Densification of powder compacts: An unfinished story

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Abstract

The focus of this review is to summarize the understanding of why the coarsening of grains and pores accompanies the densification of a powder compact. The review will initiate with a summary of the thermodynamic studies of simple particle arrays, which suggests that the growth of necks between the initial touching particles stop before the compact is dense. Results of analytical and computer studies concerning how grain growth occurs in partially dense powder compacts will be reviewed to show that grain coarsening will reinitiate the neck growth process responsible for further shrinkage. Experimental results will then be reviewed and related to the analytical studies. It will be shown that isolated pores connected to the largest number of grain boundaries, namely, avenues for rapid mass transport, will disappear first. Finally, the lack of pore periodicity will constrain the shrinkage of one region relative to another.
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1. Introduction

To understand the intent of this review, the reader must pull out their Introduction to Ceramics[1] and turn to pages 482 and 483 to study the consecutive micrographs, supplied by C. Greskovich and K. Lay, showing the microstructural development of an alumina oxide powder compact as it densifies. A quick glance should tell even the causal student that grain growth is concurrent with densification. The four micrographs on these two pages clearly show the particle size of the initial powder compact, and the size of the grains for partially dense compacts after heat treatments at $1700\,^\circ$C for periods of 1, 2.5 and 6 min. It is obvious that an enormous amount of grain growth occurs between consecutive micrographs. Recognizing that when two identical spheres combine to make one with a radius only 26% ($\sqrt[3]{2} = 1.26$) larger that either of the two smaller spheres, one must conclude that the more than half the particles have disappeared after the powder compact was heated at $1700\,^\circ$C for only 1 min, a point where the compact is still very porous.

Concurrent to the enormous growth of grains during densification, one observes a comparable growth of pores. If the large amount of grain growth does not bother the serious student expecting to understand densification, the concurrent growth of

the pores should trigger a complete lack of comprehension. That is, although the student cannot read about a comprehensive link between grain growth and densification in the chapter concerned with densification, at least the text book explains grain growth in terms of either grain boundary motion or coarsening (the mass transfer between surface of grains). On the other hand, since the book only implies that pores disappear during densification, it should be incomprehensible to the serious student to see them grow as clearly illustrated in the sequential micrographs supplied by Greskovich and Lay.

The objective here is to review the literature to explain why grain growth is a critical phenomenon to achieve densification, and why pore growth is a consequence to the constraint to densification produced by a non-periodic distribution of pores. It will be see that the grain growth of interest here is caused by coarsening, namely, a phenomenon associated with either surface diffusion or evaporation/condensation, and generally not associated with densification. Likewise, it will be shown that pore growth is also a consequence of coarsening, leading to a decrease in surface area, and thus a decrease in free energy.

The review starts with a thermodynamics of neck growth for a periodic array of identical, spherical, single crystal particles to show that neck growth will stop once the energy required to form the grain boundary between the particles exceeds the reduction in free energy due to a decrease in the particle's surface area. The second subject concerns the sintering of a smaller particles

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periodically placed between larger particles. Here it is shown that conditions exist where, after neck growth stops between all particles, the transfer of mass from the smaller particles to the larger particles will eventually cause the larger particles to touch one another to reinitiate neck growth, and thus shrinkage. Third, experimental evidence will be reviewed that confirms the first two subjects. Forth, experimental observations will be reviewed concerning isolated pores that are coordinated by either a small or large number of grains. These results show that it is not the local surface curvature that controls pore closure, but the number of grain boundaries (fast diffusion paths) that intercept the pore. Lastly, it will be shown that if the isolated pores are not periodic, pore growth will occur via a de-sintering process due to the constraint of shrinkage by one part of the body on others.

2. Thermodynamics of neck growth

To estimate the free energy change during the growth of necks between touching, identical single crystal spheres, Kellett and Lange[2] assumed that the morphological change could be simply described by a linear array of truncated spheres as shown in Fig. 1a. They assumed that only two parameters were required to develop a free energy function, namely, the initial particle radius, r_i, and an angle, ϕ, that describes the relation between the two tangents at the spherical surfaces that have a common vertex at the grain boundary shown above Fig. 1a. For a given array, r_i is fixed, ϕ is varied between 0 and π, and the volume of the cylinder or sphere remains constant, thus describing the radius of the truncated sphere as a function of ϕ. Although this model

neglects the negative curvature of the surface located in the neck region during neck growth analytically described by Pross and Exner,[3] it does produce the exact equilibrium configuration when $\phi = \phi_e$, the dihedral angle, as also reported by Cannon and Carter.[4]

