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Particle drag retardation of surface smoothing and sintering

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Diffusion-controlled capillarity phenomena in solids, including sintering and surface profile changes, can be retarded by dispersed particles which are pinned at the surfaces. A model is proposed which predicts that dispersed particles which are more wetted by the substrate material, and subsequently partially imbedded, will tend to have a lower mobility than particles which are less wetted, if the force exerted on the particles by the moving interface is sufficiently low that the particles are dragged by the surface. On the other hand, less wetted immobile particles can provide a greater restraining force than more wetted particles. For a given volume of dispersoid per unit area of substrate, larger particles will provide a greater restraint to interfacial motion. Particle drag at the surface is probably not very effective in retarding sintering brought about by grain-boundary and volume diffusion. Surface diffusion-controlled sintering and surface-shape changes can be strongly retarded by dispersed particles.

1. Introduction

It has been observed for a number of years that a dispersion of second phase particles retards densification during sintering [1–8], and it has been postulated that the particles cause a dispersion hardening of the material, thus inhibiting plastic flow contributions to sintering [4]. While this may be so, there are circumstances under which the retardation may be caused by dragging of second-phase particles by the surface of the sintering material. This is entirely analogous to the commonly observed retardation of grain growth due to the presence of a dispersed second phase, which has been treated theoretically [9–11]. It is the purpose of the present paper to propose a model for the mobility of particles pinned at a free surface as the surface moves normal to itself under the action of capillarity forces. This model will then be related to initial-stage sintering and smoothing of sinusoidal surfaces.

Tikkanen *et al.* [2] studied densification of porous compacts of Co and Ni containing dispersions of MgO and CaO. They prepared their compacts by first calcining CoO plus $MgCO_3$, for example, grinding the resulting powder and reducing it in H_2. This produced a fine dispersion of oxide, probably mostly on the metal particles. They observed that the more wetted oxide, that is, MgO in the case of Co, and CaO in the case of Ni, had the greater effect in the sintering retardation.

Kuczynski and Lavendel [12] proposed a model for retardation of sintering by particles which are immobile as the surface moves, and concluded that nonwetted particles would retard sintering more than wetted particles. In their model the particles had to be covered by the metal if the interface was to advance. The present model is for the case when the particles are dragged by the surface as it advances or recedes.

2. Model for particle mobility

It will be assumed that all surface tensions are isotropic and, therefore, all surfaces of the particles are spherical. It will be furthermore assumed that all interfacial angles are always at their equilibrium value. The geometry of a particle in the surface of a substrate is shown in Fig. 1 in

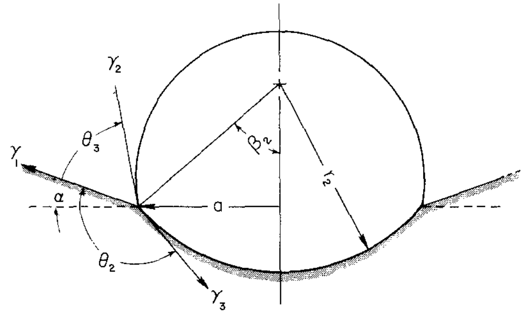

Figure 1 Inert particle pinned to an advancing surface. The surface energies of the substrate and particle are γ_1 and γ_2, respectively; the interfacial energy between these is γ_3.

which the surface is dragging the particle in the upward direction. The force exerted by the surface on the particle is given by

$$f = 2\pi a \gamma_1 \sin\alpha \tag{1}$$

where a and α are defined in Fig. 1, and γ_1 is the surface tension of the substrate material. The volume of the particle will be assumed to remain constant and is given by

$$V = \frac{\pi r_2^3}{3} C \tag{2}$$

where

$$\begin{aligned} C \equiv \frac{\sin^3(\theta_2 - \alpha)}{\sin^3(\theta_3 + \alpha)} & [1 + \cos(\theta_3 + \alpha)]^2 \\ & [2 - \cos(\theta_3 + \alpha)] \\ & + [1 + \cos(\theta_2 - \alpha)]^2 [2 - \cos(\theta_2 - \alpha)] \end{aligned} \tag{3}$$

and r_2, θ_2 and θ_3 are defined in Fig. 1. Since $a = r_2 \sin(\theta_2 - \alpha)$, we can define a dimensionless force, using Equation 2, as follows:

$$F \equiv \frac{f}{\gamma_1 a_0} = \frac{2\pi}{a_0} \left(\frac{3V}{\pi C} \right)^{1/3} \sin(\theta_2 - \alpha) \sin\alpha \tag{4}$$

where a_0 is the value of a at $\alpha = 0$.

