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Slurry-based selective laser sintering of polymer-coated ceramic powders to fabricate high strength alumina parts

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Abstract

Instead of conventional powder-based selective laser sintering, a novel slurry-based process to fabricate high strength ceramic parts is proposed. A slurry which was composed of alumina powder coated with water-insoluble semi-crystalline polyvinyl alcohol (PVA) as a structure material, water-soluble PVA as an organic binder, ammonium polymethacrylate (DARVAN C–N) as a dispersant, and deionized water as a solution, could be prepared with colloidal processing. A rigid green block could be built with a self-made rapid prototyping apparatus. The polymers contained in the scanned region were melted to connect the alumina powders, but transformed to be water-insoluble. However, the un-scanned region remained water-soluble. Due to dissolving of the polymers in water, the un-scanned region could collapse to obtain the green part. After binder removing and sintering, an alumina ceramic part could be obtained. An average flexural strength of 363.5 MPa and a relative density of 98% were achieved.

Keywords: Sintering; Alumina; Strength; Rapid prototyping

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 3D ceramic parts from CAD models without molds, have been developed over decades, such as stereolithography (SL),[1–3] selective laser sintering (SLS),[4,5] fused deposition of ceramics (FDC),[6] laminated object manufacturing(LOM),[7] computer-aided manufacturing of laminated engineering materials (CAM-LEM),[8] and slurry-based three dimensional printing(S-3DP).[9] Most of these processes can make ceramic parts with high strength.

Since the objects directly fabricated with conventional powder-based selective laser sintering (SLS) are not fully dense, the strength of the objects is low. Subramanian et al.[4] 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; however, the density and flexural strength of the sintered part were only 50% and 8 Mpa, respectively. Liu et al.[5] used 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.

Tang[10] brought up a new process: slurry-based selective laser sintering, which also named as ceramic laser sintering (CLS). Casting a layer with thickness of 10 μm is available to effectively improve the stairstepping effect occurred in layer manufacturing. However, the high strength ceramic parts also cannot be achieved. The process of slurry-based selective laser sintering, which applied in this paper, is illustrated in Fig. 1. The steps are: (1) making slurry, (2) descending platform for one layer thickness, (3) casting a thin slurry layer by a moving scraper, (4) drying the slurry layer with a heater to form a fresh green layer, (5) selectively scanning the green layer with a CO_2 laser. Particles scanned by the laser beam are consolidated; on the other hand, the un-scanned portion forms an inherent support, (6) repeating steps from step (2) to step (5) until the slicing files is executed completely to form a 3D green part, (7) immersing

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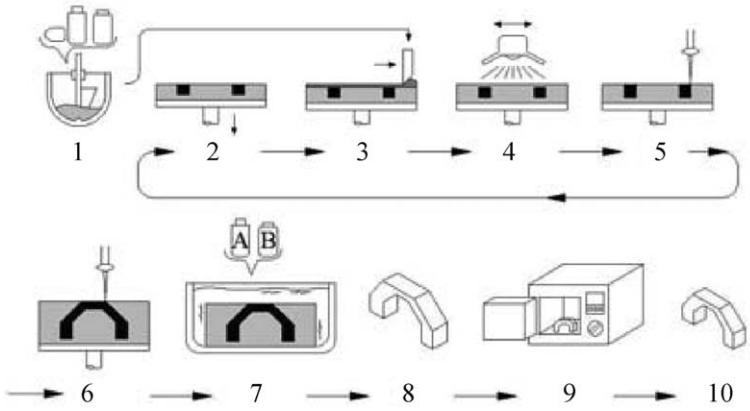

Fig. 1. The schematic of slurry-based selective laser sintering.

the green block in water to remove the un-scanned green portion with the assistance of an ultrasonic vibration, (8) taking the green part out from the ultrasonic cleaner, (9) binder burnout and part sintering in a furnace, and (10) obtaining a ceramic part.

