part. Fused deposition modeling (FDM) mixes ceramic powder and organic binder together to form a filament and then fabricates a ceramic green part with this ceramic-polymer filament by a FDM machine.[5] In three-dimensional printing (3DP), an organic binding agent is selectively spurted out in a way similar to ink jet technology, but onto a designated powder material.[6] If the powder material is ceramic, a ceramic green part can be formed. Any sheet material with adhesive backing could be used in laminated object manufacturing (LOM).[7,8] Ceramic sheet can be made from ceramic powder and polymer binder. In most of these processes, the added organic binder must be burnt out in a furnace during post-sintering. The hazardous gases released during sintering are unhealthy for human and can pollute the environment, some impurities will also be left after the sintering process. Thus, a ceramic part of 100% ceramic content cannot be obtained.

In order to avoid releasing hazardous gases and obtain a 100% ceramic part, Tang developed a process called ceramic laser fusion (CLF).[9] Ceramic powder and inorganic binder were mixed together to become ceramic slurry. After paving a thin slurry layer, an infrared heater irradiated the slurry layer. The dried and hardened ceramic green layer was impinged by a focused CO_2 laser beam and the ceramic green layer was then locally fused together to form a portion of the ceramic part. A laser power of about 50 W with a 10 mm/s scanning speed was needed to fuse a SiO_2 green ceramic layer by exceeding its melting point, about 1800 °C.

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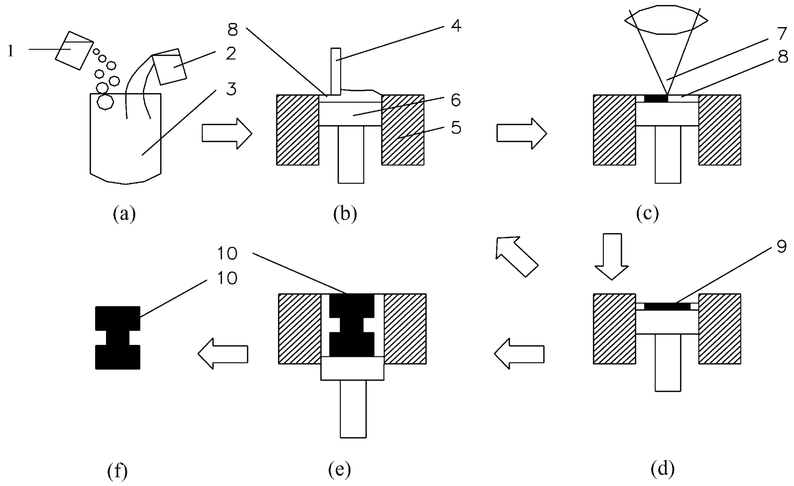

Fig. 1. Diagram of manufacturing processes of CLG: (1) silica powder, (2) nano-scaled oxide sol, (3) slurry cup, (4) scraper, (5) paving platform, (6) elevating platform, (7) laser beam, (8) slurry layer, (9) ceramic green cross-section, (10) 3D ceramic green part.

This process formed ceramic work pieces directly, requiring no conventional sintering post-treatment. However, if it is compared with the above-mentioned organic binder processes, there are some disadvantages: laser power above 50 W with a slow scanning speed means a higher capital investment, greater power consumption during operation and a low production rate. In addition, because CLF needs extra time (60 s each layer) for the drying procedure, its building time is too long to be widely adopted for industrial applications.

The primary objective of this paper is to develop a novel method, ceramic laser gelling (CLG), which will maintain the advantages of CLF, while eliminating its drawbacks. In other words, with inorganic binder used as before, the process time should be shortened, and the laser power needed for gelation of the part cross-sections should be decreased. Furthermore, a feasibility study of this process and a comparison of this process with other RP processes will be conducted. Application fields for this process will also be discussed.

2. Principle and process of CLG

The principle of CLG has it basis on the “gelling effect” of colloidal particles or sol. When a sol is gelled, it first becomes viscous, then develops rigidity, and finally links together forming three-dimensional networks.[10,11] The rate of gelling appears to be proportional to sol concentration. When a sol is evaporated, its concentration is increased. It shrinks and cracks. Although a sol may not form a coherent continuous film when dried alone, it forms a 3D network to bridge the distance between larger particles. According to our experiments, when a mixture comprised of a nano-scale silica sol and silica powder with 10 μm mean diameter was spread onto a platform to form a thin slurry film of about 100 μm thickness and then the film was dried by a laser beam, the dried portion caused by the laser beam scanning was connected together to form a solid and crack-free green network, while the portion of slurry film that was not scanned by the laser beam remained in slurry state. A CO_2 laser beam was used because the absorption rate of silica powder upon a CO_2 laser beam was above 90% and the heat affective zone caused by laser processing was narrow.

