Modeling of the densification of silver particles during sintering at controlled pressure and temperature

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1. Introduction

The sintering process involves mass transfer (atomic migration), resulting in the creation of bonds between particles. This diffusion-based phenomenon is mainly driven by temperature, but it is also sensitive to the applied pressure. It allows for the formation of nano- to microparticle aggregates of a given density from metal powders. The three stages of sintering can be summarized as follows: (i) the first stage, which has a very limited contribution to the overall shrinkage, corresponds to the creation of necks between the particles, (ii) the intermediate stage leads to most of the densification of the powder compact, with pores forming interconnected channels along the grain edges, (iii) the final stage is characterized by isolation and elimination of the pores until ultimate compaction. These stages have been well observed experimentally but improved sintering models are still needed to estimate quantitatively the effects of some important parameters for the process. The basic analytical models, which were developed by Frankel [5], Kuczinsky [6], Kingery and Berg [7] and Coble [8] are known as the first theoretical works on grain-level sintering. In this study, we will use the relationships of the two-particle model of Coble to examine the neck growth during the initial stage of sintering of a silver...
powder. Then, a continuum-based model [4] is used in the framework of the finite element method to analyze the material densification at the last stage of sintering.

2. Two-particle model for neck growth description

The two-sphere model (figure 1) is essential to understand the effects of the geometrical and physical factors on the powder compact processing, in particular during the initial stage with the creation and development of necks. In the case of surface diffusion (figure 1a), as the sintering time increases, the neck size becomes larger without a change of distance between the centers of the particles due to the fact that material transport by this mechanism results in no shrinkage. It is different from what happens in the model with shrinkage (figure 1b) because the neck size grows, in this case, by material removal from the grain boundary. The flow occurs from the region of the grain boundary under compression (its center) towards that under tension (its ends). Based on the equations associated with these different diffusion processes, as introduced in [9,10], the initial-stage sintering kinetics can be analyzed. The relative neck growth relations (normalization by the particle radius \( r \)) are expressed in equations (1) to (3) for surface diffusion, lattice diffusion from grain boundary and grain boundary diffusion, respectively:

\[
\frac{x}{r} = \sqrt[3]{\frac{56D_s\gamma_s\delta_sV_m}{RT^3}} t
\]

\[
\frac{x}{r} = \sqrt[3]{\frac{16D_lV_m}{RT^3}} \left[ \gamma_s + \left( \frac{P_a}{\pi} \right) \right] t
\]

\[
\frac{x}{r} = \sqrt[3]{\frac{48D_b\delta_bV_m}{RT^4}} \left[ \gamma_s + \left( \frac{P_a}{\pi} \right) \right] t
\]

where \( D_s, D_l \) and \( D_b \) are the respective diffusion coefficients, \( \delta_s \) and \( \delta_b \) are the diffusion thicknesses of the surface and the grain boundary, \( \gamma_s \) is the surface energy, \( P_a \) is the externally applied pressure, \( T \) is the temperature, \( R \) is the gas constant, and \( V_m \) is the molar volume. The temperature-dependent silver self-diffusion coefficients in the lattice and the grain boundary were obtained experimentally by Hoffman and Turnbull [11]:

\[
D_l = 0.895 \exp \left( \frac{-207000}{RT} \right) \text{cm}^2\text{s}^{-1}
\]

\[
D_b = 0.03 \exp \left( \frac{-84000}{RT} \right) \text{cm}^2\text{s}^{-1}
\]

The value for the surface self-diffusion coefficient, \( D_s \), is calculated based on molecular dynamics computations in Liu et al [12] who investigated several surfaces of silver, among other metals. Here, the surface (110) is considered, giving the pre-exponential factor \( D_0 = 10^{-3} \text{cm}^2\text{s}^{-1} \) and the activation energy \( E_a = 0.32 \text{eV} \) for \( D_s \) which is expressed in the Arrhenius form as:

\[
D_s = D_0 \exp \left( \frac{-E_a}{k_BT} \right)
\]

where \( k_B \) is the Boltzmann constant. Figure 2 shows the time evolution of the ratio of neck to grain radius for the various sintering mechanisms at the temperatures 700°C and 900°C. The computations have been made using a value for the surface energy taken from [13], i.e. \( \gamma_s = 1.23 \text{J/m}^2 \). Obviously, the surface diffusion is the dominant mechanism in sintering, followed by grain boundary diffusion. As for the lattice diffusion mechanism, it plays a non-negligible role in sintering only at elevated temperatures.
**Figure 1.** The two-sphere model for the first stage of sintering: (a) without shrinkage and (b) with shrinkage ($x$ is the neck radius, $r$ is the particle radius and $2\delta_{p}$ is the overlap distance).

