

Test of Cu base alloy Huadong sintering model^①

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[Abstract] Through modular pressing and sintering, the Cu-C powder metallurgy samples were made and the process was investigated. The results show that there exist expanding mechanism and shrinking mechanism in sintering process, and whether the sintering body is shrinking or expanding depends on the interacting between the two mechanisms, and the HD sintering model is in keeping with the actual sintering process.

[Key words] powder metallurgy; sintering mechanism; sintering model; Cu-C material

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1 INTRODUCTION

The HD sintering model was introduced in Ref. [1], and it considered that there always exist shrinking and expanding mechanisms during sintering process, although most PM material will shrink only phenomenally when sintered, that is to say, it is difficult to emerge the expanding mechanism. To show the expanding mechanism and its effect, three kinds of Cu-C materials are designed according to the undissolving characteristic between copper and graphite in order to consolidate the expanding mechanism and its action. Also, the dimensional change of sintering bodies during sintering is investigated to test the HD sintering model.

2 EXPERIMENTAL

The element components of Cu-C powder bodies are listed in Table 1, they were pressed in single-action die, the press direction along the direction x , the press forces were 450 MPa, and the dimension of compacts was 250 mm × 25 mm × 11 mm. The sintering protective gas was hydrogen, the geometry relationship between boat and compact sample is shown in Fig. 1.

The samples were sintered for 3 h at 25, 200,

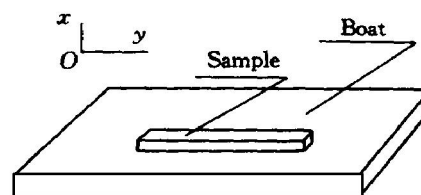


Fig. 1 Schematic diagram of sample in boat

300, 400, 500, 600, 700 and 800 °C, respectively, then cooled in the furnace, and the dimensions along the direction x and y after sintering were measured, otherwise the dimensions along the direction x and y before sintering were represented by x_0 and y_0 . Finally the values of x/x_0 and y/y_0 represented the sample dimension change after sintering. If $x/x_0 > 1$, it represents sintering expanding, and if $x/x_0 < 1$, it represents sintering shrinking, so does y/y_0 .

3 RESULTS

The relationships between sintering body dimensions and sintering temperatures were shown in Figs. 2, 3 and 4, and obviously the dimensional change along direction x was identical to the HD sintering model. The dimensional change along direction y in Figs. 3 and 4 was identical to the HD sintering model too. The reason why the expanding phenomena can not be seen in direction y in Fig. 2 is that the values of deformation as well as residual stress caused in pressing process are lower than that in direction x .

4 DISCUSSION

4.1 Cu base alloy

Table 1 Element contents of Cu-C powder (volume fraction, %)

Element	HDV0	HDV6	HDV12
Cu	75.65	70.81	65.85
Sn	10.60	10.13	9.67
Fe	10.90	10.35	9.90
Ni	2.85	2.71	2.59
C	0	6.00	12.00

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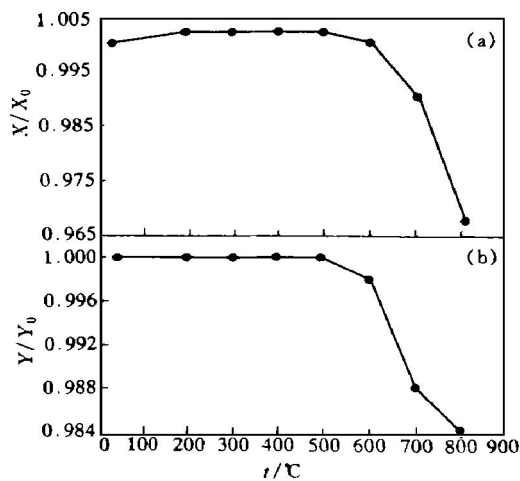


Fig. 2 Dimension change of sample vs sintering temperature (HDV0)

