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Investigation of the powder loading of gas-atomized Ti6Al4V powder using an 'in-house' binder for metal injection moulding

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Powder loading is one of the most critical factors in metal injection moulding (MIM) technology. It largely determines the success or failure of the subsequent MIM processes. A gas-atomized Ti6Al4V powder was investigated to determine an optimum powder loading. Five different kinds of powder loadings – 55, 60, 65, 68 and 70 vol.% – were selected based on tap density calculations. Feedstocks were prepared using a wax-based CSIR binder. Powder loading investigations were performed by means of rheological studies. All the feedstocks followed a pseudo-plastic behaviour, flow index behaviour $n < 1$. A 65 vol.% powder loading demonstrated the best rheological properties i.e. smallest flow index behaviour (n) and moderate activation energy (E).

Keywords: Metal injection moulding, MIM, powder loading, tap density, feedstock, pseudo-plasticity, rheology.

Introduction

Powder injection moulding (PIM) is an advanced technology for processing metal and ceramic powders and forming desired shapes at a relatively low processing cost (Zaky, Soliman, and Farag, 2009). This technique was previously restricted to polymers (called plastic injection moulding) to produce small (normally less than 400 g) complex-shaped parts in a cost-effective manner. However, these parts had limited applications due to loss of strength at elevated temperatures. By adding and increasing the metal/ceramic particulate content in a predetermined quantity of a polymeric material, PIM evolved into a process for the production of high-density metal, intermetallic, or ceramic components (Aggarwal *et al*., 2007). PIM is referred to as metal injection moulding (MIM) when the particles are metallic (Loh, Tor, and Khor, 2001). MIM consists of the following steps: feedstock preparation (mixing), pelletizing and injection moulding, debinding, and sintering. However, understanding the powder and the binder characteristics prior to feedstock preparation is important. The choice of the binder is important as it must facilitate the injection moulding and the debinding processes (Ahn *et al*., 2009). A typical MIM process is shown in Figure 1. The different steps for a system based on thermoplastic binders are as follows:

- **Feedstock preparation.** Metallic powder and binder are mixed thoroughly during this stage. The intention is to obtain a homogeneous feedstock which provides the necessary rheological properties for injection moulding. The powder-binder mix is heated to the melting temperature of the binder and then continuously mixed until a homogeneous mixture is attained. MIM feedstock should represent a balanced mixture of powder and binder for it to flow well. It is safer to prepare a feedstock of powder loading 2-5 vol.% below the critical loading to improve the flow properties (e.g. viscosity) of the feedstock. As the solid content approaches the critical loading, a dramatic increase in viscosity is observed. At and beyond the critical loading the feedstock cannot flow (Moballegh, Morshedian, and Esfandeh, 2005; German, and Bose, 1997).
- **Pelletizing and injection moulding.** The feedstock is allowed to cool after mixing and then granulated to form pellets. Rheological studies can be performed at this point. Now the feedstock is ready to be melted in an extruder and then injected into a mould cavity to form a green part with a desired shape (Moballegh, Morshedian, and Esfandeh, 2005).
- **Debinding.** Here the binder is removed from the green body to obtain a brown body. This is known to be a critical stage in obtaining a brown compact with a desired strength prior sintering. After the binder removal, the brown body becomes very fragile and the metallic particles are held together by weak Van der Waals' forces (Adames, 2007).
- **Sintering.** The brown body is sintered to a density of at least 97% of the theoretical density and a linear shrinkage that can go up to 10-20% (Moballegh, Morshedian, and Esfandeh, 2005).

Titanium and its alloys have a low density, relatively high strength, excellent corrosion resistance in many media, and are known to be biocompatible. This combination of properties makes titanium and its alloys an excellent choice for applications such as watch parts, medical devices/implants and dental components, and sports goods. These parts can be made with powder metallurgy processes such as MIM. In MIM the powder loading, i.e. the ratio of the powder to the binder, largely determines the success or failure of the subsequent processes. It is important that the powder loading in this technology is well studied and understood. The whole idea behind powder loading studies is to maximize powder loading in MIM feedstocks for good injection moulding and shape retention, good dimensional control, and minimum shrinkage of the final components. The problem that is usually encountered in MIM feedstocks of lower powder loading is dimensional variability i.e. dimensional control as the component shrinks during debinding and sintering.

