

Huadong sintering model about expansion and shrinkage^①

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[Abstract] The whole sintering course from the beginning of heating to the end of heat preservation stage was studied by taking into account the influence of pressing. It was found that there exist expanding mechanism and shrinking mechanism in the sintering process, and the expanding mechanism is always acting before the shrinking mechanism. Whether the sintering body shrinks or expands depends on the interaction between the two mechanisms. And according to this, the Huadong sintering model in account of expansion and shrinkage mechanism was given.

[Key words] powder metallurgy; sintering model; sintering mechanism; expanding mechanism; shrinking mechanism

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1 INTRODUCTION

The sintering process of powder metallurgy is so complex that it has to be investigated by model method. Generally, the investigation consists of two parts, thermodynamic analysis and dynamic discussion. The former is to determine whether or not the particles can be sintered while heated, and the latter is to study how the sintering process takes place. Up to now it was thought that the powders were spherical particles before the beginning of sintering, so the compact would shrink through mass transporting with the sintering taking place according to the rule that the total surface energy will decrease automatically during the sintering process^[1~10], and the sintering investigation was limited in the high temperature stage and so did the mass transporting mechanism. All these can explain the sintering shrinking but not the expanding. The sintering expanding does exist for some sintering materials and some sintering process^[11~13]. Even today there does not exist a sintering model which can explain both sintering shrinkage and sintering expansion.

Sintering is a process in which the compact is heated in certain atmosphere, as shown in Fig. 1. Compact is a powder billet which has been taken some elastic and plastic deformation. There exists residual stress in the compact because of heterogeneous deformation in pressing. The residual stress will relax gradually while the sintering temperature increases gradually. Obviously, the effect of sintering temperature is more important than that of sintering time, from which it is well known that only by studying the whole sintering processing and taking the molding processing into account, can the sintering mechanism as well as the dimensional change of sintering body be

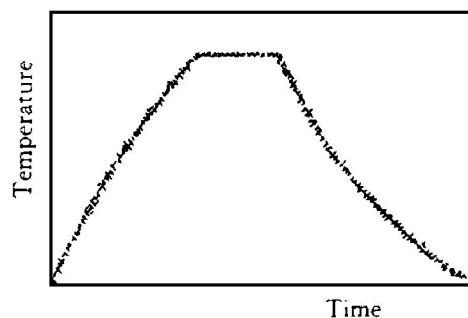


Fig. 1 Scheme of sintering process

understood.

Based on those above, the Huadong Sintering Model about both sintering expansion and shrinkage was made.

2 MOLDING INFLUENCE UPON SINTERING DIMENSIONAL CHANGE

Supposing that the particles be homogeneous spherical powders and the molding processing as well as the deformation of particles may be shown as Fig. 2, it may be known that the deformation of each particle is heterogeneous and the deformation in the X direction is greater than that in the Y direction.

If there is heterogeneous deformation, there will be residual stress and this stress is the embodiment of cold deformation storage energy^[14,15]. There are three kinds of residual stresses^[16].

I, This kind of stress is an equilibrium force among the whole powder mass, which may decrease or disappear through the plastic deformation of particles when heated.

II, This kind of stress is an equilibrium force which exists in the grain or subgrain as well as the

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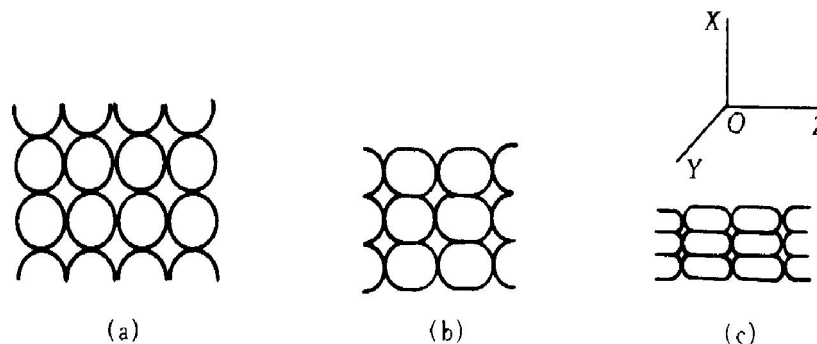


Fig. 2 Powder deformation during pressing process^[1]((a) → (b) → (c))

volume that is rounded by the slip surface, both the direction and the amount of this kind of force are disordered, and the stress has little influence on the particle size.