An equation for the velocity of the particle can be derived employing an approach reminiscent of Shewmon's [9] treatment of a particle or void dragged by a moving grain boundary. Consider first the case when $\beta_2 < \pi/2$. As the particle moves an amount dz, a volume dV of material must flow in behind it, if the surface is advancing, or out from in front of it, if the surface is receding. The flux equation for this mass flow, assuming that diffusion in the interface between the particle and the substrate material is rate limiting, is

$$j = -\frac{D_\mathrm{i}}{\Omega k T} \nabla\mu \tag{5}$$

where j is the atomic flux per unit area per unit time, D_i is the interfacial diffusion coefficient, Ω is the atomic volume of the rate limiting diffusing species, and $\nabla\mu$ is the gradient in the chemical potential of the diffusing species. It is assumed that the latter quantity can be given with sufficient accuracy as the force on the particle divided by the maximum cross-sectional area of the particle in contact with the matrix, with the average diffusion distance equal to $\beta_2 r_2/2$. Thus, for $\beta_2 < \pi/2$,

$$\nabla\mu \cong -\frac{2\Omega f}{\pi \beta_2 r_2^3 \sin^2\beta_2} . \tag{6}$$

The incremental volume, dV, which must be transported as the particle moves an amount dz, is given by

$$\mathrm{d}V = \pi (r_2 \sin\beta_2)^2 \,\mathrm{d}z = 2\pi r_2 \sin\beta_2 \delta j_\mathrm{m} \Omega \mathrm{d}t \tag{7}$$

where δ is the width of the region of enhanced diffusion at the interface between the particle and substrate, and j_m is the flux at the line of maximum girth between the particle and the substrate. Rearranging Equation 7 and employing Equations 5 and 6, the velocity of the particle is

$$u \equiv \frac{\mathrm{d}z}{\mathrm{d}t} = \frac{4\Omega\delta D_\mathrm{i} f}{\pi k T \beta_2 r_2^4 \sin^3\beta_2} . \tag{8}$$

Carrying Shewmon's results to the same point would give unity in place of $4/\pi$.

A dimensionless velocity can be defined as follows, using Equations 2 and 4:

$$U \equiv \frac{kTa_0^3}{\gamma \Omega \delta D_\mathrm{i}} u = \frac{8\pi a_0^3 C \sin(\theta_2 - \alpha) \sin\alpha}{3 V \beta_2 \sin^3\beta_2} . \tag{9}$$

For $\beta_2 \geqslant \pi/2$, $\sin\beta_2$ is replaced by unity in Equations 6, 7, 8 and 9.

A dimensionless mobility can be defined as

$$M \equiv \frac{U}{F} = \frac{kTa_0^4}{\Omega \delta D_\mathrm{i}} \cdot \frac{u}{f} . \tag{10}$$

This is plotted in Fig. 2 for various values of θ_2 and θ_3. The curves terminate either when the magnitude of F reaches a maximum, or when the curve exceeds the boundaries of the plot.

