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The Development of Pore-Free Ceramics

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ABSTRACT

In the early 1950s the techniques and understanding previously used only to study the microstructure of metals began to be applied to polycrystalline oxides (which about that time began to be called ceramics). Sintering is a phenomenon of interest to both fields, and the development of sintering science provided a bridge between physical metallurgy and the newly developing physical ceramics. The application to ceramics of the understanding of the mechanisms of grain growth in metals soon led to the production of pore-free alumina and yttria. A critical step was the prevention of discontinuous grain growth by the reduction of grain boundary mobility with additions of magnesia in alumina and thoria in yttria. Some discussion of how these additives operate is presented and a new mechanism is proposed.

INTRODUCTION

The development in the late 1950s of a process for sintering substantially pure alumina powder into a pore-free product, Lucalox alumina, dramatically demonstrated that microstructure control was as feasible in ceramics as it is in metals, and that valuable new products, such as the high pressure sodium vapor lamp, could be made with structure controlled ceramics. In this discussion of that development and subsequent work, the importance of the understanding obtained from parallel research on metals is emphasized. The

development also revealed some new relationships between sintering and grain growth, some new requirements for optimum powder characteristics and displayed some new phenomena that are even yet only partly explained. These are discussed briefly and a new suggestion for the mechanism by which MgO reduces grain boundary mobility is made. The paper is in four parts:

- (I) The work which establishes the importance of pore-grain boundary separation to the ability to make pore-free ceramics; it demonstrated that the processes of matter transport to remove pores from a sintering body, and the processes of grain growth are interlocked.
- (II) The establishment of a need for pore-free alumina, and the development of a process for making it.
- (III) The several discussions of how MgO operates to facilitate pore removal from alumina during sintering.
- (IV) A general discussion of mechanisms for reducing grain boundary mobility with additives.

I THE IMPORTANCE OF PORE-GRAIN BOUNDARY SEPARATION

The pore-free ceramic development started with an attempt to test the mid-1950s belief of many metallurgists that it should be possible to modify the composition or microstructure of ceramics to make them ductile. One of the author's colleagues at the G. E. Research Laboratory heated some sintered alumina to about 1900°C and hit it with a forging hammer. The results were instructive, and not favorable to the ductile ceramics idea: the piece broke into a number of shards. At the time the author was a metallurgist beginning to become interested in ceramics, so he polished one of the shards as metallographers do, etched it with molten potassium pyrosulfate and examined it under a metallographic microscope (an unheard-of procedure for a ceramist at the time) and observed a microstructure like that shown in Fig. 1. A reasonable interpretation supported a diffusion model of matter transport, and it led to the work reported in 'The role of grain boundaries in sintering' [1].

At that time, many people still believed that matter transport in sintering was accomplished by plastic flow. As reported in that paper, its goal was 'to present some observations which support a diffusion model for the process and to emphasize the importance of grain boundaries and grain growth to the process. The approach is to study the distribution of pores, the size of pores and the positions of grain boundaries . . . and to interpret these observations in terms of a diffusion model of matter transport' [1].

The specimen of Fig. 1 was heat-treated at 1950°C. It shows large grains with many pores inside them, and in particular, the regions near the grain boundaries are free of pores. Figure 2, using polarized light in vertical illumination to look inside the specimen shows this more strikingly (a similar phenomenon had been observed by Alexander & Baluffi [2]). The structure was interpreted to indicate that pores disappear more rapidly when in contact

