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Contributed Paper

Application of Polyethylene Glycol and Polymethyl Methacrylate as a Binder for Powder Injection Moulding of Hardmetals

Nutthita Chuankrerkkul* [a,b], Peter F. Messer [b] and Hywel A. Davies [b]

[a] Metallurgy and Materials Science Research Institute, Chulalongkorn University, Phyathai Road, Bangkok 10330, Thailand.

[b] Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield S1 3JD, United Kingdom.

*Author for correspondence; e-mail: Nutthita.C@chula.ac.th

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ABSTRACT

A binder system is successfully developed for powder injection moulding of tungsten carbide-cobalt (WC-Co) hardmetal components. The binder comprises a major fraction of polyethylene glycol (PEG), which can be removed rapidly by water leaching and a minor fraction of a finely dispersed polymethyl methacrylate (PMMA), which retains rigidity of the components. PMMA can be removed by pyrolysis during ramping up to the sintering temperature. Studies have been made to the feedstock compositions and to the process parameters in order to achieve high density components. Feedstocks having a powder loading of the WC-Co powder mixture up to 60 vol% can be injection moulded successfully. Density and strength of the specimens tend to increase with increasing PMMA content. The mouldings have green strength in the range 14-17 MPa. Specimens can retain their shapes during and after solvent debinding. The final density achieved is higher than 95% of the theoretical value.

Keywords: Powder injection moulding, tungsten carbide-cobalt hardmetal powder, PEG/PMMA binder.

1. INTRODUCTION

Powder injection moulding (PIM) is an effective process for fabricating small, complex shaped components, especially for high performance applications. The PIM process involves several steps, including feedstock preparation by mixing the powder with a removable binder, injection moulding of the mixture, debinding and sintering [1]. Tungsten carbide-cobalt (WC-Co) hardmetals are used in applications where materials with high hardness and wear resistance with sufficient ductility and toughness are required, for instance, in cutting tools for machining of metal parts or for a variety of wear- resistant components employed in the mining, textile or automobile industries [2]. Binder compositions and debinding techniques are the main differences between various powder injection moulding processes. Several classes of binder have been used but most have long debinding times which affected the economics of these processes. To overcome this

problem, a binder system was developed at Department of Engineering Materials, University of Sheffield [3]. It has been used in a number of previous studies with a range of metallic alloy powders such as stainless steels [4,5] in addition to ceramic powders [6]. In a previous pilot study, an attempt was made to use the polyethylene glycol (PEG) and polymethyl methacrylate (PMMA) composite binder to produce a feedstock with WC-Co powder for injection moulding. However, the feedstocks suitable for this process could not be prepared and the reasons for this failure were not understood, the current investigation was therefore undertaken [7].

2. MATERIALS AND METHODS

The WC and Co powders used in the present study were obtained from Marshall Hard Metals Ltd., Sheffield, U.K. Particle size data were obtained from a Coulter LS130 particle size analyzer. WC Powder, as received, had a coarse particle size with the particles being agglomerated. It is denoted WC Powder A. As the coarse-grained particles would not be suitable for sintering, they were milled to reduce size and denoted WC Powder B. The milling was carried out using a Frisch planetary mill with a WC-Co lined milling pot (500ml) and 8 milling balls (20 mm) of the same material. Some 200 grams of powder were dry milled at a time for 60 minutes. Another type of powder used in the present study was Powder Mixture D which was a 94 wt% WC - 6 wt% Co powder mixture that had been milled/mixed by the supplier. Cobalt powder was also supplied by the same company. WC Powders A or B was then mixed with 6 wt% of Co powder to produce Powder Mixtures A* and B*, respectively. Both contain 94 wt% of WC and 6 wt% of Co.

Feedstock compositions are presented in Table 1. The binder was initially composed of 85 wt% of PEG with a molecular weight of ~1500 and 15 wt% of PMMA. For some feedstocks, part of the PEG constituent was replaced with stearic acid (SA) and its effect was investigated. In two feedstocks made with Powder Mixture B*, the PMMA content was reduced from 15 wt% to 12.5 and 10 wt%, respectively, so that its effect on the mouldings could be studied.

