Average Grain Size in Polycrystalline Ceramics

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A model is proposed which realistically characterizes the grain structure of polycrystalline ceramics. The average grain size of a log-normal distribution of grain sizes with tetrakaidecahedral (truncated octahedral) shape is related to the average intercept size by a proportionality constant. This result can be used to determine the average grain size of a sintered powder compact composed of nontextured grains which shows no discontinuous grain growth.

Fig. 1. Tetrakaidecahedral grain of edge length l where α_1 and α_2 are the angles between {100},{111} faces and {111},{111} faces, respectively.

Fig. 2. Convex grain showing the caliper dimension $D(\theta)$ as a function of orientation.

I. Introduction

A PHYSICAL model for specifying the average grain size is necessary for characterizing the structure-sensitive properties of sintered ceramic materials. Such a model is developed by carefully analyzing the variables on which the grain size depends: (1) selection of a structural parameter[†] (2) structural anisotropy, (3) grain shape, and (4) grain size distribution. From the model, the average grain size is related to practical measurements which can be performed on the plane of polish.

Previous methods have inadequately defined the grain size variables, as indicated by different values for converting the average intercept size to the average grain size.[1] The structural parameter has not been systematically related to the desired physical property. Hence, the average grain size can range from the size of the smallest to the largest grain, depending on which parameter is chosen to represent the physical property.[2] Methods for determining the average grain size have been based on spherical grain geometry with a small (almost negligible) size distribution[3,4] and equiaxed grains of undefined shape and unknown size distribution.[5,6] These methods are too unrealistic and vague to be used as microstructural models.

At the present time a model which completely describes the grain structure is physically impossible. Some assumptions for the grain size variables must be made in order to specify an average grain size. These are as follows: a structure consisting of nontextured, equiaxed grains of regular polyhedral shape with a particular size distribution, where only normal (continuous) grain growth occurs. This applies to many, but certainly not to all, sintered powder compacts.

II. Development of Model

The steps followed in this analysis are (1) selecting a proper structural parameter and grain geometry, (2) selecting a proper size distribution, and (3) relating the average grain size to an average intercept size.

At present, too little is known about the correlation of structure with properties to rigorously determine which parameter should be used. Nevertheless, the S_V (grain boundary surface area to grain volume ratio) parameter has been selected. This is a good choice because: (a) It can
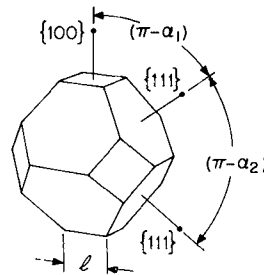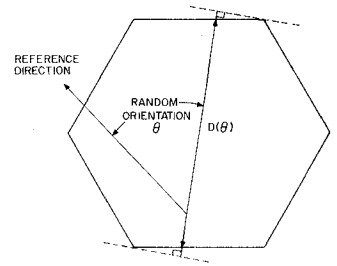
be quantitatively determined from intercept measurements on the plane of polish[7]; (b) it designates the three-dimensional structure independently of grain shape and size distribution; and (c) it describes the structural changes that occur during normal grain growth. A surface area per unit volume weighted average of the grain size may be correlated with such properties as heterogeneous nucleation, creep, and intergranular fracture strength.

A reasonable choice for the grain shape is a tetrakaidecahedron (truncated octahedron). Actually a distribution of complex polyhedra exists; however, a tetrakaidecahedron is the space-filling polyhedron which approaches the average, ideal shape for a polycrystalline structure during grain growth.[8] This shape has previously been assumed.[4,9] The geometry of a tetrakaidecahedron can be expressed by six {100} square faces and eight {111} hexagonal faces, as shown in Fig. 1. The surface area and volume of a single grain of edge length l are $6(1 + 2\sqrt{3})l^2$ and $8\sqrt{2}l^3$, respectively. Hence,

$$S_V = 2.3675 \frac{l^2}{l^3} \qquad (1)$$

The edge length in Eq. (1) is an unsatisfactory dimension to be correlated with the average intercept measurement. Therefore, a caliper dimension $D(\theta)$ is defined for any random orientation θ in a grain, as shown in Fig. 2. The average caliper dimension D is the mean perpendicular distance (averaged over all orientations) between two parallel tangent planes on the tetrakaidecahedron. This average caliper dimension will be referred to as the grain size for a single grain. For any convex polyhedron, Mack[10] derived a general expression for D in terms of l:

$$D = \frac{1}{4\pi} \Sigma \, l_i \, (\pi - \alpha_i) \qquad (2)$$

where α_i is the angle (less than π) between the faces intersecting at the ith edges of length l_i. For a tetrakaidecahedron, all of the l_i lengths are equal. The $(\pi - \alpha_i)$ values are computed for 24 edges of {100} faces intersecting {111} faces and for 12 edges of {111} faces intersecting {111} faces. The
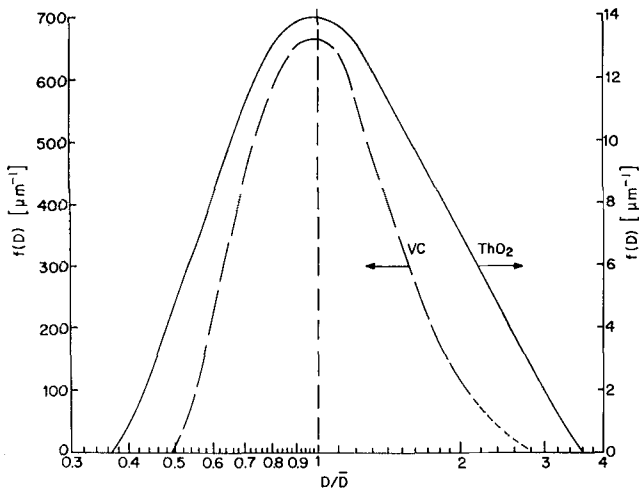
Fig. 3. Grain size distribution curves for VC sintered at 2200°C for 1 h and for ThO_2 sintered at 1800°C for 3 h (Ref. 11), with normalized grain size plotted on a log scale.

Fig. 4. Log-probability graph where σ_{VC} and σ_{ThO_2} are the standard deviations for VC and ThO_2, respectively.

total calculation using Eq. (2) gives $D = 3l$. Substituting this result for l into Eq. (1) yields

$$S_V = 7.1025 \frac{D^2}{D^3} = \frac{7.1025}{D} \cdot \frac{(D/\bar{D})^2}{(D/\bar{D})^3} \quad (3)$$

where $\bar{D}$ is a normalizing constant (defined as the average grain size of the size distribution).

A distribution of grain sizes can be more conveniently expressed as a function of a normalized grain size, rather than grain size per se. For example, the size distribution function $f(D)$, when plotted versus D, widens with time during isothermal grain growth.[11] However, if D is normalized with respect to $\bar{D}$, then $f(D)$ remains constant with time during normal grain growth.[12,13] The probability for a number of grains to range between $D/\bar{D}$ and $(D + dD)/\bar{D}$ is $f(D) \, d(D/\bar{D})/\int_o^\infty f(D) \, d(D/D)$ for the unnormalized frequency function $f(D)$. The total surface area per unit volume for all the grain sizes is the ratio of the second moment to the third moment of the size distribution, or Eq. (3) integrated over the complete distribution. Hence,

$$S_V = \frac{7.1025}{\bar{D}} \cdot \frac{\int_o^{D_m/\bar{D}} (D/\bar{D})^2 \, f(D) \cdot d(D/\bar{D})}{\int_o^{D_m/\bar{D}} (D/\bar{D})^3 \, f(D) \cdot d(D/\bar{D})} \quad (4)$$

where D_m is the maximum size.