The free energy function is give by

$$E = A_s \gamma_s + A_b \gamma_b, \tag{1}$$

where A_s is the surface area of the truncated cylinder or sphere, A_b is the grain boundary area, γ_s is the surface energy/unit area, and γ_b is the grain boundary energy/unit area. The surface energies are related through Young's relation,

$$\frac{\gamma_b}{\gamma_s} = 2\cos\frac{\phi_e}{2}, \tag{2}$$

where ϕ_e is the equilibrium dihedral angle defined by the ratio of the two interfacial energies. A_s and A_b are simple trigonometric functions of r_i, ϕ, γ_s and ϕ_e.[2]

Fig. 1a illustrates three free energy functions described by Eq. (1), normalized by the initial energy of a cylinder of unit length ($E_0 = 4\pi r^2 \gamma_s$) for three different values of the dihedral angle. As shown, with increasing values of ϕ, the free energy decreases to a minimum when $\phi = \phi_e$ where the formation of a neck between the two particles stops. This minimum occurs because any further decrease in free energy due to a decrease in the external surface energy is less than the increase in free energy due to the increasing surface area of the grain boundary. Namely, the configuration at $\phi = \phi_e$ is a metastable equilibrium configuration for neighboring particles in the linear array. This configuration is metastable because mass can still be transferred
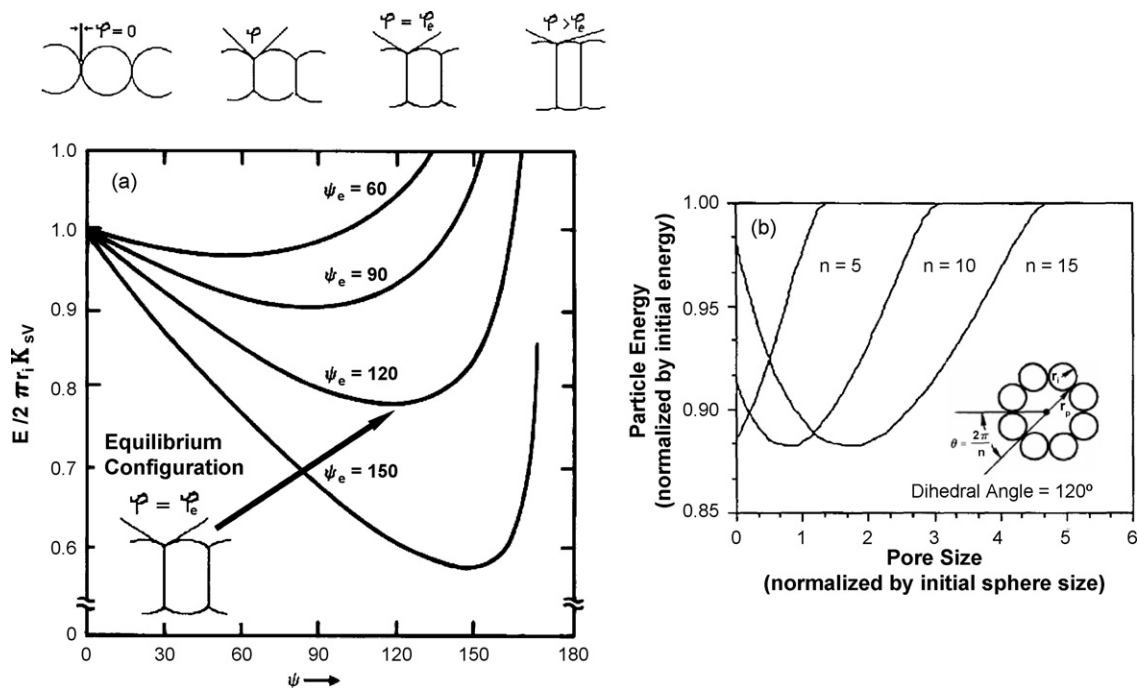

Fig. 1. Schematic for a linear array of cylinders (or spheres) showing truncated forms as a function of the contact angle ϕ ($0 < \phi_e < \pi$). (a) Normalized free energy for one truncated cylinder (or sphere) as a function of the contact angle. Lowest free energy occurs where $\phi = \phi_e$. (b) Normalized free energy of a ring array of spheres as a function of the pore radius normalized by the initial sphere size for ring arrays containing n number of spheres coordinating the pore.

between the particles to further reduce the free energy, a point that will be discussed in the next section.