Table 1. Composition of feedstocks

Feedstock	A*2	A*5	B*16	B*20	B*8	B*9	B*22	D4	D5	D6	D7
Powder loading(vol%)	54	54	60	60	60	60	60	54	54	56	57
PEG (wt%)	85	83	90	87.5	85	83	81	85	83	83	83
PMMA(wt%)	15	15	10	12.5	15	15	15	15	15	15	15
SA(wt%)	0	2	0	0	0	2	4	0	2	2	2

PEG = polyethylene glycol, PMMA = polymethyl methacrylate and SA= stearic acid

The powders, 400 grams of WC-Co mixture (6 wt% Co), were mixed with the required amount of PMMA emulsion (40 wt% of PMMA) in the same pot that was

used for milling. A pestle was employed to effect mixing. This was formed by attaching a WC-Co milling ball onto a cylindrical steel bar. This mixture was dried and then hot mixed (~ 80 °C) in the pot with the remainder of the binder, i.e. PEG or PEG/SA, for ~ 15 minutes using the pestle. Hand mixing was employed in the present study, so that smaller and cheaper batches could be prepared, i.e. to avoid the need for large volume of powder when using an available mechanical mixer. To improve the compositional uniformity, the feedstock was extruded five times using the injection moulding machine. Feedstock made with Powder Mixture D could only be moulded with 54 vol% powder loading without an addition of SA in the binder. In this case, SA was introduced into the binder not only to facilitate the mixing but also to obtain feedstocks having higher powder loadings.

Injection moulding was performed using a simple plunger-type machine, which was originally employed for plastic injection moulding. The schematic diagram is illustrated in Figure 1. The temperature used was 100 °C with 44MPa injection pressure for the mould having a square area of 5 x 5 mm and a length of 55 mm.

The mouldings were subjected to debinding study using water leaching approach. The leaching tests were performed at 40 °C or 60 °C for various times. After leaching in water, specimens were sintered in a tube furnace under a controlled atmosphere of argon. Specimens were heated at 2 °C/min, held at a temperature in the range 1375 – 1500 °C for 30, 60 or 120 minutes, and then cooled to room temperature. A Hounsfield universal testing machine was used to measure the strength of the as-moulded (after moulding) and as-leached (after leaching) specimens by a three-point bend test. Density measurements were made in as-moulded and as-leached states and after sintering. The microstructures of specimens were observed using optical or scanning electron microscopy.

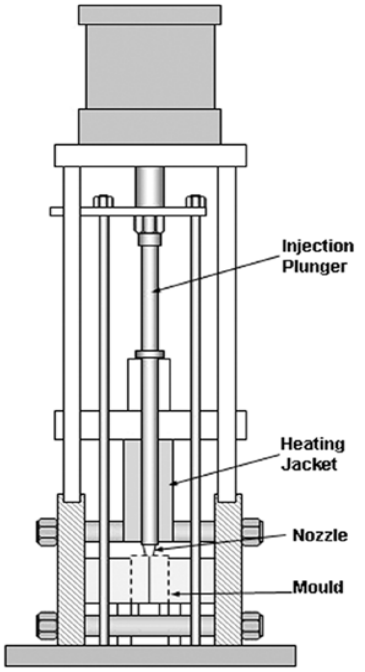

Figure 1. Diagram of a plunger-type powder injection moulding machine

Table 2. Characteristic of powders

Powder	Relative apparent density*	Relative tap density*	Median size, D_{50} (μm)
WC Powder A	36%	46%	43
WC Powder B	44%	55%	18
WC-Co Powder Mixture D	24%	37%	4.9
Co Powder	15%	25%	6.8

*The densities shown are relative to theoretical values of 15.6 g/cm^3 for WC, 14.93 g/cm^3 for WC-6Co and 8.9 g/cm^3 for Co.

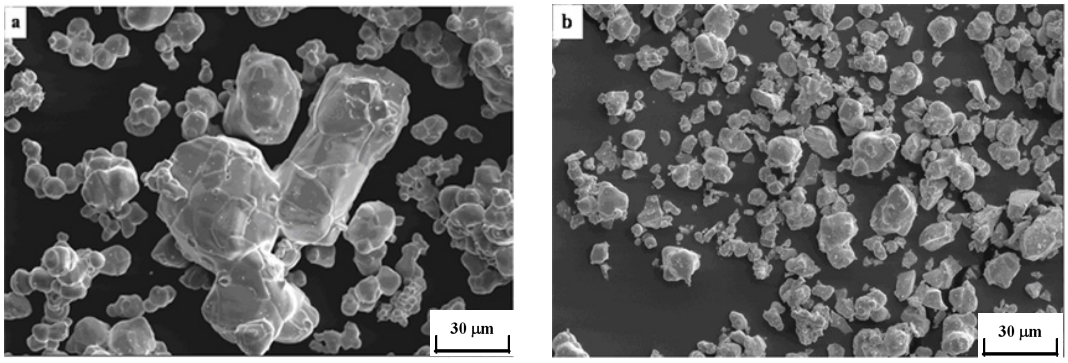

Figure 2. SEM micrographs of (a) WC Powder A (as-received) (b) WC Powder B (after milling)

