The Dependence of Strength on Particle Size in Graphite

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†Operated by Union Carbide Corporation under contract W-7405-eng-26 with the U.S. Department of Energy.

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KEYWORDS

Graphite, particle size, strength, fracture mechanics, microcracking, Dugdale model, physical properties.

Abstract

The strength to particle size relationship for specially fabricated graphites has been demonstrated and rationalized using fracture mechanics. In the past, similar studies have yielded empirical data using only commercially available material. Thus, experimental verification of these relationships has been difficult. However, the graphites of this study were fabricated by controlling the particle size ranges for a series of isotropic graphites. All graphites that were evaluated had a constant 1.85 g/cm^3 density. Thus, particle size was the only variable. The strength to particle size relationship revealed that the fracture strength was logarithmically related to initial defect size by an apparent $-1/3$ power. Application of Dugdale crack extension model with simple modifications accounting for nonspherical pores and variable defect concentrations explains the $-1/3$ power relationship. This study also considered the particle size effect on other physical properties; coefficient of thermal expansion (CTE), electrical resistivity, fracture strain, and Young's modulus.

Introduction

The increased use of graphite for structural applications has warranted a better understanding of the relationships between strength to porosity and grain size. The understanding of these relationships are particularly important in the development of optimized microstructures for specific applications. However, it is difficult to confirm proposed relationships by testing poorly defined commercially available materials. The need to have a clear understanding of the structural morphology to define the critical defect has been emphasized by earlier investigators^(1,2). The purpose of this study is twofold: (1) to furnish unambiguous experimental information that compares the various strength-to-particle size relationships, and (2) to develop, through the aid of fundamental fracture mechanics theory, a correlation of the fracture process with microstructure.

The objectives are accomplished by testing graphites fabricated using a green isotropic filler of carefully controlled particle size ranges. The graphites were made to achieve the same final 1.85 g/cm^3 bulk density. Thus, by controlling the fabrication and density, particle size is the only variable. It was found that by controlling the particle size during fabrication, the initial defect size was approximately equal to the mean particle size after graphitization. However, the test results indicated the final defect size was incrementally larger than the initial size. Further, in terms of fracture mechanics theory, this anomaly is approximated by an apparent $-1/3$ power law relating the fracture strength to initial defect size rather than the expected $-1/2$ power law relationship.

This phenomenon is explained by developing an understanding of the fracture process in conjunction with microstructural affects on the parameters of the crack theory. It will be shown that the inherent stress relief system of graphite causes an effective crack extension that can be explained by the Dugdale model⁽³⁾. 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.

Materials and Fabrication

The desired isotropy in the experimental graphites was achieved by using a green Robinson filler coke. This coke, made from an air-blown petroleum residuum has a very solid, fine, randomized optical domain structure which is approximately 3-4 μm in dia. Initially, the coke was pulverized and carefully screened to obtain the desired particle size range distributions. Table 1 gives the particle size ranges. The graphites were then made using an ORNL process⁽⁴⁾ to plasticize the outer surfaces of the green filler coke. This process is used to obtain highly efficient binding with uniform packing of moldings with fillers of a very narrow size range. Coal tar pitch 30M was used as the plasticizer. After application of the plasticizer, the filler particles were screened again to assure conformity with the specified particle size range distributions as shown in Figure 1.

Four 40 mm-dia. moldings were made using A-240 petroleum pitch as the final binder and were baked under restraint. One molding was graphitized without impregnation and a second molding impregnated with petroleum pitch before graphitization at 3000°C. The impregnation was to assure that the final graphite densities or porosities were over a common range. As shown in Table 1, a common density range was very successful, except for the two larger particle size ranges. The 430- μ m material was improved significantly by a second impregnation; however, the larger 725- μ m material was very resistant to densification. Also in this table, the shrinkage of the initial filler size in processing is calculated.

As a result of the process, the graphites exhibit a contiguous structure with no apparent particle boundaries. The pores are well rounded, having a length approximately the size of the filler particles as seen in Figure 2.

Testing and Results

The graphites were evaluated by testing a minimum of three brittle ring samples⁽⁵⁾, (18-mm-OD, 10-mm-ID, and 6.4 mm thickness). From each molded block the properties of bend strength, Young's modulus, and fracture strain were obtained. The load-deflection curve was recorded, and the stresses were calculated considering the shift in neutral axis⁽⁶⁾. Two 6.4-mm-dia. and 25.4-mm-long samples, both the across-grain and with-grain orientations, were made to determine the electrical

restivity and the 1000°C mean coefficient of thermal expansion (CTE). The porosity dependent properties were either interpolated or extrapolated for each particle size range to obtain comparisons at a common 1.85 g/cm³ density. The properties measured are given in Table 2.