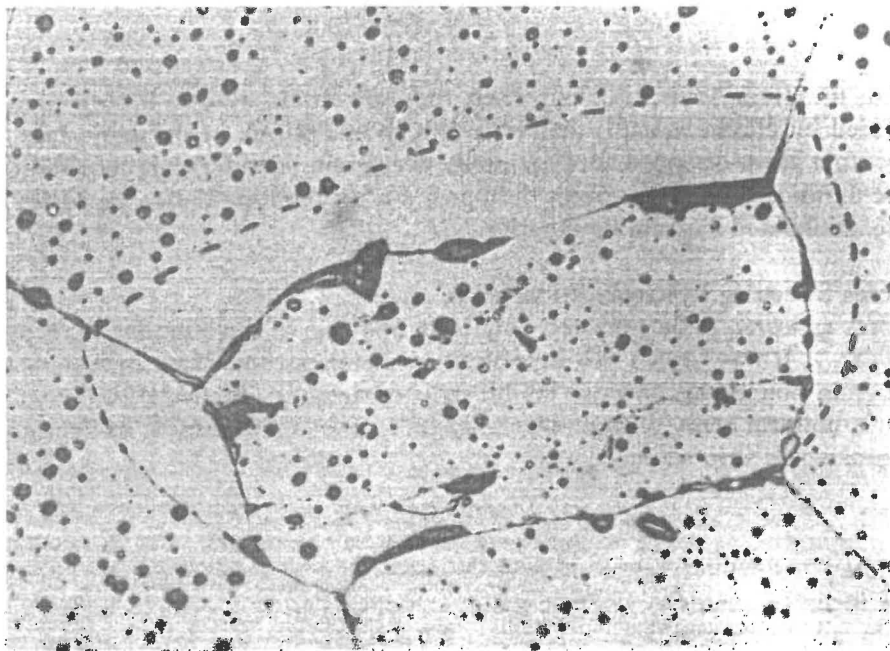


Fig. 1. Norton Company 38-900 alumina sintered 2 h at 1950°C. Grain boundary has migrated from dotted line to present position sweeping out pores between. Large voids on boundaries are chips from specimen preparation, not pores (750×).

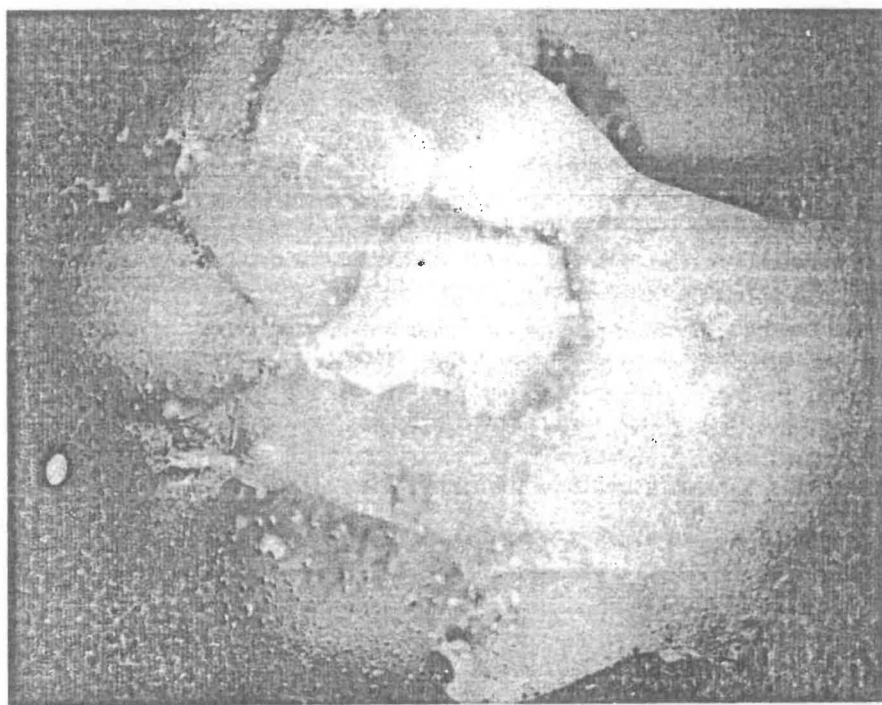


Fig. 2. Same material as Fig. 1, but examined with polarized light to eliminate surface reflections. Sub-surface pores appear bright, and dark areas are pore-free. Shows pores are preferentially eliminated near grain boundaries (750×).

with the grain boundary than when they are inside grains. If shrinkage was caused by plastic flow [3] then all pores should shrink at the same rate. The fact that pores disappear preferentially near grain boundaries is consistent with the diffusion model that pores disappear by 'evaporating lattice vacancies' that are annihilated at grain boundaries.