This paper focuses on the investigations of the powder loading of spherical Ti6Al4V using an 'in-house' CSIR binder. Some of the experimental results are summarized.

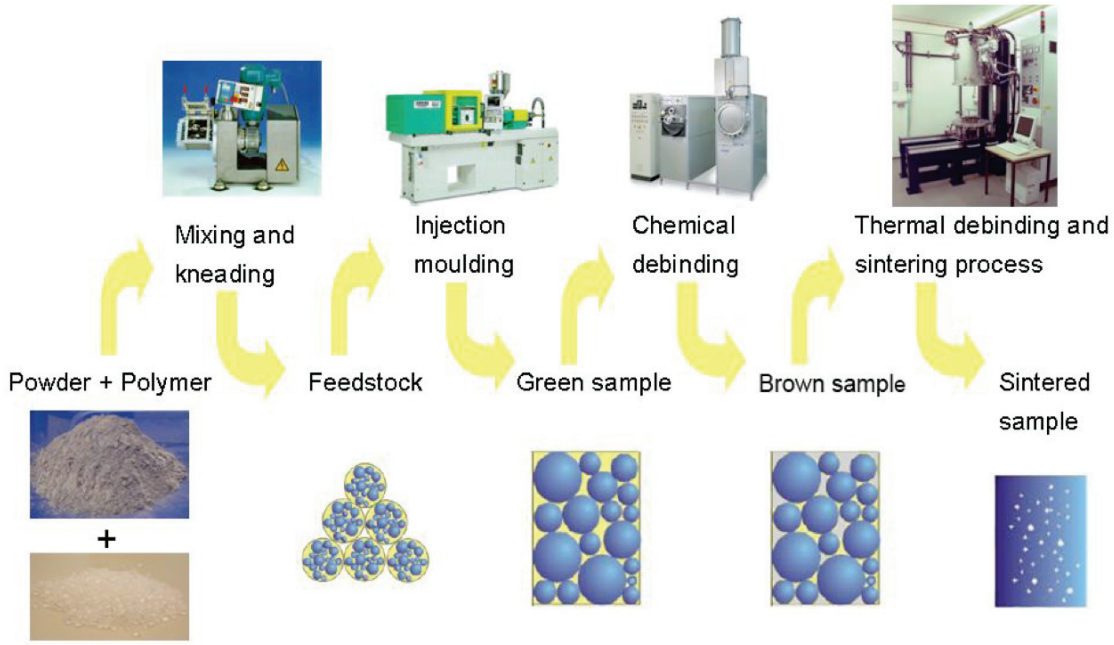

Figure 1. Metal injection moulding process (Loh, Tor, and Khor, 2001)

Experimental

Materials

Gas-atomized (GA) Ti6Al4V supplied by TLS Technik, Germany, was used. The powder characteristics and morphology are shown in Table I and Figure 2 respectively. The binder used in this study consisted of 60 vol.% paraffin wax (PW) and 40 vol.% low-density polyethylene (LDPE). PW acts as a backbone to the powder-binder mixture and provides wettability around the metal particles, thus decreasing the viscosity of the mixture. LDPE acts as a strengthening agent in the wax matrix. The polymers for the binder were supplied by Sasol, South Africa.

