Article ID: 1003－6326(2003)02－0262－05

A novel binder and binder extraction method for powder injection molding of tungsten cemented carbide①

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Abstract: An improved wax-based multi-component binder and a new debinding method termed high-pressure condensed solvent extraction were developed for powder injection molding of tungsten cemented carbide. The results indicate that a critical powder loading of 65% (volume fraction) and an ideal rheological properties were obtained by the feedstock based on the binder. High debinding rate and specimens with high strength were obtained by the debinding method. Moreover, by making high temperature holding time adjustable, it makes the subsequent thermal degradation process more flexible to debinding atmosphere and carbon content of the as debinded specimens controllable. The transverse rupture strength, hardness and density of the as-sintered specimens made by an optimized PIM process are 2.48 GPa, HRA90 and 14.72 g/cm^3, respectively. Good shape retention and about 0.02% dimension deviation were achieved.

Key words: powder injection molding; tungsten cemented carbide; binder; rheological property
CLC number: TF 125.3 **Document code:** A

1 INTRODUCTION

Powder injection molding (PIM), which is derived from plastic injection molding, is a kind of net-shape powder metallurgy forming process[1-3]. Combining high part complexity with high production quantities, it supplements the established processes like die compaction, machining and investment casting[4-6]. Comparing to conventional pressing/sintering process, the PIM has great technique and cost advantages for the production of cemented carbide components with complex shapes[7, 8]. Since hydraulic pressure is applied during injection molding, mold caves are filled up uniformly and the density gradient could be avoided. The products prepared by PIM are expected to have more homogeneous microstructure and better mechanical properties. Moreover, The fabrication cost could be eliminated by reducing machining cost and recycling use of PIM feedstock[9, 11].

Aiming at getting fundamental knowledge of each step of the process and their interaction, the work reported in this article summarizes some results from a research program investigating the application of PIM for the production of cemented carbides.

2 EXPERIMENTAL

The WC-8% Co powder mixture used was supplied by Zhuzhou Cemented Carbide Company, Hunan, China. The particle was of irregular and angular morphology and had certain degree of agglomeration. The characteristics of the powder are listed in Table 1. The binder was wax-based multi-component binder, the content and properties of each component of the binder are listed in Table 2.

Binder components were pre-mixed in a home-made mixing device at 160 ℃ for 2 h. Then the WC-8% Co powder mixture was mixed with the binder in a torque rheometer plastograph mixer at 50 r/min for 2 h. The mixing temperature was 140 ℃. Feedstock was injection-molded in an SZ-28/250 injection molding machine at 165 ℃. The injection pressure was 75 MPa and the mold temperature was 30 ℃. The injection molded specimens were debinded by high pressure condensed solvent debinding and thermal degradation method. Heptane was used as solvent. Thermal degradation was performed in a certain protection atmosphere according to schedule 1: 20 ℃ $\xrightarrow{30\text{min}}$ 600 ℃ $\xrightarrow{\text{certain time}}$ 600 ℃ $\xrightarrow{\text{furnace cooling}}$ 20 ℃. The as-debinded specimens were sintered in vacuum furnace at 1 460 ℃ with pressure of 20 Pa.

An Instron 3211 capillary rheometer was used to measure the viscosities of feedstock. The mechanical properties of the specimens were determined on an Instron material tester. The contact angles were measured by a soakage tester at 170 ℃. The carbon residual was analyzed by the infrared absorption method using a Leco CS-344 carbon analyzer.

① **Foundation item:** Project(50025412) supported by the National Natural Science Foundation of China; Project(G2000067203) supported by the National Key Fundamental Research and Development Program of China
Received date: 2002－04－27; **Accepted date:** 2002－07－09
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Table 1 Characteristics of WC-8% Co powder mixture

Total carbon content/ %	Dissociated carbon content/ %	Oxygen content/ %	Cobalt content/ %	Tap density/ ($g \cdot cm^{-3}$)	Grain size/ μm	Specific area/ ($cm^2 \cdot g^{-1}$)
5.70	0.13	0.33	8.11	4.85	3.2	3 970

