

Sintering of submicron metallic particles

J. R. BLACHERE, A. SEDEHI, Z. H. MEIKSIN

School of Engineering, University of Pittsburgh, Pittsburgh, PA 15261, USA

An approximate analytical solution to the complete sintering of submicron hemispheres under conditions relevant to the preparation of semi-continuous metallic films is derived. The sintering of two spheres controlled by surface diffusion with no grain boundary formation is broken into two distinct parts: sintering with no shrinkage followed by spheroidization. The time for each part is derived and it is found that the time for spheroidization is about 17 times larger than the time of neck growth. The results are generally in agreement with the treatment of some previous investigators. It is shown also that under normal deposition conditions the contribution of the deposition source can be neglected during a sintering event simplifying significantly the simulation.

1. Introduction

The sintering (coalescence) of small particles is a part of the growth of metallic films prepared by vapour deposition. It was considered in a larger study of the computer simulation of the formation of thin films by vapour deposition [1, 2]. The microstructure and electrical conductivity of semi-continuous films are strongly dependent on the sintering step. A major consideration in the modelling was also the time of sintering compared to those of growth by vapour deposition. An explicit mathematical expression for the time of sintering decreases significantly the memory and time requirements of the computer program. Therefore an approximate model for the sintering of spheres was set up which appears satisfactory for the vapour deposition simulation which at this stage of its development can only be semi-quantitative. However the results of this model are very close to numerical predictions at higher x/a^* ratios (Fig. 1).

2. Procedure

The sintering process includes formation of a neck between two identical spheres,[†] the growth of the neck and the spheroidization of the two into one sphere. The size of the particles is assumed below $0.1\ \mu\text{m}$; they are usually much smaller than that, and surface diffusion dominates

transport in the sintering [3-5]. Furthermore if the deposition is made on a crystalline substrate, assumed to be a single crystal, there is an orientation relationship between the particles and the substrate [6]; therefore, the particles are expected to have the same orientation and not to form a grain boundary at the neck. While it is obvious that the geometric approximations of the initial stage of sintering could not be used here, since sintering is considered until completion, it was not believed important to introduce the complexity and uncertainty of modelling the observed undercutting at the neck included in the models of Uskokovic and Exner [3], Nichols [7], and German and Lathrop [8]. The neck was taken, in the longitudinal cross section of the sphere assembly, as a circular arc tangent to the spherical particles of radius a^* . The evolution of the assembly of spheres is summarized in Fig. 1. The sintering is treated in two successive stages: (i) sintering with no approach of centre and (ii) spheroidization. The transition between the two stages is made abruptly at a neck radius of $x = 0.89a^*$ consistent with conservation of volume. At this point the two spheres have taken the shape of a cylinder of radius $0.89a^*$ (Fig. 1c). This cylinder is replaced for the modelling of the spheroidization by an ellipsoid of equal volume with a long axis of revolution $a = 2a^*$ and a short axis $b = a^*$. This

[†]It was shown that in some cases the particles forming films are nearly hemispherical [2]. They may be, however, of different sizes; this is not considered here.

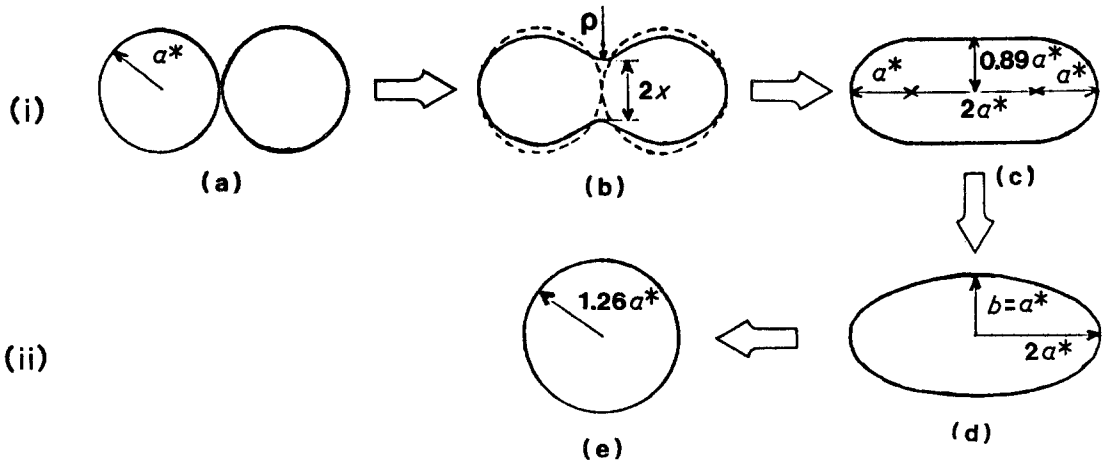


Figure 1 Sintering of two spheres (i) sintering with no shrinkage, (ii) spherodization.

ellipsoid is allowed to spheroidize into a sphere of radius $r = 1.26a^*$ as required by conservation of volume. This procedure leads to the relatively simple analytical solutions given below.