**Figure 2.** Relative neck growth for surface diffusion, lattice diffusion and grain boundary diffusion under applied pressure of 98.1 kPa at 700°C (blue) and 900°C (red), and with particles of 10 µm radius.

3. **Finite element model for densification**

The sintering continuum model introduced by Olevsky [4] is largely used because of its efficiency in various sintering field like high/low temperature sintering and SPS (Spark Plasma sintering). In this model, the strain rate tensor is considered to derive from the contributions of the mechanical stresses (external applied pressure) and the surface tensions on the particles in contact (natural sintering). The general constitutive equation for creep used by the author is the Norton’s law as given in equation (7). It relates the effective stress, $\sigma(w)$, to the equivalent effective strain rate, $w$:

$$\sigma_{eq} = Kw^m$$  \hspace{1cm} (7)

with $m = 1/n$ and $K = A^{-1/n}$. Here, $n$ is the stress exponent in the Norton creep law, $K$ is a temperature-dependent coefficient (like $A$) which represents the resistance to creep. Additionally, a local constitutive equation (8) gives the expression of the stress tensor with respect to the strain rate tensor. The law includes the loading parameters $\varphi$, $\psi$ and $P_L$, which are functions of the porosity. The parameters $\varphi$ and $\psi$ are respectively defined as the moduli related to shearing and isostatic
compression, while $P_L$ is an effective stress stemming from the surface energies of the grains in contact.

$$\sigma_{ij} = \frac{\sigma_{eq}}{w} (\varphi \dot{\varepsilon}_{ij} + (\psi - \frac{1}{3} \varphi) tr(\dot{\varepsilon}) \delta_{ij}) + P_L \delta_{ij}$$

(8)

The mass conservation is ensured during the whole process by satisfying at each increment the following condition between the rate of the relative volume change and the porosity:

$$tr(\dot{\varepsilon}) = \frac{\dot{\theta}}{1-\theta}$$

(9)

This model is implemented as a user law in the COMSOL Multiphysics and is applied on a thin cylinder (silver powder) which is submitted to a given uniaxial deformation rate along its axis ($z$-axis). In the simulations, the capillary force resulting from the curvature difference (free sintering) is neglected compared with the external applied pressure. The evolution of the relative density of the silver powder compact at 700°C and 900°C is plotted in figure 3 with respect to the sintering time. It is worth noting that the relative density reaches the peak value quite rapidly at such temperatures. Other studies established that the sintering velocity during the densification stage is sensitive to the grain size and temperature [14].

![Figure 3. Finite element computations of the relative density of a silver powder under uniaxial pressure at 700°C (blue) and 900°C (red) with respect to the sintering time.](image)

4. Conclusion

The study of the sintering process starts usually by understanding the basic analytic models like the Coble’s model even though many new approaches have been introduced since then. The first stage of sintering, corresponding to the neck growth and bonds formation, is still well described by the Coble’s model but, at the later stages, the densification evolution is difficult to estimate with the limited assumptions made in the early studies. However, the process of densification can be easily accounted for, in particular in large powder volumes, by considering models such as those based on the continuum theory of sintering. This study is only a preliminary investigation on that particular subject and simulations, based on the approach developed in the paper, can now be carried out on complex electronic assemblies to predict the formation of the sintered joint between components under a given thermal/loading profile. Also, more work remains to be done, using precise measurements of material parameters, to find the optimal conditions for sintering given the process constraints and the objectives fixed for the joint characteristics (stiffness, thermal conductivity).
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