A STUDY OF THE DEPENDENCE OF PHYSICAL PROPERTIES ON PARTICLE SIZE IN GRAPHITE*

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The relationships of strength to porosity and grain size for many polycrystalline ceramic materials have been examined extensively in numerous investigations.[1–4] These studies, through the careful preparation of fabricated ceramics and glasses, have produced several empirical formulas, generally rationalized by fracture mechanics. Extending these concepts to the applications of graphite, Knibbs, Andersson, Buch, Zimmer, and Meyer[5–8] have proposed similar relationships of strength to porosity and grain size. However, experimental verification of these proposals was obtained from testing poorly defined, commercially available materials. Buch, Zimmer, and Meyer emphasize the need for a clear definition of the structural morphology to define the critical defect. The purpose of this study is to furnish unambiguous experimental information to compare the various empirical strength-particle size relationships. This is accomplished by testing graphites fabricated using a green isotopic filler of carefully controlled particle sizes. The graphites were made to achieve the same final 1.85 g/cm³ bulk density. By controlling the fabrication and density, particle size is the single variable. This investigation also considers the particle-size effect on other physical properties; the coefficient of thermal expansion (CTE), electrical resistivity, fracture strain, and Young's modulus.

Isotropy is obtained by using green Robinson filler coke to fabricate the experimental graphites. This coke, made from an air-blown petroleum residuum, has a very solid, fine, randomized optical domain structure. The graphites were made using an ORNL process[9] to plasticize the outer surfaces of the green filler coke. This is done to obtain highly efficient bindering with uniform packing of moldings with fillers of a very narrow size range. Coal tar pitch 30M was used as a plasticizer and A-240 petroleum pitch was used as the final binder. The plasticized filler particles were carefully screened to obtain the particle size ranges given in Table I.

Four 40-mm-dia moldings were made and baked under restraint. One molding was graphitized without impregnation and a second molding impregnated with petroleum pitch before graphitization to 3000°C. This was to assure that the final graphite densities or porosities were over a common range. This was very successful, as shown in Table I, except for the two larger particle size ranges. The 430-μm material was improved significantly by a second impregnation; however, the larger 725-μm material was very resistant to densification. As shown in Table I (third column), the shrinkage of the initial filler size in processing is calculated and given.

The graphites were evaluated by testing a minimum of three brittle ring samples, 18-mm-OD, 10-mm-ID, and 6.4 mm thickness, from each block to yield the bend strength, Young's modulus, and fracture strain. Two 6.4-mm-dia samples, across-grain and with-grain, were made to determine the electrical resistivity and the 1000°C mean coefficient of thermal expansion (CTE). The porosity-dependent properties were either interpolated or extrapolated for each particle size range for comparisons to be made at a common 1.85 g/cm³ density. The properties measured are given in Table II.

Table I. Particle Size Range and Final Bulk Densities of Fabricated Graphites

Particle Size Range (μm)	Mean Particle Size		Bulk Density, g/cm³	
	As-Screened (μm)	Graphitized (μm)	Impregnation	
			Without	With One Pitch
105–125	115	90	1.84	1.91
125–149	137	110	1.86	1.89
149–177	163	130	1.83	1.90
177–210	194	155	1.86	1.87
210–250	230	180	1.86	1.90
105–149	127	100	1.81	1.87
125–177	151	120	1.84	1.86
149–210	180	140	1.87	1.90
177–250	214	170	1.84	1.84
500–590	545	430	1.75	1.78(1.86[a])
840–1000	920	725	1.69	1.71(1.73[a])

[a]Impregnated twice.

The generally accepted model for fracture of polycrystalline graphite is that a crack propagates from pore to pore normal to the stress axis, following paths of least resistance. This may be along optical domain boundaries or around the boundaries of misaligned particles. There actually exists microcracking well below the failure stress which increases in number with increasing applied stress. The microcracking is associated in magnitude to the nonlinear component of the stress-strain behavior of graphite. The ability of a graphite to achieve large strains to failure is limited by the ability of the structure to accommodate homogeneous microcracking without resulting in rapid crack propagation to failure. The microcracking is actually a stress-relief system which differentiates graphite from classically brittle ceramic materials.