Table I. Characteristics of Ti6Al4V powder

Powder type	***Size distribution (μm)**	***D_{50} (μm)**	**Theoretical density (g/cm^3)**	**Oxygen content (wt %)**	**Shape**
Ti6Al4V	-25+6	13.42	4.43	0.22	Spherical

* -25+6 denotes a distribution of particle sizes less than (-) 25 μm but greater than (+) 6 μm
* D_{50} is the mean particle size (mean diameter) of the given particle size distribution

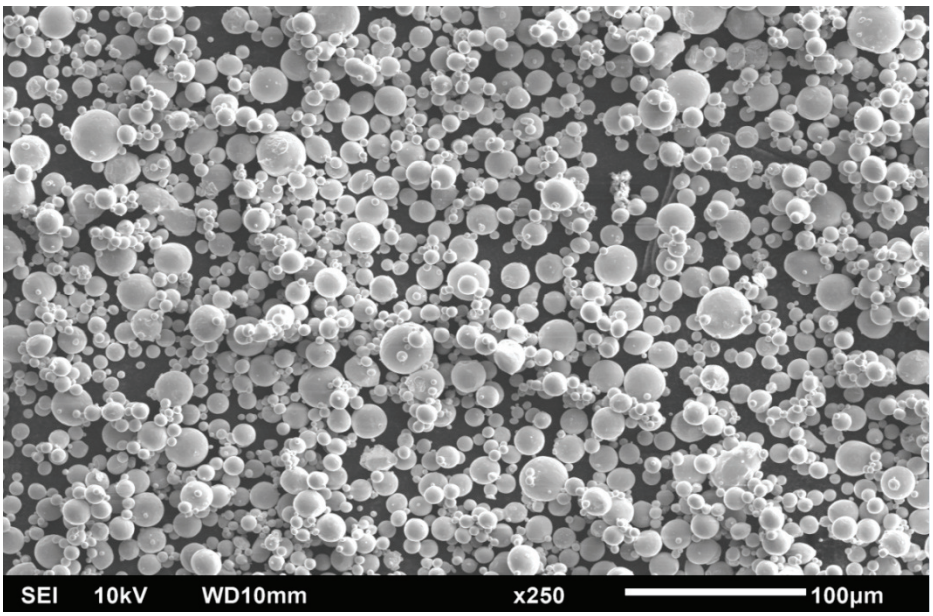

Figure 2. SEM photomicrograph showing the spherical morphology and particle size of the Ti6Al4V powder

Experimental procedure

Tap density determination

The maximum possible packing of the spherical particles was estimated using the tap density method. Previous studies indicated that a critical loading of 72 vol.% of Ti6Al4V can be achieved depending on the particle size distribution and shape (Guo *et al*, 2006). Based on tap density calculations, five different kinds of feedstocks – A, B, C, D, and E, with powder loadings of 55, 60, 65, 68, and 70 vol.% respectively were selected for this study.

Feedstock preparation

The feedstocks were prepared using a Z-blade shear mixer (4223, Jones Industrial mixer). In preparing each feedstock, the LDPE was first melted in the Z-blade mixer at 175°C and a fraction of the powder was added to break up the dense melt of LDPE. The temperature was reduced to 150°C and the paraffin wax (PW) was added together with the remaining powder. The materials were allowed to mix for 2 hours. The feedstock was allowed to cool after mixing and was granulated for rheology investigations.

Rheology

Rheological behaviour of the feedstocks was studied using a capillary rheometer (Smart RHEO, maximum piston force = 20 kN, piston model: 8.09 PT, capillary disc of L/D = 5) at temperatures varying from 110-130 °C. The piston speed was varying from 1-10 mm/s. The rheological studies were done to investigate the pseudo-plasticity of the feedstocks. Homogeneity and stability behaviours were investigated, using the same capillary rheometer, at a fixed piston speed of 3 mm/s.

