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Contributed Paper

Study on Binder Removal and Green Properties of Tungsten Carbide-Nickel Hardmetals Fabricated by Powder Injection Moulding

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Abstract

This works aims to investigate the as-injected properties of the tungsten carbide-nickel (WC-Ni) hardmetal powder. Tungsten carbide containing 6wt% nickel blended with a binder mixture of polyethylene glycol (PEG) and polyvinyl butyral (PVB). The powder loadings (the powder to binder mixture ratios) covered 48:52, 50:50 and 52:48 %v/v. The hardmetal powders were initially mixed with PVB in ethanol, followed by PEG, to prepare powder feedstock. Then, the obtained feedstock was injected into a set of steel die at 120-140 ^{o}C to get the injected specimens. The green properties, i.e. green strength and density, were examined. Debinding behaviours of PEG by a stagnant water at ambient temperature from 0.5-5 hours were observed. The preliminary study revealed that powder loading governed injection ability as well as injection temperatures. Density of the green specimens depended strongly on powder loading meanwhile the green strength values did not. PEG removal rate of WC-Ni hardmetals were relatively high at the very beginning and became slow with longer debinding times and also affected by powder loadings.

Keywords: hardmetals, tungsten carbide-nickel, powder injection moulding

1. Introduction

Tungsten carbide-nickel (WC-Ni) hardmetals are widely used as cutting tools and high wear resistant parts employed in textile, mining and automobile industries as well as metal forming process. The hardmetals or cemented carbides have advantages because of their high hardness and high toughness which are rarely obtained from metals or ceramics on their own [1]. The types of materials provide a combination of excellent strength, wear resistance and hardness as well as reasonable ductility and toughness [2-3]. Hardmetals have usually been produced by powder metallurgy and researchers are interested in fabrication of hardmetals by powder injection moulding in order to provide alternative ways for making small, complex and near-net-shaped components [4-8]. Powder injection moulding (PIM) technique allows the large number of small and complicated parts to be fabricated at a time. It has 4 main steps including feedstock preparation, injection moulding, debinding and sintering. The PIM of very fine particles of cemented carbide powders using paraffin wax (PW) and polypropylene (PP) binder system were reported by Yang and German [4]. Zhu *et al.* also investigated on solvent debinding of hardmetals components using wax-based binder system [5]. The water-soluble binder system composed mainly of polyethylene glycol (PEG) and a minor constituent of polymethyl methacrylate (PMMA) was employed in powder injection moulding of WC-Co hardmetals [1]. It was found that the highest density of 97% of the theoretical value could be achieved. The binder systems comprising PEG and polyvinyl butyral (PVB) were recently reported for PIM of alumina-zirconia composites [9] as well as metallic titanium alloys [10]. Several research work in PIM focused on binder selection and debinding process but a study on PIM of hardmetals using water-soluble binder is quite limited. This work, therefore, focused on processing of WC-Ni hardmetals using PEG as a main binder ingredient while PVB is used as a backbone polymer that holds particles when PEG was removed during water leaching.

2. Materials and Methods

Ultra-fine tungsten carbide-nickel (WC-Ni) hardmetal powder (GWC-75™, ATI Alldyne, USA) containing 6wt% nickel, the density of which is 15 g/cm^3, was used in the study. The powder feedstocks were prepared using the cemented carbide and a mixture of PEG (average molecular weight of 1500, density 1.125 g/cm^3) and PVB (average molecular weight of 80000, density 1.1 g/cm^3) binders. The volume ratio between PEG and PVB throughout the experiment was 85:15. The feedstocks with 3 different powder loadings were investigated, the powder to binder volumetric ratios included 48:52, 50:50 and 52:48, designated as WCN48, WCN50 and WCN52, respectively. To thoroughly blend hardmetal powder with both binders, PVB was firstly dissolved in ethanol into solution and the powder was added and vigorously stirred in order that PVB solution covered particles. The solution containing cemented carbide was then dried in an oven at 80 ^{o}C. The dried powder was later mixed with the PEG that heated into viscous forms. The obtained feedstock was placed in a cylinder of a plunger-type laboratory scale injecting machine, heated up between 120-140 ^{o}C. The powder feedstocks were injected 4-5 times to ensure homogeneity before injecting the mixture into a preheated steel die. After being left to cool down, the as-injected specimen was demoulded, providing the bar specimens with square cross sectional area. The dimension of each bar specimen, according the size of the die cavity, was approximately 5mm × 5mm × 55mm, as shown in Figure 1. The green density values of the specimens were calculated by a mass to volume ratio while flexural strength of those were achieved using a 3-point bending test. To investigate the debinding behaviour, it was noted that PEG removal was only focused. Water-soluble PEG in the as-injected specimens was removed by leaving them in stagnant water at ambient temperature from 0.5 to 5 hours. The changes in weight of the wiped-dry specimens after 0.5, 1, 2, 3, 4 and 5-hour water immersion were measured and evaluated in the term of the degree of PEG removal in percentage.

