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Reprinted from *The Journal of The American Ceramic Society*, 40(3), 1957, pp. 80-5

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Role of Grain Boundaries in Sintering*

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During sintering, grain boundaries act either as sinks or as diffusion paths for lattice vacancies. Thus the configuration of the grain boundaries will have an important effect on the rate of sintering. Grain growth during sintering changes the configuration of grain boundaries relative to pores and thus may markedly influence the shrinkage rate; for example, for uniformly distributed pores the shrinkage rate will increase as the grain size decreases. Impurity additions will increase the sintering rate if they increase diffusion rates, but they may also increase sintering rates by impeding grain-boundary movement. Some experimental evidence is presented to support these conclusions.

I INTRODUCTION

In recent years the mechanism of matter transport during sintering has been discussed in a number of papers. Two major mechanisms have been proposed: plastic flow¹ and atomwise diffusion.² The object of this paper is to present some observations which support a diffusion model for the process and to emphasize the importance of grain boundaries and grain growth in the process. The general approach is to study the distribution of pores, the size of the pores, and the positions of the grain boundaries on polished surfaces of pure sintered alumina specimens and to interpret these observations in terms of a diffusion model of matter transport.

* Presented at the Fifty-Seventh Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 27, 1955 (Basic Science Division, No. 21).

II MICROSCOPIC STUDY OF DISTRIBUTION OF PORES

The distribution of pores in a ceramic is readily studied by examining a polished surface with vertically incident reflected light in a conventional metallograph. Figure 1 shows such a specimen of 900-mesh alumina powder, pressed and sintered for 1 hour at 1800°C. The grains have been revealed by etching for about 30 seconds in molten potassium pyrosulfate, made by heating potassium bisulfate in a platinum crucible until strong fumes of sulfur trioxide are evolved.

Figure 1 was photographed at $\times 500$. The average grain diameter is about 15μ ; thus the grains are about the same size as the original 900-mesh powder. All, or almost all, pores lie on grain boundaries, which is to be expected since the pores are formed by the misfit of the original single-crystal particles of alumina powder.

Figures 2 through 5, taken at a magnification of $\times 100$, show the change in structure which occurs on further heating. Figure 2 is taken from the same specimen as Fig. 1 and shows the distribution of pores at the grain boundaries. Figure 3 shows a similar specimen after 1 hour at 1900°C. Extensive grain growth occurred during this further heating; the average grain size is now more than 300μ . Thousands of pores are found within each large grain, but the

