付加製造技術（3Dプリンタ）用セラミック原料粉末の高次設計 ～レーザ直接3D造型を目指して～

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Design of Ceramics Powder for Additive Manufacturing Technology
～ For Direct Laser 3D Printing ～

直接レーザー焼結による付加製造のための静電統合造粒を使用したセラミック顆粒の製造に関する実現可能性を調査した。平均サイズが140nmのアルミナ粒子を出発原料として単分散な球状のアルミナ顆粒を作製した。この構造によって、流動性とハンドリング性が向上した。アルミナ顆粒を二酸化炭素レーザーで照射して、粉末の焼結および溶融を誘導した。レーザー出力や走査速度などのパラメーターを調査した結果、レーザー照射パラメーターを調整することにより､直接焼結または溶融を制御できることが明らかになった。機能性添加材料をセラミック顆粒に組み込むなどのさらなる開発は、機能性複合セラミックスの付加製造に向けて有益である。

The feasibility of ceramic granules fabricated using electrostatic integrated granulation for additive manufacturing via direct laser sintering has been investigated. Monodisperse and spherical alumina (Al_2O_3) granules were obtained using Al_2O_3 particles with an average size of 140nm, which exhibit an improved flowability and handling ability. The granules were then irradiated with a CO_2 laser to induce sintering and melting of the powder. Parameters such as laser power and scanning speed were investigated. The results obtained indicate a possible control of direct sintering or melting by adjusting the laser irradiation parameters. Further development such as incorporation of functional additives into ceramic granules would be beneficial toward additive manufacturing of functional composite ceramics.

1. Introduction

1.1 Additive manufacturing

Ceramics have desirable properties but are difficult to mould using conventional techniques [1-3]. Additive manufacturing technology, including 3D printing, offers a potential solution by enabling the production of complex ceramic parts without the need for expensive moulds [4]. While polymer-based 3D printing is already widely used, it is challenging to use this method for ceramics due to their high melting point [4]. Two methods are currently being researched for ceramic 3D printing: indirect manufacturing of a sintered body and direct moulding using melted materials or laser irradiation of raw material powders. These approaches offer new possibilities to produce ceramic materials with complex shapes and at high speeds. However, the bottleneck of additive manufacturing is the development of functional materials using this technique [5]. A homogeneous distribution of powder is indispensable in obtaining composite ceramics exhibiting desired properties via additive manufacturing. A continuous "layer-by-layer" additive manufacturing of multifunctional ceramic composites is challenging due to the inability to precisely obtain a controlled distribution of composite powder due to tendency of fine particles toward agglomeration [6]. One possible solution is to simultaneously apply laser sintering to a continuous feed of granulated powder with homogenous distribution of nanosized particles. Therefore, fundamental investigation and the feasibility with laser sintering of granulated ceramic powder is carried out in this study.

1.2 Indirect laser sintering

There are various methods of indirect manufacturing of sintered bodies, such as stereolithography, indirect laser sintering, binder jet method, and thin film lamination method. Stereolithography involves dispersing raw material ceramics in a photocurable resin, irradiating it with an ultraviolet laser, hardening and forming a monolayer outline, applying a photocurable resin to the surface, and performing the following steps. After that, a curing step is required. The formed green body is then sintered to produce the final ceramic part. The advantages of this method include the ability to use a wide range of ceramic materials, high production speeds, and low material waste. However, the resolution of the final product is limited, and there may be some residual binder left in the sintered body, which can affect the mechanical properties. These indirect methods can produce complex shapes without the need for expensive moulds, but they require careful consideration of the material properties and processing conditions to ensure the quality of the final product [7].