Pores Sweeping by Grain Boundaries

Pores *appeared* to be removed only from one side of the boundary as is shown in Fig. 1. It was known that in unstrained metals second phase inclusions bond to grain boundaries and can inhibit their movement. Zener [4] computed that for a uniform array of immobile solid inclusions, grain growth in fine grained metal would stop when [5]

$$f = (4/3)(R_i/D) \quad (1)$$

where f = volume fraction of inclusions (pores) in the specimen, R_i = radius of the inclusions and D = average grain diameter.

In any polycrystalline specimen, the surface tension force driving grain growth tends to move grain boundaries toward their centers of curvature. Pores behave the same as solid second phase inclusions and inhibit this motion, with one important difference: pores touching a grain boundary shrink rapidly and disappear so the boundary is freed to move further toward its center of curvature until it encounters more pores. Thus, as it migrates, it appears to sweep volumes of the specimen free from pores as seen in Fig. 1. The boundary remains in contact with pores on the concave side.

Pore-Grain Boundary Separation

The question now became: how did the pores get inside the grains? Specimens prepared from the same powder but heated to a lower maximum temperature had a small grain size, with all pores on grain boundaries, but the pore-pore distance is about the same as in specimens heated to 1950°C (Fig. 1). Pores are formed because the initial powder particles do not fit perfectly, hence initially, all pores must lie on grain boundaries. The pores entrapped inside grains, observed in Fig. 1, must have resulted from boundary migration past the pores. Again there was a precedent for understanding the phenomenon from grain growth work in metals [6,7].

Two kinds of grain growth are observed in metals:

- (1) Continuous, or ideal grain growth. All the grains are about the same size, the larger grains consume the smaller ones, and the average grain size increases but the grain size distribution does not change as growth proceeds.
- (2) Discontinuous growth (secondary recrystallization, germination, exaggerated grain growth or abnormal grain growth). In it a few large grains grow rapidly, consume the small matrix grains, and a duplex grain size distribution develops. The phenomenon had been known for decades:

Archer and Jeffries described and illustrated it in 1924 [8]. An example in zinc is shown in Fig. 5. A few large grains grow and consume the small matrix grains which remain of constant size. Beck *et al.* [9] showed it could occur when grain growth is inhibited in a uniform grain size specimen by a fine dispersion of inclusions and the specimen is heated to a temperature where the inclusions just begin to dissolve. Burke [7,10] explained that in such an array, the sides of the uniform grains are only slightly curved and are readily pinned by second phase inclusions. As they dissolve a few grains will grow and add sides. Having more sides, the topological requirement that all grain boundaries radiate from triple points at 120° angles demands that the sides of the larger grains be more strongly curved outward (Fig. 3) [7], and thus have a stronger driving force for growth. Von Neumann [11] stated it simply: the growth force of a grain is proportional to $(N - 6)$ where N is the number of sides. The boundaries of the new many-sided grains migrate easily past inclusions that inhibit the movement of uniform-sized matrix grains.

As described in Ref. 1: 'Now, as was indicated previously, all pores which are formed between grains as the result of the misfit of powder particles lie on the grain boundaries in the early stages of sintering. These pores . . . 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