Table 2 Binder composition and properties of components

Component	content/ %	Monomer structure	Melting point, / ℃	Density/ ($g \cdot cm^{-3}$)
Paraffin wax	60	C_nH_{2n+2}	58.0	0.900
Liquid paraffin wax	5	C_nH_{2n+2}	–	0.855
High-density polyethylene	10	$\{CH_2—CH_2\}_n$	139.0	0.950
Polypropylene	10	$\{CH_2—CH(CH_3)\}_n$	142.0	0.900
Dioctyl phthalate	5	$C_{24}H_{38}O_4$	18.1	0.978
Ethylene propylene diene monomer	5	$\{CH_2—CH_2—CH(CH_2)—CH_2\}_n$	–	0.860
Stearic acid	5	$CH_3[CH_2]_{16}COOH$	66.0	0.960

3 RESULTS AND DISCUSSION

3.1 Binder and feedstock

The binder plays a very important role in PIM process. In order to obtain feedstock with high solid powder loading and suitable rheological properties for injection molding, an improved wax based binder named ZB-5 was developed (Table 2). Comparison of feedstock based on ZB-5 and a typical wax-based binder (80% PW + 20% HDPE) is listed in Table 3. The solid powder loading of feedstocks used for steady state torque testing is 57% (volume fraction). The transverse rupture strength of the as-molded specimens was tested to appraise the strength of the binder. The dimension of the specimens was 6 mm × 6 mm × 42 mm and the solid powder loading was 62% (volume fraction). Table 3 indicates that feedstock based on ZB-5 can obtain a higher solid powder loading and a lower steady state torque in mixing. It is because that liquid paraffin wax and dioctyl phthalate added as modifier improve the rheology of the feedstock significantly. Stearic acid helps to strengthen the interaction between binder and powders, which would improve powder loading of the feedstock and overcome phase separation phenomenon during injection molding. The ash content of ZB-5 is low and it will benefit the mechanical properties of the as-sintered specimens.

Rheology of the feedstock (with ZB-5 as binder and a powder loading of 62% (volume fraction)) is shown in Table 4. It indicates that the viscosity of the feedstock decreases with the increase of shear rate and temperature, which accords with the pseudoplastic behavior. For a pseudoplastic fluid, there is

$$\tau = k\dot{\gamma}^n, \quad \eta = \tau/\dot{\gamma} \tag{1}$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate, k is a constant, n is a flow behavior exponent, η is viscosity of the feedstock. The value of n indicates the degree of shear sensitivity, which is very important in producing complex and delicate parts. Plotting the logarithm of shear stress against the logarithm of shear rate for the temperature of 160 ℃, 170 ℃ and 180 ℃ as shown in Fig. 1, values of n were determined as 0.331, 0.360 and 0.374 respectively.

The dependence of viscosity on temperature

Table 3 Comparison of feedstock based on ZB-5 and typical wax-based binder

Binder	Critical powder loading/ %	Steady state torque/ (N·m)	Strength/ MPa	Contact angle/ (°)	Ash content/ %
ZB-5	65	2.05	19.2	3.78	0.25
Typical wax-based binder	56	2.75	17.3	6.92	0.35

Table 4 Viscosity of feedstock at different shear rates

Temperature/ ℃	Viscosity/ (Pa·s)				
	12.11 s^{-1}	36.12 s^{-1}	121.3 s^{-1}	356.7 s^{-1}	1 185 s^{-1}
160	1 189.0	634.8	276	127.5	57.84
170	974.5	479.4	235	119.0	52.24
180	869.1	439.0	196	104.0	51.52

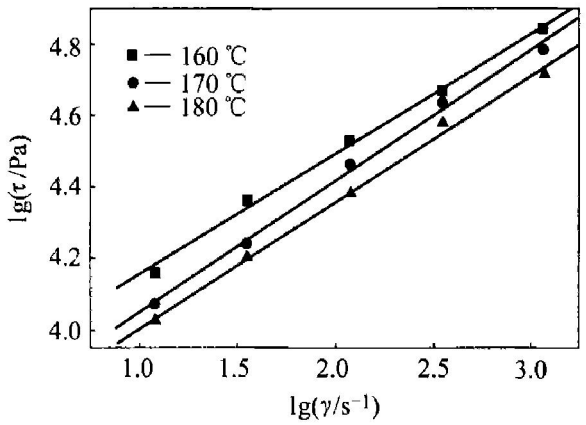

Fig. 1 Correlation of shear stress and shear rate

can be expressed by an Arrhenius equation[11]:

$$\eta(T) = \eta_0 \exp(E/RT) \quad (2)$$

where E is the flow activation energy, R is the gas constant, T is temperature, η_0 is reference viscosity. The value of E expresses the influence of temperature on the viscosity of the feedstock. If the value of E is low, the viscosity is not so sensitive to temperature variation. That means a small fluctuation of temperature during injection molding will not result in a sudden viscosity change, which is the cause of undue stress concentration in the molded specimens. On the condition that the shear rate is 1 185 s^{-1}, which falls into the normal range of shear rate during powder injection molding, by plotting the common logarithm of viscosity against the reciprocal of temperature, as shown in Fig. 2, the flow activation energy E was determined as 24.6 kJ/mol.

A mouldability index α_{stv} which was defined as

$$\alpha_{stv} = \frac{1}{\eta_0} \frac{\left| \frac{\partial(\lg \eta)}{\partial(\lg \dot{\gamma})} \right|}{\frac{\partial(\lg \eta)}{\partial(1/T)}} \quad (3)$$

can be introduced to evaluate the general rheological properties of the feedstock. Where η is viscosity, η_0 the reference viscosity, $\dot{\gamma}$ shear rate, T temperature. Simplifying the above equation gives

$$\alpha_{stv} = \frac{1}{\eta_0} \frac{|n-1|}{E/R} \quad (4)$$

where n is a flow behavior exponent, E the flow activation energy, and R the gas constant. The subscripts s, t, v of α_{stv} represent the effect of shear

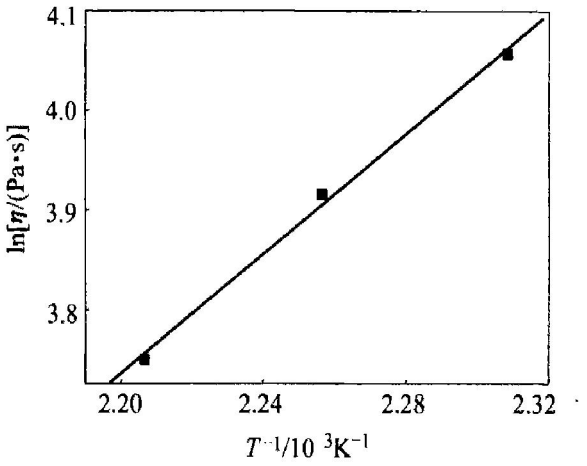

Fig. 2 Correlation between viscosity and temperature

sensitivity, temperature sensitivity, and viscosity respectively. The higher the value of α_{stv}, the better the general rheological properties. Taking 160 ℃ as a reference temperature and 1 185 s^{-1} as a reference shear rate, the values of α_{stv} of the feedstocks were calculated. After multiplying the results by 10^6 to give number between 1 and 10, the α_{stv} value is 3.65, which is a relatively high value for feedstock with a 62% (volume fraction) powder loading.

3.2 High pressure condensed solvent debinding

Fig. 3 is the sketch drawing of the high pressure condensed solvent debinding device. By controlling the solvent temperature on different levels, the vapor pressure of the solvent is different in the two containers. The vapor flows from the high-pressure end to the low-pressure end and condenses on the surface of the specimens that are placed on the porous substrate. Binder is then removed to the surface by inter-diffusing of binder and condensed solvent. The binder-solvent solution flows to the base of the specimen and absorbed by the porous substrate. By importing Ar or N_2 continuously from a pressure-constant source, certain atmosphere pressure is maintained in the containers. A temperature difference of 10 ℃ between the two containers and a 0.202 MPa pressure in the containers are proved suitable for a rapid and defect free debinding by pre-experiments and it is adopted by the following experiments. Fig. 4 shows the relationship among soluble binder loss ratio, debinding temperatures (of solvent in the container filled with specimens) and debinding time. Clearly, 80 ℃ is a suitable debinding temperature and the soluble binder is nearly completely removed in 5 h. High pressure in the container ease up, or in another word, neutralizes binder swelling and stress relaxing of compacts. As a result, the as-debinded specimens has an integrated structure and it is absolutely defect free. The transverse rupture