CLS employs the slurry composed of ceramic powder, inorganic binder, and water to fabricate ceramic parts. After layer drying, ceramic powders are connected by the inorganic binder and consolidate to form a solid support which can prevent green block surface from damaging caused by the force generated during the thin layer casting. Fig. 2 shows the green block is formed by layer manufacturing. The green block contains the green part which is a region formed through selective laser scanning, and the support which is un-scanned region surrounding the green part. Immersing the green block in water, the inorganic binder (clay) in the un-scanned region can be dissolved in water; the support is disintegrated, and the clay in the scanned region is converted to be water-insoluble. Therefore, the green part can retain its original shape and dimension. But, sintering at high temperature, the ceramic parts produced by this process cannot achieve high density; their flexural strengths are only $10 \sim 20$ MPa.

The reason why the ceramic parts fabricated by existing slurry-based selective laser sintering cannot achieve high strength is that clay is used in the slurry as a binder, so 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, CAM-LEM. Instead of clay, polyvinyl alcohol (PVA) as a binder was used in this paper to fabricate the ceramic parts with high strength.

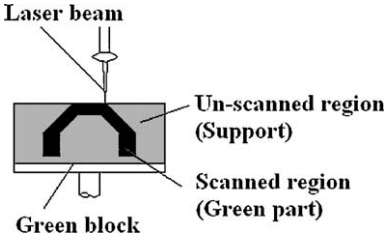

Fig. 2. The green block formed by layer manufacturing (the step 6 of Fig. 1).

PVA is a regular organic binder, which can effectively bind ceramic particles. After irradiating by laser beam, sub-partially hydrolyzed PVA cannot be transformed to be water-insoluble as clay does even though it is water-soluble at room temperature. Thus, we cannot only use of sub-partially hydrolyzed PVA as a binder for preparing slurry. In this study, we just employed a little amount of sub-partially hydrolyzed PVA. The main binder was fully hydrolyzed PVA, which is not dissolved in water at room temperature. Furthermore, the fully hydrolyzed PVA was coated on the surface of ceramic particles. Afterward, the polymer-coated ceramic particles could undergo re-crystallization with heat treatment to further reduce the water solubility of the PVA. Fig. 3 illustrates the states of the green layer before and after laser irradiation. In Fig. 3(a), the water-soluble PVA in the un-scanned region connects the water-insoluble polymer-coated ceramic particles; therefore, the binder will be dissolved and the polymer-coated ceramic particles will be dispersed if this region is immersed in water. In Fig. 3(b), two kinds of PVA in the laser scanned region are liquefied and mixed each other to connect ceramic particles to form a water-insoluble composite.

Therefore, if the green block is immersed in water, the un-scanned region will be dissolved, 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. The aim of this paper is to prove that the new approach of the slurry-based selective laser sintering can fabricate ceramic parts with high strength.

2. Experimental procedure

2.1. Fabricating and conditioning polymer-coated alumina powder

Coating process is illustrated as following: Firstly, 1 g of ammonium polymethacrylate (DARVAN C–N, R.T. Vanderbilt Co., Inc., Norwalk, CT) as the dispersant, and 24 g of deionized water as the solvent were added to every 100 g of Al_2O_3 powder (AES-11 C, purity 99.8%, $D_{50} = 0.5\,\mu m$, Sumitomo Chemical Co., Japan) as the ceramic phase to make

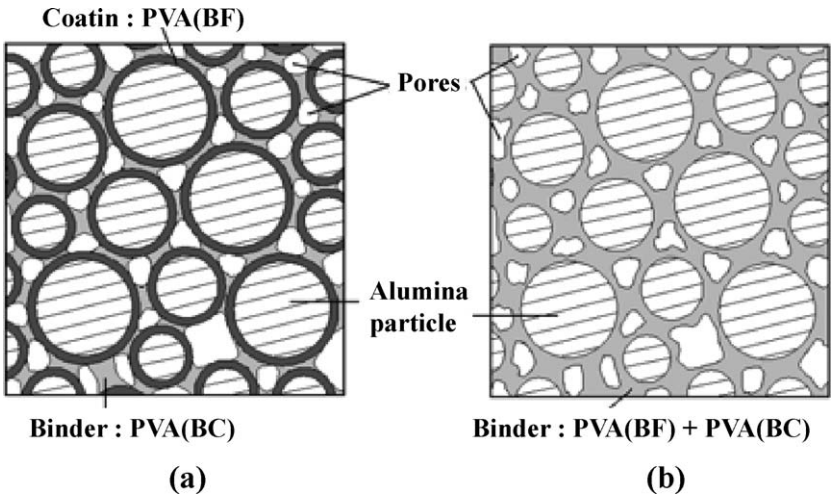

Fig. 3. Schematic of the property transformation of PVA (a) before laser irradiating; (b) after laser irradiating.

