Disappearance of grain boundaries in sintering

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(Received 30 November 1989; accepted for publication 9 November 1990)

An exactly solvable model of grain boundary annealing in sinters is introduced and studied for a range of particle sizes. The model explains well the cluster fusion events observed by high-resolution transmission electron microscopy.

In sintering processes, powder particles fuse together under the influence of surface tension and the starting material shrinks as much as 30% in volume. In the beginning of sintering, small necks are formed between adjacent particles. The necks subsequently grow and the pores between the particles fill in, resulting in the shrinkage. However, since the particles are randomly oriented in the starting material, grain boundaries form between the adjacent particles in the initial stage of sintering. These grain boundaries may act as major avenues for material transport during further sintering. In fact, there is substantial experimental evidence that a pore which still remains when the pores have lost connectivity will anneal out only when connected to a grain boundary. However, the pressure of grain boundaries is obviously not energetically favorable and many of them anneal out during the early stages of sintering.

In order to control grain boundaries during the sintering process to optimize particular final properties, one needs to develop a comprehensive theory of sintering and grain boundary annealing. The most frequently encountered goal in sintering is to achieve the maximum possible densification and strength; the empirical rate-controlled sintering process[1] has been developed in order to preserve many more grain boundaries than in the standard constant temperature sintering. The resulting material has a higher density, fewer remaining pores, a smaller average grain size, and a greater strength than standard sinters.

In this letter, we discuss an explicit mechanism for grain boundary annealing related to a qualitative description by Greskovich and Lay,[2] present results of calculations for a model of this process in an isotropic medium, and show that these results are consistent with experimental observations of grain boundary annealing during the coalescence of small metal particles, as revealed by real-time high-resolution transmission electron microscopy (HRTEM).[3,4] The present theory follows naturally from a recent solution to the problem of finding the figure of minimum free energy for any given amount of material transported into the neck of a sinter via an arbitrary combination of surface and grain boundary transport.[5]

The model in its simplest form is this: two spherical, randomly oriented single-crystal particles with radii R_1 and R_2 initially have one point of tangency and we assume that $R_1 > R_2$. This geometry has long been used in the modeling of sintering properties by Kuczynski and others.[6] As the sintering process proceeds through its first stage, material is transported to the neck region by diffusion on the surfaces of the spheres and by grain boundary diffusion from the contact region. Each sphere retains its single-crystal structure, so the area of the grain boundary grows as the neck thickens. Figure 1(a) is a sketch of the model. The model assumes that the sinter evolves along a path that, at every instant, minimizes the total free energy subject to the constraint that a specified amount of material has been transported to the neck up to that instant.

The free energy of a slab containing the grain boundary is greater than that of a slab of the same dimensions in the bulk crystal; if this excess per unit area is Δf, the excess free energy of the interparticle grain boundary of area A is $A\Delta f$. To the degree that it may be considered a quasi-equilibrium process, the fact of sintering indicates that $A\Delta f$ remains less than the reduction of free energy due to the decrease in the surface area of the sintering figure. The assumption of a quasi-equilibrium, minimum free energy that evolves under slowly changing constraint implies that the sinter continually assumes a figure in which the neck is a region of constant mean curvature, so that growth of the sinter is essentially a continuous reduction in this curvature. The general solution[5] indeed has this property.

The configuration shown in Fig. 1(a) is that of a local minimum in the free energy because the grain boundary falls at a local minimum in area. We choose the z axis on the line of centers as in Fig. 1, and suppose for the present that Δf is constant. The grain boundary is pinned at the plane where $\partial A/\partial z = 0$ and $\partial^2 A/\partial z^2 > 0$. As the neck grows, the minimum in area and thereby the grain boundary may move along the z axis under certain conditions (see below), but the grain boundary remains pinned until the diameter of the neck grows to equal the diameter of the smaller sphere. This happens when the z coordinate of the grain boundary is equal to the z coordinate of the center of the smaller sphere. At this point the grain boundary is free to move; the driving force is the reduction in the area of the grain boundary

$$F = -\Delta f \partial A/\partial z. \tag{1}$$

When the local minimum disappears, the sinter can be expected to evolve spontaneously in the direction corresponding to $\delta A < 0$. The three vertical cuts in Fig. 1(c) show, from left to right, the evolution of the sinter from