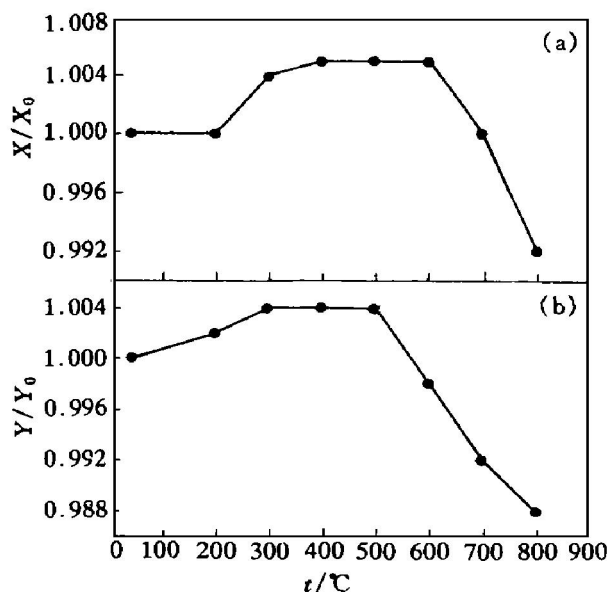


Fig. 3 Dimension change of sample vs sintering temperature (HDV6)

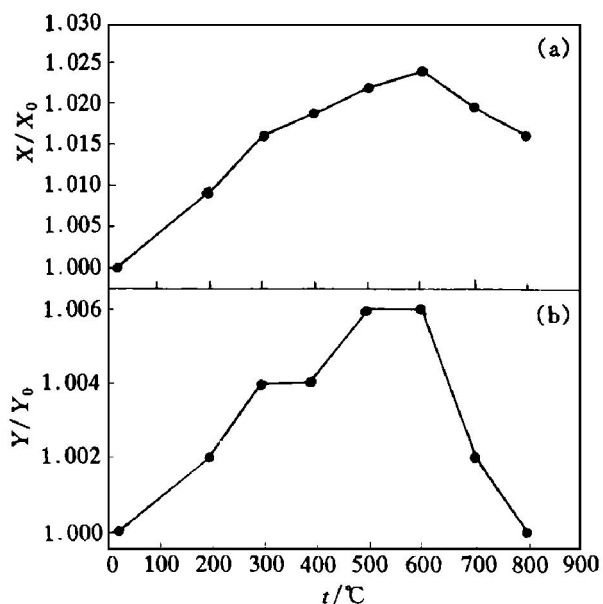


Fig. 4 Dimension change of sample vs sintering temperature (HDV12)

It is found that^[2,3] the particles in compact will plastically deform when the molding pressure is more than 3 times of the particles yield limit. During pressing process, the particle deformation is heterogeneous, thus, there is residual stress in particles. For the Cu base powders, the molding pressure is much more than 3 times of the particles yield limits (Table 2), so there will be residual stress in Cu base powder particles.

Table 2 Yield strength ($\sigma_{0.2}$) of elements^[4,5] (MPa)

Cu	Fe	Ni	Sn
48	98	60	< 48

The compact in mold^[6] bears not only the vertical pressure p_x but also the horizontal pressure p_y , and the relationship between p_y and the pressure p can be shown as^[2]

$$p_y = \xi p \quad (1)$$

where ξ is the coefficient of horizontal pressure. The values ξ of elements Fe, Sn, Cu are 0.31, 0.39 and 0.43, respectively^[2]. As the values ξ is lower than 1, there is always $p > p_y$, this would lead the values of residual stress and distortion energy in direction x higher than that in direction y . From Fig. 2 it might be known that during the primary sintering stage, there were $x/x_0 > 1$ and $x/x_0 > y/y_0$, this is identical to the HD sintering model. Now, according to the reciprocity of elements, the sintering process of material HDV0 is discussed as follows:

1) Room temperature~ 200 °C

There always is a dense structural oxide film on the particle surfaces of element Sn, this film would baffle the diffusion between element Sn and Cu, and there would not take diffusion among other elements. All these made it impossible to form neck, but the annealing may relax the residual stress because the sintering temperature t is over the residual stress relaxing temperature t_r . The t_r of element Cu is 149 °C^[1], the residual stress relax would make the sintering body expand, so the maximum value of x/x_0 equals 1.002, higher than 1.

2) 300~ 600 °C

Since the melting point of element Sn is 232 °C, the Sn particle would melt and appear liquid metal during this temperature range. As there exist inter-dissolving between elements Cu and Sn and good wettability of liquid Sn on Cu^[2,7,8], it would be possible to take this sintering as liquid sintering. But the experiment did not show so, and this means that this sintering is different from the liquid sintering.

