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Preparation of feedstock containing water-soluble binder for powder injection moulding of silver

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Abstract

Feedstock for powder injection moulding of silver was prepared using water-soluble binder composed of polyethylene glycol (PEG) and polyvinyl butyrol (PVB). Silver powders with particle size in range of 1 μm to 20 μm can be mixed with PEG/PVB binder system to form feedstocks having powder loadings of 42 vol% and 45 vol%. PEG can be removed using water leaching method while PVB can be removed by thermal debinding. Specimens retained their shapes during debinding and after debinding. Components fabricated with relatively higher powder loading resulted in higher density with lower porosity. Density of specimens containing powder loading of 42 vol% and 45 vol% and heated at 700°C is about 43% and 46% of the theoretical value, respectively. Therefore, it can be further developed for porous materials applications.

1. Introduction

Silver is generally known as a precious metal which can be used in various applications such as jewelry, electronic parts, water purification and dental amalgams. Silver (Ag) is a soft and ductile materials which can be produced conventionally by powder metallurgy or investment casting (lost-wax technique) [1,2]. However, investment casting consists of many processing steps and this method produces several waste materials such as ceramic moulds during the production. Powder injection moulding (PIM) is a cost effective process that can produce near-net-shaped, small and complex-shaped components using the combination of particulate materials flexibility and of polymeric binder diversity [3,4]. The use of PIM for the fabrication of precious metal jewelry, watch cases and bracelet parts was earlier stated.[5,6]. PIM can also be used to produce both dense and porous materials in addition to macro and micro sized components depending on the specific requirement of each application [7,8].

PIM processing steps include feedstock preparation by mixing powder and binder, injection moulding to form components, debinding to remove binders from moulded specimens and sintering to densify parts and improve properties or to control porosity for specific applications. Binder selection and binder constituents is one of the important part in the PIM process. Many research work has been carried out with a variety of binder systems for the PIM of metallic, ceramic and composite materials. Some of them required organic solvents such as hexane or heptane for the removal of binder [9,10]. Due to environmental concerns and economic of process, water-soluble binder system is of interest for many researchers [11-13]. However, the research work of silver powder injection moulding using water-soluble binder was very limited.

For the research activities at Metallurgy and Materials Science Research Institute, Chulalongkorn University, polyethylene glycol (PEG), which is a water-soluble binder, together with polyvinyl butyral (PVB) that acts as backbone binder, has previously been used. The PEG/PVB composite binder was applied for injection moulding of a variety of powders to avoid the use of organic solvents. These include ceramic powders such as alumina, zirconia and alumina-zirconia composites [12,14,15] in addition to metal-ceramic composite materials such as stainless steel-tungsten carbide powder and tungsten carbide-nickel hardmetal powder [16,17]. The injection moulding of titanium alloys using the PEG/PVB binder system was also reported [13]. As metallic silver can be used in various applications especially for jewelry, a near-net-shape fabrication technique is necessary. Therefore, this work aimed to prepare feedstock using water-soluble binder consisting of PEG and PVB for powder injection moulding of silver and to investigate the processing parameters for successfully injection moulding of silver powder for certain applications such as biomedical and jewelry design.

2. Materials and method

The silver powder has theoretical density of 10.49 $g \cdot cm^{-3}$, obtained from Inframat, Advanced Materials. Polyethylene glycol (PEG, average molecular weight of 1500, 4000 and 6000) and polyvinyl butyral (PVB, average molecular weight of 80000) were purchased from Acros Organics, and used as received.

To select the appropriate binder materials, the thermal properties of all binder materials, PVB and PEG with various molecular weights, 1500, 4000 and 6000 were investigated using the differential scanning calorimetry (NETZSCH DSC 3500 Sirius). The polymeric binder samples were heated from 20°C to 180°C, with a temperature ramp of 10°C·min^{-1} and kept isothermal for 2 min. Then the samples were cooled down to 20°C with the temperature ramp of 10°C·min^{-1}. After that, the samples were again heated up to 200°C with the same heating rate at 10°C·min^{-1}. All measurements were performed under nitrogen atmosphere.

The feedstocks were prepared using the silver powder and a binder mixture of PEG (average molecular weight of 1500) and PVB (average molecular weight of 80000). The ratio between PEG and PVB was kept constant at 85:15 by weight. This PEG/PVB ratio was adapted from the previous works [14,15]. PEG provides appropriate feedstock viscosity that can flow into the mould cavity while PVB helps retain shape of components during and after water debinding. The feedstocks with 3 different powder loadings were prepared. As shown in Table 1, the powder to binder ratios were 42:58, 45:55 and 48:52 by volume, designated as S-42, S-45 and S-48, respectively. The obtained feedstocks were subjected to injection moulding using a plunger-typed, laboratory-scaled injection moulding machine at temperature of 190°C. The shape of mould is in a disc form with diameter of 20 mm and thickness of 1.8 mm.