ceramic slurry after mixing. The pH value of the slurry was regulated to 8.1. Afterwards, after 2 h mixing in a ball mill, the slurry was well dispersed. Secondly, 42.5 g of a 6% aqueous solution of fully hydrolyzed PVA (BF-17S, degree of hydrolysis of 98.5 ~ 99.2 mol% and an average molecular weight of 74,800 g/mol, Chang Chun Petrochemical Co. Ltd., Taipei, Taiwan) as the organic binder was added. After ball milling for 1 h, the slurry was ready. Then, the steps of drying and wind sieving were followed; the well-mixed slurry was decanted into a vessel of the mixer and dried by hot air. The slurry was then transformed to be many solid cakes which were gradually pulverized during the drying and mixing process. The PVA-coated alumina particle less than 1 μm was collected with a vacuum dust collector. Eventually, the PVA-coated alumina powder was heated at 180 °C in an electric oven for 10 min to enhance its property of water resistance.

2.2. Slurry preparation

The slurry was composed of 1 g of Darvan C–N, and 24 g of deionized water for every 100 g of water-insoluble PVA-coated Al_2O_3 powder. After regulating its pH value to 8.1 the slurry was then milled for 24 h. Afterwards, 24 g of 6% aqueous solution of sub-partially hydrolyzed PVA (BC-05, degree of hydrolysis of 72 ~ 76 mol%, Chang Chun Petrochemical Co. Ltd., Taipei, Taiwan) as the organic binder were added to slurry. The slurry was milled for another hour. Finally, the slurry was defoamed by adding a defoaming agent and de-aired in a vacuum chamber for a few minutes. After all, the slurry stayed still under ambient conditions for 24 h, and then the residual bubble could continuously escape from the slurry.

2.3. Parts fabrication

In accordance with the steps from (2) to (5) in Fig. 1, the green parts were fabricated by a self-made rapid prototyping apparatus. Laser scanning parameters of the step (5) were studied in this paper. Four laser powers (1.5, 2.0, 2.5, 3.0 W), three scanning speeds (370, 580, 870 mm/s), and constant hatch spacing were selected to carry out laser scanning. Each parameter combination with layer thickness of 20 μm was employed to fabricate 3 pieces of green part with dimension of 10 mm × 10 mm × 1 mm. After a formability analysis, one of the parameter combinations was selected to fabricate 6 pieces of green part.

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 min 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 h. The topography of the fracture surface of the green parts and the sintered parts were observed by a scanning electron microscopy (SEM). 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).

According to ASTM C1161-02,[11] six specimens with dimensions of 25 mm(L) × 2 mm(W) × 1.5 mm(H) of each were fabricated for flexural strength test. The flexural strength of the sintered parts was measured in 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.

3. Results

Using suitable laser scanning parameters can fabricate a green part layer by layer. The principle of part forming is the organic binder melts in a very short time and binds the adjacent ceramic particles when the dried green layer is scanned selectively with a laser; the laser scanning parameters should lead to binder melting rather than evaporating. The property of scanned region will be transformed to be water-insoluble, and the depth of this transformation region must be near 40 μm, which is two times of the layer thickness, to ensure the adjacent two layers can connect each other. The experimental results revealed that only two of twelve scanning parameter combinations (2.5 W

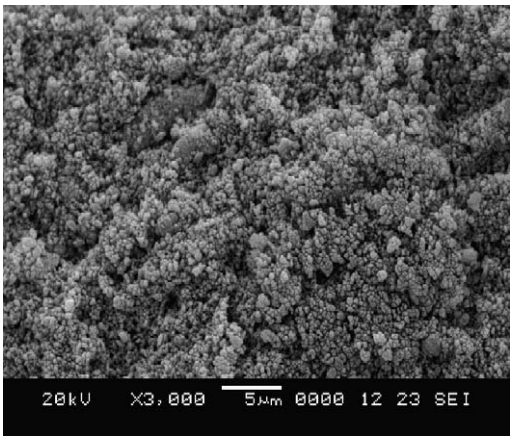

Fig. 4. The fracture surface micrograph of the scanned region formed with scanning parameter of 2.5 W-870 mm/s.