The fracture strength as a function of initial particle size is compared with the results of a acicular grade graphite in Figure 3. It should be mentioned that agglomeration of particles in graphite do lead to structures having defect sizes greater than the particle size. We found that very fine green Robinson filler particles (i.e., particle sizes less than 90 μm) did tend to agglomerate and could not be considered in this study. The agglomeration is a particular problem in considering commercial graphites and was one of the incentives to fabricate controlled graphites.

Young's modulus was also measured. Figure 4 shows the modulus decreasing with increasing particle size. This result is significant because porosity is generally assumed spherically shaped, and the modulus would be independent of pore size. To account for this result a rationalization of Young's modulus must include the effects of non-spherical porosity which would reduce the inherent spring constants within the structure. This effect can be considerably intensified in graphites with defective particles and with highly anisotropic structures with aligned porosity.

The degree of isotropy was evaluated by comparing the electrical resistivity and CTE in the with-grain and across-grain directions. In every block, both the electrical resistivity and the CTE in both directions were within 2-5% of each other confirming the isotropic structure. In Figure 5 the electrical resistivity is shown as a function of particle size for the 1.85 g/cm^3 dense material. The decreasing resistivity with increasing particle size is a result of reduced boundary resistance as the particle boundary area becomes smaller.

The CTE is compared with an anisotropic acicular grade in Figure 6. In this figure, because of the anisotropy in the acicular grade, the volumetric CTE (sum of the three linear directions) is compared. For the Robinson grade only, the linear CTE is simply one third of the volumetric value. The CTE for both types of graphites apparently approaches the same value as the particle size is reduced. The CTE is affected by the defect concentration within the particle; therefore, as the particle size is reduced by breaking the particles through the defects, the defect concentration is reduced, and the CTE increases. For each curve in Figure 6, the slope is a reasonable measure of the defect concentrations in a particular filler coke. As observed, the defect concentration within the Robinson filler particle is much less than in acicular filler cokes.

The fracture strain obtained from testing these graphites is shown in Figure 7. The stress-strain characteristic of graphite is nonlinear and the total strain (ϵ_t) to fracture can be separated into two components, the elastic strain (ϵ_e) and a nonlinear strain (ϵ_c) resulting from crack extension:

$$\epsilon_t = \epsilon_e + \epsilon_c \quad (1)$$

The elastic strain can be calculated and subtracted from the total strain

$$\epsilon_t - \frac{\sigma_f}{E} = \epsilon_c \quad (2)$$

to give the nonlinear component of strain. Also given in Figure 7 are the elastic and crack strains obtained from this test series. It is very significant to note that the crack strain did not vary with particle size.

Discussion

The accepted model of deformation, as discussed by Jenkins⁽⁷⁾, describes the initial application of stress accommodated by interlamellar shearing and limited slip due to the inadequate number of slip systems. Simultaneously, the large macropores cause local strain concentrations in adjacent grains which open pre-existing microcracks normal to the stress axis. These microcracks actually act as a stress relief mechanism much like the plastic zone of a ductile material. The size of this psuedo-plastic zone is determined by the stress concentrations at the macropores. The growth of the individual microcracks within the process zone may be obstructed by a boundary or by a obstacle such as a pore. The microcrack may then either terminate or deviate onto a less suitably oriented weakness plane where growth is discontinued. Growth of the microcrack will continue only when the strain energy increases to allow the crack to pass either through or around the obstacle.

These co-existing stress relief mechanisms are indistinguishable at low stresses; however, at higher stress levels, the size of the microcrack process zone increases and becomes the dominate contributor to the deformation process. Eventually, coincidental alignment of this discontinuous array of microcracks cause them to link-up, and macrocrack growth occurs. Ultimately, a critical effective crack length is reached, and catastrophic failure occurs.

