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Design of water debinding and dissolution stages of metal injection moulded porous Ti foam production

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ABSTRACT

Foams are advanced materials with controlled meso- and micro-structure, with huge potential in a variety of applications such as in the biomedical and automotive sectors. One promising technique for the production of Ti foams is Metal Injection Moulding in combination with Space Holders (MIMSH). Most existing work in the literature on MIM-SH foams reports very long debinding and dissolution periods that can extend for more than two days. In this paper, the effect on process speed of different water debinding and dissolution techniques of MIM-SH Ti foams will be investigated. Furthermore, the temperature influence on the debinding and dissolution behaviour of a PEG based binder and KCl space holder will be examined. In addition, some debound samples will be sintered in order to verify their suitability for the production of Ti foams. The results show that a heated ultrasonic bath is the fastest and most effective technique in removing the PEG and space holder, while increasing the temperature increased the removal rate up to a certain temperature (80 °C) where a significant swelling occurred, leading to a slower removal rate. The results make it possible for a more rapid production method to be designed systematically.

1. Introduction

Ti foams have gained a wide interest in a variety of applications in the last decade due to them offering a unique combination of properties, such as high strength to weight ratio, high permeability and excellent biocompatibility [1]. There are several techniques for the production of Ti foams with different pore sizes and shapes, many of which are based on powder metallurgy (e.g. [2]). One such method is Metal Injection Moulding (MIM) in combination with the space holder method. MIM itself offers several advantages as a production process, and there is ongoing development of new binder systems adapted to different materials [3–5]. For foams, this technique offers several advantages over other foaming techniques, such as the potential for high volume production and the ability to produce complex near net shapes without the need for subsequent grinding and machining, which can result in closure and contamination of the pores with wear debris [6]. The MIM-space holder technique involves mixing of the metal and space holder powders with a multi-component binder and moulding them into the desired shapes before debinding and sintering. One crucial step in the success of the process is choosing the right binder and debinding it in an effective and economical way. There are two main methods for debinding, namely: thermal debinding and solvent debinding. The former usually results in more contamination and needs to be done carefully and at a slow rate to avoid the formation of cracks and slumping of the samples [7]. The latter is usually carried out in either water or other solvents such as hexane. Hitherto, most of the reports on the production of Ti foams via MIM-space holder method used paraffin wax as a major binder constituent and organic solvent debinding for binder removal [8,9]. However, one significant problem is that the debinding and space holder removal processes can often take a very long time (up to 72 h) [10]. Another problem is that environmentally unfriendly organic solvents are used for paraffin wax debinding such as Chloroform [9] and hexane [8,10,11]. In this paper, the use of water soluble polymer, namely Poly ethylene glycol (PEG) as a main constituent in the binder and its debinding behaviour will be studied for the production of Ti foams by the MIM-space holder method. In addition, different water debinding and space holder dissolution techniques will be explored and a comparison will be made among those techniques. Furthermore, the effect of the temperature on the removal of the binder and space holder will be examined. This knowledge will allow the design of a more efficient process.

2. Experimental procedure

2.1. Starting materials

Commercially pure Ti grade 2 (Arcam AB, Sweden) powder with spherical particles was used in this study. The particle size distribution of the Ti powder was analysed via a Malvern Mastersizer 3000

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Table 1
Characteristics of starting materials.

Name	Dx (10)	Dx (50)	Dx (90)	Density, g/cm^3
Ti powder	52 μm	72.5 μm	102 μm	4.5371
KCl powder	188 μm	307 μm	476 μm	1.9866
PEG 1500	–	–	–	1.1300
PMMA	–	–	–	1.2060
Stearic acid	–	–	–	1.0075

using the wet dispersion method. Potassium chloride (Sigma-Aldrich, Steinheim, Germany) was used as a space holder and its particle size distribution was analysed using a Malvern Mastersizer 3000 with the dry analysis method. Table 1 summarises the size distribution and density of the powders used. The morphologies of both the Ti powder and KCl space holder are shown in Fig. 1A and B. The space holder was sieved through a 500 micron sieve. The binder consisted of PEG1500 (Sigma-Aldrich, Steinheim, Germany), Poly methyl methacrylate (PMMA, Sigma-Aldrich) and stearic acid with purity of ≥97% (Fluka, Sigma-Aldrich). The density of the powders and binder constituents were measured using an AccuPyc II 1340 Pycnometer, Micromeritics, USA.

KCl particles were cubic with a hopper-like shape in some cases. This shape usually results from a crystal growth mechanism where atoms add preferentially at the edges, leading to a faster growth at the edges compared to the centre. Ti particles, produced by gas atomisation, were approximately spherical in shape.

