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Solvent debinding of water-soluble binder in powder injection moulding^①

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Abstract: The solvent debinding of water-soluble binder in powder injection moulding (MIM) was investigated systematically, including the effects of solvent types, temperature and the thickness of green parts on the solvent debinding rate. After studying the debinding of a green part with a thickness of 4.26 mm, it was found that, the debinding rate of polyethylene glycol (PEG) in water and alcohol was high initially, and then decreased; however, it would increase with temperature increasing. At room temperature, the dissolution rate of PEG in water was higher than that in alcohol, but the latter would be much faster with temperature increasing because the debinding activation energy in alcohol was $51.44 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, much higher than $24.23 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ in water. With a green part thickness larger than 4.26 mm, the debinding was controlled by diffusion; but with that smaller than 2.36 mm, the debinding was controlled by both dissolution and diffusion.

Key words: powder injection moulding; water-soluble binders; solvent debinding

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1 INTRODUCTION

Recently many debinding techniques have been studied in metal powder injection molding (MIM), including thermal debinding, capillary debinding, catalyzed debinding etc^[1~5]. Compared with other debinding techniques, the solvent debinding has the advantages of little deformation, high rate and easy control of the carbon content^[6]. Currently, the researches on solvent debinding are most aiming at increasing the debinding rate, and seldom at the debinding theory. Moreover different experiments found different debinding rules. Kevin had established that the debinding duration was proportional to the thickness of green parts^[7], while Lin had found that the square of the debinding duration was proportional to the thickness of green parts^[8]. PEG based binder has been considered as a very promising water-soluble binder for MIM. PEG can be dissolved in water and alcohol, but as for its dissolution rates in those solvents there is still uncertainty^[9,10]. This work aims at studying

the solvent debinding dynamic of PEG based binder in water and alcohol.

2 EXPERIMENTAL

2.1 Preparation of samples

Carbonyl Fe-2Ni powder with mean particle sizes of $3.97 \mu\text{m}$ and $2.60 \mu\text{m}$, and the binder consisting of 70% PEG and 30% polymethyl methacrylate (both in mass fraction) were used. The metal powder and binder were mixed at 150°C for 1.5 h, and then injection molded to $\phi 20$ mm cylinders with different thickness.

2.2 Solvent debinding

The lateral side of the green parts was sealed, in order that it contacted the solvent only through longitudinal side. The green parts were immersed in distilled water or alcohol. When using distilled water, in case of the oxidation of metal powder, N_2 was filled for 5 min. After debinding, the green part was dried and weighted to calculate the loss of PEG.

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3 RESULTS

3.1 Effect of debinding temperature and solvent on debinding rate

The relationships between PEG loss and immersion time in water and alcohol are shown in Fig.1 and Fig.2 respectively (with a sample thickness of 4.26 mm) . Both figures show that PEG loss increases initially very fast with debinding time, then slowly; and is accelerated with temperature increasing. It is also found that at 25 °C PEG loss rate in alcohol is slower than that in water, but is higher when temperature increases. For example, at 40 °C for 6h, 65.77 % (mass fraction, %) PEG dissolved in water while 83.33 %(mass fraction, %) in alcohol. The difference in the debinding dynamic in those two solvents accounts for the different results of references [9] and [10]; reference [9] reported that the debinding rate in water was higher than that in alcohol while reference [10] was on the contrary.

3.2 Effect of sample thickness on debinding rate

The effect of the sample thickness on the debinding rate is shown in Fig.3 . It can be seen that for all the samples the PEG loss increases with debinding time, but PEG loss rate decreases with the sample thickness increasing. The results are different from that in reference [6],

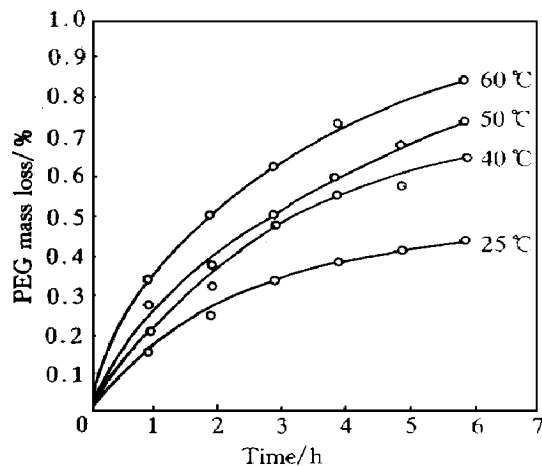


Fig.1 Influence of temperature on water debinding rate

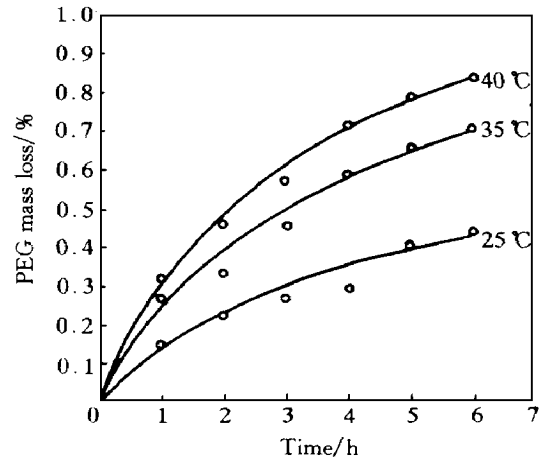


Fig.2 Influence of temperature on alcohol debinding rate

Fig.3 Influence of part thickness on debinding rate

which reported that there was a linear relationship between the debinding time and the sample thickness (< 10 mm) .

