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FEASIBILITY OF DISPERSED PHASE GRAIN REFINEMENT IN CERAMICS

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ABSTRACT

The feasibility of dispersed phase grain refinement in ceramics is assessed. Conditions for grain size stabilisation of normal grain growth are derived using a Zener type analysis for random dispersions and for the case in which all particles are located at specific sites upon a grain boundary. The calculations predict the relative stabilising effects of particles located at grain boundaries, triple-grain edges and four-grain corners. Other factors reviewed include the effects of particle size instability, nucleation of discontinuous grain growth, and possible methods for its prevention. It is concluded that dispersed phase grain refinement in ceramics is feasible. The general predictions are applied to the case of a BeO moderator and used to predict the most promising additives for further investigation.

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1. INTRODUCTION

Many of the properties of fabricated ceramic materials depend critically upon microstructure. Among such structure-dependent properties are mechanical strength, creep resistance, thermal conductivity and stability under neutron irradiation. Realisation of optimum behaviour for any specific application may require achievement of a particular combination of bulk density and grain size.

Some independent control over final density and grain size can be achieved by careful selection of starting material, forming, and firing methods. However, it has frequently been found that during sintering, grain growth and densification proceed with the same apparent activation energy (Coble 1961; Bruch 1962; Bannister 1964a). This implies that for a specific powder and given starting conditions, as long as the minimum sintering time is used to obtain a particular bulk density, the same grain size will be obtained regardless of the sintering temperature.

The use of additives to obtain independent control over density and grain size shows some promise of providing the desired flexibility. One possible method is to reduce the rate of grain growth by means of an inert dispersed phase which will pin the grain boundaries without affecting the rate of densification. The feasibility of grain boundary pinning in metals has long been recognised. The best known case is the use of thoria to inhibit grain growth in tungsten lamp filaments. Developments in the use of grain size inhibitors in metals have been reviewed by Beck et al. (1949). However, application of dispersed phase grain refinement in ceramics has been very limited.

This report reviews previous applications of this method of grain refinement in ceramics and provides a theoretical basis for proving the feasibility of the concept and determining the characteristics required for a suitable second phase particle. The specific problem of grain refinement in the BeO matrix of a dispersion type fuel element is discussed.

2. APPLICATION OF DISPERSED PHASE GRAIN REFINEMENT IN CERAMICS

Elyard et al. (1963) found that UO_2, with the addition of 0.06 weight per cent. of finely dispersed platinum, sintered at 1200 °C in argon to a density of 10.63 g/cm^3, compared with 9.92 g/cm^3 without Pt and the grain size was 3 microns compared with greater than 10 microns, respectively. This method was subsequently used as the basis for a patent (B.Pat.934,254).

The experiments of Duderstadt and White (1963) using specimens of UOX-BeO containing 3 weight per cent. ZrO_2 sol, indicated that marginal grain refinement (that is, lower grain size for a given density than without the additive) was obtained by sintering in a hydrogen atmosphere, within the range 1500 °C to 1700 °C. In dry air, the rate of grain growth of the specimens containing the ZrO_2 sol was also definitely lower than that for pure UOX.

Hot pressing experiments by Langford (1965) showed that graphite can act as a grain growth inhibitor in BeO. At a density of 99.7 per cent. theoretical, 1 weight per cent. carbon limited the grain size to 4 microns compared with 14 microns for specimens without carbon. A patent (U.S. Pat. 3165417) was later taken out to cover the fabrication of BeO containing carbon or carbides by sintering in a hydrogen atmosphere. Similar hot pressing experiments at this establishment (Wulf and Bardsley, A.A.E.C., Unpublished) confirmed that a dispersion of graphite in UOX-BeO produced grain refinement. At the level of addition 1 to 5 volume per cent. carbon, the grain size was limited to 3 to 4 microns compared with the normal 8 microns for hot pressed UOX at 99.3 per cent. theoretical density. Other hot pressing experiments showed that 1 to 5 volume per cent. ZrO_2 sol had little grain refining effect, while similar additions of Y_2O_3 sol had a deleterious effect due to the formation of a liquid grain boundary film at 1500 °C or lower. A 1 to 5 micron tungsten powder had no refining effect and appeared to agglomerate and sinter together into large particles.

Hill, O'Neill, and Livey (1966) found that a dispersion of sub-micron SiC particles in BeO containing 1 weight per cent. MgO restricted grain growth during sintering. Compacts containing 8 weight per cent. SiC sintered to a density of 2.94 g/cm^3 after 4 hours at 1750 °C with a mean grain diameter of 5 microns.

3. ANALYSIS OF PARTICLE LIMITED GRAIN BOUNDARY MIGRATION

In the case of a particle situated on a grain boundary, the combined surface free-energy of the particle and boundary is lowered, compared with when a particle is situated adjacent to a boundary. Work must be done to detach the particle from the boundary and such a particle may form an impediment to grain boundary movement. A simple theory of the restraining effects of an insoluble particle, based upon interfacial tensions between the particle and the grain boundary, was proposed by McLean (1957). However, Bannister (1964b) showed that a better estimate of the forces involved can be calculated from the work-energy relationship involved in removing the particle from the boundary. The results of these calculations are listed in Table 1; the forces resisting displacement of a particle are generally larger than those predicted by the McLean treatment.

When a grain boundary is moving through a matrix containing second-phase particles, the grain boundary tends to "stick" at the particles owing to the extra energy required for the boundary to break free. If the particles are relatively immobile compared to the mobility of the boundary regions free of particles, the boundary tends to cusp. The resultant grain boundary geometry is complex; however, Zener (1949) showed that the effect of second phase particles upon grain boundary mobility can be taken into account (a) by assuming that the grain boundary geometry is unaffected, that is, the interfaces remain planar, and (b) by introducing into the model an hypothetical backstress exerted by the particles upon the boundary.

Grain growth occurs in a polycrystalline matrix as the grains consume each other in order to decrease the total grain boundary area and minimise the associated interfacial energy. During "normal" grain growth, most of the grains have a size which is nearly equal to the mean size, and grain growth is said to be continuous. When normal grain growth is inhibited in the matrix, some grains with a greater number of sides than the average grain grow unimpeded and reach very large sizes. This phenomenon is termed "discontinuous" or "exaggerated" grain growth.

3.1 Effect Upon Normal Grain Growth

The presence of second phase particles may affect normal grain growth by:

(i) Stabilising the grain size.

(ii) Affecting the rate of grain growth.

The simple model of Zener (1949) predicted a limiting grain size for normal grain growth in the presence of the second phase particles. A more fundamental mathematical analysis of particle limited grain growth has been carried out by Hillert (1965). His two-dimensional model assumed the introduction of "defect" grains with fewer than six sides, into a regular array of hexagonal grains and second phase particles. The model predicted two stable grain sizes for particle limited, normal grain growth, (Figure 1); the first corresponds to the locking of all defective grains with greater than four sides, while the latter corresponds to the complete locking of all defective grains. Hillert's model is strictly applicable only to a two-dimensional array of grains, although it is reasonable to assume that the trends shown by the model will still be apparent in three-dimensional systems, that is, there are always two grain size limits. Moreover, normal grain growth occurs below the lower limit of grain size but cannot be initiated at larger grain sizes since all "defect" grains with greater than four sides are locked and grain growth depends initially upon the shrinkage of such "defect" grains. The upper limit determines the maximum possible grain size in the absence of discontinuous grain growth. Discontinuous grain growth is likely to be initiated between the grain size limits and continue above the upper limit, unless the grain size and particle distribution is particularly uniform.

3.1.1 Grain size stabilisation

The upper grain size limit predicted by Hillert's model (Figure1) can be calculated from a Zener type analysis. The simple model of Zener (1949) was based upon a random dispersion of uniform spherical particles and it considered the effect at the boundaries of a uniform array of spherical grains. It ignored the effect of particles located at triple-grain edges and four-grain corners.

To elucidate these additional effects, the Zener type model is now applied to the case of uniform spherical particles and a uniform array of tetrakaidecahedral grains. The relationships for stabilisation of normal grain growth by particles located at various sites are calculated in Appendix 2. The meanings of symbols used in the text are listed in Appendix 1.