2.2. Feedstock preparation

The feedstock was prepared by mixing the Ti powder with the KCl space holder using a centrifugal Speedmixer 800 FZ (Hauschild; supplied by Synergy Devices Ltd., UK). Four cylindrically shaped dispersion media made of zirconia were added to mixture. Next, PMMA and stearic acid were added to the mixture and the mixing process continued according to the following mixing programme (See Table 2).

The mixing programme was chosen so that the heat generated from friction as the constituent mix was sufficient to melt the PMMA. It consists of 2 sets of increasing speeds, intended to build up the heat each time. PEG was added in the last three stages of the mixing programme in order to guarantee that the PMMA first gets melted and homogenised in the mixture before adding the PEG, as the latter has a low melting temperature in comparison with the former. It should be noted that the temperature of the mix cannot be directly measured in the equipment, so visual observation of molten state was used to determine when the temperature was sufficient. The total period of mixing, 16 min, is much shorter than that reported in the literature (e.g. over 1 h for the same binder components for MIM of stainless steel powder,

Table 2
Mixing programme of feedstock.

Mixing speed (rpm)	1300	1600	1800	1400	1600	1800
Time (min)	4	4	2	2	2	2

with a blade mixer at a speed of 30 rpm and a temperature of 70 °C [12]) due to the effectiveness of the high speed centrifugal mixer with the dispersion media in mixing and homogenising the powders and polymers. The mixture was then pelleted by extruding it twice through a plunger type injection moulder at 150 °C and cutting it into small pellets. The pellets were then allowed to cool for 5 min before carrying out any subsequent processing. The volume percentage of the solid part was equal to 55% of which 50% was space holder and 50% was Ti, while the volume percentage of the binder was equal to 45% of which 65% PEG, 30% PMMA and 5% stearic acid.

2.3. Differential scanning calorimetry (DSC) and thermogravimetric (TG) analyses of the binder

These analyses were performed in order to find out the melting and decomposition behaviour of the binder and according to which the injection temperature and debinding temperature were set. The DSC analysis of the binder and its constituents was performed using a DSC 6, Perkin Elmer, USA. The thermogravimetric analysis was carried out under argon atmosphere using a Pyris 1 TGA instrument, Perkin Elmer, USA.

2.4. Rheological characteristics of the feedstock

The viscosity of the feedstock was measured using a twin bore barrel capillary rheometer (Rosand RH2000, Malvern, UK). The test was carried out at 150 °C and at a shear rate in range of 900 to 5000 s^{-1} using a tungsten carbide die. The die had a diameter of approximately 2 mm and a length of 16 mm. Rabinowitsch correction was applied to the results in order to get absolute viscosity readings by correcting the shear rate value and obtaining the true shear rate as the flow of the feedstock is pseudoplastic (non-Newtonian) [13]. The flow behaviour index was calculated using the following power law equation [14]:

$$\eta = K\dot{\gamma}^{n-1} \tag{1}$$

where η is the viscosity, K is a constant, $\dot{\gamma}$ is the shear rate and n is the flow behaviour index, which is equal to 1 for Newtonian fluids and less than 1 for pseudoplastic fluids.

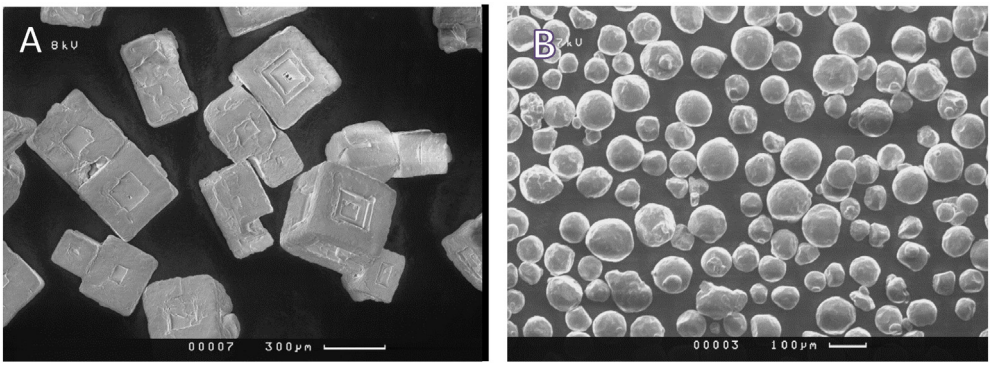

Fig. 1. A. KCl powder, B. Ti powder.