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Effect of nanopowder ratio in bimodal powder mixture on powder injection molding

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ABSTRACT

One of the significant advantages of nanopowder is activated sintering and better surface finish of the final components. However, because of its drawbacks like higher cost and low formability, the mixture of nano and micro powder emerged as an effective solution. In this research, effects of nanopowder in nano/micro bimodal feedstock were studied. Bimodal powder in feedstock was prepared with nano and micro sized powders. These powders were mixed with different nanopowder volume ratio from 0 to 50%. The effects of nanopowder vol.% on the critical solids loading was investigated with rheometer experiments. From debinding behavior, apparent debinding activation energy for each feedstock was determined. Sintering behavior of micro and bimodal feedstocks were analyzed by dilatometer and compared with die compacted specimen. Nanopowder effect on sintered density and hardness of the samples were verified as well.

1. Introduction

Powder injection molding (PIM) is an advanced manufacturing technology for the production of complex, high volume net-shape components with the high production rate [1–2]. This technology combines advantages of plastic injection molding and conventional powder metallurgy [3]. PIM process consists of 4 steps; mixing, injection molding, debinding and sintering. In the mixing step, polymers with powder form a feedstock, and it is molded into a mold cavity. After shaping, the polymeric binder system is extracted by solvent or thermal heat, the product is sintered, often to near-theoretical densities [3–5].

Nanopowder has been introduced in PIM process for fabrication of micro sized components [6]. It is known that nanopowder shows more isotropic sintering behavior and its sintered body has the finer surface roughness than micro powder sintered body [7]. Low sintering temperature due to its low activation energy is also one of the representative advantages of nanopowder [6–8]. However, since nanopowder has large surface area because of its small size, it easily agglomerates and has high interparticle friction. As a result, nanopowder shows low packing density, low solids loading and high feedstock viscosity [6,9–10]. Low packing density and solids loading can induce a high shrinkage rate followed by shape distortion and difficult dimensional control. High feedstock viscosity also makes injection molding become difficult. Its high price is also the problem has to be solved for applying nanopowder in PIM process. These problems can be overcome by using nano/micro bimodal powder, which is the mixture of two different sized powders.

M. E. Sotomayor et al. [11] investigated bimodal effect on feedstock. They analyzed the change of the critical solids loading and the viscosity of each feedstock while small powder ratio increased from 0 to 100%. They showed higher small powder ratio decreased the critical solids loading and increased the feedstock viscosity. However, the smaller powder they used in the study was micro sized powder rather than nanopowder, and particle size ratio was just about 2 that was too small value to show bimodal effect [12]. B. N. Mukund et al. [13] also used the micro sized bimodal powder. They investigated the critical solids loading for various bimodal feedstocks, and the conditions for minimizing powder-binder separation and distortions. K. H. Kate et al. [14] studied the effect of AIN bimodal powder on injection molding. They used 18 wt.% nanopowder in bimodal powder and found that nanopowder increased the density, freeze time and required injection pressure. J. P. Choi et al. [15–16] showed 25 vol.% nanopowder improved sintered density, and explained this phenomenon by analyzing the microstructures of samples. V. P. Onbattuvelli et al. [17] reported the existence of optimal nanopowder ratio in bimodal feedstock for achieving the maximum solids loading with AIN and SiC powder. They conducted rheological study as well and concluded that bimodal feedstock had lower viscosity than monomodal feedstock. M. Müller et al. [18] showed small amount of nanopowder in bimodal feedstock led to reduction of the shear viscosity, but the critical solids loading was the same as the value of sub-micro sized powder. J. Rajabi et al. [19] studied the effects of nanopowder weight ratio in bimodal feedstock on mechanical and

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physical properties. W. K. You et al. [20] investigated low temperature-pressure powder injection molding with 25 vol.% nanopowder. Although they did not used backbone polymer, the nanopowder provided sufficient strength during process. Those studies investigated nanopowder effect in bimodal feedstock, but they mainly focused on the properties of sintered body, and most of experiments dealt with small amount of nanopowder, which was less than 30%. The changes of debinding and sintering behavior by nanopowder ratio should be analyzed to understand nanopowder effect in bimodal feedstock and optimize PIM process with bimodal feedstock. In this study, the effect of nanopowder ratio from 0 to 50% in bimodal feedstock has been examined. Effects of volume percentage of nanopowder on solids loading, debinding and sintering behavior were verified.

2. Experiments

Commercial stainless steel 316L powders were used in this study. 4 μm powder was provided from ATMIX Corporation in Japan, and 100 nm powder was provided from nanotechnology in Korea. Bimodal powder was fabricated by mixing nano and micro powders as 25:75 and 50:50 volume ratios with tubular mixer (KMC, KMC-T21) for 40 min. The characteristic of each powder is summarized in Table 1. Particle size of micro and bimodal powders were measured by particle size analyzer (HORIBA, LA-960) in wet condition. The morphologies observed by scanning electron microscopy (JEOL, JSM-6390LV) are shown in Fig. 1. Both of the nano and micro powder had spherical shape, and in bimodal powders, the nanopowder was stuck to the surface of micro powder rather than filled the interparticle space of micro particles. For this reason, increase of packing density, which is the effect of bimodal powder, was not observed in the tap density. A wax-based binder system had been accepted due to a beneficial melting range and nontoxicity. The binder system consisting of paraffin wax (PW), polypropylene (PP), polyethylene (PE) and stearic acid (SA) was used to provide the flowability during injection molding. Table 2 summarizes the physical properties of each polymer in the binder system.