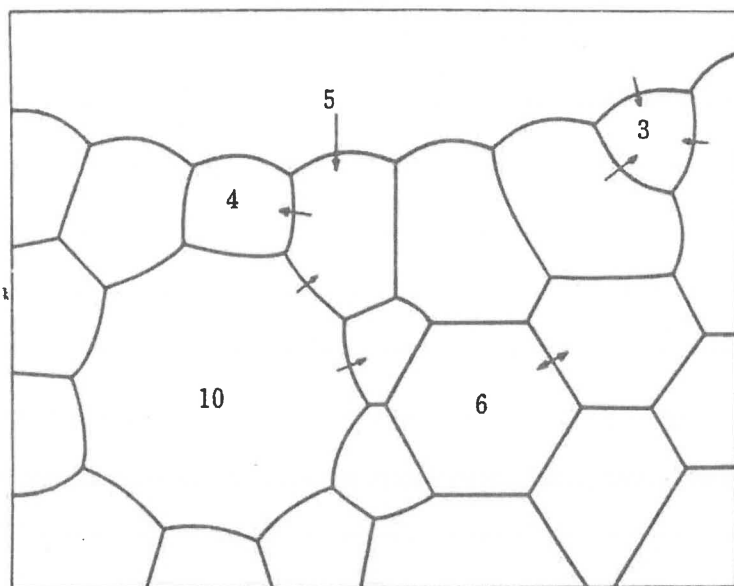


Fig. 3. Schematic drawing of polycrystalline specimen. The sign of the grain boundary curvature changes as the number of sides increases from less than six to more than six, and the radius of curvature is less the more the number of sides differs from six. Arrows indicate the direction boundaries will move.

sintering proceeds, the volume fraction of pores gradually decreases, and finally the conditions of eqn (1) are fulfilled, and the disappearance of a few more pores will permit a few grains to grow somewhat and thus to gain more sides than their neighbors...'. Then, as described above, the more strongly curved boundaries of these larger grains can migrate past the pores, the grains will add yet more sides, and their growth force will increase even more. Discontinuous grain growth will have been initiated and entrapped pores will be found inside the new generation of grains and they will, for practical purposes, be permanent.

Complete Removal of Pores

The discussion of Ref. 1 concluded: discontinuous growth and pore-grain boundary separation will frequently occur in a late stage of sintering and pores will be entrapped permanently inside grains. If, for example, some other second phase inclusions were to be present in a concentration high enough to prevent grain boundary migration, then all pores will remain on grain boundaries until they have disappeared and essentially theoretical density should be obtained. Figure 4 (from that paper) showed complete pore removal during sintering in a specimen in which discontinuous grain growth had been inhibited by a (then) unknown impurity.

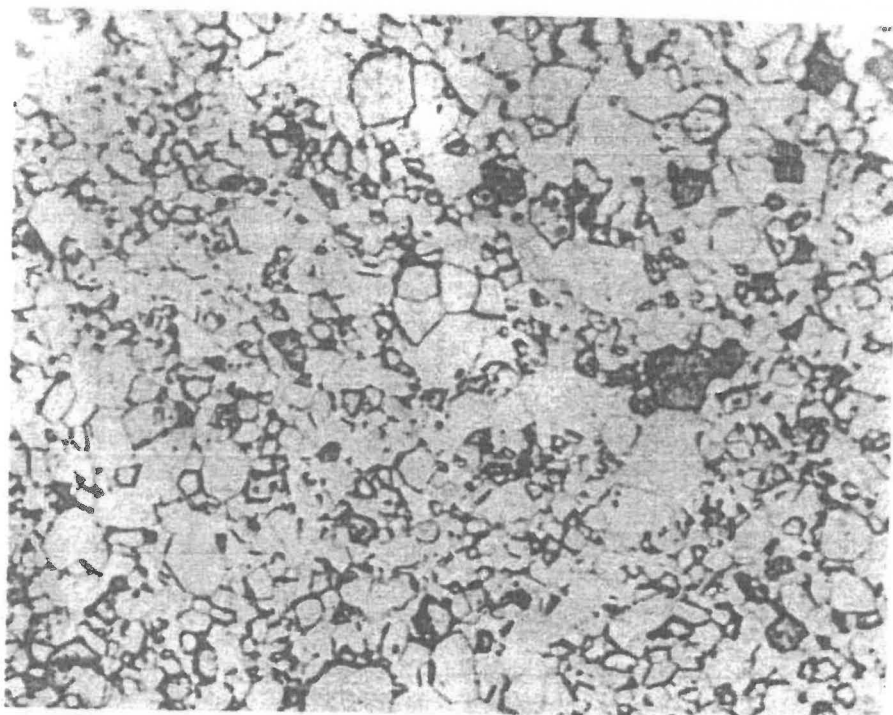


Fig. 4. Fine-grained pore-free specimen of aluminum oxide made from special batch of Norton 38-900 alumina containing (then) unknown impurity which prevented discontinuous grain growth [1].