The removal of PEG was investigated by leaching in water i.e. leaving the moulded specimens in still water at ambient temperature from 0.5 h to 6 h. The weight of specimens after 0.5, 1, 2, 4 and 6 h water immersion were measured and compared with the moulded specimens and also evaluated in the term of PEG removal percentage. The deviation of the measured PEG removal values were calculated from three different test pieces. The specimen's shape retention was also observed.

In addition, the thermal stability of the leached specimens was carried out using the NETZSCH TG 209 F3 thermogravimetric analyzer under a temperature range of 30°C to 900°C at a heating rate of 10°C·min^{-1} in oxygen and in argon atmosphere. The results presented in this work focused mainly for the characterization of binder and of the feedstocks. The preparation of feedstock, the injection moulding and binder removal were also investigated. The preliminary trial for thermal debinding and subsequent pyrolysis of the leached specimens was performed at 700°C in argon atmosphere. The density measurement of the specimens was carried out using Archimedes' method. The dimension stability of specimens was observed by measuring the shrinkage. For the future work, the sintering of silver components made by powder injection moulding will be systematically studied. The as-leached specimens were planned to be sintered at various sintering conditions and the sintered properties will be reported.

Table 1. Composition of feedstock for silver injection moulding.

Feedstock	Powder loading (vol%)	PEG (wt%)	PVB (wt%)
S-42	42	85	15
S-45	45	85	15
S-48	48	85	15

3. Results and discussion

3.1 Materials characteristic

Morphology of the silver powder is shown in Figure 1. It has irregular shape with some agglomeration. Size of silver powders were in range of 1 μm to 20 μm as estimated by SEM. The thermal properties of binder materials are presented in Figure 2. As expected, the glass transition temperature (Tg) of PVB is higher than those of the PEG, due to the higher molecular weight (80000). For PEG, the lower the molecular weight, the lower the Tg. For water soluble binders, in particular PEG, the depression of the Tg that corresponded to the smaller molecular weight, could indicate the ease of water solubility. Thus, the PEG with the molecular weight of 1500 were selected for feedstock preparation.

Although previous works that employed PEG/PVB binder system were successfully injected hardmetal feedstock of 52 vol% powder loading into the mould [17], the feedstocks of silver containing powder loading of only up to 42 vol% and 45 vol% (S-42 and S-45)

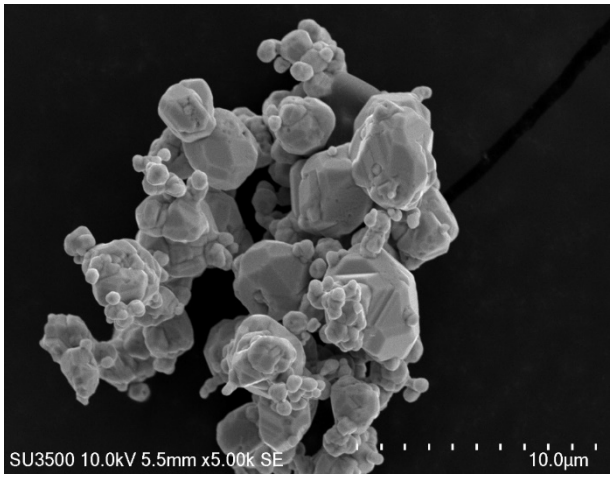

Figure 1. SEM micrograph of silver powder.

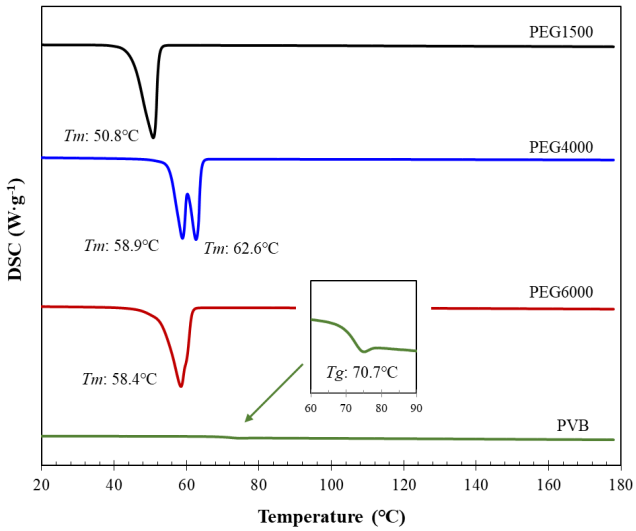

Figure 2. DSC thermogram of polyethylene glycol (PEG) and polyvinyl butyral (PVB).

