THERMAL DEBINDING OF A NEW BINDER[①]

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ABSTRACT　The thermal debinding of new binder in cemented carbide's extruding compacts and its debinding mechanism have been studied here. When the low molecular mass components (LMMC) in these new binder systems are changed, their thermogravimetric analysis (TGA) curves are very different. As the paraffin wax is the main LMMC, the new binder has been removed in two different temperature zones; while the temperature is at 240 ℃, the LMMC have been almost totally debinded. When a kind of short-time polymer X is the main LMMC, there are no zones of low temperature debinding in the TGA curves. The differential thermal analysis curves show that a new single-phase microstructural material composing with X and polymer A has been made in these cases.

Key words　cemented carbide　extrusion pressing　binder　formulation　thermal debnding

1　INTRODUCTION

The formulation and debinding of binders are very important while the cemented carbide parts are moulded by extrusion process techniques. It is a very important factor which decides the part's properties and costs. The extrusion process requires that the surface of the extruding gross-parts be very smooth and the interior zones be not damaged and the operations be easy and stable, therefore the binder systems composed of only one kind of polymer can't satisfy above needs about the binder and good design of binder formulation is very necessary. On the other hand, because the general used thermal debinding technique about the cemented carbide extruding gross-parts possess rather large production costs, the debinding rate must be available, and the binder can be effectively expelled without a risk of parts cracking and the effect on the carbide weight percent is small. The newly developed binder systems must be easy to extrusion moulding and debinding. In recent years, a lot of research jobs on new binders have been carried on[1-3]. In China, some factories and institutes try to develop practical new binder systems. In this paper, general considering of the requirements of extrusion moulding and debinding together, we probe into the newly developed binder formulation and its thermal debinding mechanism.

2　EXPERIMENTIAL PROCEDURES

In this paper, the weighted middle-diameter of WC-Co powder is 3.34 μm, the tap density is 4.80 g·m^{-3}, and the pycnometer density is 14.05 g·cm^{-3}. The SEM photograph of WC-Co powder is shown in Fig. 1. The LMMC in the newly developed binder systems is praffin wax (PW) and/or stearic acid (SA) and/or a kind of short-time polymer (X), these LMMC and a kind of polymer A were plasticized by the XSS-300 rheometer, then the binder and WC-Co composite powders were mixed and plasticized. The prepared feedstocks compounded with new binder and WC-Co were extruded on the XSS-300 rheometer. The extruding rod's surface is very smooth, which shows good extruding performance. The feedstock's formulation and the

extrusion parameters are listed in Table 1 and
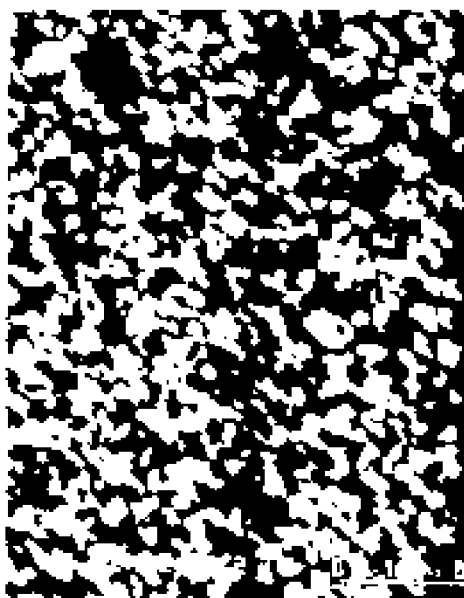
**Fig. 1 Scanning electron micrograph of
WC-Co copowders**

Table 1   Formulation of feedstocks(%)

Constituents	BP_1	BP_2
PW	1. 57	/
SA	0. 39	0. 48
X	/	1. 95
A	2. 94	3. 62
WC-Co	95. 10	93. 95

the machine conditions used during compounding are as follows:

Screw diameter/ mm 20

Screw L/D ratio 25

Screw speed / r•min^{-1} 31

Barrel temperatures, 95– 105– 110– 100
  feed to exit/ ℃

The DTA experiments were performed on Dupont-1600DTA under the following conditions: (1) reference sample, α-Al$_2$O$_3$; (2) heating rate, 5 ℃ • min^{-1}; (3) atomsphere, high pure N$_2$, flow rate 100 ml•min^{-1}. For a part of the samples the changing temperature and isothermal TGA tests were carried out by means of Dupont-9900 TGA. The TGA experimental conditions are the same as DTA except the temperature procedures. In TGA experiments, for changing temperature processes the heating rate was 5 ℃•min^{-1}; for isothermal measurements,

the heating procedures were : firstly, from room temperature to (T– 40) ℃ (T is the isothermal temperature), heating the sample with a heating rate of 20 ℃•min^{-1}, then at (T– 40) ℃ for 3 min; and following that heating the sample to (T– 20) ℃ with a heating rate of 2 ℃•min^{-1}, again at (T– 20) ℃ for 3 min; lastly with a heating rate of 20 ℃•min^{-1}, heating the sample to the isothermal temperature T, and then at this temperature for 1~ 3 h.

3 RESULTS AND DISCUSSION

The mass percent of polymer A in the newly developed binder systems is 60% and the LMMC' mass percent is 40%, their volume percents are almost the same as the mass percent for the difference of density of all kinds of components in the new binders is very small. If the mixture with the even microstructure is formed when the polymer A is mixed with LMMC, the mixture's glass-change temperature (T_g) should be lower than that of polymer A. The difference ΔT_g between them should be in direct proportion to the volume percent of LMMC[4]. Fig. 2 shows the DTA curves under our experimental conditions. The glass-change temperature T_g of sample BP$_1$ is about 105 ℃ and that of sample BP$_2$ is about 95 ℃. And we know that the T_g of polymer A is 100 ℃[4]. So we can surely deduce that the LMMC in sample BP$_1$ is not effectively mixed with polymer A and in sample BP$_2$ a new melting-mixture with the even microstructure has been formed after mixing process (from Fig. 3 we can also deduce the result). In fact, we have observed that paraffin wax can not effectively disperse to the degree of molecular scale in the bone of polymer A and that the paraffin wax accumulates in the interface of polymer A chains with the shape of micro-points. And we also find that SA is easy to disperse and it is an effective surface active agent and lubricant.

Fig. 3 shows the TGA curves of sample BP$_1$ and BP$_2$ under the changing temperature. We can deduce that the debinding process of sample BP$_1$ can been divided into two zones: while the temperature is lower than 240 ℃, there is a
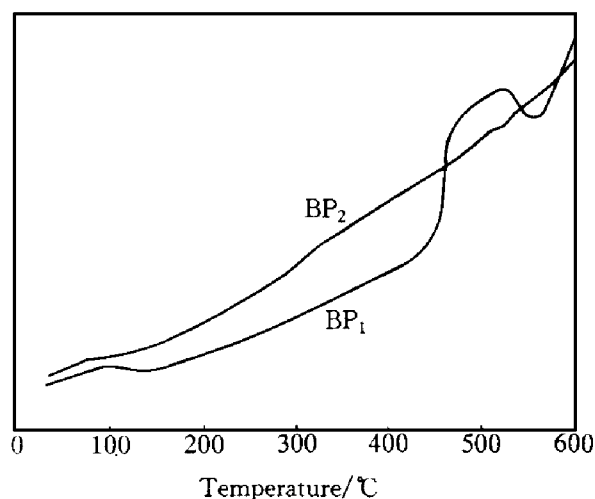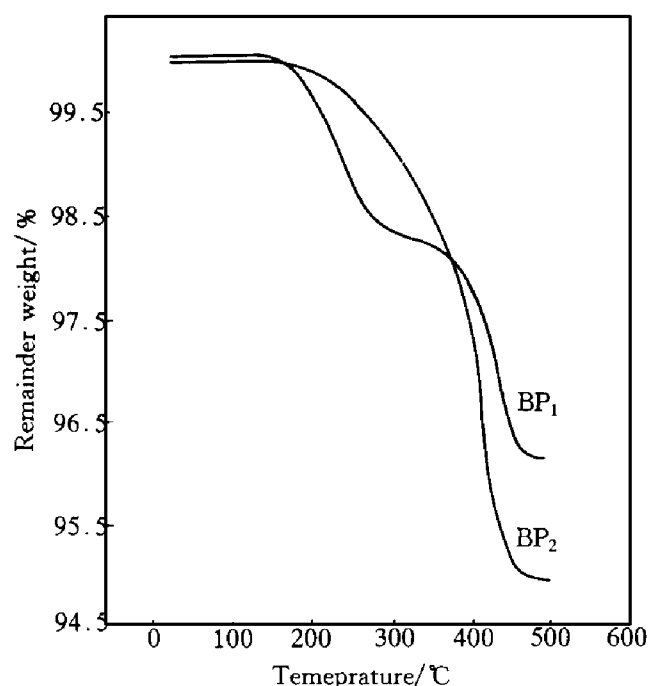
Fig. 2   DTA curves