Particles at Grain Boundaries

Random Dispersion of Particles: The volume fraction of particles required for grain size stabilisation is given by:

$$V_f = 0.3\ (d/D). \tag{1}$$

The derivation given in Appendix 2 is a modification of that used by Zener (1949) who obtained a very similar equation:

$$V_f = 0.75\ (r/R).$$

Particles Located Entirely at Grain Boundaries: The requirements for grain size stabilisation are given by:

$$V_f = 0.6\ (d^2/D^2). \tag{2}$$

Particles at Triple-Grain Edges

Random Dispersion of Particles: The requirements for grain size stabilisation are given by:

$$V_f = 1.05\ (d/D). \tag{3}$$

Particles Located Entirely at Triple-Grain Edges: The requirements for grain size stabilisation are given by:

$$V_f = 1.86\ (d^3/D^3). \tag{4}$$

Particles at Four-Grain Corners

Random Dispersion: The probability of particles from a random dispersion filling 0, 1, 2, 3...... of the four-grain corner sites for a particular grain may be calculated from successive terms of the expansion:

$$\exp - Z, \quad Z \exp - Z, \quad (Z^2/2!) \exp - Z, \quad (Z^3/3!) \exp - Z, \quad \ldots\ldots$$

where

$$Z = 7\ (V_f\, D^3/d^3). \tag{5}$$

Thus, the probability of these sites being filled from a random dispersion would be very small. For example, the probability that none of the sites would be filled in a 2 micron matrix containing a 0.1 volume fraction of 0.1 micron particles is greater than 0.99.

Particles Located Entirely at Four-Grain Corners: Where all sites at four-grain corners are filled, the conditions for grain size stabilisation are given by:

$$(d/D) = 3.1\ , \tag{6}$$

and if only one in every possible six sites are filled the conditions become:

$$(d/D) = 18.7\ .$$

3.1.2 Rate of normal grain growth

In a polycrystalline body with a uniform grain size, the rate of normal grain growth is inversely proportional to the size of the grains (Burke 1949), that is:

$$dD/dt = K/D,$$

or, integrating and evaluating the integration constant at $t = 0$,

$$D^2 - D_0^2 = Kt \quad . \tag{7}$$

When the initial grain size D_0 is small compared with D, it can be ignored and the equation is often written in the form:

$$D = K^1 t^n \quad , \tag{8}$$

where n is equal to 0.5. The rate constant K varies with temperature according to the equation:

$$K = K_0 \exp(-\Delta Q/RT) \quad . \tag{9}$$

Impurities in ceramic materials generally increase the value of the apparent activation energy ΔQ, and in systems of gross impurity, cause the grain growth to follow a relationship similar to Equation 8 but with a time exponent of 0.3 (Burke 1959; Coble 1961). This is indicative of the slowing of grain growth due to the increasing accumulation of impurities at the grain boundaries as the grains grow larger.

The effect of second phase particles upon the rate of normal grain growth is best considered in terms of the relationship between the driving force for grain growth F_D and the restraining force exerted by the particles F_R. In the early stages of grain growth the radius of curvature of the grains is small and F_D (proportional to 1/R) is large. Generally, $F_D >> F_R$ and the particles have little restraining effect upon the rate of grain growth. Under these conditions, the rate of grain growth would be expected to follow the normal grain growth relationship, Equation 8, with a time exponent of 0.5. As grain size increases, the driving force for grain growth diminishes owing to straightening of the grain boundaries, and a point is reached when $F_D = F_R$. All the grain boundaries would become locked, the grain size stabilised and the time exponent in Equation 8 equal to zero. Between these limits, the time exponent in Equation 8 would be expected to vary between 0.5 and 0 depending on the proportion of grain boundaries locked at that particular time. If particle coalescence occurs after prolonged grain growth without the initiation of discontinuous grain growth, Hillert's model suggests that the time exponent will approach a value of 0.3.

A hypothetical grain growth curve obtained from Equation 8 by plotting the logarithm of the grain size versus the logarithm of time is shown in Figure 2. The actual shape of an observed curve will depend upon the time taken for most boundaries to be locked.

3.2 Effect Upon Discontinuous Grain Growth

Burke (1950) showed that exaggerated or discontinuous grain growth may occur in the presence of grain growth inhibiting particles. The analysis of Hillert (1965) indicates that discontinuous grain growth may be initiated between the two limits of normal grain growth (Figure 1) if the following conditions are simultaneously fulfilled:

(i) normal grain growth is restrained owing to the presence of second phase particles;

(ii) the average grain size is below the upper limit;

(iii) there is at least one grain much larger than the average size.

However, the risk of developing a grain large enough to grow discontinuously may be slight under ordinary stabilised conditions (that is, stable second phase particles). The risk of developing a large grain is much higher if the stabilised limits of normal grain growth slowly move to larger sizes by coalescence and/or dissolution of the second phase particles.

Hillert (1965) suggests that a method of avoiding discontinuous grain growth would be to decrease the distance between the two normal grain size limits by using a large volume fraction of particles and a large particle size. Discontinuous grain growth is unlikely to occur in a material when the particles are stable and observed to be situated entirely at the grain boundaries.

3.2.1 Grain size stabilisation

Hillert's results (1965) indicate that if discontinuous grain growth occurs, the presence of second phase particles has no stabilising effect upon the ultimate grain size limit. When a large grain is growing discontinuously in a matrix of smaller grains, the curvature of local boundaries is increased and the associated driving force for grain growth F_R is much greater than the retarding force exerted by inclusions, F_D. Such grain growth is only limited by the impingement effects of other equally large grains and/or when the grain size approaches the size of the ceramic body.

3.2.2 Rate of discontinuous grain growth

Under conditions where discontinuous grain growth is possible (see Section 3.2), the presence of particles at grain boundaries has little retarding effect upon the rate of growth of the large grains, since $F_D >> F_R$.

Cutler (1959) showed that under conditions of discontinuous grain growth in Linde A alumina, the rate of growth of the large grains follows a linear relationship:

$$D - D_o = Kt . \qquad (10)$$

However, later work by Patrick and Cutler (1964) indicated that the rate of growth of seed crystals of high purity alumina in a high purity alumina matrix followed a normal grain growth relationship (Equation 7). The larger grains grew more rapidly than predicted by Equation 7 which describes the growth of small grains, but less rapidly than the rate predicted by the linear relationship. The latter results cause some doubts as to whether the linear law represents discontinuous grain growth dependent solely upon interfacial energy relationships or whether it is due to segregation of impurities at grain boundaries.

If discontinuous grain growth develops after grain size stabilisation of the matrix, the time exponent of the grain growth relationship, Equation 8, should be substantially larger than 0.5 and may be close to 1.0. This is shown diagrammatically in Figure 2.

4. EFFECT OF GRAIN SIZE STABILISATION ON SINTERING

During the intermediate and final stages of sintering in ceramics, volume diffusion of vacancies between the pores and neighbouring grain boundaries becomes the most important mechanism for densification. Grain boundary migration affects the vacancy diffusion flux by varying the distance between the vacancy source (pore) and the vacancy sink (grain boundary). However, during periods of normal grain growth the porosity is continuously reduced in size and volume because every pore is swept a number of times by a passing grain boundary. If discontinuous grain growth occurs during the final stages of sintering, the boundaries move rapidly with little time for annihilation of pores and the pores will generally be swept only once. Pores become isolated within the large grains and the grain size ultimately stabilises owing to impingement effects. Unless sintering is continued for extremely long times, a limiting density is apparent at this stage of the process.

If the presence of second phase particles and porosity impedes grain boundary migration and maintains a relatively small grain size so that pores remain at the boundary or at an extremely short distance from the boundary until eliminated, an enhanced rate of sintering will result from the decrease in diffusion distance and the associated increase in the vacancy flux. Higher ultimate densities will be achieved if discontinuous grain growth is prevented or its initiation delayed. Sintering for longer times at relatively low temperatures where grain growth takes place slowly, would appear to be advantageous since there is a greater probability under these conditions that particles will be stable and remain at, and lock, grain boundaries.

