Paper

Fabrication of Carbon-decorated Al_2O_3 Composite Powders using Cellulose Nanofiber for Selective Laser Sintering

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ABSTRACT

In this study, systematic investigation using cellulose nanofiber (CellNF) as a carbon source for selective laser sintering (SLS) of Al_2O_3 was conducted. A composite powder that consisted of CellNF and Al_2O_3 was fabricated using electrostatic adsorption (EA) method in aqueous suspension. Heat-treatment temperature of 500 and 800°C was compared for the conversion of CellNF to carbon residue (CR) in the Al_2O_3 composite. After that, the parameters involving the volume fraction of CR and effect of Al_2O_3 particle size in the CR- Al_2O_3 composite particle were also investigated in order to obtain an optimized condition of the CR- Al_2O_3 composite particle for SLS. From the results obtained, 1.5 wt% CR- Al_2O_3 with alumina size of 0.8 μm that was heat-treated at 800°C exhibited optimum laser sinter ability owing to the good CR distribution over a higher surface area that promoted good laser adsorption for the alumina sintering.

KEY WORDS

additive manufacturing, selective laser sintering, cellulose nanofiber, electrostatic adsorption, nano-assembly technique

1 Introduction

Additive manufacturing (AM) technology is regarded as next generation's manufacturing technique that allows complex shape formation without requiring molds. AM technique also enable rapid production compared to traditional manufacturing techniques (for example, dry pressing, slip casting, tape casting, and injection molding). Precise sophisticated components are indispensable for breakthrough advanced technologies such as aerospace industry and therefore selective laser sintering (SLS) have recently attracted significant attention due to its feasibility to produce complex parts using pinpoint sintering or melt-solidification process. SLS involves the usage of high-energy laser beam for fusion or consolidation of powder granules¹⁾. During SLS process, inefficient transfer of the energy to the powder would hinder sintering process while too much energy would result in complete powder meltdown. Therefore, adaptation of SLS for new material sintering is complex as it is highly dependent on the material composition in the compound/composite which would alter the physical properties and amount of energy transfer during laser sintering despite being irradiated under similar condition²⁾. There are mainly two approaches to fabricate ceramic parts by SLS, which are indirect

SLS and direct SLS. Indirect SLS uses an organic polymer binder and ceramic composite particles as the raw materials. Upon laser irradiation, the melting of polymer binder would then bind the ceramic particles together. The green bodies obtained are then subsequently sintered to achieve higher density and strength. Complex fabrication of polymeric or metallic parts by indirect SLS have been well reported³⁾, however, there are only few studies on the direct SLS of ceramics without any polymer binder. Ceramics manufacturing by direct SLS is very challenging as ceramic materials possess high melting point, low thermal shock resistance and poor ductility.

Another obstacle faced using SLS on ceramics is that ceramic oxides exhibit poor absorptivity towards near-infrared laser⁴⁾. Although ceramic oxides show high absorptivity to CO_2 laser, its large laser spot size resulting from its long wavelength would be a setback towards fabrication of high precision complex components¹⁾. Therefore, a near-infrared laser with a wavelength of near-infrared that has smaller laser spot size is more suitable to be used for SLS even if it provides poor absorptivity for ceramic oxides. To improve the absorption of near-infrared laser, additive materials are added into the ceramic matrix. Using a smaller laser spot size (near-infrared laser) on materials with improved near-infrared laser adsorption, higher level of precision manufacturing of industrial

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components could be achieved. Chang et al. reported the fabrication of 3D porous SiO_2 structures by SLS with carbon additive that exhibited high absorptivity⁵⁾. With the addition of 0.2 mass fraction of carbon into silica, the laser absorptivity was increased 8 times in comparison to pure silica which then allowed the conversion of silica into good crystallized quartz structure after laser irradiation. Their work had demonstrated that incorporation of carbon additive into ceramics could improve the laser absorption property that can be used for direct SLS in ceramics manufacturing.