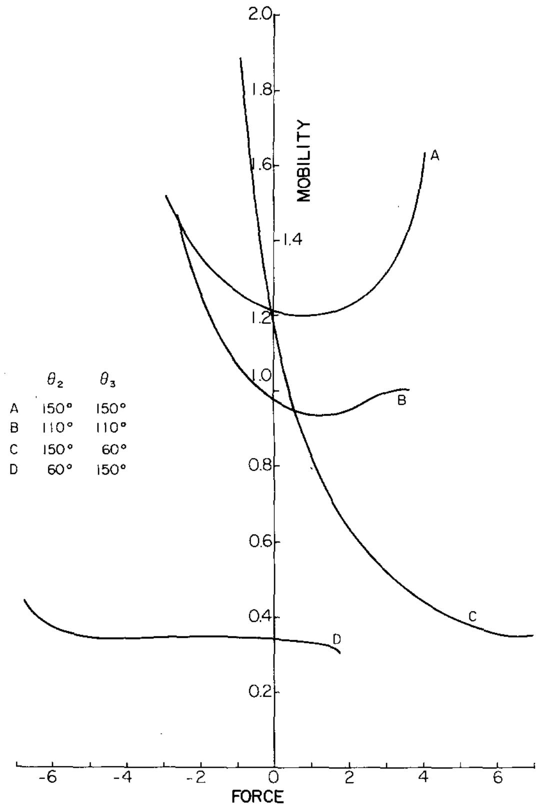

Figure 2 Plot of dimensionless mobility versus force for particles pinned to a moving surface. Positive branches of the curves terminate at maximum possible restraining force that the particles can exert on the surface. A negative force means a receding interface. θ_2 and θ_3 are defined in Fig. 1. Curves A and B are for symmetric lenticular particles; C and D are for less wetted and greater wetted particles, respectively.

A number of conclusions can be drawn from Fig. 2. Non-wetted particles can restrain greater forces than wetted particles for advancing interfaces, in agreement with Kuczynski and Lavendel's model [12]. However, the mobility of non-wetted particles is very high for receding interfaces. The wetted particles are far superior in restraining receding interfaces both in mobility and in the magnitude of maximum restraint possible. It can be noted at this point that sintering involves both advancing and receding interfaces.

3. Smoothing of a sinusoidal surface

The foregoing results can be applied in a straightforward manner to the surface-smoothing models of Mullins [13]. The following treatment assumes that surface diffusion is the primary mechanism of surface smoothing; extension to vapour transport and volume diffusion is trivial.

The flux equation for surface diffusion on a sinusoidal surface is

$$j \simeq -\frac{D_s}{kT}\frac{\mathrm{d}p}{\mathrm{d}x} \tag{11}$$

where D_s is the surface self-diffusion coefficient, p is the pressure beneath the surface, which is assigned positive values under convex portions of the surface. The presence of uniformly distributed identical particles attached to the surface will yield a drag which can be represented as a back-pressure on the pressure generated by the curvature, as follows:

$$p = -\gamma_1 K + fN \tag{12}$$

where K is the local value of the curvature and N is the number of particles per unit area. It is assumed that this equation holds, provided the interparticle spacing is less than about 10% of the surface-profile wavelength. The surface profile is given by

$$z(x, t) = A(t)\sin\omega x \tag{13}$$

where $A(t)$ is the time-dependent amplitude and ω is the angular frequency of the surface profile. In the small slope approximation (amplitude much less than wavelength), $K \simeq \mathrm{d}^2z/\mathrm{d}x^2$, which gives

$$p \cong \gamma A\omega^2 \sin\omega x + fN \tag{14}$$

where A has been written instead of $A(t)$ for simplicity. The velocity of a surface element is

$$\frac{\mathrm{d}z}{\mathrm{d}t} = -\Omega^2\nu\frac{\mathrm{d}j}{\mathrm{d}x} \tag{15}$$

where ν is the surface concentration of diffusing atoms. Substituting Equations 11 and 14, and performing the indicated operations, gives

$$\frac{\mathrm{d}z}{\mathrm{d}t} = \frac{\Omega^2\nu D_s}{kT}\left(-\gamma A\omega^4\sin\omega x + N\frac{\mathrm{d}^2f}{\mathrm{d}x^2}\right). \tag{16}$$

If particles are being dragged by the surface, the particle velocity and the surface-element velocity are equal and Equation 16 becomes

$$u = -AB\omega^4\sin\omega x + \frac{NB}{\gamma m}\frac{\mathrm{d}^2u}{\mathrm{d}x^2} \tag{17}$$

where $B \equiv \gamma\Omega^2\nu D_s/kT$ and use has been made of the definition of mobility, $m \equiv u/f$. The solution of this equation is

$$u = -\frac{AB\omega^4 \sin \omega x}{1 + (NB\omega^2/m\gamma)}\,. \tag{18}$$

The rate of decay of the amplitude, $\mathrm{d}A/\mathrm{d}t$, is the value of u at the maxima of the surface profile, where $\sin \omega x = 1$. Using Equation 10,

$$\mathrm{d}A \quad = -\frac{AB\omega^4}{1 + (Na_0^4\omega^2/R_\mathrm{D}M)} \tag{19}$$

where $R_\mathrm{D} \equiv \delta D_\mathrm{i}/\Omega\nu D_\mathrm{s}$. This differs from Mullins' result by the added term in the denominator.