1.3 Direct laser sintering

A typical direct moulding method is the direct laser sintering method. Laser irradiation on an uniformly spread powder on a stage leads to sintering or melting forming layered sintered artifacts. The step is repeated forming a multilayer sintered artifact to obtain a three-dimensional object. The main drawback is the large thermal shock resulting in cracks formation. However, unlike indirect moulding, polymer binder is not used and therefore, no degreasing step or post-sintering step is required. In order to improve the direct laser sintering of ceramics with the feasibility to induce desired properties in ceramic composites, this study investigated the fundamental of direct laser sintering of granulated alumina (Al_2O_3) powder. Using ceramic granules with good flowability at a continuous feeder for laser sintering process, this could enable a more efficient and lean additive manufacturing process. Furthermore, it is envisaged that desired functional materials can be fabricated by incorporating additives into the composite granules during additive manufacturing.

1.4 Electrostatic integrated powder assembly

By using electrostatically integrating surface-charged modified particles, composite particles and granules design can be achieved [6, 8]. The controlled assembly of particles in nano- and submicron-sized forming composite particles enabled the fabrication of functional composites for various applications such as selective laser sintering [9, 4], batteries [10], optical properties of aerosol-deposited composite films [11], improved mechanical properties of green body [7] and ceramic composites [12] have been reported.

Recently, by using electrostatic integrated granulation of particles with similar size, formation of composite granules with controlled microstructure have been reported. By effectively incorporating functional additives such as carbon nanotubes and hexagonal boron nitride into the ceramic granules with improved handling ability, a controlled property such as electrical [13] and heat conduction [14] of the sintered ceramic artifacts have also been demonstrated. Therefore, it is of interest to investigate the feasibility to obtain a controlled laser sintering of ceramic granules obtained by electrostatic integrated granulation method. The findings from this fundamental investigation can be a useful reference for future development of functional ceramic composites by direct laser sintering process.

2. Experimental procedures

The Al_2O_3 granules (average particle size 140 nm, Taimei Chemical Co., Ltd) were prepared using electrostatic integrated granulation method. As Al_2O_3 particles exhibit positive surface change in aqueous suspension, they were used as received and polysodium styrenesulfonate (PSS) (an average molecular weight of 70 000, Sigma-Aldrich) was used as electrolyte to induce a negative surface charge. Details for the electrostatic integrated granulation process are reported elsewhere [13, 15]. The ratio of the positively and negatively charged suspensions used was 1:1 and the mixed suspension was rotated in a glass vessel at 5 to 30 rpm for one week. After that, the granules obtained were dried in an oven at 80 oC for 24 h.

As for the laser irradiation, the granules were affixed onto an alumina plate and irradiated with a carbon dioxide laser (wavelength of 10.6 μm and a spot size of 0.2 mm). The granules obtained were observed using a laser microscope (Olympus, OLS 4100) The microstructure of laser sintered artifacts obtained were observed using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800).

3. Results and discussion

The Al_2O_3 granules obtained after electrostatic integrated granulation are shown in Fig. 1. Spherical monodisperse granules with an average size of 500 μm, exhibiting good flowability and handling ability compared to their powder state was obtained. SEM image of a granule irradiated with a laser at 8 W and 1 mm/s is shown as Fig. 2. The image is taken in the direction of laser irradiation from left to right. In the left region of the granule, it can be observed that sintering did not occur and as the laser gradually moved to the

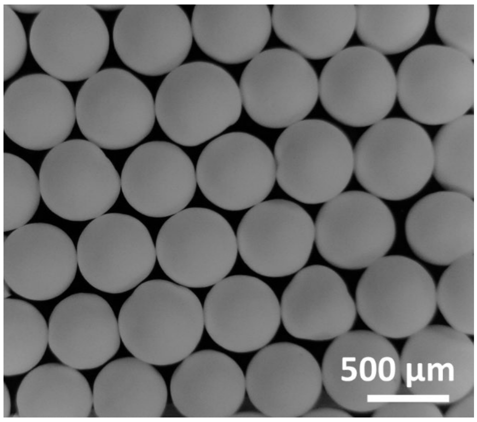

Fig. 1: Optical miscrope image of the Al_2O_3 granules obtained using electrostatic integrated granulation process.

right region, temperature increase during a continuous laser led to sintering or melting, which can be observed at the surface of the granule. As the diameter of the laser used is smaller than the diameter of the granule, only a partial region of the granule was irradiated and underwent a sintering or melting process. Cracks were also observed on the surface of laser irradiated granules which could be caused by the thermal shock during laser sintering process[4]. Although it is difficult to obtain a complete and uniform sintering process of the entire granule, this study provides the fundamental observations on the feasibility for direct laser sintering of Al_2O_3 granules and the morphological transformation which could be beneficial for future development and study.