3. Results and Discussion

3.1 Injection Behaviour

According to some literatures [11] using a PEG and PVB binder system, the Al_2O_3 and Al_2O_3/WC could easily be injected at 190-200 ^{o}C. At the very first attempt, it was found that the temperature was too high to apply to the cemented carbide. The 190 ^{o}C injection was possible but this provided a low viscosity mixture that could not completely fill up the mould cavity. The mixture tended to penetrate through the seam lines of the mould (see Figure 2a) and spill over the mould sprue. To promote viscous flow, the optimization of injection temperature was carried out. Another drawback of 190 ^{o}C injection was the PEG loss due to burnout or evaporation. In

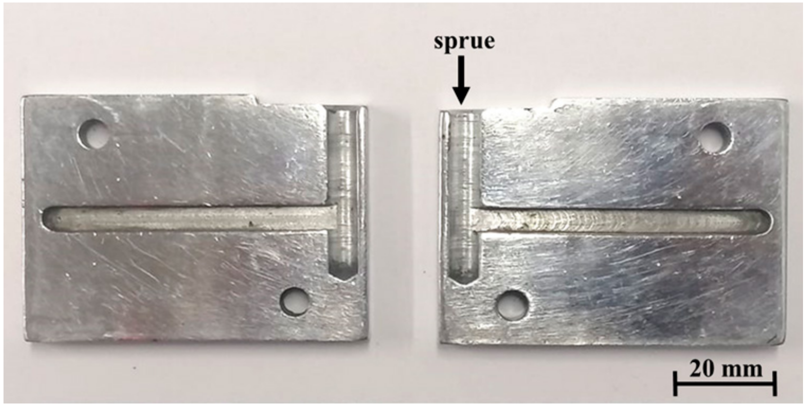

Figure 1. A set of steel die used for powder injection moulding in this experiment.

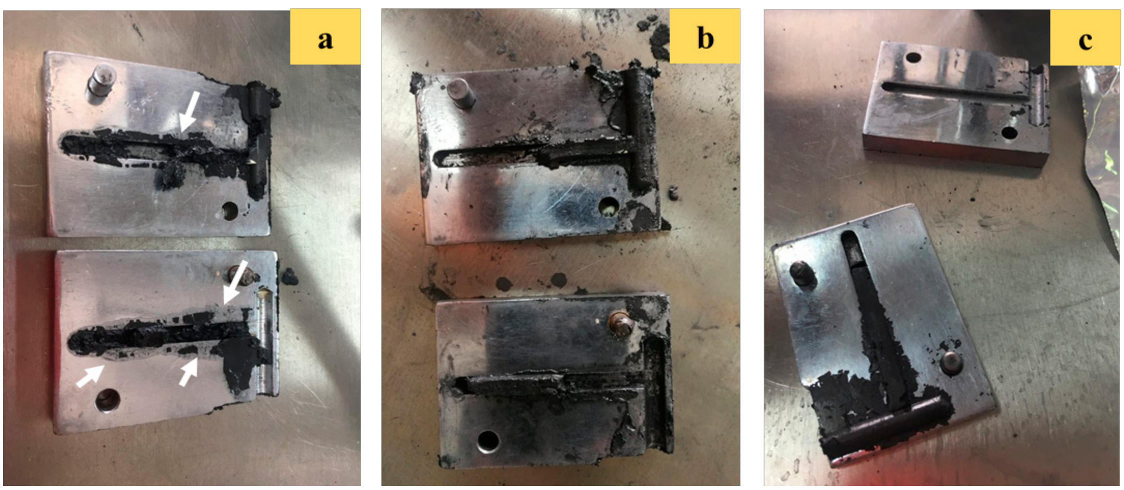

Figure 2. Injection ability of the WCN48 feedstocks at (a) 190 °C (b) 160 °C (c) 120 °C.

