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of the
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LOS ALAMOS • NEW MEXICO

CMF-13 Research on Carbon and Graphite

Report No. 5

Summary of Progress from
February 1 to April 30, 1968

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This LA...MS report presents the summary of progress of CMF-13 research on carbon and graphite at LASL. Previous summary of progress reports in this series, all unclassified, are:

LA-3693-MS

LA-3821-MS

LA-3758-MS

LA-3872-MS

This report, like other special-purpose documents in the LA...MS series, has not been reviewed or verified for accuracy in the interest of prompt distribution.

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

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CMF-13 Research on Carbon and Graphite
Report No. 5
Summary of Progress from
February 1 to April 30, 1968

by

Morton C. Smith

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CMF-13 RESEARCH ON CARBON AND GRAPHITE

REPORT NO. 5: SUMMARY OF PROGRESS FROM FEBRUARY 1 TO APRIL 30, 1968

I. INTRODUCTION

This is the fifth in a series of progress reports devoted to carbon and graphite research and development in LASL Group CMF-13, and summarizes work done during the months of February, March and April, 1968. It should be understood that in such a report many of the data given are preliminary, incomplete, and subject to correction, and that many of the opinions and conclusions stated are tentative and subject to change. This report is intended only to provide up-to-date background information to those who share the interests of the programs described in it, and should not be quoted or used as a reference publicly or in print.

Research and development on carbon and graphite were undertaken by CMF-13 primarily to increase understanding of their properties and behavior as engineering materials, to improve the raw materials and processes used in their manufacture, and to learn how to produce them with consistent, predictable, useful combinations of properties. The approach taken is microstructural, based on study and characterization of natural, commercial, and experimental carbons and graphites by such techniques as x-ray diffraction, electron and optical microscopy, and porosimetry. Physical and mechanical properties are measured as functions of formulation, treatment, and environmental variables, and correlations are sought among properties and structures. Raw material and manufacturing techniques are investigated, improved, and varied systematically in an effort to create specific internal structures believed to be responsible for desirable combinations of properties. Prompt feedback of information among these activities then makes possible progress in all of them toward their common goal of understanding and improving manufactured carbons and graphites for the ultimate benefit of science and industry in general, and of the United States Atomic Energy Commission's reactor programs in particular.

II. CMF-13 "STATE-OF-THE-ART" GRAPHITE

A. General

Lot AAQ1 graphite is a relatively large sample of extruded, resin-bonded graphite which was manufactured in CMF-13 primarily to: (1) Demonstrate the state of the art of graphite manufacturing techniques in CMF-13, and particularly the quality and uniformity possible in such a graphite when each step of the manufacturing process is closely controlled; (2) Determine the properties and explore the behavior of a good graphite of this type, free of dispersed fuel particles and in the condition in which it would exist after normal graphitization or after service at high temperature; (3) Establish a reliable base line against which to compare the results of other CMF-13 experiments in which filler materials, binder, and manufacturing procedures are varied systematically.

The raw materials and manufacturing processes used to produce Lot AAQ1, and some of its properties, have been described in the last previous report in this series (LA-3872-MS). Additional data since collected are reported below. This is one of the most uniform and now one of the most fully characterized lots of graphite ever made.

B. Raw Materials

Additional information collected on the Thermax carbon black, which was part of the filler mix for Lot AAQ1, is summarized in Table 1. The "fuzziness ratio" shown is the ratio of specific surface area measured by nitrogen adsorption to that calculated from Micromerograph size-analysis sample statistics, with the assumption that each particle is a smooth-shelled sphere. That given in Table 1 is one of the lowest ever determined, and indicates that in this case the assumption of smooth-shelled spheres is realistic. It also confirms the relatively low helium-density value (1.880 g/cm^3) in indicating that most of the internal porosity of the Thermax particles is not surface-connected. The particle diameter of monosized spheres which would have specific surface area equal to that measured by gas adsorption was 0.359μ , in good agreement

TABLE 1

SAMPLE DATA ON LOT TP-3 THERMAX CARBON BLACK

Specific Surface:Measured = $8.90 \text{ m}^2/\text{g}$ Calculated = $7.43 \text{ m}^2/\text{g}$

Fuzziness Ratio = 1.198

Chemical Analysis: H_2O = 0.03%

Ash = 0.23%

S = 0.04%

Fe = 20 ppm

Si = 900 ppm

Ca = 30 ppm

Mg = 15 ppm

B < 1 ppm

(All other common impurities below detection limits of semi-quantitative spectrochemical analysis.)

Crystalline Parameters: L_c = $17.4 \text{ \AA}$ d_{002} = $3.47 \text{ \AA}$ Bulk Density = 0.92 g/cm^3

Amorphous Carbon = ~47%

Unassociated Layers = 13%

with the average particle diameter of 0.328μ determined by an optical count. (The slightly higher calculated value would be expected from the fact that the size distribution is positively skewed and has non-zero variance.)

A small sample of TP-3 Thermax, contained in a graphite crucible, was heat treated for 30 min at 2800°C and then examined by electron microscopy and by x-ray diffraction. As has previously been reported by others, the external shapes of individual Thermax particles in general changed from spherical to polyhedral, usually with quite well-developed facets. Crystallite size increased markedly, L_c increasing from $17.4 \text{ \AA}$ to $225 \text{ \AA}$, and interlayer spacing decreased from $3.47 \text{ \AA}$ to $3.378 \text{ \AA}$. This degree of graphitization was not expected in a carbon black, and the possibility of interaction with some cata-

lyzing impurity derived from the crucible will be investigated.

C. Properties1. Electrical Resistivity

Electrical resistivity parallel to the extrusion axis has been measured over the temperature interval ambient to 2300°C ; with the results plotted in Fig. 1. From ambient temperature to 800°C , the temperature sensor used was a shielded chromel-alumel thermocouple. From 900° to 2300°C , temperature measurements were made with a disappearing-filament optical pyrometer. Since the specimen was heated resistively and radiated freely to a relatively cool environment, radial temperature gradients were known to exist in it. The resistivity reported at each temperature is therefore actually an average value over a small temperature interval. However, a calculation of probable error from this source indicates that it is distinctly less than that resulting from measurement uncertainties.

2. Shear Modulus

Shear modulus normal to the extrusion direction was measured at room temperature on one specimen of AAQ1 graphite, by an eddy-current technique involving use of closely-fitting aluminum sleeves on each end of the specimen. The measured value was $0.748 \times 10^6 \text{ psi}$.

3. Elevated-Temperature Tensile Properties

Tensile tests have been made on longitudinal ("with-grain") specimens of AAQ1 graphite over the temperature interval ambient to 2750°C , with the results shown in Fig. 2. All elevated-temperature tests were made in a static helium atmosphere at a positive pressure of 3 psi, and at a constant rate of crosshead motion of 0.005 in./min . Between room temperature and 1750° , ultimate strength increased almost linearly with temperature, from about 3000 psi at room temperature to about 4250 psi at 1750° . Between 1750° and 2325° the strength increase was much more rapid, to a maximum of about 8050 psi at 2325° . At higher temperatures strength decreased sharply as temperature increased, to about 4650 psi at 2750° .

Fig. 1. Electrical Resistivity of AAQ1 Graphite Measured Parallel to the Extrusion Direction

A 0.2% yield strength distinct from the ultimate strength first appeared at 2250°C. At higher temperatures the yield strength decreased with increasing temperature at about the same rate as did the ultimate strength.

As measured at room temperature on reassembled tested specimens, percent elongation of the 1-in. long gage section was about 0.1 to 0.2% at all temperatures below 2250°C. Above 2250° it increased with temperature to about 1.0% at 2750°.

Fracture surfaces were generally almost flat and approximately normal to the tension axis, with a finely-crystalline appearance. In spite of a small taper toward the center of the gage section, most specimens broke near one of the radii in which the gage section terminated.

Apparently because of the notch sensitivity which this fracture behavior indicates, the high temperature gradient in the specimen ends, and the very rapid increase of strength with temperature in the interval 1750° to 2325°C, most tests made on standard 0.250-in. dia specimens in this temperature range resulted in fracture through the threaded specimen ends where they entered the loading grips. As is indicated in Fig. 2, most successful tests in this interval were made on specimens on which gage diameter had been reduced to either 0.225 or 0.200 in.

4. Notch Sensitivity

Because of the fracture behavior described above, a qualitative exploration of the notch sensitivity of AAQ1

Fig. 2. Longitudinal Tensile Properties of AAQ1 Graphite Tested in Helium

graphite was undertaken. A small group of sharply-notched tensile bars was tested at a variety of temperatures under the same conditions used for standard test bars, with the results plotted in Fig. 2. The notches used were circumferential V-grooves at the center of length of

the gage section, having 60° included angle, root radius of 0.0014 to 0.0017 in., and reducing the gage diameter from 0.250 in. to 0.125 in. (According to Peterson's tables¹, such a notch should produce a stress-concentration factor, K_t , of about 4.5.) For such a specimen, the

TABLE 2
ROOM-TEMPERATURE TENSILE PROPERTIES OF AAQ1 GRAPHITE

Type of Test	Type of Specimen	Specimen No.	Ultimate Strength, psi
Tension, 0.005 in./min.	Standard	10A	2975
	Standard	10B	2689
	Standard	<u>10C</u>	<u>3044</u>
	Standard	Average	2903
		σ	188
Tension, 0.020 in./min.	Standard	17A	3178
	Standard	17B	3178
	Standard	<u>17C</u>	<u>2893</u>
	Standard	Average	3083
		σ	164
Tension, 0.020 in./min.	Full cross-section rod	113A	3083
	Full cross-section rod	113B	3632
	Full cross-section rod	64A	3368
	Full cross-section rod	<u>64B</u>	<u>3069</u>
	Full cross-section rod	Average	3288
		σ	268

ratio of notched to unnotched ultimate tensile strength was about 0.5 to 0.7 over the temperature range ambient to 2250°, then increased at higher temperature to almost unity at 2500°. This relatively high degree of notch sensitivity at the lower temperatures was unexpected. Its decrease at the higher temperatures suggests that a limited amount of real plasticity exists at and above 2325°.

5. Effects of Strain Rate and Extrusion Skin on Tensile Strength

In separate room-temperature tests made in air using another testing machine and different loading fixtures, the longitudinal tensile strength values listed in Table 2 have been measured. Three standard 0.250-in. dia specimens were tested at the rate of crosshead motion (0.005 in./min) used in tests described above, and gave strength values which agreed well with those shown in Fig. 2.

Three other standard specimens were tested at a rate of

crosshead motion four times this great (0.020 in./min), giving strength values which did not differ significantly from those measured at the lower testing rate.

Four specimens were tested at their full as-extruded cross section by use of metal grips glued to the ends of unmachined rod sections. Results scattered broadly enough so that sample statistics are poor. However, a comparison of individual and average strength values suggests that the extrusion skin has a small strengthening effect, as is often the case among extruded materials.