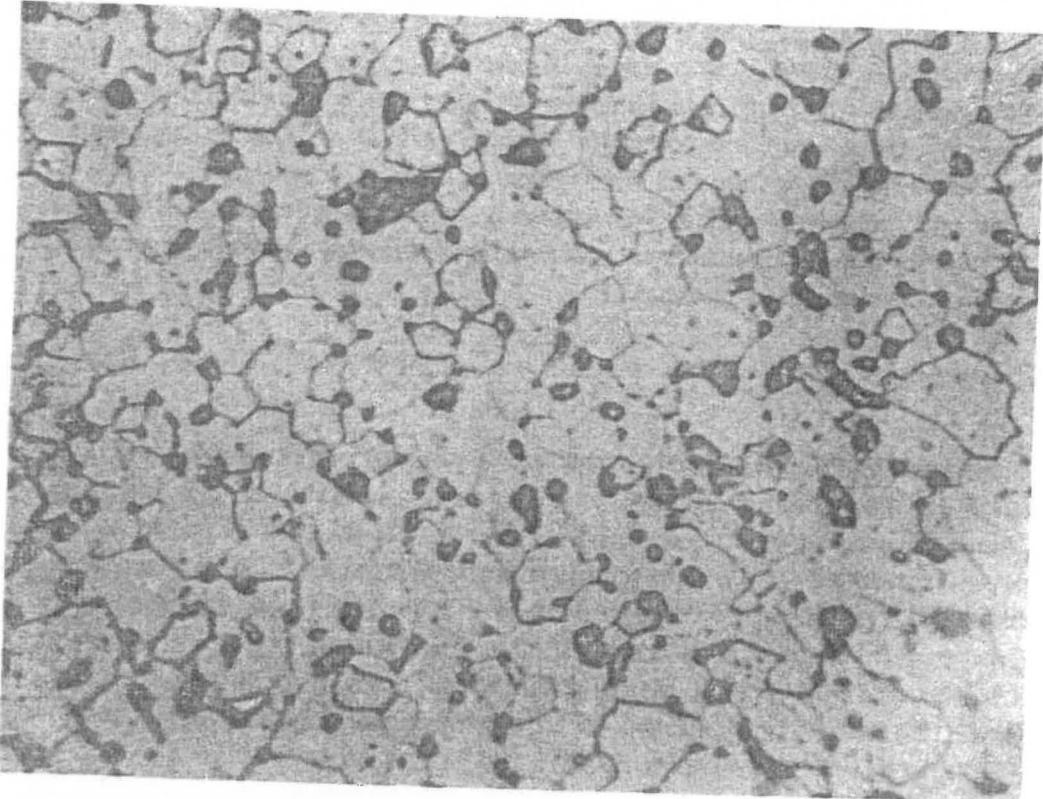


Fig. 1. Distribution of pores in alumina powder sintered 1 hour at 1800°C. Etched in hot $K_2S_2O_7$. Vertical illumination ($\times 500$).

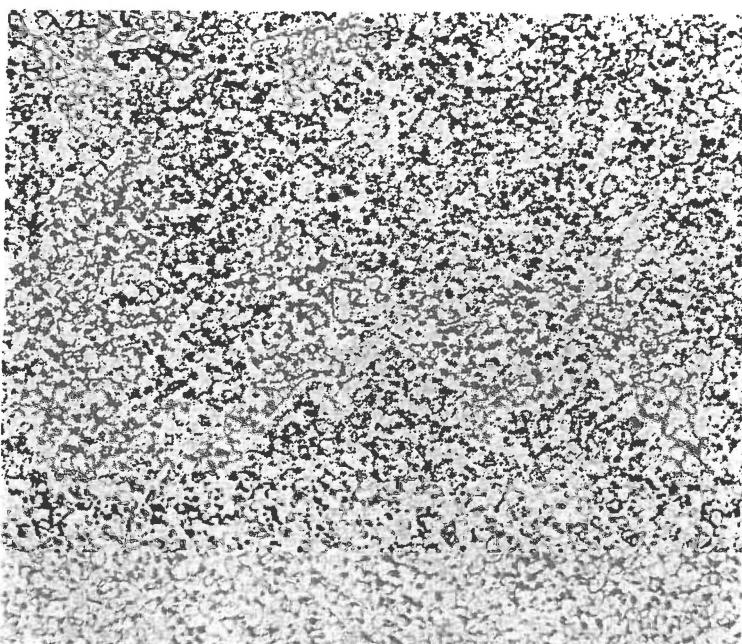


Fig. 2. Taken from same specimen as Fig. 1 ($\times 100$).

average separation of pores is about the same before and after this heat-treatment, indicating that grain growth without much further densification has occurred. After heating for 2 hours at 1950°C . (Fig. 4), some of these pores disappear and the others grow somewhat larger. The disappearance is particularly marked near the grain boundaries, as is shown more clearly in Fig.



Fig. 3. Alumina powder sintered 1 hour at 1900°C . Unetched grain boundaries are revealed by cracking. Exaggerated grain growth has occurred and many pores are isolated inside the grains. ($\times 100$.)

