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Original Article

Frozen slurry-based laminated object manufacturing to fabricate porous ceramic with oriented lamellar structure

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ABSTRACT

The freeze drying-based additive manufacturing can be used to process porous ceramics. However, the lack of freezing direction leads to the disorderly porous structure. This paper proposes a frozen slurry-based laminated object manufacturing (FS-LOM) for processing porous ceramics. Slurry was composed of water, alumina powder, and organic binder. The water in the fresh slurry layer crystallized to obtain a good support strength. The outline of 2D pattern was cut with laser to gasify ice crystal and binder. After stacking, the ice crystal freeze dried to obtain a porous structure. The lamellar ice crystals were induced to growth vertically by layer-by-layer freezing. The uniformity and orientation of the pore structure were improved, and the compression strength of the parts were improved. Due to the support of frozen slurry, the deformation of the green part was avoided.

1. Introduction

Porous ceramics have important applications in many fields, such as filtration, catalyst carrier, thermal insulation, biological medicine, sound absorption and so on [1,2]. Some additive manufacturing (AM) methods can be used to process porous ceramics with complicated shapes, such as three-dimensional printing (3DP) [3,4], selective laser sintering (SLS) [5], fused deposition modeling (FDM) [6], selective laser gelling (SLG) [7], selective laser burn-out (SLB) [8], and selective laser gasifying of frozen Slurry (FSLG for short) [9]. These methods can be used to process parts with bimodal porosity. A milimeter scale porosity processed by controlling the machining path (i.e. the pore size depends on the precision of the mechanical control system), and residual μm-level porosity after sintering due to binder reaction/melting-solidification or solvent evaporation. However, the processes of binder reaction/melting-solidification or solvent evaporation are difficult to control, resulting in poor designability of micrometer scale macroporous structure.

In order to improve the designability of the macroporous structure, the properties of the material must be controlled in the whole process of processing. Through the direct extrusion process (without changing the physical and chemical properties of the material), the ceramic parts with macroporous structure can be obtained by combining the corresponding post-processing technology. Direct ink writing (DIW) takes shear thinning ceramic ink as the material [10–12]. It is extruded from the slim-hole nozzle into threadiness, and then the 3D part is constructed through the accumulation of layers. Emulsion/foam templating has the advantages of simplicity and strong applicability to processing porous structure. As a raw material, the emulsion/foam dispersion system with a stable rheological performance is used in DIW to process ceramic parts with pore structure [13]. The freeze drying method uses the sublimation principle of the frozen solvent to obtain a designed porous structure [14]. Porous ceramics with lamellar structure can be obtained by the freeze form extrusion fabrication (FEF) [15]. Unlike FEF, ceramic/camphene-based slurry is used as raw material in 3-dimensional ceramic/camphene-based extrusion (3D-Ex) process, the frozen solvent can be sublimated at room temperature [16,17]. In these freeze drying-based processes, the crystals growth randomly during the freezing process, resulting in a lack of orientation in the lamellar structure. In addition, the extruded slurry filament can easily cause the deformation of cantilever structure due to gravity.

The aim of this study is to propose a frozen slurry-based laminated object manufacturing (FS-LOM) method, which employed laser cuts the two-dimensional contour of frozen slurry layer, and used freeze drying to obtain porous structure. The new method enhances the orientation of the lamellar pore structure. Compared with extrusion process, the deformation of cantilever structure is avoided.

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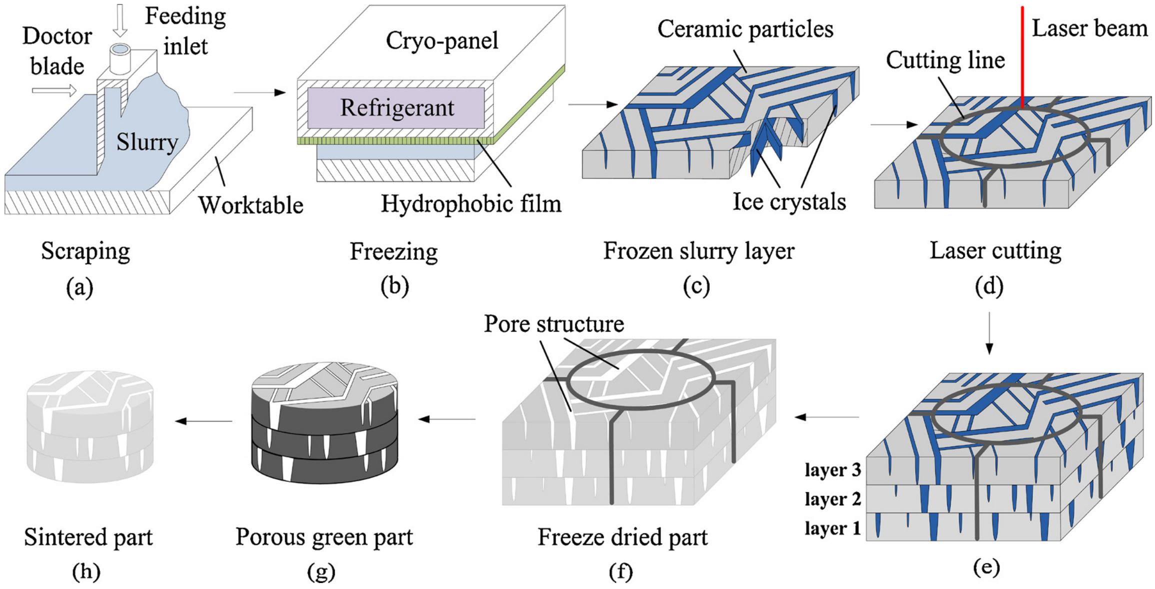

Fig. 1. Diagram of the manufacturing steps of FS-LOM.