3. Time of sintering

Nichols and Mullins [9] has shown that the flux J_s along a surface is

$$J_s = -\frac{D_s \gamma \Omega \nu}{kT} \nabla_s K \quad (1)$$

in which D_s is the surface self-diffusion coefficient (isotropic), γ is the surface tension, Ω is the atomic volume, ν is the number of diffusing atoms per unit surface area, k is Boltzmann's constant, T is the temperature, $\nabla_s K$ is the surface curvature gradient, and K is the surface curvature [$K = (1/R_1) + (1/R_2)$] where R_1 and R_2 are the principal radii of curvature. This equation is true for all geometries. For an arbitrary body of revolution Nichols and Mullins [9] showed that it can be written as:

$$\frac{\delta n}{\delta t} = \left(\frac{B}{y}\right) \left\{ \frac{\delta}{\delta s} \left[y \left(\frac{\delta K}{\delta s} \right) \right] \right\} \quad (2)$$

where δn is the outward normal increment of distance travelled by a surface element during the time δt , δs is the incremental arc length measured along a section through the axis of revolution, y is the distance of a given point of this section to the axis of revolution and

$$B = \frac{D_s \gamma \Omega^2 \nu}{kT} = \frac{D_s \gamma \Omega \Delta_s}{kT}$$

where Δ_s is the thickness of diffusion.

Changing Equation 2 for sintering, when $y = x$

the neck radius (Fig. 1b) then

$$\frac{\delta x}{\delta t} = \left(\frac{B}{x}\right) \left(\frac{\delta x}{\delta s} \frac{\delta K}{\delta s} + x \frac{\delta^2 K}{\delta s^2} \right)$$

however, $\delta y/\delta s = \delta x/\delta s = 0$ at the minimum. Therefore the equation for the growth of the neck becomes $\delta x/\delta t = B(\delta^2 K/\delta s^2)$ which with a circular profile for the neck becomes

$$\frac{\delta x}{\delta t} = BK^3 \quad (3)$$

if one assumes that $\rho \ll x \ll a^*$ and then takes $\rho = x^2/2a^*$, integration of Equation 3 leads to the well-known expression for the initial stage of sintering of two spheres under surface diffusion control:

$$\frac{x^7}{a^{*3}} \approx 56Bt \quad (4)$$

The constant in Equation 4 actually depends on the arc length considered and was obtained in different ways [9–11].

For sintering until completion $\rho = x^2/2a^*$ cannot be used and the relation:

$$\rho = \frac{x^2}{2(a^* - x)} \quad (5)$$

is obtained from simple geometry. The rate of neck growth may be approximated by:

$$\frac{dx}{dt} = 2BK'^3 \quad (6)$$

in which K' is the difference in curvature which is driving the sintering, as discussed by Ashby [11]. It is taken as $K' = (1/\rho) - (1/x) + (2/a^*)$ which is not adjusted arbitrarily as done by Ashby who forced $K' \rightarrow 0$ for $x = a^*$. It does not appear