In this study, alumina which is one of the commonly used ceramic oxide was used as the matrix material while TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-oxidized cellulose nanofiber (TOCN⁶⁾) with high aspect ratios (>100 ; diameter of 3~4 nm and several microns in length) as well as high specific surface area ($>650 \text{ m}^2/\text{g}$) was added as a carbon source. Cellulose nanofibers (CellNF) possess good reusability, biodegradability and abundance with estimated yearly-production of 10^{10} tons. Due to its rich carbon content of 44.4 mass fraction, CellNF is even thought to be an eco-friendly precursor to supply carbon nanofiber by pyrolysis⁷⁾. Hence, CellNF- Al_2O_3 composite particles were prepared and converted to carbon residue (CR)- Al_2O_3 composite by heat treatment prior to direct SLS. The samples obtained after SLS were systematically characterized and evaluated.

2 Experimental

2.1 Electrostatic adsorption (EA) assembly method

Up to now, conventional mechanical mixing method such as the mechanical ball-milling technique is commonly used to obtain powder mixture. However, the homogeneity of the powder obtained using mechanical milling is rather insufficient to meet today's precision technology requirement. Moreover, the volatile force and motion during the mixing process would destroy and alter the original crystallinity and the shape of the materials such

as nanofibers and nanorods. To solve these issues, a new method; electrostatic adsorption assembly method that allows homogeneous preparation of nano/micro-composites has been developed^{8,9)}. The EA assembly method used in this study is shown in Fig. 1. Firstly, the primary alumina particles were mixed into a solution of polyelectrolyte (such as polydiallyldimethyl ammoniumchloride (PDDA) as polycation and polysodium styrenesulfonate (PSS) as polyanion), in order to induce desired surface electric charges on the particles' surface. As alumina possesses positive zeta potential charge, adsorption of polyanion electrolyte on its surface would modify the surface charge to negative zeta potential. Then the particles were washed and immersed into polycation electrolyte which would then generate positive surface charge. The alternate layer coating would induce higher zeta potential as well as improved stability. Repetition of this multiple layer coating is also known as layer-by-layer (LbL) coating process¹⁰⁻¹²⁾, where the zeta potential of a set of particles can be controlled. Finally, samples with the opposite zeta potential induced in separate suspension prepared by LbL technique were mixed together. Due to the EA force, finer electrostatically charged particles (secondary) were pulled towards and attached onto the bigger particles (primary) forming the nano/micro-composites. In this study, zeta potential of alumina which was used as matrix was positively induced while CellNF which served as an additive was used as it was due to its original strong negative surface charge.

2.2 Materials and methods

Alumina particles (AA-3, AA-1.5 and AA-07, Sumitomo Chemical Co., Ltd., Japan) and CellNF (Rheocrysta, DKS Co. Ltd., Japan) were used as starting materials for this study. The average particle sizes of alumina used were approximately 3.4, 1.6, 0.8 μm , respectively. The average diameter of CellNF was approximately 3~4 nm with length reaching several micrometers. The as received CellNF in Rheocrysta gel is TEMPO-oxidized cellulose nanofiber (TOCN)

Fig. 1 Schematic illustration of nano/micro-composite particles fabrication using layer-by-layer (LbL) and electrostatic adsorption assembly (EA) technique.

that possess good dispersion. Alumina and CellNF exhibit positive and negative zeta potential, respectively. Only surface charge of alumina was modified by electrostatic adsorption technique using designated polyelectrolytes as CellNF possess strong negative zeta potential (-75 mV). Polydiallyldimethyl ammoniumchloride (PDDA) was used as polycation, while polysodium styrenesulfonate (PSS) was used as polyanion. As alumina exhibits positive charge in water, the alumina particles were immersed into the following sequence of polyelectrolytes; PSS, PDDA, and PSS solution in order to create high and stable positive zeta potential charge on the surface. Then, the positively surface charged alumina and negatively surface charged CellNF were mixed together to fabricate CellNF- Al_2O_3 composite particles.

Firstly, the effect of heat treatment temperature of CellNF- Al_2O_3 was investigated at different temperature of 500 and 800°C while alumina particle size and mass fraction of CellNF were fixed. Then, the effect of laser absorbent ratio was studied. 16 and 11 wt% CellNF- Al_2O_3 composite particle with alumina matrix of 0.8 μm was prepared and heat-treated at 800°C for 2 h in order to obtain 1.5 and 1.0 wt% CR- Al_2O_3 , respectively. Finally, the effect of alumina particle size was investigated using alumina with different diameter of 3.4, 1.6 and 0.8 μm while the heat treatment temperature and mass ratio of CR was fixed at 800°C and 1.5 wt%, respectively.