According to this principle, a rapid prototyping process called “ceramic laser gelling” was developed to form a three-dimensional ceramic green work piece. As shown in Fig. 1, this process includes the following steps: (a) preparing slurry, (b) paving the slurry onto the mold space formed between the elevating platform and the paving platform, (c) irreversible gelling of the irradiated portion of slurry after selective scanning by a high-power energy beam, thus, a layer of the ceramic green cross-section has been formed, (d) lowering the elevating platform with a distance of thin slurry layer thickness, repeating the steps from (b) to (d), paving a thin slurry layer and then scanning the thin slurry layer with a high-power energy beam. After stacking a series of overlapped cross-sections, a 3D ceramic green work piece is completed (Fig. 1e). The slurry surrounded the gelled work piece is separated, and then a 3D ceramic green work piece is obtained (Fig. 1f).

3. Experiments

3.1. Experimental setup and materials

An experimental rapid prototyping machine using “ceramic laser gelling” was constructed as shown in Fig. 2. This equipment comprised a feeding device, a paving system, a laser scanning system, and a control system. The feeding device was a commercial screw pump with a small screw diameter. The paving system included a paving platform, an elevator with elevating platform, and a scraping device.

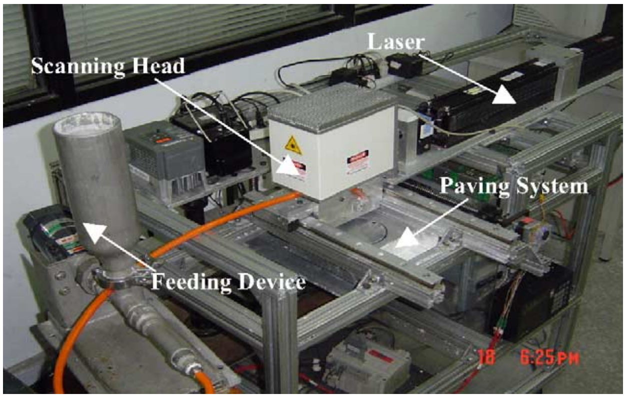

Fig. 2. Rapid prototyping machine using CLG.

The laser scanning system consisted of a Syndrat 10 W CO_2 laser and a scan head with 110 mm × 110 mm working area. A process computer, with a built-in laser power control card and a scan route control card, coordinated the laser power on-off and laser scanning path. This computer could also control the scraper, the elevator and the feeding device via a programmable logic controller (PLC) which was connected to a RS232 interface.

Slurry, consisting of water, silica sol with 40–50 nm particle diameters and silica powder with an average diameter of 10 μm, was used in the following series of experiments. Mixing silica sol and silica powder in a proportion of 40 to 60 wt.% could form a high-quality slurry with suitable viscosity and to provide good paving behavior.

3.2. *Experimental procedures*

As seen in Fig. 1b, slurry was fed on the mold space formed between the elevating platform and the paving platform and then scraped with a scraper along the surface of the paving platform. The height of the slurry surface was equal to that of the paving platform surface. The paving platform surface level or slurry surface level was arranged on the focus point of the scan head F-θ lens. The slurry layer thickness could be accurately controlled by setting properly the lowering distance of the elevating platform. As shown in Fig. 1c, a laser beam scanned the surface of the slurry layer via manipulating the X–Y mirror of the scan head according to the working path program of the cross-section of a 3D work piece. Upon laser radiation, water in the slurry would be evaporated, the silica powder in the scanned area was bonded together by the gelled nano-scale silica sol. By changing laser power or/and scanning speed, different gelled thickness could be obtained. In order to bond a layer with the underneath layer, the gelled thickness had to be greater than one-layer thickness. Because gelling is an irreversible reaction, the gelled portion would not be dispersed in water; on the other hand, ungelled slurry remained fluid. After taking the ceramic green part out of the elevator platform and washing the remaining slurry away from the surface of the part by water jet, a ceramic green part could be obtained.

Important parameters affecting the accuracy, strength, or processing time of the work piece were laser power, scan pitch, and scan speed. Furthermore, layer thickness was another geometric parameter which determines the resolution of the 3D work piece. A series of experiments was conducted to determine the suitable laser and scanning parameters for several specific layer thicknesses. Moreover, a series of layer paving experiments was conducted to determine the smallest pave-able layer thickness. In order to show the feasibility of producing delicate parts, a complex 3D part was manufactured by CLG rapid prototyping machine with suitable processing parameters. Finally, in order to verify that this process can produce pure silica parts, an EDS experiment was conducted to determine the elements contained in the produced part.