A frequency function was assumed from the data of Oel.[11] From polished cross sections of sintered powder compacts, Oel measured the apparent spherical diameters of the grains with a Zeiss particle size analyzer and determined their frequency within a given size range for the total distribution.[14] He plotted $f(D)$ as a function of D', the spherical diameter. Since D' differs from D by a conversion constant, c, where $D' = cD$ and $\bar{D}' = c\bar{D}$, Oel's data can be used when $f(D)$ is plotted as a function of $\ln D'$ or $\ln D/\bar{D}$, as shown in Fig. 3 for VC and ThO_2. These distributions appeared to be log-normal. The hypothesis test for the log-normality of an experimental size distribution is determined by plotting the cumulative probability of the frequency function against the normalized grain size on a logarithmic scale. A straight line passing through the most probable grain size, i.e. $D/\bar{D} = 1$ at 50%, confirms that the distribution is log-normal. From Fig. 3 the cumulative areas under the curves were integrated with a planimeter for increasing $D/\bar{D}$ values and plotted on the log-probability
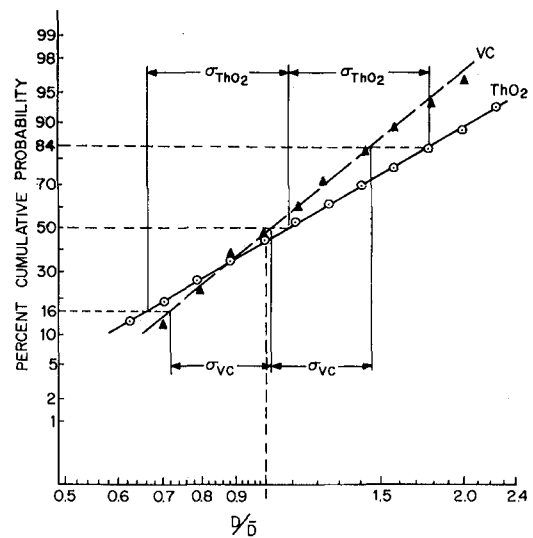
graph in Fig. 4. These data above about 15% closely approximated straight lines, passing through $D/\bar{D} \approx 1.02$ and 1.08 for VC and ThO_2, respectively, at 50% probability. These results satisfactorily agreed with the conditions for log-normality. Log-normal size distributions have also been determined for sintered MgO[11] and UO_2.[15] The author is unaware of size distribution data for other sintered ceramic materials. Due to the paucity of data, a log-normal distribution cannot be assumed to be general for all materials. Nevertheless, the known data for specific materials seem to favor a log-normal size distribution.

From the above information, a log-normal distribution, symmetrical about $D/\bar{D} = 1$, is assumed. This relation is obtained by substituting $\ln D/\bar{D}$ for $D/\bar{D}$ in a Gaussian distribution function. Thus,

$$f(D) = K \exp - \frac{1}{2} \left[\frac{\ln D/\bar{D}}{\ln \sigma} \right]^2 \quad (5)$$

where K is a constant (μm^{-1}) and $\ln \sigma$ is the standard deviation of the log-normal distribution. When Eq. (5) is substituted into Eq. (4),

$$S_V = \frac{7.1025}{\bar{D}} \cdot \frac{\int_o^{D_m/\bar{D}} (D/\bar{D})^2 \exp - \frac{1}{2} \left[\frac{\ln D/\bar{D}}{\ln \sigma} \right]^2 \cdot d(\ln D/\bar{D})}{\int_o^{D_m/\bar{D}} (D/\bar{D})^3 \exp - \frac{1}{2} \left[\frac{\ln D/\bar{D}}{\ln \sigma} \right]^2 \cdot d(\ln D/\bar{D})} \quad (6)$$

In the above expression the ratio of the second moment to the third moment of the log-normal distribution has previously been evaluated.[16,17] Equation (6) becomes

$$S_V = \frac{7.1025}{\bar{D}} (\exp - 2.5 \ln^2 \sigma) \quad (7)$$

for noncontiguous grains. For a polycrystalline structure S_V depends on both the average grain size and the shape of its log-normal distribution. During isothermal normal grain growth $\bar{D}$ increases with annealing time, whereas $\ln \sigma$ should remain constant.

III. Average Grain Size Measurement

The average intercept size can be measured by using the intercept analysis of Smith and Guttman[7] for contiguous grains:

Table I. $\bar{D} = k\bar{L}$

Grain shape and size distribution	Proportionality constant, k	Refs.
Tetrakaidecahedra, log-normal size distribution		
ThO_2 ($\ln\sigma = 0.487$)	0.981	This work
VC ($\ln\sigma = 0.367$)	1.268	This work
Single size ($\ln\sigma \to 0$)	1.776	This work, 19
Spheres, single size	1.5	3,4,19
Cubes, single size	2.25	19
Equiaxed grains, unknown shape and size distribution	1.126	5
Extruded, oriented grains, unknown shape and size distribution, taken on transverse planar section	1.273	6

$$\bar{N}_L \simeq \frac{1}{2} S_V \qquad (8)$$

Here $\bar{N}_L$ is the expected number of grain boundary intersections per unit line length of a test figure (straight line, circle, etc.), which is randomly applied to the plane of polish. Since the grains in a microstructure are contiguous, each boundary in Eq. (7) is shared by two grains, and $\bar{N}_L$ is equal to one-quarter of the surface area-to-volume ratio for non-contiguous grains. Hence,

$$\bar{N}_L \simeq \frac{1}{\bar{L}} = \frac{1}{4} S_V \qquad (9)$$

where $\bar{L}$ is the average intercept length over a large number of grains as measured on the plane of polish. By substituting Eq. (7) into Eq. (9) for S_V, a direct relation is obtained between the average grain size and average intercept length:

$$\bar{D} = 1.7756 \, (\exp - 2.5 \ln^2\sigma)\bar{L} \qquad (10)$$

When an intercept analysis is used, $\ln\sigma$ must be determined to convert $\bar{L}$ to $\bar{D}$. To obtain $\ln\sigma$, the size distribution must be experimentally determined. However, if the size distribution is determined, $\bar{D}$ can be directly obtained from the data[14,18] without the use of Eq.(10), but this is laborious. A general value of $\ln\sigma$ can be estimated without grain size distribution data, and this will be subsequently discussed.

Equation (10) holds for a log-normal distribution whose standard deviation is confined within certain limits. For the lower limit the distribution disappears as $\ln\sigma \to 0$, and $\bar{D} = 1.7756\bar{L}$. This agrees with the result previously determined for tetrakaidecahedra of a single size.[19] An intuitive upper limit can be estimated at $\bar{D}/\bar{L} \simeq 1$. At $\bar{D} = \bar{L}$ the plane of polish intersects the most probable dimension of the grains in the distribution. $\bar{D}$ is related to $\bar{L}$ by a proportionality constant k, where $\bar{D} = k\bar{L}$. As the size distribution for tetrakaidecahedra increases, the proportionality constant decreases from 1.776 toward unity. As an example, the proportionality constants for VC and ThO_2 were obtained by estimating $\ln\sigma$ from Fig. 4. The standard deviation occurs at about 68% probability, i.e. between 16% and 84% cumulative probabilities. When these $\ln\sigma$ values were substituted into Eq.(10), the values of k were calculated and compared to those from previous methods, as shown in Table I. For ThO_2, $k = 0.981$, which is near the upper limit. Any value of k which is much less than unity can be due to abnormal grain growth.[12] As expected, k varies with grain geometry. For example, by considering grains of a single size, k for tetrakaidecahedra (1.776) is between that for spheres (1.5) and cubes (2.25), and it is greater than the values for the poorly defined structures.[5,6]

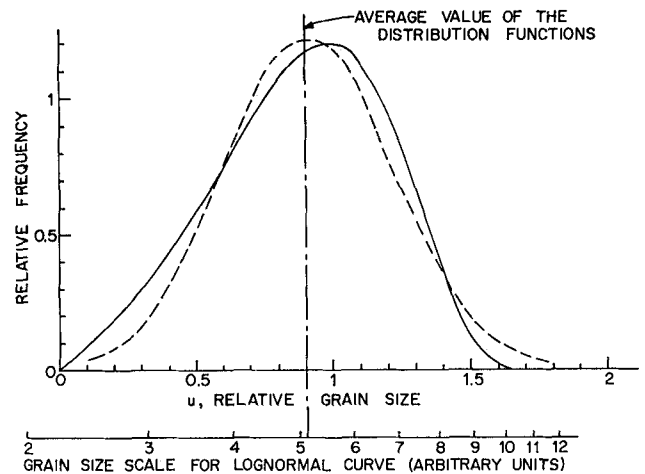A general proportionality constant can be estimated from both theoretical and experimental size distribution functions. Hillert[12] has quantitatively proposed an equilibrium, fixed size distribution during normal grain growth. This distribution is similar to a log-normal distribution but is skewed to the right and has a maximum relative grain size at $\lesssim 2$ as shown in Fig. 5. By assuming Hillert's distribution function, the relation between $\bar{D}$ and $\bar{L}$ was calculated in the Appendix:

