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Analysis of rheological behaviour of titanium feedstocks formulated with a water-soluble binder system for powder injection moulding

G. Thavanayagam [a,*], K.L. Pickering [a], J.E. Swan [a], P. Cao [b,**]

[a] School of Engineering, University of Waikato, Hamilton 3240, New Zealand
[b] Department of Chemical and Materials Engineering, University of Auckland, Auckland 1142, New Zealand

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ABSTRACT

Binder selection and formulation are critical in powder injection moulding. Binders play a key role in controlling the rheological properties of a feedstock and influence whether the resulting feedstock can be successfully injection moulded, debound and sintered without defects. A four-step process was used to mix hydride-dehydride titanium alloy (processed) powder (Ti–6Al–4V) with a polyethylene glycol (PEG) based water soluble binder system. The rheological properties, including flow behaviour index, flow activation energy, fluidity and melt flow index of the homogeneous feedstock, were determined with a capillary rheometer. All feedstock formulations exhibited shear thinning flow behaviour. The optimum feedstock consisting of 60 vol.% powder content, 32 vol.% PEG, 6 vol.% polyvinyl butyryl and 2 vol.% stearic acid was suitable for titanium injection moulding.

1. Introduction

In spite of many unique properties such as high specific strengths and high resistance to corrosion, titanium alloys are restricted to high value products such as the aerospace and biomedical sectors where their high manufacturing costs can be fully justified. Powder injection moulding (PIM) offers a solution in reducing the cost and hence produces affordable titanium parts [1]. This innovative moulding technique is used to produce complex shaped components from feedstock of metal powders with thermosetting or thermoplastic binders, which provide the required fluidity for successful injection moulding [2].

Having a suitable binder system is a major factor in obtaining feedstock with good rheological properties and good mechanical properties in the final products. In general, a binder system is composed of at least three components: a backbone polymer that retains the shape of a moulded part during debinding and sintering, a low viscosity polymer that gives the feedstock suitable viscosity and which can be easily extracted during solvent debinding, and an additive that improves wettability of powder particles and binder [3]. A good binder system must have good flow characteristics, be comparatively low cost, have good interactions with metal powders, enable easy debinding, be easily disposed of, and be environmentally safe [4]. Binder removal in a multi-component binder system is carried out sequentially; otherwise the debound parts would collapse during debinding and sintering. In general, the low-melting-point polymer is removed either via solvent debinding or low temperature thermal debinding. Upon complete removal of most of the low-melting-point polymer, the high-melting-point polymer can still retain the shape and geometry of the moulded part. Also, the open pores formed during the first stage of debinding (either solvent debinding or low temperature thermal debinding) provide the extraction pathways for removing the backbone (i.e. high-melting-point polymer) [5]. The decomposition mechanisms of the polymers depend on the nature of the polymers used and the temperature or medium they are exposed to.

To produce a homogeneous feedstock for PIM, the powder and binder must be miscible and have desired rheological properties. Therefore, the appropriate mixing conditions need to be identified. A typical feedstock [6] was formulated using polyethylene glycol (PEG), high density polyethylene (HDPE), polyvinyl butyryl (PVB) and stearic acid (SA). These ingredients were kneaded for 5 min at 180 °C and then 10 min at 160 °C. In another report [7] the PIM feedstock was made by dry mixing both zirconia powder and a binder system made of PEG, PVB, HDPE, SA and an anti-oxidant in a Type R02 intensive mixer at room temperature for 15 min, then extruded using a twin-screw extruder at 150 °C–181 °C. The powder contents were in the range from 40 to 50 vol.% [7]. Although these authors claimed two extrusion passes were sufficient for feedstock homogeneity, there was no direct evidence supporting the homogeneity claim [7].

* Correspondence to: G. Thavanayagam, School of Engineering, University of Waikato, Private Bag 3123, Hamilton 3240, New Zealand. Tel: +64 22 6577024.
** Corresponding author. Tel.: +64 9 9236924; fax: +64 9 3737463.
E-mail addresses: vinthant@yahoo.com (G. Thavanayagam), klp@waikato.ac.nz (K.L. Pickering), jswan@waikato.ac.nz (J.E. Swan), p.cao@auckland.ac.nz (P. Cao).

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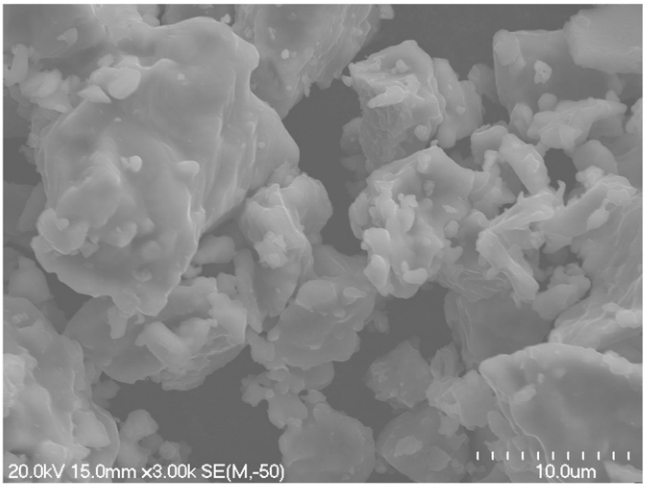

Fig. 1. Particle morphology of HDH Ti–6Al–4V.

