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## Development of wax oil polyethylene binder for Fe-2Ni powder injection molding<sup>①</sup>

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**[ Abstract ]** A new wax-oil-polyethylene binder was developed for Fe-2Ni powder injection molding. The advantages of both wax-based and oil-based binders were acquired. Moreover, the debinding solvent could be recycled. The miscibility of the binder ingredients and the characteristics were evaluated. The results show that the maximum powder loading can reach 60% (volume fraction), and the two-direction debinding rate is over 2 mm/h. The drying time for 6.37 mm thick samples is less than 20 min. The recycle ratio of the debinding solvent is over 95%.

**[ Key words ]** metal injection molding; binders; solvents

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### 1 INTRODUCTION

Metal injection molding (MIM) is a newly developed technology for forming complicate-shaped metals and alloys<sup>[1,2]</sup>. Debinding is the controlled step in MIM, researches of binders are core of this technique. The usual method for removing binder is thermal debinding, however, the great quantity of gas produced by evaporation and degrading of the binder produced many defects, such as bubbles and cracks in the molded parts; so thermal debinding has to be done very slowly and needs quite a long time<sup>[3]</sup>. Solvent debinding is an effective means to reduce degreasing time, the solvent dissolves binder ingredients from surface to internal of the green part, thus, defects are not easily formed and binders can be removed at a rate of several millimeters per hour<sup>[4]</sup>; but organic solvents used also bring up environment pollution. The effective recycle of the solvent is very important in practical use.

Wax-polyolefin binder systems are widely used in practice, because these binders have quite good rheology and green strength. Thermal debinding is often used for wax-based systems. Solvents are also used for debinding in some papers<sup>[5-9]</sup>, but the degreasing temperature is high and debinding rate is low. Oil-polyolefin binders are reported to have high degreasing rate, however, the green strengths are low and synthetic performances of these binders are not reported<sup>[8,9]</sup>.

In this paper, oil is added into the wax-polyethylene binder in order to get a quickly solvent-removable binder and to acquire the multiple advantages of wax-based and oil-based binders. Moreover

drying and recycle of the solvent selected to dissolve the binder are also investigated.

### 2 EXPERIMENTAL

Carbonyl iron and nickel powders were used as element powders. Wax (PW), oil, polymers were mixed in a self-made mixer for 2 h to form a binder. The binder and Fe-2Ni powders were then mixed for 1 h to get a feedstock for molding. Green strength was tested in three-point bending test using an Instron mechanical tester. Solvent debinding was processed by immersing green parts into a thermal-static solvent. X-ray diffraction patterns were measured by a Japanese Rigaku 3014<sub>z</sub> diffractometer. Heat capacities of the binder and ingredients were obtained by a Duppon 910 DSC instrument. The volume swell ratio of polymers were got by comparing the volume of the polymers before and after their immersing in a solvent.

### 3 RESULTS AND DISCUSSION

#### 3.1 Selection of wax ingredients

The oil and polyethylene (PE) were determined first, then different kinds of wax were added respectively into this oil-PE system. Performances of the wax-oil-PE are listed in Table 1.

The carbonate wax and microcrystal wax were reported to increase the adhesion of the binder and powder, i.e. resulting in higher powder loading<sup>[10]</sup>, but these two kinds of wax were not suitable in CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub> debinding system for their insoluble in these two solvents.

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**Table 1** Influence of wax on performances of wax-oil-PE binder

Wax sort	Compatibility	Green strength	Solubility in CH <sub>2</sub> Cl <sub>2</sub> or CHCl <sub>3</sub>
Carbonate wax	Bad	Middle	Bad
Microcrystal wax	Good	High	Bad
Paraffin wax A(PW)	Good	Middle	Good

**3.2 Determination of debinding solvent**

The solvent is preferable to be dried and recycled at a lower temperature. The boiling point of CHCl<sub>3</sub> is 65 ~ 68 °C, while CH<sub>2</sub>Cl<sub>2</sub> is 39 ~ 41 °C. The debinding abilities of the two solvents at room temperature were compared in Fig.1, which indicated that CH<sub>2</sub>Cl<sub>2</sub> dissolves wax and oil faster than CHCl<sub>3</sub>. So CH<sub>2</sub>Cl<sub>2</sub> was selected as the debinding solvent.