III, This kind of stress is a force which exists among the grain boundary or sliding surface, and exists as a subequilibrium state. It is a static distortion and has no influence on the particle size.

For convenience, kind I residual stress is represented as residual stress, kind II and kind III residual stresses as distortion energy. Residual stress σ_r is an elastic stress, which is proportional to elastic modulus E and elastic strain ε , that is, $\sigma_r = E\varepsilon$. As the temperature increase, the E would decrease little by little, so the σ_r would decrease. To metal particles, as the temperature increases, its yield strength limit σ_s would decrease and this decreasing is more than that of σ_r ^[15] (see Fig. 3). At the critical temperature t_1 , the value of σ_r is equal to that of σ_s , above t_1 , the material would get rid of some residual stress through plastic deformation. As the temperature increases, the residual stress will relax gradually, and all these make the particle size in Fig. 2 change from (c) to (b), which will induce the compact expansion in the X direction.

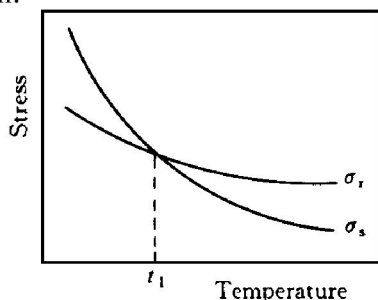


Fig. 3 Plot of σ_r and σ_s vs temperature^[15]

The distortion energy has no influence on particle size, but enhances the quantity of disfigurement, makes the free energy of the particle increase and favors the atom diffusion. Thus, the distortion energy will be favorable to the atom diffusion among particles and neck forming as well as the neck growing. All these above favor the compact densification.

The relaxation of residual stress is nearly proportional to the increase of temperature (see Fig. 3), but the relationship between the diffusion coefficient D and temperature T is exponential and may be given as follows:

$$D = D_0 \exp(-Q/RT) \quad (1)$$

where D_0 is the frequency gene, Q the diffusion activation energy, R the gas constant.

Now, it may be concluded generally that the compact would expand when sintered at low temperature, and shrink at high temperature.

3 SURFACE ENERGY CHANGING DURING SINTERING

Surface energy which consists of free and fethering energy, may be expressed by^[1]

$$E_s = F_s - TS_s \quad (2)$$

where E_s is the surface energy, which represents the total inner energy for the surface molecules, F_s the surface free energy, S_s the surface entropy, TS_s the surface fether energy.

When compared to F_s , the TS_s may be negligible^[17], thus, the E_s mainly depends upon the F_s . If a spherical particle has surface area A , and the surface energy per unit is γ , then there exists

$$\gamma = \delta F_s / \delta A \quad (3)$$

So the particle surface free energy may be expressed by

$$F = \gamma A \quad (4)$$

When a spherical particle is transmitted to a non-spherical particle (see Fig. 2), the value of γ remains unchanged, but the particle surface area would enlarge. So it may be known that as the spherical particle is pressed to deform into another shaped particle, its A will accretion and F enhance, the particle would be in an unstable thermodynamic state, so there exists a tendency to retransmute to the stable thermodynamic state automatically. While heated, this tendency will be transmuted into reality.

There are two passes for the particle to reduce its surface energy when heated.

1) When the heating temperature is lower than

T_s at which the atoms begin to diffuse, the particle shape may change to the spherical shape through relaxing the residual stress. This will reduce the surface area and the value of F . This process is called anneal factor in this paper. It makes the pore volume between the particles enhance (see Fig. 2(c) \rightarrow (b)), and belongs to the sintering expanding mechanism.

2) When the heating temperature is higher than T_s , there may be two changes to take place in the compact.

I. If the neck may be formed between the particles, the atoms in and on the particles may diffuse to the interface of particles to form neck and make the neck grow up, which makes the interface of particles transmute into the grain boundary or two particles link or several particles consolidate into one particle. All these will reduce the surface area of particles and the value of F , and this process makes the pores volume to reduce, the volume of compact reduce (see Fig. 4), and is sintering shrinking mechanism. With the hoisting of sintering temperature, the acting of this mechanism is increasing and taking the exponent forming (see formula (1)), at this stage, the annealing factor may exist also, but its influence will be swallowed gradually with the increasing of sintering temperature.