It is instructive to examine the effectiveness of surface particles in retarding surface smoothing. Consider first the minimum wavelength for which no part of the surface is moving fast enough to break away from the particles. The corresponding angular frequency will be called ω_c; particles will be dragged by the surface if $\omega < \omega_\mathrm{c}$. The following treatment applies to those particles for which the mobility is approximately equal for both advancing and receding interfaces (see Fig. 2). Let the amplitude and wavelength of the profile be related through $g \equiv A\omega$ and define $v \equiv \omega_\mathrm{c}g^{2/3}/N^{1/2}R_\mathrm{D}^{1/6}$ and $w \equiv a_0N^{1/2}/R_\mathrm{D}^{1/6}g^{1/3}$. Using these and the first parts of Equations 9 and 10, Equation 19 can be rearranged to give the following:

$$v^3 - F_\mathrm{m}wv^2 - U_\mathrm{m}w^{-3} = 0 \tag{20}$$

where F_m and U_m are the magnitudes of the breakaway dimensionless force and velocity, respectively. Note that g is not independent of time; it is merely a convenience to give Equation 20 a simple form, and decreases with time.

Fig. 3 shows Equation 20 plotted for $\theta_2 = 60°$ and $\theta_3 = 150°$; the region beneath the curve represents conditions under which the surface would drag all particles. The small slope approximation [13] requires $g < \pi/5$. The model probably requires that particle spacing is substantially less than the surface wavelength (say $\omega < N^{1/2}/2$), and the particles cannot overlap (say $a_0 < (3N^{1/2})^{-1}$). Using these, the model should be valid for $v < 0.4R_\mathrm{D}^{-1/6}$ and $w < (3R_\mathrm{D}^{1/6}g^{1/3})^{-1}$. Breakaway is not anticipated under most experimental conditions.

Assuming that the particles are retained by the surface, the expected influence of dispersed particles on the rate of amplitude decay can be examined. Equation 19 can be written as

$$\dot{A} = \frac{\dot{A}_0}{1 + (Na_0^4\omega^2/R_\mathrm{D}M)} \tag{21}$$

where $\dot{A}_0$ is the amplitude decay rate without particles. Besides the obvious relationships shown in this equation, note that the volume of dispersed phase per unit area is proportional to Na_0^3, so that the second term in the denominator is proportional to the dispersed particle size for any given system at constant volume of dispersed phase. Thus, spontaneous coarsening of the dispersed particles would produce a decrease in $\dot{A}/\dot{A}_0$ with time. Based on the restrictions on particle spacing and size discussed above, the

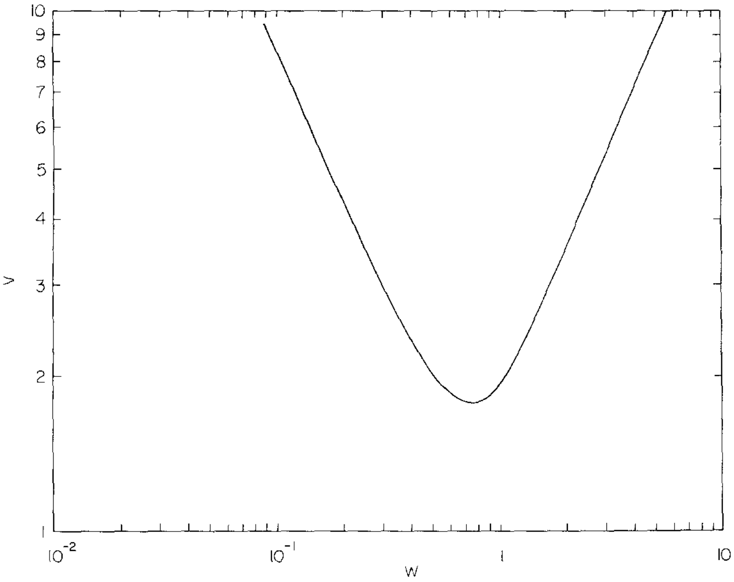

Figure 3 Breakaway curve for sinusoidal surfaces, Equation 20, for $\theta_2 = 60°$ and $\theta_3 = 150°$. The region beneath the curve represents conditions under which the surface would drag all particles.

minimum value of $\dot{A}/\dot{A}_0$ obtainable under the most favorable conditions (nearly dense packing of large particles) is $(1 + 0.003/R_DM)^{-1}$, or, in other words, R_D must be less than 10^{-3} in order for the particles to have a significant effect. Of course, greater reductions in decay rate would be realized for larger particles (at the required lower particle density) than those for which the current model would be applicable.