The same model can be used to estimate the free energy change for circular arrays of cylinders or spheres and polyhedra arrays of spheres.[2] As shown in the insert of Fig. 1b, one additional thermodynamic parameter is needed for the free energy function, namely the number of particles, n, that surround the pore. For these arrays, it can be shown that the radius of the pore, R_p, is a function of r_i, ϕ, and n, e.g., R_p decreases with increasing ϕ. Fig. 1b illustrates the normalized change in free energy for a circular array with different number of coordinating cylinders. As shown, when $n > n_c$, where $n_c = 2\pi/(\pi - \phi_e)$, pores shrink to their metastable equilibrium configuration, when $\phi = \phi_e$, but do not disappear. More recently, Wakai et al.[5] reached the same conclusions via a numerical method.

The thermodynamic analysis of neck growth by Kellett and Lange[2] lead to two major conclusions. First, for conditions where the dihedral angle is $<\pi$, the growth of necks between the initially touching particles in a powder compact will stop after some period of mass transport. Second, because real powder compacts are formed of connective, particle polyhedra, Kellett and Lange concluded that not all pores would disappear during the initial period of neck growth. Much earlier, Hoge and Pask[6] reached this same conclusion by determining the equilibrium configuration achieved by identical spheres that formed a periodic, three-dimensional (e.g., simple cubic) array. Namely, they showed that the periodic pores (e.g., those coordinated by 8 particles within the simple cubic arrangement) would not disappear, after the particles formed necks, for conditions where the dihedral angle was less than a critical angle. Similar to Lange and Kellett, Hoge and Pask reached this conclusion with the assumption that mass distribution between the identical particles would not occur.

To test the validity of the above conclusions, namely that neck growth between initially touching particles would stop and many pores defined by the initial touching particles would not disappear, Slamovich and Lange[7] investigated the densification behavior of particles synthesized as either single crystal or polycrystalline ZrO_2 spheres via the electrostatic atomization of an aqueous Zr- and Y-acetate solution (0, 3 and 10 mole% Y_2O_3). The ZrO_2 spheres (1–2 μm diameter) containing either 0 or 10 mole% Y_2O_3 spheres quickly converted, via grain growth, into single crystals after heating to 1350 °C, whereas, as expected,[8,9] those containing 3 mole% Y_2O_3 remained polycrystalline after prolonged heating (>64 h) at 1400 °C.

Figs. 2 and 3 summarize the results of this study. As shown in Fig. 2a, when compacts of the spherical single crystal particles are heat treated at 1400 °C for periods up to 64 h, neck growth is observed for short heating periods between 1300 and 1400 °C (A in Fig. 2a), but necks stop growing after very short periods at 1400 °C. Fig. 2a is part of a series of micrographs taken at the same surface location after the specimen was heated, then cooled for SEM observations, and then reheated and cooled for observations, for many cyclic heating periods. It can be seen that most of the particles retain their identity from one micrograph to the next, whereas others (usually smaller particles) are consumed by neighboring particles, via coarsening. That is, once necks quickly form between touching particles, neck growth stops and coarsening becomes the dominate phenomenon associated with morphological changes. Identical observations are observed for both single crystal powders, namely, ZrO_2 containing either 0 or 10 mole% Y_2O_3.

Fig. 2b illustrates the same heating sequence for the spherical, polycrystalline particles (see insert). Unlike the single crystal particles, after ≈10 h at 1400 °C, the polycrystalline particles begin to loose their identity, and are no longer recognized after extended periods. Although grain growth was observed in the dense polycrystalline particles, the grains were always much smaller than the initial particles themselves. Likewise, when isolated pairs of particles are heat treated in the same way, it was also observed that neck growth stops for the single crystal particles, whereas neck growth between the polycrystalline particles does not stop until the two particles become one larger polycrystalline sphere.[7]

Fig. 3 illustrates the density of powder compacts made from the three powders, heat treated for different periods from room temperature to 1400 °C and then at 1400 °C for extended periods. It can be seen that powder compacts formed with either single crystal powder exhibit most of their shrinkage (increasing their relative density from ≈0.4 to ≈0.63) during the period of neck growth (between 1300 and 1400 °C), whereas little densification continues for extended periods at 1400 °C. That is, shrinkage is concurrent with neck growth, i.e., via grain boundary diffusion. After neck growth ceases, the rate of shrinkage is much less.