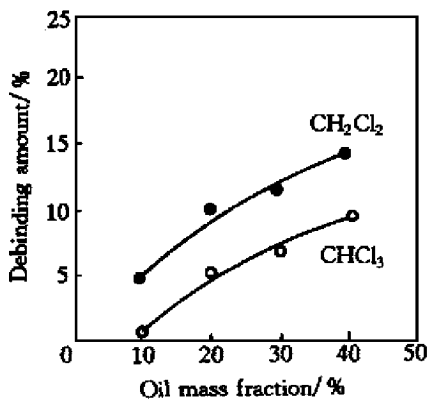


Fig.1 Variation of debinding ability vs oil mass fraction

**3.3 Influence of polymer kinds on debinding process**

Two kinds of polymer, PE and ethylene-vinyl acetate copolymer (EVA) were chosen to investigate their influences on the debinding process. The molded part cracked after immersion for 0.5 h when containing 20 ~ 30 % EVA as bone polymer. Samples containing 20 % ~ 30 % PE existed no defect after immersing in CH<sub>2</sub>Cl<sub>2</sub>. This may be due to the different volume swell ratio of PE and EVA in CH<sub>2</sub>Cl<sub>2</sub>. Fig. 2 shows that the volume swell ratio of EVA is much

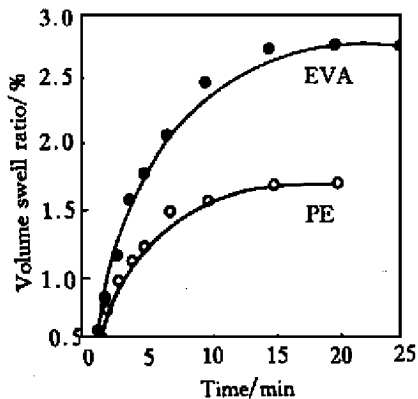


Fig.2 Variations of volume swell ratio of EVA and PE vs time in CH<sub>2</sub>Cl<sub>2</sub> at 35 °C

larger than that of PE. So as the solvent diffusing into the molded part, it swells in the polymer molecules. When the volume swell ratio is large enough, the great stress causes bubbles or cracks.

**3.4 Structure and compatibility of binder**

Fig. 3 shows the X-ray diffraction patterns of the wax-oil-PE and its constituents. This means that wax, oil, PE keep their own structure in the binder system, no chemical interaction exists among these constituents, and the binder is a physical mixture of the ingredients.

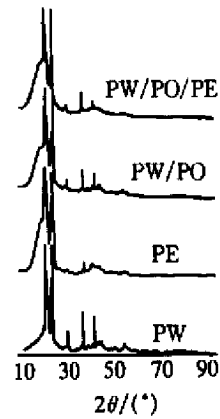


Fig.3 X-ray patterns of P W- P O- P E binder and ingredients

**3.5 Influence of oil addition on mixing torque and maximum powder loading**

Fig. 4 shows the effects of oil addition on mixing steps. The torque of mixing steps decreased with the increase of oil content. Oil flowed and covered the powder to act as a lubricant and reduced the friction between the feedstock and the mixing vessel. Barrels of molding machines were also protected in injection step.

The maximum powder loading ( $\varphi_p$ ) decreased about 1 % (volume fraction) with the addition of oil.

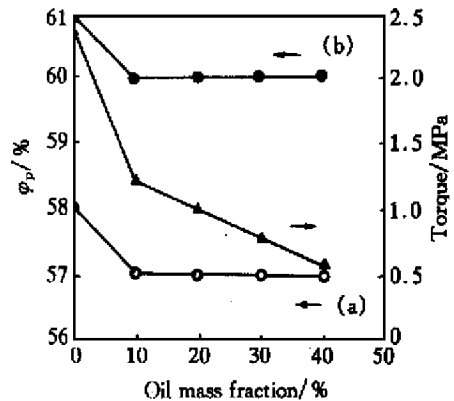


Fig.4 Influences of oil on mixing torque and maximum powder loading  
(a) —PE with high molecular weight;  
(b) —PE with low molecular weight

This may due to the slightly different of rheological behavior between wax and oil. When the molecule weight of the PE was decreased,  $\varphi_p$  was elevated from to 57% ~ 60%.

