Powder layer manufacturing of alumina ceramics using water spray bonding

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For powder layer process of additive manufacturing, alumina granules containing methylcellulose as organic binder were used to form a firm powder layer by spraying water to the granules, and the powder layers were stacked to obtain a green body. Good shape retention with bonded alumina granules was confirmed in the green body. Debinding and post-sintering of the green body were conducted, resulting in an alumina sintered body without visible gap or interface between the stacked layers.

Key-words : Additive manufacturing, Binder jetting, Alumina, Granule, Water spray, Methylcellulose

1. Introduction

Additive manufacturing, which has been developed for fabrication of plastic and metal parts, is now very important processing technology in the field of ceramics as well, since complex-shaped parts with desired compositions can be directly generated from a virtual model in computer by adding material, without hard-tooling (e.g., dies or molds) and post-machining (subtracting material).¹-³ There are several techniques in additive manufacturing;³ among them the binder jetting (or indirect printing), where a liquid bonding agent is selectively deposited to bind powder materials on a powder layer, is one of the most widely used approaches, because of the high degree of geometric freedom, the low-cost equipment, high speed production, etc.

Methylcellulose is a water soluble polymer and has been used very extensively as binders in a variety of ceramic processes such as extrusion, injection molding, and sheet forming, due to several beneficial characteristics including, thermal gelation property, surface activity (reducing surface tension of aqueous solution), non-ionic property (little interaction with other processing aids), water retentive ability (improving plasticity and workability), lubricity (reducing inter-particle friction), and non-toxicity.⁴-⁸ In this study, we investigated powder layer process of ceramics in binder jetting approach, using spray-dried alumina granules which contain methylcellulose as organic binder. We tried to bond the alumina granules by spraying water into them and dissolving the contained methylcellulose in the water, taking advantage of water solubility of methylcellulose. A green body obtained by stacking the layers was debinded and post-sintered, followed by investigating the microstructure of the sintered body.

2. Experimental procedure

Commercially available alumina granules (AES-11, Marusu Glaze Co., Ltd., Aichi, Japan), which was produced by spray-drying alumina powder (AES-11E, Sumitomo Chemical Company, Limited, Tokyo, Japan; average particle size: ~0.5 μm), was used as the starting material. This granule contains 4.2 vol.% organic binder consisting of 0.5% methylcellulose, 3.4% ethylene-vinyl acetate, 0.2% wax, and 0.1% stearic acid. Among these, only methylcellulose is soluble in water. This granule is denoted as “MC granule” hereafter.

As a preliminary experiment, the granules were put into a cylindrical container with a base of 20 mm in diameter so that the height reached ~1 mm, and water at 18°C of 1 cm³ was sprayed onto them [Fig. 1(a)] and the wet condition was kept for 1 min, followed by drying at 150°C for 5 min. The shape retention was evaluated from the external appearance and the bonding behavior between the granules was observed by scanning electron microscopy (SEM; JEM-5600, JEOL Ltd., Tokyo, Japan). For comparison, the same experiment otherwise was conducted using alumina granules prepared by spray-drying alumina powder (AL-160SG-4, Showa Denko K.K, Tokyo, Japan; average particle size: ~0.6 μm) with binder of ~2 vol.% polyvinyl butyral, which is insoluble in water. This granule is denoted as “PVB granule”.

Fig. 1. Schematic illustrations of water spray onto granules in a container (a) and powder layer stacking process using granules by water spray (b).
hereafter.

Next, a green body was fabricated using the MC granule by powder layer stacking process. A square layer of the granules with an approximate thickness of 500 μm and an area of 45 mm × 45 mm was formed over a stage by a conventional recoating system with a scraper, as schematically shown in Fig. 1(b). Water of 3 cm³ was sprayed onto the layer, which was subsequently left 10 min for drying. The stage is lowered by one layer thickness, and a new layer of the granules was formed on top of the layer previously prepared. This process was repeated 10 times for making the thickness 5 mm, followed by drying at 150°C for 5 min. The obtained green body was heated up to 600°C at a rate of 1°C/min and kept there for 2 h in air for removing the binder. Then it was further heated up to 1600°C at a rate of 5°C/min and kept there for 2 h in air for post-sintering. The microstructure of the sintered body was observed by SEM.