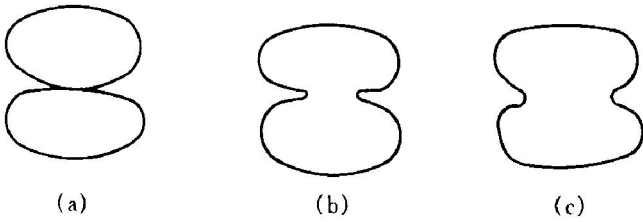


Fig. 4 Schematic sketch of sintering shrinkage mechanism ((a) \rightarrow (b) \rightarrow (c))

II. If the neck can not be formed between particles, in order to reduce the compact surface energy, the only way is to readjust the particle shape, that is, to transmute the particle shape to or near the spherical shape to reduce the value of particle surface area. This process is called circularizing factor, and it induces the compact to expand, therefore it belongs to the sintering expanding mechanism. For convenience, the circularizing factor is neglected temporarily when the Huadong sintering model is built up, and the influence of this factor will be discussed after the Huadong sintering model has been built up.

4 SINTERING MODEL

4.1 Thermodynamics analysis for sintering process

The beginning sintering temperature may be defined as T_s , and it nearly equals $(0.43 \sim 0.50) T_o$, where T_o is the melting point of the material; the highest sintering temperature as T_x , and nearly

$(0.67 \sim 0.85) T_o$. But during the sintering process, the residual stress of particles will relax because of the plastic deformation of particles (see Fig. 3), and the temperature of residual stress almost completely relaxing may be defined as T_r . The recrystallization temperature of powder metallurgy as T_z , then there exists the relation of $T_x > T_z > T_s > T_r$ (see Table 1).

Table 1 Several characteristic temperature values of elements^[1, 14, 18]

Element	T_r	T_s	T_z	T_x	T_o
Cu	422	583~ 678	679	909~ 1153	1357
Ni	547~ 589	743~ 854	863	1156~ 1467	1726
Fe	700~ 866	777~ 904	904	1212~ 1537	1809

Since $T_s > T_r$, the acting of expansion mechanism is always before that of shrinkage mechanism as well as the co-acting of shrinkage and expansion mechanism in the sintering process, and the influence of expansion mechanism will disappear gradually while the sintering temperature increases step by step.

There are three ways for the free energy of sintering system to reduce, that is:

- 1) Reducing the overall surfaces and surface free energy of particles.
- 2) Reducing the overall volume and surface area of pores inside compact.
- 3) Reducing/relaxing the distortion energy inside particles.

When the sintering process is finished, there are always many imperfections of thermodynamic balance in the compact, and from this, it may be known that the reduction of distortion energy is subsidiary as compared with that of surface energy. It is very difficult to calculate the sintering motivity through thermodynamic way because of the complexity of sintering system and process, so the sintering motivity is calculated by the model method set up by Kuczynski^[17].

1) In primary sintering stage ($T < T_s$), the sintering motivity is the releasing of residual stress and the decreasing of particles surface energy.

After pressing, the strain energy W_o , storage energy per unit volume, is given by^[19]

$$W_o = \frac{1}{2} E \varepsilon^2 \quad (5)$$

where E is the elastic modulus of the particle, and ε is the elastic strain. When the sintering temperature $T > T_s$, the residual stress will relax nearly completely and this means that the drift has been relaxed, so the particle shape would renew a spherical shape (see Fig. 2) and the compact expands. As T is far off below T_z , the change of distortion energy may be neglected. Thus, if the overall particle volume of the compact is V , and the released elastic strain energy is

W , there exists:

$$\Delta W = 0 - W_0 V = -\frac{1}{2} E \varepsilon^2 < 0 \quad (6)$$

Specially it should be pointed out that while $T < T_r$, the elastic strain energy had been relaxed gradually.

The surface energy changing during the primary sintering stage may be discussed as follows: if the overall particle number is N , the changing value of surface area is ΔA , and $\Delta A < 0$, when the particle shape transmuted toward spherical, the total surface energy changing ΔF may be shown as

$$\Delta F = N \gamma (\Delta A) < 0 \quad (7)$$

thus, the free energy changing of sintering body ΔZ may be given as

$$\begin{aligned} \Delta Z &= \Delta W + \Delta F \\ &= -\frac{1}{2} E \varepsilon^2 + N \gamma (\Delta A) < 0 \end{aligned} \quad (8)$$

As $\Delta Z < 0$, the sintering process should be the automatic process in thermodynamics, and the ΔZ is the sintering motivity.