In a separate experiment, a rod 0.250, 2 in. dia was cored from extruded Rod 93, leaving intact a shell of material 0.081, 8 in. thick which included the extrusion skin. This shell was too fragile to be tested in tension, but its density was 1.889 g/cm³ and its longitudinal Young's modulus was 2.29 x 10⁶ psi. The density of the core was 1.907 g/cm³, its Young's modulus was 2.35 x 10⁶ psi,

and presumably its tensile properties were similar to those of 0.250-in. dia tensile bars machined from other rods of AAQ1 graphite. The slightly lower density and elastic modulus of the shell suggest that its strength should be lower than that of the core instead of higher, as was suggested above. Unfortunately, the detailed relations among density, preferred orientation, and properties are not well understood, and this apparent anomaly cannot yet be explained.

6. Diametral Compression Tests

In an attempt to measure across-grain tensile strength, diametral compression tests were made on seven full cross-section segments of an AAQ1 extrusion, cut from Rod 30. Results are listed in Table 3. While they are reasonably consistent, these values are quite low relative to the longitudinal strength, even for a relatively anisotropic material. (According to W. C. Chard of Battelle Memorial Institute, this is typical of diametral compression tests on graphite. The strength calculated from such a test is normally appreciably lower than that measured in direct tension, by a factor which varies from one graphite to another.) Accordingly, the strength values listed in Table 3 are assumed not to be reliable on an absolute basis, but are expected to be useful for comparisons with

TABLE 3
TRANSVERSE TENSILE STRENGTHS
FROM DIAMETRAL COMPRESSION TESTS

Specimen No.	Ultimate Strength, psi
30A	1545
30B	1572
30C	1319
30D	1398
30E	1494
30F	1452
30G	1359
Average	1477
σ	106

TABLE 4
ROOM-TEMPERATURE FLEXURAL STRENGTH
OF AAQ1 GRAPHITE

Specimen No.	Ultimate Strength, psi
56A	4676
56B	5022
63A	4802
63B	4959
Average	4865
σ	156

other generally similar graphites.

7. Flexural Strength

Room-temperature flexure tests were made on four full cross-section rod segments, using four-point loading over a four-inch span. Results are listed in Table 4.

8. Compressive Properties

Compression tests have been made in air at room temperature on eight specimens of AAQ1 graphite, cut from four different rods, with the results listed in Table 5. Specimens were full cross-section segments of the

TABLE 5
ROOM-TEMPERATURE COMPRESSIVE PROPERTIES
OF AAQ1 GRAPHITE

Specimen No.	Ultimate Compressive Strength, psi	Yield Strength (0.2 %), psi
2C	11,430	9,560
2D	11,188	9,896
44C	10,386	9,269
44D	11,133	9,865
90C	10,922	9,438
90D	10,453	9,304
117C	10,977	9,770
117D	10,839	9,642
Average	10,916	9,593
σ	357	243

extruded rod, each 1.5 in. long. They were tested at a constant rate of crosshead motion of 0.020 in./min, between removable tool-steel platens lubricated with "Fluoro Glide", a commercial fluorocarbon lubricant. No load vs. compression data were collected, but the load vs. time records were good enough so that yield strengths at 0.2% compression could be estimated quite accurately, as an indication of deformation behavior. In most cases fracture occurred near the center of specimen length, apparently from some combination of tension and shear, and with much local shattering of the graphite at the moment of fracture. The permanent increase in specimen diameter could not be measured accurately because of cracking associated with the fracture, but in general appeared to be between 0.1 and 0.3% and to average about 0.2%. In only one case could a broken specimen be re-assembled for a length measurement. A very uncertain measurement of it indicated a decrease in specimen length of about 2.1% as a result of the compression test.

9. Creep Properties

Tensile creep tests have been made at 2300° and 2500°C in a static helium atmosphere at a positive pressure of 2 psi, using AAQ1 graphite specimens 0.220-in. in diameter with a one-inch gage length.

To evaluate the uniformity of the material and the reproducibility of the testing procedure, fifteen tests were made at 2500°C and 5260 psi tensile stress. Under these conditions creep rates were essentially constant after about 5 min under load. These "constant" rates are listed in Table 6, together with percent permanent extension preceding rupture and time to rupture. For this group of tests, standard deviation from the average steady-state creep rate was about 18% of the average. The estimated uncertainty in creep rate due to stress variations in the testing system is $\pm 10\%$, and that due to temperature variations of $\pm 10^\circ\text{C}$ is $\pm 20\%$. Apparently temperature and stress measurements reproduced well, and the graphite structure was remarkably uniform from specimen to

TABLE 6
TENSILE CREEP PROPERTIES OF AAQ1 GRAPHITE AT 2500°C AND 5260 PSI

Specimen No.	Creep Rate, (in./in.) $\times 10^{-4}$ /min.	Strain to Rupture, %	Time to Rupture, Min.
45A	3.3	1.3	37
45B	2.6	1.7	50
45C	3.3	1.2	30
23A	5.1	1.4	21
23B	3.4	1.2	35
23C	3.4	1.5	34
110A	3.4	1.3	32
110B	3.5	1.4	34
110C	3.7	1.1	23
30A	4.7	1.7	29
30B	3.3	1.5	39
30C	2.9	1.6	50
95A	4.0	1.5	30
95B	3.8	1.5	33
95C	3.2	1.4	34
Average	3.57	1.41	34.0
σ	0.63	0.18	7.8

Fig. 3. Tensile Creep Rate vs. Stress for AAQ1 and ATJ Graphites at 2300° and 2500°C

specimen.

Results from tests at 2300° and 2500°C at a variety of stresses are shown in Fig. 3. In all cases creep rates for AAQ1 graphite were much lower than those determined by Seldin² for commercial ATJ graphite tested at similar temperatures and stresses. Creep curves for the two graphites were similar in shape. The slopes of the lines in Fig. 3 indicate that for AAQ1 graphite creep rate is proportional to about the eighth or ninth power of stress, while for ATJ graphite it is proportional to about the fourth power of stress.

Time to rupture is plotted as a function of stress in Fig. 4, for creep tests on AAQ1 graphite at 2300° and 2500°C. The trends of both curves are those which would be expected if, at each temperature, strain to fracture were constant, and indicate that a very large increase in time to rupture will result from a relatively small reduction in stress.

The apparent activation energy for creep of AAQ1 graphite was determined by three different methods. The first of these was the ΔT method, in which -- in a creep test at constant stress -- creep rates of the same specimen are compared just before and just after a sudden temperature change. This gave an apparent activation energy of about 250 kcal/mole. In the second method two specimens are tested at the same stress but different temperatures, and creep rates are compared at the same value of prior creep strain. This gave a value of 225 kcal/mole. In the third method tests are made on two specimens at the same stress but different temperatures, and the times required to achieve a given amount of strain are compared. This gave a value of 220 kcal/mole. Agreement among the results of the three methods is considered good.

10. Thermal Expansion

The thermal expansion of AAQ1 graphite parallel to the extrusion direction has been measured by three different investigators using five different dilatometers. One used a differential method (quartz dilatometer) over the range 20°K (liquid hydrogen) to 300°K, on one specimen from Rod 93. The second used a different quartz dilatometer over the range 76°K (liquid nitrogen) to 350°K,

using the same specimen, and an optical method over the range 25° to 2475°C, using a specimen cut from Rod 86. The third investigator used a third quartz dilatometer over the range 25° to 700° on three specimens, the one from Rod 93 used by the other investigators and one each from Rods 28 and 80. He also used a different optical system over the range 950° to 2500°C on specimens machined from Rods 34 and 75. All optical measurements were made on relatively long (~9 cm) specimens to minimize refractive effects.

All data collected by all three investigators were plotted together, and the single curve shown in Fig. 5 was drawn through the points in such a way that every point was contained in a band whose upper limit was 4% above the curve and whose lower limit was 4% below the curve. The vertical bars in the figure represent estimates of standard deviations.

Thermal expansion normal to the extrusion direction was measured by the third of the above investigators, using a quartz differential dilatometer over the range 25° to 700°C and an optical extensometer over the range 950° to 2450°C. Specimens were constructed from stacked discs machined so that their cylinder axes were normal to the extrusion direction. Two specimens were used over each temperature interval, one built up of discs machined from Rod 28 and the other of discs from Rod 80. All data were well represented by the upper curve of Fig. 5.

11. Thermal Conductivity

Over the temperature interval -150° to 500°C, the thermal conductivity of AAQ1 graphite normal to the extrusion axis was measured by the flash-diffusivity technique^{3,4}. Between 840° and 2500°C it was measured by a radial heat flow method^{3,4}, using a disappearing-filament optical pyrometer to measure specimen temperature and a specially-built differential radiation pyrometer to measure temperature differences between two adjacent cylindrical holes drilled radially to different depths in the specimen. At specimen temperatures above 2000°C these differences become large enough so that they could also be measured with the optical pyrometer with good accuracy. All data collected on thermal conductivity meas-

Fig. 4. Time to Rupture vs. Tensile Stress for AAQ1 Graphite at 2300° and 2500°C

Fig. 5. Thermal Expansion of AAQ1 Graphite

Fig. 6. Thermal Conductivity of AAQ1 Graphite Measured Normal to the Extrusion Direction

measurements normal to the extrusion axis are plotted in Fig. 6.

Thermal conductivity parallel to the extrusion axis was measured over the temperature interval -140° to 325°C by the flash diffusivity method. From 210° to 575°C it was measured by a series comparison method using Armco iron comparison standards. From 600° to about 750°C the same method was used but with molybdenum as the comparison standard. Above 1000°C the method used was that of Jain and Krishnan⁵ for determining thermal conductivity of a resistively-heated rod radiating freely in an evacuated environment. All data on thermal conductivity measured parallel to the extrusion direction are plotted in Fig. 7.

D. Structure

1. Microradiography

Thin longitudinal and transverse slices cut from Rod 22 have been impregnated with sulfur and microradiographed by Group GMX-1 at section thicknesses of about 0.005, 0.010 and 0.020 inch. Because sulfur is more opaque to x-rays than is carbon, voids entered by the sulfur appear as light areas on the radiograph. In the case of AAQ1 graphite, the microradiographs show a relatively large region of low porosity near the center of the extruded section, believed to be associated with merging in the die of six separate streams of material emerging from openings in the breaker plate. A faint "chevron" pattern is visible near the edges of the longitudinal section, appar-

Fig. 7. Thermal Conductivity of AAQ1 Graphite Measured Parallel to the Extrusion Direction

ently representing a tendency for flakelike particles to assume orientations in which they are inclined at about 30° to the surface of the extrusion die. A tendency toward a tangential arrangement of these particles is evident in the transverse section.

An attempt was made to detect an increase in accessible porosity in the vicinity of the fracture of a tested tensile bar, by sulfur impregnation and microradiography. It was not successful, indicating that the increase, if any, was small.

