LOW TEMPERATURE THERMAL DEBINDING BEHAVIOR
OF WAX-BASED MULTI-COMPONENT BINDER
FOR TUNGSTEN HEAVY ALLOY[①]

Fan Jinglian, Huang Baiyun, Qu Xuanhui and Li Yiming
State Key Laboratory for Powder Metallury,
Central South University of Technology, Changsha 410083, P. R. China

ABSTRACT   To control the defects in thermal debinding stage, low temperature thermal debinding behavior of wax in the multi-component binder for tungsten heavy alloy was studied. The wax burnout temperature is below 250 ℃, at which the defects mainly occur. The debinding rate is controlled by the diffusion of wax in the polymer to the inner surface of pores and then to the external environment. The experiment proved the amount of removed wax as an exponential function of time, the reciprocal sample thickness and temperature coeffcient.
Key words   thermal debinding   multi-component binder   tungsten   heavy alloy

1   INTRODUCTION

Powder injection moulding (PIM) is a new process for manufacturing near net shape parts with advantages of low cost, high performance and shape complexity[1]. In PIM, the thermal debinding process has been considered to be the most critical step[2-4], the quality of the sintered part and the production cost are strongly determined by this step, incorrect debinding process could lead to crack, pore, bubble and the dilatory response of powder compacts. Many researchers have investigated the thermal debinding process[5-10] and mechanism. Using single component system, German[1,11] has modeled thermal debinding by three mechanisms: diffusion control, permeation control, fluid wicking. The binder removal may behave quite differently in multi-component binder system[12] and agglomerated irregular fine particles[13]. In two or multi-component system, Wang *et al*[2,3] considered the removal rate is controlled by the degradation of low temperature binder component such as stearic acid and wax in the initial thermal debinding stage, Barone[14] proposed liquid transport and evaporation of wax controlled the initial stage, and Angermann[15] suggested the debinding rate of SA is controlled by diffusion of SA in the thermoplastic in two component system. Raman[16] simulated binder removal mechanism and validated diffusion is important. Particle size and shape also affect binder removal[17,18], irregular and fine particles easily give rise to adsorbed layer on the high energy surface, the thickness of the absorded layer can reach 150 nm[19,20]; particularly, wax and polymer can priorly attach to the inner pores of the agglomerated fine particles[21]. The layers prevent binder flow and diffusion. Therefore, binder removal behavior would be much more complex in the multi-component binder and agglomerated fine particles, correct understanding binder removal behavior is important to control the defects. In the present work, paraffin wax was used as a main low temperature binder component, and its removal behavior was studied in the multi-component binder and tungsten heavy alloy with agglomerated fine tungsten powders.

2　EXPERIMENTAL

Wax based multi-component binder system was used , with paraffin wax (PW) as main component , high density polyethylene (HDPE) and polyethylene vinylacetated (EVA) as backbones , and stearic acid (SA) as coupling agent . Binders were prepared by heating and stirring 74 %(mass fraction , %) PW , 25 %(HDPE + EVA) and 1 % SA for 2 h . EVA has good adhesion on metal powder and lower melting point and lower viscosity[16] . Mixed 95 % tungsten powder with balance of 3 .5 % nickel powder and 1 .5 % iron powder , with mean particle sizes of 2 .91 , 2 .66 and 6 .50 μm respectively . The binder and mixed powders were then mixed in the z-blader mixer for one more hour , powder loading is 54 %(volume fraction , %) , mixed temperature is 115 ℃; then after pelletizing and moulding , three kinds of samples were prepared , whose thickness are 2 .40 , 3 .90 and 10 .50 mm respectively . Finally , buried the samples in the 8 .25 μm alumina powder , heated the samples to different temperature at 3 ℃/ min and held them for different hours and investigated PW removal behavior .