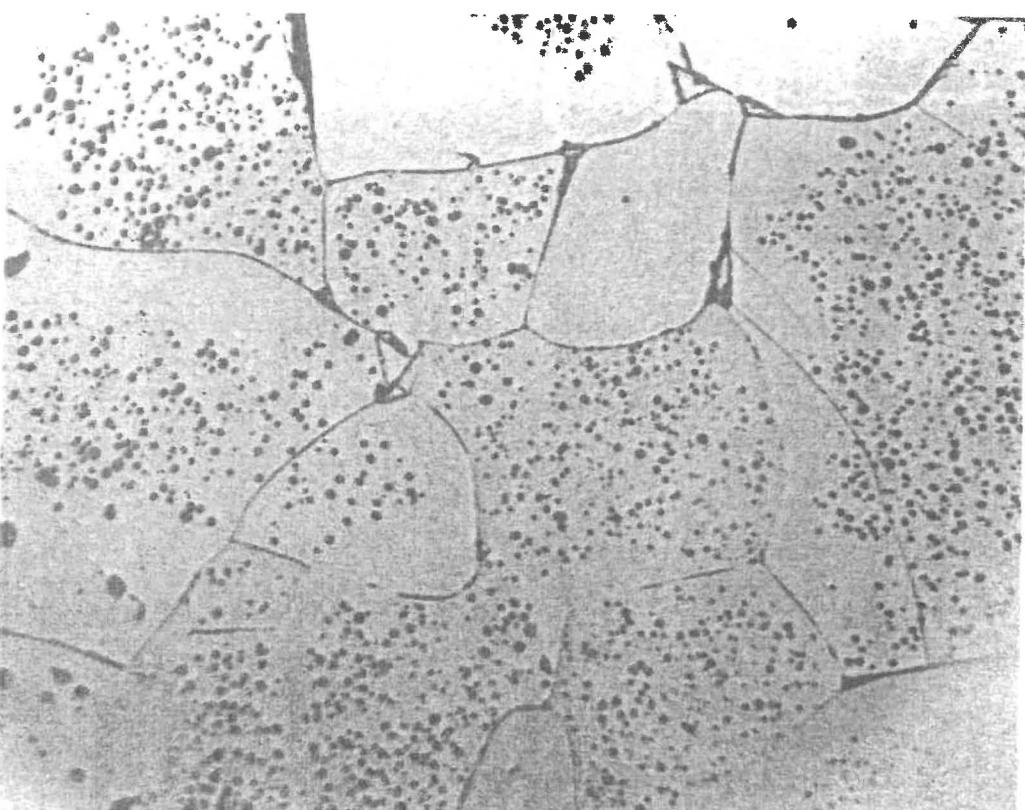


Fig. 4. Alumina powder sintered 2 hours at 1950°C. Unetched grain boundaries are revealed by cracking. Many pores have been eliminated, particularly near grain boundaries. Bright-field vertical illumination. ($\times 100$.)



Fig. 5. Same field as Fig. 4 photographed with polarized light to eliminate surface reflection. Dark areas at grain boundaries indicate elimination of porosity. ($\times 100$.)



Fig. 6. Alumina powder sintered 2 hours at 1950°C. Growth is shown of some pore that are isolated from grain boundaries. Polarized vertical illumination. ($\times 250$.)

5. This photomicrograph shows exactly the same field as Fig. 4, but the specimen was illuminated with vertically incident polarized light and was observed through a crossed analyzer. This method of observation eliminates the reflection from the upper surface of the specimen and permits an 'optical section' below the surface to be observed. Spherical pores depolarize the incident beam and thus appear bright. Pore-free regions of the material appear dark, and it can be readily seen that each crystalline grain is outlined by a dark region of essentially pore-free corundum.

Figure 6, taken at $\times 250$ with polarized light, shows the individual pores more clearly and demonstrates that after 2 hours at 1950°C, some pores have grown larger; indeed, some are even larger than any of the powder particles that were initially present in the specimen.

III MECHANISM OF MATTER TRANSPORT

The most pertinent observation is that pores near the grain boundaries shrink and disappear more rapidly than those in the center of the grains, as has previously been noted in copper by Alexander and Balluffi.³ If the reason for shrinkage were indeed that the surface tension of the pores applied the equivalent of an external hydrostatic stress, so that pore shrinkage occurred by plastic flow,^{1(b), (d)} then all pores should shrink at approximately the same rate

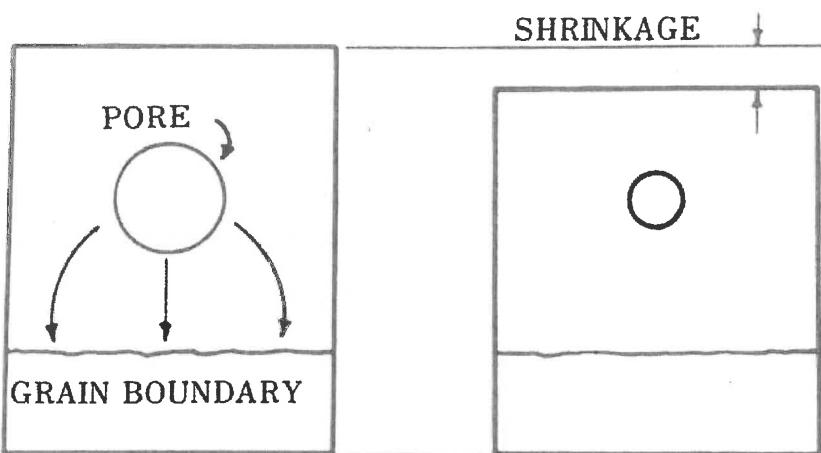


Fig. 7. Grain-boundary sink model in a bicrystal. Vacancies diffuse from the surface of a pore to a grain boundary where they collapse. The pore shrinks and the grains move together to produce an external shrinkage in a direction perpendicular to the grain boundary.