3.3. *Experimental results*

A gelled layer was constructed with 100 mm/s scan speed and 150 μm scan pitch on a slurry layer of approximately 1 mm thickness by a CO_2 laser of 400 μm beam spot diameter. The relationship between the gelled depth of the slurry layer and laser power is shown in Fig. 3. The gelled depth formed by laser power under 3.4 W was too small to be measured. As laser power increased from 3.4 to 10 W, the gelled depth was increased from 140 to 440 μm. The slope between 3.4 and 8.6 W was greater than that between 8.6 and 10 W. According to this relationship, a part with 150 μm thickness layer could be manufactured by a 7 W laser power, which gave a 300 μm gelled thickness layer. The SEM micrograph shown in Fig. 4 is the side-view of a part with 150 μm layer thickness, which verifies that the ceramic green layers can be connected together under the said working condition.

Without additional support structure, the sensible layer thicknesses achieved were between 200 and 80 μm. A layer thicker than 200 μm is not practical because the necessary high-energy density used for its production caused a decrease in part accuracy. A layer thinner than 80 μm is not sensible because the paved layer could be removed during scraping operation. Utilizing suitable processing parameters for building layers of 150 μm thickness, namely laser power 7 W, scan speed 100 mm/s, scan pitch 150 μm, we can demonstrate the ability of the CLG process to manufacture a

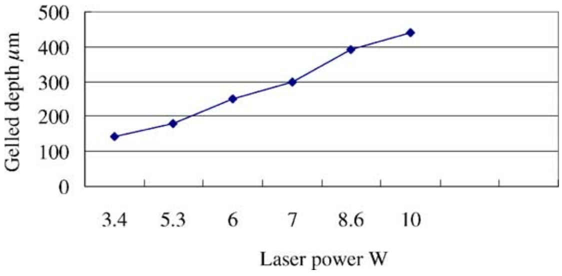

Fig. 3. The relationship between gelled depth and laser power.

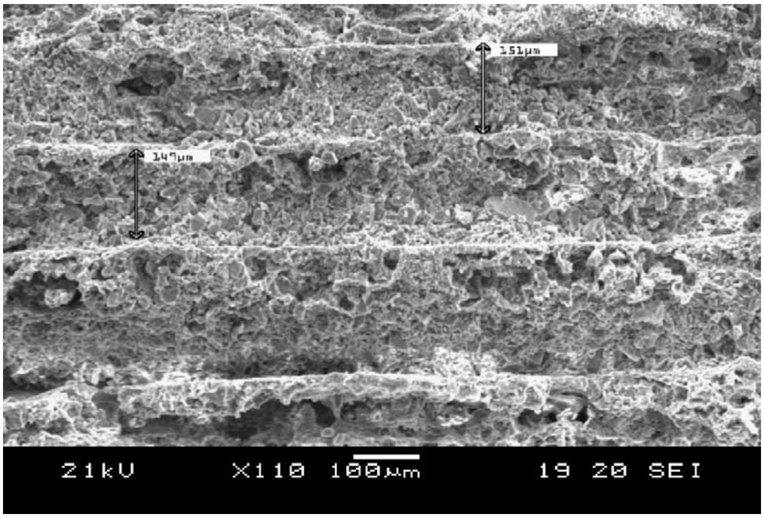

Fig. 4. SEM micrograph of 150 μm layer thickness.

Fig. 5. Fan blade made by CLG.

delicate 3D ceramic green part. A manufactured fan blade is shown in Fig. 5. It had an outer diameter of 56 mm and a total height of 12 mm (80 layers). The total building time was 160 min, inclusive of slurry paving time and laser scanning time. Fig. 6 is an EDS elemental analysis, which showed only two elements (Si, O) existing in the finished ceramic green part. The silica percentage in this part reached 100%.

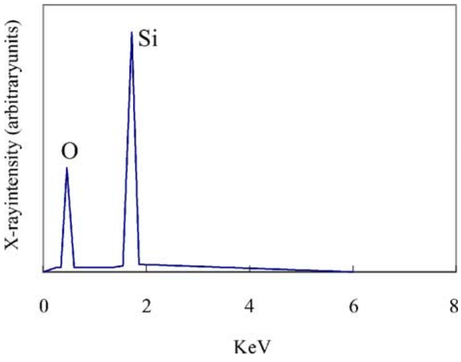

Fig. 6. EDS elemental analysis of ceramic green part.