When sintering below 600 °C, as there is no interdiffusion among the elements Cu, Fe and Ni, and no self-diffusion for elements Fe and Ni, the influence of Fe and Ni on the sintering of Cu-Sn may be negli-

gible^[9]. When Sn particle is being melted, the abutment probability between metals Cu and Sn is 1 for the fluidity of melting metal and the wettability of Sn liquid on Cu particles. By Sn-Cu phase diagram, the alloying process between Cu and Sn may be discussed as follows:

As sintering t approaches 300 °C, the phases α (Cu_2Sn_3) and β ($\text{Cu}_{31}\text{Sn}_{19}$) would be formed through some Cu atoms dissolving in Sn liquid.

By the same way, the alloying process may be discussed when t being 400 °C, 500 °C and 600 °C. While sintering among 300~ 600 °C and with increasing t , the Sn liquid will appear, but with the process of Sn-Cu alloying, the Sn liquid would disappear gradually^[8], so the sintering will remain to be solid sintering.

While the sintering temperatures are 300 ~ 600 °C, the diffusion only takes place in Cu particles (Table 3), the self-diffusion coefficient is very small (Table 4) and it is very difficult to form neck among the Cu particles. After sintered at 600 °C, the metallographic structure of compact showed that the neck formed, but the proportion of particles formed neck was very low and the effect of necking on compact shrinking was very small^[9]. At the same time, the Fe and Ni particles had some effect on compact expanding through the effect of anneal and circumstance. Then, during the sintering at 300~ 600 °C, the compact dimension remained unchanged nearly.

3) 600~ 800 °C

With increasing sintering temperature, the self-diffusion and inter-diffusion coefficients among

Cu, Fe, Sn, Ni elements would enhance and the self-diffusion and interdiffusion would take place. These made the neck form and grow, and made the compact shrink. As the residual stress of particles being relaxed, there did not exist annealing. Then the compact would shrink.

Table 3 shows that there would exist Kirkendall domino effect because of the difference among the diffusion coefficients, this would make the compact expand, but its effect was too small to display.

4.2 Cu-C material

The Cu-C materials sintering experiment (Figs. 3, 4) shows that:

1) As the sintering temperature increased, the compact dimensional changes in direction x were greater than those in direction y , and the curve shape was similar to that of alloy HDV0.

2) Obviously, there existed shrinking mechanism and expanding mechanism during sintering process.

3) With increasing content of C, the expanding value of the compact increases, this means that the element C may strengthen the expanding mechanism^[10].

4) The expanding in direction x is greater than that in y .

During sintering process, the element C remained solid phase, it did not dissolve into element Cu and Sn, its solid solubility in Fe and Ni was very small (0.035% and 0.2%, respectively), and its self-diffusion was too difficult to carry through. Only when the element C is contacting with element Fe and Ni it is possible for C to dissolve into Fe and Ni, but the adjoin probability of C to Fe and Ni was very low (Table 5). And for this reason, it might consider that element C did not dissolve into any element and take self-sintering. The atoms of Cu, Sn, Fe and Ni cannot diffuse through that of C. Thus, the sintering of Cu-C material may be divided into two parts, the sintering among metal elements and the sintering between metal elements and C:

Table 5 Adjoining probability of powders

HDV6			HDV12		
M-M	M-C	C-C	M-M	M-C	C-C
0.883 6	0.056 4	0.003 6	0.774 4	0.105 6	0.014 4

1) The sintering among metal elements

This is the same as that of alloy HDV0.

2) The sintering between M and C

When the M powder particles was contacting with C, considering the C powder shape being squamelliform and the deformation of M powder in pressing process, the schematic diagram of M-C sintering might be shown as Fig. 5. With the deforming in pressing process, the powder stacking took der-

Table 3 Relationship between diffusion coefficient and temperature^[3]