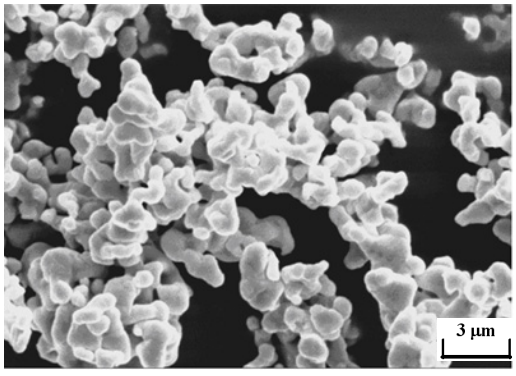

Figure 3. SEM micrograph of Co powder

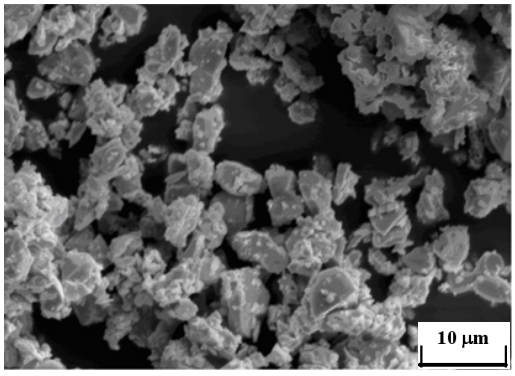

Figure 4. SEM micrograph of Powder Mixture D

3. RESULTS AND DISCUSSION

After milling, the WC particle size was reduced and the apparent and tap densities were improved. The characteristics of powders are presented in Table II. SEM micrographs of WC Powders A and B (powder as received and powder after milling) are shown in Figures 2a and 2b, respectively. Figure 3 shows a SEM micrograph of Co powder. SEM micrograph of Powder Mixture D is presented in Figure 4.

The properties of the mouldings produced from feedstocks with various amounts of PEG and PMMA are listed in Table 3**.** As expected, the as-leached strength of mouldings increased with increasing PMMA. As PMMA has been shown to bond only to Co [8], it is considered that ligaments of PMMA molecules that joined to Co particles and formed a three-dimensional network hold the mouldings, in the as-leached state, together. The as-moulded strength of mouldings did not show any statistically significant trend [9]. This is possibly because the as-moulded strength will be affected by both the PEG and PMMA contents in the mouldings. Clearly, the presence of the PEG in the as-moulded state increased the strength substantially over that of the as-leached state. The contribution to the strength from the PEG would be reduced by the reduction in PEG content, whilst the contribution to the strength from the PMMA would be increased by an increase in its content.

Table 3. Properties of the mouldings produced with various proportions of PMMA

Powder Mixture	Binder Composition (wt%) (PEG/PMMA)	Strength (MPa)		Density (g/cm^3)	
		As-moulded	As-leached	As-moulded	As-leached
B*	90/10	15.1 ± 2.4	3.4 ± 0.5	9.34± 0.03	9.02 ± 0.03
(60 vol%)	87.5/12.5	17.6 ± 1.0	4.0± 1.2	9.37± 0.03	9.01± 0.06
	85/15	16.8 ± 0.5	5.1± 0.3	9.53± 0.06	9.22± 0.05

(mean ± 95% confidence limit, n=5)

The densities of the as-moulded and as-leached mouldings generally increased with increasing PMMA content. This observation cannot be explained on the basis of any change in the density of the binder as a result of different compositions. It is necessary to assume that the voidage in the mouldings decreased with increasing PMMA content. That is, as the PMMA content increases, the Co particles are pulled together more strongly. This will cause the WC particles to pack more densely. Hence, densitites of the mouldings increased.

In the present study, the highest powder loadings for feedstocks that could be moulded were 60 vol% and 57 vol% for those made with Powder Mixtures B* and D, respectively. It was found in a previous study by Wong [6] that a time of 8 hours was required to mix a whiteware feedstock with 64 vol% solids, which was close to the maximum that could be moulded, whereas one made with 61 vol%

required only 1 hour for mixing. This suggests that, with the short time employed to hand mix the feedstocks, it is probably only possible to produce a feedstock with ~90% of the critical powder loading. Moreover, the feedstocks were probably not as uniform in composition with respect to the binder and powder as they might have been if a prolonged machine mixing had been employed.

Solvent debinding tests were carried out to investigate time required for the removal of the PEG, at temperatures below and above its melting point (~43-46 °C). The results are presented in Figure 5. Interconnected pores are formed after water leaching, which allows faster removal of the remaining PMMA by subsequent pyrolysis during ramping up to the sintering temperature. Injection moulded specimens retained their shapes during and after leaching at both temperatures and for all times. Water leaching at elevated temperature resulted in faster removal of the PEG. Figure 5 also shows that leaching is rapid in the initial stage. Furthermore, for mouldings made with Powder Mixture D, the rate of removal of the PEG is lower than that for Powder Mixtures A* or B*.