II THE DEVELOPMENT OF A PROCESS FOR MAKING PORE-FREE CERAMICS

A Need is Established

Although it is clear from the foregoing description that it was possible to make a pore-free alumina ceramic, nothing was done about it until about 1956 when George Inman of the General Electric Company Large Lamp Department pointed out to the authors that it might be possible to make a useful new kind of lamp using an envelope of refractory 'transparent' pore-free alumina, and it was agreed to start a project in the Ceramic Studies Section of the Laboratory to attempt to make such a product. Robert L. Coble had been studying the kinetics of the initial stage of sintering and agreed to put that work aside for a time to carry out the new program.

Development of a Fabrication Process

The initial assumption was that if pore-grain boundary separation could be prevented it would be possible to sinter alumina to a pore-free state. Again, earlier metals work was helpful: Burke [12] had reported that discontinuous grain growth in high purity zinc (containing a small dispersion of ZnO) was eliminated by the addition of 0.7 wt% silver (see Figs 5 and 6) the effect was attributed to reduction of grain boundary mobility (the terminology then was 'restrained grain boundary movement'). Mobility was presumed to be reduced because the movement of the adsorbed excess of atoms had to be accomplished by diffusion while the grain boundary would move faster alone by simpler processes. It was thus reasonable to assume that some additive had prevented pore-grain boundary separation in the alumina specimens discussed in the last section, and to seek it. By this time, Cahoon & Christensen [13] had examined the effects of many additions upon the sintering of alumina, and by examining thin sections (then the only microscopic technique used by ceramists) they established that additions of very small amounts of magnesium oxide were particularly effective in inhibiting the discontinuous grain growth they encountered in most of their specimens.

Magnesia was the first addition Coble tried. The powder selected was of ammonium alum. It had been procured because it was the purest alumina powder readily available; it turned out to have been a critically important selection because the uniform particle size was particularly suited to the removal of all pores, and on the first attempt the specimen sintered to theoretical density. It had been assumed that a possible role of magnesia would be to make a dispersion of spinel particles that would inhibit grain growth, and there were quite a few present in the first specimens. In the course of the investigation he demonstrated that the magnesia addition could be reduced until no second phase was present and discontinuous grain growth still did not occur and the specimens continued to sinter to theoretical density, and had very good light transmitting power [14,15], Fig. 7. It was clear that in this case also an addition in solid solution was operating. Another interesting observa-

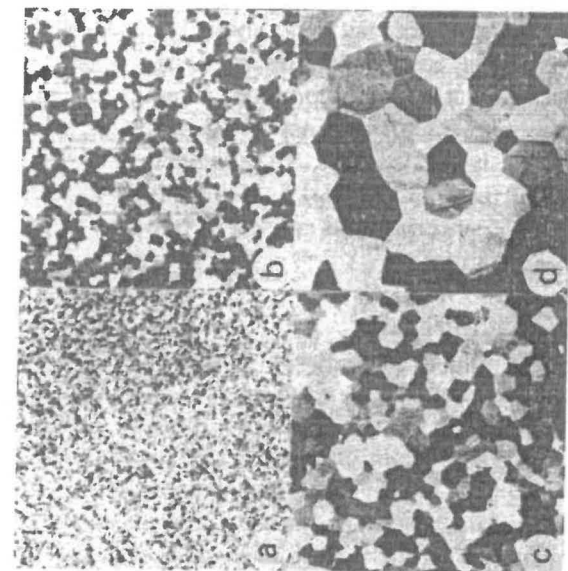


Fig. 6. Shows continuous grain growth and inhibition of discontinuous growth by the addition of 0.7% silver in solid solution.