3　NUMERICAL RESULTS AND DISCUSSION

3 .1　Influences of various parameters on PW removal

In the initial thermal debinding stage , main low melting point binder PW was firstly removed , while SA removal was neglected , and small pore channels left . The amount of PW removal increased with the increasing of temperature and the reciprocal sample thickness and time , as shown in Fig .1 and Fig .2

With increasing temperature and sample thickness , the risk of crack increased greatly , the amount binder loss at low temperatures increased slowly . For the sample thickness above 10 mm , little binder could be removed and crack easily occurred even below 140 ℃ . As the temperature reached 200 ℃ , crack formed even for 2 .40 mm thin compacts .

3 .2　Liquid phase transport and evaporation

In the initial stage , main low temperature binder PW firstly begin to be soft , molten and less viscous and dilatant . This gives rise to strong capillary force between fine tungsten powders , and liquid transport takes place . The prerequisite for sufficient liquid transport to surface is that the capillary force of wicking powder is over that of the metal powders , that is[1]

$$D_c > D_w , \quad \alpha_w > \alpha_c \qquad (1)$$

where　D_c —the diameter of compact powder , D_w —the diameter of wicking powder , α_w —the permeability of wicking powder , α_c —the permeability of compact powder .

Otherwise , sufficient liquid flow couldn't occur . Powder factors also affect debinding .
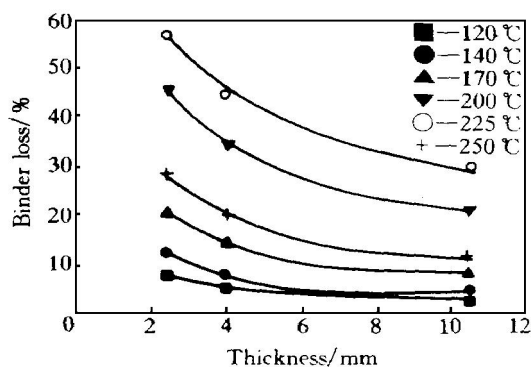

Fig .1　Amount of removed binder as a function of temperature and sample thickness
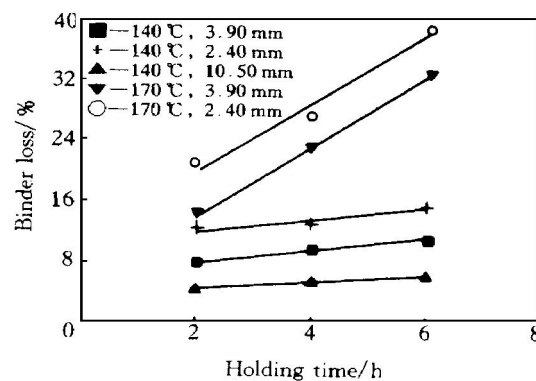

Fig .2　Amount of removed binder with debinding time

Pores shape, size and surface determine the flow resistance. Irregular fine particles have high energy surface and various pores, adsorbed layer easily forms on the high energy surface and inner pores of agglomerated powder. Pendulous binding is easily formed and precluded liquid transport. Thus, liquid transport could not be the rate-control factor of PW removal.

Curved surface affects the vapor pressure as described by the Kelvin equation:

$$KT\ln(\ p/p_0) = \sigma_{LV}\ \Omega\omega(1/\ Y_1 + 1/\ Y_2)$$

$$(2)$$

where p_0—the equilibrium vapor pressure, p—the vapor pressure over the curved surface described by the curvatures Y_1 and Y_2, K—Boltzmann constant, T—the absolute temperature, σ_{LV}—the liquid-vapor surface energy, ω—the atomic volume.

The vapor pressure over fine particle curved surface is even lower than the expansion pressure at low temperature[1], so debinding by PW vaporation is not dominant. If the rate of PW removal is controlled by vaporation, the vaporation rate will remain constant[1] at certain temperature, and the vapor pressure is: $\Delta p \sim p_e \exp(-Q/KT)$, here p_e—the vapor pressure constant, Q—the activation enthalpy. The vaporation rate will be proportional to the vapor pressure at different temperatures, therefore the ratio of removed binder is as an exponential function of the reciprocal temperature, this is:

$$\ln(1 - \frac{m(t)}{m(0)}) \sim -\frac{1}{T} \qquad (3)$$

where $m(t)$—the amount of residual binder of sample after debinding, $m(0)$—the amount of binder of sample without debinding.