As shown in Fig. 3, the compacts formed with the polycrystalline particles exhibit a much larger change in density (from ≈0.4 to ≈0.9) relative to those formed with the single crystal particles. For this case, the densification rate decreases at 1400 °C as the pores become isolated for relative densities >0.85. Micrographs of polished and etched bodies formed with the polycrystalline particles and heat treated at 1400 °C for 64 h, only revealed isolated pores. Whereas, micrographs of bodies formed with the single crystal particles also heated for the same period revealed an open, sintered particle network, penetrated by a co-mingled pore phase. Namely, the single crystal particles were readily identified, and appear similar to that shown in bottom micrograph of Fig. 2a.

The results for the experimental studies for single crystal particles clearly agree with the thermodynamic analysis, namely, the neck growth between single crystal particles will stop when the particles form a metastable equilibrium configuration. It is also clear that further densification must involve some other phenomenon, which is very sluggish at 1400 °C. As discussed below, it is shown that coarsening, i.e., the disappearance of smaller grains and the growth of larger grains appear to be the phenomenon that would continue densification.

After observing that neck formation between polycrystalline particles does not stop, Slamovich and Lange,[7] recognized that no new grain boundary forms between the polycrystalline particles. In fact, it was obvious that grain boundaries actually disappear during neck formation, and thus, unlike single crystal particles, the polycrystalline particles will never achieve a metastable equilibrium configuration.
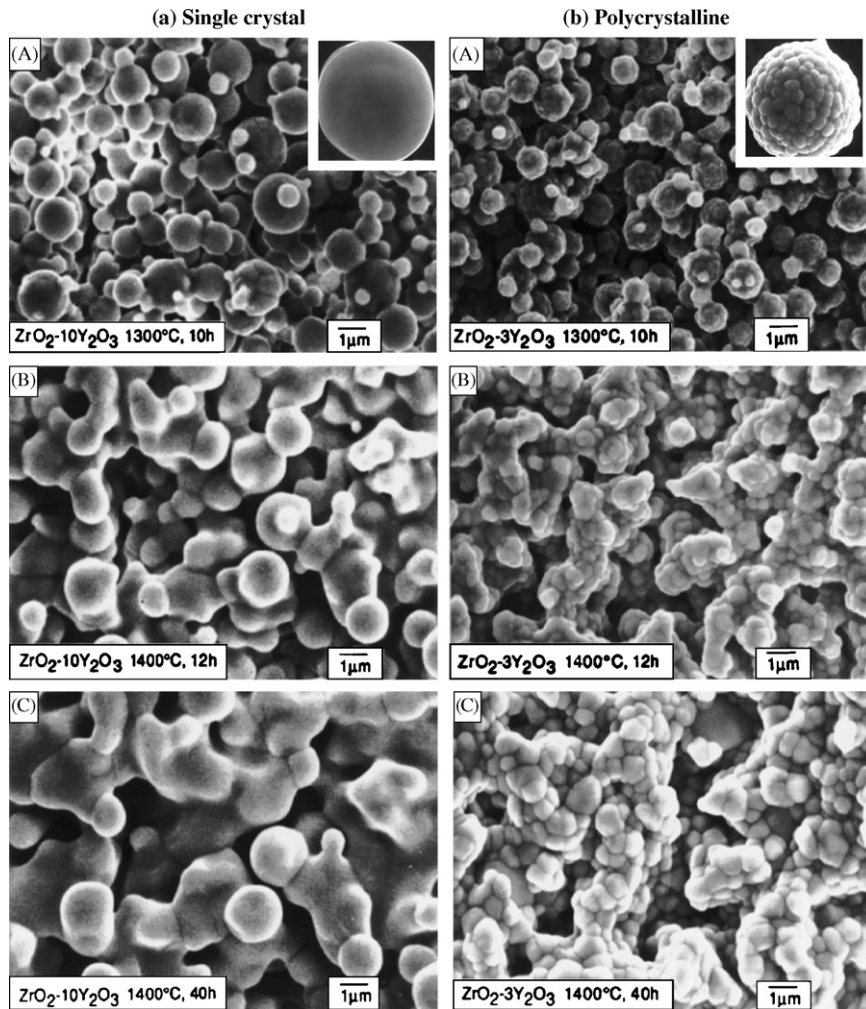
Fig. 2. (a) Identical areas for single crystal ZO₂ (10 m/o Y₂O₃) compact heated to 1300 °C–10 h (A), 1400 °C–12 h (B), and 1400 °C–40 h (C). Note: single crystal spheres do not lose their identity. (b) Identical areas for polycrystalline ZO₂ (3 m/o Y₂O₃) compact heated to 1300 °C–10 h (A), 1400 °C–12 h (B), and 1400 °C–40 h (C). Note: polycrystalline spheres do lose their identity.