5. STABILITY OF PARTICLE SIZE

The relationships derived in Appendix 2 for stabilisation of normal grain growth by particles located at various grain boundary sites show that particle size has a major effect upon the amount of additive required. The restraining force per unit area of boundary (F_R) is equal to the number of particles per unit area of boundary ($\propto 1/d^n$) times the force per unit area exerted by each particle ($\propto d$). Thus:

$$F_R \propto d/d^n \propto 1/d^{n-1} \quad ,$$

where n is normally equal to or greater than unity. This indicates that for a given volume fraction of particles, the smallest discrete particle size is desirable and subsequent increases in particle size will lead to less favourable conditions for stabilisation.

There are two major processes which can effectively contribute to particle growth:

(1) Segregation and agglomeration of particles during powder preparation, subsequently sintering to a larger particle size during fabrication.

(2) Particle growth during sintering, due to particle instability.

5.1 Segregation and Agglomeration

A uniform distribution of the second phase particles is required for homogeneity of product and properties. The tendency for powders to segregate and agglomerate during mixing is influenced by several factors, including:

(i) specific gravity of components,

(ii) particle size distribution of components,

(iii) particle shape of components,

(iv) particle surface conditions of components,

(v) mixing media.

Relatively tenacious agglomerates can be formed as a result of inter-particle attractive forces and the sintering of agglomerates of sub-micron particles will be rapid owing to the driving force associated with the large surface area.

5.2 Instability of Particles

If there is some solubility of the components of the dispersed phase in the matrix, a concentration gradient may exist between small and large particles and the diffusion of constituent atoms or ions through the matrix may result in dissolution of the finest and the growth of the larger particles (Lifshitz and Slyozov 1958, Dromsky et al. 1962; Komatsu and Grant 1964). The inter-particle spacing and size of particles may change to less favourable dimensions. Coalescence of a dispersed phase at elevated temperatures is a manifestation of its lack of stability. The chief factors that promote stability of a dispersed phase (Goetzel and Bunshah 1961) include:

(i) high free-energy of formation,

(ii) large particle radius,

(iii) high density of the dispersed phase,

(iv) low values of the diffusion coefficients of the components of the dispersed phase in the matrix,

(v) low solubility of the dispersed phase and components in the matrix,

(vi) low interfacial energy between the dispersed phase and matrix,

(vii) increased complexity of the crystal structure of the dispersed phase.

Lifshitz and Slyozov (1958) investigated the coalescence of spherical particles. They showed that there is a tendency towards a fixed distribution of relative sizes and the rate of coalescence can be represented by the relationship:

$$r^3 = Kt.$$

The average particle size $\bar{r}$, will asymptotically approach:

$$\bar{r}^3 = 4/9\,(kt)$$

and the largest particle should be 3/2 times as large as $\bar{r}$.

The effect of particle instability upon grain growth (Hillert 1965) is to shift the stabilised limits of normal grain growth to higher grain sizes and enhance the possibility of discontinuous grain growth.

If the second phase particles are unstable and the components have a slight solubility in the matrix, the retarding effect of particles, which is a function of particle size and distribution, will be temperature dependent. This will affect the normal temperature dependence of the growth rate constants. Burke (1949) pointed out that materials containing inclusions show a much higher apparent activation energy for grain growth (ΔQ in Equation 9) than is observed for pure materials. Turnbull (1951) explained this observation in terms of the effect of temperature upon the dispersion of inclusions which modify the free energy decrease in boundary migration such that:

$$\Delta F = \Delta F' - I\ ,$$

where $\Delta F'$ is the driving free energy in the absence of inclusions. If the particles coalesce, the term I, an energy term due to the particles and their dispersion, will decrease with increasing time and temperature. If, at a constant temperature, I reaches a constant value in a time that is short relative to the period of grain growth, then with respect to grain boundary migration, I will be a function of temperature only. However the temperature dependence of grain growth is best predicted by Equation 9:

$$K = K_o \exp(-\Delta Q/RT) = D^n/t\ .$$

The effect of the temperature dependence of I upon this relationship is shown in Figure 3, for values of I associated with various dispersions of particles at grain boundaries (dotted curves). If particle coalescence occurs, the effect is shown schematically by the solid curve in Figure 3. The apparent activation energy, ΔQ (slope) of the curve decreases as temperature increases owing to progressive solution and is generally much higher than if particles are absent, that is:

$$\Delta Q_{\text{Observed}} = \Delta Q_{\text{True}} - \delta T,$$

where δ is a function of particle size, number and distribution, and decreases with increasing temperature.

Instability of the particles may affect the rate of sintering by:

(i) permitting discontinuous grain growth to develop,

(ii) solution of cation or anion components of the particles in the vicinity of pores and grain boundaries, thus affecting the vacancy concentration gradient,

(iii) formation of a liquid phase.

The effect of discontinuous grain growth on sintering was discussed in Section 3. When ions of different valency are dissolved in an ionic host lattice, a method of charge compensation is necessary to maintain electrical neutrality. The main method of compensation in ceramics is by changes in the defect structure. A cation of higher valency should create a higher local concentration of cation vacancies and a lower concentration of cation interstitials and anion vacancies in the host lattices. If sintering is controlled by the rate of migration of cation interstitials or anion vacancies, solution of a higher valency ion should reduce the rate of sintering. Similarly, if sintering is dependent upon the rate of migration of cation vacancies, the rate of sintering should be enhanced by the addition of higher valency ions. Thus, the effect of the solution of foreign ions from the dispersed particles upon the rate of sintering is dependent upon (a) the charge and valency of the solute ion in relation to those of the host lattice, (b) the identity of the ionic species associated with the rate-controlling steps during sintering and (c) the induced change in the equilibrium concentration of the rate-controlling species at the sintering temperature.

The formation of a liquid phase at the grain boundaries, with its associated increase in diffusion coefficients, leads to enhanced sintering and grain growth kinetics, and is therefore undesirable.

6. DISCUSSION

6.1 Particle Limited Normal Grain Growth

In considering the dispersion of particles throughout a matrix two limiting types of distribution are evident. These correspond to a random dispersion and to the situation where all particles are located at sites on the grain boundary. The relationships calculated in Appendix 2 for stabilisation of normal grain growth by particles located at various sites are collated in Table 2. The volume percentage of 0.5 micron particles required to stabilise a 2 micron grain size are also listed in Table 3 for comparison.

Random Dispersions: Calculations show that for a random dispersion, only particles at grain boundaries and triple-grain edges have significant stabilising effects upon grain size (Table 3). These relationships are illustrated in Figure 4. The effect of particles located at four-grain corners can be ignored since the probability of these sites being filled in any particular grain is very small.

All Particles Located at Boundaries: Particles located at grain boundaries and triple-grain edges have a major stabilising effect upon grain sizes with the latter being relatively more effective (Figure 4). The calculations indicate that even if particles are located at four-grain corners, the particle size must be three times as large as the grain size for stabilisation to be achieved. Therefore, the effect of particles at four-grain corners can be ignored.

Particles located on the grain boundary will be partitioned between the boundary planes and triple-grain edges, with the majority being situated on the former since the boundary plane has a greater number of sites upon which particles can collect. The resultant stabilisation relationship will be intermediate between those calculated for grain boundaries (d^2/D^2) and triple-grain edges (d^3/D^3) (Figure 4), lying closer to the former.

The particles are normally added to a ceramic powder and initially will be located entirely at the crystallite boundaries. During the initial stages of sintering, particles will have little stabilising effect since the driving force for grain growth is so large. The dispersion becomes effectively more random as grain growth continues since a greater proportion of the particles lie within grains and the initial crystallite size becomes small compared with the grain size. When particles become effective in locking boundaries, a grain boundary will continue to move until locked by particles. The number of particles at grain boundaries will be greater than predicted by the probability of a random plane passing through them, since the boundaries are free to move until they meet particles and are locked.