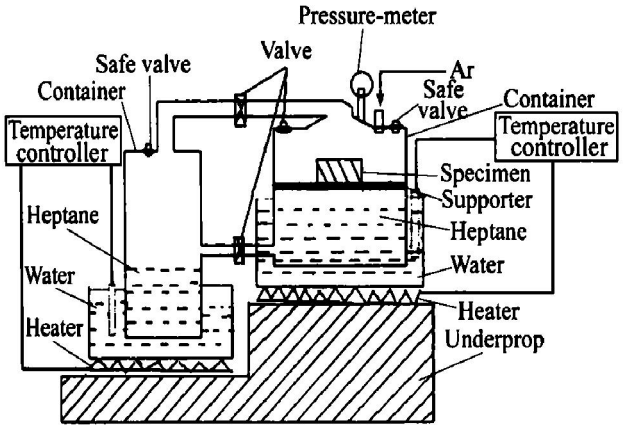

Fig. 3 Schematic drawing of high pressure condensed solvent debinding device

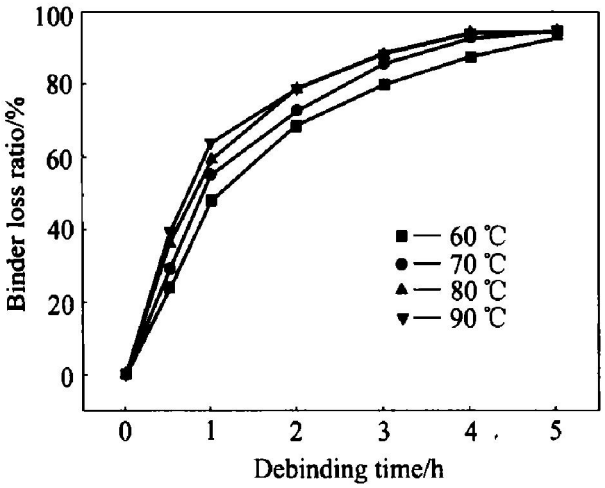

Fig. 4 Correlation among binder loss ratio, debinding temperature and debinding time

strength of the as-debinded specimens achieves 0.384 MPa, which is higher than those of specimens debinded by conventional solvent debinding method.

3.3 Carbon control

Carbon control is the most important issue in manufacturing WC-Co cemented carbide by PIM. It determines not only the mechanical properties but also the dimensional stability[7]. The condensed solvent debinding won't change the original carbon content of WC-Co powder, but the subsequent thermal debinding step does. Fig. 5 shows the effect of thermal debinding time and debinding atmosphere on carbon content of the as-debound specimens. It was found that binder remaining in the compacts after condensed solvent debinding is almost removed completely after thermal debinding when specimens were held at 600 ℃ for 1.5 h according to schedule 1. Specimens debinded in H_2 and 75% N_2/25% H_2 mixture respectively are nearly on the same carbon content level. It is because that the high temperature holding time is

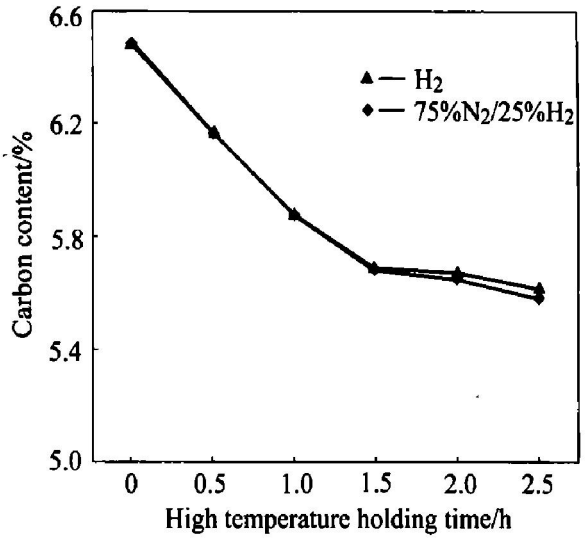

Fig. 5 Correlation between hold time(600 ℃) and carbon content of as-debinded specimens

short enough to avoid decarburization caused by H_2 atmosphere, which indicates that the two step debinding method is endowed much flexibility to debinding atmosphere. By controlling the high temperature holding time, the carbon content of the as-debinded specimens could be adjusted in a certain range, which would benefit control of PIM process.