3. Coarsening of grains during densification

It is well know that the transport of mass from the surface of one particle (or grain) to another via either surface diffusion or evaporation/condensation will not cause the densification of a powder compact.[10] But, as shown in this section, surface diffusion will cause smaller grains sandwiched between larger grains to disappear to reinitiate the neck growth process and thus, shrinkage between the larger particles. Thus, the cyclic neck growth (sintering), coarsening, and reinitiated neck growth was hypnotized[11] to allow densification to proceed after neck growth between the initially touching particles ceased.

Fig. 4a shows the sequential mass transport between a small and large particle for a given dihedral angle, ϕ_e. As reviewed above, neck growth will initially dominate any mass transport phenomenon because of the net negative curvature at the neck region where the particles join together. Here, as above, it will be assumed that neck growth is dominated by grain boundary diffusion, namely, mass in each of the two adjoining particles diffuses along the grain boundary to the surface to formed the neck, to reduce the distance between their mass centers, and thus produce shrinkage. When the size ratio of the adjacent particles is less than a critical value, neck growth will stop when the equilibrium condition is achieved as discussed above for identical particles.

Although neck growth terminates, a driving force for mass transport still exists due to the differential size of the two grains. This driving force results in mass transport between the grains, by surface diffusion (or evaporation–condensation), causing the smaller grain to 'donate' its mass to the larger grain, reducing the surface to volume ratio, and thus, the free energy of the system. The change in free energy for coarsening is related to the inverse radii of the two grains, and is thus much smaller relative to the driving free energy for neck growth due to the negative curvature in this region. In addition, the mass transport path is much larger relative to the grain boundary path. Thus, coarsening is expected to be much slower and should require higher temperatures.

Once neck growth ceases, it is obvious that the two sintered grains shown in Fig. 4a could further reduce their free energy if the grain boundary were to move through the smaller grain and disappear. This could happen, but as pointed out by Lange and Kellett,[11] the grain boundary would have to first increase its area, namely, there exist an energy barrier for the movement of
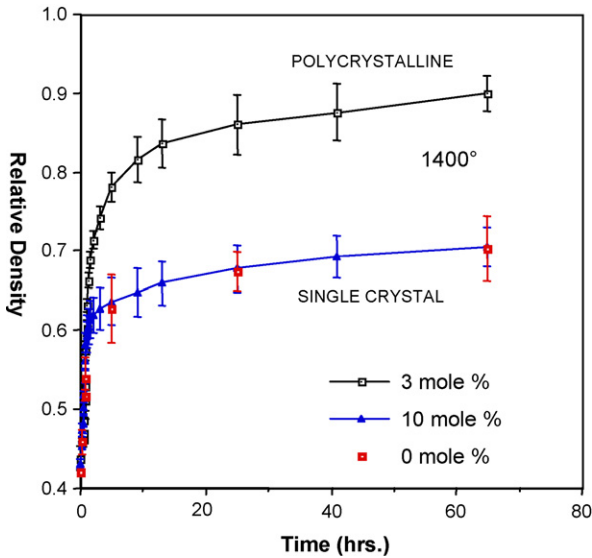
Fig. 3. Relative density vs. time at 1400 °C for three powder compacts composed of spherical, single crystal ZO_2 particles (0 and 10 mole% Y_2O_3) and spherical polycrystalline ZO_2 particles (3 mole% Y_2O_3). Per discussion in text, most of the densification for single crystal particles occurs during heating to 1400 °C.

the grain boundary though the smaller grain. Kellett and Lange showed that for a given dihedral angle, a special configuration (configuration c in Fig. 4a) could be achieved via coarsening where the energy barrier for grain boundary motion is reduced to zero. More than decade later, the same conclusions were reached by Zhang et al.[12] via computation modeling and very unique experiments.