Therefore, the volume fraction of particles required to stabilise a specific grain size will be intermediate between the values predicted by Equations 1 and 2, with a tendency towards the latter values. The relationships are illustrated in Figures 4, 5, and 6.

Figure 6 shows the relationship between particle size and the volume percentage of particles for stabilisation of grain sizes in the 1 to 3 micron regions. For a given grain size, the lines representing the stabilisation relationships for a random dispersion and for all particles located at grain boundaries converge at higher values of particle size and volume fraction of particles. This indicates that at these higher values a greater proportion of the randomly dispersed particles lie upon grain boundaries.

It is of interest to calculate the unique relationship when all the randomly dispersed particles are located at grain boundaries, that is, when $0.3\,(d/D) = V_f = 0.6\,(d^3/D^2)$,

$$D = 2d\,,$$

and the volume fraction:

$$V_f = 0.3\ (d/D) = 0.3\ (d/2d) = 0.15\,.$$

Thus, at 15 volume per cent. particles, and a particle size equal to half the grain size, stabilisation will be achieved and all the particles distributed in the matrix will be situated at grain boundaries. The conditions are identical with the points of intersection in Figure 6.

The grain diameter D in the above equations refers to three-dimensional grains. Mean grain diameters determined from a planar section can be corrected by the relationship derived by Fullman (1958):

$$\begin{aligned} D &= 1.5/N_L \\ &= 1.5\,D_L \end{aligned}$$

to provide a more realistic estimate of grain diameter for use in this analysis.

6.2 Application of Dispersed Phase Grain Refinement to Ceramics

The analysis of particle limited grain boundary migration presented earlier indicates that it is feasible to achieve grain refinement in ceramics by the addition of an inert dispersed phase. However, the choice of particle composition, size, and level of addition to a specific ceramic can only be made with a knowledge of the application and final properties required from the ceramic.

Two methods can be used to obtain the desired dispersion of particles:

(i) addition of a solute followed by precipitation of the particles during densification;

(ii) addition of discrete particles to the ceramic powder prior to densification.

The latter process is the most favoured one owing to greater control over particle size, shape, and level of addition.

6.3 Application of Dispersed Phase Grain Refinement to BeO

In a nuclear moderator such as BeO, the volume fraction of any parasitic diluent should be kept to a minimum to avoid deleterious effects upon the nuclear and physical properties. The properties of BeO which it is desirable to retain include:

(a) the low thermal neutron absorption cross section and the advantages of neutron economy from the (n,2n) reaction of beryllium,

(b) the high temperature stability and oxidation resistance of BeO,

(c) the fairly high thermal conductivity and mechanical properties,

(d) the irradiation stability and resistance to microcracking,

(e) the ability to sinter to high densities at moderate temperatures.

Any diluent, with the exception of carbon, will increase the thermal neutron absorption cross section, since Be and O have the lowest cross sections of any cation or anion, respectively, except carbon. Dilution will also reduce the contribution of the (n,2n) reaction to neutron economy. Different thermal expansions of the dispersed phase and the matrix may cause stresses to be set up in both the particles and the matrix. The dispersion may have an adverse effect upon mechanical properties of BeO if the particle size exceeds 8 microns or the volume fraction is so large that the stress fields surrounding the particles overlap (Rotsey and Veevers, A.A.E.C., unpublished). Similar considerations apply to the effect of a dispersion upon irradiation stability particularly if the particles are situated at grain boundaries where the maximum stress is generated in irradiated BeO due to anisotropic expansion. Stress problems may be aggravated by irradiation damage of the matrix and dispersed phase. Elleman et al. (1965) showed that fission-fragment-induced-expansion increased in the order:

$$MgO < SiO_2 < BeO < \text{graphite} < Al_2O_3 < ZrO_2 < \text{pyrolytic carbon} < SiC.$$

Low temperature neutron damage (Hickman, A.A.E.C., private communication) produces expansions which increase in the order:

$$SiC \simeq Al_2O_3 \simeq MgO < BeO < \text{graphite} < \text{pyrolytic carbon} < SiO_2 .$$

Materials with a greater irradiation-induced expansion than BeO would contribute to the general tensile stress field developed at the grain boundaries.

The ability to sinter BeO to high densities at moderate temperatures is desirable to reduce fabrication problems and minimise costs. Reeve (1966) has reviewed the effect of impurities upon the sinterability of nuclear grade BeO powders. Si and Al, either singly or in combination, have the most unfavourable effect upon the sintering of BeO, particularly below 1500 °C.

These factors suggest that particle size and level of addition should be maintained as low as possible, preferably less than 4 microns and perhaps, 1.0 volume per cent. At a level of addition of 1.0 volume per cent., the maximum particle size that can be used for stabilisation of a 1.0 micron grain size is 0.04 microns for a random dispersion and may increase to 0.13 microns if all the particles are located at grain boundaries (Figure 6). Under these conditions, the maximum stable particle size which can be used is probably 0.1 microns.

However, particle instability and coalescence may cause the particle size and distribution to change to less favourable dimensions. Analysis of these effects upon normal and discontinuous grain growth (Section 5) indicates a greater probability of grain size stabilisation if large particle sizes and high volume fraction of particles are used. However, this may be undesirable for neutron economy.

A method of overcoming this problem in a dispersion type fuel element is to use the fuel particles to achieve grain size stabilisation. For example, in a BeO based fuel element containing 2 - 3 volume per cent. of fissile-fertile oxide particles ($(UTh)O_2$, $(PuTh)O_2$, or $(PuU)O_2$), use of 4μ or smaller fuel particles would provide grain size stabilisation in the BeO matrix.

6.3.1 Choice of particles

The following materials have been considered for particle additions to a BeO matrix:

(i) Oxides - These compounds are attractive owing to their inherent high temperature stability and the fact that they can be produced as sub-micron sols. Both ZrO_2 and ThO_2 sols are available and have small particle sizes (0.005 to 0.01 microns) so low levels of addition may be satisfactory. Sols have the advantage of producing an initial uniform dispersion of adsorbed particles at crystallite surfaces due to the repulsive forces between sol particles within the solution. Excess or unadsorbed sol may gel within the interstices of the drying powder and subsequently sinter to larger particle sizes. In general, the stability of oxide particles in an oxide matrix may be questionable because of the tendency to form a continuous oxide lattice with the BeO matrix at high temperatures, thus reducing the initial "barrier" to cation diffusion. Bulk solubility of foreign cations in BeO is generally very limited but grain boundary diffusion can be rapid.

(ii) Metals – These are not favoured owing to the large particle size (0.5 to 5.0 microns) of most commercially available metal powders. Submicron metal powders are available but these tend to be pyrophoric, explosive in contact with air, and very difficult to handle. Refractory metal powders tend to segregate during mixing owing to their much higher densities relative to BeO and this causes aggregation and particle growth during subsequent sintering, with an associated decrease in grain refining capacity. The overall corrosion resistance of beryllia may be affected by the metal addition.

Platinum is the most attractive metal addition owing to its colloidal nature when decomposed from salt solutions. Temperatures less than 1600 °C would have to be maintained during sintering to prevent volatilisation.

(iii) Carbon and Carbides – The experimental results discussed in Section 2 have demonstrated the feasibility of using colloidal graphite to obtain grain refinement in sintered and hot-pressed BeO. This material is objectionable from an oxidation viewpoint particularly as the oxidation products are gases. There is the possibility of interconnected porosity being formed by the oxidation of particles segregated at grain boundaries. For this reason, colloidal graphite could not be used in any outer coating on a fuel element designed to improve fission product retention.

Carbides, particularly silicon carbide, appear to be the most promising particle material. Silicon carbide overcomes the disadvantages of other materials associated with thermal conductivity, oxidation resistance, and general stability. It has the added advantage of having relatively good nuclear properties and is becoming available in sub-micron particle sizes. It has the disadvantage that it contains Si and if the particles are not stable, this could have a deleterious effect upon sintering.

The most attractive materials for use as grain size stabilisers in a BeO matrix would, therefore, appear to be silicon carbide, oxide sols, colloidal platinum, and colloidal graphite, in that order.

