

The selection of grain-growth control additives for the sintering of ceramics

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SUMMARY. The close interrelation between sintering and grain growth is discussed critically, and the necessity for control, but not suppression, of grain growth is established. A distinction between discontinuous and exaggerated grain growth is drawn, and the superiority of grain boundary films as grain-growth control agents is demonstrated. Work on the establishment of tentative criteria for the selection of grain-growth control additives for alumina is reviewed and discussed, and the extension of these ideas to the selection of NaF as a successful aid for magnesia is described.

THE term sintering, as used in ceramics, refers to the process by which an assembly of discrete particles is transformed into a more-or-less porous solid mass by the application of heat not sufficient to melt the material of which the particles are composed. The driving force for the consolidation observed in sintering is universally agreed to be the excess surface energy possessed by a given amount of material in the form of a fine powder relative to the surface energy of the same amount of material in a solid lump. It would therefore be expected that sintering would continue until all internal surface associated with porosity was eliminated, but this behaviour is very seldom observed, and sintering normally stops for all practical purposes before all porosity has disappeared.

Although a very great deal of theoretical study of the sintering process has been made, the most important result embodied in the current view of the sintering process is the empirical observation by Alexander and Balluffi (1950) that pores in a body undergoing sintering cease to shrink when they become isolated from grain boundaries by the movement of these boundaries in the process of grain growth. It is therefore necessary, if it is desired to sinter to an essentially pore-free state, to control the grain growth in a ceramic in such a way that the grain boundaries do not move away from the pores. Pore-free material possesses properties that are different from those of porous materials in various ways, most noticeably in being transparent or translucent in comparison with the opacity characteristic of porous bodies.

In recent years the author has been associated with several pieces of work whose general aim was to establish criteria for the selection of suitable additives that would control grain growth in particular materials and enable their sintering to proceed to its theoretical limit of zero porosity. This branch of activity is to be distinguished from that aimed at accelerating the rate at which sintering occurs, which can be of considerable technological importance. Such phrases as 'enhancement of sintering' are sometimes used without the reader (or possibly the author) being clear as to whether it is the rate of sintering or the ultimate relative density at which it effectively

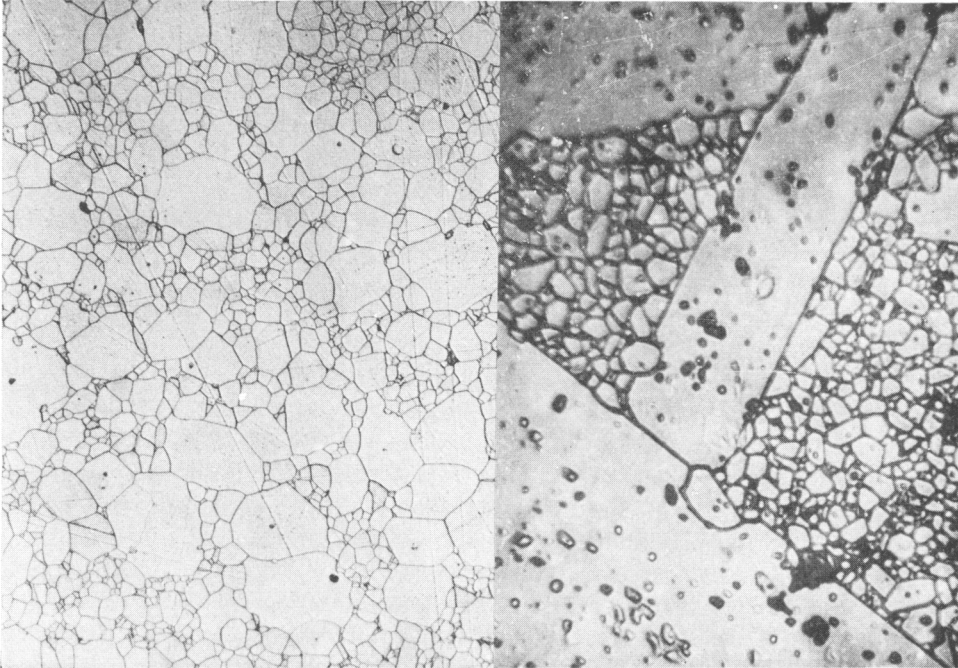
terminates that is being increased. Since these two desirable ends can be to some extent mutually exclusive, it is important to be clear as to which is being pursued. As some of the work has been published elsewhere, the aim of this paper is to convey the general principles and to pay particular attention to aspects of sintering that are often discussed somewhat uncritically.