Several attempts have been made to define the relationships between the strength of brittle polycrystalline solids to porosity and grain size. We found that the particle size data may be described by the Petch relationship; however, for these data the asymptotic (σ_∞) stress was not equal to zero, as indicated in other studies for graphite. Therefore, the more convenient Knudsen relationship for particle size combined with the Ryshkewitch-

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Table II. Properties of 1.85 g/cm³ Graphites

Particle Size (μm)	Fracture Strength (MPa)	Fracture Strain (%)	Modulus of Elasticity (GPa)	Resistivity (μΩ-cm)	1000°C CTE ($C^{-1} \times 10^{-6}$)
725	46.2	0.68	10.3	850	6.35
430	52.4	0.71	11.3	880	6.50
180	68.3	0.75	12.3	1000	6.55
170	71.0	0.80	13.0	970	6.76
155	75.8	0.81	13.3	955	6.74
140	79.3	0.84	13.4	970	6.79
130	77.9	0.86	13.0	960	6.87
120	80.0	0.86	13.4	990	6.86
110	81.4	0.88	13.4	960	6.91
100	84.1	0.89	13.7	1000	6.93
90	86.9	0.91	13.4	950	6.75

Duckworth expression for porosity is used:

$$\sigma_f = \sigma_0 \, e^{-\alpha p} \, D^{-m} \qquad (1)$$

where σ_f = fracture strength (MPa), σ_0 = zero porosity strength (644 MPa), p = fractional porosity, α,m = constants (α = 3.47, m = 0.312), D = particle size (μm). The independence of porosity and particle size is assumed; however, while the particle size-strength relationship is demonstrated over a log cycle, the strength-porosity data were only available from 15 to 22% for the 430-μm material.

These graphites made using a filler with uniform 3–4 μm optical domains compared to a minimum 70 μm particle size emphasize the interparticle pore as the possible weak link controlling fracture. However, it must be realized that the pore size is controlled by the filler particle size. The value of m = 0.312 (less than 0.5) suggests that the critical size or pore size does not decrease proportionately with decreasing particle size. This can be shown to be associated with the known tendency for agglomeration with decreased particle size increasing the effective length of the pores.

Young's modulus was found to have a similar exponential function of porosity; however, the generally assumed independence of particle size was not observed. We found the following expression necessary to describe the decreasing modulus with increasing particle size:

$$E = E_0 \, e^{-\beta p} \, D^{-n} \qquad (2)$$

where E = Young's modulus (GPa), E_0 = zero porosity modulus (31.6 GPa), β,n = constants (β = 2.2, n = 0.11), p = fractional porosity, D = particle diameter (μm). This implies that a rationalization of the modulus of elasticity must include the effects of nonspherical porosity and defective particles which reduce the inherent spring constants within the structure.

The total strain (ε_T) to fracture can be separated into two components, the elastic strain (ε_e) and a nonlinear component (ε_c) resulting from crack extension.

$$\varepsilon_T = \varepsilon_e + \varepsilon_c \qquad (3)$$

The elastic strain can be represented by

$$\varepsilon_e = \sigma_f/E = \sigma_0/E_0 \, e^{(\beta-\alpha)p} \, D^{n-m} \qquad (4)$$

from Eqs. (1) and (2). Subtracting the elastic strain from the total strain to failure, we found that the nonlinear strain was constant and independent of particle size. However, the fracture strain did increase with decreasing porosity, as expected.

$$\varepsilon_c = 3.2 \times 10^{-3} \, e^{-1.5p} \qquad (5)$$

and

$$\varepsilon_T = \sigma_0/E_0 \, e^{(\beta-\alpha)p} \, D^{n-m} + 3.2 \times 10^{-3} \, e^{-1.5p} \qquad (6)$$

This suggests that there exists, for each structural morphology, a strain component due to microcracking that is independent of particle size.

The less-than-theoretical value of CTE is a result of the material expanding into the defect structure. Therefore, as the particle size is reduced by breaking the particles through the defects, the defect concentration is reduced. The CTE is shown to increase with reduced particle size as

$$(1000°C) \; CTE = 8.57 \, D^{-0.047} \qquad (7)$$

No apparent effect of porosity was observed. The very small defect structure in these particles is obvious by the very large CTEs shown in Table II for this material and the fairly small increase due to reduced particle size.

Finally, it is noted that while electrical resistivity (ρ) has a strong dependence upon porosity, it is thought to be independent of particle size. We found, again like the modulus, that a logarithmic function represents the 1.85 g/cm³ data fairly well.

$$\rho = 1500 \, D^{-0.083} \; \mu\Omega\text{-cm} \qquad (8)$$

In summary, this study has yielded experimental data which describes the dependence of physical properties upon particle size. These data emphasize the need to describe the structural morphology in detail, particularly in defining the microstructural defect-controlling fracture. These results clearly describe a defect which is not equal to nor linearly related to the particle size; however, as suggested by Knudsen, it is logarithmically related to the particle size. It is also shown that while the total fracture strain increases with reduced particle size, the nonlinear or crack strain is constant for constant porosity. While not expected, both the modulus of elasticity and the electrical resistivity increased with decreasing particle size. The coefficient of thermal expansion also increased with decreasing particle size, but was less than expected.

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