### 3.6 Effect of oil addition on cooling step and green strength

DSC was used to measure heat capacity ( $C_p$ ) of oil and feedstocks, the  $C_p$  of oil is about 0.24 J/g during 50 ~ 100 °C.  $C_p$  of feedstock is about 0.8 J/g. Different from wax and PE, there was no phase transition and volume shrinkage for oil during cooling after mold was filled. Oil absorbed a part of heat from the powder and decreased the volume shrinkage of the binder, which resulted in the reduction of heat and mechanical stress.

Effect of oil addition on the green strength is illustrated in Fig.5. The green strength decreased a lot with increasing the oil content in the binder. This is because oil is a liquid with no strength. Addition of oil not only causes the decline of the percentage of wax and PE, but also decreases the forces between wax and PE molecules by dispersing in PW crystal and PE molecule chains. In Ref.[11], with the addition of oil to PP or PS, the green strength decreased to as low as below 2 MPa in most cases. German<sup>[1]</sup> concluded that the suitable green strength for metal injection molding should be larger than 5 MPa. So oil content in the binder should be less than 30% in this binder system. When oil content is 40%, oil may have fulfilled wax crystal and PE chains, oil will flow out of the feedstock when the injection pressure is higher.

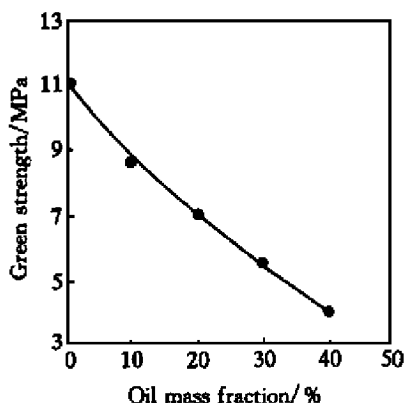


Fig.5 Variation of green strength vs oil content

### 3.7 Effect of oil on debinding rate

Parts of 6.37 mm thick were molded to investigate the debinding rate. Results are shown in Fig.6. The debinding rate was slow without oil in the binder. With increasing the content of oil, the debinding rate increased a lot because liquid-stated oil dissolved and diffused quickly in liquid solvent. However, dissolution of solid-state wax was slower. As temperature increased, the dissolution and diffusion

of wax in  $CH_2Cl_2$  became quicker, so the debinding rate increased. Debound at 35 °C for 3 h could remove 45% of binder. Interconnected tunnel were formed in the binder. So the debinding rate was over 2 mm/h for two direction debinding.

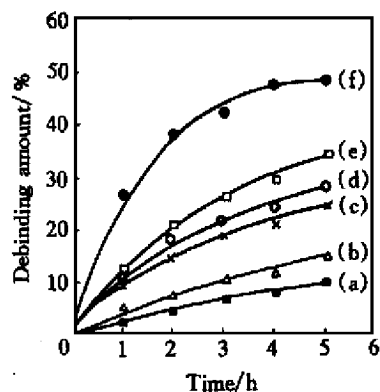


Fig.6 Variations of debinding percentage vs time  
 (a) -20 °C,  $c_0 = 0$ ; (b) -20 °C,  $c_0 = 10\%$ ;  
 (c) -20 °C,  $c_0 = 20\%$ ; (d) -20 °C,  $c_0 = 30\%$ ;  
 (e) -20 °C,  $c_0 = 40\%$ ; (f) -35 °C;  $c_0 = 30\%$

### 3.8 Drying of brown parts and recycle of solvent

The quick drying of brown parts after solvent debinding is also important for decreasing total process time. The 6.37 mm thick brown parts were dried and weighed to calculate the solvent remained in the sample. Fig.7 shows the drying time was less than 25 min at 40 °C for samples of 6.37 mm thick. When drying temperature was elevated to 50 °C, the drying time dropped to 20 min. This time is much less than immersion debinding time. This can be explained as the solvent boils into "vapor" state and move out through the inter-connected tunnel. Elevating the drying temperature results in the diffusion rate increase, so drying gets quicker.