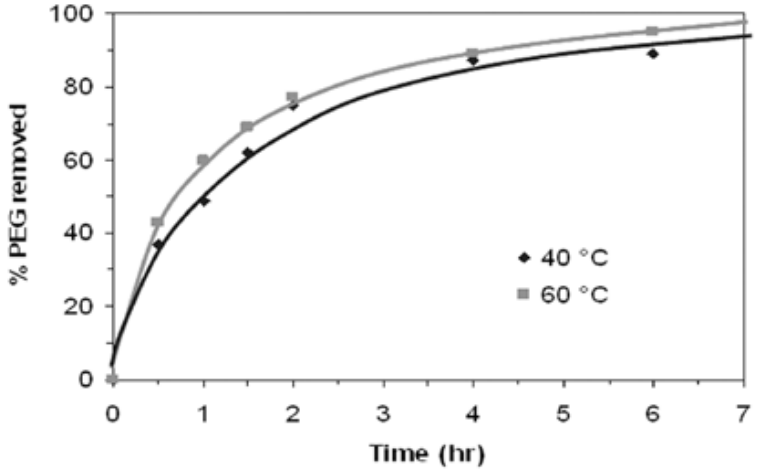

Figure 5. Results of leaching of B*8 specimens at 40 °C and 60 °C

Sintering was performed in an argon atmosphere. The measured sintered densities for mouldings made with Powder Mixture A*, prepared with 54% powder loading, are in the range 12.86-13.09 g/cm^3 (86-88 % of the theoretical density), while those for the mouldings made with Powder Mixture D with the same powder loading are 14.35-14.36 g/cm^3 (96 % of the theoretical density). This clearly indicates the importance of using fine WC particles which can produce mouldings having the Co distributed on a finer scale. In addition, when stearic acid was introduced into feedstocks based on Powder Mixture D, feedstocks having higher powder loadings could be prepared and injection moulded. This allowed components with a slightly higher sintered density, i.e. 14.46 g/cm^3 (97 % of the theoretical density) to be obtained. The densities of specimens prepared with Powder Mixture B* using various binder compositions based on a 60 vol% powder loading were not significantly different. The final densities of these specimens were in the range 14.00-14.23 g/cm^3 (94-95 % of the theoretical density). Although the powder loading for

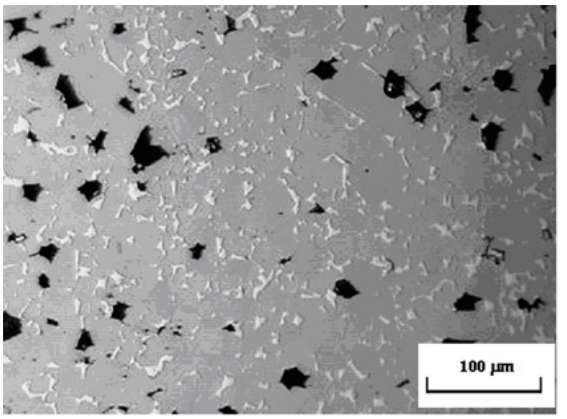

Figure 6. Optical micrograph of moulding made with Powder Mixture B* sintered at 1450 °C for 60 minutes

these feedstocks was higher than those made with Powder Mixture D, the distribution of Co was not as favourable because the WC particles were coarser. Moreover, the linear sintering shrinkage for mouldings made with Powder Mixtures A* and B* was 13-14 % while the value of 19-20 % was for those made with Powder Mixture D. An optical micrograph, for example, of a specimen made with Powder Mixture B*, sintered at 1450 °C for 60 minutes is shown in Figure 6.

Despite the fact that, other workers, had achieved sintered densities between 95%–99% of theoretical maximum values using different binder systems, particle sizes, cobalt contents or sintering conditions [10-15]. The highest density which can be achieved in the present study, as sintered in an argon atmosphere, is 97% of the theoretical value.

4. CONCLUSIONS

It has been found possible to fabricate WC-Co hardmetals by powder injection moulding technique using the water-soluble, multi-component binder. The mouldings retain their shape during and after leaching of the PEG. The highest density achieved thus far is 97% of the theoretical value. It is possible that a higher density might be obtained if the feedstocks made with Powder Mixture D (finer particle size) and the PEG/PMMA/SA binder could be prepared with higher powder loading, using a mechanical mixer. Furthermore, the use of vacuum sintering might also be advantageous.

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