Fig. 3   Changing temperature TGA curves

low-temperature debinding, while the temperature is high up to 350~ 450 °C, there is a high-temperature debinding process. The two debinding zones are almost introduced due to the debinding characteristics of LMMC or polymer A, respectively. Fig. 3 also shows that the feedstock of sample BP₂ can't possess the debinding characerisitics such as sample BP₁. Here when the temperature is lower than 250 °C, the debinding rate is rather slow, and the debinding weight fraction is very small, while the temperature is 370~ 450 °C, the binder components are debind-

ed fastly, as the temperature is not lower than 470 °C, the binders are almost expelled over. The TGA curve of sample BP₁ also strongly proves that the LMMC in sample BP₁ are separated from polymer A in the scale of microstructure and they can not be effectively mixed.

The purpose of adding LMMC into binder systems is to increase the binder's plasticity, so that the extruding process is easy to operate and control. On the other hand, more important purpose may be to change the debinding characteristics. Fig. 4 shows the TGA isothermal curves of sample BP₁ under different temperatures. When the temperature is lower than 147 °C, the debinding rate is very slow, the debinding weight fraction is very small, and prolonging the debinding time is not very effective; while the temperature is up to 237 °C and retained for about 2 h, the LMMC in the binder is basically debinded. The low-temperature zone's curves show the exponential function rule of debinding. This result is rather identical with Fig. 3. We also have studied the LMMC' debinding and its mechanism and observed that the LMMC' debinding mechanism in the PW/A model binder system is under the control of diffusion process. Because the debinding process under the low-temperature zone is located at the initial stage, so it is very sensitive to defect
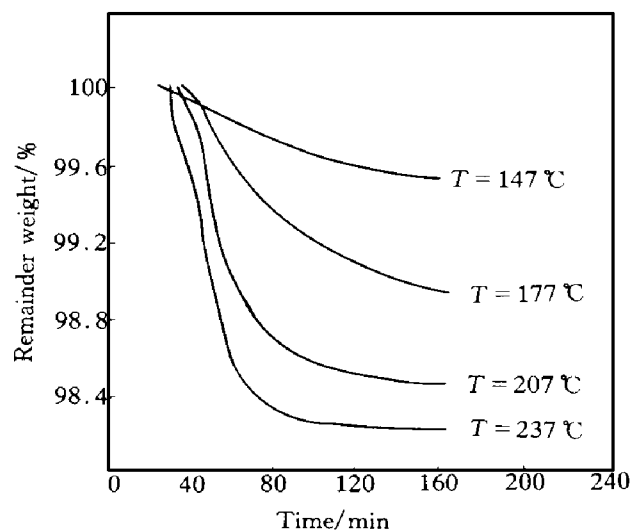

Fig. 4   Isothermal TGA curves

formation in extruding rods. By controlling the debinding temperature, heating rate and atmosphere, the preliminary large hollow defects, the surface's cracking and blisters can be avoided during the thermal debinding process, so that the pre-sintering rods with good performance can be formed after the debinding procedures. But for sample BP_2 feedstock, because the binder's debinding mass fraction is very small when the temperature is lower than 250 ℃, we did not probe into the thermal debinding mechanism under the low-temperature stage.

4 CONCLUSIONS

Both of feedstock with two kinds of different binder formulations can be extruded successfully, but the binder's microstructure is different. By changing the LMMC' formulation, the binder's TGA curves are very different. This reflects the different debinding characteristics. When the LMMC are PW and SA, there is a low-temperature debinding zone which is useful to debinding procedure; when the LMMC are short-time polymer X and SA, the debinding rate is very slow at low-temperatures. These low-temperautre debinding characteristics can cut down the micro-hole defects' forming rate in the initial debinding stage. It is useful to the debinding procedure's controlling and operations, so as to make excellent debinding pre-sintering rods.

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