The solids loading has significant effect on rheological properties of feedstock. Its optimal value can be determined by considering the critical solids loading. The critical solids loading is defined as the ratio at which the powders are tightly packed and the binder fills all the voids between the particles [3]. In this study, the critical solids loading was measured with a torque rheometer (Thermo scientific, HAAKE PolyLab QC Lab Mixer). The powder and binders were mixed in a twin-screw mixing chamber at 150 °C with 150 rpm. The powder was added into the mixing chamber as an increment of 1 vol.% of solids loading and the mixing torque was recorded. The procedure was repeated until the stabilized mixing torque rapidly increased, which indicated an excess amount of powder in the mixture. The optimal solids loading was determined as 2 vol.% lower than the critical solids loading for the process flexibility.

Feedstock mixing process was carried out with a twin-screw extruder type mixer. The mixing temperature was 160 °C, and mixing speed was 30 rpm. The same mixing procedure had been performed 4 times to achieve homogeneous feedstocks. Capillary rheometer test was conducted for homogeneity evaluation. The viscosity of feedstocks was measured with capillary rheometer (Malvern, Capillary Rheometry Rosand RH7) under the constant shear rate of 1000 s^{-1} and 160 °C.

Table 1
Characteristic of each powder.

Powder		Micro	25:75	50:50
Nano power ratio (vol.%)		0	25	50
Particle size (μm)	D_{10}	2.10	0.48	0.14
	D_{50}	4.16	3.84	2.58
	D_{90}	7.64	7.56	5.95
Distribution slope parameter (S_w)		4.56	2.14	1.57
Pycnometer density (g/cm^3)		7.84	7.74	7.63

Thermogravimetric analysis (METTLER TOLEDO, TGA/DSC 1) was carried out to record the binder decomposition behavior. The experiment was performed with three different heating rates, 2, 5 and 10 °C/min, from 30 °C up to 600 °C in a hydrogen atmosphere. Based on the debinding behavior of feedstocks, the apparent debinding activation energies of each feedstock were calculated.

Cylindrical shaped green bodies were fabricated by an injection molding machine (Sodick, TR30EH). Dimension of these samples were 8 mm in diameter and 13 mm in height for dilatometric sintering. The feedstocks were injected at 160 °C under 40 MPa, and defect-free green parts were fabricated. The green bodies were debound with a furnace (Kejia, KJ-1600G) at two different isothermal temperatures, 250 °C and 450 °C. The condition of thermal debinding process was determined based on the thermal decomposition behavior of the binders in the feedstock. In order to prevent binder from remaining in brown body, thermal cycle was determined as more than 10 h. Continuously 3 different pre-sintering conditions were applied. Since nanopowder is sintered from lower temperature than micro powder, the bimodal feedstocks were pre-sintered at 700 °C whereas the micro feedstock was pre-sintered at 900 °C. Similar brown body density had been obtained by changing pre-sintering temperature and time to minimize the effect of different solids loading on sintering behavior. Fig. 2 depicts the debinding and pre-sintering thermal cycles.

Dilatometric sintering was carried out to analyze the densification behavior during sintering with a dilatometer (NETZSCH, DIL 402C). 3 different heating rates, 2, 5 and 10 °C/min, were applied from 600 °C to 1350 °C, and after 2 h of isothermal section, sintering process was finished. Fig. 3 shows the thermal cycle of sintering process. Both of debinding and sintering process were conducted in a hydrogen atmosphere.

After sintering, the density of each sample was measured with an archimedes densimeter (AND, GH-200D). For each condition, at least 5 measurements were performed and the average value was used. The contents of impurity element can be increased by large surface area of nanopowder. In order to investigate the contamination of specimens, the chemical composition of C, S, N and O in powders and sintered parts were analyzed by C/S analyzer (LECO, CS230) and N/O analyzer (LECO, TC-600). Vickers hardness measurements were also performed by a microhardness tester (Future-tech, FM-700) with 2 kgf and a dwell time of 15 s. The hardness reported in this paper was the average value of 7 measurements taken at random spots on the sample. The average grain size of the micro and bimodal sintered specimens was calculated by measuring the area of about 100 randomly selected grains. The samples were etched with the mixture of nitric acid, hydrochloric acid and methanol, and microstructures were observed with SEM.

3. Results and discussion

3.1. Feedstock preparation

The average mixing torque after stabilization is shown in Fig. 4. The torque increased as solids loading increased in the feedstock. The average torque rapidly increased at some points, and they were the critical solids loading of each feedstock. The critical solids loading was verified with density measurement. When the solids loading exceeds its critical value, the binder system fails to fill the interparticle space of powders. As a result, insufficient binder system leads to formation of voids and relatively low density [3,21]. Fig. 5 shows the density of feedstocks depending on the solids loading, and the result was well matched with the torque rheometer results. As nanopowder ratio increased in Fig. 4, the critical solids loading decreased whereas the mixing torque increased due to large specific surface area of nanopowder. Conventionally most feedstocks are formulated with slightly less powder than the critical solids loading value to provide more flowability during injection molding process [3]. In this study, the optimal solids loading was determined as 2 vol.% lower than the critical solids loading value. Feedstock