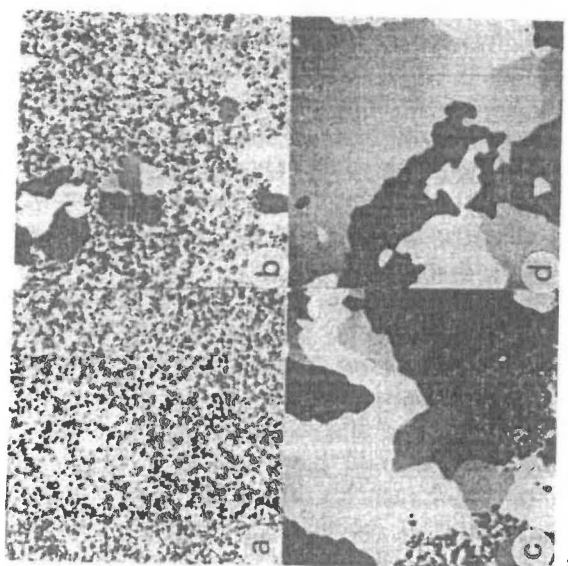


Fig. 5. Shows discontinuous grain growth in high purity zinc containing a small amount of second phase zinc oxide.

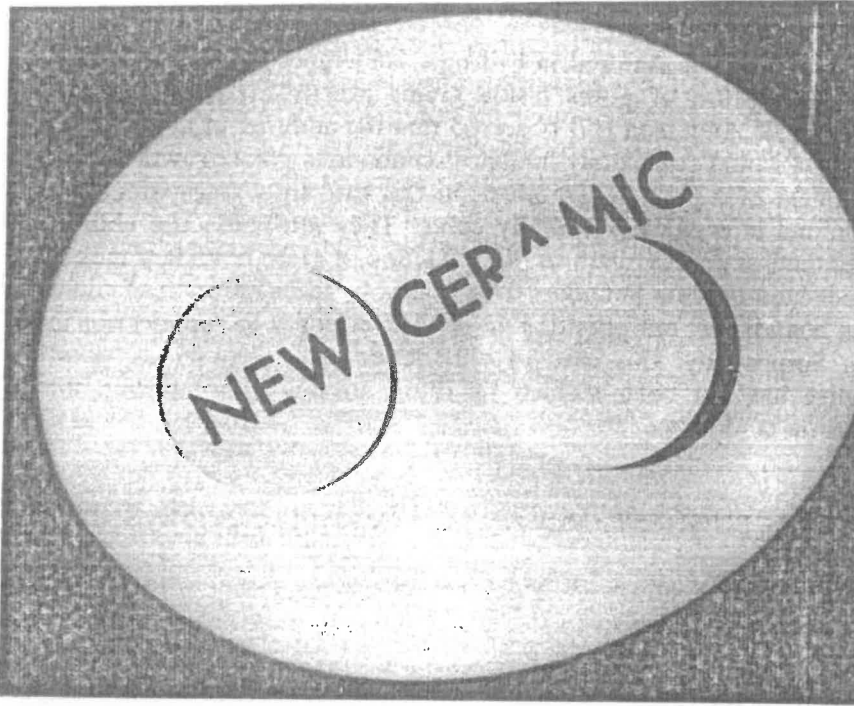


Fig. 7. Demonstration of light transmitting ability of new pore-free (Lucalox) alumina ceramic (1962 photograph).

tion was subsequently made: theoretical density could be obtained if the specimen were sintered in hydrogen or oxygen, but if sintered in air, residual pores remained. Both oxygen and hydrogen diffuse fast enough to permit pore closure, but nitrogen is inert and stabilizes the pores.

Following this, a great deal of detailed work was done to develop a reproducible manufacturing process for pore-free alumina. Much of it was done by Charles Bruch [16] and the results are reported in that reference. The transition to a process to make tubes for high pressure sodium vapor lamps was done most expertly by Nelson Grimm of the GE Lamp Glass Department, and the process was controlled by him for many years. Critically important steps were found to be:

- (1) Using sub-micrometer powder in which all the particles are substantially of the same size.
- (2) Milling the powder to remove aggregates, to insure that the maximum pore size in the green compact is related to the misfit between ultimate powder particles, not between particle aggregates.
- (3) Sintering in an atmosphere (usually hydrogen, never air) that can readily diffuse through the alumina and be eliminated after it is trapped in closed pores.