It seems more probable that the mechanism involved is a diffusional one, like that proposed by Nabarro⁴ and by Herring⁵ to explain the apparently viscous flow observed by Udin, Shaler, and Wulff⁶ in fine polycrystalline wires heated close to their melting points and subjected to externally applied stresses of the order of those applied by their own surface tension. As applied to the sintering process, the Nabarro-Herring model would assume that atoms diffuse from grain boundaries to neighboring pores and fill them, and that the grains move together to fill the space left by the missing atoms. Stated differently, lattice vacancies are present in excess of the equilibrium concentration in the crystal lattice near pores. These vacancies can diffuse to the grain boundaries and collapse there, to produce an externally detectable shrinkage as illustrated schematically in Fig. 7.[†]

IV GRAIN-BOUNDARY VERSUS LATTICE DIFFUSION

One might argue that shrinkage does not result from the collapse of vacancies at grain boundaries, but rather that grain boundaries act as pipes to conduct vacancies to the surface where they are discharged. The grain-boundary collapse model predicts a shape change of the type shown in Fig. 7, whereas the grain-boundary pipe model would produce a shape change of the type shown in Fig. 8. Balluffi and Seigle⁷ have presented evidence which indicates

[†] Since this paper was originally presented, Seigle and Pranatis have also called attention to this model (L. L. Seigle and A. L. Pranatis, "Mechanism of Sintering of Nonvolatile Metals and Oxides," *Metal Progr.*, **68**(6), 86-90 (December 1955); *Ceram. Abstr.*, 1956, May, p. 106g).

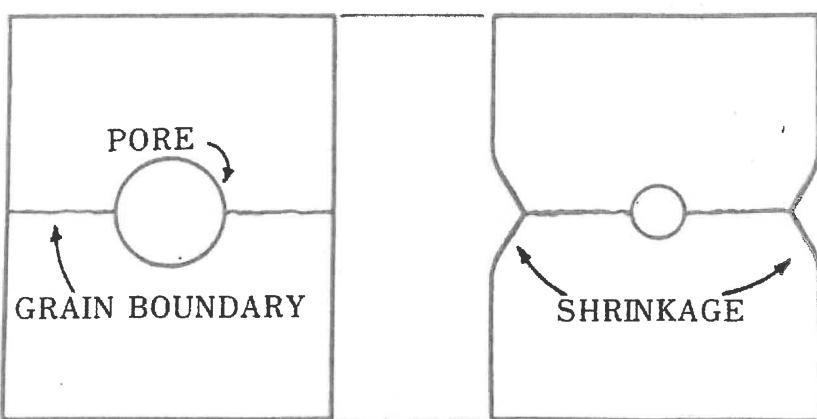


Fig. 8. Grain-boundary channel model. Vacancies diffuse from pore along grain boundary to the surface where they are discharged, leaving a depression.

that the grain-boundary collapse model is more probable. They studied the distribution of pores in sheet specimens of α -brass in which an excess of lattice vacancies had been produced by dezincification. In their thin sheet specimens, they observed that pores precipitated in the centers of the grains but that no pores precipitated near the grain boundaries. Since their specimens were thin, the grain boundaries were perpendicular to the sheet surface. They observed that specimen shrinkage occurred predominantly in the plane of the sheet, i.e., normal to the grain boundaries as indicated in Fig. 7. It may thus be concluded that grain boundaries act as vacancy sinks and not as pipes to conduct vacancies to the specimen surface.

The fact that pores disappear much more rapidly when they lie near grain boundaries than when they lie in the interior of grains might lead to the conclusion that grain-boundary diffusion is the predominant mechanism of matter transport. However, there is ample evidence to indicate that lattice diffusion is also important in producing densification during sintering.

Numerous observations have been made that minor additions of second components, which produce lattice defects and thus increase the diffusion rate through the lattice, increase the rate of sintering. Marshall, Enright, and Weyl,⁸ for example, report that the addition of TiO_2 to ZnO , which addition increases the number of oxygen vacancies, decreases the temperature at which shrinkage can be observed in pressed zinc oxide powder. Although such an addition can introduce lattice vacancies and thus facilitate diffusion through the lattice, it seems unlikely that it would have much effect on the structure of, or on the diffusion rates through, highly disordered grain boundaries. Thus, the fact that additions like this are effective in increasing the sintering rate indicates that a major amount of the diffusion occurs through the lattice.

As can be seen in Fig. 6, certain pores which are isolated from boundaries may increase tremendously in size during sintering. These large pores undoubtedly grow because they act as vacancy sinks and compete with grain boundaries for vacancies diffusing away from smaller pores. The fact that these

pores which do not lie on grain boundaries can grow so large again indicates that an important amount of lattice diffusion does occur.

It can also be deduced qualitatively what the effect of pore diameter and temperature is on the relative importance of grain-boundary and lattice diffusion, for a pore that lies on a grain boundary. Consider a pore of diameter d which lies on a grain boundary. In the lattice and boundary immediately surrounding the pore there will be an excess of vacancies. These vacancies must diffuse to and along the boundary to collapse and produce shrinkage. If the vacancies diffuse along the boundary only, they must diffuse away from the pore through an area that is proportional to δ , the boundary thickness. If they diffuse through the lattice, they will diffuse away from the pore through an area that is proportional to d , the diameter of the pore.