4 DISCUSSION

4.1 Debinding model

The solvent debinding process includes following steps: low molecular solvent diffuses into the green part and contacts the binder, the solvent expands and dissolves the soluble binder, the dissolved binder diffuses to the surface of the green part and finally to the solvent. Both of the

dissolution of the binder and the interdiffusion between the binder and the solvent may be control steps in debinding. Therefore, there are two possible rules for solvent debinding:

(1) At a large sample thickness and high dissolution rate, as the diffusion path of the solvent and the dissolved binder is long, diffusion control is more possible.

When debinding is controlled by diffusion, it can be deduced from the Fick's second law^[7]:

$$-\ln F = D_{bs} t \pi^2 / 4 L^2 \quad (1)$$

$$\ln(-\ln F) = \ln \frac{D_0 t \pi^2}{4 L^2} - \frac{E}{R} \cdot \frac{1}{T} \quad (2)$$

while

$$D_{bs} = D_0 \exp(-E/RT) \quad (3)$$

where $F = C_R / C_i$ —the residual fraction of the soluble binder, D_0 —experience constant, D_{bs} —the diffusion coefficient of the soluble binder in binder-solvent at T_k , t —debinding time, L —half of the sample thickness, T —debinding temperature, E —activation energy, R —constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$).

(2) At a low dissolution and diffusion rate of the binder, debinding is controlled both by diffusion and dissolution of the binder. Suppose the dissolution of the binder is one-order reaction, then the initial concentration C_i for diffusion is controlled by dissolution. Also suppose C_0 is the concentration of soluble binder, then from the one-order reaction dynamics, there is

$$C_i = C_0 e^{At} \quad (4)$$

where A is reaction constant. Combined with equations (1) and (4), there is

$$-\ln F' = -At + D_{bs} t \pi^2 / 4 L^2 \quad (5)$$

where $F' = C_R / C_0$, still the residual fraction of the soluble binder. In both equations (5) and (1), $(-\ln F)$ and $(-\ln F')$ have a linear relationship with $1/L^2$, the difference lies in that

the intersection is zero under diffusion control and is non-zero under mixed control.

4.2 Verification of model

From Figs. 1 ~ 3, $\ln(-\ln F)$ and $\ln F$ can be calculated. Combining with the sample thickness $2L$, the relationships between $\ln(-\ln F)$ vs $1/T$ and $-\ln F$ vs $1/L^2$ are found in Figs. 4 ~ 6.

It can be inferred from the linear relation in Fig. 4 and Fig. 5 that at the sample thickness of 4.26 mm the debinding in water and alcohol is controlled by diffusion. According to Eqn. (2) and the slope of the lines, the activation energy E can be obtained. Also D_0 was obtained from the intersection of the lines, and the diffusion coefficient of the soluble binder in binder-solvent system at 25 °C was obtained from the D_s vs D_0 relationship Eqn. (3), as shown in Table 1.

Fig. 4 Relationship of $\ln(-\ln F)$ vs $1/T$ in water debinding

The data in Table 1 indicate that the diffusion coefficients of solvent debinding are all at the order of $10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$, very similar to that in

Table 1 Kinetic parameters of solvent debinding process

Debinding parameter	Water	Alcohol
Diffusion coefficient / $10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$, 25 °C	1.57	1.32
Activation energy / $\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	24.23	51.44
Kinetic equation	$-\ln \frac{C_R}{C_i} = \frac{2.51 \times 10^{-6} t}{L^2} \exp(-\frac{2900}{T})$	$-\ln \frac{C_R}{C_i} = \frac{1.33 \times 10^{-6} t}{L^2} \exp(-\frac{6187}{T})$

Fig.5 Relationship of $\ln(-\ln F)$ vs $1/T$ in alcohol debinding

reference [8], and that the activation energy of alcohol debinding is $51.44 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, far higher than that of water debinding. This result accounts for the debinding rate in alcohol varied from slower to higher than that in water.

Fig.6 indicates that the controlling factor of solvent debinding varies with the green part thickness. There are two lines in this figure. At thickness larger than 4.26 mm (8.10 mm, 10.40 mm) the line passes the origin point, suggesting a diffusion control at large green part thickness; at thickness smaller than 2.36 mm (1.52 mm, 1.00 mm) the line does not pass the origin point, suggesting a mixed control.

5 CONCLUSIONS

Investigation on the PEG based binder for MIM shows that at room temperature the debinding rate in water is faster than that in alcohol, while at 40 °C it is slower because the debinding activation energy in alcohol is higher than that in water. At sample thickness larger than 4.26 mm, the debinding is controlled by diffusion, and at sample thickness smaller than 2.36 mm, it is controlled by both solvent dissolution and diffusion.

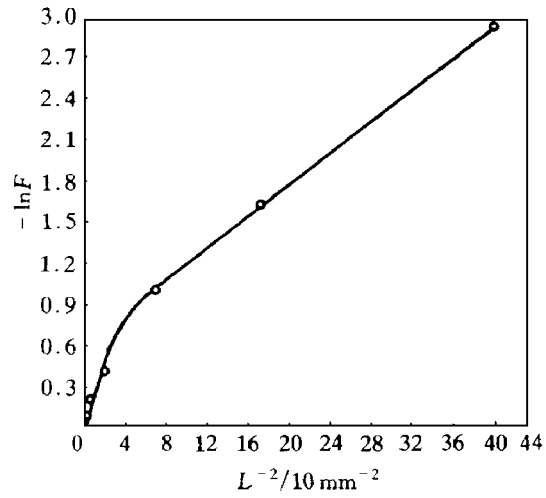


Fig.6 Relationship of $(-\ln F)$ vs $1/L^2$ in water debinding

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