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PROGRESS REPORT

CMB-13 Research on Carbon and Graphite

Report No. 21

Summary of Progress from February 1 to April 30, 1972

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This report presents the summary of progress of CMB-13 research on carbon and graphite at LASL. The four most recent reports in this series, all unclassified, are:

LA-4770-MS
LA-4917-PR

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CMB-13 RESEARCH ON CARBON AND GRAPHITE
REPORT NO. 21: SUMMARY OF PROGRESS FROM FEBRUARY 1 TO APRIL 30, 1972

by

Morton C. Smith

I. INTRODUCTION

This is the twenty-first in a series of progress reports devoted to carbon and graphite research in LASL Group CMB-13, and summarizes work done during the months of February, March, and April, 1972. It should be understood that in such a progress report many of the data are preliminary, incomplete, and subject to correction, and many of the opinions and conclusions are tentative and subject to change. This report is intended only to provide up-to-date background information to those who are interested in the materials and 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 CMB-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 materials 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.

Since its beginning, this research has been sponsored by the Division of Space Nuclear Systems of the United States Atomic Energy Commission, through the Space Nuclear Propulsion Office. More recently additional general support for it has been provided by the Office of Advanced Research and Technology of the National Aeronautics and Space Administration. Many of its facilities and services have been furnished by the Division of Military Application of AEC. The direct and indirect support and the guidance and encouragement of these agencies of the United States Government are gratefully acknowledged.

II. RAW MATERIALS

A. Krecabeads (R. D. Reiswig, L. S. Levinson, J. A. O'Rourke)

Four samples of spherical carbon beads called "Krecabeads", were obtained from the Kreha Corporation of America, and have been examined by optical and electron microscopy and by x-ray diffraction. These beads are manufactured from "pitch" by the Kureca Chemical Industry Co., Ltd., of Tokyo, and are stated to have relatively high particle density ($1.5-2.0 \text{ g/cm}^3$), to be isotropic, and to be available in a variety of size fractions for various applications.

TABLE I
MICROMEROGRAH SAMPLE STATISTICS FOR KRECABEADS

Grade	Mean Diam, $\bar{d}_3, \mu$	Variance, $s^2_{d_3}, \mu^2$	Calc. Surface Area, $S_W, m^2/g$	Coeff. of Variation, CV_d
SC	64.7	1859	0.145	1.08
SG	98.7	1281	0.906	1.08
MC	164.6	1651	0.022	0.23

In each of the samples examined the beads were found to contain many cracks and pores, some of which were inaccessible to the mounting resin at 2000 psi.

Grade SC Krecabeads are nominally less than 50 μ diam, and are said by their manufacturer to have been heat-treated to 1000°C. X-ray measurements indicated an L_c of less than 11.0 Å and d_{002} of about 3.53 Å, representing one of the most disorganized carbons ever examined here. Micromerograph analysis indicated the presence of a significant weight fraction of particles greater than 50 μ diam, and particles as large as 130 μ diam were measured optically. Helium density was 1.738 g/cm³.

Grade SG beads are nominally less than 100 μ diam and are stated to have been heat-treated by the manufacturer to 2800°C. However, x-ray diffraction measurements gave $L_c = 70.5$ Å, $d_{002} = 3.393$ Å, indicating that they had graphitized poorly. Most of each bead was optically isotropic and featureless in microstructure, resembling a glassy carbon. Some graphitic material occurred as inclusions, pore linings, and thin surface layers. Maximum particle size was about 140 μ . Helium density was 1.612 g/cm³.

Grade MG beads are nominally 100 to 250 μ diam, and are also stated to have been heat-treated to 2800°C. Their x-ray parameters were $L_c = 56.1$ Å and $d_{002} = 3.402$ Å, indicating even less development of the graphite structure than in the SG beads. However, microstructures of the two grades of beads were very similar. Maximum particle size of the MG beads was about 300 μ , and their helium density was 1.586 g/cm³. A thin, discontinuous layer of lamellar materials was found on the

surfaces of many beads, and some beads also contained large internal patches of lamellar material.

Grade MC beads have the same nominal size range as MG beads, but are stated to have been heat-treated only to 1000°C. Their x-ray parameters were $L_c < 11.0$ Å and $d_{002} \cong 3.54$ Å, representing a degree of disorganization similar to that of the SC beads. Maximum bead diameter was about 300 μ , and microstructures were essentially featureless except for small, frequently spherical inclusions about 1 to 20 μ diam. Helium density was 1.746 g/cm³, which was unexpectedly high relative to that of the grade MG beads.

Micromerograph sample statistics for the SC, SG, and MC grades are listed in Table I. None of these particle-size distributions was well approximated by the log-normal model, and the statistics given are therefore based on the finite interval model.

B. Fluid Coke (R. D. Reiswig, L. S. Levinson, J. A. O'Rourke)

Samples of coke from the Humble Oil Co. fluidized-bed coker at Billings, Montana, have been examined with regard to microstructure and x-ray parameters.

The fluid coke itself consists largely of spherulites up to about 300 μ diam, each having a generally circumferential orientation of basal planes much like that in a Gilsocarbon. Heat-treating the fluid coke for 0.5 hr at about 2815°C increased L_c from 13.7 to 198 Å and reduced d_{002} from 3.47 to 3.378 Å, indicating that it graphitizes reasonably well but not to a large crystallite size.

A lump scraped from the inner wall of the coker consisted of fluid coke spherulites cemented together with material resembling pyrolytic carbon, and of bulk material made up of large, randomly oriented domains

interspersed with structures resembling large growth cones in a pyrolytic graphite. Upon heat-treatment for 0.5 hr at about 2815°C, L_c of this sample increased from 13.5 to 183 Å, and d_{002} decreased from 3.45 to 3.380 Å. Thus, there was very little difference in graphitizing behavior between material from the coker wall and the fluid coke itself, in spite of the more disorganized appearance of the latter.