Assuming that the concentration gradient of vacancies is the same in the lattice as in the grain boundary, the flux of atoms through the boundary will equal that through the lattice when

$$D_b\delta = D_l d \quad (1)$$

where D_b and D_l are the diffusion coefficients for vacancies in the boundary and lattice, respectively. It may thus be concluded that at a given temperature, increasing the pore size will increase the relative importance of lattice diffusion. Furthermore, at least in metals, it has been observed⁹ that the activation energy for lattice diffusion is greater than the activation energy for grain-boundary diffusion. Thus it is also concluded that lattice diffusion will be favored at higher temperatures.

Of course, pores which lie on or near a grain boundary always disappear more rapidly than pores far removed from grain boundaries because the concentration gradient of vacancies is much steeper when pores lie near a grain-boundary sink than when they are far removed.

V GRAIN GROWTH DURING SINTERING

We shall now inquire into the effect of grain growth which may occur during sintering on the shrinkage of pores and on the residual porosity which remains after long sintering times. First, we shall look at the process of grain growth in a polycrystalline single-phase material.

The results of most investigations of grain growth show¹⁰ that on heating, grain boundaries in polycrystalline specimens tend to migrate toward their centers of curvature. In this process, some grains disappear and the average size of the remaining grains increases. In general the grain size remains uniform during this process and growth continues at a rate which is inversely proportional to the instantaneous grain size until the average grain diameter is of the order of the minimum dimensions of the piece.

Second-phase inclusions may inhibit this grain-boundary migration, as shown in Fig. 9. Direct evidence of the impeding effect of pores on grain-boundary

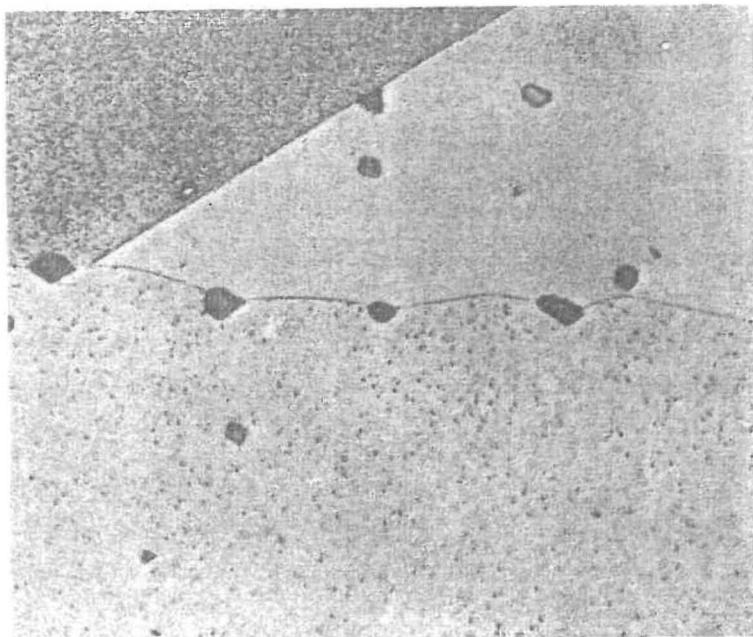


Fig. 9. Inhibition of grain-boundary movement by second-phase inclusions in alpha brass. Scallops appear on boundary where inclusions inhibit movement. ($\times 500$.)

migration may also be deduced from Fig. 10. Notice in this figure that the grain boundary lies on one side of the void-free region. This is because the boundary tends to migrate toward its center of curvature but is stopped by impeding pores. The pores touching the boundary disappear. As soon as this impediment is removed, the boundary moves to a new position of stability in contact with the next layer of pores. Thus the boundary appears to move slowly through the specimen and to sweep the region through which it moves free of pores.

As a result of this inhibition by pores or other second-phase inclusions, continuous grain growth stops in the presence of a dispersed phase when the following condition is fulfilled:¹¹

$$D = d/f \quad (2)$$

D = average diameter of grains.

d = average diameter of inclusions or pores.

f = volume fraction of inclusions or pores present.

It has been long realized, however, that under certain conditions, particularly in the presence of growth-inhibiting inclusions, an exaggerated or discontinuous grain growth may occur.¹² An example is shown of a large grain growing in a matrix of small grains (Fig. 11, a commercial ferrite). As a result of such growth, many pores become isolated inside grains, and after isolation they disappear only very slowly.