III. RAW MATERIALS

A. Solid Raw Materials (H. D. Lewis)

1. Characterization of Carbon Blacks

An optical particle-size count has been made on a sample of Thermatomic Carbon Company's Grade P33 carbon black, taken from CMF-13 Lot No. T(P-33)-2. This is a furnace black, quite similar to "regular" Thermax but distinctly finer. The sample was prepared by L. S. Levinson using an ultrasonic deagglomeration technique, and he also made the electron micrographs used for counting. An Endter counter was used to make two optical counts on each of four fields of view: (1) The number of individual spherical particles in each range of particle diameters, including those composing agglomer-

ates; (2) The number of agglomerates in each range of equivalent circular areas, including as agglomerates all individual spherical particles isolated from other particles. In order to generate an agglomerate sample size sufficient to define the sample distribution of agglomerates, a total sample size, N , of more than 5000 individual particles was used.

Sample distribution curves for the four-field composite particle and agglomerate counts are shown in Fig. 8, and computed sample statistics are summarized in Table 7. The ratio N/N_A is the average number of particles composing one agglomerate (considering isolated single particles as agglomerates also) and can perhaps be considered a measure of the "deagglomerability" of the material under the "standard" conditions used in preparing the sample. The particle-size distribution curve is displaced toward smaller sizes from that for regular Thermax (reported in LA-3872-MS), peaks more sharply,

TABLE 7
SAMPLE STATISTICS FOR P33 THERMAX,
LOT T(P-33)-2

	Particle Count	Agglomerate Count
Total Number Counted, N	5814	1334
Mean Diameter, $\bar{d}$, μ	0.2151	0.3650
Variance, s_d^2	0.00636	0.03295
Standard Deviation, s_d	0.0798	0.18153
Skewness, g_d	1.5621	1.5964
Most Probable Value of d , M_d	0.1850	0.2675
Mean Diameter Ratio, $\bar{d}_A/\bar{d}$		1.70
Average No. Particles per Agglomerate, N/N_A		4.36

Fig. 8. Composite Particle and Agglomerate Counts, P33 Thermax, Lot T(P-33)-2

and is more highly skewed. However, the $\bar{d}_A/\bar{d}$ and N/N_A ratios are about the same for the two materials.

Specific surface area of P33 Thermax calculated from optical count data (with the assumption that all particles were smooth-shelled spheres) was $11.38 \text{ m}^2/\text{g}$. Specific surface area measured by nitrogen adsorption was $12.35 \text{ m}^2/\text{g}$, giving a "fuzziness" ratio of only 1.085 and indicating that the assumption of smooth-shelled spheres was valid. The calculated particle diameter of monosized spherical particles having specific surface area equal to that measured by nitrogen adsorption was 0.260μ , in remarkably good agreement with the mean particle diameter (0.215μ) from the optical count.

Helium density of P33 Thermax was 1.87 g/cm^3 , compared with 1.88 g/cm^3 for "regular" Thermax. Except for mean particle diameter and some details of the

size distribution, the two materials are very much alike.

2. Particle-Size Analyses of Ground Products

Sample statistics derived from Micromerograph analyses of the products of fluid-energy grinding natural graphite and a high-expansion coke are listed in Table 8, together with similar statistics determined for several graphite flours and one coke flour of interest for mixing experiments. The ground natural graphites are identified by the symbol "T(NA)" followed by a number indicating the number of times the material has passed through the Trost fluid-energy mill. The high-expansion coke is identified by "T(HCTE)", followed by a number again indicating number of passes through the mill.

These sample statistics indicate very different grinding behaviors for the two materials. For the natural graphite, all statistics decrease monotonically as number

TABLE 8
MICROMEROGRAPH SAMPLE STATISTICS FOR GROUND NATURAL GRAPHITE, SERIES T(NA),
FOR GROUND HIGH-EXPANSION COKE, SERIES T(HCTE), AND FOR SIX GRAPHITE FLOURS AND ONE COKE FLOUR

Sample	$\hat{\mu}_{x3}$	$\hat{\sigma}_x^2$	$\hat{\mu}_x$	$\bar{d}_3$ microns	$\bar{d}$ microns	s_d^2 microns ²	S_W cm ² /gm	CV_d
T(NA)-1	1.8684	0.4257	0.5914	8.015	2.235	2.651	5070.	0.728
T(NA)-2	1.5659	0.3506	0.5141	5.704	1.993	1.667	6608.	0.648
T(NA)-3	1.4813	0.3284	0.4959	5.183	1.935	1.456	7113.	0.624
T(NA)-4	1.4407	0.3184	0.4855	4.953	1.905	1.361	7370.	0.612
T(NA)-5	1.4002	0.3367	0.3902	4.800	1.748	1.223	7746.	0.633
T(HCTE)-1	4.2426	1.9121	-1.4937	181.0	0.584	1.967	1206.	2.402
T(HCTE)-4	3.4944	1.2980	-0.3996	63.02	1.283	4.384	1875.	1.632
T(HCTE)-7	2.9772	1.4542	-1.3852	40.62	0.518	0.880	3399.	1.811
T(HCTE)-10	2.3814	1.2243	-1.2916	19.96	0.507	0.617	5499.	1.550
T(HCTE)-13	1.9439	0.8034	-0.4664	10.44	0.937	1.084	6900.	1.110
T(HCTE)-17	1.5857	0.6620	-0.4003	6.80	0.933	0.817	9199.	0.969
G-17 (-100 mesh)	4.2610	1.3499	0.2112	139.2	2.426	16.811	766.	1.690
G-14 (-325 mesh)	3.3471	0.8378	0.8336	43.21	3.499	16.056	1472.	1.145
G-19	2.8956	1.1379	-0.5180	31.96	1.052	2.347	2650.	1.456
G-19 (-325 mesh)	2.8068	1.1423	-0.6201	29.31	0.952	1.935	2902.	1.461
G-20	2.9121	1.1729	-0.6068	33.07	0.980	2.142	2653.	1.494
G-20 (-325 mesh)	2.7938	0.9380	-0.0202	26.12	1.566	3.815	2667.	1.247
C-5	2.7563	1.1463	-0.6826	27.92	0.896	1.725	3347.	1.465

of passes increases, except for the final value of the variance ($\hat{\sigma}_x^2$) and of course specific surface area (S_w). In general, then, as grinding progressed, both the mean and the variance of the size distribution decreased continuously.

The grinding behavior of the high-CTE coke was much more complex. Weight-fraction mean diameter ($\bar{d}_3$) and weight-fraction median diameter (antilog $\hat{\mu}_{x3}$) decreased monotonically with successive passes, but the weight-fraction variance ($\hat{\sigma}_x^2$) -- and hence the number-fraction mean diameter, $\bar{d}$, and variance, s_d^2 -- did not. The data suggest that successive passes through the mill did not affect large particles and small particles in the same way. Apparently the first pass generated a relatively large weight fraction of fines without eliminating large particles (of the order of 200 μ dia), thus giving a large $\hat{\sigma}_x^2$ value and a relatively small $\bar{d}$. The next three passes apparently produced considerable comminution of these large particles, producing particles of intermediate size and considerably reducing $\hat{\sigma}_x^2$ and $\hat{\mu}_{x3}$. The net effect was to increase the number-fraction mean diameter, $\bar{d}$, because of the relation $\bar{d} = \exp [\hat{\mu}_{x3} - 2.5 \hat{\sigma}_x^2]$. The next three passes apparently generated a relatively large fraction of fines, increasing $\hat{\sigma}_x^2$ and decreasing $\bar{d}$. This "stepwise" comminution of coarse fractions and then fine fractions appears to have continued through the 17 grinding passes.

CV_d , the coefficient of variation of d , changed monotonically for the natural graphite series and for a similar grinding series on YBF graphite (reported in LA-3872-MS). For the high-CTE graphite it showed a maximum at seven passes, suggesting that T(HCTE)-7 should produce higher density in molded or extruded pieces than any other flour in the series except T(HCTE)-1.

3. Surface-Area Analyses

A redetermination of the specific surface area of one T(NA) sample was made by the BET nitrogen-adsorption method, using an adsorption equilibration period of 60 min instead of the "standard" 20 min previously used. This was found to increase the measured value of S_A by 18 %, which is significant -- although far from enough to explain the large difference between these results and those reported by Walker and Seeley⁶ for ball-milled natural

graphite. (An important difference in grinding mechanism between the ball mill and the fluid-energy mill is suspected to exist.) Surface areas of the T(NA) series have therefore been redetermined using a compromise equilibration time of 45 min, the longest that will permit two surface-area measurements to be made per day. These results are summarized in Table 9, together with those for the T(HCTE) series. Because of the very long (1.5 hr) equilibration periods required by the latter, surface areas were measured on only 6 samples of the total of 17 produced. In the table, d_o is the diameter of monosized spherical particles which would have surface area equal to that measured by gas adsorption, and may be compared with $\bar{d}$, the mean particle diameter from Micromerograph analysis, listed in Table 8. The "Fuzziness" Ratio listed in Table 9 is the ratio of surface area measured by gas adsorption, $\bar{S}_A$, to that listed in Table 8 as S_w , which is calculated from Micromerograph data with the assumption that each particle is a smooth-shelled sphere.

"Fuzziness" ratios for the T(NA) series of ground natural graphites are nearly constant, indicating that the grinding process did not significantly change the surface character of the particles. For the high-expansion coke series, however, the ratio was much higher and did change

TABLE 9
SURFACE AREA SAMPLE STATISTICS
FOR GRINDING PRODUCTS

Sample	$\bar{S}_A, m^2/g$	s_S	d_s, μ	"Fuzziness" Ratio
T(NA)-1	8.07	---	0.329	15.92
T(NA)-2	10.59	0.037	0.251	16.02
T(NA)-3	11.98	0.184	0.222	16.85
T(NA)-4	12.95	0.099	0.205	17.73
T(NA)-5	13.91	0.187	0.191	17.95
T(HCTE)-1	5.82	0.68	0.621	48.09
T(HCTE)-4	14.62	0.25	0.247	77.76
T(HCTE)-7	25.31	0.35	0.143	74.44
T(HCTE)-10	34.25	0.05	0.106	62.27
T(HCTE)-13	46.64	0.88	0.077	67.59
T(HCTE)-17	55.75	0.67	0.065	60.60

significantly. It is speculated that during the first several passes through the mill, fracture not only created new external surfaces but also opened to these surfaces a system of voids which were not previously surface-connected. Then, with further grinding, particle dimensions became smaller than the spacing of such voids, and fuzziness ratio decreased. In any case, these data indicate -- as did the particle-size data -- a much more complex comminution mechanism for the T(HCTE) material than for natural graphite and the YBF graphite previously investigated.