7. CONCLUSIONS

(i) Dispersed phase grain refinement in ceramics is feasible.

(ii) The grain size stabilisation relationship for normal grain growth is deduced using a Zener type analysis:

(a) Random dispersion:

$$V_f = 0.3\ (d/D) \quad .$$

(b) All particles located at grain boundaries:

$$V_f = 0.6\ (d^2/D^2) \quad ,$$

or at triple-grain edges:

$$V_f = 1.86\ (d^3/D^3) \quad .$$

(iii) Discontinuous grain growth cannot be stabilised by second phase particles but nucleation may be prevented by using stable particles and/or a large volume fraction and large particle size.

(iv) The choice of particle composition, size, and level of addition to a specific ceramic can only be made with a knowledge of the application and final properties required from the ceramic.

(v) The most attractive materials for use as grain size stabilisers in the matrix of a dispersion type fuel element based on BeO would appear to be silicon carbide, oxide sols, and colloidal platinum.

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APPENDIX 1

DEFINITIONS OF SYMBOLS USED

d	Diameter of a spherical particle
ℓ	Length of a tetrakaidecahedron edge
n	A constant for a given material
r	Radius of a spherical particle
$\bar{r}$	Average radius of spherical particles
t	Time
D	Grain diameter
D_L	Mean linear intercept between grain boundaries in a planar section of a polycrystalline body
F_D	The driving force per unit area of grain boundary
F_R	The restraining force per unit area of grain boundary
ΔF	The free-energy decrease in boundary migration
$\Delta F'$	The free-energy decrease in boundary migration in the absence of inclusions
I	An energy term due to particles and their dispersion
K	A constant for a given material
N_L	Number of intercepts per unit length which a line makes with grain boundaries in a planar section
ΔQ	Apparent activation energy for grain growth
R	The effective radius of grain boundary curvature
T	The absolute temperature
V_f	Volume fraction of spherical particles
Z	The average number of particles situated at four-grain corners per unit volume
δ	A constant for a given material which is a function of particle size, number and distribution
λ	The interfacial energy

APPENDIX 2

PARTICLE LIMITED NORMAL GRAIN GROWTH

A Zener type model of grain size stabilisation is applied to the case of uniform spherical particles and uniform tetrakaidecahedral grains to determine the stabilising effect of particles located at grain boundaries, triple–grain edges and four–grain corners.

In such a model the volume and surface area of each grain is given by 11.31 ℓ^3 and 26.78 ℓ^2 respectively. For the tetrakaidecahedral grain model with planar surfaces, the radius of curvature R is infinite but spherical grains having the same surface area as the model grains would have the value:

$$R = 1.46\,\ell = D/2 \ ,$$

where D is the grain diameter. In practice, grain boundaries are straighter than for hypothetical spherical grains. Cole et al. (1954) found that generally $R \simeq D$ during periods of normal grain growth, and thus a more realistic value of R would be:

$$R = 1.46\,\ell = D \ .$$

Particles at Grain Boundaries

Since each grain boundary is shared by two grains, the grain boundary area per unit volume $= 1/2\,(26.78\,\ell^2/11.31\,\ell^3)$

$$= 1.18/\ell \ ,$$

The volume of each inclusion $= \pi d^3/6$.

Thus, the number of inclusions per unit volume of sample $= 6\,V_f/\pi d^3$.

(a) Random Dispersion of Particles

Fullman (1958) stated that in a random dispersion of particles, the average number of particles per unit area situated upon a plane intersecting the array is equal to the number of particles per unit volume times the probability that the plane of unit area will intersect a single sphere positioned at random within the unit volume. He deduced that the probability of such a plane intersecting a randomly placed sphere of diameter d is d . The number of particles per unit area of grain boundary

$$= (6\,V_f/\pi d^3) \times d$$

$$= 6\,V_f/\pi d^2 \ .$$

The maximum restraining force per unit area exerted by each particle upon the grain boundary (Bannister 1964b) $= \pi \lambda d$.

Thus, the restraining force per unit grain boundary area:

$$F_R = (6\,V_f/\pi d^2) \times (\pi \lambda d)$$

$$= 6\,V_f\,\lambda/d \ ,$$

The driving force per unit grain boundary area for grain growth (McLean 1957):

$$F_D = 2\,\lambda/R \ .$$

Since $R \simeq D$:

$$F_D = 2\,\lambda/D \ .$$

(continued)

APPENDIX 2 (continued)

For grain stabilisation, $F_R = F_D$, that is:

$$(6\ V_f\ \lambda/d) = (2\ \lambda/D)\ ,$$

and the volume fraction of particles required for stabilisation is given by

$$V_f = 0.3\ (d/D)\ . \qquad (1)$$

(b) Particles Located Entirely at Grain Boundaries

Since all the particles are located at grain boundaries, the number of inclusions per unit grain boundary area:

$$= (6\ V_f/\pi\ d^3)/(1.18/\ell)$$

$$= 5.07\ V_f\ \ell/\pi d^3.$$

Since $\quad R = 1.46\ \ell \simeq D\ ,$

$$F_R = 3.47\ V_f\ \lambda\ D/d^2\ ,$$

and the volume fraction of particles required for grain stabilisation is given by:

$$V_f = 0.6\ (d^2/D^2)\ . \qquad (2)$$

Particles at Triple-Grain Edges

The tetrakaidecahedral model has 36 edges shared by 3 neighbouring grains. The edges can be assumed to have an effective area equivalent to the cross-sectional area of particles situated upon it.

(a) Random Dispersion of Particles

The situation is similar to that discussed in Section (a) above and the volume fraction of particles required for stabilisation is given by:

$$V_f = 1.05\ (d/D)\ . \qquad (3)$$

(b) Particles Located Entirely at Triple-Grain Edges

Each triple-grain edge is shared by three neighbouring grains and the effective triple-edge area per unit volume

$$= 1/3\,(36\ \ell\ \pi d^2/4d)/11.31\ \ell^3 = 0.833\ d/\ell^2\ .$$

With all particles situated at the triple-edge, the number of particles per unit area of triple-grain edge

$$= (6\ V_f/\pi d^3)/(0.833\ d/\ell^2) = 2.29\ (V_f\ \ell^2/d^4).$$

The requirements for stabilisation ($R = 1.46\ \ell \simeq D$) are given by:

$$V_f = 1.86\ (d^3/D^3)\ . \qquad (4)$$

Particles at Four-Grain Corners

The model tetrakaidecahedron has 24 corners each shared by four neighbouring polyhedra.

(continued)

APPENDIX 2 (continued)

(a) Random Dispersion of Particles

If the number of second phase particles is large compared with the number of sites available at four–grain corners, then the number of opportunities to fill these sites is large, the probability of such a single event is small, and the filling of a site represents an isolated event in a continuum of volume. Therefore, the probability of sites at four–grain corners being filled by particles from a random dispersion can be predicted by a Poisson distribution. The actual probability of 0, 1, 2, 3 ..... sites being filled may be calculated from successive terms of the expansion

$$\exp - Z, \quad Z \exp - Z, \quad (Z^2/2!) \exp - Z, \quad (Z^3/3!) \exp - Z \ldots\ldots \text{etc.},$$

where Z is the average number of possible occurrences and in this model will be represented by the average number of particles per grain volume, that is,

$$Z = (6V_f / \pi d^3) \times 11.31\, \ell^3 .$$

For spherical grains having the same surface area as the tetrakaidecahedral model and R = D:

$$Z \simeq 7\ (V_f\, D^3/d^3) . \qquad (5)$$

(b) Particles Located Entirely at Four–Grain Corners

If we consider the optimum case where all sites at four–grain corners are filled, the number of particles in sites at four–grain corners per unit grain boundary area $= (24/4)\ [(26.78/2) \times \ell^2]$. The maximum restraining force per unit area exerted by each particle upon the grain boundary (Bannister 1964b) = $0.67\ \lambda d$.