The relationship between sintering and grain growth. As the sintering of an assembly of particles proceeds, the original contact points of the particles develop into areas of grain boundary and the inter-particle spaces shrink to become pores, which are situated on the grain boundaries. The minimizing of the free energy of the grain boundaries themselves eventually begins to be a significant factor in the over-all process and leads, in the case of grain boundary energy that is independent of the degree of misorientation across it, to a grain boundary arrangement that is the same as that of a soap foam, except that the pores are still present at the corners where four grains meet. The geometry of this arrangement has been very thoroughly discussed by Smith (1964); the basic features are that grain faces meet in threes at 120° , and grain edges in fours at $109^\circ 28'$. Some curvature of the grain faces and edges necessarily results from the reconciliation of these requirements. Continued shrinkage necessarily involves movement of the grain boundaries, and this movement must be in such a direction that the total area (and hence the total energy) of the boundaries decreases. Shrinkage must thus be accompanied by grain growth. Although this point appears to be obvious, its significance does not seem to be well appreciated, although all ceramists know that shrinkage and grain growth occur together and at one time the terms 'sintering' and 'grain growth' were treated as being synonymous.

Although it is easily seen that energy is required to pull a grain boundary away from a pore, such separation does occur when abnormal grain growth occurs and the grain-boundary pattern departs from the ideal soap-foam configuration. The usual explanation for 'discontinuous grain growth', as it is often called, is that if one grain happens to acquire rather more sides than average, then these sides will be more strongly curved than average (because the correct angles between grain boundaries are preserved by surface-energy equilibrium at their intersections) and will therefore have a greater tendency to move because the energy gain by their straightening will be large. A grain slightly larger than its fellows will thus tend to get even larger and a population of large grains will develop in a small-grained matrix. This explanation is undoubtedly valid in some cases, and fig. 1 shows an example of an alumina body that has undergone discontinuous grain growth, and in which the porosity is almost entirely confined to the larger grains. This type of abnormal grain growth is to some extent self limiting, because once the larger grains have consumed most of the smaller ones they begin to impinge upon each other, and a more uniform structure begins to re-emerge.

There is, however, another form of abnormal grain growth, which is geometrically distinct from that shown in fig. 1, and an example of this form is shown in fig. 2. It seems worth while to distinguish these two forms and to reserve the term 'exaggerated grain growth' for the second form. The characteristic feature of exaggerated grain

growth is that the large grains have very straight sides, which are not deflected very much by the impingement of smaller grains as they would be in a soap-foam configuration: the disparity in size between large and small grains is usually very much greater than in discontinuous grain growth. One explanation of this behaviour was suggested by Kooy (1962), who postulated the existence of a small amount of a liquid



FIGS. 1 and 2: Fig. 1 (left). Discontinuous grain growth in an alumina body. The large grains are about $40\ \mu\text{m}$ in diameter. (Photograph by M. O. Warman.) Fig. 2 (right). Exaggerated grain growth in an alumina body. The small grains are about $5\ \mu\text{m}$ in diameter. (Photograph by M. O. Warman.)

phase (originating from impurities) with a finite dihedral angle at the sintering temperature, resulting in a grain virtually growing from solution and exhibiting a characteristic growth habit. This type of abnormal growth also leads to the isolation of pores inside grains, as can be seen in fig. 2, and renders unsuitable for use materials that are otherwise suitable for sintering. Some method must therefore be found for controlling exaggerated grain growth.

Control of discontinuous grain growth is also desirable, but the accepted explanation of this behaviour is such as to leave doubt as to whether it can be completely controlled: some non-uniformity in grain size must always exist, and will get worse as grain growth proceeds.

The theory that some degree of discontinuous grain growth is almost inevitable receives some support from a consideration of figs. 1 and 2, for the material in fig. 1 differs from that in fig. 2 by the addition of a grain-growth inhibitor, which has

completely suppressed exaggerated grain growth. Sintering has proceeded to such a degree in fig. 1 that almost all porosity has been removed, and such small pores as do remain are situated in the large grains of the population produced by discontinuous grain growth.

The control of grain growth. In order to sinter to zero porosity, grain boundary movement must be controlled, but it must not be absolutely prevented. This control can be effected by second-phase particulate inclusions, of which pores are a special case, or by some form of grain-boundary film phase. Pores are excluded, by definition, from use in the present instance. Particulate inclusions are almost immobile so that grain boundaries are totally impeded by them unless they somehow manage to escape completely, when they are free to move in an uncontrolled manner. Grain boundary films thus offer the most promising means of controlling grain growth, as they will move with the boundary at a moderate speed, and will swamp any effects due to orientation differences between different boundaries.

It has been known for many years that small amounts of magnesia can be used to control grain growth in alumina, and this fact was exploited by Coble (1961) to enable him to sinter alumina to a pore-free condition. This was the first occasion on which this feat had been performed on any material and in order to achieve the desired result it was necessary to use a carefully selected powder and to sinter in an atmosphere of a gas that could readily diffuse out of closed pores in the partially sintered piece. These two conditions are very important, but they will not be discussed in this paper.

Further investigations by Jorgensen and Westbrook (1964) established that the magnesia additive was preferentially concentrated at grain boundaries in the densified alumina, and they also demonstrated a correlation between the effect of an additive on grain boundary hardening and the final density achieved by its use. Such a correlation, however, does not enable an experimenter to predict what additives might be of use in a particular material, so that a programme of work to establish predictive techniques was started.