Results and discussion

Influence of powder loading on the rheological properties of the feedstock

Tap density calculations estimated the critical powder loading (Φ_{max}) to be 0.604 by volume and the maximum pore fraction (ε) to be 0.396 (Table II). Guo *et al.* (2006) have proposed that the critical powder loading of Ti6Al4V must be around 72 vol.% for irregular Ti6Al4V (-45+25 microns) and spherical Ti6Al4V (-45 microns). Some feedstocks, in this work, were prepared with their powder loadings exceeding the critical powder loading estimated from tap density measurement. This was done because the calculated critical powder loading was relatively low, which was probably due to particle agglomeration (fine particles agglomerate easily). The selection of a well-balanced mixture of the powder and binder is a very critical stage in MIM. Hence, the feedstock rheological properties are critical in this study since

they reveal the flowability and homogeneity of the feedstock (Li, Li, and Khalil, 2007). A MIM feedstock showing pseudo-plastic (shear thinning) flow behaviour is defined by Equation [1] (Huang, Liang, and Qu, 2003):

$$\tau = k\dot{\gamma}^n \quad [1]$$

where τ is the shear stress (in Pa), $\dot{\gamma}$ is the shear rate (in 1/s), n is the flow behaviour index, and k is a constant. For a Newtonian fluid $n = 1$ and $k = \eta$ where η is the viscosity of the fluid in Pa.s, $n < 1$ indicates that the fluid is pseudo-plastic i.e. it indicates the degree of shear sensitivity thus the lower the value of n the more quickly the viscosity of feedstock changes with shear rate (Li, Li, and Khalil, 2007; Li, Huang, and Qu, 1999). A MIM feedstock is desired to follow pseudo-plastic behaviour. The most important rheological property for MIM feedstocks is viscosity, which is defined as follows (Huang, Liang, and Qu, 2003) :

$$\eta = \frac{\tau}{\dot{\gamma}} \quad [2]$$

In general, feedstock viscosity is a function of shear rate ($\dot{\gamma}$), temperature (T), powder loading (φ), and binder viscosity (η_b). Equations [1] and [2] can be manipulated to determine the shear rate dependence of viscosity as follows (Huang, Liang, and Qu, 2003):

$$\eta = k\dot{\gamma}^{n-1} \quad [3]$$

The influence of temperature on viscosity can be expressed by the Arrhenius equation as follows:

$$\eta(T) = \eta_0 \exp(\tfrac{E}{RT}) \quad [4]$$

where E is the flow activation energy (in J mol^{-1}), T is the temperature (in K), R is the gas constant (in J K^{-1} mol^{-1}), and η_0 is the viscosity at the reference temperature. The value of E indicates the sensitivity of viscosity to temperature i.e. if E is low, the viscosity of the feedstock is not too sensitive to temperature change and *vice versa* (Li, Huang, and Qu, 1999). The evaluation of the feedstock rheological properties is based on the sensitivity of viscosity to shear rate and temperature. The test shear rates and temperatures were very high for feedstocks A and B, which failed the tests; hence these materials were excluded from further test work. By plotting the logarithm of shear stress against the logarithm of shear rate (Figure 3) at a temperature of 120 °C, the n values (flow behaviour indexes) can be determined for each feedstock. Table III shows the n values of the three remaining feedstocks. It is seen that all the feedstocks follow a pseudo-plastic behaviour ($n < 1$). Feedstock C has the smallest flow behaviour index as compared to feedstocks D and E (Table III). It can be deduced that feedstock C's viscosity is more sensitive to increasing shear rates. The sensitivity of viscosity to shear rate is also shown in Figure 4.

Table II. Tap density of Ti6Al4V of a given PSD, ρ_{real} = 4.43 g/cm^3

*Trial #	Measured volume (cm^3)	Mass (g)	Compact volume	Tap density (g/cm^3)	Φ_{max}	ε
1	36.0	95.6	21.5	2.66	0.599	0.400
2	34.5	92.4	20.8	2.68	0.604	0.395
3	34.5	91.9	20.7	2.67	0.601	0.398
4	36.0	96.0	21.6	2.67	0.602	0.398
5	35.5	96.3	21.7	2.71	0.612	0.387
Average	**35.3**	**94.5**	**21.3**	**2.68**	**0.604**	**0.396**

* At least 300 taps per trial, compact volume = mass/ρ_{real}, tap density = mass/$V_{measured}$, $\Phi_{max} = V_{compact}/V_{measured}$, $\varepsilon = 1 - \Phi_{max}$