Related to the influence of pressing and sintering primary stage on the particle shape and pore volume between particle, it may be concluded that the sintering body would expand in the sintering primary stage because of the acting of annealing factor.

2) In mid temperature sintering stage ($T_s < T < T_x$), the sintering motivity is the decreasing of particle surface energy.

Since the sintering temperature in this stage is over the beginning diffusion temperature of material, it is possible for the neck between particle to form through atom diffusing, and this would decrease the particle surface area and surface energy. As $T > T_r$, the annealing factor has little effect.

Taking two particles from Fig. 4(a), zooming in them as shown in Fig. 5, and it may be described that the neck is the same as that of Kuczynski sintering model, and the stress σ acting on the neck is given as follows from the Kuczynski sintering model:

$$\sigma = \gamma \left(\frac{1}{x} - \frac{1}{\rho} \right) \quad (9)$$

as $x \gg \rho$, so

$$\sigma = -\frac{\gamma}{\rho} \quad (10)$$

where the symbol “-” represents that σ is tensile

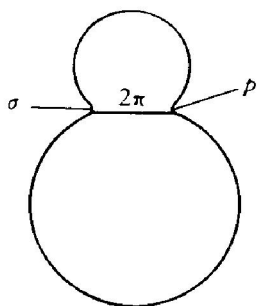


Fig. 5 Two ball model^[1]

stress, and its acting direction towards outer of neck. With the acting of σ , the vacancy concentration would change^[1]. The heat equilibrium concentration of vacancy C_v in the crystal may be calculated by statistical thermodynamics as

$$C_v = \exp(S_f/k) \cdot \exp(-E_f/kT) \quad (11A)$$

where E_f is the vacancy formation energy, k the Boltzmann's constant, S_f the total form entropy except mixing entropy, T the absolute temperature.

Inside crystal lattice, the vacancy concentration in tensile stress region is higher than that without stress. With the acting of σ , the energy of creating a vacancy is equal to the work that the stress does to the vacancy volume. If Ω represents the volume of a vacancy, there is $\sigma\Omega = -\gamma\Omega/\rho$, where minus represents that the σ makes the vacancy formation energy reduce. Then the required energy to create a vacancy among tensile stress region is

$$E'_f = E_f - \sigma\Omega \quad (12)$$

where E_f is the vacancy formation energy of no stress region. Taking formula (12) into formula (11A) may get the equation as

$$C_v = \exp(S_f/k) \cdot \exp(-E_f/kT) \cdot \exp(\sigma\Omega/kT) \quad (11B)$$

let C_0 represents the vacancy equilibrium concentration of no stress region, there is

$$C_0 = \exp(S_f/k) \cdot \exp(-E_f/kT) \quad (13)$$

then

$$C_v = C_0 \cdot \exp(\sigma\Omega/kT) \quad (11)$$

The magnitude of $\sigma\Omega/kT$ may be estimated to be $10^{-1} \sim 10^{-2}$ according to Refs. [1, 20, 21], which means that $\sigma\Omega/kT \ll 1$. Spread by series, there is

$$\exp(\sigma\Omega/kT) \approx 1 + \sigma\Omega/kT \quad (14)$$

then, if the equilibrium vacancy concentration difference between the region of tensile stress and that of no stress near neck is expressed by ΔC and the three formulas above are colligated, there is

$$\Delta C = C_v - C_0 = C_0 \sigma\Omega/kT \quad (15)$$

Supposing that the surplus vacancy concentration district only exists among the circularity with the radial ρ in the neck surface, then the surplus vacancy concentration gradient on the particle surface $\Delta C/\rho$ caused by σ may be given as follows:

$$\Delta C/\rho = C_0 \sigma\Omega/kT\rho \quad (16A)$$

Taking formula (10) into (16A), the following formula may be gotten:

$$\Delta C/\rho = -C_0 \gamma\Omega/kT\rho^2 \quad (16B)$$

Formula (16) makes out that the tensile stress σ on neck arouses vacancy concentration gradient round the neck, and this gradient causes the atoms diffuse to the neck, makes the neck grow up, and with this growing, the particle surface and surface energy will decrease.