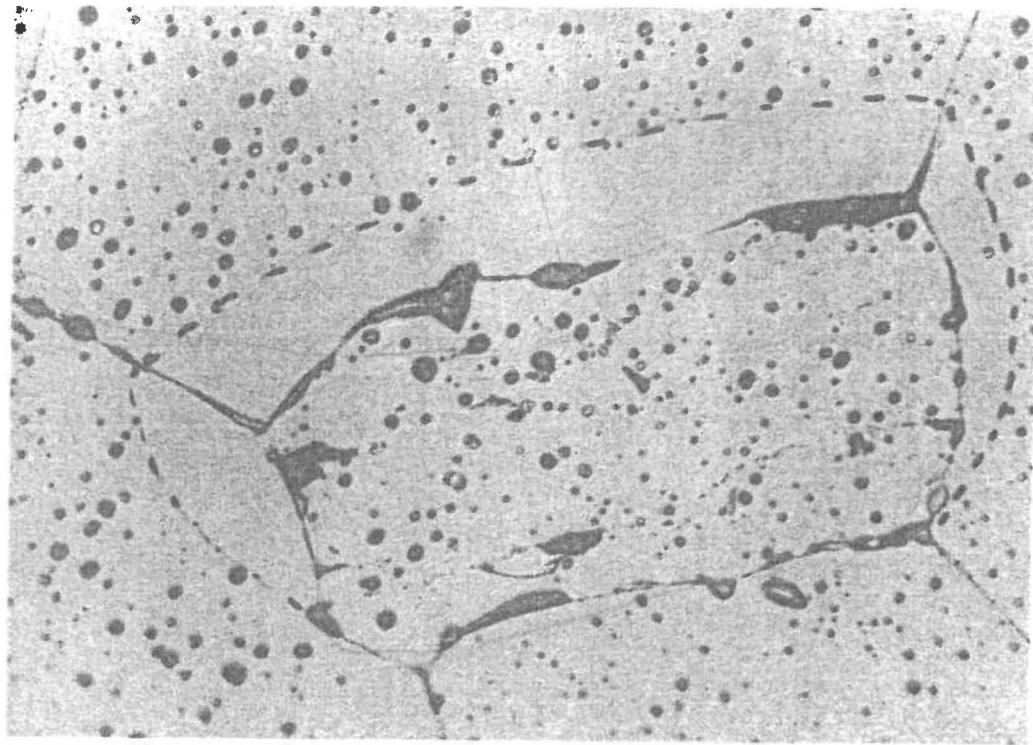


Fig. 10. Sweeping out of pores by grain-boundary migration. The original position of the grain boundary is shown by the dotted lines. The apparent porosity on the present boundary is the result of chipping when the specimen was polished. ($\times 250$.)