4. Sintering

Particle drag can be incorporated into the initial stage sintering models [14]. These models describe the first few percent of linear shrinkage of a compact of uniform spheres, or a pair of spheres of equal size, and the formation of a neck between pairs of spheres. At first, it will be assumed that the sintering takes place by a combination of volume and grain-boundary diffusion, with no surface-diffusion contribution. It will be assumed that all of the material to build the neck between the spheres is transported from the grain boundary in the neck. The model is based upon the sintering model presented earlier [14], and is identical to it, except for the incorporation of a drag force caused by the presence of a surface dispersion of particles. It is assumed that the particles are uniformly distributed over the surface of the neck, and that the surface dispersoid particle density is fixed with time. Neither of these can be precisely true because of the nature of evolution of the neck, but the calculation will, nevertheless, permit a fairly accurate estimation of the effectiveness of particles in retarding sintering by this mechanism.

The atomic flux equation for either grain-boundary or volume diffusion of atoms from the grain boundary to the neck surface is given by

$$j = -\frac{D}{kt} \nabla p(r) \tag{22}$$

where D is either the grain-boundary or volume-diffusion coefficient and r is the radial distance from the centre of the neck. Material continuity requires that the divergence of the flux be constant, or,

$$\nabla^2 p(r) = \text{constant}. \tag{23}$$

The boundary conditions are Equation 12 and the following:

$$\frac{\mathrm{d}p(0)}{\mathrm{d}r} = 0 \tag{24}$$

and

$$\int_0^x r p \mathrm{d}r = \gamma x. \tag{25}$$

The solution of Equation 23, subject to these boundary conditions, is

$$j = \frac{4\gamma D(x+\rho)}{kTx^2\rho}\left[1 - \frac{Nfx\rho}{\gamma(x+\rho)}\right], \tag{26}$$

where $K = 1/\rho - 1/x$, ρ is the minimum radius of curvature of the neck surface, and x is the neck radius. The grain-boundary groove at the neck surface has been neglected; its effect on sintering kinetics is small. Assuming that the chemical potential gradients for grain-boundary and volume diffusion are the same, the total flux arriving at the neck surface is

$$J = \frac{4\gamma(A_nD_v + 2\pi xbD_b)(x+\rho)}{kTx^2\rho}\left[1 - \frac{Nfx\rho}{\gamma(x+\rho)}\right] \tag{27}$$

where A_n is the neck surface area – the area for volume diffusion – D_v and D_b are the volume and grain-boundary diffusion coefficients, respectively, and b is the region of enhanced diffusion at the grain boundary. The force, f, is the neck growth rate divided by the mobility of the dispersoid particles. Under the assumption that all of the material to fill in the neck comes from the grain boundary, the following relationship exists between the neck growth rate, $\dot{x}$, and the fractional shrinkage, $\dot{y}$;

$$2\pi x^2 a\dot{y} = A_n\dot{x}. \tag{28}$$

Thus,

$$f = \frac{2\pi x^2 a}{mA_n}\dot{y} \tag{29}$$

The relationship between the total flux and shrinkage rate is

$$j = \frac{2\pi x^2 a\dot{y}}{\Omega} \tag{30}$$

Using Equations 28, 29, 30 and 10 in Equation 27, gives

$$\dot{y} = \dot{y}_0 \Big/ \left[1 + \frac{4Na_0^4(D_v + 2\pi XbD_b/aA'_n}{XMa\delta D_i}\right] \tag{31}$$

where A'_n and X are the neck surface area and neck radius normalized to the sphere radius, and $\dot{y}_0$ is the shrinkage rate without particles, given by [14]

$$\dot{y}_0 = \frac{2\gamma\Omega(A'_n D_v + 2\pi X b D_b/a)\,(X+R)}{\pi k T X^4 R a^3}. \tag{32}$$