The conditions for stabilisation are:

$$(d/D) = 3.1 . \qquad (6)$$

If only one in every possible six sites are filled at four–grain corners, the conditions for stabilisation become:

$$(d/D) = 18.7 .$$

TABLE 1

FORCES BETWEEN SPHERICAL PORES AND GRAIN BOUNDARIES – BANNISTER MODEL

Particle Location	Displaced to	Force
Grain boundary	Grain interior	$\pi \lambda d$
3–grain edge	Grain boundary	λd
4–grain corner	3–grain edge	$0.67\ \lambda d$

TABLE 2

REQUIREMENTS FOR GRAIN SIZE STABILISATION OF NORMAL GRAIN GROWTH

Particle Location	Random Dispersion	Particles Located Entirely at Site
Grain boundary	$V_f = 0.3\ d/D$	$V_f = 0.6\ d^2/D^2$
3–grain edge	$V_f = 1.05\ d/D$	$V_f = 0.6\ d^3/D^3$
4–grain corner	–	$d/D = 3.1$

TABLE 3

VOLUME PERCENTAGE OF 0.5 MICRON PARTICLES REQUIRED TO STABILISE A 2 MICRON GRAIN SIZE

Particle Location	Random Dispersion	Particles Located Entirely at Site
Grain boundary	7.5	3.8
3–grain edge	26.2	2.9
4–grain corner	–	Not possible

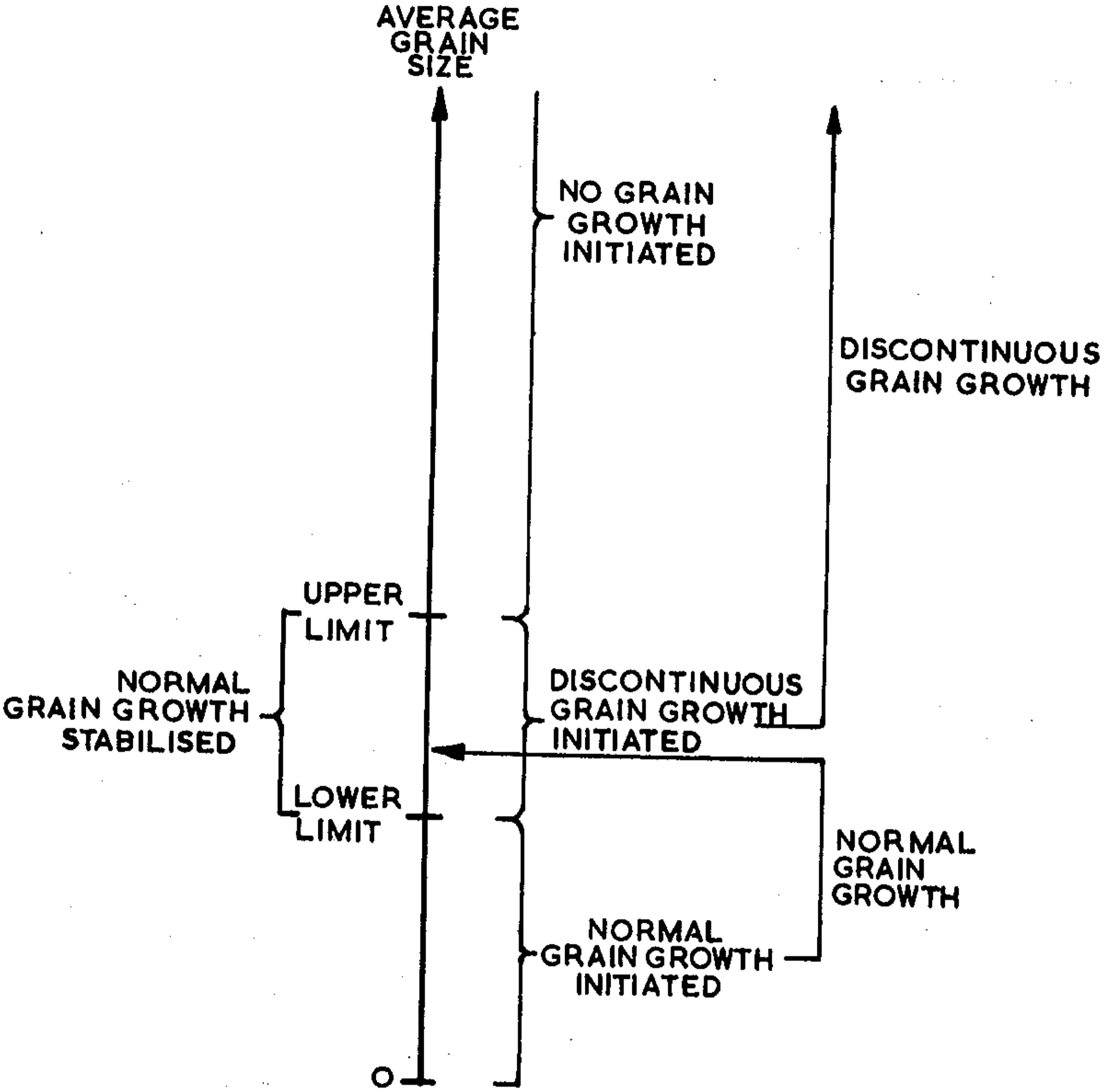

FIGURE 1. EFFECT OF SECOND PHASE PARTICLES UPON GRAIN GROWTH

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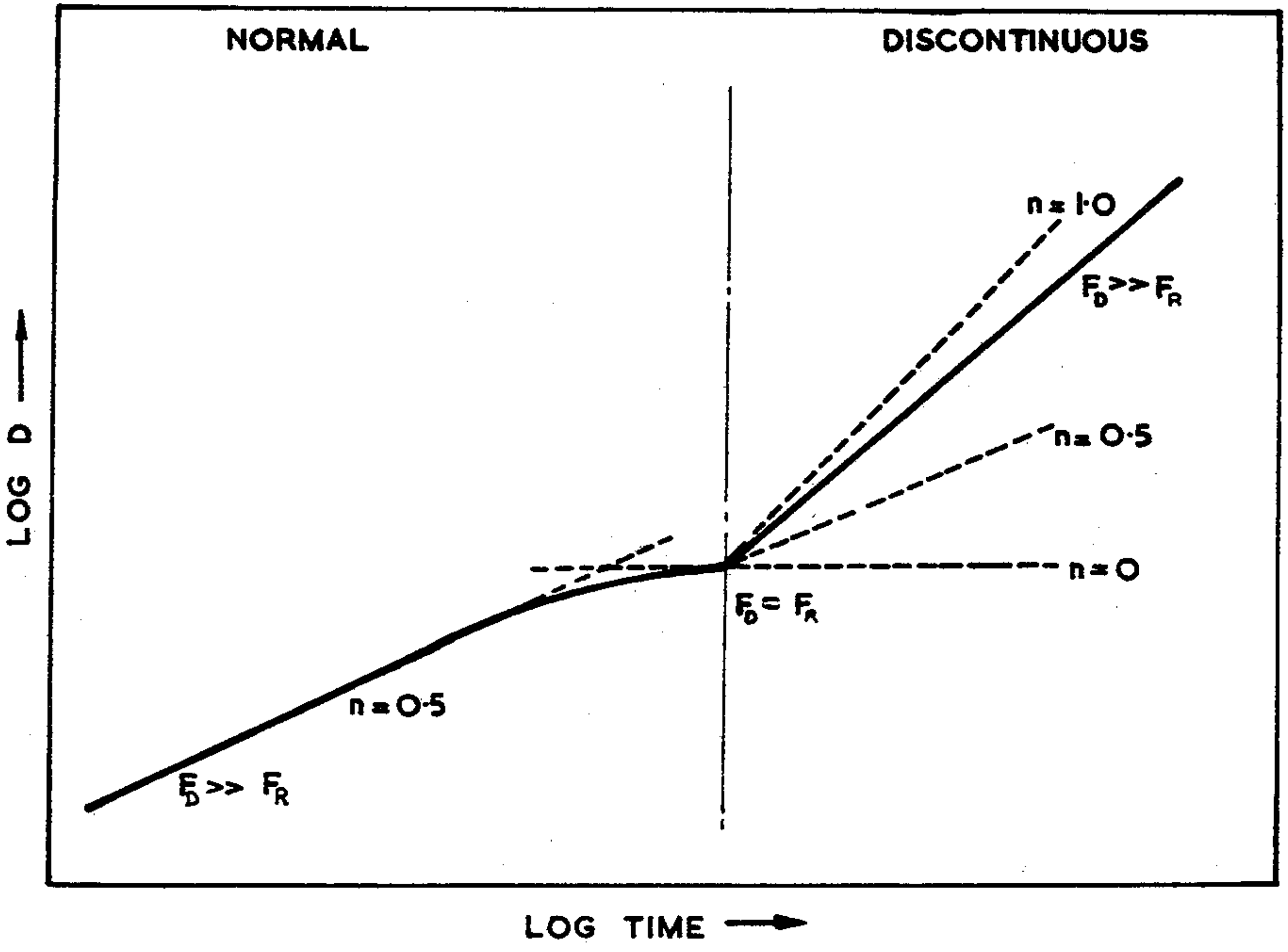

