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Effect of nanoparticles in bimodal powder on physical and mechanical properties of powder injection molded parts

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ABSTRACT

This paper presents investigation of how nanoparticles in bimodal powder that contains both nanoparticles and microparticles affect the physical and mechanical properties of injection-molded parts. As the starting materials, a pure-micropowder, and three different nano/micro-bimodal powders were prepared and mixed with a wax-based binder system. Addition of nanoparticles slightly decreased the critical solids loading and the feedstock homogeneity, and significantly increased the flexural strength and strain of green bodies. Addition of nanoparticles increased the density, decreased the grain size and provided superior surface finish of the sintered samples, and thereby improved their mechanical properties. The Vickers hardness of the samples increased as the nanoparticles content increased. Tensile strength was also improved by addition of small amounts of nanoparticles. However, the large passivation area of the nanoparticles raised the oxide content in the bimodal powder samples and degraded the strength and elongation. As a result, tensile strength was the highest in the sample fabricated from the bimodal powder that contained 12% nanoparticles.

1. Introduction

Powder injection molding (PIM) is a specialized process to manufacture for complex three-dimensional structures with a high production rate (Sidambe et al., 2013; Sardarian et al., 2017). It consists of four steps: mixing, injection molding, debinding and sintering (German and Bose, 1997). PIM uses the injection molding technique for shaping, and therefore has much higher design flexibility than conventional powder metallurgy process (Fayyaz et al., 2014). It also has advantages of near net shaping with a tight tolerance (Zhang et al., 2016). Because of these merits, PIM technique is an appropriate process for micro-fabrication (Attia and Alcock, 2011).

In PIM, the particle size is an important factor because the mean particle size should be less than one-tenth of the minimum structure dimension (Rajabi et al., 2014). For this reason, nanopowder has been used in PIM for micro-fabrication. Use of nanopowder in PIM (nanoPIM) increases structural details and improves surface finish. NanoPIM also archives low sintering temperatures and improved mechanical properties with fine grains (Rajabi et al., 2012; Lee et al., 2016). However, the small particle size causes various complications in nanoPIM process. The large surface area of the powder decreases both powder content in feedstocks and feedstock homogeneity, which results in shrinkage related defects (Yu et al., 2009). The large surface area also increases the feedstock viscosity, and thereby hinders the injection molding process and may require increase in injection temperatures and pressures (Han et al., 2016). Decomposition temperature changes of binder systems and unique densification behaviors should also be considered (Oh et al., 2018, 2017b). Moreover, an increase of material cost is a critical limitation of nanopowder. Nano/micro-bimodal powder (nmBP) that contains both nanoparticles (NPs) and microparticles (MPs) is a solution to overcome these drawbacks of nanoPIM.

nmBP can be obtained by mixing NPs and MPs. nmBPs have the benefits of NPs, but its disadvantages are suppressed. Most previous researches on use of nmBPs in PIM process has focused on feedstock rheology and physical properties of sintered samples. Müller et al. (2005) developed low-pressure injection molding process with a nmBP. They found the nmBP produced relatively high solids loading and low feedstock viscosity compared with those of NPs and MPs. Similar results were reported by Onbattuvelli et al. (2013) and Nishiyabu et al. (2007). Especially, Nishiyabu et al. (2007) used Cu nmBP and stated nmBP had relatively low viscosity as a result of the roller bearing effect of the NPs. Oh et al. (2017a) investigated NPs effects on feedstock homogeneity

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and moldability. They showed NPs in nmBP feedstocks decreased the feedstock homogeneity, and small amounts of the NP addition could improve the feedstock moldability. Kate et al. (2013) also verified that a nmBP feedstock provided more desirable mold-filling behavior than a conventional MP feedstock with a simulation. Choi et al. (2014) and Oh et al. (2016) analyzed sintering behaviors of nmBP samples. They demonstrated that NPs in nmBPs increased the sintered density and suppressed grain growth. Mechanical properties of nmBP samples were studied by only a research group despite its importance. Rajabi et al. (2014) added NPs into a micropowder up to 30 wt. % and showed tensile strength and hardness of the sintered samples were improved as the NPs content increased. However, the density varied among the samples, so the comparison may be invalid. Due to the low sintering temperature, the density of some samples was < 90%, and only one sample showed density > 95%. The density of sintered parts profoundly affects their properties, so the mechanical properties must be properly compared with near-fully-dense samples.

In this study, properties of nano/micro-bimodal powder injection molded samples were investigated. To consider the influences of NPs in nmBP, three nmBPs were prepared. The PIM process for each powder was optimized to obtain sound samples. Thereafter, the effects if NP on physical and mechanical properties were analyzed.

2. Experiments

2.1. Material

316L stainless steel was used as the starting material; it is widely used in PIM. Commercially available 100-nm and 4-μm powders were provided from Nanotechnology in Korea and Atmix in Japan, respectively. The powders were blended using a tubular mixer (KMC, KMC-T21) for 40 min to formulate nmBPs. The prepared materials were micropowder and three nmBPs with NP contents of 12, 25 and 50 vol. %. These four powders were termed micropowder, 12:88, 25:75 and 50:50 nmBPs, respectively (Table 1). Particle-size distribution was measured by a particle size analyzer (HORIBA, LA-960) after ultrasonic treatment for 10 min, and tap density was measured using a tap density volumeter (Bettersize Instruments Ltd., BT-300). Pycnometer density was also measured using an automatic helium pycnometer (Micromeritics, Accupyc 1330). Morphology of the powders (Fig. 1) was observed using a scanning electron microscope (JEOL, JSM-6390LV) and FE-SEM (JEOL, JSM-7401 F). A wax-based binder system was used to fabricate feedstocks. The binder system was composed of 57.5 wt. % paraffin wax (PW), 25 wt. % polypropylene (PP), 15 wt. % polyethylene (PE) and 2.5 wt. % stearic acid (SA).