While a substantial amount of research has only resulted in low and moderate powder contents, some research reports higher powder contents. For instance, Krauss et al. [8] obtained a homogeneous feedstock with 55 vol.% powder content and enhanced rheological properties by mixing alumina powder and a binder system made of PEG, PVB and SA in a sigma-type blade mixer for 30 min at 180 °C, followed by further mixing for 30 min at 160 °C. Weil et al. [9] obtained a 65% vol.% homogeneous feedstock for reactive metal based PIM by mixing Ti–6Al–4V powder with an aromatic-based binder system of naphthalene, ethylene vinyl acetate and stearic acid at 90 °C for an unspecified time in a Hake Record 90 mixer. Amin et al. [10] obtained a 64 vol.% homogeneous feedstock with good rheological properties by mixing stainless steel powder with a binder system made of PEG, polymethyl methacrylate (PMMA) and SA in a Z-blade type mixer for 30 min at room temperature followed by 60 min of mixing at 70 °C [10]. There have been other reports on formulating feedstock using different binders, various mixing conditions and powder contents. Recently, Wen et al. [11] published a comprehensive overview on the development of binder systems specifically used for titanium injection moulding.

A direct indicator of feedstock quality is its rheological properties. A feedstock with low viscosity, low activation energy and low flow behaviour index has better rheological properties for effective injection moulding [12]. During PIM, the temperature of a feedstock changes throughout the moulding process, starting from the feed section (medium temperature, 60 °C–100 °C), intermediate section (high temperature, 120 °C–200 °C) to the end mould (low temperature, 25 °C–50 °C). Viscosity can significantly change with temperature and is a critical factor in analysing rheological properties of a feedstock. Flow activation energy is widely used to analyse the temperature dependency of viscosity and depends on the composition of a binder and a feedstock [2]. A high flow activation energy indicates a strong effect of temperature on viscosity. Therefore, a small change in temperature during PIM may cause a significant change in feedstock viscosity.

Table 1
Feedstock formulations.

Feedstock no.	Powder content (vol.%)	PEG (vol.%)	PVB (vol.%)	SA (vol.%)	Binder ratio (vol.%) (PEG:PVB:SA)
F1	55	33.8	9.0	2.3	75:20:5
F2	60	30.0	8.0	2.0	75:20:5
F3	55	36.0	6.8	2.3	80:15:5
F4	60	32.0	6.0	2.0	80:15:5

In this research, feedstocks were formulated by mixing hydride-dehydride (HDH) titanium Ti–6Al–4V alloy powder with a PEG based water soluble binder system. The hydride-dehydride (HDH) process involves hydrogenating titanium sponge, crushing the TiH_2 and then dehydrogenating the TiH_2. In general, spherical gas-atomised Ti–6Al–4V powder is preferred for formulating titanium feedstock because this powder has higher purity and the preferred spherical particles. Unfortunately, such a powder with required small particle size is expensive and usually unavailable commercially. On the other hand, HDH Ti–6Al–4V powder is more affordable and commercially available with many options of particle sizes and purity levels.

2. Experimental procedures

2.1. Materials

Feedstocks of various compositions were prepared using HDH Ti–6Al–4V alloy powder and a water soluble binder system consisting of PEG, PVB and SA. The following materials were used for this research: HDH Ti–6Al–4V powder (Xi'an Baode Powder Metallurgy Co. Ltd., Xi'an, China), PEG with a molecular weight of 8000 g/mol and a melting point of 65 °C (Union Chemical Ltd, Albany, New Zealand), PVB with a molecular weight of 50,000 and a melting point of 185 °C (Sigma Aldrich, Australia), and SA with a molecular weight of 285 g/mol and a melting point of 74 °C (Sigma Aldrich, Australia). Scanning electron micrographs showed the HDH Ti–6Al–4V alloy powder had irregular shaped particles (Fig. 1). The average particle size (Fig. 2) was 70 μm.

2.2. Methods

2.2.1. Mixing and blending

The homogeneous feedstock was manufactured using four successive mixing stages. A mix of titanium alloy powder and binder

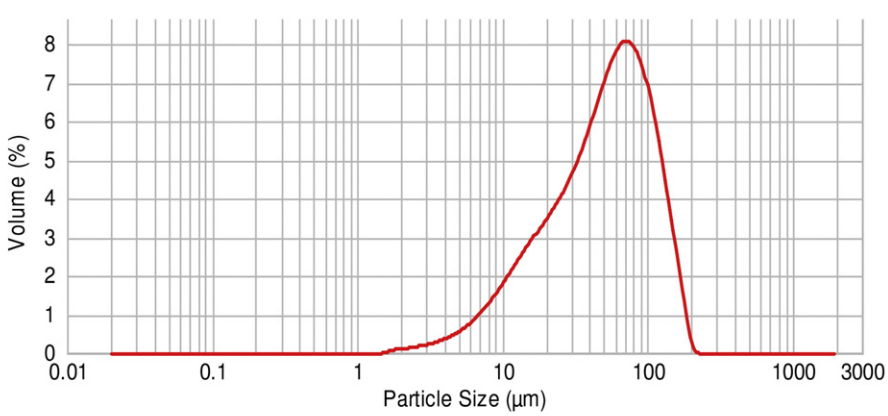

Fig. 2. Particle size distribution of HDH Ti–6Al–4V.