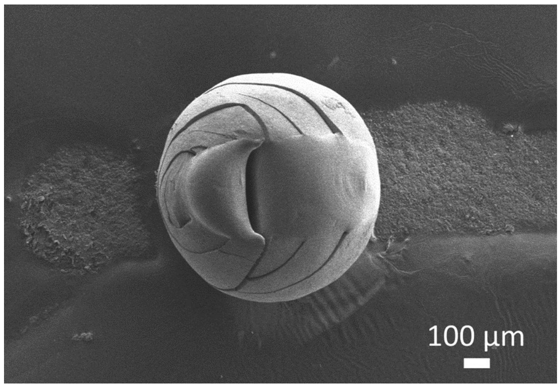

Fig. 2: SEM image an Al_2O_3 granule after laser irradiation at 8 W with a scan speed of 1 mm/s.

Different laser irradiation parameters were used for the laser sintering process of the Al_2O_3 granules and SEM images showing the surface morphologies obtained are shown in Fig. 3. From the SEM images, molten state was observed when laser irradiated at 4 and 6.4 W with a scan speed of 1 to 10 mm/s as shown in Fig. 3 (a)-(c) and (f)-(g), respectively. At higher laser irradiation power of 8 W, molten state was observed for all the scan speed from 1 to 20 mm/s as shown in Fig. 3 (k)-(o).

At a low scan speed and low laser power, sufficient heat generation for melting was obtained. However, upon irradiation at a lower laser irradiation power of 4 W with a high scan speed of 15 to 20 mm/s, sintering or melting was not obtained due to insufficient heat conversion and generation as shown in Fig. 3 (d) and (e). A higher magnification of the microstructure obtained after laser irradiation at 4 W with a scan speed of 20 mm/s is shown

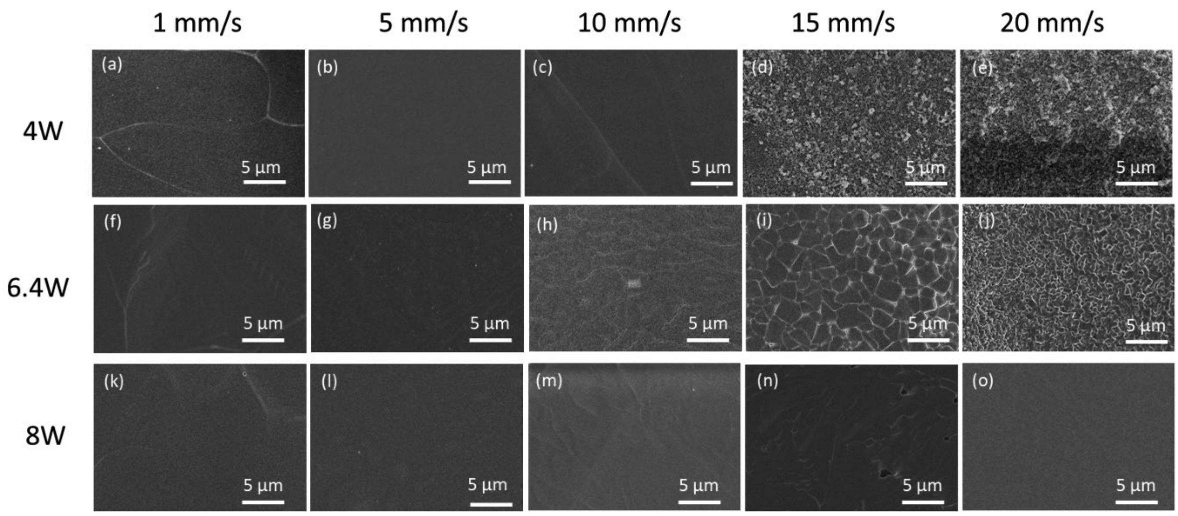

Fig. 3: Surface morphologies SEM showing the microstructure obtained at the surface of Al_2O_3 granules using different laser sintering parameters.

in Fig. 4. It can be clearly seen that particulate Al_2O_3 particles that match the size of the starting materials used.