The obtained powders were then subjected to uniaxial pressing at 50 MPa to form pellets and followed by 80 W laser irradiation on the pellets at a scanning rate of 1 mm/sec. The laser-irradiation system used consisted of a continuous direct diode laser ($P_{\text{max}} = 120$ W, ML-5120A, AMADA MIYACHI CO., LTD., Japan) with a wavelength of 915 nm and a laser beam focusing diameter of ~ 1 mm.

2.3 Characterization

The laser irradiated area of the samples were carefully observed by field emission scanning electron microscopes (FE-SEM, S-4800, Hitachi High-Technologies Corporation, Japan). Laser Raman spectrophotometer was used to investigate the carbonization of CellNF (NRS-3100, JASCO Corporation, Japan). The UV-Vis-NIR spectra were obtained using a V-670 UV-Vis-NIR spectrophotometer (JASCO Corporation, Japan). Thermogravimetric analysis and differential thermal analysis (Thermo plus EVO2 TG 8121, Rigaku

Fig. 2 TG result of the oven-dried CellNF at 500 and 800°C for 2 h in N_2 atmosphere. Solid lines indicate the mass change at different heating temperature of CellNF while dotted lines indicate heating temperature profiles.

Corporation, Japan) were used in the range from room temperature to 500 and 800°C in a flowing N_2 atmosphere with a heating rate of 5°C/min.

3 Results and discussion

3.1 Profiling of starting materials

Fig. 2 shows the TG results of the oven-dried CellNF that were heat-treated at 500 and 800°C for 2 h (heating rate 5°C/min). The results indicated that 28.7 and 8.1 mass percent of carbon residues remained after dehydration and thermal decomposition of cellulosic rings which led to the formation of gaseous products such as CO , CO_2 and tar⁶⁾. Using the aforementioned results as base reference, 5.0 wt% of CellNF- Al_2O_3 was used in order to obtain 1.5 wt% CR- Al_2O_3 when heat-treated at 500°C. Similarly, 11 and 16 wt% CellNF- Al_2O_3 were used to obtain 1.0 and 1.5 wt% CR- Al_2O_3 upon heat treatment at 800°C. Using alumina with diameter of 3.4 μm , the composite that consist of 16 wt% CellNF- Al_2O_3 is shown in Fig. 3 and upon heat treatment at 800°C the image of 1.5 wt% CR- Al_2O_3 obtained is shown in Fig. 4. In the high magnification image shown in Fig. 3 (b), CellNFs strains were observed on the surface of alumina particle while spherical dome-like CR were observed on the surface of alumina particle after heat treatment (Fig. 4). The dome-like CR (opened and closed structure) observed on alumina were most likely generated during pyrolysis. Similar phenomenon was also observed on the composite particles in the investigation of different parameters such as particle size and relative mass

Fig. 3 SEM images of CellNF- Al_2O_3 composite particle using alumina with diameter of 3.4 μm . Fig. (b) is the high magnification SEM image of (a).

Fig. 4 SEM images of CR- Al_2O_3 composite particle using alumina with diameter of 3.4 μm . Fig. (b) is the high magnification SEM image of (a).

Fig. 5 (a) Raman spectra of the oven-dried CellNF and CR obtained after heat-treatment at 500 and 800°C and (b) UV-Vis-NIR spectra of 1.5 wt% CR- Al_2O_3 (alumina diameter: 0.8 μm) heat-treated at 500 and 800°C.

ratio. However, when the CellNF- Al_2O_3 composite was heat-treated at 500°C, the dome-like structures were not observed. Although the mechanism is still unclear, it is observed that the CR retained its fiber shape at 500°C and converted into a film-like structure as shown in Fig. 4 upon heat treatment at 800°C. It is deduced that the dome-like CR structure was generated due to the volume expansion caused by thermal decomposition of the gaseous phase components. This observation indicated that heat-treatment temperature is vital for pyrolysis of CellNF to occur. The results obtained is tally with the finding reported by Jazaeri et al. where CellNF was converted to CR during pyrolysis up to 600°C due to a series of phenomena which include thermal decomposition, aromatization, dehydration and depolymerisation⁷. The as-obtained CR- Al_2O_3 composite particles were then used for the subsequent experimental investigation.