The use of fracture mechanics is helpful in understanding the microstructural defect controlling fracture. Simply stated, the Griffith-Irwin^(8,9) crack theory for elastic materials describes the fracture criterion in terms of the applied stress, material properties, and inherent defects within the material;

$$\sigma_f = \left[\frac{E G_{Ic}}{\pi c (1-\nu^2)} \right]^{1/2} \quad (3)$$

where:

- ν - Poisson's ratio varies from 0 to 0.30 dependent on active void volume that will expand or decrease during loading. Poisson's ratio for Robinson graphite is 0.28, indicating a relatively defect-free material.
- E - The apparent Young's modulus, an average of the total microstructural effect, is a function of micro and macro-porosity which occurs either within or between particles and the preferred orientation. These variables also determine the materials ability to absorb external strain primarily by allowing material expansion into the macrovoids. Therefore, the change in elastic modulus may be used as an indicator of the material's ability to concentrate strains at the crack tip.

G_{IC} - The strain-energy release rate, a measure of strain energy released per unit area of fracture surface (e.g. twice the surface energy for elastic materials), is the work to create new surface. This is constant at failure for a given type of filler particle and processing schedule. The material's resistance to crack propagation has been shown to be a function of all microstructural features except particle size⁽¹⁰⁾.

c - The length of the inherent macrocrack before loading is a function of the size and distribution of the filler particles and packing efficiency. These large disparate voids will act as weak-links and ultimately determine the fracture path.

The difficulty in applying any deformation model is that it must be consistent with the apparent $-1/3$ power shown in Figure 3. The fracture mode in graphite actually excludes its implicit description as a linear elastic brittle material. Therefore, some consideration must be given to the crack growth and the microcracking to reduce the stress concentrations. This behavior can be modeled similarly to plastically-induced failure by assuming the pseudo-plastic zone at the crack tip effectively increases the crack length. The theoretical plastic zone adjustment for the general class of elastic-plastic materials is considered by Dugdale⁽³⁾. He approximates the size of the plastic zone and assumes that the presence of this limited process zone effectively increases the crack length:

$$R = \left[\frac{\pi E}{8 \sigma_y^2} \right] G_{Ic} \quad (4)$$

where

R = plastic zone size at fracture

σ_y = yield stress

The extent of crack growth before failure is implied to be constant (i.e., independent of particle size), as indicated by the experimentally determined constant crack strain (nonlinear strain component) at fracture as shown in Figure 7. Also, as previously discussed, E is a measure of the structural compliance of the material and must be considered in the approximation of the Dugdale plastic zone size. This approximation is accomplished by simply using a geometric factor, δ , calculated by the ratio, $\frac{E}{E_0}$, where E is the modulus at failure and E_0 is the stabilized modulus measured (exhibited by the smaller particle size range). The approximation corrects for deviations due to nonspherical porosity and variable defect concentrations.

Applying this modification to the Griffith-Irwin equation, the relation becomes

$$\sigma_f = \left[\frac{E G_{IC}}{\pi (c + \delta\bar{R}) (1 - \nu^2)} \right]^{1/2} \quad (5)$$

where the term $(c + \delta\bar{R})$ is the final defect size. G_{IC} was experimentally determined using short-bar specimens to be 222 Pa.m⁽¹¹⁾.

Given in Table 3, the final defect sizes are calculated, $a = c + \delta\bar{R}$, and compared to the initial defect sizes from particle size considerations. The difference is found to be a constant $\delta\bar{R}$ equal to $98 \pm 7 \mu\text{m}$. This is the value of the modified mean psuedo-plastic zone size generated by the microcracking mechanism to reduce the defect stress concentration. The apparent yield stress of the material can be calculated from Equation 4 to give $\sigma_y = 110 \text{ MPa}$ which is consistent with the fracture results. The use of constant plastic zone size to calculate the final defect size is illustrated in Figure 8. This figure shows the comparison of the apparent -1/3 power relationship as given by the initial defect size to the calculated final defect size obtained by simply adding the constant plastic zone size to the -1/3 power relationship yielding, the -1/2 power relationship. Obviously, as the defect size increases, the crack growth should become a small insignificant part of the overall strain. Therefore, there should exist a break in the initial defect size curve taking the slope of -1/2.

Conclusion

This study has provided graphites of the same basic structure in which the only fabrication variable was controlled particle size. Experimental data was generated which describes the dependence of physical properties on particle size. These results clearly describe a final defect size which is not equal to nor linearly related to particle size but requires an addition of a crack growth size as suggested by Dugdale. 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. An unexpected feature is that 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 less than was expected.

These data emphasize the need to describe the structural morphology of graphite when defining the fracture mechanisms. Based on the Dugdale modified Griffith-Irwin crack theory, the strength dependency of graphite on its microstructure was demonstrated. The fracture process was shown to exhibit a constant effective crack extension independent of particle size which occurred by the microcracking stress relief mechanism acting as a psuedo-plastic zone. Because the effective crack growth and actual crack growth are indistinguishable, this model does not imply that crack extension completely consisted of effective crack extension. Presently, statistical analyses are being developed^(1,2,10) which are based on the Griffith theory in order to model the coincidental alignment of microcracks in the fracture process.