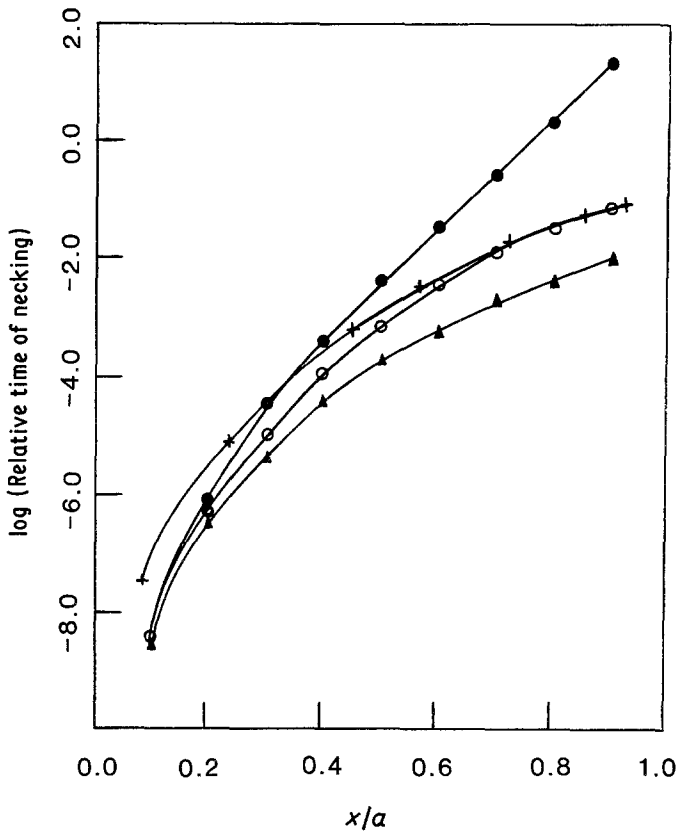


Figure 2 Relative time of neck growth according to various treatments (Δ) initial stage approximation; (\bullet) Ashby [11]; (+) Nichols [7]; (\circ) this work, Equation 7.

necessary since this sintering stage as defined earlier, stops at $x = 0.89a^*$. Then setting $\beta = a^*/x$ Equation 6 integrates to

$$\int_{a^*/x}^{\infty} \frac{1}{\beta^2(2\beta^2 - 3\beta + 2)^3} d\beta = \frac{2B}{a^{*4}t} \quad (7)$$

which is consistent with Equation 4 for the initial stage of sintering. Numerical integration of Equation 7 with the limit for β corresponding to $x/a^* = 0.89$ gives:

$$t = \frac{0.032}{B} a^{*4} = \frac{0.032kT}{\gamma_s \Omega \Delta_s D_s} a^{*4} \quad (8)$$

This relations gives a time of sintering (stage 1) which is about 8 times greater than that given by Equation 4 for the initial stage of sintering. The modified value of K' suggested by Ashby gives times to $x/a^* = 0.89$, about 2000 times greater than those based on the initial stage of sintering. These results and those of Nichols [7] are shown on Fig. 2. It is remarkable that as x/a^* increases the times predicted by Nichols and by Equation 7 are essentially the same, within 20% near $x/a^* = 0.89$. Thus it appears that Equations 7 and 8 predict well the times of sintering say for $x/a^* > 0.5$ to 0.6.

The discrepancy at lower x/a^* values is due to the under cutting of the simple geometric profiles by surface diffusion which has considerable influence over the times for the early stages of sintering and is included in Nichols treatment. However at higher x/a^* values it has little influence and the times of the early stages are extremely short (about 10^{-3} to 10^{-4} sec for the conditions used in the Appendix) so as to make them irrelevant to modelling of vapour deposition of thin films.

4. Times of spheroidization

As shown in Fig. 1 and stated in the procedure, the cylinder of Fig. 1c is approximated by an ellipsoid of revolution of the same volume with $a = 2a^*$ and $b = a^*$. Maintaining constancy of volume requires that $ab^2 = 2a^{*3}$ during spheroidization and the elliptic profile changes as shown in Fig. 3, becoming finally a circle of radius $r = 1.26a^*$ ($= 2^{1/3}a^*$). For this calculation, Equation 2 is applied to the evolution of the elliptic profile as a function of time. The motion of the profile is calculated specifically at its maximum $x = 0$ (Fig. 3) for which

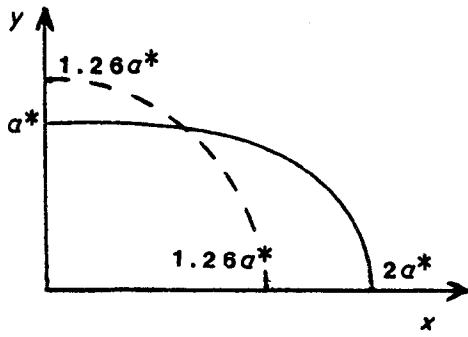


Figure 3 Profile evolution during spheroidization (---) initial; (—) final.

$$K = \frac{\delta^2 y}{\delta x^2}.$$

Near $x = 0$,

$$\frac{\delta K}{\delta s} = \frac{\delta K}{\delta x} = \frac{\delta^3 y}{\delta x^3} = -\frac{3b^6 x}{a^4 y^5}$$

Equation 2 becomes

$$\frac{dy}{dt} = \frac{B}{y} \frac{\delta}{\delta x} \left(y \frac{\delta^3 y}{\delta x^3} \right) = \frac{B}{y} \frac{\delta}{\delta x} \left(-\frac{3b^6 x}{a^4 y^4} \right)$$

After differentiation and simplification considering that $a = 2a^{*3}/b^2$ and $b = y$ at the maximum one obtains

$$\frac{dy}{dt} = -\frac{3B}{16a^{*12}} y^9 \quad (9)$$

Separation of variables and integration between $y = a^*$ and $y = 1.26a^*$ gives the time of spheroidization:

$$t_{\text{sph}} = \frac{0.5617kT}{\Omega\gamma\Delta_s D_s} a^{*4} \quad (10)$$

This equation is of the same form as Equation 8 for stage 1; however the time of spheroidization is much longer than that for sintering, $t_{\text{sph}}/t_{\text{sint}} = 0.56/0.032 \approx 17$. Nichols' treatment predicts that spheroidization would be about 12 times longer than sintering.