These are all now recognized to be important parameters in processing ceramics.

Pore-Free Yttrium Oxide

Pure yttrium oxide sintered in hydrogen undergoes discontinuous grain growth with the capture of pores inside grains exactly as aluminum oxide does. Jorgensen & Anderson [17] observed that the addition of about 10% thoria to the yttria would completely inhibit discontinuous grain growth and permit the attainment of a pore-free product, in this case truly transparent because the compound is crystallographically cubic. They attributed the ability to avoid discontinuous grain growth to the reduction of grain boundary mobility by the introduction of grain boundary drag caused by the adsorption of additive to the grain boundaries, but provided no explicit evidence to support this interpretation. Surprisingly, this case of elimination of discontinuous growth by an additive has not been studied by those attempting to explain the role of magnesia in alumina.

III SUGGESTIONS AS TO THE ROLE OF MAGNESIA

The remarkable effect of MgO in permitting alumina to be sintered to theoretical density has attracted wide interest in the ceramic community, and a succession of explanations and suggestions for its role have been presented.

Although Coble [14] suggested that the MgO addition did not reduce grain boundary mobility, but changed the shape of the pores or speeded up sintering, Coble & Burke [18] suggested that MgO was adsorbed at grain boundaries and that the adsorbate reduced boundary mobility by the grain boundary drag model mentioned above, and by now discussed theoretically by Lücke & Detert [19] and Cahn [20] and demonstrated experimentally by Aust & Rutter [21,22] for tin alloys. Coble and Burke assumed that the pores were immobile inclusions and that the adsorbate would slow down the rapidly moving boundaries of large grains and prevent their breaking away from pores until the pores had disappeared.

Greenwood & Speight [23], Nichols [24] and Kingery & Francois [25] demonstrated that pores can have quite high mobility, hence the further condition must be added [26] that grain boundaries can break away from pores only if the velocity of the boundary V_b can be greater than the velocity of the pore, V_p , or

$$V_b = F_b M_b > V_p = F_p M_p \quad (2)$$

where F_b and F_p are the driving forces for boundary and pore movement and M_b and M_p the mobilities of the boundary and pore respectively. Even, or perhaps especially, with mobile pores, reduction of grain boundary mobility is the way to prevent pore-grain boundary separation.

At about this time several workers, notably Marcus & Fine [27] and Johnson & Stein [28], demonstrated that very little if any magnesium was segregated at the grain boundaries, and this was taken for several years to prove that the hypothesis that the MgO addition decreased grain boundary mobility in

alumina was incorrect. For example, Heuer [29] suggested that the role is to increase the pore mobility in alumina.

Then came several explicit demonstrations that the MgO addition does indeed decrease true grain boundary mobility in alumina [30–32]. Monohan and Halloran, for example, observed that the growth rate of sapphire seeds in hot-pressed alumina powder was 25 times higher in pure alumina than in alumina containing 200 ppm magnesia. Since the grain size of the matrix grains was the same in both experiments, the relative growth rates were a direct measure of relative boundary mobility.

Thus, after much discussion, the present understanding is much as it had been early on: as summarized recently by Berry and Harmer [32] 'The role of MgO in the sintering of alumina was attributed mainly to its ability to lower the grain boundary mobility'.

IV DISCUSSION

Can Solute Drag Operate in Ceramics?

In metals it is commonly observed that grain boundary mobility is reduced by solute drag (many references to recent work may be found in Smith *et al.* [33]) and in Ref. 12 it was shown that a solid solution addition to zinc would prevent discontinuous grain growth in that metal. If one were to seek an additive to prevent pore-boundary separation in a new compound to be sintered, the most rational approach would be to seek a solute that would segregate at the grain boundaries and provide solute drag. The mechanism must work in ceramics as it does in metals, and there is no reason to suppose that it is not, for example, the mechanism by which thoria inhibits discontinuous growth and permits the sintering of yttria to a pore-free product.