4. Mixture Calculations

The XOPMIX computer program has been developed to calculate the proportions by weight in which two powders (for which particle-size distribution statistics are available) should be mixed in order to maximize $\hat{\sigma}_x^2$, the variance of $\ln d$, for the mixture. It also calculates the weight fractions required to produce a binary mixture for which the distribution curve has zero skewness ($\hat{\gamma}_x = 0$), and CV_d , the coefficient of variation of particle diameter, at the composition at which variance is maximized. Presumably the mixing fraction at which maximum packing density will be achieved is somewhere between that required to maximize variance and that which gives zero skewness, and CV_d gives an indication of what that density will be relative, for example, to the unmixed components.

As a guide to mixing experiments described below, the XOPMIX code has been used to compute optimum mixtures for all possible binary combinations of graphite flours T(YBF)-1, -2, -3, -4, -5, and -12, prepared by grinding commercial YBF graphite and described in LA-3872-MS. It has also been used for combinations of several commercial flours and for mixtures of screen-fractions of Lot G-18 flour (a Great Lakes 1008 graphite flour). These computations made it apparent that two long-standing problems must be resolved before much further progress can be made in improving particle size distributions to increase density of formed graphite bodies: (1) Because the lognormal model assumes an infinite range of particle sizes, it does not provide an adequate description of distributions which are truncated as a re-

sult of screening out certain size fractions or for some other reason. In effect, it supplies particles mathematically to make the distribution fit the lognormal assumption. (2) The change in coefficient of variation, CV_d , with proportions of a binary mixture can not be examined analytically for a maximum value as can the variance, $\hat{\sigma}_x^2$ or s_x^2 . Since CV_d seems to be related significantly to the packing behavior of powders and powder mixtures, this is unfortunate.

To correct the second of these deficiencies, the COFVARD computer program has been developed. This calculates and plots CV_d as a function of mix composition at small composition intervals. If it exists, a maximum value of CV_d is discovered by examining the numerical printout of the program, or the graph which it produces. COFVARD is now being used to examine binary combinations of powders of current interest. An example of its output is shown in Fig. 9, which shows the variation of CV_d with composition for mixtures of flours G-14 and G-17 (which are considered further below). This shows a maximum in CV_d at 17 wt % flour G-14 in the mixture.

Fig. 9. COFVARD Plot of CV_d vs. Composition for Mixtures of Flours G-14 and G-17

Fig. 10. COFVAR Plot of $\hat{\sigma}_H^2$ vs. Composition for Mixtures of Flours G-14 and G-17

A similar plot of $\hat{\sigma}_x^2$ vs. mix composition for the same pair of flours is shown in Fig. 10. This indicates maximum variance at 2 wt % G-14 flour (compared with 1.99 wt % from the XOPMIX calculation). It is evident that mix composition to maximize CV_d is not the same as that required to maximize $\hat{\sigma}_x^2$, and it must be decided by experiment which is the better indicator of maximum packing density. However, at least the region of compositions which deserves experimental investigation has been identified.

Like the XOPMIX code, COFVAR assumes lognormal particle-size distributions, and so has the first of the two deficiencies noted above. In an attempt to correct this, a program is now being written which will compute size-distribution statistics from size-interval data (the "non-functional" model). This will contain a version of COFVAR as a subroutine.

B. Liquid Raw Materials (E. M. Wewerka)

1. Furfuryl Alcohol Resins

Recently it has been observed that the viscosities of

certain experimental resins were increasing slowly with time. Repeated viscosity measurements over a period of several weeks indicated that many of these resins were relatively stable, while the viscosities of others changed at rates up to 10%/week. This behavior is believed to be due to some inconsistency in the procedure used to neutralize the resin during polymerization. During the course of future resin preparations, the effects of various neutralizing methods will be examined. In the meantime, no significant uncertainty is involved in using resins now on hand providing that not more than a week or two elapses between the viscosity measurement and incorporation of the resin into a fabrication experiment.

As is further discussed below, experiments are in progress to determine whether or not correlations exist between successful heat-treating cycles in graphite manufacture and the thermal behavior of the binder as this is revealed by differential thermal analysis. In the initial experiments, a high-viscosity (2700 cp) furfuryl alcohol resin is being tested using a variety of linear heating rates to 425°C, to determine the maximum heating rate at which specimen integrity is maintained. When this has been determined, both resin properties and heating cycles will be varied systematically.

2. Indene Polymers

A few indene polymers have been synthesized successfully. Polymerization techniques and analytical methods are now being evaluated. Some of these polymers will soon be available for fabrication experiments.

3. Equipment

The gel permeation chromatograph has been improved by addition to it of a new type of micrometer-adjusting solvent pump and a refractometer conversion unit. Each should considerably reduce the attention required during operation of the apparatus. Other improvements made at the same time included modification of the solvent reservoir to allow faster filling without danger of airlock and solvent spillage, and elimination of the stabilizing transformer in the power supply, which was a source of much noise. Some resolution has been lost by the gel columns, and they will be replaced with a new set as soon as possible. However, for better correlation with previous re-

sults, the old set will be used until the current series of fabrication experiments is completed.

A differential calorimeter cell has been obtained for the differential thermal analysis unit. It will give direct, quantitative values of the energies involved in thermal transitions, requires no reference sample, and has permanent thermocouples which are isolated from the sample.

IV. EXPERIMENTAL GRAPHITE MANUFACTURE

A. Grinding Research (R. J. Imprescia)

1. Grinding of High-Expansion Coke

Initial results from grinding of an air-blown, nearly isotropic, high-CTE coke in a Trost fluid-energy mill

were reported in LA-3872-MS. This series of experiments has been terminated, after 17 passes of the material through the mill. Particle-size and surface-area data are reported above, where the ground products are identified as the T(HCTE) series. Feed rates and screen-size analyses are listed in Table 10. Relative fineness and specific surface area are plotted in Fig. 11 as functions of number of passes through the mill.

The great difficulty encountered in grinding this material is indicated by the fact that even after 17 passes through the mill more than 25 wt % of it was coarser than 5 μ .

2. Grinding of Commercial Needle Coke

A series of fluid-energy grinding tests is in progress

TABLE 10
EFFECTS OF REPEATED FLUID ENERGY GRINDING ON SCREEN-SIZE ANALYSIS OF ISOTROPIC COKE

Grind No.	Feed Rate Lb/hr	Cumulative Weight % Coarser Than								Fineness % < 5 μ
		710 μ (#25)	350 μ (#45)	177 μ (#80)	88 μ (#170)	41 μ	21 μ	10 μ	5 μ	
Raw Feed *		2.5	24.5	59.0	78.1	90.8	94.4	94.9	95.3	4.7
T(HCTE)-1	4.6	2.2	21.0	43.5	57.5	78.2	84.2	88.6	90.7	9.3
-2	4.0	2.0	17.0	31.0	45.8	67.2	77.0	83.8	88.3	11.7
-3	4.1	1.5	16.0	27.5	34.8	56.4	72.0	79.4	81.6	18.4
-4	4.1	1.0	9.5	17.0	27.0	44.9	59.7	75.9	80.3	19.7
-5	3.9	0.5	9.0	15.5	21.7	39.8	56.2	70.1	73.7	26.3
-6	3.8	0.5	6.0	11.0	16.5	32.5	46.3	65.2	73.0	27.0
-7	3.9	trace	4.0	9.0	10.4	25.7	41.7	61.5	70.7	29.3
-8	3.5	trace	3.0	5.5	9.5	16.7	32.9	56.1	64.4	35.6
-9	3.0	trace	2.0	4.0	4.5	11.3	26.9	52.8	59.9	40.1
-10	3.0	trace	1.5	2.5	3.1	7.6	18.2	47.2	54.1	45.9
-11	2.6	0	0.5	1.0	1.3	3.1	9.6	35.7	53.3	46.7
-12	2.6	0	trace	0.3	0.6	1.8	5.5	26.0	49.6	50.4
-13	2.7		0	0.1	0.3	0.9	3.3	20.6	43.1	56.9
-14	2.8		0	trace	0.2	0.6	2.4	13.9	39.8	60.2
-15	2.7			0	0.1	0.4	0.9	10.6	31.9	68.1
-16	2.6			0	trace	0.3	0.6	7.3	27.3	72.7
-17	2.7				0	0.1	0.2	6.9	25.9	74.1

* CP(HCTE)-2

Fig. 11. Relative Fineness and Specific Surface Area of High-Expansion Coke, Series T(HCTE), as Functions of Number of Fluid-Energy Grinding Passes

on a commercial needle coke, Lot CNL-1 (a lump coke purchased from Carbon Products Division of Union Carbide Corporation). By a series of preliminary crushings in a jaw mill and a Williams hammer mill, the coke was reduced to a particle-size distribution similar to that of the crushed high-CTE coke used as the starting material for the experiments described above.

Initial results indicate that during the first few passes through the Trost mill this needle coke grinds even more easily than does the YBF graphite discussed in earlier reports. After about 5 or 6 passes, however, the difficulty of further grinding increases markedly.

3. Effects of Feed Rate

The effect of mill variables on the rate at which a given material is reduced in a Trost fluid-energy grinding mill will be investigated in a series of experiments just started. The first of these will examine the effect of feed rate on the grinding of YBF graphite.

Three different size fractions of coarsely ground YBF graphite have been separated for use as feed materials, by repeated screening of Lot GP(YBF)-6 graphite flour

on a SWECO Vibro Energy Separator. These were a coarse (-34 +62 mesh), a medium (-62 +100 mesh), and a fine (-100 +200 mesh) fraction. In the first grinding series, the coarse fraction will be ground at several feed rates with air pressure kept at 100 psi on the feed side and 80 psi on the air-jet side, and the discharge orifice kept at 1.25-in. dia. (Both air jets have previously been kept at 100 psi. With this material, however, it has been necessary to reduce pressure on the jet opposite the feed side by 20 psi, to prevent blow-back of the feed.)

B. Hot Molding (R. J. Imprescia)

1. Ground YBF Graphite Fillers

Hot-molded, pitch-bonded, graphite specimens have been manufactured from five of the fine graphite flours produced by grinding commercial YBF graphite in the Trost fluid-energy mill, in grinding experiments previously described. They were pressed in 2.5-in. dia graphite dies at 4000 psi and 900°C except for specimen S-2A, which was heated only to 800°C. Runs S-2A and S-3 were interrupted by failures of graphite components in the hot-molding system. In both cases the failed components were replaced and the run resumed, but the effects of these interruptions -- if any -- are not known. All specimens were graphitized in helium at about 2900°C.

Density and shrinkage data for these graphites are summarized in Table 11. The coarsest filler, No. CP-(YBF)-6, was the raw feed for the grinding experiments. The finer fillers were the products of 1, 2, 4, and 12 passes through the Trost mill, as indicated by the final number in the filler identification. All specimens had similar densities in the baked (i.e., hot-molded) condition, but their volume and density changes during graphitizing varied systematically with fineness of the filler. Only for the finest filler, flour T(YBF)-12, did density increase during graphitization. With the coarser fillers density decreased during graphitization, the density decrease becoming greater as the filler became coarser.

