DEBINDING MECHANISM AND KINETICS FOR PW IN PW-WC FEEDSTOCK UNDER AIR ATMOSPHERE①

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ABSTRACT The feedstock, a binder-powder plastic body consisting of paraffin wax (PW) and WC powder, is of great importance for hard metal injection molding (MIM) and extrusion processing. The debinding mechanism and kinetics for a specific PW-WC feedstock under air atomsphere have been investigated in terms of the experimental results of differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The investigations have shown that it is a very complex chemical and physical process, in which the paraffin wax ketonization and the sublimation of both the binder and the binder ketonization products are involved. The kinetic behavior obeys one order reaction law, with activation energies of 60.1 kJ·mol^{-1} and 95.6 kJ·mol^{-1} for PW system and PW-WC feedstock system respectively.

Key words MIM PW-WC feedstock debinding process mechanism kinetics

1 INTRODUCTION

Metal injection molding (MIM) and metal powder extrusion technology are new emerged technologies in powder metallurgy for manufacturing complex metallic components in near net-shape. Their preferable features include near net-shaping, complex shape production, high performance and productivity, relatively wide range of applications, and advancement of formability for new advanced materials[1]. However, many aspects of these new technologies have to be further studied before their benefits can be fully realized, among which the binder removal process is a very important step. This is because the debinding process for the MIM or extrusion forming part is a process that can take several days. From the economical point of view, the time duration shortening for this technological step is of great benefits. For this reason, many investigators, like Angermann *et al*[2] and Rhee *et al*[3], focus on the fundamental research for the debinding process. In this article, the mechanism and kinetics for a specific PW-WC ingredient debinding process have been investigated on the base of DTA and TGA and fourier transform infrared spectrometry (FTIR) experimental results.

2 EXPERIMENTAL PROCEDURES

2.1 *Feedstock Preparation*

The starting materials used in the experiments were commercial WC powder with less than 10 μm mean particle size and paraffin wax (PW) with chemical purity grade. The feedstock with 92∶8 ratio of WC powder and PW in weight was mixed at 373 K in a sigma mixer made in Germany for 4 h. The prepared feedstock was extruded on the Dorst extruder made in Germany and showed good extruding performance.

2.2 *Experimental Conditions*

(1) DTA experimental conditions

This experiment was performed on a TAS-100 DTA apparatus under the following terms:

a) reference sample: α-Al_2O_3

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b) heating rate: $10\ K \cdot min^{-1}$

c) thermal differential measurement range: $\pm 50\ mV$

d) atmosphere: air

(2) TGA experimental conditions

The experiments were carried out on Dupont 9900 TGA instrument under the following conditions:

a) heating rate: 5 and $10\ K \cdot min^{-1}$

b) samples: PW and PW-WC feedstock

c) atmosphere: air

3 RESULTS AND DISCUSSION

The typical DTA pattern for PW used in the feedstock as a binder is shown in Fig. 1. There was an endothermic peak at about 329 K due to the melting of the paraffin wax. A broad exothermic peak was present at 530 K. Between 517 K and 650 K, a thermal oscillation with a temperature period of about 25 K was formed. For the feedstock system, the result was the same as the above pattern. The TGA curves for PW and the feedstock are presented in Fig. 2. They indicated that for PW system the weight loss became noticeable at 429 K, and violent from 453 to 548 K, but for the feedstock system, the former temperature was 453 K, the temperature range for quick weight loss was 453 ~ 573 K. These differences suggested that due to the introduction of WC powder, the paraffin wax removal process be retarded. In terms of the DTA experimental results that a broad exothermic peak was formed from 457 to 573 K, which coincided with the quick weight loss temperature range of the feedstock system, it could be inferred that the binder was oxidized during the above temperature range. Meanwhile, the weight loss (77%) calculated from TGA curves suggested that the binder sublimation process take place during the same temperature range as mentioned above. Fig. 3 is the FTIR patterns given by Zhang[4] for the binder at different temperatures under the air atmosphere. It showed that with the temperature increase, the absorption band at $1456\ cm^{-1}$ resulted from the unsymmetrical vibration of the $+CH_2+$ base group in the binder molecule was weakened, but the absorption band at $1\ 703\ cm^{-1}$ produced by carbonyl base group symmetrical vibration was merged and enhanced. This meant that when temperature was high enough, binder would be carboxylated. According to the works of Pan[5], the products of the binder carboxylation were ketonic compounds. Thus, the following reaction mechanism could be postulated.

$$\ldots\!-\!R'\!-\!CH_2\!-\!R''\!-\!CH_2\!-\!R'''\!- \ldots (1) + \frac{3}{2}O_2(g) \rightarrow \ldots -R'\!-\!CO\!-\!R''\!-\!CO\!-\!R'''\!- \ldots + H_2O(g) \quad (1)$$

Fig. 1 The typical DTA pattern for the paraffin wax (PW)