It is noteworthy that a sintered morphology was obtained upon laser irradiation with laser power of 6.4 W and a scan speed of 15-20 mm/s as shown in Fig. 3 (i) and (j). Higher magnification SEM images of the sintered microstructure obtained at 6.4 W with scan speed if 15 and 20 mm/s are shown as Fig. 5 (a) and (b), respectively. At a scan speed of 15 mm/s, a distinguished grain boundary can be observed. At a higher scan speed of 20 mm/s, a rather low degree of sintering was obtained. The morphologies observed are comparable with those of sintered ceramic powder obtained using powder metallurgy technique.

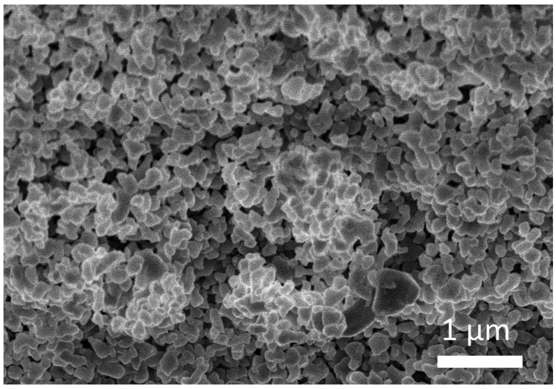

Fig. 4: High magnification SEM image of the microstructure obtained after laser irradiation at 4 W with a scan speed of 20 mm/s.

The findings from this study indicates the feasibility to obtain a controlled direct laser sintering or melting of Al_2O_3 granules formed using electrostatic integrated granulation method. However, as the size of the granules obtained is larger than the diamter of the laser used, further investigation and control in the formation of granule size is necessary and will be carried out. Using granules with average size that is equivalent or smaller than laser irradiation spot size, it is envisaged that a more uniform selective laser sintering or melting can be obtained.

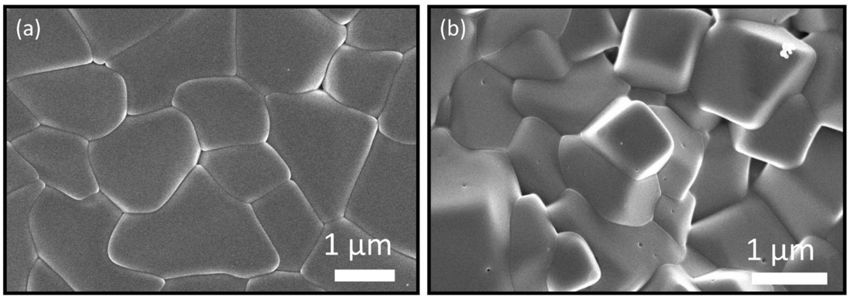

Fig. 5: High magnification SEM image of the microstructure obtained after laser irradiation at 6.4 W with a scan speed of (a) 15 and (b) 20 mm/s.

4. Conclusions

In this study, a fundamental investigation on the feasibility of direct laser sintering of Al_2O_3 granules obtained using electrostatic integrated granulation process. Using the Al_2O_3 granules with improved flowability and handlingability, different degrees of sintering or melting was obtained by altering the laser irradiation power and scan speed. This indicates a potential to use ceramic granules for additive manufacturing via a continuous feeder. Nevertheless, further investigation is still required to obtain a desired size of granules and incorporation of functional additives toward a possible fabrication of functional composite materials with desired properties using additive manufacturing.

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