The flow activation energy (E) of the three feedstocks can be determined by plotting the natural logarithm of viscosity against the reciprocal of the temperature from Equation [4]. The slope of the curve is used to calculate E, where R = 8.3145 J K^{-1} mol^{-1} (Figure 5). Also the flow activation energies of the feedstocks are shown in Table III. As expected, $E_C > E_D$, E_E due to its high binder content, thus, the higher the binder content the faster the viscosity change

with increasing temperature. On the other hand $E_E > E_D$, according to (Li, Li, and Khalil (2007), this increase in flow activation energy at the higher powder loading may be due to the interaction between the metal's particles and the binder matrix, whereby a higher particle content weakens the sensitivity of the binder viscosity to temperature, thus, a wider temperature range is required for higher powder loadings.

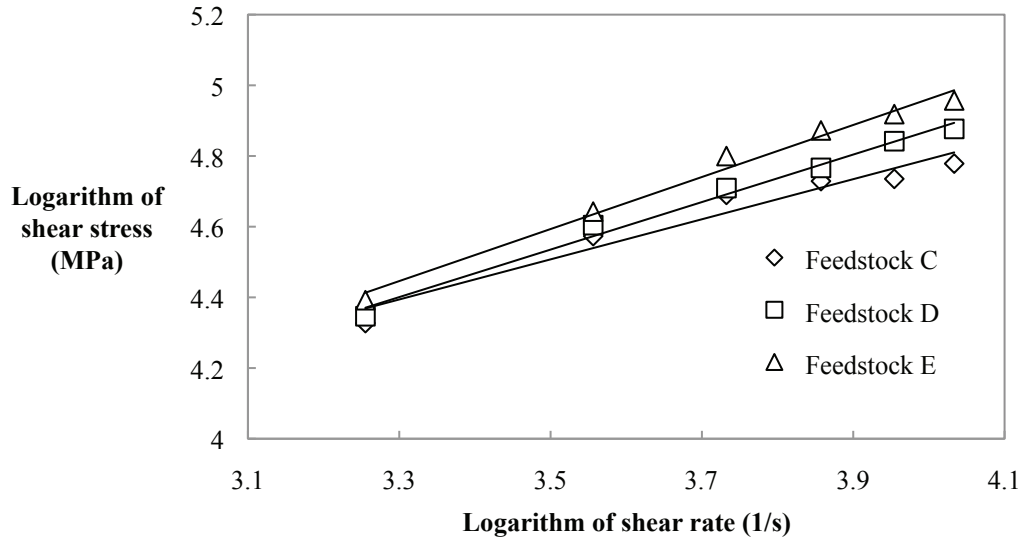

Figure 3. Variation of shear stress with shear rate for feedstocks C, D, and E at 120°C