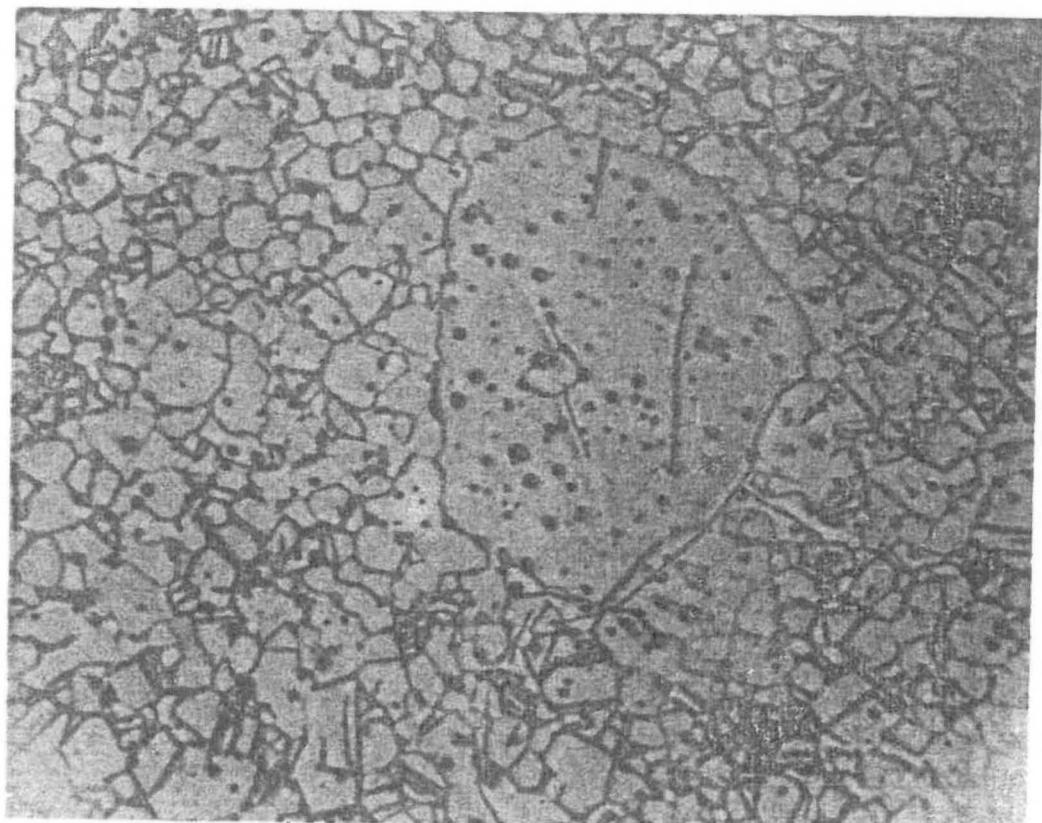


Fig. 11. Discontinuous grain growth in a commercial ferrite. Note pores isolated inside large grain. ($\times 100$.)

The conditions necessary for such discontinuous grain growth are as follows.¹² Equation (2) holds for grain growth in a specimen where the grain size is uniform; i.e., as seen on a polished section all the grains will be about the same size and the number of sides on each grain will range from 3 to 8 or 9. Under these conditions the growth force is relatively small, since Von Neumann¹³ has shown that for a given grain the growth force is proportional to $(N - 6)$, where N is the number of sides on a grain. If as a result of some local perturbation one grain with many sides is introduced into such a specimen, it will be able to grow past the inhibiting inclusions or pores, because its growth force is greater, although the growth of all other grains will be inhibited by the inclusions present.

Now, as was indicated previously, all pores which are formed between grains as a result of the misfit of particles lie on grain boundaries in the early stages of sintering. These pores act like any other second-phase inclusion to inhibit the migration of grain boundaries. In the early stages of sintering, the volume fraction of pores is so large that essentially no grain growth occurs. As sintering proceeds, the volume fraction of pores gradually decreases and finally the conditions of equation (2) are fulfilled. Now, the disappearance of a few more pores will permit a few grains to grow somewhat, and thus to gain more sides than their neighbors. By the Von Neumann criterion, the growth force of these grains is increased so they will continue to grow, to gain yet more sides, and to grow more rapidly. One thus has the situation where a few grains grow at the expense of many neighbors to produce a discontinuous increase in grain size like that shown in Fig. 11.

Once such exaggerated grain growth or secondary recrystallization has occurred, many pores will be isolated in the centers of grains, far removed from grain boundaries, and will of course disappear only very slowly. Unless sintering is continued for very long times, shrinkage will seem to have stopped at this stage. It is interesting, therefore, to inquire into what residual porosity might exist when the conditions for exaggerated grain growth obtain.

If pores are the only second phase inhibiting grain growth, then the conditions of equation (2) are fulfilled when f and d represent the volume fraction and average diameter of the pores. For example, if the average pore diameter is about one-tenth that of the grains, exaggerated growth will occur when the porosity is about 10% and the limiting density will be about 90% of theoretical. If other second-phase inclusions that inhibit grain growth are present, the volume fraction of pores will be smaller than that computed above before exaggerated growth will occur; thus the limiting density will be higher. If the concentration of other second-phase inclusions is so high that complete removal of pores does not lead to the satisfaction of equation (2), then all pores will remain on grain boundaries until they have disappeared and essentially theoretical density should be obtained.

An example of this is shown in Figs. 12 and 13.† Figure 12 shows a specimen

† These specimens were called to the author's attention by Louis Navias.