3. Results and discussion

Figures 2(a) and 2(b) show SEM images of the MC and PVB granules, respectively, before water spray. Both the granules had spherical shape with an average size of about 60 μm. Both also show smooth surface with hollow or dimple structure, which is typical with spray-dried ceramic granule particularly when the deflocculant level is high or the slurry yield stress is low. During spray-drying, slurry droplet shrinks and rigid shell forms, leaving an internal void. A crater may form from the inward collapse of the granule surface, resulting in the above structure.

For the sample after spraying water onto the MC granule in the container and drying, good shape retention was observed as shown in Fig. 3, while such shape retention was not obtained for the PVB granule. Figures 4(a) and 4(b) show the SEM images of the samples from the MC and PVB granules after spraying water and drying, respectively. In the MC granule sample, substantial amount of product which was formed on the surface played a role of bonding the granules together. On the other hand, neither such product on the surface nor bonding between the granules was observed in the PVB granule sample. The product observed in the MC granule sample is most likely caused by solution of methyl cellulose contained in the binder in the sprayed water and precipitation on the surface after drying. It has been well known that, in ceramic wet forming, organic binders and small ceramic particles tend to migrate, or move, together with evaporating medium (water in this case) to the surface of the green body during drying, since the solvent medium evaporates from the surface. The movement of water to the surface is enhanced substantially by capillary forces. If the binders are in solid state particle form, the migration occurs only when their size is sufficiently smaller than the moving path. However, when the binders are soluble in water, such limitation is not applied. Methylcellulose dissolved in water inside easily moves into the surface, and precipitates there after water evaporation to form the solid product, or residue, which bonds the granules. By this way, even such a small amount of methylcellulose as 0.5% can produce the substantial amount of the product on the surface as observed. For the PVB granule sample which does not contain water-soluble binder, such product product...
was not observed as above-stated.

Figures 5(a) and 5(b) show the green body fabricated using the MC granule by the powder layer stacking process, and the body obtained dewaxing and post-sintering the green one, respectively, both indicating relatively good shape retention. Particularly for the sintered body, obtained was a relatively good rigidity which allows its easy handling. The relative density of the green and sintered bodies was 45 and 48\% respectively, which was determined by Archimedes’ method. In order to measure the density for the green body without binder, a sample was cooled down after the 600°C heat-treatment for the debinding. The small difference between the green and sintered densities indicates little densification during the post-sintering.

Figure 6 shows the SEM image of the sample prepared using the MC granule after the dewaxing and post-sintering. The shape of granules apparently maintains their original spherical ones and there is no significant change in the granule size, agreeing with the limited sintering and densification as above-noted. It can be assumed that large spaces among the granules suppress mass transfer or diffusion between them, resulting in little change in the bulk density. However, between the stacked layers, there is no visible gap or interface, suggesting good sintering and bonding behaviors of the powder layers in the forming and post-sintering processes, respectively. Figure 7 shows a magnified view of two granules. Considering that the original average particle size of the alumina powder used for the MC granule is 0.5\,\mu m, it is obvious that grain-growth occurred due to some mass diffusion inside the granule during the post-sintering. Partial formation of necks is observed at the interface between the two granules, suggesting mass diffusion was generated at such a limited area, similarly to that inside the granule. The neck growth between the granules most likely causes the relatively good rigidity of the sintered body.

4. Conclusions

We investigated powder layer process of ceramics in binder jetting approach, using spray-dried alumina granules which contain methylcellulose as organic binder. The alumina granules were successfully bonded by spraying water into them and dissolving the contained methylcellulose in the water, taking advantage of water solubility of methylcellulose. Good shape retention with bonded alumina granules was confirmed in the green body prepared by stacking the powder layers. Debinding and post-sintering of the green body were conducted, resulting in the alumina sintered body with the neck growth between the granules and no visible gap or interface between the stacked layers.

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