The experimental results in Table 1 showed that Eq. (3) is confirmed just at 105 ℃, 120 ℃ and 140 ℃. It is suggested that little amount of PW removal is dependent on surface vaporation. With increasing temperature, the ratio of PW removal is not exponential to the reciprocal temperature, the debinding rate is not held constant at one temperature, as shown in Fig. 3 and Fig. 4.

3.3 Diffusion and permeation

With increasing temperature, liquid or gas

diffusion and gas permeation take place, due to PW vaporation and degradation. For a mixture of liquid and vapor, the gas has no permeability

Table 1 Holding two hours at different temperature, the value of

$$\ln(1 - \frac{m(t)}{m(0)})/\frac{1}{T}$$

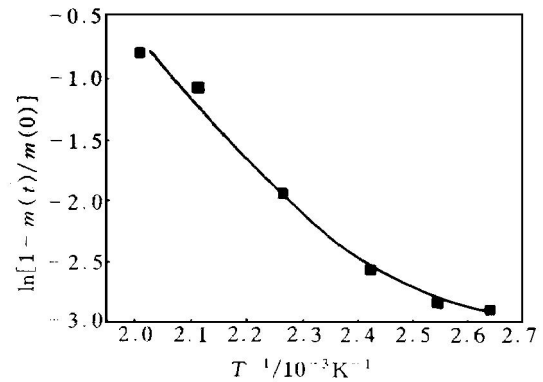| $T/$ K	$\ln(1 - \frac{m(t)}{m(0)})/\frac{1}{T}$
378	- 1.12
393	- 1.12
413	- 1.06
443	- 0.86
473	- 0.51
498	- 0.39
523	- 0.84

Fig.3 Logarithm of PW loss $\ln(-\frac{m(t)}{m(0)})$ against reciprocal temperature
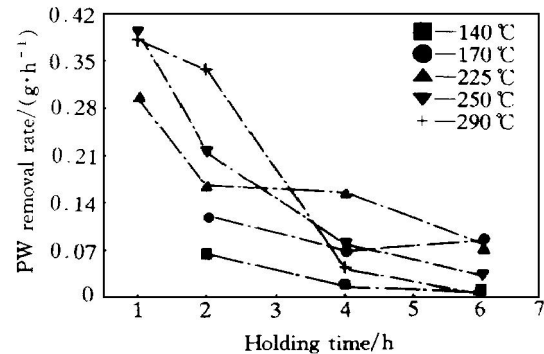

Fig.4 Debinding rate against debinding time

beyond 90 % saturation , gas permeability is gradually dominant only at the liquid saturation below 60 %[10]. Furthermore , particle size , shape and pores also affect permeability , agglomerated irregular fine powders greatly lowered permeability . Therefore , diffusion of liquid and gas may be the main way of P W removal .

Assuming that P W removal determined by diffusion rate of P W in the polymer and pores within a compact , the following equations[15] will be considered :

$$\frac{m(t)}{m(0)} = \frac{8}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \exp[-(2n+1)^2 \cdot \frac{\pi^2 D_{eff}}{4 l^2} t] \tag{4}$$

and

$$\frac{\pi^2}{4} \frac{D_{eff}}{l^2} \propto \frac{1}{d} \tag{5}$$

where l —the diffusion path length , D_{eff} —the effective diffusivity of P W , d —the sample thickness .

When $n = 0$ for equation (4) , then

$$\ln \frac{m(t)}{m(0)} = C - \frac{k}{d} t \tag{6}$$

or

$$1 - \frac{m(t)}{m(0)} = 1 - C' \cdot \exp(-\frac{k}{d} t) \tag{7}$$

where C and C' are constant , $k = \frac{\pi^2 D_{eff}}{4 l^2} d$.