Of greater interest for the densification of powder compacts is the case where the smaller particle is sandwiched between larger particles as shown in Fig. 4b. With the same sequence of mass diffusion paths, namely, initial neck formation (sintering) via grain boundary diffusion (a to b) and then coarsening (grain growth, b to c) via surface diffusion, the same condition that allows the grain boundary to move without an energy barrier is

achieved with coarsening as shown by c. In addition, it can be shown[11] that the same condition cause the two larger grain to touch one another and initiate neck growth once again. Thus, the second cycle of neck growth (c to d) reinitiates shrinkage. It can also be shown[11] that when the dihedral angle is >120°, the coarsening step (b to c in Fig. 4b) does not lead to shrinkage. Thus, by numerous steps of neck growth and coarsening, a powder compact can continue to undergo shrinkage. But because the driving energy for coarsening is relatively small, the period required for the cyclic neck growth and coarsening is expected to dominate the densification kinetics. To further illustrate this point, Lange[13] showed that during heating, the densification rate of a powder compact will reach a maximum value after achieving a certain relative density, and then rapidly decline, despite the higher temperatures. It was thus concluded by Lange and Kellett[11] that coarsening was an essential phenomenon in the densification of a powder compact. This is certainly consistent with the observations of Greskovich and Lay reported on pages 482 and 483 of "Introduction to Ceramics".

It should be pointed out here that the application of an external pressure (hot-pressing and hipping) would deform the partially dense network to continually cause particles to touch and sinter. It could be concluded that the application of pressure would avoid the need for coarsening to achieve full densification.

4. Coarsening of pores during densification

The Greskovich and Lay micrographs[11] not only illustrate grain growth during densification, but they also illustrate concurrent pore growth. It has been shown that particles that formed necks during the initial stage of densification can de-sinter if either the particles connected by the necks undergo coarsening and are constrained from shrinking or are pulled apart due to tensile forces applied to the sintered particles by the densification of one part or the compact relative to another. The first of these two phenomena can be illustrated by examining configuration b in Fig. 4b. If the smaller grain were to redistribute its mass
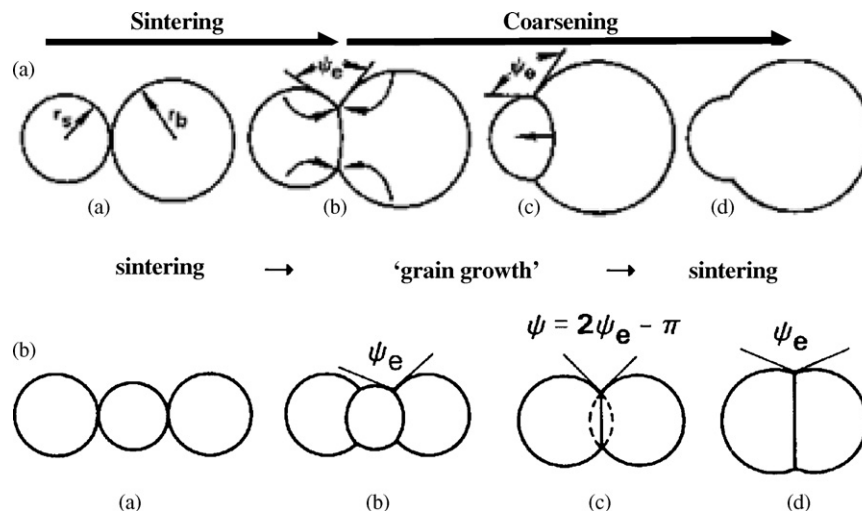