Acknowledgment

This research was supported, in part, by the Naval Surface Weapons Center under contract No. N-60921, The authors also wish to acknowledge their appreciation of assistance from Fred Jeffers for his help in the laboratory and Dr. W. F. Flanagan for his stimulating comments and advice.

References

1. J. D. Buch, AS*-STP-605, pp. 124-144, 1976.
2. J. E. Zimmer and R. A. Meyer, 12th Biennial Conference on Carbon, p. 95, 1975.
3. D. S. Dugdale, J. Mech. Phys. Solids, 8, 100 (1960).
4. C. R. Kennedy, 11th Biennial Conference on Carbon, pp. 304, 973, 1973.
5. S. A. Bortz and H. H. Lund, "The Brittle Ring Test", Mechanical Properties of Engineering Ceramics, Interscience Publ., 1961, pp. 383-404.
6. S. Timoshenko and J. N. Goodin, Theory of Elasticity, 2nd Edition, McGraw-Hill, NY, 1951, pp. 116-123.
7. G. M. Jenkins, Chemistry and Physics of Carbon, 11, 189-242, 1973.
8. A. A. Griffith, Proc. Int. Cong. Appl. Mech., 55, (1924).
9. G. R. Irwin, Encycl. of Phys., Vol. VI, Springer, Heidelberg (1958).

10. C. A. Anderson and E. I. Salkovitz, 11th Biennial Conference on Carbon, p. 273, 1973.

11. F. H. Shipman, Resource Enterprises, Private Communication.

Table 1 - Particle Size range and final bulk densities of fabricated graphites

Particle Size Range, μm	Mean Particle Size		Bulk Density, g/cm^3	
	As-Screened, μm	Graphitized, μm	Without Impregnation	With 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*)
840-1000	920	725	1.69	1.71 (1.73*)

*Impregnated twice

Figure 1 -
THE PARTICLE SIZE OF THE ISOTROPIC FILLER WAS CAREFULLY CONTROLLED

Figure 2 -

THE STRUCTURE OF THE GRAPHITE IS CONTIGUOUS WITHOUT
APPARENT PARTICLE BOUNDARIES

100 200 MICRONS 600 700
100X
0.005 0.010 INCHES 0.020 0.025

Table 2 - Properties of 1.85 g/cm³ graphites

Particle Size, μm	Fracture Strength, MPa	Strain, %	Modulus of Elasticity, GPa	Resistivity, μΩ - cm	1000°C CTE, C ⁻¹ x 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

Figure 3 - The Brittle Ring Strength of Robinson Graphites

Figure 4 - The Modulus of Elasticity Decreases With Increased Particle Size

Figure 5 -Electrical Resistivity Decreases With Increased Particle Size

Figure 6- The Coefficient of Thermal Expansion Decreases
With Increased Particle Size for Most Graphite

Figure 7- Decreasing the Filler Particle Size Increases the Total Fracture Strain to the Point of Agglomeration. The Crack Strain is Independent of Particle Size

Table 3 - Calculation of the Dugdale plastic zone size

Particle Size, μm	Elastic Modulus, GPa	Half Initial Defect Size(c), μm	Calculated Half Final Defect Size(a),*	R=a-c, μm	$\delta^\ddagger$	δR , μm
775	10.3	336	371	8	.77	6
430	11.3	215	316	101	.84	85
180	12.3	90	203	113	.92	104
170	13.0	85	198	113	.97	110
155	13.3	78	178	100	.99	99
140	13.4	70	164	94	1.00	94
130	13.0	65	165	100	.97	97
110	13.4	55	155	100	1.00	100
100	13.7	50	149	99	1.02	101
90	13.4	45	136	91	1.00	91
						<u>98±7</u>

*Calculated by Griffith - Irwin equation for plane strain, using measured

$$a = \frac{E G_{Ic}}{\pi \sigma^2 (1-\nu^2)} \quad \text{fracture strengths.}$$

$$\ddagger \delta = E/E_0 \quad \text{where } E_0 = 13.4 \text{ GPa}$$

Figure 8-A Comparison of the Initial Defect Size to Final Defect Size With a Constant $98\mu\text{m}$ Crack Growth