The other properties of these graphites also varied systematically with filler fineness, particularly with regard to anisotropy of properties. As was reported in LA-3872-MS, microscopic examination of the grinding

TABLE 11
PROPERTIES OF HOT-MOLDED GRAPHITES AS FUNCTIONS OF FILLER FINENESS

Run and Specimen No.	S-2A	S-3	S-4	S-5	S-6
Filler No.	T(YBF)-12	T(YBF)-4	T(YBF)-2	T(YBF)-1	GP(YBF)-6
Filler Fineness, % < 5 μ	99.1	43.3	16.7	10.4	2.6
Bulk Density, g/cm ³					
As-Baked	1.858	1.908	1.861	1.884	1.841
Graphitized	1.865	1.887	1.827	1.835	1.788
Change, %	+0.4	-1.1	-1.8	-2.6	-2.9
Young's Modulus, 10 ⁶ psi					
With-grain	3.04	2.76	1.78	1.49	1.08
Electrical Resistivity, $\mu\Omega\text{cm}$					
With-grain	973	838	1016	1026	1152
Across-grain	5102	3945	2663	1803	1740
Anisotropy Ratio	5.24	4.71	2.62	1.76	1.51
Thermal Expansion Coeff., $^{\circ}\text{C}^{-1}$					
With-grain	2.02×10^{-6}	2.06×10^{-6}	2.90×10^{-6}	3.20×10^{-6}	3.84×10^{-6}
Across-grain	9.92×10^{-6}	7.68×10^{-6}	6.07×10^{-6}	5.14×10^{-6}	6.06×10^{-6}
Anisotropy Ratio	4.91	3.73	2.09	1.61	1.58
Preferred Orientation					
Dacon Anisotropy Value	2.96	2.73	1.69	1.41	1.36
M Value	5.85	5.34	2.85	1.74	1.58

products here used as fillers suggested that the particles composing them became progressively more plate-like in shape as grinding progressed, which is reflected in the increasing degree of preferred orientation produced when they were molded into solid bodies. Microscopic examination of the graphitized bodies suggests the presence of a slight excess of binder, with generally good mixing of binder and filler for the three finer fillers and less-good mixing for the two coarser ones. Specimen S-6, made from the coarsest filler, showed the poorest mixing and contained many large voids and some very large c-face cracks. Voids became smaller and less interconnected as filler fineness increased.

2. Ground High-Expansion Coke Fillers

A series of hot-molded specimens similar to that discussed above is now being manufactured using as fillers the products of repeated grinding of an essentially isotropic, high-CTE coke. This grinds to much blockier particle

shapes than does YBF graphite, and should shrink much more during molding and graphitizing.

C. Comminution During Blending (R. J. Imprescia)

In the course of the mixing experiments discussed below, seven series of molded specimens were prepared, each series including the same compositions in the G-17/G-14 binary series. All series showed similarities in the trend of packed filler density vs. mix composition, but density differences among corresponding members of the various series were often large. This suggested that particle-size characteristics of one or both of the fillers might be changing during blending of the two graphite flours composing the mix, producing corresponding changes in compactability of the mixture.

To explore this possibility, the coarser component -- flour G-17 -- was blended by several different techniques with a fixed proportion of stearic acid lubricant and then,

TABLE 12
EFFECTS OF BLENDING ON SCREEN SIZE ANALYSES OF G-17 PLUS STEARIC ACID MIXTURE

Screen Fraction (U.S. Std. Series)	As Rec'd	Weight % in Screen Fraction				
		Sample 1 (TSB-N)	Sample 2 (TSB-I)	Sample 3 (10FC)	Sample 4 (20FC)	Sample 5 (30FC)
+25	Trace	Trace	Trace	Trace	Trace	Trace
-25 +45	9.5	10.0	7.1	2.5	2.3	2.0
-45 +80	79.1	80.2	71.5	43.4	44.8	42.0
-80 +170	10.5	9.0	16.9	29.1	28.9	29.8
-170 +325	0.4	0.3	2.5	10.4	9.4	10.3
-325	0.6	0.5	2.1	14.6	14.6	15.9

TSB-N --- Twin-shell blending 20 min. with NO intensifier

TSB-I --- Twin-shell blending 20 min. with Intensifier

FC --- Food Choppings

after the lubricant was removed by evaporation, was examined by screen analysis. Results are listed in Table 12. Twin-shell blending without the use of an intensifier bar ("Sample 1" in the table) had no significant effect on screen-size distribution. Twin-shell blending with an intensifier bar ("Sample 2") significantly changed the size distribution. Further blending by passing Sample 2 through the food chopper 10, 20, and 30 times produced still greater changes in size distribution, the greatest changes apparently occurring in the first few passes.

Fortunately, most of the fillers so far used in fabrication experiments are considerably finer than either G-17 or G-14 flour, and are believed to have been much less affected by comminution during blending than was the G-17 flour here examined.

D. Mixing Experiments (R. J. Imprescia, J. M. Dickinson)

1. The G-17/G-14 Binary Series

The G-17/G-14 binary mixing experiment initially described in LA-3872-MS has been resumed using twin-shell blending of the mix components without use of an intensifier bar. Results are summarized in Fig. 12, where most of the points plotted are averages of 2 or 3 independent determinations using unidirectional pressing and the lubricant-evaporation technique. Standard devi-

Fig. 12. Packed Filler Density as a Function of Filler Composition, G-17/G-14 Series

ations of density values were small, and the curve is believed to represent quite well the packed filler density profile for this series. It is much more complex than would be expected from Fig. 9 and Fig. 10, which represent initial attempts to treat this system theoretically.

The small peak in Fig. 12 at 4% G-14 may correlate with the maximum in Fig. 10, and the hump in Fig. 12 at about 25% G-14 with the maximum in Fig. 9.

The AAR series of extruded graphites was also made to investigate filler packing in G-17/G-14 binary mixtures. The two graphite flours were mixed in various proportions with 27 pph Varcum binder, and extruded as 0.5-in. dia rod. Agreement between duplicate runs was poor, perhaps again due in part to blending procedures, but largely because of the presence of fine cracks in most of the graphitized extrusions. In an attempt to correct this, several extrusions were made using 85 parts of the G-17/G-14 mix plus 15 parts of Thermax carbon black, and these did not crack. Packed filler densities were much higher than for molded specimens, in the ranges 1.50-1.56 g/cm³ without the Thermax addition and 1.61-1.66 g/cm³ with it. Curves of packing density vs. mix composition, both with and without Thermax, show trends which suggest a small density minimum near 2% G-14 and a small maximum near 4% G-14, in agreement with Fig. 12. They also suggest a broad density maximum near 75% G-14, not evident in Fig. 12. Unfortunately, scatter was too great in graphites without Thermax and differences were too small in graphites containing it for these results to be conclusive.

It is clear that much remains to be learned about the packing behavior of fillers.

2. The T(YBF)-1/T(YBF)-2 Binary Series

A density profile has also been prepared for a binary system based on mixtures of two flours prepared by grinding YBF graphite to different degrees of fineness, and is shown in Fig. 13. Most of the points plotted represent the averages of either 2 or 3 independent determinations by pressing and lubricant evaporation, among which agreement was excellent. Because the supply of raw materials was limited, the composition interval was wide except in the vicinity of 55 wt % T(YBF)-2, where the maximum-variance model predicts a maximum in packing density. While the density curve is irregular here, it shows no pronounced maximum.

Fig. 13. Packed Filler Density as a Function of Filler Composition, T(YBF)-1/T(YBF)-2 Series

3. The G-18/G-19 Binary Series

The AAT series of extruded graphites was made to investigate filler packing in a system for which the maximum-variance model predicted that no maximum in packing density would occur. The two graphite flours, G-18 and G-19, were mixed in various proportions with Varcum binder in an amount (27.5 to 37.6 pph) determined experimentally to produce the best extrusions, and the mix was extruded as 0.5-in. dia rod. No carbon black was added to the mix and some cracking occurred, although much less than in the AAR series described above. The graphite made from 100% G-18 flour was the best in the series, and there was no indication of a maximum in the curve of packing density vs mix composition. In fact, there was some evidence of a shallow minimum in this curve at about 95% G-19.

E. Binder Residue in Hot-Molded Graphites (R. J. Imprescia)

Further examination of data from two series of hot-

molding experiments described in LA-3821-MS has indicated that a correlation exists between percent binder residue and initial proportion of binder present, and that the relation between the two is not precisely that which would have been predicted.

The experiments in question were intended to determine optimum binder concentration for hot molding of two quite different fillers. For both, the binder used was Allied Chemical Co. Grade 30MH coal-tar pitch, whose initial concentration was varied over a wide range. In Series 26D, the filler was a graphite flour-Thermax mix, and optimum binder concentration was about 29 pph. In Series 26E the filler was a coke flour, and optimum binder concentration was about 38.5 pph.

In Fig. 14, binder residue (% of original binder weight retained in the graphitized specimen) is plotted against initial pitch concentration for both series. In hot molding by the technique used here, binder in excess of the optimum proportion squeezes out of the die and is lost, so that the measured binder residue is less than the binder's actual coking value. However, for mixes containing binder in the optimum proportion or less, no squeeze-out

would be expected and it is generally assumed that binder residue will remain essentially constant (at the coking value of the pitch). As Fig. 14 shows, in these two series of experiments binder residue continued to increase as pitch concentration diminished to far below its optimum value.

One possible explanation of this behavior depends upon the observation that as a raw mix becomes increasingly deficient in binder an increasing proportion of the total filler-particle surface is not wet by the binder. These unwet particle surfaces may serve as condensation sites for heavy hydrocarbon gases produced by pyrolysis of the pitch, which are subsequently carbonized or graphitized on these surfaces instead of being evolved and lost. Differences in binder residue between the two series of specimens may reflect differences between the fillers used with regard to specific surface area or the activities of the surfaces exposed, both of which might influence condensation and retention of pyrolysis products.

F. Extrusion (J. M. Dickinson)

1. Effects of Particle-Size Distribution (Series AAP)

As was discussed in LA-3872-MS, the AAP Series of extruded graphites is intended to explore the effects of filler particle size and size distribution on manufacturing procedures and graphite properties. Additional members of the series made recently are listed in Table 13 (which supplements Table 13 in LA-3872-MS). The fillers used were graphite flours made by Carbon Products Division of Union Carbide Corporation from an air-blown, high-CTE coke. Flour G-25 had a screen analysis similar to that of Great Lakes 1008 flour, while G-24 was very fine, essentially all through 325 mesh.