The influence of particles on the shrinkage rate can be anticipated by calculating the magnitude of the second term in the denominator of Equation 31. Using restrictions on particle spacing and particle size that are similar to those employed in the sinusoidal decay model, the maximum value of the product Na_0^4 is $\rho^2/30$. Substituting this and the mobility for the particles with $\theta_2 = 60^\circ$ and $\theta_3 = 150^\circ$ gives a magnitude of this term of $4 \times 10^{-4} a(D_v + 27.8\, bD_b/a)/\delta D_i$ for 1% linear shrinkage ($X = 0.20$, $R = 0.014$, $A'_n = 0.045$). It can be seen that this term is not large unless the interfacial diffusion coefficient is very much less than the volume diffusion coefficient, and substantially less than the boundary diffusion coefficient. This is not surprising, considering the relatively long distance that atoms must be transported in order for shrinkage to take place, compared with the distance they must be transported to allow the surface dispersoid particle to move. It is not known whether the observed retardation in shrinkage caused by dispersed oxide particles [1–8] is brought about by the mechanism discussed above, or whether the particles interfere with the densification mechanisms in other ways.

The influence of dispersed particles on neck growth by surface diffusion can be estimated with the help of a simplified surface-diffusion sintering model. The flow of atoms into the neck by surface diffusion is given by

$$J_s \cong -\frac{4\pi x \Omega \nu D_s}{kT}\,\frac{\mathrm{d}p}{\mathrm{d}s} \tag{33}$$

where $\mathrm{d}p/\mathrm{d}s$ is the surface derivative of the pressure beneath the surface approximated by

$$\frac{\mathrm{d}p}{\mathrm{d}s} \simeq \frac{\Delta p}{\Delta s} = \frac{p_n - p_s}{2\rho} = \frac{\gamma[\rho - x - (2x\rho/a)]}{2x\rho^2} \left\{1 + \frac{fNx\rho}{\gamma[\rho - x - (2x\rho/a)]}\right\}. \tag{34}$$

In this equation, p_n is given by Equation 12 and p_s is the pressure at the surface of the spheres, $2\gamma/a$. The assignment of $\Delta s = 2\rho$ is made on the basis of the computer-generated surface-diffusion sintering model of Nichols and Mullins [15]. The total flux is related to the neck growth rate by $J_s\Omega = A_n\dot{x}$. Using this and Equations 33, 34 and 10, and remembering $f = \dot{x}/m$, we obtain the following:

$$\dot{X} = \dot{X}_0 \Big/ \left(1 + \frac{2\pi N a_0^4 X}{M R_D A'_n R a^2}\right) \tag{35}$$

where $\dot{X}_0$ is the normalized neck growth rate without particles given by

$$\dot{X}_0 = \frac{2\pi\gamma\Omega^2 \nu D_s (X - R + 2XR)}{kTa^4R^2A'_n}. \tag{36}$$

The second term in the denominator of Equation 35 can be examined using geometric parameters obtained from Nichols and Mullins' [15] work. At $X = 0.2$, $A'_n = 0.13$, $R = 0.039$, and using $Na^4 = \rho^2/30$ and $M = 0.34$, the second term in the denominator of Equation 35 is $0.037/R_d$. It is quite likely that the magnitude of R_d is less than 10^{-3}, so that surface diffusion-controlled sintering will likely be strongly affected by the presence of dispersoid particles.

Although the sintering models are clearly approximations, they, nevertheless, indicate trends that can be expected. It is more likely that surface diffusion-controlled sintering will be more strongly inhibited than grain-boundary and volume diffusion-controlled sintering. This means that the sintering in the low temperature regime, where surface diffusion is more important, will be more sensitive to the presence of dispersed particles which retard sintering by this mechanism.

5. Conclusions

Dispersed inert particles tend to impede the motion of free surfaces under capillarity-induced morphological changes, such as sintering and surface smoothing. A number of predictions can be made on the basis of the models presented above. For a given dispersoid particle size, a particle which is more buried within the sintering material will have a lower mobility, but also a lower maximum restraining force, than one which is more nearly resting on the surface. The latter particles offer little restraint to a receding interface. Since sintering involves both advancing and receding interfaces, it is likely that the more buried particles will be more effective in overall sintering retardation. The magnitude of the effects are such that they should be measurable using the well established technique of sinusoidal surface smoothing. For a given volume of dispersoid particles per unit area, larger, more widely separated particles will be more effective in restraining surface motion than smaller, more closely spaced particles. Surface dispersoids are more likely to inhibit surface diffusion sintering than grain-boundary and volume-diffusion sintering by the mechanisms discussed above.

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