FIGURE 2. EFFECT OF SECOND PHASE PARTICLES UPON THE RATE OF GRAIN GROWTH

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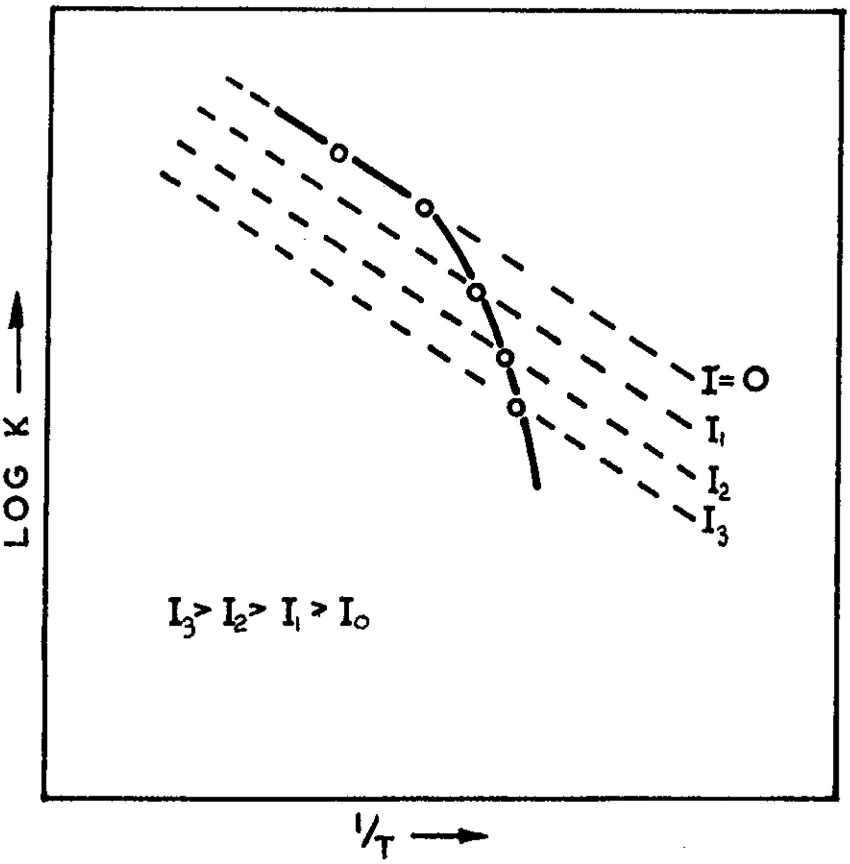