3.2 Effect of heat-treatment temperature

After determining the amount of CR composition in the CR- Al_2O_3 composite based on the amount of CellNF deposited as mentioned above, the effect of heat treatment temperature at 500 and 800°C on the CR formation was then investigated. To confirm the existence of CR after heat-treatment, Raman and UV-Vis-NIR characterization were conducted. Fig. 5 (a) shows the Raman spectra of oven-dried CellNF and CR obtained after heat-treatment at 500 and 800°C while Fig. 5 (b) shows the UV-Vis-NIR spectra of 1.5 wt% CR- Al_2O_3 (alumina diameter: 0.8 μm) heat-treated at 500 and 800°C. The intensity of the Raman band at 1650 cm^{-1} which is attributed to G-band increased with higher

Fig. 6 Photograph of the laser-irradiated surfaces of 1.5 wt% CR- Al_2O_3 pellets (alumina diameter of 0.8 μm) which were heat-treated at different temperature of (a) 500 and (b) 800°C.

heat treatment temperature (Fig. 5 (a)) indicating higher amount of carbon presence. As for the UV-Vis-NIR results shown in Fig. 5 (b), the sample heat-treated at 800°C exhibited higher absorbance at wavelengths between 900~1000 nm compared to the sample heat-treated at 500°C. For comparison, sample consist of only alumina was also measured which demonstrated very low absorbance (almost negligible). Both Raman and UV-Vis-NIR results corroborate that laser absorption rate increased with higher carbonization that was achieved at higher heat-treatment temperature of 800°C. In order to investigate the effect of heat treatment temperature to laser-irradiation, CR- Al_2O_3 composite powders were laser-irradiated. Fig. 6 shows the photograph of the laser-irradiated surfaces with sample of 1.5 wt% CR- Al_2O_3 (alumina diameter: 0.8 μm) which were heat-treated at 500 (Fig. 6 (a)) and 800°C (Fig. 6 (b)). By comparing the laser irradiated CR- Al_2O_3 powder that were heat-treated at 500 and 800°C, the

sample heat-treated at 500°C did not exhibit any sign of fusion or melting (Fig. 6 (a)) but the sample heat-treated at 800°C exhibited complete melting along the laser irradiated line as shown in Fig. 6 (b). This finding indicated that carbonization of CellNF to CR is indispensable to induce laser absorbing characteristic that would assist with the sintering of alumina.

3.3 Effect of CR volume fraction

In the investigation of CR volume fraction effect, heat-treatment temperature of 800°C was fixed while comparison between CR volume fraction of 1.0 and 1.5 wt% were compared. UV-Vis-NIR spectra of 1.0 and 1.5 wt% CR- Al_2O_3 composite powders shown are in Fig. 7. The results show that CR composition could affect the absorptivity of powder bed. For further confirmation, the surface and cross-sectional images of the samples after laser-irradiation were observed using SEM and the images are shown in Fig. 8. By comparing Fig. 8 (a) (i) and (b) (i), it can be observed that the composite sample with 1.0 wt% CR exhibited irregular groove depth while a smooth and even groove was obtained using the

composite sample with 1.5 wt% CR. It is thought that the irregular groove structure was caused by uneven heat distribution during laser irradiation due to the insufficient amount of CR in the 1.0 wt% CR- Al_2O_3 sample. Although electrostatic adsorption technique could promote good adsorption of CellNF on alumina, insufficient CellNF amount could cause non-uniform distribution of CR after pyrolysis which then affect the subsequent laser sintering process. On the other hand, composite sample with 1.5 wt% of CR possesses sufficient CR content to be distributed evenly across the surface of alumina to allow more uniform laser adsorption enabling better heat distribution during the melting process as a smoother melted groove was obtained as shown in the SEM image in Fig. 8 (b) (i). From the cross-sectional view shown in Fig. 8 (a) (ii) and (b) (ii), 1.5 wt% CR sample exhibited better depth and smoothness at the melted groove area after laser irradiation compared to the 1.0 wt% CR sample. The area between the molding resin and the black-dotted line represents the heat affected zone (HAZ). The high magnification images of the HAZ are shown in Fig. 8 (a) (iii) and (b) (iii).

