Journal of Materials Processing Technology 209 (2009) 5785–5792

Contents lists available at ScienceDirect

Journal of Materials Processing Technology

journal homepage: www.elsevier.com/locate/jmatprotec

Preparation and selective laser sintering of nylon-12 coated metal powders and post processing

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ARTICLE INFO

Article history:
Received 20 October 2008
Received in revised form 20 May 2009
Accepted 18 June 2009

Keywords:
Selective laser sintering
Nylon-12
Metal powders
Dissolution–precipitation process

ABSTRACT

A dissolution–precipitation process was successfully developed to prepare nylon-12 coated carbon steel powders. The SEM and laser diffraction particle size analysis results show that the metal particles are well coated by nylon-12 resin; therefore, an effective method for preparing nylon-12 coated metal powders is provided. Green parts were formed from the coated powders by selective laser sintering (SLS) process, and when the nylon-12 content in the coated powder was 1.0 wt% and the applied laser energy density was 0.06 J/mm^2, the SLS green parts had sufficient strengths for features as small as 0.1 mm to be built and post-processed, and relatively high dimensional accuracy. The SLS green parts were post-processed by binder decomposition and epoxy resin infiltration, and the obtained epoxy-infiltrated parts have the dimensional errors in the X, Y and Z directions of -0.30, -0.32 and -0.25% respectively, and the bend strength, bend modulus, tensile strength and impact strength of 93.4 MPa, 14.7 GPa, 70.3 MPa and 12.4 MPa respectively.

1. Introduction

SLS is a powder-based rapid prototyping (RP) process, which directly forms solid components according to a three-dimensional CAD model by selective sintering of successive layers of powdered raw materials (Kumar, 2003). While the capability of SLS to produce functional objects directly from metals is still under development, indirect methods of producing functional objects from metals have been widely used. In an indirect method of SLS process, the laser is used to melt a polymer binder and produce a “green” part in which the metal particles are bound together by polymer–polymer bonds. The green part is usually porous, has low mechanical properties and need to be post-processed. This green part is processed in a high temperature furnace to remove the polymer binder, and then the binder-free part is sintered or further post-processed to form a nearly full density part with geometric precision that is comparable to that of the green part (Beaman et al., 1997).

At present, two methods have been used to add polymer binder to metal powders. One method is to mechanically mix polymer binder powders with metal powders. Liu et al. (2006, 2007) manufactured metal parts via the indirect SLS process, using admixtures of metal and epoxy resin powders. Epoxy resin contents in these admixtures were 4–5 wt% (about 24–29 vol%). Sercombe and Schaffer (2003, 2004) formed the green parts by laser sintering the blend of aluminium alloy and 4 wt% (10 vol%) copolymer polyamide 6–12 binder. In general, the mechanical mixing method has the advantage of simple process. However, Beaman et al. (1997) revealed that the mixed powders have obvious disadvantages of powder segregation during shipping and poor binder efficiency. The other method is to prepare polymer binder coated metal powders. Joel and Neal (2000) reported that coated powders are readily handled, conveniently shipped and may be stored for long periods of time without the separation of components encountered in mixed powders. More importantly, at the same binder content, the green strengths of coated powders are found to be much higher than those of mixed powders. Balasubramanian (1995) indicated that SLS green parts made from coated metal powders were found to yield higher strengths than those made from mixed powders at the same polymer content. Subramanian et al. (1995) revealed that the bend strengths of the spray-coated alumina powders are three to four times those of the mixed powders at the same binder volume fraction. Nowadays, the most commonly used coating technology is a spray drying process. The materials used in this process are a class of emulsified amorphous polymer binders, based on poly(methyl methacrylate) (PMMA), copolymers of MMA (methyl methacrylate) and BMA (butyl methacrylate) monomers, which have been developed at the University of Texas to permit the formation of metal parts by the indirect SLS process. In the spray drying process, polymer emulsion is first synthesized by emulsion polymerizaion, and then the binders are coated on to metal particles by spray drying a slurry of metal powders in the polymer emulsion. Agglomerated, porous particles are formed by this coating process, which

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doi:10.1016/j.jmatprotec.2009.06.010

Table 1
Properties of the nylon-12 resin according to its specification.

Property	Test method	Nylon-12
Melting temperature (°C)	ISO-1346	178
Melt Flow Index (g/10 min)	ISO-1133 230 °C × 2.16 kg	84
Density	ISO-1183	1.01
Tensile strength (MPa)	ISO-527	60
Charpy notched impact strength (kJ/m^2)	ISO-179	5

typically contain about 20 vol% polymer (Beaman et al., 1997). The PMMA-based binder coated powders has been successfully used to prepare metal and ceramics shapes by the indirect SLS process. For instance, Subramanian et al. (1995) formed alumina parts by the indirect SLS process from PMMA coated Al_2O_3 particles; Vail et al. (1996) developed a thermal of polymer degradation during selective laser sintering of PMMA or poly(MMA–BMA) coated ceramic powders; Balasubramanian (1995) prepared injection molds by the indirect SLS process from PMMA or poly(MMA–BMA) coated metal powders. However, the polymer binder contents in these coated powders are relatively high, which goes against accuracy of final parts, and Chua et al. (2004) pointed out that the spray drying technique to produce polymer coated powders gives rise to some problems such as a labor-intensive preparation process and high requirements for materials and equipment.