Fig. 4. (a) Sequential mass transport between two touching particles; steps: a to b, sintering; b to c, coarsening; c to d, grain boundary motion. (b) Sequential mass transport for two larger particles sandwiching smaller particle; steps: a to b, sintering; b to c, coarsening; c to d, sintering between larger touching particles.
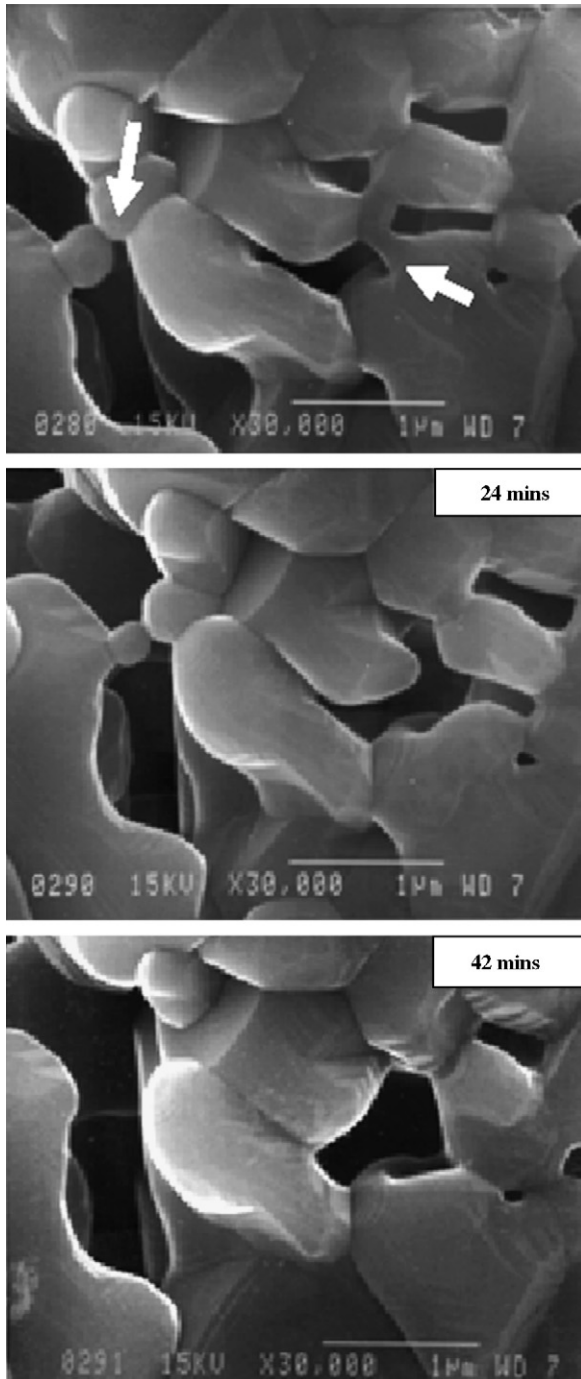
Fig. 5. Series of three micrographs of a partially dense alumina body, take at the same location after heating to 1600 °C for different periods (see inserts). Note the two white arrows where de-sintering occurs.

to the larger grains and the larger grains were constrained from moving together, the smaller grain would break-away (de-sinter) from one of the larger grains and be adsorbed by the other. This is shown at two locations in the sequential micrographs (see two white arrows) of Fig. 5.

De-sintering is a phenomenon commonly observed for the densification of polycrystalline thin films biaxially constrained by a substrate.[14] It occurs when grain growth occurs either in a polycrystalline fiber[15] or a dense polycrystalline thin film[16] that

is constrained by either a surrounding matrix, or a substrate, respectively. De-sintering occurs within a powder compact that is constrained from shrinking caused either by a network of inclusions[17] or simply by a distribution of denser regions. Pore growth occurs to reduce the surface to volume ratio of a powder compact, when the compact is either constrained from shrinking, or when surface diffusion and/or evaporation condensation are the only mass transport paths. For the case of interest here, pore growth will occur in regions where densification is locally constrained, whereas the partially dense body will globally undergo densification as described in the next section.

5. Disappearance of isolated pores

Prior to this section, portions of the partially dense body were consider to contain an interconnected pore phase much like that shown in Fig. 5. Isolated pores will be considered here, a condition usually considered to occur when the relative density is >0.90. Until the report by Kingery and Francois,[18] pores within a polycrystalline material were treated as spherical voids. The relation between the driving energy that drives mass to the pore was simply given by $\sigma = 2\gamma/R_p$, where γ is the surface energy/unit area and R_p is the radius of the pore. Kingery and Francois pointed out that because grain boundaries intersected the pore, and Young's relation between the grain boundary and pore surface must be obeyed, the real surface curvature of the pore would be either convex or concave. They argued that pores with concave surfaces would grow and those with convex surfaces would shrink and disappear. Kellett[19] recognized that the mass to fill the pore had to come form the external surface of the polycrystalline body. Kellett therefore compare the free energy of an isolated pore to that of the external surface to show that convex pores would shrink to an equilibrium size, and not grow as suggested by Kingery and Francois. Kellett showed that this condition was related to the grain size, dihedral angle and the number of coordinating grains. He also showed that convex pores would shrink and disappear. Because this thermodynamic argument was compelling, it was hypothesized that grain growth must be linked to the disappearance of isolated pores. Namely, since the curvature of pores was related to the number of coordinating grains, it was postulated that grain growth was required to change the surface curvature from convex to concave.
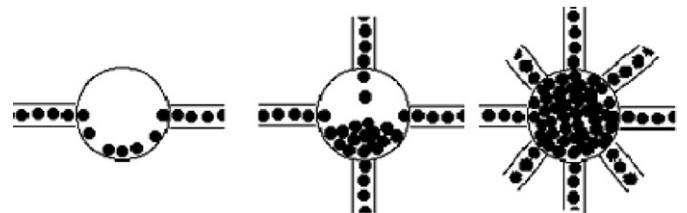