FIGURE 3. EFFECT OF PARTICLE INSTABILITY UPON THE OBSERVED ACTIVATION ENERGY FOR NORMAL GRAIN GROWTH

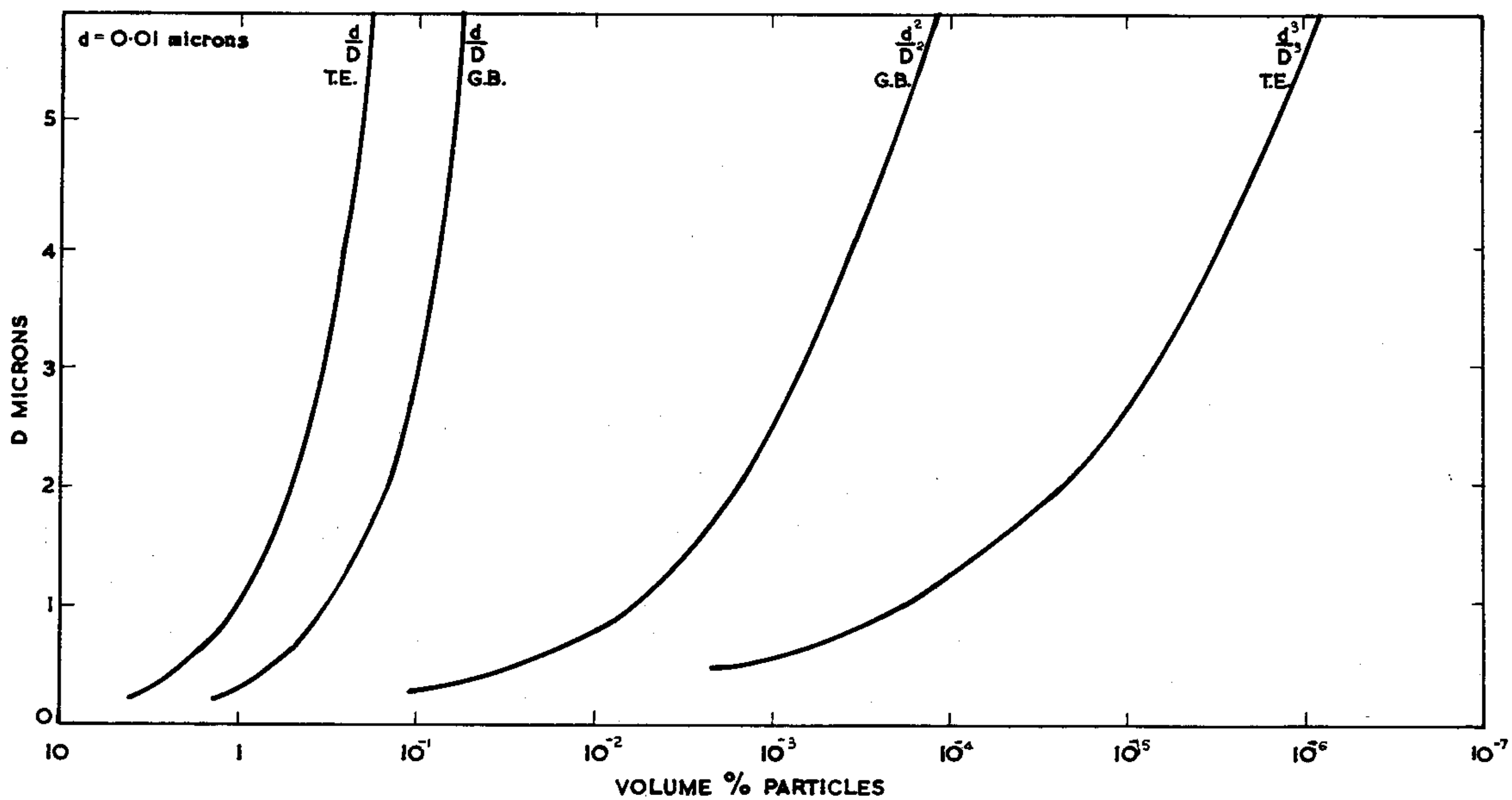

FIGURE 4. VOLUME PERCENTAGE OF 0.01 MICRON PARTICLES REQUIRED TO STABILISE GRAIN SIZES IN THE 0.25 TO 5.0 MICRON REGION

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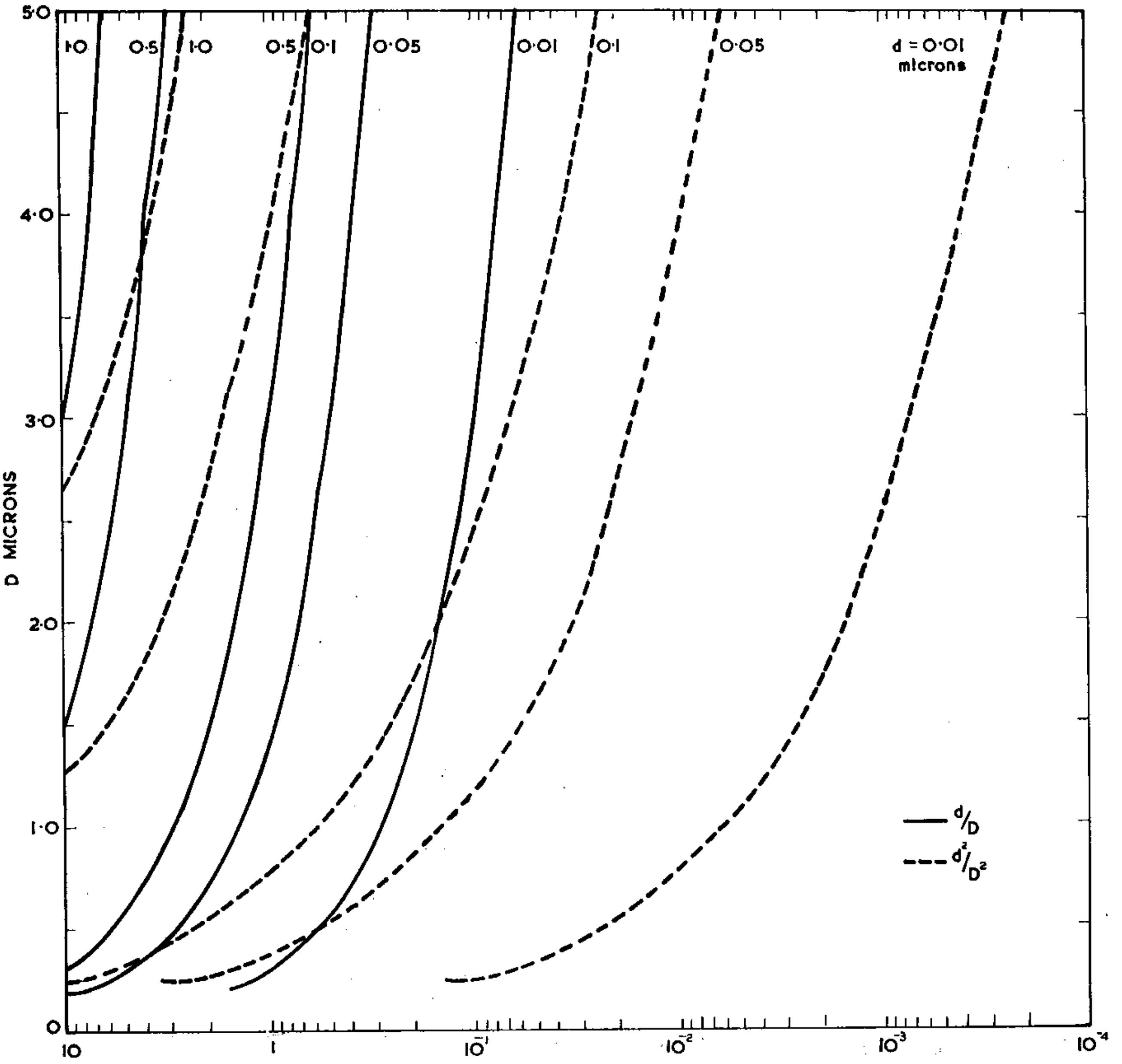

FIGURE 5. VOLUME PERCENTAGE AND PARTICLE SIZE RELATIONSHIPS REQUIRED TO STABILISE GRAIN SIZES IN THE 0.25 TO 5.0 MICRON REGION

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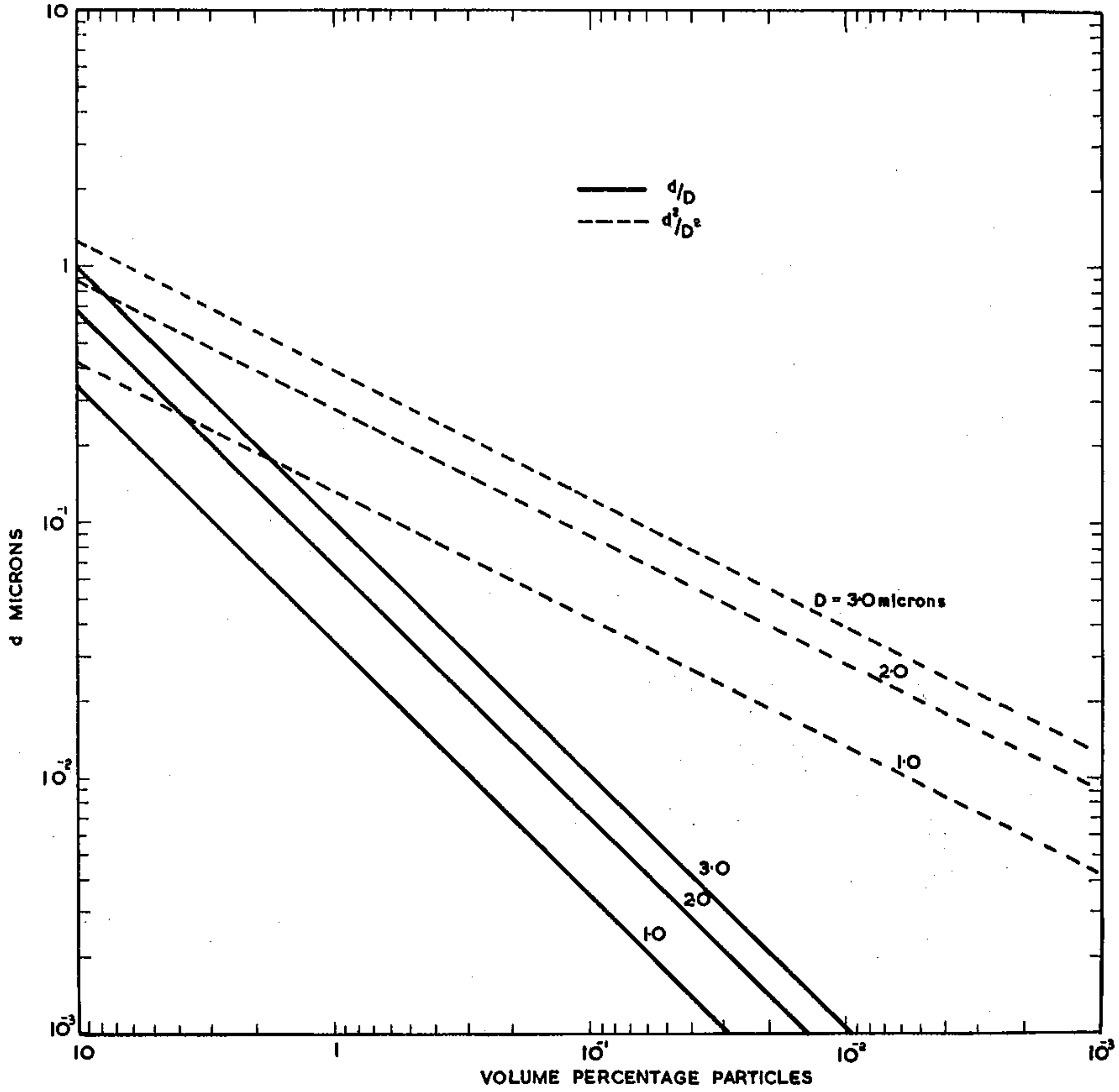

FIGURE 6. VOLUME PERCENTAGE AND PARTICLE SIZE RELATIONSHIPS REQUIRED TO STABILISE GRAIN SIZES IN THE 1.0 TO 3.0 MICRON REGION

P11/5