Advanced Powder Technology xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

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

Original Research Paper

Segregation measurement of powder injection molding feedstock using thermogravimetric analysis, pycnometer density and differential scanning calorimetry techniques

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ARTICLE INFO

Article history:
Received 18 September 2014
Received in revised form 23 March 2015
Accepted 12 April 2015
Available online xxxx

Keywords:
Segregation
Powder injection molding (PIM)
Thermogravimetric analysis (TGA)
Pycnometer density
Differential scanning calorimetry (DSC)

ABSTRACT

In this study, three measurement techniques were experimentally compared to quantify the effects of segregation on powder injection molding feedstock. In a powder metallurgy process, particle or phase segregation generates a fluctuation of the particle distribution in powder–binder mixture from point-to-point. Such demixing occurs generally before or during the injection process and can lead to the formation of defects such as cracks, distortions or heterogeneous shrinkage of the sintered parts. Thermogravimetric analysis, pycnometer density and differential scanning calorimetry were used to measure respectively the mass loss after binder burnout, the density and the enthalpy of fusion on several feedstocks with different solid loadings. It was demonstrated that the variation in solid loading can be measured with a sensitivity of at least ±0.5 vol.% of powder using the TGA and PD techniques only. It was also shown that the thermogravimetric analysis and the pycnometer density results are independent of feedstock formulation and can be obtained without the use of a calibration curve. The thermogravimetric analysis and the pycnometer density measurement are complementary and well-adapted experimental methods to measure the effects of segregation on powder injection molded green components.

1. Introduction

Segregation of powder mixture or powder–binder mixture is a nonuniform distribution of powder particles by size, shape, density or quantity and is of practical importance in many industries using powder metallurgy such as automotive, biomedical, aerospace, and many others [1]. Shaping of powder metallurgy components could be done for example by compaction of a dry powder mixture or by injection of a powder–binder mixture (feedstock). In the compaction method, the dry powder mixture is poured into a die, compacted by the application of pressure and then sintered to obtain the required final properties. In the powder injection molding method (PIM), a polymeric binder is used as a temporary vehicle for transportation of metallic or ceramic powder into a mold cavity and as a media supporting the powder particles until the final processing debinding–sintering steps [1,2]. The segregation of particulate materials is a well-known and generally unwanted phenomenon that occurs during processing, transportation and handling of powder or feedstock mixture [3,4]. In powder metallurgy, the segregation occurs generally in two forms, (i) particle segregation refers to a demixing of a granular mixture in motion while (ii) phase segregation represents the separation of the binder from the powder.

Particle segregation of dry powder particles has been studied by die filling, shear blender, rotating blender, vibrated shaker, Hele Shaw cells and fluidized beds using measurement techniques such as optical techniques, particle image velocimetry, radioactive particle tracking and infrared or near-infrared spectroscopy [5–14]. It is well accepted that size and density are the two main factors responsible for particle segregation. When a dissimilar granular material is subjected to vibration or shear force, the larger (or lighter) particles rise to the top while the smaller (or denser) particles move to the bottom [3]. For a given volume of powder, this movement of particles leads to a change in particles size distribution from point-to-point.

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http://dx.doi.org/10.1016/j.apt.2015.04.005
0921-8831/

Phase segregation of PIM feedstock is generated by gravity, improper mixing method, high-speed variation and high-pressure gradient before or during the molding process [4,15,16]. Although the particles size distribution may stay unchanged after phase separation, this type of segregation leads to a change in volume fraction of powder from point-to-point in a feedstock. Regardless of the segregation process (segregation of particles and/or phase separation), fluctuation of the particle distribution in feedstock may lead to distortions, cracks, voids, warping and heterogeneous shrinkage of the sintered parts [1,2]. To evaluate the intensity of segregation from point-to-point on a component or from part-to-part on a batch of components, several methods are available including measurement of density, heat capacity, thermal conductivity, electrical conductivity, binder burnout, rheology or microscopic examination [17–25]. These methods involve a punctual measurement of volume fraction of powder (also called the solid loading) at different places on injected part. In general, the segregation tendency of feedstocks decreases as the solid loading increases.