$$\bar{D} = 1.570\bar{L} \qquad (11)$$

On the other hand, Feltham[13] used a log-normal distribution function to fit experimental grain growth data having a maximum grain size of $2.5\bar{D}$, or $D_m/\bar{D} \simeq 2.5$. If this maximum grain size is assumed to occur at four standard deviations from the mean, giving a probability of 99.994% that D_m is the largest occurring grain size,

$$4 \ln\sigma = \ln(D_m/\bar{D}) = \ln 2.5$$

and

$$\ln\sigma = 0.2291 \qquad (12)$$

When Eq. (12) is substituted into Eq.(10),

$$\bar{D} = 1.558\bar{L} \qquad (13)$$

This result is very close to Eq.(11) and is slightly higher than that for spheres of a single size. Because the experimental data for normal grain growth in metals seem to favor a log-normal distribution with $D_m/\bar{D} \simeq 2.5$,[20] Eq. (13) can be used as a general estimate of the proportionality constant. This assumes that $\ln\sigma$ has a unique value. However, $\ln\sigma$ may differ for different materials (as shown for ThO_2 and VC in Table I) or may be dependent on their prior processing. Since this is not well understood, a proportionality constant of 1.56 can be used as an estimate until more representative values are obtained for various materials with specific processing conditions.

IV. Conclusion

The grain structure of polycrystalline ceramics undergoing normal grain growth was characterized by nontextured grains of tetrakaidecahedral shape having a log-normal size distribution. Based on the physical properties being correlated with the S_V parameter, the relation between the average grain size and

the average intercept size was determined by Eq. (10). The proportionality constant was a function of the standard deviation of the log-normal distribution. This constant could be experimentally determined and was estimated as 1.56.

APPENDIX

Equation (4) must be changed to accommodate Hillert's analysis. Instead of normalizing D with respect to $\bar{D}$, $9/8\bar{D}$ (the critical grain size) is used; and a new parameter $u = 8/9(D/\bar{D})$ is defined as the relative grain size. Making these alterations to Eq. (4),

$$S_V = \frac{8 \ (7.1025)}{9\bar{D}} \cdot \frac{\int_0^{u_m} u^2 f(u) \cdot du}{\int_0^{u_m} u^3 f(u) \cdot du} \qquad (A1)$$

where u_m is the maximum relative grain size $\lesssim 2$. Hillert, following the procedure of Lifshitz and Slyazov,[21] calculated a true three-dimensional distribution:

$$f(u) = (2e)^3 \cdot \frac{3u}{(2-u)^5} \exp - \left[\frac{6}{(2-u)} \right] \qquad (A2)$$

When this relation is substituted into Eq. (A1) and numerically integrated (on a computer using the Runge-Kutta method[22]) between the limits of 0 and 1.90, the result is

$$S_V = \frac{6.2787}{\bar{D}} \qquad (A3)$$

Substituting this result into Eq. (9) gives the final result:

$$\bar{D} = 1.570\bar{L} \qquad (A4)$$

Acknowledgment

The writer is indebted to J. E. Hilliard for helpful criticisms.

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Steam Oxidation Kinetics and Oxygen Diffusion in UO₂ at High Temperatures

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Results of steam oxidation measurements of UO₂ cylinders from 885° to 1835°C may be expressed by the equations:

$$K_p = 2.44 \times 10^5 \exp \frac{-52,100 \pm 2800}{RT} \, mg^2/cm^4 \cdot s$$

for the parabolic rate of oxidation and

$$D_c = 99 \exp \frac{-56,900 \pm 1800}{RT} \, cm^2/s$$

for the chemical oxygen diffusion coefficient. K_p and D_c, obtained from thermobalance measurements to 1500°C and from pre- and post-test weights for the higher temperatures, were independent of sample weight from 10 to 149 g and of surface-to-volume ratios from 2.34 to 18.74 cm^{-1}. D_c varied as the 0.65 power of the final average excess oxygen (x in UO$_{2+x}$). The oxidation was accompanied by considerable grain growth. A bulk diffusion mechanism was verified by analyses of partially oxidized samples using both X-ray diffraction and analytical chemistry; an oxygen gradient was demonstrated by each technique.