Diffusion coefficient/ ($\text{cm}^2 \cdot \text{s}^{-1}$)	Temperature range/ °C
$D_{\text{Fe-Fe}} = 2.01 \text{EXP}(-28900/T)$	770~ 884
$D_{\text{Cu-Cu}} = 0.10 \text{EXP}(-23700/T)$	300~ 1061
$D_{\text{Ni-Cu}} = 0.27 \text{EXP}(-30700/T)$	775~ 1050
$D_{\text{Ni-Sn}} = 0.83 \text{EXP}(-29200/T)$	700~ 1350
$D_{\text{Cu-Ni}} = 3.80 \text{EXP}(-28600/T)$	695~ 1061
$D_{\text{Cu-Sn}} = 0.84 \text{EXP}(-22600/T)$	737~ 1047
$D_{\text{Fe-Ni}} = 1.40 \text{EXP}(-29200/T)$	600~ 680
$D_{\text{Fe-Cu}} = 3.00 \text{EXP}(-34100/T)$	772~ 880
$D_{\text{Fe-Sn}} = 5.40 \text{EXP}(-27900/T)$	700~ 760
$D_{\text{Cu-Fe}} = 1.01 \text{EXP}(-25700/T)$	716~ 1056

Note: D_{A-B} represents diffusion coefficient of element B in A

Table 4 Copper self-diffusion coefficient (D) in different temperatures^[4]

Temperature/ °C	$D / (\text{cm}^2 \cdot \text{s}^{-1})$	Temperature/ °C	$D / (\text{cm}^2 \cdot \text{s}^{-1})$
300	1.09×10^{-19}	600	1.62×10^{-13}
400	5.08×10^{-17}	700	2.64×10^{-12}
500	4.84×10^{-15}	800	2.56×10^{-11}

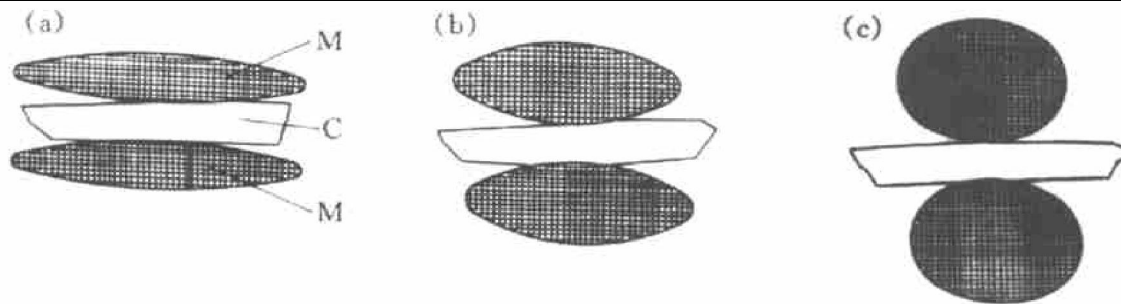


Fig. 5 Sketch diagram of M-C sintering change ((a) \rightarrow (b) \rightarrow (c))

se stacking mode (Fig. 5(a)), when heated, the annealing would affect the pressure and make the powder shape to transmute to near spherical shape and cause the sintering body expand (Figs. 5(b) and (c)). Even the sintering temperature over that of forming neck for M powders, the M powders did not form neck because the C powders interdicted the atom diffusion channel of M. It was impossible to form neck between the M and C too. Even there did not exist the annealing, the M powders would transmute their shapes to near spherical shape in order to reduce their surface energy. All these would make the sintering body expand.

As temperature increases, the yield strength of powder M would decrease, this means that with increasing temperature, the resistance of M powders transmuting their shapes to near spherical shape would decrease. Then, the higher the temperature, the greater the extent of powder M to be spheroidized, and the greater the sintering body expansion. Otherwise, the higher the C content, the greater the adjoining probability between powders M and C, and the greater the sintering body expansion. These were just shown in Figs. 3 and 4. As powders C shape is squamelliform, the adjoining probability in direction x is greater than that in y , thus the expanding in direction x is greater than that in y .

4.3 General discussion

Both sintering shrinking and expanding mechanisms can affect the volume and shape of the samples in the sintering process in Cu base alloy. But the sintering of Cu-C materials consists of three parts: M particles, M-C particles and C particles. The sintering shrinking and expanding mechanisms can affect only for the sintering of M particles. For the sintering of M-C and C, only sintering expanding mechanism has effect. And the Cu-C materials sintering body dimensional change depends on the general action of these three parts, and the element C is a factor in favor of sintering expanding mechanism. This is the reason why the experimental results in Figs. 2, 3 and 4 were gotten.

5 CONCLUSIONS

- 1) There does exist sintering expanding and shrinkage mechanism during sintering process.
- 2) The sintering dimensional change may be under control through adjusting the interaction between sintering expanding mechanism and shrinkage mechanism.
- 3) The HD sintering model is identical to the PM sintering process.

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