3.4 Effect of alumina particle size

In the investigation of the effect of alumina particle size on the laser sintering process, alumina particles with different diameter of 0.8, 1.6 and 3.4 μm were used for comparison while heat-treatment temperature and CR volume fraction were fixed at 800°C and 1.5 wt% CR, respectively. Fig. 9 shows UV-Vis-NIR spectra of all three samples. The composite powders with alumina diameter of 1.6 and 3.4 μm exhibited higher laser absorption than the 0.8 μm composite powder. Fig. 10 shows the surface and cross-sectional SEM images of 1.5 wt% CR- Al_2O_3 samples with 0.8, 1.6 and 3.4 μm diameter of alumina, respectively. The images denoted with (i), (ii) and (iii) represent the surface morphology, cross-sectional view and high magnification of the bottom area, respectively. As shown in Fig. 10 (a) (ii), (b) (ii) and (c) (ii), the samples with alumina size of 0.8 μm exhibited a rather smooth curved melted groove compared to those of 1.6 and 3.4 μm which exhibited a melted V-shaped groove. With bigger particle size of 1.6 and 3.4 μm , the surface area available for CR distribution was smaller and therefore higher amount of CR adsorbed on the alumina's surface resulted in higher laser adsorption upon

Fig. 7 UV-Vis-NIR spectra of 1.0 and 1.5 wt% CR- Al_2O_3 (alumina diameter: 0.8 μm) heat-treated at 800°C.

Fig. 8 SEM images of the pellets prepared by heat-treatment at 800°C using CR- Al_2O_3 with different CR volume fractions of (a) 1.0 and (b) 1.5 wt% after laser irradiation. Images denoted with (i), (ii) and (iii) represent the surface morphology, cross-sectional view and high magnification of the bottom area (highlighted with dotted lines), respectively.

Fig. 9 UV-Vis-NIR spectra of 1.5 wt% CR- Al_2O_3 using different alumina diameter of 0.8, 1.6 and 3.4 μm after heat treatment at 800°C.

Fig. 10 SEM images of the pellets prepared using 1.5 wt% CR- Al_2O_3 with different alumina particle sizes of (a) 0.8, (b) 1.6 and (c) 3.4 μm after laser irradiation. Images denoted with (i), (ii) and (iii) represent the surface morphology, cross-sectional view and high magnification of the bottom area (highlighted with dotted lines), respectively.

irradiation causing volatile heat scattering effect (Fig. 9). From the surface morphological observation, higher amount of ball-shaped sintered particles are observed for the sample fabricated using 3.4 μm alumina (Fig. 10 (c) (i)) compared to those of 1.6 μm (Fig. 10 (b) (i)). The sample with alumina size of 0.8 μm exhibited the best melted morphology demonstrating smooth interface owing to its higher total surface area that allowed better distribution of CR on its surface. The more homogeneous CR distribution would then promote better heat transfer and distribution during laser irradiation. The area between the molding resin and the black-dotted line represent the HAZ in the images denoted with (ii) and (iii).

4 Conclusion

In this study, CR- Al_2O_3 composite particles that exhibited laser adsorption characteristic were fabricated by heat treatment of electrostatically adsorbed CellNF on alumina. The conversion of CellNF- Al_2O_3 composite to CR- Al_2O_3 composite was confirmed using Raman and UV-Vis-NIR indicating the presence of CR and good adsorption at the laser wavelength region of 900–1000 nm (laser wavelength: 915 nm). The CR- Al_2O_3 composite particles were then pressed into pellet form and used for selective laser sintering test. From the systematic study carried out in this work, sample that consisted of 1.5 wt% CR- Al_2O_3 heat-treated at 800°C with alumina size of 0.8 μm exhibited the optimum melted structure owing the higher surface area of alumina which allowed better CR distribution and coverage on alumina surface that improved the laser absorption as well as heat transfer upon irradiation.

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