In this study, nylon-12 resin was used as a polymer binder, and a dissolution–precipitation process was developed to prepare nylon-12 coated carbon steel powders. In the dissolution–precipitation process, the metal powder was firstly dispersed in the nylon-12 solution by stirring intensively at about 160 °C. Then, the suspension liquid was cooled gradually and nylon-12 recrystallized to uniformly coat on the surfaces of the metal particles. Finally, when the solvent was recovered, nylon-12 coated metal powders were prepared. The green parts made from the coated powder with 1.0 wt% (about 7 vol%) nylon-12 have sufficient strength for features as small as 0.1 mm to be built and post-processed and relatively high dimensional accuracy. After the binder in the green parts was removed by a decomposition process, the binder-free parts were infiltrated with a high temperature resistance epoxy rein, and fully dense carbon steel/epoxy functional parts were manufactured.

2. Experimental

2.1. Materials

The nylon-12 pellets were obtained from Degussa Co. in Germany. The properties of the nylon-12 resin according to its specification are listed in Table 1. Selecting nylon-12 as the polymer binder for the indirect SLS process was largely governed by the previous works (e.g. Caulfield et al., 2007), which suggested that nylon-12 SLS parts have relatively high densities and strengths, and nylon-12 has good interfacial adhesion with metals. The carbon steel powder was provided by Powder Metallurgy Research Institute of Central South University, China, and its composition is given in Table 2. The metal powder was treated with dilute hydrochloric acid before use. The mixed solvent was comprised of 95 wt% ethanol, 4.5 wt% butanone, and 0.5 wt% distilled water. The phenolic epoxy resin (F-51) with the epoxy value of 0.51 mol/100 g and curing accelerator of 2,4,6-tris(dimethylaminomethyl) phenol (DMP-30) was obtained from Baling Petrochemical Company of China. The curing agent of nadic methyl anhydride (MNA) was purchased from Polynt S.p.A. of Italy.

2.2. Powder preparation

The procedure of the dissolution–precipitation process for preparing the nylon-12 coated carbon steel powder was as follows: add the nylon-12 pellets, mixed solvent (1:7 w/w) and carbon powder into a 10 L reactor; vacuum the reactor and add N_2 gas to protect the reactants from being oxidized; elevate the temperature to 145 °C to resolve the nylon-12 pellets thoroughly; stirring intensively, cool at a speed of 10 °C/h to 105 °C or so at which nylon-12 began to precipitate, keep the temperature until precipitation was complete and distill out the mixed solvent. The obtained precipitation materials underwent vacuum drying and ball milling, and the coated powder was then obtained. The nylon-12 coated carbon steel powders with nylon-12 contents of 0.6, 0.8, and 1.0 wt% were prepared, denoted as CP0.6, CP0.8 and CP1.0 respectively.

A mechanically mixed nylon-12/carbon steel powder with 0.8 wt% nylon-12 (denoted as MP0.8) was also prepared for comparison. The preparing procedure was as follows: prepare a neat nylon-12 powder by the dissolution–precipitation process; mix the carbon steel and neat nylon-12 powders, and ball-mill the admixture for 2 h.

2.3. Selective laser sintering process

The sintering experiments were carried out in an atmosphere of nitrogen gas using an HRPS-III SLS system made by Huazhong University of Science and Technology (HUST), P.R. China. The SLS system was equipped with a continuous wave CO_2 laser (wavelength = 10.6 μm), the power of which could be continuously adjusted from 0 to 50 W. Ho et al. (1999) has shown that one of the key processing parameters in the SLS process is the energy density (ω), which is defined as the relative applied laser energy per unit area and can be calculated by Eq. (1),

$$\omega = \frac{P}{H \times v} \tag{1}$$

where P is fill laser power, H is scan spacing, and v is laser beam speed. In this work, v was 2000 mm/s; H was 0.1 mm; P was in the range from 8 to 24 W. Therefore, ω was in the range from 0.04 to 0.12 J/mm^2. The part bed temperature was 165 °C and the powder layer thickness was 0.1 mm. All test specimens were fabricated using the scanning method that scans each successive layer in alternate, perpendicular directions. Therefore, a three-point bend specimen (80 mm × 10 mm × 4 mm) will have alternate layers of short scan vectors, 10 mm, and long scan vectors, 80 mm.

2.4. Post processing

The nylon-12 binder in the green parts formed via the SLS process was completely removed in H_2 atmosphere furnace. Then, the binder-free parts were infiltrated with a high temperature resistance epoxy resin, which was synthesized by well-mixing F-51, DMP-30 and MNA at the mass ratio of 100:0.5:90 at 80 °C. The infiltrating procedure was as follows. First, the temperature of the epoxy resin was elevated to 100 °C. Second, the binder-free parts were immersed in the epoxy resin for about 10 min and the resin infiltrated the parts through capillarity action. Finally, the epoxy-

Table 2
Percentage composition by weight of the carbon steel powder.

Main element	C	Si	Mn	P	S	Ni	Mo	Cr	Fe
Content (wt%)	0.23	0.22	1.35	0.017	0.012	0.02	0.01	0.05	Remained