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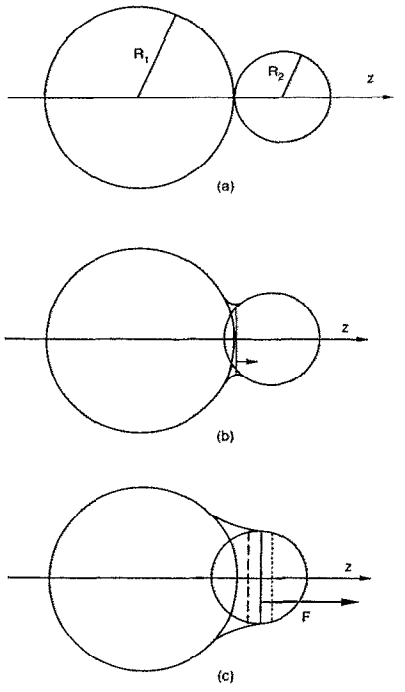

FIG. 1. Two-sphere geometry used in the calculations. (a) Initial stage, the spheres have only one point of tangency. (b) The two-sphere complex has shrunk and a neck has formed between the spheres. The grain boundary in the neck region is pinned at z_{grain}, the point of minimum cross-sectional area of the neck. The material for neck formation has come by GBT from the overlap of the two spheres in this case, and the shape of the neck has been calculated using methods described in Ref. 5. (c) The unpinning stage. The position of the grain boundary is shown just before the unpinning (dashed line), at unpinning (solid line), and just after unpinning (dotted line); prior to that (dashed line) the neck has an interior minimum, at the pinning point.

just prior to the transition point, through that point, to a slightly later point along its history. The sinter's evolution must continue until the grain boundary disappears into the void adjacent to the smaller particle or, if the smaller particle is in contact with still another particle, until the grain boundary described here meets and coalesces with another grain boundary.

This model is based on the assumption that the grain boundary is planar or nearly so. This assumption is entirely plausible so long as the grain boundary is pinned; moreover, the pinned grain boundary is perpendicular to the cluster's tangent surface and the dihedral angle is assumed for convenience to be 180° (see below). The discussion following will show that under some circumstances the grain boundary may migrate even while pinned, because the pinning point migrates. As soon as unpinning occurs, either the grain boundary no longer meets the cluster's surface as a perpendicular, or the grain boundary is no longer planar, or perhaps both. Our model is based on the former choice. These two are extreme cases; the real situation must be somewhere between. If local equilibrium governs the evolution of the sinter, where the real sinter falls between the two cases depends on the balance between the free energy to bow the grain boundary and the free energy to bend the angle of intersection of the grain boundary with the cluster surface away from the perpendicular.

If the smaller particle is adjacent to the void, then beyond the unpinning, dA/dz in Eq. (1) is simply $2\pi(z-c)$, where c is the z coordinate of the center of the smaller sphere. We an then insert the force F from Eq. (1) into either a friction-dominated evolution equation with friction coefficient γ

$$\frac{dz}{dt}=C\gamma(z-c) \tag{2}$$

or an equation for a Newtonian system

$$\frac{md^2z}{dz^2}=C'(z-c) \tag{3}$$

for the z coordinate of the grain boundary. The resultant equations have simple exponential solution provided the friction coefficient or effective mass m is independent of area—a rather unlikely condition. An effective form for the solutions is likely to be an exponential multiplied by a modifying function, or perhaps a stretched exponential.

The unpinning mechanism, as we can now call it, follows naturally from the general solution for the sinter figure, Eq. (6) of Ref. 5, because that solution gives $A(z)$ explicitly for arbitrary R_1 and R_2. The special case in which $R_1=R_2$ cannot be treated within the context of that analysis alone because the symmetry about the pinning point keeps z_{grain} midway between the centers of the spheres until the instant of unpinning. Then the neck becomes a point of neutral equilibrium, so the grain boundary moves only as a result of fluctuations. As more material flows to z_{grain}, a bulge develops and the equilibrium becomes unstable. From that instant on, fluctuations provide the mechanism for breaking the symmetry and destabilizing the position of the grain boundary, triggering its movement toward smaller area $A(z)$.

The annealing of a grain boundary between two spheres was previously discussed in qualitative terms by Greskovich and Lay,[2] by Pask,[7] and then by us,[8] but the first explicit calculations are presented in this letter. The calculations have been done for two limiting cases for the source of material. In the first case, all the material is transported to the neck via grain boundary and volume diffusion. The shrinkage occurs thus by the approach of the centers of the coalescing spheres while their radii remain constant. The volume of the transported material is equal to the overlap of the original spheres. In the second extreme case, all the mobile material comes from the shrinkage of the smaller sphere. In this case the shrinkage of the sinter is due to the change in the diameter of the smaller sphere. In the following, these two cases are denoted "grain boundary transport" (GBT) and "surface transport" (ST), respectively. We can set $R_1=1$ and $R_2\leqslant 1$; all other cases may be obtained by scaling.