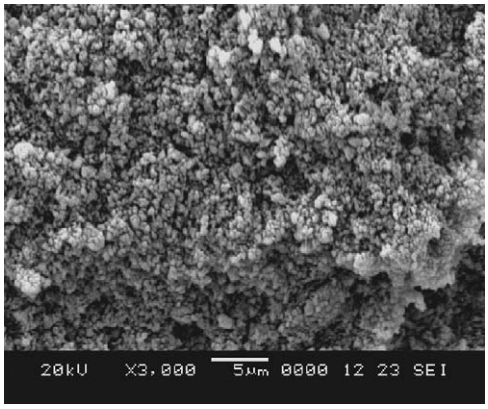

Fig. 5. The fracture surface micrograph of the un-scanned region.

-870 mm/s and 2.0 W-580 mm/s) could be employed to fabricate parts. The temperature generated from the laser scanning with low energy density, such as 2.0 W-870 mm/s, was too low to create a scanning depth greater than 40 μm for binding the adjacent two layers together. However, a high energy density, such as 3 W-870 mm/s, generated a high temperature to vaporize a part of the organic binder; the part could not be fabricated successfully also. In this paper, the scanning parameter combination of 2.5 W-870 mm/s was selected.

Figs. 4 and 5 show the fracture surface micrograph of the scanned region formed with scanning parameter 2.5 W-870 mm/s and the un-scanned region, respectively. The microstructures were almost identical. This result indicated that the selective scanning only brought about minor variation in the microstructure of the material. The relative density of the green part was 56.7%.

The sintered ceramic parts are shown in Fig. 6. The relative density of the sintered ceramic parts was increased to 98%. Fig. 7 shows the fracture surface micrograph of the sintered part, which still contained a few closed pores. The average flexural strength was 364.6 MPa with a standard deviation of 54.4 MPa.

Fig. 8(a) demonstrates a 3D complex green part "lion", which was about 40 mm and fabricated by this process. Fig. 8(b) shows the sintered part shrunk to be smaller.

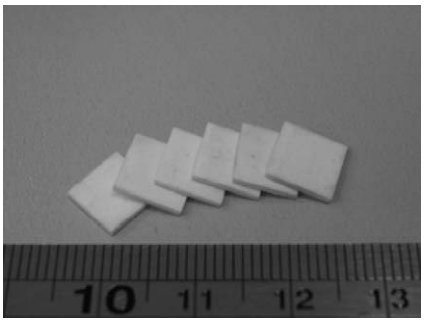

Fig. 6. Sintered parts (10 mm × 10 mm × 1 mm, sintered at 1600 °C for 2 h).

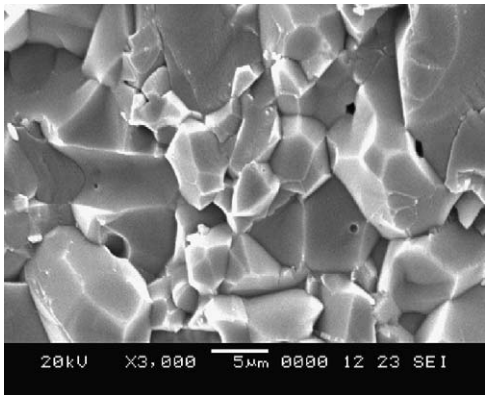

Fig. 7. The fracture surface micrograph of an alumina part (sintered at 1600 °C for 2 h).