5. Discussion

Both Equations 8 and 10 have an a^{*4} particle size dependence as anticipated from Herring scaling law [12] and is in agreement with other treatments of sintering [4, 8, 10]. The agreement between the results of Equation 8 for the growth of a neck (stage 1) and those of Nichols gives confidence in its use and that of Equation 7 to calculate the size of large necks. Strings of spheres of equal size sinter according to this treatment into filaments

of final radius $0.89a^*$. The remarkable agreement with the results of Nichols for the times of sintering at larger relative neck sizes suggests that while the undercutting by surface diffusion at the root of the neck is very important in the initial stage of sintering, it does not affect significantly the results later in the sintering, and can be safely neglected in treatments concerned with the formation of necks of large relative diameters (x/a).

Thin films produced by vapour deposition are usually formed by nucleation and growth of "islands". This requires that the atoms deposited have sufficient mobilities on the substrate. There are few direct observations of thin films [13–15] at various stages of deposition and in particular there is no quantitative correlation between the microstructure and properties of thin films during their formation. At the beginning of the deposition, the number of stable nuclei increases until a saturation value is reached; after that the islands continue to grow. When islands physically touch each other they are observed to coalesce "instantly" [13] resulting in the reduction of the number of islands and eventually in the transformation of the granular (island-type) film into a connected filamentary network called a semi-continuous film. Further growth results in a continuous film by filling the voids in the porous film. The islands generally tend to be equiaxed in the plane of the substrate [14, 15] and although they may be faceted [6] or have the shape of truncated cones [16], an hemispherical cap appears to be a good approximation to their shape when the islands are large enough to touch and less than $0.1 \mu\text{m}$ in size. The contact angle between the islands and the substrate is not usually well known under the specific deposition conditions. It has been reported [17] to be about 90° for the deposition of gold on cleaved sodium chloride at 150°C with a deposition rate of $1.4 \times 10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$.

Deviations of the contact angle (θ) from 90° are not thought to affect greatly the time of sintering. Contact angles larger than 90° do not change the results since the previous derivations were performed for two spheres. $\theta < 90^\circ$ gives caps with heights smaller than their radius of curvature and the geometry of the two caps in contact is altered leading to opposite tendencies on the sintering time: transport requirements are decreased but the driving force is decreased also. The lowering of the driving force can be estimated by comparing the results of Equations 8 and 10

for a^* as the radius of curvature of the cap or as the radius of the circular area of contact between the cap and the substrate. Then using simple geometry an upper limit to the increase in sintering times is obtained. The sintering time is increased by a factor of $(\sin \theta)^{-4}$ for $\theta < 90^\circ$. For $\theta = 80^\circ$ this upper limit is 6%. Furthermore for many systems, the surface energies of the deposited materials are not expected to be much smaller than those of the substrates so that in many cases θ should not be much smaller than 90° . Therefore it may be concluded that deviations from the calculated sintering times due to the contact angle will be generally small.

The times calculated for the complete sintering by Equations 8 and 10 show that the sintering is essentially instantaneous during the vapour deposition process and therefore no significant error is made by neglecting the contribution of the evaporation source to the sintering process. This conclusion which is in agreement with the qualitative reports of instantaneous coalescence [13] can be demonstrated by a simple numerical calculation (see Appendix). This greatly simplifies the simulation.

Appendix: Representative calculation

For the following conditions, representative of practical deposition conditions for the deposition of silver on a single crystal substrate of sodium chloride at a rate of 10^{15} atoms $\text{cm}^{-2} \text{sec}^{-1}$ for a temperature $T = 500 \text{ K}$, the time of complete sintering for particles of radius $a^* = 30 \text{ nm}$ is less than 0.1 sec according to

$$t = \frac{0.594kT}{\Omega\gamma\Delta_s D_s} a^{*4} \quad (\text{Equations 8 and 10})$$

with $\Omega = 2.8 \times 10^{-24} \text{ cm}^{-3}$, $\gamma = 1120 \text{ erg cm}^{-2}$, $\Delta_s = 3 \times 10^{-8} \text{ cm}$, $D_s = 0.16 \exp(-5183/T)$. D_s is for silver surface self diffusion [18].

By simple geometric considerations it can be shown that the volume captured by two islands of radius $a^* = 30 \text{ nm}$ during vapour deposition for 0.1 sec is less than 1% of the volume of the neck formed between the two spheres.

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