3.4 Properties and microstructure

Properties of WC-8% Co cemented carbide made by PIM are listed in Table 5. Fig. 6 is the optical micrograph of its cross-section. It is found that the density of PIM specimens is close to the theoretic value, the void ratio is less than 0.02%, the microstructure is homogeneous and free of the third phase, the transverse rupture strength and hardness of specimens sintered at 1 460 ℃ for 2 h achieve 2.48 GPa and HRA90 respectively, which are similar to those of specimens made by conventional pressing and sintering technology.

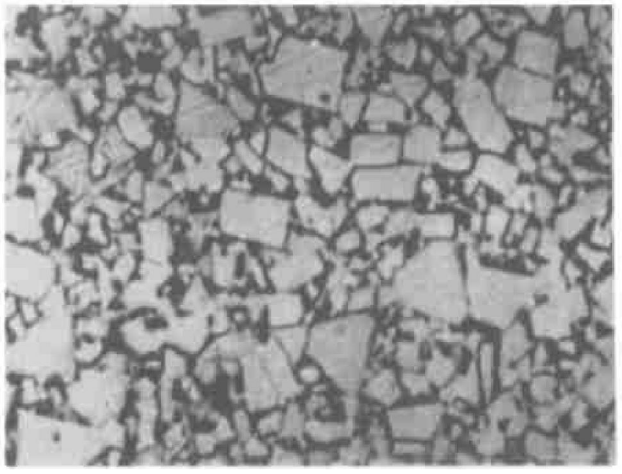

Fig. 6 Optical micrograph of WC-8% Co formed by PIM

Table 5 Comparisons of tungsten cemented carbide made by PIM and pressing/sintering process

Process	Composition	Strength/GPa	Hardness (HRA)
PIM	WC-8% Co	2.48	90
Pressing/Sintering	WC-8% Co	2.48	89

Process	Coercivity/($kA \cdot m^{-1}$)	Density/($g \cdot cm^{-3}$)	Void/%	Grain size/μm
PIM	8.95	14.72	< 0.02	2
Pressing/Sintering	6.53	14.72	< 0.02	2

3.5 Dimension precision

Table 6 shows the effect of solid powder loading on dimension precision of the rectangular specimen(6 mm × 6 mm × 42 mm). Camber τ was defined as

$$\tau = \frac{\text{real value in length of crooked specimens}}{\text{linear value in length of crooked specimens}}$$

to evaluate the distortion of the as-sintered specimens. The results indicate that dimension precision increases as sintering shrinkage of the specimens decreases. High solid powder loading of feedstock would reduce sintering shrinkage and benefit dimension precision and shape retention.

Table 6 Effect of solid powder loading on dimension precision

Powder loading/%	Linear shrinkage/%	Relative density/%	Deviation/mm	τ(camber)
55	17.5	99.1	0.10	1.002 81
57	16.2	99.2	0.06	1.001 68
60	14.7	99.6	0.03	1.000 84
62	14.1	99.8	0.02	1.000 56

4 CONCLUSIONS

1) The improved wax-based multi-component binder named ZB-5 is suitable for powder injection molding of tungsten cemented carbide. It endowed the feedstock with a critical powder loading of 65% and an ideal rheological properties. The flow behavior exponent n, flow activation energy E and general rheological index α_{stv} of feedstock with a powder loading of 62% (volume fraction) are 0.331, 24.6 kJ·mol^{-1} and 3.65 respectively.

2) High debinding rate and specimens with high strength are obtained by high pressure condensed solvent debinding method. Moreover, by making high temperature holding time adjustable, it makes the subsequent thermal degradation process more flexible to debinding atmosphere and carbon content of the as-debinded specimens controllable.

3) WC-8% Co cemented carbide components can be made by PIM. The transverse rupture strength, hardness, coercivity and density of the as-sintered specimens made by an optimized process are 2.48 GPa, HRA90, 8.95 $kA \cdot m^{-1}$ and 14.72 g/cm^3 respectively. Good shape retention and about 0.02% dimension deviation can be achieved.

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(Edited by HUANG Jin-song)