While the characterization of these flours and of the graphites made from them is not yet complete, the information already collected is of unusual interest. Two of the three graphites containing Thermax cracked, while both of the Thermax-free graphites were sound. This is the opposite of the experience with most other fillers. Further, binder requirements for these flours were relatively low, favoring relatively high density. Graphite AAP-26, made with 100 parts of the fine G-24 flour, had

Fig. 14. Binder Residue as a Function of Initial Pitch Concentration

TABLE 13
MIX COMPOSITIONS AND PROPERTIES OF AAP GRAPHITES

Specimen No.	Graphite Flour Parts	TP-3 Thermax, Parts	Varcum Binder, pph	Dia. of Green Extrusion, In.	Density, g/cm ³	Condition
AAP-26	100 G-24	---	27.1	0.503	1.900	OK
AAP-27	85 G-24	15	28.43	0.501	1.910	Cracked
AAP-25	100 G-25	---	26.17	0.505	1.838	OK
AAP-24	85 G-25	15	23.95	0.499	1.913	Cracked
AAP-28	85 G-25	15	20.72	0.502	1.906	OK

* Including 4% maleic anhydride catalyst

by a considerable margin the highest density of any Varcum-bonded, Thermax-free graphite so far made here.

These unusual graphite flours will, of course, be used in other experiments, including mixing with other fillers.

2. Effects of Vacuum Degassing (Series AAU)

Particularly during preparation of samples for gas-adsorption surface-area analysis, it has been observed that a large decrease in bulk volume often occurs during vacuum degassing of graphite flours. To explore the possibility that the compaction which this represents might result in increased density of an extruded graphite, two lots of graphite were prepared by vacuum degassing the filler (at 400°C and 10⁻⁵ Torr), then hand-mixing it with binder in a helium-filled dry box. One lot was made from 85 parts G-18 graphite flour to 15 parts TP-3 Thermax with 27 pph Varcum binder, the other from 100 parts G-19 graphite flour with 38 pph Varcum. The first lot produced graphite having a density of 1.867 g/cm³ when the degassing treatment was used, compared with 1.870 g/cm³ for a parallel sample mixed as usual, in air. The second produced a graphite having density of 1.757 g/cm³ with vacuum degassing and 1.755 g/cm³ without it.

At least for these filler materials and this relatively simple degassing procedure, there is no evident advantage in vacuum degassing of the solid raw materials to be used in graphite manufacture.

3. Effects of Binder Characteristics (Series AAS)

In the AAS series, the effects of viscosity and molecular distribution of furfuryl alcohol resin binders on manufacturing procedures and the properties of extruded graphites are being investigated. Binders having the same viscosity but widely different molecular distributions will be used, as well as binders having a wide variety of viscosities.

Previous studies have indicated a tendency toward cracking of extruded rods made with furfuryl alcohol resins having viscosities much greater than about 250 cp. An essential part of this investigation is, therefore, the development of techniques which will reduce the cracking tendency of graphites made with higher viscosity binders. In particular, modified heat-treating cycles, based on differential thermal analysis studies of the individual binders, are being developed.

Because of the large number of variables being considered, the number of specimens so far given any particular treatment is small. However, certain behavior patterns have appeared which will be investigated more intensively. For example, a rod from Lot AAS-7, made from a CMF-13 binder having a viscosity of 2600 cp, was observed to be uncracked after curing to 200°C and cracked after baking to 900°C. This suggested that the exothermic reactions shown by DTA to occur in the binder at 300° to 400°C might be a source of damage. Rods from Lot

AAS-9, also made from a high-viscosity binder, were therefore cured by extending the curing cycle upward to about 425°C and heating to this temperature in a variety of schedules. Results indicate that heating over the range 185° to 400°C at more than 10°/min caused cracking, while heating at 6°/min or less did not.

Graphitized rods from Lot AAS-9 had densities of 1.901 to 1.906 g/cm³. Similar rods made from the same filler mix with the same proportion of binder, but using commercial Varcum instead of the high-viscosity experimental resin, had densities of 1.871 to 1.884 g/cm³. When conditions are found under which sound graphites can be made using the higher-viscosity binders, a significant increase in graphite density can be achieved. This should be reflected in other properties as well.

4. The Role of Carbon Black in Graphite

The carbon black (Thermax) which has been part of the filler in most of the CMF-13 experimental graphites so far made has been found to affect binder requirement in formulating the raw mix, most steps in the manufacturing procedure, and essentially all properties of the finished graphite. In several of these aspects its effects are large, and in general they are not well understood.

One of the properties most affected by the presence or absence of Thermax is density. Density is important of itself, and interacts strongly with many other properties. Further, in affecting density, the Thermax is apparently modifying the packing behavior of the filler, which is currently being studied in other CMF-13 programs. For these reasons an investigation of the role of Thermax in graphite has been undertaken, beginning with a study of its effect on the compaction behavior of a well-characterized graphite flour.

The graphite flour being used in the first phase of this program is from CMF-13 Lot G-18. (This is a Great Lakes Grade 1008 graphite flour, which is identified by Group CMB-6 as "M3 flour".) It is pressed in a 1.5-in. dia, double-acting, unidirectional steel vacuum die which is sufficiently thick-walled so that changes in diameter of the die cavity are negligibly small at the maximum pressures used. Bulk density of the compact is determined as a function of pressure by measuring

(with a cathetometer, to the nearest 0.01 mm) the difference in height of two scribe marks on the opposing punches, and subtracting the height difference between the same two marks previously measured when the same pressure was applied to the empty die. Specimens are weighed to the nearest milligram before and after pressing, and weight loss is usually about 1 part in 3000. Whenever possible, bulk density of the compact is calculated from physical measurements made after it is ejected from the die. Initial runs have been made in vacuum to a maximum pressure of 28,000 psi. After a holding time of 2 min, no change in specimen height has been observed with further holding under pressure for up to 30 min.

A typical pressure vs bulk density curve for dry G-18 flour is shown in Fig. 15. At 28,000 psi, bulk density was 2.125 g/cm³, which is 96.6% of the particle density and 127.2% of the calculated packing density. (Packing density is the bulk density which would be achieved by close-packing of monosized spheres, and equals 74% of the particle density.) As pressure was reduced bulk density dropped rapidly to 1.915 g/cm³ at 566 psi and 1.659 g/cm³ at 14 psi. Upon removal from the die the specimen expanded to a bulk density of 1.351 g/cm³. Results of other runs are given in Table 14, and agreement among duplicate runs is good.

Fig. 15. Pressure vs. Bulk Density for Dry-Pressing of G-18 Graphite Flour.

TABLE 14
DENSITY OF DRY-PRESSED G-18 GRAPHITE FLOUR ALONE AND WITH ADDITIONS OF FINES

Spec. No.	Composition		Particle	Packing	DENSITY			Out of the Die
					Pressure			
					28 KSI	566 PSI	14 PSI	
	G-18	Fines						
		None						
ABA1-1	100	---	2.2	1.67	2.125	1.915	1.659	1.351
-2	100	---	2.2	1.67	2.124	1.916	1.655	1.359
-3	100	---	2.2	1.67	2.125	1.914	1.713	
		TP-3						
ABA2-1	95	5	2.18	1.66	2.089	1.883	1.635	---
-3	90	10	2.17	1.65	2.046	1.849	1.643	1.409
-4	85	15	2.15	1.64	1.989	1.810	1.621	1.373
-2	80	20	2.14	1.62	1.994	1.766	1.615	1.422
-6	50	50	2.04	1.55	1.692	1.551	1.479	1.385
-5	--	100	1.88	1.42	1.403	1.274	1.232	---
		Linde A						
ABA3-1	50	50	3.085	2.35	2.094	1.953	1.752	1.567
-2	80	20	2.554	1.941	2.118	1.804	1.700	1.564
-3	90	10	2.377	1.807	2.130	1.922	1.683	1.363
-4	0	100	3.97	3.017	2.028	1.958	1.914	1.799
		Germantown Black						
ABA4-1	80	20	2.146	1.63	1.856	1.646	1.483	1.286
-2	95	5	2.187	1.662	2.057	1.839	1.597	1.322
-3	0	100	1.926	1.464	1.196	1.079	0.837	---

When bulk density exceeds theoretical packing density, then either the initial particle size and shape distributions are such that the particles pack more densely than would monosized spheres, or else the particles are deformed under pressure so that they do so. In the case of the G-18 flour, as is shown in Table 15, bulk density considerably exceeded packing density when pressure was high, but fell well below it as pressure was reduced. Evidently the high density was not achieved because of initial particle sizes or shapes, but rather by an elastic (or anelastic) deformation of particles which disappeared

when the load was removed. The amount of elastic deformation possible in the system, as indicated by the density change on unloading, was far greater than was expected.

Thermax carbon black consists of a distribution of sizes of essentially spherical particles. It would be expected to compress into an approximately close-packed array with the finest particles in interstitial positions among the coarser ones, and so to reach bulk densities well above 100% of packing density. In fact, even at 28,000 psi, only 99% of packing density was reached with TP-3 Thermax, and this was reduced to 87% at 14 psi.

TABLE 15
PERCENT OF PARTICLE DENSITY AND OF PACKING DENSITY
ATTAINED IN DRY-PRESSING G-18 GRAPHITE FLOUR ALONE AND WITH ADDITIONS OF FINES

Spec. No.	Composition		% of Particle Density				% of Packing Density Based on Particle Density			
	G-18	Fines	28 ksi	566 psi	14 psi	Out of the Die	28 ksi	566 psi	14 psi	Out of the Die
None										
ABA1-1		---								
-2	100	---	96.6	87.0	75.4	61.4	127.2	114.7	99.3	80.9
-3	100	---	96.5	87.1	75.2	61.8	127.2	114.7	99.1	81.4
-4	100	---	96.6	87.0	77.9	---	127.2	114.6	102.6	---
TP-3										
ABA2-1	95	5	95.8	86.1	75.0	---	125.8	113.4	98.5	---
-3	90	10	94.3	85.2	75.7	64.9	124.0	112.1	99.6	85.4
-4	85	15	92.5	84.2	75.4	63.9	121.3	110.4	98.8	83.7
-2	80	20	93.2	82.5	75.5	66.4	123.1	109.0	99.7	87.8
-6	50	50	82.9	76.0	72.5	67.9	109.2	82.2	79.5	89.3
-5	0	100	74.6	67.8	65.5	---	98.8	89.7	86.8	---
Linde A										
ADA3 1	50	50	67.0	60.3	56.8	50.8	80.1	80.1	71.6	66.7
-2	80	20	82.9	70.6	66.6	61.2	109.1	92.9	87.6	73.7
3	90	10	89.6	80.9	70.8	57.9	117.9	106.4	99.1	75.4
-4	0	100	51.1	49.3	48.2	45.3	67.2	64.9	63.4	59.6
Germantown Black										
ABA4-1	80	20	86.5	76.7	69.1	59.9	113.9	101.0	91.0	78.9
-2	95	5	94.1	84.1	73.0	60.4	123.8	110.6	94.5	79.5
3	0	100	62.1	56.0	43.5		81.7	73.7	57.2	

Either packing is badly disturbed by the presence of strongly-bonded aggregates or, even at high pressure, movement of particles to occupy voids is very limited. When pressure was reduced on a Thermax compact the elastic springback was appreciably less than for the graphite flour. This might be attributed either to the internal structure of the particles or, more probably, to their shape.