this experiment, the injection ability was likely to be improved at lower injection temperature, such as at 160°C, relative to that undergone at 190 °C, as seen in Figure 2b. This might be caused by the cemented carbide powders generally contain a small amount of polymer or organic additives to attain some specific requirements [2], such as paraffin wax to prevent agglomeration and enhance compaction when pressed. Unlike the ceramic powder-based, hardmetal powders provide better flowing manners according to a presence of attached additives. More additional polymer binders in hardmetal feedstock and being injected at the temperature above softening points of the two binders, resulted in better powder fluidity compared to ceramic powders with the same amount of additional binders. As far as the WCN fabricated by injection moulding at 160 °C was considered, sprue overflow was no longer observed but the specimens could not yet gain the as-injected strength to be demoulded and handled. A decrease in injection temperature from 160 °C to 120 °C led to the expected viscous flow, the feedstocks could fill up the die cavity and the specimens could

Table 1. Green density and flexural strength of the as-moulded WC-Ni specimens.

Specimens	Volume ratios		Green density (g/cm^3)	Green flexural strength (MPa)
	Hardmetal powder	PEG and PVB binder		
WCN48	48	52	5.71 ± 0.14	2.13 ± 0.27
WCN50	50	50	5.82 ± 0.25	2.32 ± 0.23
WCN52	52	48	6.60 ± 0.23	2.15 ± 0.22

also be demoulded quickly without any breakage as shown in Figure 2c.

However, the injection temperatures were slightly varied from one powder loading to another, i.e. higher powder loading required slightly higher temperatures to facilitate the feedstock to travel through runner and fill the die cavity. Higher powder loadings indicate that less amount of binder being used so viscous flow needs higher temperatures. Therefore, the feedstocks of WCN50 and WCN52 were necessary to be injected at the temperatures slightly above 120 °C.

3.2 Green Strength and Green Density

The density and green flexural strength values of the injected specimens are exhibited in Table 1. The experimental suggested that the density values of the injected specimens were up to powder loadings. Greater volume fraction of WC-Ni cemented carbide attributed more weight at a certain volume. Thus, the density of WCN52 ranked the highest, followed by WCN50 and WCN48, respectively. Nonetheless, the higher green density did not reflect higher green flexural strength. Flexural strength of the as-injected specimens were about the same levels because the strength gain came from PEG and PVB binders, not particle bonding. PEG binder, which had bigger volume fraction to PVB, dominated green strength holding the hardmetal particles together and helped handling at room temperature. Also, the particles of the WCN hardmetals were assumingly coated by PVB and the outermost later were covered by PEG, according to the experimental procedures. After PEG debinding, the brown strength solely came from PVB. Therefore, it could be implied that it was reasonable if the green strength values of the injected specimens were quite similar as long as (1) the volume fraction of PEG and PVB was fixed (2) the difference in powder loading of the feedstocks was small an (3) the hardmetal powder and binders were thoroughly and uniformly mixed. Fracture surfaces of the green specimens with various powder loadings are exhibited in Figure 3, showing the coverage of binder mixture onto the hardmetal particles.

3.3 Binder Removal Rate

Figure 4 illustrates the PEG removal rate at various debinding time. At the first few hours, the debinding rate was relatively high and later low at the longer times. The PEG in specimen WCN48 could be removed with higher rates compared to WCN50 and WCN52 because it contained higher volume fraction of PEG and PVB binders. Lower powder loadings contributed to lower powder packing and offered PEG to glue the particles together more evenly (see Figure 3). The more fraction of binders, literally higher volume of PEG, the more PEG removal. It was also noticed that the degree of PEG removal of the injected WC-Ni hardmetal was low compared with those of the ceramic-based [8,9], only 30% maximum after 5 hours. This might be caused by stagnant water at room temperature. The degree of PEG removal could possibly induced by rising the water temperature [9] and using running water instead of the stagnant one.