2.2. Powder injection molding process

The powder content in a feedstock has significant effects on the product quality (Attia and Alcock, 2011). Therefore, feedstocks should be formulated with the optimal solids loading; this value is generally determined based on the critical solids loading, which is defined as the condition in which particles are packed as tightly as possible without external pressure, and all space between the particles is filled with binder (German and Bose, 1997). When the solids loading in a feedstock exceeds the critical solids loading, the feedstock viscosity rapidly raises due to insufficient content of binders. Thus, the critical solids loading can be measured by observing the change in mixing torque as solids loading is increased. In the present work, the critical solids loading of each powder were measured using a torque rheometer (Thermo scientific, HAAKE PolyLab QC Lab Mixer). The powders and the binder system were mixed at 150 °C and 150 rpm, and the mixing torque was recorded at each solids loading. For process flexibility, the optimal solids loading was set as 2 vol. % lower value than the critical solids loading (German and Bose, 1997).

Table 1
Characteristics of micropowder and bimodal powders.

Powder		Micro	12:88	25:75	50:50
Nanoparticle content (vol. %)		0	12	25	50
Particle size distribution (μm)	D_{10}	2.10	1.55	0.48	0.14
	D_{50}	4.16	3.98	3.84	2.58
	D_{90}	7.64	7.60	7.56	5.95
Tap density (g/cm^3)		4.12	3.69	3.26	2.72
Pycnometer density (g/cm^3)		7.84	7.81	7.74	7.63

The optimal amounts of the powders were mixed with the binder system by a twin-screw extruder at 160 °C and 30 rpm. To obtain homogeneous feedstocks, the feedstock was mixed four times. Thereafter, the feedstock homogeneity was evaluated by measuring viscosity fluctuations using a capillary rheometer (Malvern, Capillary Rheometry Rosand RH7) at 160 °C and the shear rate of 50 s^{-1}.

Two types of green bodies were fabricated using an injection molding machine (Sodick, TR30EH). Rectangular samples (60 mm × 20 mm × 7 mm) were injected for a green body bending test. Dog-bone samples (Fig. 2) were fabricated for a tensile test; after sintering, the samples had cross-section of 2.5 mm × 3.3 mm and gauge length of 14 mm. All samples were injected at 160 °C and 25 MPa, and the resulting green bodies showed no visible defects.

During debinding, samples become vulnerable because the amount of backbone binders decreases and the porosity increases. Furthermore, the high internal pressure and thermal gradient during the process increase the possibility of defect formation (Páez-Pavón et al., 2016). NPs also increase the difficulty of the process by narrowing the interparticle spaces (Rajabi et al., 2012; Onbattuvelli et al., 2014). To minimize the defects in the samples, both solvent debinding and thermal debinding were used in the study. PW and SA in the green bodies were dissolved in 50 °C *n*-hexane, then the remaining PP and PE were thermally decomposed. To determine the process time for the solvent debinding, the dog-bone samples were immersed in the solvent for various times, and the content of the residual binders was measured using weight change after drying. The thermal debinding was performed in a tube furnace (Kejia, KJ-1600 G) in a hydrogen atmosphere. The heating cycle was determined by considering the thermal decomposition behavior of micropowder feedstock, analyzed using thermogravimetric analysis (METTLER TOLEDO, TGA/DSC 1). The test was conducted from 30 to 600 °C with a heating rate of 2 °C/min in a hydrogen atmosphere. As a result, two isothermal stages were set at 250 and 450 °C. Thereafter, the samples were pre-sintered at 900 °C to provide enough strength for handling. The diagram of the thermal debinding cycle is presented in Fig. 3.

All samples were sintered in a tube furnace (AJEON, AJ-SKT3) in a hydrogen atmosphere. The sintering was conducted at 1350 °C for 2 h with a heating rate of 5 °C/min and the cooling rate 10 °C/min (Fig. 4).

2.3. Characterization of samples

The mechanical property of the rectangular green samples was analyzed using a three-point bending test conducted on a universal testing machine (R&B, RB 302 ML) with testing rate = 0.33 mm/min. The density of the sintered samples was measured using an Archimedes densimeter (AND, GH-200D). The microstructure of the samples was observed by SEM after etching with a Marble's reagent, and the average grain size of each sample was measured. Surface profiles of the samples were examined using an alpha-step device (KLA-Tencor, Alpha-Step IQ). Mechanical property of the sintered dog-bone samples was measured with a tensile test using a universal testing machine (Instron, 8801); the samples were clamped and pulled at a strain rate of 10^{-3} s^{-1}. Vickers hardness was measured using a microhardness tester (Futuretech, FM-700) at 2 kgf with dwell time of 15 s. The samples were cut and polished with 3-μm diamond suspension, and the hardness was measured at random spots on the cross-section. The bending and tensile