Fig. 2 TGA curves for PW system (●) and PW-WC system (○)

solid line —10 K·min^{-1}; dash line —5 K·min^{-1}

...—R—CH_2—R″—CH_2—R‴— ... (l) → ...–

...—R′—CH_2—R″—CH_2—R‴— ... (g) (2)

By this reaction mechansim, some experimental facts could be explained. For instance, the thermal oscillation within the temperature range of 457 ~ 573 K on DTA pattern might originate from the interaction between reaction (1) exothermic effect and reaction (2) endothermic effect. During the debinding process, reaction (2) took the main responsibility for the weight loss. Due to the binder sublimation and ketonization, the proportion of the carbonyl was increased, which resulted in increase of the intensity of the absorption peak at 1 703 cm^{-1} base group, just as shown in Fig. 3. When the temperature was higher than 573 K, the main part of the binder was removed, the residual of the binder was present in ketonic products. With further increase of temperature, those compounds were oxidized and sublimated, and the thermal oscillation emerged once again on the DTA pattern from 573 to 650 K.

The relationship curves between the weight loss and the reaction time for PW system and the feedstock system are presented in Fig. 4. It could be found that the heating rate had great effect on the weight loss. When it rised from 5 to 10 K·min^{-1}, the time required for the same weight loss would be doubled. For example, it took about 53.5 min for PW system to lose 80% binder at the heating rate of 5 K·min^{-1}, but only about 26.6 min at the heating rate of 10 K·min^{-1} for the same weight loss. For the feedstock system, to lose 80% binder needed 53.5 min at 5 K·min^{-1}, but 29.2 min at 10 K·min^{-1}. When the heating rate was slow, like lower than 5 K·min^{-1}, the curves plotted by the weight loss *vs* the reaction time for both systems resemble in appearance and amount. The reason was that in this case there was enough time for the binder to move out from the inner part of the feedstock by diffusion and infiltration, that is, the resistance of the WC powder on the binder removal was not significant. On the other hand, once the heating rate was high enough, like over 10 K·min^{-1}, the mechanism as mentioned above was gone, and the hindrance effect of the WC powder on the debinding process would be observed.

According to the Coasts-Redfern's[6] non-isothermal kinetic analysis method, the kinetics for the debinding process could be described by the following equation:

Fig. 3 The typical FTIR patterns for PW at different temperatures under air atomsphere[4]

Fig. 4 The relationships between the weight loss and the reaction time for PW system and PW-WC system

○—PW-WC; ●—PW;
solid line—10 K·min^{-1};
dash line—5 K·min^{-1}

$$\frac{d\alpha}{dt} = K(1-\alpha)^n \quad (3)$$

where α is the weight loss fraction, t is the reaction time, K is the reaction rate constant, and n is the reaction order. The dependence of the reaction rate constant on temperature could be expressed by Arrhenius equation as

$$K = A\exp[-E/(RT)] \quad (4)$$

where E is the debinding activation energy, and R is the gas constant, A is the pre-exponential factor. If $dT/dt = \beta$ is a constant, for the reaction process with $n = 1$, the kinetic equation can be simplified as

$$\lg[-\frac{\lg(1-\alpha)}{T^2}] = \lg\frac{AR}{\beta E}(1-\frac{2RT}{E}) - \frac{E}{2.3RT} \quad (5)$$

For the reaction process with $n \neq 1$, we have

$$\lg[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}] = \lg\frac{AR}{\beta E}(1-\frac{2RT}{E}) - \frac{E}{2.3RT} \quad (6)$$

In general, the binder removal process follows equation (5), and the first term on the right hand side, $\lg\frac{AR}{\beta E}(1-\frac{2RT}{E})$, could be regarded as a constant approximately. On the base of the TGA experimental results, α and T values could be determined. Thus, the activation energy could be obtained by $\lg[-\lg(1-\alpha)/T^2]$ *vs* $1/T$ plots. The results are shown in Fig. 5, which indicats that equation (5) could describe the kinetics for the binder removal process properly. The activation energies were 60.1 kJ·mol^{-1} for PW system and 96.5 kJ·mol^{-1} for the feedstock system. The difference of the activation energies for both systems suggested that the WC powder introduction increase the energy rampart for the debinding process.

Fig. 5 The relationships between $\lg[-\frac{\lg(1-\alpha)}{T^2}]$ and $\frac{1}{T}$ for PW system and PW-WC system

1—PW-WC; 2—PW

4 CONCLUSION

For the binder removal process of the feedstock formed by PW mixed with WC powder, which is widely used in MIM or extrusion technology, two kinds of physical and chemical process are of great importance. One is PW ketonization, and the other is PW and its ketonization product sublimation. The binder removal process for PW system and PW-WC feedstock system are subject to the one order reaction law with activation energies of 60.1 kJ·mol^{-1} for PW system and 96.5 kJ·mol^{-1} for PW-WC feedstock system.

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