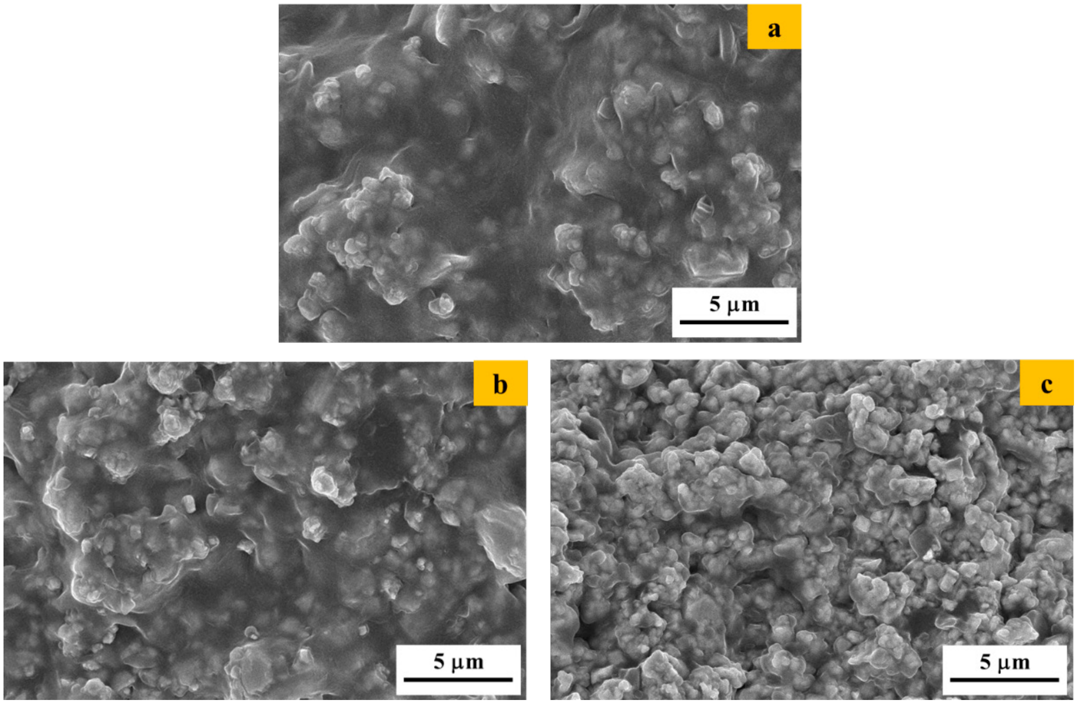

Figure 3. Fracture surfaces of the as-moulded specimens with different powder loadings: (a) WCN48 (b) WCN50 and (c) WCN52.

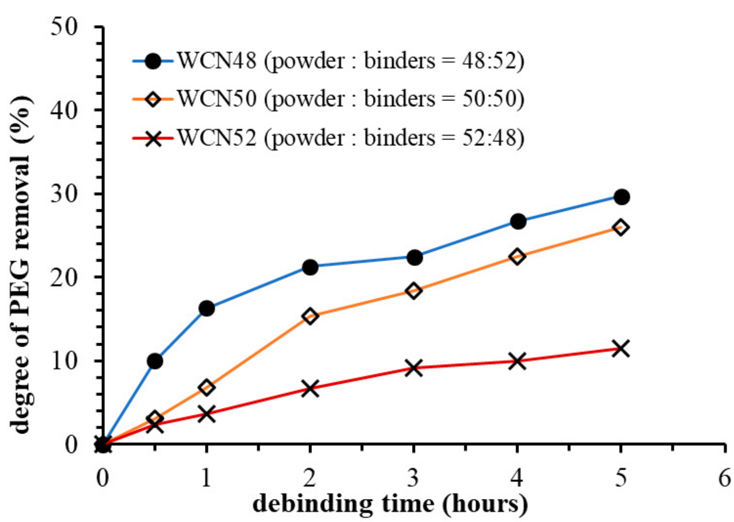

Figure 4. PEG removal of the injected WC-Ni specimens at various debinding times.

4. Conclusions

The preliminary study on green properties and debinding behaviour of the WC-Ni hardmetal fabricated by injection moulding was successfully accomplished. The hardmetal feedstocks prepared using the mixture of PEG and PVB were injected at the temperatures of 120-140 ^{o}C which was relatively lower than the ceramic-based feedstocks. The injection temperatures could possibly varied slightly due to powder loadings. PEG contents governed green flexural strength whereas powder loading determined green density. The PEG removal rate was quite low and powder loading somewhat took parts in debinding behaviour.

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