Figure 3. Feedstock S-48 containing 48 vol% powder loading that could not be injected.

were able to be injected into the mould in this work. Feedstock S-48 that contained 48 vol% powder loading could not be injected into the mould. The appearance of the S-48 feedstock was shown in Figure 3. Feedstock was too dry and would not be possible to flow into the mould with desired shape. It has been reported that flow and deformation of the PIM feedstocks was considered to occur by a slip band mechanism which was in similar ways to those observed in clay and water system [18]. Hence, feedstock that was too dry would not be able to flow and then would not be suitable for injection moulding. It is generally known that the pseudoplastic behavior i.e. non-Newtonian shear-thinning, where viscosity decreased with increased shear rate, was a required rheology for powder injection moulding feedstock [4,19-21].

3.2 Binder removal

For the solvent debinding using water as a debinding medium, PEG was removed from the components in order to create open pore channels for the remaining PVB that could subsequently be removed by pyrolysis. The standard deviation of the PEG removal at each time interval was in small numbers at less than 3%, therefore they are not presented in the graph. The percentage of PEG removal by water leaching is shown in Figure 4.

The removal of PEG was fast at the initial stage because PEG can be removed from the surface where the mass transfer path between specimen and water is short and the concentration of the PEG is also high. However, the rate of PEG removal was relatively low at the longer time. This observation of high rate of PEG removal at initial stage is in agreement with other works previously reported elsewhere [12,14,17]. It was also reported that solvent debinding of the PEG at initial stage was a dissolution controlled mechanism and change to be a diffusion controlled mechanism at the later stage [13]. In addition, the surface area to volume ratio would also affected the PEG removal behaviour where the higher ratio, the faster binder removal. The shorter debinding time was normally required to reduce cost of manufacturing. The combination of solvent debinding and thermal debinding, therefore provided faster processing time when comparing with process that employed only thermal debinding method. Figure 5 shows silver components after PEG removal by water leaching. The silver components retained their shapes during and after water leaching and no crack was observed.

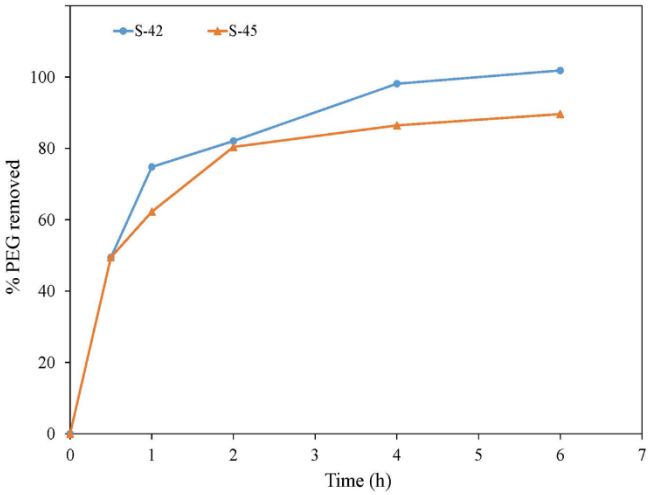

Figure 4. PEG removal of the silver mouldings by water immersion at various times.

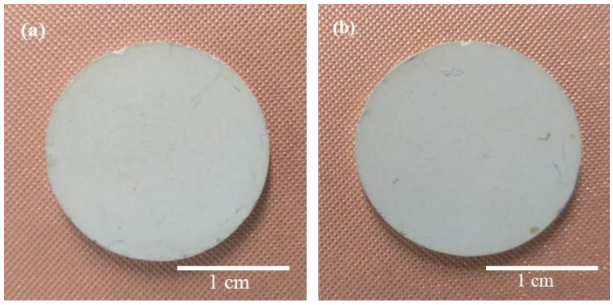

Figure 5. Silver injection moulded specimens (a) S-42 and (b) S-45 after water immersion.