By What Mechanism Does MgO Operate?

The evidence that there is no easily measurable excess concentration of magnesium at the grain boundaries of sintered aluminum oxide is convincing, and we must seek to explain the fact that MgO reduces grain boundary mobility by mechanisms other than the drag imposed by impurity atoms diffusing behind or along with a moving boundary.

It is suggested that very small amounts of solute adsorbed at grain boundaries can reduce grain boundary mobility in an alternate, very different, way: it can actively interfere with the growth process by poisoning the sites from which atoms detach themselves and the sites to which they attach themselves as the grain boundary migrates. This will result in longer times and longer diffusion distances for the atom movements associated with boundary movement, and a lower grain boundary velocity for the same driving force.

Modern concepts of grain boundaries, supported by extensive electron microscopy are that they are quite highly structured [34]. Gleiter [35] has suggested that during boundary migration atoms are detached from steps on

the locally shrinking grain and make a number of diffusive steps before becoming attached to *steps* on the locally growing grain, and other work is reviewed by Smith *et al.* [33]. It is akin to the mechanism of growth of crystals from the liquid or vapor phase, or their solution or evaporation. It seems reasonable to suggest that grain boundaries in alumina migrate in this fashion and that certain highly specific atoms such as magnesium can poison these sites and make it more difficult for an atom to detach or attach itself there. The consequence would be longer diffusion times and longer diffusion distances to find a suitable site, and experimentally one would observe reduced grain boundary mobility.

Such poisoning is commonly observed in the growth of crystals from the liquid phase, a text-book example is the ability of a trace of urea to change the habit of sodium chloride crystals growing from aqueous solution from cubes to octahedra. Gilman *et al.* [36] have documented in detail the fact that a trace of ferric ion (1.2 ppm) in the distilled water etching solution permits etch pits to form at dislocations on $\frac{1}{2}100\frac{1}{2}$ faces of lithium fluoride, while pure distilled water dissolves the surfaces with no pit formation. They demonstrate convincingly that the mechanism is to poison solution steps on the {100} surfaces so they do not propagate across the crystal and leave a smooth surface. There is also evidence for impurity effects in influencing relative boundary mobility in metals. Lücke [37] reports that small amounts of phosphorus in iron lead to different recrystallization textures but not to different deformation textures. Recrystallization textures in metals arise from deformation textures because grains with certain orientation relationships to the deformed matrix have higher boundary mobility than others. The finding of a different recrystallization texture induced by an addition indicates that relative grain boundary mobilities have been changed.

Unfortunately, such poisons are usually very specific, and there are apparently no general rules for their selection.

CONCLUSIONS

Discontinuous grain growth and pore-grain boundary separation may occur in many sintering ceramics, and entrap pores inside grains so they cannot be removed by heat treatment. Reducing grain boundary mobility is an important way to avoid this phenomenon, and permit the attainment of theoretical density.

In a great number of metal systems grain boundary mobility can be reduced by pore drag imposed by a component adsorbed at the grain boundary, and this mechanism should operate in ceramics as well; probably it does in thoria-doped yttria as was initially proposed. That suggests that a generally useful approach to prevent pore-grain boundary separation and pore entrapment inside grains in sintering ceramics is to seek a solute that can reduce grain boundary mobility by solute drag.

An MgO addition to alumina greatly reduces grain boundary mobility and prevents pore-grain boundary separation, but very little if any magnesium is segregated at the grain boundaries of MgO-doped alumina, thus solute drag cannot be invoked to explain the reduction in boundary mobility. Instead, it is suggested that grain boundary migration occurs by the movement of atoms from steps on the receding grain to steps on the growing grain, and that these steps can be 'poisoned' by specific foreign atoms such as magnesium so that the transfer is retarded and boundary mobility reduced. Such phenomena are observed in the growth and solution of crystals from the vapor and liquid, and in some metal grain boundaries.

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