2. Materials and methods

2.1. Materials

The alumina powder (structural material, $D_{50} = 0.3\,\mu m$), carboxymethylcellulose sodium (binder, 1 wt.%), Ammonium polyacrylate (dispersant, 2 wt.%) are mixed thoroughly in the ball mill to prepare a water-based ceramic slurry (alumina content: 50, 55, 60, and 65 wt.%).

2.2. Process of FS-LOM

FS-LOM processing includes paving, freezing, cutting, freeze drying and sintering, as shown in Fig. 1. The vertical motion worktable is placed in a −20 °C processing environment. After the worktable is lowered one layer, the prepared slurry is supplied to doctor blade through the feeding inlet and scraped on the worktable (Fig. 1a). Then a cryo-panel with internal circulation of refrigerant is used for freezing. A layer of hydrophobic film applied to the lower surface of the cryo-panel to avoid the bonding of frozen slurry (Fig. 1b). After the slurry is frozen to the temperature below eutectic point, the ice crystals are fully grown and the ceramic particles are squeezed together (Fig. 1c); Then the laser gasification is used to incise the outer contours of the 2D pattern (Fig. 1d); The slurry in the region where the laser did not scan remains frozen. When a new layer is just paved, the micro ice crystals on the surface of the former frozen slurry are melted. After the new layer is frozen, the water produced by the micro-melting is crystallized together with the water in the new layer, and a combination of adjacent layers is achieved. After layers are accumulated, the 3D green part wrapped by frozen slurry is obtained (Fig. 1e). Then the entire sample is placed in a vacuum freeze dryer (Fig. 1f). After drying is completed, the periphery excess material should be removed, and the ceramic green body is obtained (Fig. 1g). Finally, the ceramic parts with pore structure were obtained after sintering (Fig. 1h).

Fig. 2 shows the principle of laser cutting. The CO_2 laser is used because the ice has a high absorption coefficient (158,000/m) for a laser with a wavelength of 10.6 μm. The temperature of the materials rises instantly by laser irradiation. When the temperature exceeds the boiling point, the ice crystals and organic additives are gasified directly to form a gasification area, which makes the ceramic particles free from bondage. Some free particles are ejected by the rapidly escaping gas, and the others remain on the scanning line. In the gasification area, some organic additives that have no contact with the air are high-temperature carbonized by laser. With the increase of laser incident depth, the attenuation of energy increases. Below the gasification area, the laser energy is not enough to make the ice crystals gasified, but it can make the ice crystals melt to form a transition area. In the transition area, the ceramic particles are separated from the extrusion of the ice crystals, redistribute in the molten area. Finally, the transition area is refrozen by the surrounding low temperature frozen slurry.

2.3. Experimental procedure

The eutectic point of the ceramic slurry (solid content: 50 wt.%) measured by a differential scanning calorimeter (DSC823e, Mettler-Toledo, Switzerland) is −14 °C (test temperature range: 20 to −50 °C, cooling rate: 10 °C/min). The slurry layer of 2 mm thickness is scraped on the worktable, then frozen by the cryo-panel (temperature: −60 °C) to −20 °C (about 5 s). Different laser parameters (spot size : 500 μm, power P: 30 W – 41 W, speed V: 100 mm/s–250 mm/s) were used on the frozen samples for the scanning cutting experiment. Then the samples were dried in a vacuum freeze dryer (LGJ-10, Songyuan, China) for 18 h (temperature:10 °C, vacuum degree: 3 Pa). A scanning electron microscope (VEGA-II XMU, TESCAN, Czech Republic) was used to observe the change law of the shape of the cut.

The slurries (alumina content: 50, 55, 60, and 65 wt.%) were frozen by layer-by-layer (layer thickness: 200 μm) and frozen as a whole. Then the samples were freeze-dried for 36 h (temperature:10 °C, vacuum degree: 3 Pa), and sintered by a high-temperature box resistance furnace (KSL-1700X, Kejing, China) at 1650 °C in air for 120 min (heating rate: 2 °C/min). In order to calculate the porosity, partial samples were boiled for 3 h in boiling water to make it fully soaked, then the changes of sample weight before and after immersion were measured, and the volume of the soaked sample were measured by using the Archimedes principle. Then the porosity of the sample can be calculated. A diamond wire saws (STX-202A, Kejing, China) is used to cut the samples into test blocks of 15 mm × 15 mm × 15 mm (length × width × height). The vertical compressive strength of 28 test blocks (4 kinds of solid content, 7 samples per species) were respectively measured by a microcomputer controlled electronic universal testing machine (CTM2500, Xieqiang, China) at the pressure loading rate of 1 mm/min.

In order to illustrate the characteristics of FS-LOM, 3D parts were processed with appropriate laser parameters and layer thickness.