Viscosity and density are widely used parameters to evaluate the impact of mixing and injection conditions on homogeneity and stability of the feedstock during its preparation and injection. Viscosity of the feedstock can be measured using a capillary or rotational rheometers. It was demonstrated that a decrease in the volume fraction of powder or an increase in the homogeneity of the feedstock, in the temperature or in the shear rate lead to a decrease in the viscosity [17–20,23,24]. Density of feedstock is obtained using a pycnometer and a balance. It was shown that variations in local apparent density in the molded components were attributed to segregation defects [20,21]. Supati et al. [20] demonstrated that the measurement of the density can be correlated with the solid loading for three feedstocks of 52, 54 and 57 vol.% of powder. Evaluation of degradation temperature of the binder, thermal stability of the feedstock and debinding rate are generally done using thermogravimetric analysis (TGA). These values are useful to optimize the thermal debinding procedure. In addition, measurement of the binder content of a feedstock was realized by evaluating the weight loss according to temperature during the binder burnout performed by TGA [17,18,26]. Chung et al. [17] performed TGA measurements to study the pyrolytic behavior and to determine the binder content of simple powder–binder mixtures. Cao et al. [18] used TGA measurements to reveal the phase segregation occurring after viscosity measurement and to compare qualitatively the homogeneity of different PIM feedstock. The variation of solid loading between the gate and the green part was demonstrated by Rhee et al. [26] using TGA measurements. Although TGA measurements are widely used to estimate the binder content, the sensitivity of this technique to quantify the variation of volume fraction of powder has not been clearly demonstrated. Melting temperature, recrystallization temperature, enthalpy of fusion and the heat capacity of the binder can be obtained using differential scanning calorimetry (DSC). These values are useful to determine the injection temperature, the maximum temperature of the mold, the minimum temperature of the barrel/tank and the thermal parameters needed for simulation of injection [17,18,22,24,26]. Chung et al. [17] demonstrated that the thermal behavior of the feedstock is affected by the volume fraction of powder and can be predicted from the heat capacities and weight fractions of the powder by using a simple rule of mixtures equation. On the other hand, the sensitivity of the DSC method for measuring the volume fraction of a powder–binder mixture has not been evaluated. The present work aims to compare the sensitivity of thermogravimetric analysis, pycnometer density and differential scanning calorimetry methods for measuring the solid volume fraction of feedstock.

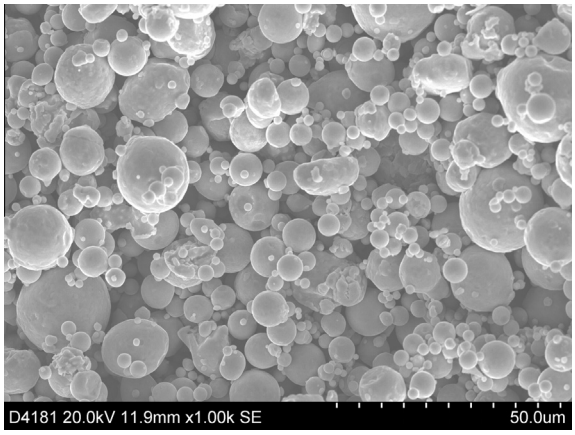

Fig. 1. SEM micrograph of Inconel 718 powder.

2. Experimental procedures

Thermogravimetric analysis, pycnometer and differential scanning calorimetry were used to measure (i) the mass loss after binder burnout (ii) the density and (iii) the enthalpy of fusion from several feedstocks with different powder proportions. For these three measurement techniques, each testing condition was repeated five times with different specimens. In the range of interest of 60–65 vol.% of powder, dots and error bars on Figs. 4–10 mark the average values and the variation of the measurements. Due to the small number of samples used for each solid loading, the variation around each average value was calculated by the confidence interval using a Student's t distribution with a confidence level of 95%. Assuming that no variation in solid loading has occurred during mixing of each calibrated feedstock, the confidence interval of each average value of the thermogravimetric analysis, the pycnometer density or the differential scanning calorimetry was used to quantify the sensitivity of each measurement technique. Sensitivity refers to the smallest variation of the solid loading that the instrument can measure. For a given measurement technique, the sensitivity could be evaluated by the highest value of the variation (i.e. confidence interval) measured in the range of interest of 60–65 vol.% of powder. However, in this study it was decided to define conservatively the smallest sensitivity at ±0.5 vol.% representing the half of the increments between each calibrated feedstock (i.e. 1.0 vol.% of powder). In other words, this value represents the highest acceptable variation of the measurement technique in order to differentiate two different calibrated feedstocks used in this work. Finally, thermogravimetric analysis was also used to evaluate the variation of solid loading throughout two different geometries of injected parts.

2.1. Materials, mixing and injection

Gas-atomized Inconel 718 superalloy powder (Osprey Sandvik, Neath, UK) with a typical spherical shape and an average particle size of 12 μm was used (Fig. 1). The binder was composed of paraffin wax (PW) as a main component to control fluidity, stearic acid (SA) as a surfactant and ethylene vinyl acetate (EVA) as a backbone component. These low melting point constituents are generally used in a low-pressure powder injection molding process [27]. The physical properties of the constituents are given in Table 1. The melting point, enthalpy of fusion and temperature of degradation of binders were determined using a differential scanning calorimetry and thermogravimetric analysis while the density of all components were measured with a gas pycnometer. The binder was mixed with the metallic powder to form several mixtures of

Please cite this article in press as: V. Demers et al., Segregation measurement of powder injection molding feedstock using thermogravimetric analysis, pycnometer density and differential scanning calorimetry techniques, Advanced Powder Technology (2015), http://dx.doi.org/10.1016/j.apt.2015.04.005