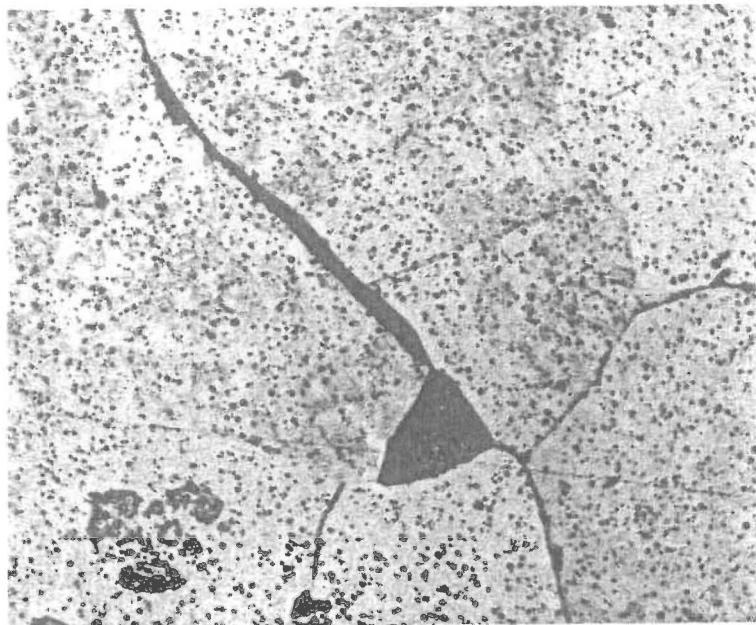


Fig. 12. Alumina powder sintered 2 hours at 1950°C. Coarse grained. Density is about 95% of theoretical. ($\times 100$.)

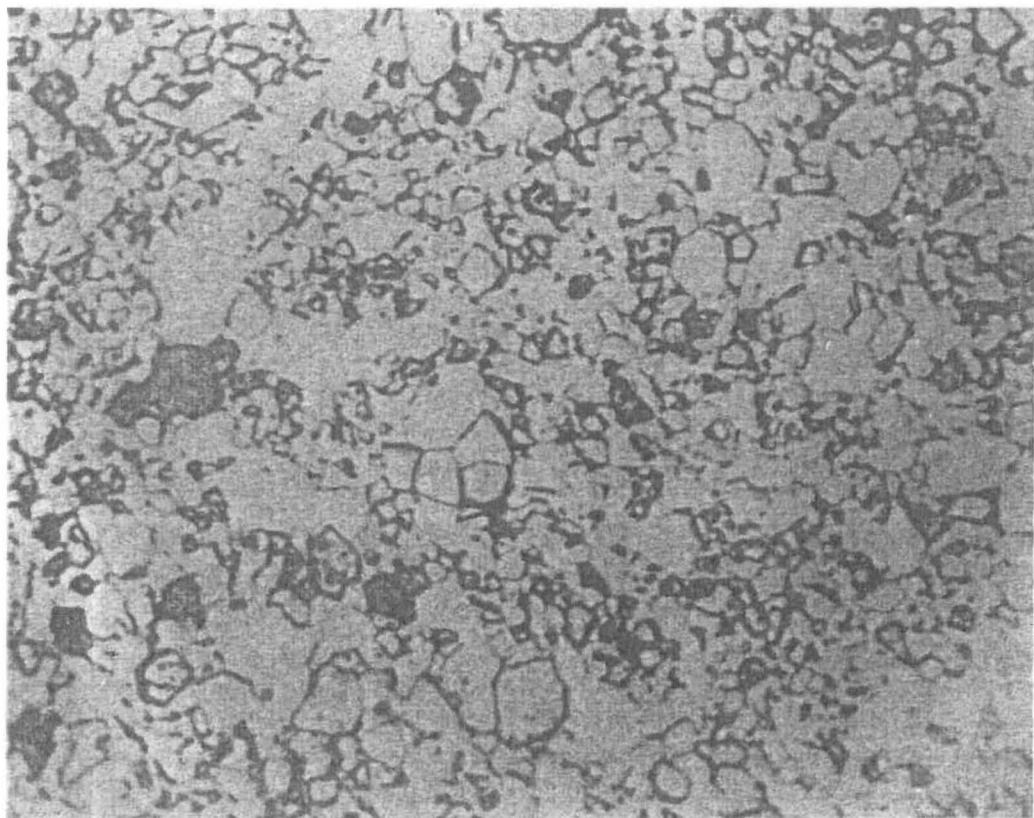


Fig. 13. Alumina powder sintered 2 hours at 1950°C. Grain growth was inhibited by impurities. Density is 99.5% of theoretical. ($\times 250$.)

of alumina fired for 2 hours at 1950°C. Exaggerated grain growth has occurred, and many pores are left inside the grains; the ultimate density is about 95% of theoretical. Figure 13 shows an almost identical specimen in which grain growth did not occur, presumably because of unidentified impurities that were present. The density is essentially theoretical and the grain size is little larger than that of the original particles.

VI CONCLUSIONS

It is found that the preferred disappearance of pores near a grain boundary is consistent with the atomwise diffusion of matter from grain boundaries to pores, with a concurrent shrinkage. The observations are not consistent with a plastic-flow model of sintering. Since grain boundaries play such an important role in the process, their mobility is of great importance in controlling the ultimate density of a specimen; the greatest densities will be attained when grain growth is inhibited.

ACKNOWLEDGMENT

The author would like to acknowledge helpful discussions with R. L. Coble. Mrs. J. Tomlinson prepared most of the photomicrographs.

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