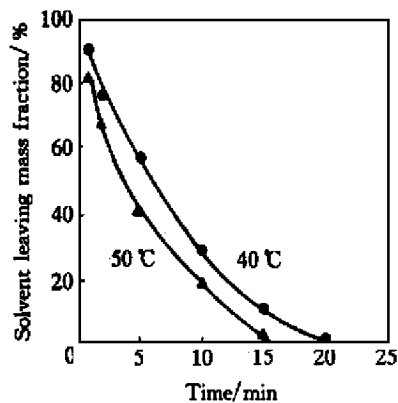


Fig.7 Variations of solvent leaving vs time for 6.37 mm thick parts

The recycle of solvent is a key in MIM production.  $CH_2Cl_2$  solution containing different concentrations of wax and oil was distilled and condensed to get pure  $CH_2Cl_2$ . The Data is plotted in Fig.8. With in-

creasing wax and oil content in the solution, the solvent recycle ratio decreased a little. But it was still as high as 95% even the concentration of wax and oil reached 160 g/L.

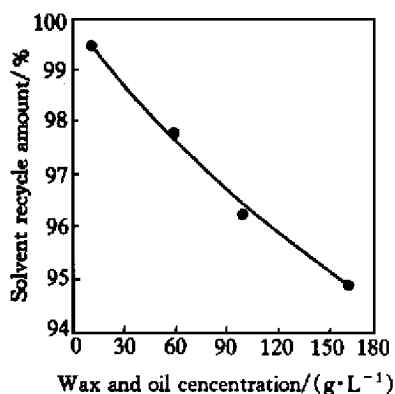


Fig.8 Variation of solvent recycle percentage vs wax and oil concentration for  $\text{CH}_2\text{Cl}_2$

#### 4 CONCLUSIONS

1) Wax-oil-polyethylene is a physical mixing binder system, and every ingredient keeps its own structure.

2) Addition of oil decreases the green strength and maximum powder loading. But it also decreases torque during mixing and increases debinding rate greatly.

3) Feedstock with wax-oil-EVA as binder cracks when debinding in  $\text{CH}_2\text{Cl}_2$ . This is due to the great volume swell ratio of EVA in  $\text{CH}_2\text{Cl}_2$ .

4) The preferable formulation for wax-oil-polyethylene binder is 40:30:30. When using  $\text{CH}_2\text{Cl}_2$  as the debinding solvent to remove wax-oil-PE

binder, debinding rate reaches 2 mm/h, drying time for 6.37 mm thick part is less than 20 min, and solvent recycle ratio is over 95%.

#### [ REFERENCES ]

- [ 1 ] German R M. Powder Injection Molding [ M ]. MPIF NJ, 1990.
- [ 2 ] Wiech R E. Manufacture of Parts from Particulate Materials [ P ]. US 4197118, 1980.
- [ 3 ] Wiech R E. Method and Means for Removing Binder from a Green Body [ P ]. US 4305756, 1981.
- [ 4 ] Lin S T and German R M. Theory of Thermal Debinding [ J ]. Int J Powder Metall, 1987, 23(4) : 237.
- [ 5 ] Yang M J, Atre S V and German R M. Wax-based and PEG-Based Binder Systems Development for Metal and Ceramic Powders [ A ]. Cadle T M and Narasimhaks. Advance in Powder Metallurgy & Particulate Materials Vol.5 Part 19 [ C ]. Princeton, NJ: MPIF 1996. 225.
- [ 6 ] Hens K F and German R M. Advanced processing of Advanced Materials via Powder Injection Molding [ A ]. Lawley A and Swanson. Advance in Powder Metallurgy & Particulate Materials Vol.5 [ C ]. Princeton, NJ: MPIF, 1993 : 153.
- [ 7 ] German R M and Bose A. Injection Molding of Metals and Ceramics [ M ]. Princeton, NJ: MPIF, 1997.
- [ 8 ] Johnson K P. Process for Fabricating Parts from Particulate Materials [ P ]. US 4765950, 1988.
- [ 9 ] Johnson K P. Metal injection molding by the injectamax process [ A ]. Metal Injection Molding ( II ) [ M ]. Princeton, NJ: MPIF, 1989. 17.
- [ 10 ] Martyn M P, James P J and Haworth B. Injection moulding of hardmetal components [ J ]. Metal Powder Report, 1988, 43(12) : 816.
- [ 11 ] Hens K F, Lee D and Lin S T. Integrity of Complex Shape Products by Powder Injection Molding [ J ]. Powder Metallurgy International, 1991, 23(1) : 15.

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