The addition of Thermax to G-18 flour would be ex-

pected to improve packing by providing many small particles to fill interstitial voids in the G-18 packing array. However, at pressure, both actual density (Table 14) and percent of packing density (Table 15) were reduced when Thermax was added, and the reduction was greater at higher Thermax content. This was not true of compacts after ejection from the die. Both bulk density and percent packing density were greater for the ejected compacts which contained Thermax, indicating that some of the

TABLE 16
SPRING BACK OF DRY PRESSED SPECIMENS

Specimen Comp.	Spring Back of Specimens - Percent [*]		
	28 ksi to 566 psi	28 ksi to 14 psi	28 ksi to atm.
G-18/TP-3			
100/0	9.6	21.2	35.2
95/5	9.8	20.9	---
90/10	9.1	18.6	29.4
85/15	8.3	17.1	28.6
80/20	10.7	17.7	26.8
50/50	6.9	10.4	15.0
0/100	6.8	9.1	---
G-18/German Town Lamp Black			
100/0	9.6	21.2	35.2
95/5	11.7	22.8	35.4
80/20	9.8	17.4	26.6
0/100	6.1	18.6	---
G-18/Linde "A"			
100/0	9.6	21.2	35.2
90/10	8.7	18.8	32.3
80/20	12.3	16.3	21.7
50/50	4.6	11.1	17.1
0/100	1.8	2.9	5.8

^{*} The units are percent of the particle densities of the mixed powders.

Thermax did enter voids in the G-18 packing arrangement. Evidently, however, from density comparisons at pressure, not much of it did so. Instead of seeking and filling existing voids, or acting as ball-bearings to facilitate relative motion of the particles of graphite flour, it appears that most of the Thermax particles acted as rigid separators of flour particles, reducing their ability to deform and fill the voids themselves.

Two series of pressings were made in which the Thermax addition to the G-18 flour was replaced by additions of Linde A, an α -alumina abrasive whose particle size is similar to that of Thermax, and of German Town lamp black, a carbon black which is much finer than

Thermax. In both cases -- as with Thermax -- the pressing behavior of mixtures was intermediate between that of the G-18 flour alone and that of the fine addition alone. As indicated by the fraction of packing density attained, both carbon blacks (whose particles are nearly spherical) packed in denser arrays than did the Linde A, whose particles are shaped like bent rods.

Table 16 lists percent springback of compacts of the various pure materials and mixtures as pressure on the die cavity was reduced. Pure G-18 graphite flour shows the greatest springback, and pure Linde A the least. In general high packing density and high springback occur together, and appear to depend on some of the same factors.

Since the packing behavior of a mixture seems to be intermediate between those of its two components, it appears desirable that the "fines" added to a filler mix have high packing density when compacted alone, as well as high particle density.

The mechanism by which a fine addition, such as Thermax, reduces maximum density attained under pressure is not understood. Neither is it clear why the addition has an even greater effect on elastic springback, so that its net effect is a density increase of the finished compact.

V. STRUCTURAL STUDIES

A. X-Ray Diffraction (J. A. O'Rourke)

1. Technique Development

A new experimental x-ray diffraction technique has been developed which greatly reduces the corrections that must be applied to measurements of crystallite sizes (L_c) and interplanar spacings (d_{002}) of graphitic materials, and correspondingly reduces the uncertainties involved in such measurements. In general the new method gives larger and more reproducible values of crystallite size than did the "standard" method previously used, and much more consistent measurements of interplanar spacing. Its details will be reported when a study of its advantages and limitations, now in progress, has been completed. This, however, has already progressed to a point at which accuracy and reliability of the method are believed to have been well established, and its results are now being used with confidence. Its usefulness is indicated by the data reported in the next section.

2. Reexamination of Ground Graphites

In the last previous report in this series, LA-3872-MS, x-ray measurements were listed for a series of ground commercial and natural graphites, the T(YBF) and T(Na) series respectively. These were made in an attempt to determine whether appreciable fragmentation of crystallites had occurred during grinding of these materials in a fluid-energy mill. While differences were detected in the crystalline parameters of the various grinding products they were not large, and scatter was

TABLE 17
CRYSTALLINE PARAMETERS OF GROUND GRAPHITES

Sample Designation	d_{002} (Å)	L_c (Å)
T(YBF)-1	3.361	595
-2	3.360	595
-4	3.361	580
-6	3.360	565
-8	3.360	525
-10	3.360	480
-12	3.360	480
T(Na)-1	3.356	1450
-2	3.355	1420
-3	3.355	1250
-4	3.355	1080
-5	3.355	910

broad enough to obscure any trend in the relation of crystallite size to number of grinding passes.

These materials have been reexamined using the measuring technique discussed above, with the results listed in Table 17. Here the final number in the sample designation indicates the number of times each sample has passed through the Trost mill. For both YBF and natural graphite, a progressive reduction in crystallite size is seen to occur as the average particle size is reduced by successive passes through the mill. Comparison of these results with those of Table 14 in LA-3872-MS shows that the new measuring technique gives more consistent values of d_{002} and both larger and more sensitive measurements of L_c than did the old method. The new results are believed to be reliable, and indicate that indeed some fragmentation of individual crystallites does occur during fluid-energy grinding of graphite.

3. CMB-8 Pyrolytic Carbons

The degree of crystallinity and, in some cases, the crystalline anisotropy have been measured on a number of samples of pyrolytic carbons and graphites prepared by Group CMB-8. Samples were in the form of leached shell-fragments, discs, and coated beads. Results of these measurements are listed in Table 18, together with

TABLE 18
X-RAY PARAMETERS OF CMB-8 PYROCARBONS

CMB-8 Sample No.	Type of Sample	Bulk Density, g/cm ³	L _c , Å	d ₀₀₂ , Å	M ⁽¹⁾	Heat Treatment	Component ⁽²⁾	Remarks
L-10, C-23 (1, 2)	Fragments	0.97	24.4	3.47		None	Pyro C	
			800	3.36			Xyl C	
GA-XEK-4444	Fragments	0.92	55.5	3.46		None	Pyro C	
L-10, C-12 (1, 2)	Fragments	0.87	47.5	3.43		4 hr @ 2300°C	Pyro C	
			445	3.35			Xyl C	
L-10, C-16 (1, 2)	Fragments	0.68	49.7	3.43		4 hr @ 2300°C	Pyro C	
			595	3.36			Xyl C	
L-10, C-23 (1, 2)	Fragments	1.07	99.5	3.43		4 hr @ 2300°C	Pyro C	
GA-XEK-4444	Fragments	0.97	136	3.39		4 hr @ 2300°C	Pyro C	
L-10, C-12A	Disc	1.47	42.4	3.427	0.4	4 hr @ 2300°C	Pyro C	
L-10, C-16 (2)	Disc	1.53	53.5	3.422	8.2	4 hr @ 2300°C	Pyro C	
L-10, C-23 (2)	Disc	1.89	25.8	3.48	<0.1	None	Pyro C	
GA-XEK-4444	Disc	2.18	1100	3.390	200-230	4 hr @ 2300°C	Pyro C	
L-5, C-67, H-4	Beads	2.15	148	3.43		None	Pyro C	Undoped-Al control
			>1000	3.360			Pe C	
L-6, C-3, H-2	Beads	2.15	150	3.43		None	Pyro C	Al doped-310 ppm Al
			>1000	3.358			Pe C	
L-5, C-67, H-4	Beads	2.15	157	3.43		3 hr @ 2300°C	Pyro C	Undoped-Al control
			>1000	3.358			Pe C	
L-6, C-3, H-2	Beads	2.15	137	3.415		3 hr @ 2300°C	Pyro C	Al doped-310 ppm Al
			>1000	3.358			Pe C	
L-5, C-67, H-2	Beads	2.15	147	3.43		None	Pyro C	Undoped-Zr control
			>1000	3.358			Pe C	
L-6, C-3, H-22	Beads	2.15	149	3.43		None	Pyro C	Zr doped-1.6 w/o Zr
			>1000	3.358			Pe C	
L-6, C-3, H-16	Beads	2.15	138	3.43		None	Pyro C	Zr doped-6.0 w/o Zr
			>1000	3.361			Pe C	
L-5, C-3, H-2	Beads	2.15	163	3.43		3 hr @ 2300°C	Pyro C	Undoped-Zr control
			>1000	3.359			Pe C	
L-6, C-3, H-22	Beads	2.15	182	3.424		3 hr @ 2300°C	Pyro C	Zr doped-1.6 w/o Zr
			475	3.366			Xyl C	(3)
L-6, C-3, H-16	Beads	2.15	153	3.418		3 hr @ 2300°C	Pyro C	Zr doped-6.0 w/o Zr
			430	3.364			Xyl C	(4)

Footnotes:

- (1) The L-10, C-12A and L-10, C-23(2) discs showed slight three dimensional anisotropy.
- (2) Pe C - Abbreviation for proeutectic carbon.
- (3) This sample exhibited about 10-15% of a more crystalline component - most of which was not the proeutectic carbon.
- (4) This sample exhibited nearly 50% of a more crystalline component.

the bulk densities used in making the necessary absorption corrections. (For consistency with results reported previously, "standard" techniques were used throughout this group of measurements.)

An interesting effect of doping on crystallite size distribution was observed. Aluminum doping, even in small percentages, seems to enhance crystallite growth during heat treatment at 2300°C, which is accompanied by an improvement in layer stacking. However, L_c for the doped material appears to decrease as a result of heat treatment. This is because stacking order is improved in only part of the material, increasing the range of d-spacings and thereby producing broader diffraction lines. The same phenomenon apparently occurs during heat treatment of zirconium-doped samples, but in this case accompanied by formation of a more highly graphitic component -- perhaps around sites of high zirconium concentration. This crystalline component shows a tendency toward improved stacking as the zirconium concentration increases.

B. Optical and Electron Microscopy (R. D. Reiswig, L. S. Levinson)

1. High-Expansion Coke and Graphite Flour

CMF-13 Lot CL(HCTE)-2 is a sample of an air-blown, essentially isotropic coke produced by Carbon Products Division of Union Carbide Corporation. It has been calcined in vacuum to 800°C by the manufacturer, is in lump form, and is the "high-CTE" starting material for the grinding experiments described above. In its original condition it consists of large, approximately equiaxed particles which, even at electron-microscope magnifications, appear to be nearly structureless and almost free of internal voids. Under polarized light in the optical microscope, an internal structure is revealed, consisting of very small, randomly-oriented optical domains.

Several of the products of grinding this coke have been examined. Their internal structures were, of course, unchanged by grinding. The external shapes of individual particles were in general relatively equiaxed down to the limit of optical resolution, with the larger

particles quite well rounded. Electron microscopy showed that the finest grinding product, Sample T(HCTE)-17, consisted chiefly of particles smaller than 1μ dia, many of which were only 0.1 to 0.2 μ dia. Even the finest particles were more nearly equiaxed than those usually observed in coke and graphite flours, although there appeared to be some increase in acicularity in the finest size ranges.