3) In high temperature sintering and heat preservation stage ($T = T_0$), the sintering motivity is the decreasing of particles surface energy.

With the neck growing, the pore volume among the particles will diminish and even form some close pores (see Fig. 4), but the gas in the pores will counteract the neck growing, that is to counteract the pores to diminish. Then, the stress σ_s on the neck will be given by^[1]

$$\sigma_s = p_v - 2\gamma/r \quad (17A)$$

where p_v is the gas pressure of pores, r the pore radius.

From the ideal gas equation $p_v V = nRT$ and $V = 4\pi r^3/3$, there is

$$p_v = 3nRT/4\pi r^3 \quad (18)$$

Let constant $C_1 = 3nRT/4\pi$, then formula (17A) may be rewritten as

$$\sigma_s = \frac{C_1}{r^3} - \frac{2\gamma}{r} \quad (17B)$$

Formula (17B) represents that as the pore volume diminishes, the sintering motivity σ_s decreases also. Let σ_s be zero, the last radius r_c of close pores may be calculated by the following equation:

$$r_c = \sqrt{\frac{3nRT}{8\pi\gamma}} \quad (19)$$

Formula (19) represents that the r_c is related only with the sintering temperature T , the powder particle surface tensile stress γ as well as the gas content n of pores.

4.2 Huadong sintering model (I)

Based on the analysis mentioned above and using the investigation achievement of Kuczynski and Rhines^[17,22,23], the Huadong sintering model about expansion and shrinkage is made out, and it is shown as Fig. 6.

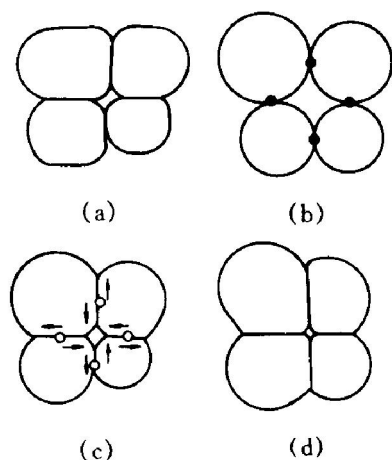


Fig. 6 Huadong sintering model

Sintering is a process in which the particle surface energy and stored energy decrease; so does the free energy of the sintering body. Sintering is a spontaneous process in thermodynamics:

1) In primary sintering stage ($T < T_s$), with the relaxation of residual stress of powder particle, the particles shapes change from their original shapes

to the spherical shapes, and this causes the pores among the particles to enlarge, and all these induce the compact to expand (see Fig. 6(a) \rightarrow (b)).

2) In mid temperature sintering stage ($T_s < T < T_x$), the stress caused by surface tensile stress (see formula (1)) and the atom diffusion makes the matter flow to the touch region of particles, the neck forms, and the pores dwindle. All these will make the sintering body volume shrink (see Fig. 6(b) \rightarrow (c)).

3) In high temperature sintering and heat preservation stage ($T = T_0$), with the prolonging of sintering time, the neck will grow up, the pore will dwindle gradually and transmit from interconnecting pores to close pores, and become spherical pore at last (see Fig. 6(c) \rightarrow (d)).

4.3 Huadong sintering model (II)

The model shown in Fig. 6 is a sintering shrinking model at last, but it shows there exists an expanding stage of sintering body during the primary sintering stage. If this expanding stage remains till the sintering process ends, or if the circularizing factor takes its acting in sintering process, the model would be a sintering expanding model, so that the Huadong sintering model is a model about sintering expansion and shrinkage.

The sintering of material Cu-C is an excellent example that both sintering expansion and shrinkage mechanisms give their effects during the sintering process^[24].

5 CONCLUSIONS

The sintering motivity is the decreasing of particle surface energy and the relaxing of particle storage energy. There are two paths to do so, i. e. forming neck among particles and circularizing of particles, but the former induces the sintering body to shrink, and the latter to expand. There always exist shrinking and expanding mechanisms during the sintering process. As the acting of expanding mechanisms is always before that of shrinking, there is an expanding stage in the primary sintering stage. The Huadong sintering model based on these can explain the sintering expansion as well as sintering shrinkage.

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