4. Discussion

4.1. Comparison of CLG with other RP processes

A comparison of the CLG with other RP processes for production of ceramic green parts, such as Stereolithography Apparatus (SLA), SLS and CLF, is shown in Table 1. It becomes evident that this process has two unique features. The first feature is that its principle is an irreversible gelling of nano-scale sol and therefore it needs just a relatively small power laser. The slurry type material in CLG process is gelled by evaporating the water contained in the slurry. Because water evaporates at a temperature of 100 °C, an infra red CO_2 laser of relatively smaller power, about 4 W, is sufficient for this process condition. The SLA applies the principle of polymerization of photo-curable resin in the ceramic resin. The polymerization is initiated by irradiating a small power (<1 W) chemical ultraviolet laser on the photo-curable resin. The SLS process applies the principle of solidifying after melting of polymer-coated ceramic powder. The polymer on the powder surface melted when a physical infrared laser is focused on the powder surface. The melted polymer connects the particles upon solidification. Because this is a thermal process, an infra red CO_2 laser with medium laser powder, about 25 W, is sufficient to melt the polymer, whose melting point is about 200 °C.[3] The CLF process applies the principle of solidifying after melting of ceramic green body layer. Because ceramic has a very high melting point, for instance, 1800 °C for SiO_2 powder, a higher power CO_2 laser of above 50 W is needed to raise the working temperature up to a temperature over melting point.

The second feature is that CLG uses slurry type material and it provides a "slurry" support for the building part. The slurry under the gelled cross-section can provide a support against downward forces. If an extra solid support structure is built, resistance against downward forces and upward

Table 1
Comparison of CLG with other RP processes for production of ceramic green parts

Process	Principle, laser type and power		Material, support	
CLG	Irreversible gelation of nano-scale sol	CO_2 laser <10 W	Slurry	Slurry support or extra solid support structure
SLA	Polymerization of photo resin	UV laser <1 W	Slurry	Slurry support or extra solid support structure
SLS	Solidifying after melting of polymer-coated ceramic powder	CO_2 laser >20 W	Powder	Powder support
CLF	Solidifying after melting of ceramic powder	CO_2 laser >50 W	Slurry	Solid support

forces is available. In this case, a post-gelling step for support removal is necessary. Because the SLA process also uses a slurry type material, a ceramic resin which comprises ceramic powder and photo-curable resin, to form the work piece, its support is almost the same as the CLG process. The SLS process uses powder type material as its raw material. When powder is melted to form the part, the powder underneath the part portion can provide resistance against downward forces, but not against upward forces. An upward distortion due to thermal processing can not be prevented in case of powder support. The CLF process uses slurry type material as its raw material. The slurry is paved to form a thin slurry layer. It is then dried and hardened to form a solid green body layer by an infrared heater. This solid green body layer provides a solid support for a fused part portion, which is formed when laser impinges on the surface of a green body layer over it. Although the CLF process includes an extra drying procedure, and it needs additional drying time, the solid support provides resistance against deformation in both of downward and upward directions.[12]

In summary, the CLG process has several advantages compared with SLA, SLS, and CLF. First, due to its unique principle it can use, in contrast to SLA and SLS, environmental compatible water-soluble inorganic binder and cost-effective ceramic powder as raw materials. Second, it needs a lower power laser and a shorter processing time compared with the CLF process. It can be one of the most cost-effective, fast, human and environmental friendly processes.

4.2. Application and prospect

SLS and SLA can be used to produce a master pattern for investment casting, the manufacturing time for the master pattern is minimized, but the time-consuming works like slurring, sanding and drying remain unchanged. CLG process is suitable for direct fabrication of a ceramic shell mold, which can be used in investment casting process, because a ceramic shell mold of silica can resist temperature of above 1200 °C. By using CLG, the time-consuming iterative process steps of slurring, sanding, drying and dewaxing can be eliminated, so that metal prototypes could be manufactured in a shorter time.

In other RP processes, the material is composed of photo-curable resin, organic binder, or other impurities; these impurities must be removed by post-processing in order to fabricate 100% pure ceramic parts. As shown in EDS analysis of Fig. 6, a pure silica green part can be manufactured by CLG. Furthermore, silica sol is not a unique commercially available nano-scale ceramic sol. Other materials, such as a alumina sol and zircania sol, can also be used as a binder of the same compositional ceramic powder. Therefore, future work can focus on other material systems like alumina sol–alumina powder, zircania sol–zircania powder and so on. This could create more useful industrial applications.

5. Conclusions

The principle of CLG has it basis on the irreversible gelling effect of a nano-scale silica sol. Slurry obtained by mixing silica sol with silica powder was used as raw material to investigate the feasibility and the features of this process. The primary objective of this paper is fulfilled. Gelled part portion can be directly formed by the exposure of a low-power CO_2 laser; drying procedure in CLF is eliminated in this process and the processing rate of CLG is significantly faster than that of CLF. With inorganic binder and ceramic powder as raw materials, this process is one of the most human and environmental friendly processes. In addition, CLG could fabricate intricate 100% pure ceramic 3D green parts; the smallest pave-able layer thickness was 80 μm. The process has a potential to fabricate ceramic shell molds for the investment casting process for producing various types of metal parts in a short time.

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