3.3 Feedstock characteristic

In order to investigate characteristic of the prepared samples, the thermal stability of the leached specimen made from feedstock S-45 was conducted from 30°C to 900°C, at 10°C·min^{-1} under oxygen and argon atmosphere as shown in Figure 6. The mass loss represented the mass of PVB that was pyrolysis during the TGA measurement. The onset decomposition temperature of the binder appeared at around 297°C and 327°C under oxygen and argon atmosphere, respectively. The decomposition process under the oxygen atmosphere seems to be faster than under the argon atmosphere. A similar endset decomposition temperature was found around 460°C. The reason was that the feedstock has same concentration of PVB. However, a noticeable mass difference was evident, demonstrating that oxygen could facilitate the burn-out of organics like PVB. PVB might not be completely burnt out in argon, resulting in approximately 0.5 wt% remaining as shown in Figure 6. It was previously reported that final residue of PVB was zero at 700°C when it was analyzed by TGA under nitrogen atmosphere using a linear heating rate of 20°C·min^{-1}. [22] However, under the argon atmosphere operated in this work, the decomposition was produced entirely at a higher temperature. The noticeable decomposition occurred again in the argon atmosphere at around 720°C (T_{d2}). The slower the decomposition would lead to specimens that had a good shape retention and would not be cracked during thermal debinding and subsequently sintering.

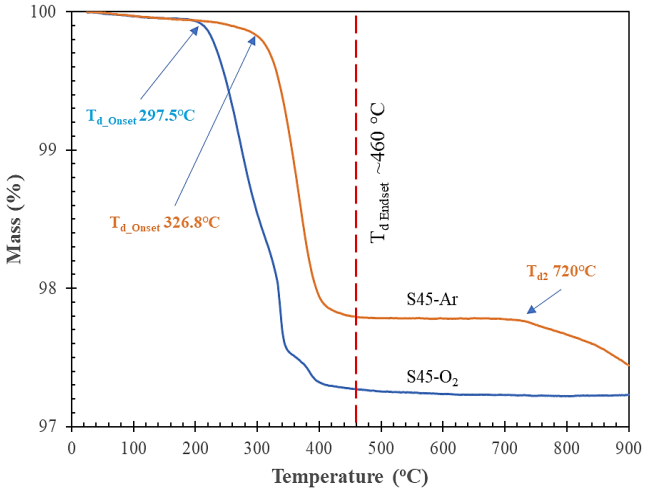

Figure 6. TGA thermogram of S-45 leached specimens tested under oxygen and argon atmosphere.

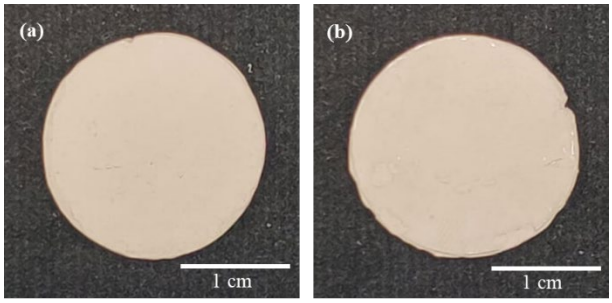

Figure 7. Silver components (a) S-42 and (b) S-45 after thermal treatment at 700°C in argon atmosphere.

Figure 7 shows components made from feedstock S-42 and S-45 and subjected to thermal treatment at 700°C. Shrinkage of specimens after heated at 700°C in argon atmosphere were in range 1% to 3%. In general, shrinkage around 15% to 20% would have been expected in components made by PIM, depending on their powder loadings and sintering conditions. Small number of shrinkage of silver specimens observed in this work might occur due to the swelling of silver. The swelling of silver has previously been investigated [2]. It was proposed that the air-trap in closed pores that formed during fabrication process as well as the release of oxygen from particle surface, resulted in swelling of silver components. Density measurement for specimens, made with S-42 and S-45, after heated at 700°C were 43% and 46% of the theoretical value, respectively. It has been reported that relative density of 54% to 56% was obtained from silver components (grain size of 0.4 μm) when they were densified at temperature of 600°C under argon or oxygen atmospheres [23]. Therefore, further study will be carried out to investigate the effect of various sintering parameters on the properties of the injection moulded silver components. This might be useful for the fabrication of materials in applications that the controlled porosity was required such as for biomedical implants or for certain jewelry design.

4. Conclusions

The feedstock of silver for powder injection moulding was successfully prepared using water-soluble polyethylene glycol (PEG) together with polyvinyl butyral (PVB). Materials and feedstock were systematically characterised. Feedstock having powder loading of up to 45 vol% was able to be injected into the mould using the plunger-typed injection moulding machine employed in this work. The moulded components retain their shapes during solvent debinding using water as a medium. No crack was observed when components were subsequently heated at 700°C in argon atmosphere. The systematic studies for sintering parameters and their effects on properties of the injection moulded silver components will be carried out for the future work.

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