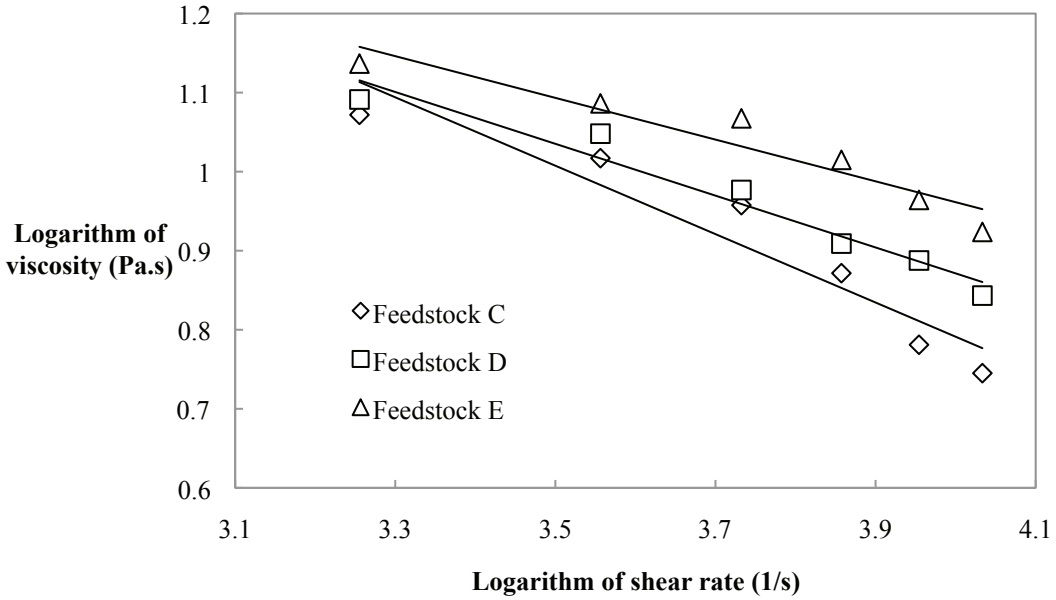

Figure 4. Variation of viscosity with shear rate for feedstocks C, D, and E at 120°C

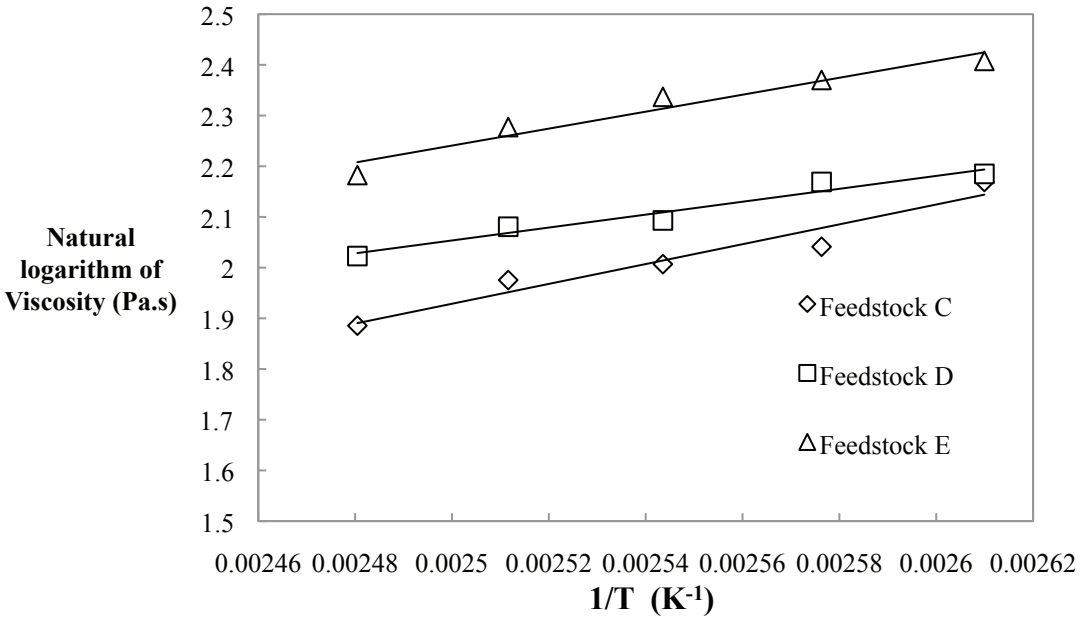

Figure 5. Variation of viscosity with temperature for feedstocks C, D, and E at 7200 s^{-1}

Table III. Flow behaviour indexes and flow activation energies of the feedstocks (shear rate = 7200 s^{-1})

Feedstock	*n*	*E* (kJ mol^{-1})
C	0.5673	16.27
D	0.6722	10.58
E	0.7361	13.90

Conclusion

Five feedstocks of different powder loading were studied using an 'in-house' wax-based CSIR binder. Rheological studies were conducted and discussed. Three feedstocks, C, D, and E, followed a pseudo-plastic behaviour; however, it was found that feedstock C gave desired rheological results in terms of *n* and *E* values. Therefore an optimum powder loading of 65 vol.% for spherical Ti6Al4V, with a size distribution of -25+6 microns, is viable for subsequent MIM processes.

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