Figure 2(a) shows the percentage of shrinkage along the z axis of the two-sphere complex at the point of unpinning as a function of the radius of the smaller sphere for the two limiting cases. Figure 2(b) shows the reduction of surface area of the complex at this point. Note that, although there are substantial differences in the linear

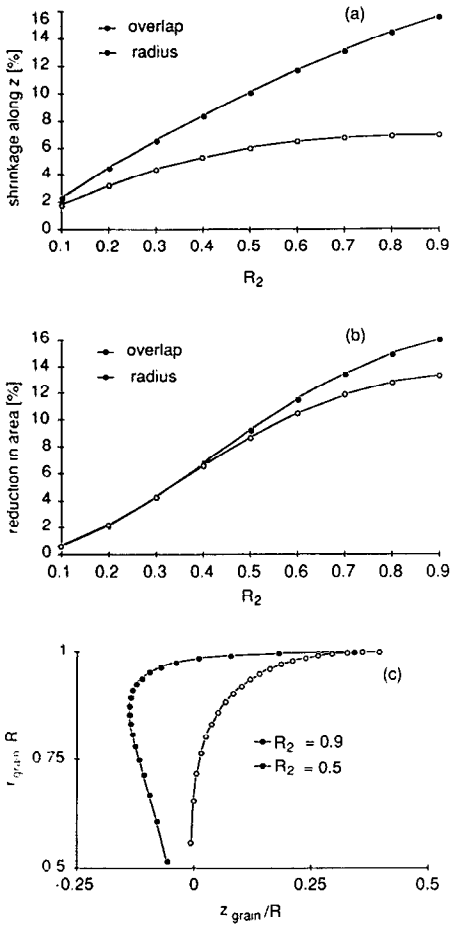

FIG. 2. (a) Relative shrinkage along the z direction at a point of unpinning for the two-sphere complex with $R_1 = 1 > R_2$ as a function of R_2 for the two mechanisms considered in the text. (b) Relative reduction in the surface area at the point of unpinning as a function of R_2. (c) Scaled radius of the grain boundary as a function of its position along the z axis for $R_2 = 0.9$ and 0.5, respectively.

shrinkage at the point of unpinning for larger sphere sizes, the surface areas are very similar. In Ref. 5, which studied the shrinkage of identical spheres, it was shown that GBT always reduces the surface area more than ST for a given amount of mobile material. The same is true for the case of two unequal spheres.

With GBT, if the radius of the smaller sphere is greater than ~ 0.5, the grain boundary, which is pinned to the minimum of the cross-sectional area of the neck, moves towards the center of the larger sphere before changing direction and eventually annealing out. This is illustrated in Fig. 2(c), where the scaled radius of the grain boundary is plotted as a function of its scaled position along the z axis for $R_2 = 0.9$ and 0.5, respectively, until the unpinning point is reached. With ST, the grain boundary moves monotonically out in the positive z direction and towards the unpinning point.

The annealing sequence described above has already been observed experimentally by Wallenberg,[3] and by Iijima and Ichihashi,[4] in HRTEM. Similar fusion events recorded by Iijima and Ichihashi have also observed a folding of a high index grain boundary during its motion.[4]

The theory as formulated can be elaborated to be more realistic. Thus far, the theory does not take explicit cognizance of the crystalline structure of the particles.[9] The evolution of shapes of real particles is of course governed by the differences in free energies of different crystal faces and the specific interfacial tensions at the boundaries where they meet at a well-defined angle. Moreover, the movement of the grain boundary must also be influenced by the crystalline structure of the particles as well as by imperfections, so that a real boundary does not move as a plane along the line of centers. No account has been taken of the randomness of the relative orientations of the particles in contact. Furthermore, the formulation presented here deals only with a dihedral angle of 180°; the theory applies in a slightly modified form if the dihedral angle is less than 180°. Specifically, the bisector of the dihedral angle tips as the neck fills; unpinning occurs at the first instant that $d^2A < 0$, an instant that can be determined by computation if the dihedral angle is known.

In summary, we have introduced an exactly solvable model for grain boundary annealing during sintering. The driving force for the annealing is the reduction in the area of the grain boundary. The model assumes the presence of a distribution of particle sizes in the powder. The greater the disparity in the sizes of the particles in contact, the greater the driving force for annealing and, presumably, the faster it will occur. The present model depends only on the initial distribution of particle sizes and the packing density, which makes it suitable to large-scale computer modeling. Kinetic effects, i.e., the influence of the thermal history on the final grain distribution, introduce additional complications which have yet to be included.

We wish to thank R. Wallenberg for communicating to us his results and for the permission to use his photographs as Fig. 3 of this letter. We also are grateful for the hospitality and stimulating environment of the Telluride Summer Research Center where part of this work was carried out. This work was supported by the Office of Naval Research, grant No. N00014-88-K-0491.

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