Samples from Lot CL(HCTE)-2 were also examined after heat treatment at 2000° and at 3100°C. A slight increase in optical anisotropy may have occurred, and there was some evidence of graphitization in the appearance of a few short lamellae, no more than a few microns long. The principal change in microstructure was the appearance of numerous cracks, which were surface-connected and should facilitate comminution.

CMF-13 Lots G(HCTE)-23, -24, and -25 are graphite flours produced by Carbon Products Division by graphitizing the high-CTE coke described above. As was true of the ground coke, particle shapes in these flours were more nearly equiaxed than in most graphite flours. Internally, the particles showed randomly-oriented lamellar domain structures with a domain size of about 2μ . Very few internal voids were observed, and relatively few cracks.

2. Other Cokes and Graphite Flours

A 100-mesh Gilsocarbon flour produced by American Gilsonite Co., identified by CMF-13 as Lot C-3, was examined as-received and after heat treatment at 2000°C and at 3100°C. Some particles had well-developed lamellar structures, some contained a high proportion of carbon black and had the appearance of a pitch-binder residue, and some contained both types of structure. The particles were more nearly equiaxed and contained fewer large internal voids than most cokes. The heat-treated samples showed evidence of graphitization, but differed from the as-received material chiefly in containing metallic inclusions within the coke particles plus small amounts of precipitated graphite of the type known to be associated with the presence of certain metallic impurities. Electron-beam microprobe analysis by J. A. O'Rourke showed that the inclusions consisted principally of iron, zirconium,

and mixtures of the two in various proportions. Neither metallic inclusions nor precipitated graphite was detected in the as-received material, but chemical analysis by Group CMB-1 showed it to be relatively high in both iron (0.17%) and zirconium (0.2%).

CMF-13 Lots C-4 and C-5 are 200-mesh and 300-mesh Gilsocarbon flours. Except for finer particle sizes, they appear to be the same as Lot C-3. However, chemical analysis by Group CMB-1 showed the presence of 0.10% iron and less than 10 ppm of zirconium in Lots C-4 and C-5. Apparently Lot C-3 was contaminated at some point in its manufacture, shipment, or handling here, although at what point cannot now be determined.

Several other commercial coke and graphite flours in CMF-13 stock have been examined and characterized with regard to structure. They have been found to vary considerably in size and number of intraparticle voids, degree of development and planarity of lamellar structures, proportion of fines present, and quantity and type of tramp particles observed. However, no other great surprises have been experienced in examining these.

3. Carbon Blacks

Eagle Brand lamp black, produced by Columbian Carbon Co., was dispersed ultrasonically by the usual technique and examined in the electron microscope. The basic particle was found to be nearly spherical and about 0.05μ dia. However, the material did not in general disperse into individual particles but rather into clumps or irregular strings of particles, typically 1 to 4μ long.

As has been reported above, particles of regular Thermax carbon black (Lot TP-3) developed faceted surfaces during heat treatment at 2800°C . "Stainless" Thermax, similarly heat treated, did not; individual particles remained essentially spherical.

4. Natural Graphite Filler Addition

An extruded, resin-bonded, experimental graphite, Lot 27C6, was examined in the cured, baked (900°C), and graphitized (2860°C) conditions. It contained 41 parts of finely-ground natural graphite flour to 100 parts of coke flour, and was examined particularly for evidence that the natural graphite had deformed to fill voids between the hard, irregularly shaped coke particles. Optically it

was seldom possible to distinguish between the natural graphite and the coke. This was also true in the electron microscope in the case of the graphitized material, but here, for cured and baked specimens, the very acicular graphite flour was easily identified. To some extent the natural graphite flakes did conform to the contours of coke particles, but they showed no tendency to bend sharply around such particles, and many voids remained unfilled.

5. Cracking of AAP Graphites

The five new members of the AAP series of graphites have been discussed above under "Extrusion". They were made with high-CTE graphite as the principal filler, with and without Thermax additions, and commercial Varcum binder. Two of the Thermax-containing lots developed cracks, while the third did not. Neither of the Thermax-free lots cracked.

In preparation for microscopic examination, specimens are normally vacuum-impregnated with an epoxy resin. The extent to which the epoxy penetrates the structure is an indication of the degree to which the voids in that structure are interconnected. Among these AAP-series graphites, the three which did not crack were all well penetrated by the resin, indicating that gases evolved during their heat treatment could probably have passed out of the structure quite freely. The two lots which did crack were penetrated only very superficially by epoxy, suggesting that the interconnected porosity needed for free escape of gases was not available. The cracks in Lot AAP-24 were of the "central" type -- wider at the center than at the ends, typically not extending to the rod surface, and suggesting by their appearance that they were created by internal gas pressure. The cracks in Lot AAP-27 were of the "radial" type, which typically do reach the surface and which appear to have been caused by inhomogeneous contraction of the rod. Such cracks are not obviously related to gas evolution, although local entrapment of gases could conceivably be involved in the inhomogeneous deformation believed to produce them.

From the data listed in Table 13, which describes these graphites, it is seen that similar densities can be attained in different ways. One of these ways -- the addition of Thermax -- in this case seems to promote cracking,

perhaps by inhibiting the escape of evolved gases. Apparently, however, this tendency can be offset by reducing the proportion of binder in the raw mix. Another way is the use of a very fine flour, with which good density is achieved without the Thermax addition.

6. Scaly vs. Lamellar Microstructures

It has previously been shown that a reasonably well-developed graphite structure may have either of two characteristic microstructural appearances. These are described as "scaly" and "lamellar", and a given structure may appear in either of these aspects depending upon the angle at which the section inspected cuts the basal plane of the graphite. If this angle is high, then the microstructure observed is lamellar; if it is low, the appearance is scaly.

To evaluate more completely the effect of orientation on microstructural appearance, pyrolytic graphites annealed at 2690° and at 2860°C have been sectioned at various angles to the average basal-plane orientation and examined in the electron microscope. A section at 5° to the average basal plane had a fine scaly appearance. At 15° the scaly structure was coarser, and a few lamellae appeared. At 30° the structure was still mostly scaly, but with a higher proportion of lamellar regions. At 45° lamellar structures predominated, but with a few scaly areas. The 50° and 90° sections appeared to be entirely lamellar.

Because annealing did not eliminate growth cones from the structure of the pyrolytic graphite, there was ambiguity in these experiments with regard to orientation of the basal plane. This will be eliminated by examining sections through a swivelled pyrographite from which, locally, the growth-cone structure has been eliminated by torsional strain at a high temperature.

7. Microradiography

In addition to the examination of AAQ1 graphite described above, samples of several other extruded CMF-13 experimental graphites have been impregnated with sulfur and microradiographed by R. A. Morris, Group GMX-1. Of particular interest was the observation of 6-fold symmetry in the porosity distribution of a rod from graphite Lot AAB8. Evidently this is associated with use of a

6-hole breaker plate, which divides the raw mix into 6 separate streams as it enters the extrusion die. Since a high-density region was observed at the axis of the extruded rod, where all 6 streams merge, it appears that in this case porosity may have been reduced locally where individual material streams merged in the die.

The thinnest (0.0054-in. thick) longitudinal section of AAB8 graphite which was sulfur-impregnated and radiographed clearly shows a "chevron" arrangement of long, thin pores near the cylindrical rod surface. Apparently this results from inclination of acicular filler particles at about 30° to 45° to the extrusion axis.

A 0.006-in. thick longitudinal section of a rod from Lot AAH7 showed, radiographically, a well-defined, centrally-located stripe which differed significantly in structure from the rest of the section. This was verified by microscopic examination to be an axial region from which, somehow, coarse particles had been excluded completely.

VI. PHYSICAL AND MECHANICAL PROPERTIES

A. Elastic Properties of POCO Grade AXF Graphite

(P. E. Armstrong)

Elastic modulus measurements on a group of specimens machined from a 4-in. dia bar of POCO Grade AXF graphite are summarized in Tables 19 and 20. Young's modulus and internal friction were measured between ambient temperature and 1475°C by an improved capacitive technique, and Young's modulus between ambient and 2000°C by a tensile wire technique.

With respect to Young's modulus, this material was essentially isotropic. However, some anisotropy appeared in internal friction. One room-temperature measurement of shear modulus was made and, assuming isotropic behavior, Poisson's ratio was calculated to be 0.28.

A maximum in Young's modulus was found to occur at the relatively low temperature of about 1100°C, with a corresponding minimum in internal friction at the same temperature. Above 1100° Young's modulus diminished to a value at 2000°C which was 6% lower than the room-temperature value. At 1100° internal friction was only about one-fifth of the room-temperature value. At higher

TABLE 19
ROOM TEMPERATURE PROPERTIES OF POCO TYPE AFX GRAPHITE, FOUR-INCH DIAMETER BILLET

<u>Sample Configuration</u>	<u>Number of Samples</u>	<u>Average Density g/cc</u>	<u>High/Low</u>	<u>Average Young's Modulus 10⁶ psi</u>	<u>High/Low</u>	<u>Average Internal friction x 10³</u>	<u>High/Low</u>
1/4 inch dia rods, axis parallel to billet axis	9	1.792	1.762/1.809	1.820	1.849/1.794	1.57	1.82/1.36
1/4 inch dia rods, axis perpendicular to billet axis	6	1.810	1.834/1.799	1.795	1.826/1.776	2.03	2.26/1.83
0.475 inch dia rods, axis parallel to billet axis	3	1.808	1.818/1.801	1.840	1.861/1.827	1.60	1.72/1.36
				<u>Shear Modulus 10⁶ psi</u>		<u>Poisson's Ratio</u>	
1/4 inch dia rod, axis parallel to billet axis	1	1.800	---	0.715		0.28	---

temperature this increased, to about one-half of the room-temperature value at 1500°C.

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TABLE 20

YOUNG'S MODULUS AND THERMAL EXPANSION OF ONE SAMPLE OF POCO TYPE AXF GRAPHITE

<u>Temperature</u> <u>Degrees Centigrade</u>	<u>Young's Modulus</u> <u>10⁶ psi</u>	<u>Internal Friction</u> <u>x 10³</u>	<u>Change in length</u> <u>length at 25C</u> <u>x 10³</u>
25	1.827	1.04	0
100	1.832	1.00	0.5
200	1.837	.93	1.4
300	1.844	.86	1.9
400	1.850	.78	2.7
500	1.856	.70	3.5
600	1.865	.61	4.4
700	1.874	.50	5.3
800	1.883	.39	6.2
900	1.891	.30	7.2
1000	1.893	.23	8.2
1100	1.896	.21	9.3
1200	1.892	.25	10.4
1300	1.887	.30	11.5
1400	1.878	.38	12.7
1500	1.867	.49	13.8
1600	1.855		14.9
1700	1.807		16.0
1800	1.809		17.1
1900	1.765		18.3
2000	1.712		19.4