Fig. 6. Three pores, each connected to a different number of grain boundaries. Black circles are 'packets' of mass being delivered to the pore via the grain boundaries. The pore can be visualized as a 'roundabout', and the back circles as speeding cars that fill the 'roads' to become 'stuck' within the roundabout (pore).
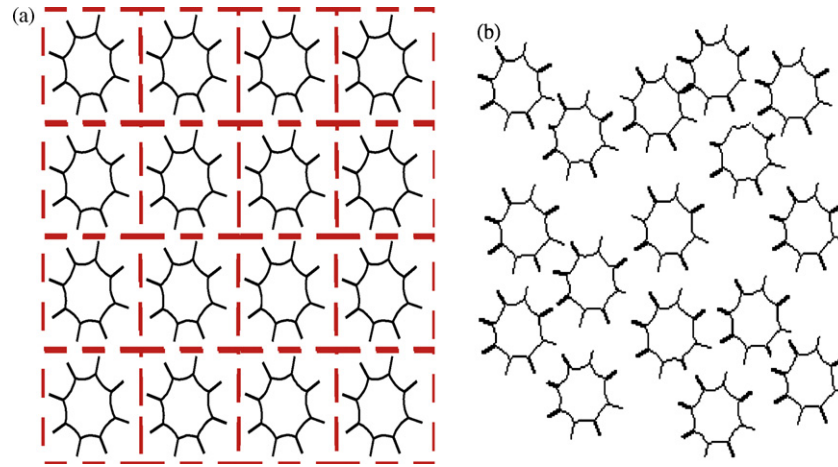
Fig. 7. (a) Periodic unit cells each containing a pore. Each cell exhibits identical shrinkage vs. time and thus mimics the shrinkage of the body. (b) Pores are not periodic; thus the shrinkage of each pore is mechanically constrained by others.

Slamovich and Lange[20] tested this hypothesis by preparing specimens containing large pores produced when identical, dispersed polymer spheres disappeared during the heating of a powder compact. In one set of specimens, grain growth was so rapid that all pores had concave surfaces after short periods at high temperatures. Whereas, for the second set of specimens grain growth was so sluggish, the pores were always coordinated by many grains and their surfaces were concave. These experiments disproved the initial hypothesis. Namely, pores surrounded by a large number of grains disappeared despite their convex curvature, whereas pores surrounded by large grains were very sluggish to shrink, despite their concave curvature. To reconcile the experimental findings with the thermodynamics relating surface curvature to pore disappearance, it was first postulated that in reality, pores with concave curvatures were generally larger than their equilibrium size, and thus, the pore should be considered as a simple sphere with a negative curvature. Second it was recognized that since grain boundaries are the only rapid paths for mass transport, the greater that number of grain boundaries intercepting the pore, the faster mass can be delivered to the pore, thus, the greater the rate of pore disappearance. Fig. 6 illustrates this idea, with pores (roundabouts) connected by 2, 4 and 8 roads (grain boundaries). Cars (units of mass), always filling the roads, all stream into the roundabout at a rate that is governed by the driving energy, $\sigma = 2\gamma/r$. Pores connected to many roads fill faster than those connected by fewer roads.

It was further suggested that if the pores are identical and are periodic as shown in Fig. 7a, and if the pores were to shrink at the same rate, each 'unit cell' containing a single, identical pore would shrink identically as all others. Since the unit cells are connected to one another, the shrinkage of one cell would mimic all others, and thus the body, as a whole, would mimic that of the unit cell. If this were the case, each cell would contribute mass from its external surface, and thus, the distance needed to move mass to the pore would be related to half the distance between the pores. This idea lead to a simple expression relating the densification rate, $\dot{\rho}$, to the number of grain boundaries

intersecting the pore, n, the driving free energy, $\sigma = 2\gamma/R_p$, and the half distance between the periodic pores, h,

$$\dot{\rho} \propto \frac{2n\gamma h}{R_p}. \qquad (3)$$

As pointed out by Sir Richard Brook in 1969,[21] pores not connected to grain boundaries, but embedded within the grain, are the least likely to disappear.

In reality, pores are never periodically distributed, but are randomly distributed as shown in Fig. 7b. Thus, because the pores are not periodically distributed and have different sizes, choosing the smallest volume element (a unit cell that contains a number of pores) that shrinks in an identical manor as the body itself is not a trivial task, and part of the unfinished story of densification.

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