It is suggested that the amount of residual binder or the amount of removed binder is exponential to time and the reciprocal sample thickness . In Eq .(7) , when $k/d \ll 1$, that is , the effective diffusivity is much smaller compared to the diffusion path , the exponential function can be expanded as $\exp(-\frac{k}{d} t) \approx 1 - \frac{k}{d} t$. Eq .(7) can then be rewritten as

$$1 - \frac{m(t)}{m(0)} = 1 - C' + At$$
$$(A = C' \cdot k/d) \tag{8}$$

or

$$\ln(1 - \frac{m(t)}{m(0)}) \propto \ln t \tag{9}$$

The experimental Figs .5 and 6 show that the logarithm of residual binder of sample is proportional to the reciprocal sample thickness and time at temperature below 250 ℃ . This confirms Eq .(6) . The experimental Figs .7 and 8 also confirm Eqs . (8) and (9) at temperature below 250 ℃ .
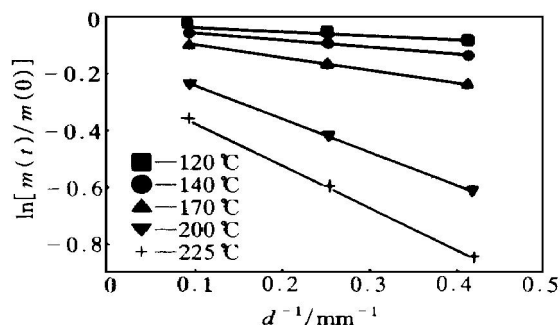

Fig .5 Logarithm of residual binder
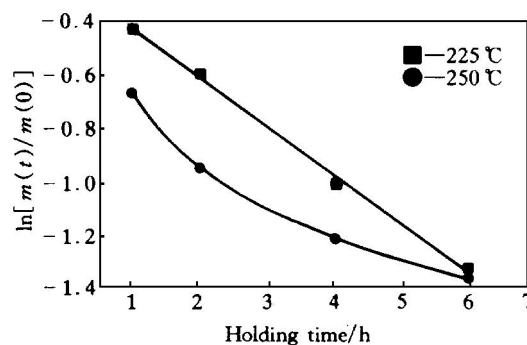$\ln \dfrac{m(t)}{m(0)}$ against reciprocal sample thickness

Fig .6 Logarithm of residual binder
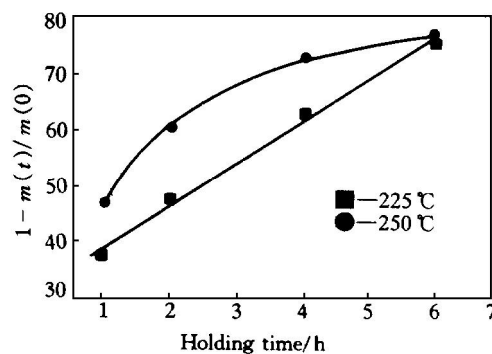$\ln \dfrac{m(t)}{m(0)}$ against time

Fig .7 Ratio of removed binder at 225 ℃ and 250 ℃ as a function of holding time
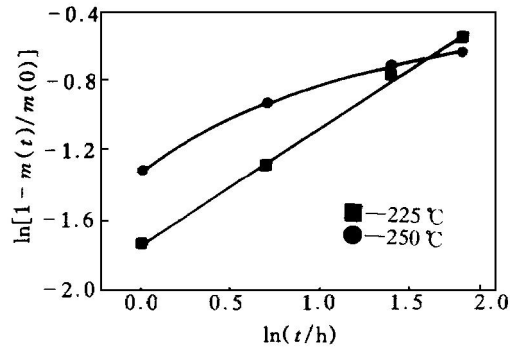
Fig .8　Logarithm of binder loss at 225 ℃ and 250 ℃ against logarithm of holding time

Linear regression analysis also verified the linear relations from Fig .5 to Fig .8 . Therefore , P W removal is controlled by the diffusion of a main low temperatute binder in the polymer and pores below 250 ℃ , P W could be removed completely at this temperature after a long time . The amount of P W removal is an exponential function of time and the reciprocal sample thickness and temperature cofficient . Beyond 250 ℃ , P W degradation increases greatly , and gas permeation becomes dominant .