Additives for grain growth control in alumina. The most significant feature of the behaviour of magnesia when added to alumina is that it affects all grain boundaries equally, even though the amount added is usually only about 0.25 % by weight. This behaviour suggests that the additive can distribute itself very readily through the initially porous specimen, and Warman and Budworth (1967) demonstrated that transport through the vapour phase was certainly possible and was therefore the probable mechanism in practice.

The action of the additive once it reaches the grain boundary must in some way be a function of its chemical nature, and Jorgensen and Westbrook (1964) had shown that the rather similar compound NiO could be substituted for MgO as a grain-growth control additive for alumina. Warman and Budworth (1967) therefore investigated a carefully selected series of additives and showed that the criteria of ionic size and valence of the cation, together with volatility of the additive at the normal sintering temperatures of around 1700 °C, seemed to account for the success or non-success of an additive. Thus CoO and ZnO were added to the list of successful additives, with

ions Co^{2+} of radius 0.72 \AA and Zn^{2+} of radius 0.74 \AA compared with Mg^{2+} of radius 0.65 \AA and Ni^{2+} of radius 0.70 \AA . All four of these additives form spinel-type compounds with alumina, and the specimens containing these additives adopted the colours of the appropriate spinels. It was necessary to use different sintering atmospheres for the different additives in order to preserve the desired oxidation states. It was also found that the non-spinel-forming additive SnO_2 , containing the Sn^{4+} ion of radius 0.71 \AA , could be successfully used to control grain growth in alumina. The valence of the cation is different from that of the host Al^{3+} (of radius 0.50 \AA), but also differs from that of the other successful additives, and SnO_2 is therefore particularly interesting. There is a eutectic in the $\text{SnO}_2\text{-Al}_2\text{O}_3$ system at about 1620°C , but no difference in sintering behaviour occurred between 1600 and 1700°C , apart from acceleration of the densification, due solely to the effect of temperature, at the higher temperature. It may be that the existence, chemical nature, and distribution of a second phase are the major influences on sintering, and the question as to whether this phase is liquid or solid is secondary.

The general picture of the action of a suitable additive constructed from these experiments is thus that the additive first distributes itself throughout the specimen by vapour-phase transport, and then remains at the grain boundaries in film form because it is not quite sufficiently chemically similar to the matrix material to go into solution and not sufficiently chemically different to form a distinct second particulate or partly wetting phase.

Further studies of the effects of MgO , ZnO , and NiO on grain growth in densified alumina were carried out by Haroun and Budworth (1970). The conclusion was drawn that, at additive levels of about 0.25% by weight, the additive was present both as discrete particles and as a grain boundary film. The distribution of the additive between the two locations was not established, but a guide to the amount present as grain boundary film is probably given by the observation (confirming that of American workers) that the minimum amount of additive needed to control grain growth was about 0.05% . With the type of alumina powder employed for the experiments, the critical stage of sintering, when the pores and their restraining influence on grain-boundary movement are disappearing and the grain boundary film is therefore required, occurs at a grain size of a few microns. It is easily seen that the thickness of the grain-boundary layer of additive at this grain size corresponds to about one lattice spacing, e.g. at a concentration of additive of 5×10^{-4} and a grain size of $3 \mu\text{m}$, the grain-boundary layer will be about 5 \AA thick. The most realistic way to regard the effective minimum amount of the grain-boundary phase is thus as the sort of mono-molecular layer familiar in other contexts.

Grain-growth control in magnesia. During the currency of the sintering studies of alumina, the production of transparent magnesia by hot pressing was also being studied. The known process for producing dense, transparent magnesia involved the use of about 1% of LiF as an additive. Unwilling to believe that the process was unique to LiF , experiments were started with NaF , which was the most similar compound that seemed convenient, and eventual success was achieved with this compound

also (Smethurst, 1968). (The use of fluoride instead of oxide additives was because of the difficulty of handling the oxides: fluorine is the nearest anion to oxygen in size and seems to cause no special problems.) In the course of this hot-pressing work, however, it was found that specimens produced with the aid of NaF had smaller grain size than those produced with the aid of LiF, and the idea arose that NaF might act as a grain-growth control agent for the pressureless sintering of magnesia. NaF is volatile at the sintering temperatures used for magnesia, which are similar to those used for alumina, and the size ratio of Mg^{2+} to Na^+ is 0.68, which is similar to the ratio of the sizes of Al^{3+} to the sizes of the various divalent or quadrivalent ions used to control grain growth in alumina: the criteria which appeared to be adequate for alumina were thus satisfied also for magnesia by NaF.

After some empirical development, it was found that very dense magnesia could indeed be produced by sintering with the aid of small amounts of NaF. The work could not be continued as far as was desirable, but specimens that were transparent for much of their bulk were produced, and no porosity could be seen under the microscope in the transparent regions (Banerjee, 1968). It is hoped to publish this work in more detail in another place.

Conclusion. It is felt that the criteria originally proposed by Warman and Budworth (1967), although crude, have some value in establishing a pattern of the behaviour of grain growth control additives. In particular, they enable predictions to be made of which additives are likely to be useful, on the basis of information that is readily available.

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