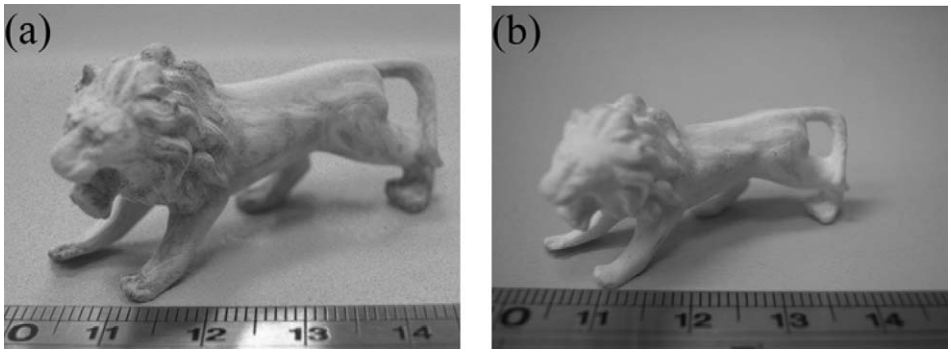

Fig. 8. (a) 3D green part; (b) 3D sintered part.

4. Discussion

The proposed material system in this study could be transformed from a water-soluble state to a water-insoluble state through selective scanning by the laser beam. Finch C.A.[12] reported that the aqueous solubility of PVA can be reduced when PVA re-crystallized by heat treatment. The current process applied this principle to reduce the aqueous solubility of the green part through re-crystallization of PVA (BF-17S) which coated on the surface of alumina particle. Besides, total amount of the binder was 3.95 wt% of the slurry; the water-insoluble PVC coated on alumina powder and the water-soluble PVC binder (BC-05) were 2.55 wt% and 1.4 wt%, respectively. Obviously, the former was the major component of the binder. After drying and laser scanning, the water-soluble green material was transformed to be a composite material which is completely water resistant at 40 °C.

The colloidal science was 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%. Although the slurry-based CLS was a wet process using inorganic binder, such as clay, there was no dispersant in the slurry and the pH value of the slurry was not adjusted. Therefore, agglomeration of the ceramic powders could occur 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, we used ammonium polymethacrylate as a dispersant to form an absorptive layer on the ceramic particle surface for obtaining a strong steric effect. Furthermore, the pH value was adjusted to 8.1 to increase the electrostatic repel force between the particles. As a result, an optimal dispersion of the slurry could be achieved. This is the reason why the density of the green part and the sintered part could be 56.5% and 98% individually.

The new slurry-based selective 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. Fortunately, the slurry-based selective laser sintering can fulfill these two demands. The water-soluble PVA in the slurry is helpful for avoiding delamination and cracks. Detail is discussed as following:

In the step 2 of Fig. 1, working platform was descended a distance of 15.5 μm. In the step 3 of Fig. 1, a fresh slurry layer, about 29 μm, was overlaid on top of previous dried-layer. The water content in the slurry was about 70 vol% and the porosity of the previous dried-layer was about 44 vol%. The liquid phase in the fresh layer, including water and the dissolved binder, penetrated into pores in the previous dried-layers; the thickness of the fresh layer reduced to about 15.5 μm. As a result, a layer contained saturated water was formed. This saturated layer, which included the fresh layer and a part of the previous dried-layers, was approximate 46 μm thick. The penetrated liquid could locally and partially dissolve the water-soluble polymer which was precipitated on the surface of the powder during the step 4 (layer drying), and could connect the individual polymer-coated ceramic particles. After drying a strong connection between adjacent layers were established. Upon laser irradiation a two 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[10] 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 binder would be precipitated to connect ceramic particles during the layer drying, and then a rigid 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. Grau et al.[13] reported that cracking occurs when the layer is thicker than the critical saturation thickness (CST). 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 45 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 nano-powder is the cracking.[14] Because the new process could cast extreme thin layer, using the presented slurry based selective laser sintering to fabricate monolithic ceramic components from nano-particles may be possible.

5. Conclusions

In this paper, the inorganic binder in the process of slurry-based selective laser sintering was replaced by the organic binder. The principle of colloidal science was applied to improve the dispersion of the slurry. The sintered alumina ceramic parts with a mean density of about 98% were made successfully. Furthermore, because the proposed slurry-based process can produce the parts free from delamination and cracks, a mean flexural strength of about 363.5 MPa was achieved.

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