4　THEORETICAL ANALYSIS

P W has molecular structure similar to HDPE and EVA , the miscibility between them is good . When mixed and melted , they diffuse into each other , but the diffusion of polymer into P W is much more slower than that of P W into polymer . The diffusion is mainly P W chains driving to curved high molecules , the interfunction between chains decreases , the degradatiion easily occurs . Therefore , in P W removal , P W firstly diffuses to pores from polymer , then diffuses outside from pores .

The diffusivity of P W in the polymer decreases with increasing viscosity of binder[22] i .e .:

$$\ln(\frac{D_0}{D}) = \ln(\frac{\eta}{\eta_0}) \tag{10}$$

where　D_0 —the self-diffusivity of P W , D —the diffusivity P W in binder , η —the viscosity of binder , η_0 —the viscosity of P W .

Feedstock also affects the diffusivity of P W following Braggerman model[19] :

$$\frac{D}{D_2} = (1 - V_1)^{3/2} \tag{11}$$

where　D —the diffusivity of P W in feedstock , D_2 —the diffusivity of P W in binder , V_1 —the volume fraction of powder .

Particle shape and size also affect the diffusion . The diffusion of P W within a compact is dependent on the diffusion of P W through the surface connected pores . The pore size and shape depend on the particle size , shape and the porosity . The pore shape is highly variable within a compact , the pores have a high level of interconnectivity and are tortuous . The effective diffusivity of binder through pores is

$$D_{eff} = D E / \tau \tag{12}$$

where　E —the porosity of the powder-binder compact , D —the real diffusivity of binder in feedstock , τ —the tortuosity of the diffusion path (for sphere monor particle , $\tau = 3$, for agglomerated particle , $\tau = 7$) .

According to Eqs .(10) , (11) , (12) , the effective diffusivity of P W in the multi-component binder and powder compact is

$$D_{eff} = \frac{\eta_0 \cdot D_0 \cdot E}{\eta \cdot \tau}(1 - V_1)^{3/2} \tag{13}$$

The higher the viscosity of binder , the powder loading or tortuosity of pores , the lower the effective diffusivity of P W within the compact . When the porosity is very low , the diffusion rate of P W within the compact is very low too . At higher temperatures , when the rate of P W removal by diffusion can't reach that of the moved binder driven by the inner pressure (vapor pressure , expansion pressure , capillary force and decomposed gas pressure) , the sample will be easily cracked . Therefore , the rate of P W removal is controlled by the diffusion of P W in the polymer and pores . In the initial stage , surface pores opened , the diffusion path increased , which is helpful to P W removal . When the binder removal is beyond 70 % , a large amount of interconnected pores forms , gas diffusion is not precluded , the rate of binder removal is then controlled by gas permeation .

P W burnout may involve several mecha-

nisms : P W melting , liquid flow , surface vaporation , P W chains fracture . The diffusion of P W in the polymer and pores is difficult and dominates the removal rate and the quality of brown part .

5　CONCLUSIONS

(1) Before 120 ℃ , liquid transport and surface vaporation remove limited P W , open little surface pores ; P W removal caused by diffusion of P W is negilible . The amount of removed P W is exponentially related to the reciprocal temperature .

(2) At temperatures between 120 ℃ and 225 ℃ , P W removal is mainly controlled by the diffusion of P W in polymer and pores in the compact , the amount of P W removal is an exponential function of time and the reciprocal sample thickness and temperature coefficient , that is

$$1 - \frac{m(t)}{m(0)} = 1 - C' \exp(-kt/d)$$

(3) The P W removal in the multi-component binder and agglomerated fine tungsten powder is complex . In the debinding stage , the defects are mainly due to the incorrect debinding process . Correct understanding the way of P W removal is important to control the part quality in this stage .

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