From its microstructure it appears that this fluid coke, used as a filler, should produce an isotropic graphite having a very high coefficient of thermal expansion.

III. THE USE OF ORGANOMETALLIC COMPOUNDS TO MODIFY THE STRUCTURES OF CARBONS DERIVED FROM FURFURYL ALCOHOL RESINS (E. M. Wewerka, R. J. Imprescia, J. A. O'Rourke)

It is well known that, in the absence of filler materials, the pyrolysis and high-temperature heat-treatment of furfuryl alcohol resins results in the formation of amorphous or glass-like carbons. Similar heat treatments in the presence of a filler result in formation of a moderately graphitic residue from resins of the same type. This is thought to be the result of a structural alignment which develops in the resin as it shrinks around filler particles during curing and the early stages of baking.

Whether the furfuryl alcohol resin is used alone as a carbon precursor or instead is used as a binder in the manufacture of conventional carbons and graphites, it would be very desirable to control the degree to which its carbon residue graphitizes, since this strongly affects the properties of the residue. A program intended to develop this type of structural control has therefore been conducted over a period of several months.

Seemingly, the most straightforward way to modify the structure of a resin-derived carbon is to modify chemically either the basic structure of the precursor resin or the manner in which it crosslinks during curing. In several experiments, however, when both the resin structure and its initial crosslinking and pyrolysis behavior were significantly altered, it was found that the crystallographic parameters of the heat-treated carbon residue were not detectably changed. This result is not completely

understood. We believe, however, that it is traceable to the latter stages of resin pyrolysis, in which structural scissioning and other extensive molecular rearrangements erase the evidence of earlier chemical structures or transformations. In any case, since no control over the structure of the carbon residue was developed by modifying the structure of the precursor resin, other means of achieving this end were sought.

A number of instances have been discussed in the literature in which metals or metallic compounds have been used to cause structural reorganizations of amorphous or glass-like carbons into more graphitic ones. Independent studies by Fitzer *et al.* (Carbon, 6, 433 [1968]) and by Gillot *et al.* (Ber. Deut. Keram. Ges., 45, 224 [1968]) have led to the postulation that such reorganizations result from phase interactions which cause amorphous carbon to dissolve in metal carbides at moderate to high temperatures and subsequently to reprecipitate as well-organized carbon. In the few reported instances in which metallic compounds have been added directly to various thermosetting resins prior to crosslinking and carbonization (Yokokawa *et al.*, Carbon, 4, 459 [1966] and Carbon, 5, 475 [1967]) appreciable increases were observed in the degree of ordering of the resulting carbon. It was not known, however, whether the structural modification of carbon produced by using a metal-doped precursor resin resulted from a mechanism similar to that proposed for the reorganization of amorphous carbons by metallic additives.

Little work has been done on this behavior in the specific case of furfuryl alcohol resins -- these having been included only as a small part of general surveys of the effects of a limited number of metallic additives on the carbons derived from a rather large variety of thermosetting resins. Accordingly, we decided to investigate the use of metallic additives as a possible means of developing some degree of control over the structures of furfuryl-alcohol-resin carbons. For this purpose we obtained a wide variety of organometallic compounds.

The use of organometallic additives is a marked departure from the kinds of additives that have been used in the past. We reasoned that the organic parts of these

TABLE II
THE EFFECTS OF ORGANOMETALLIC ADDITIVES ON THE STRUCTURES OF CARBONS
DERIVED FROM FURFURYL ALCOHOL RESINS

Additive	% Metal ^a	Apparent Solubility	Carbon Yield, % ^b	L_c , Å ^c	Remarks
None	---	---	37	27	
Maleic Anhydride	---	Complete	53	28	
Titanium Oxyacetylacetonate	0.9	Complete	47	218	
Vanadium Acetylacetonate	0.7	Complete	49	194	
Zirconium Acetylacetonate	0.9	Complete	43	153	
Cobalt Acetylacetonate	1.2	Complete	41	83	
Iron Acetylacetonate	0.8	Complete	40	81	
Nickel Acetylacetonate	1.0	Complete	32	79	Major Phase (74 %)
Copper Acetylacetonate	1.1	Partial	32	38	Major Phase (74 %)
Scandium Oxalate	1.3	Partial	28	35	Major Phase (71 %)
Manganese Acetate	1.1	Poor	29	31	
Antimony Triacetate	2.0	Poor	44	28	Major Phase (96 %)
Zinc Acetylacetonate	1.1	Complete	37	27	
Palladium Acetylacetonate	1.7	Partial	34	27	Major Phase (98 %)
Cadmium Acetate	2.1	Poor	39	26	
Magnesium Acetylacetonate	0.6	Poor	37	26	
Pentaethylantate	1.4	Complete	46	23	

^a Percent metal in resin due to organometallic addition.

^b Percent of original resin remaining after heat-treatment to 2800°C.

^c In cases where resin carbon had two phases present, the L_c of only the major phase is given.

compounds would render them more easily dispersable in the furfuryl alcohol resins than were the pure metals, metal carbides, and inorganic metal compounds used in earlier work, or better yet might make them soluble. Whatever the functions of the metal atoms during formation or reorganization of the resulting carbon structures, seemingly they would be better served if the metal atoms were as well dispersed as possible throughout the precursor resin prior to carbonization. Further, the interpretation of experimental results would be complicated by the presence of the dispersed metallic additive in particles large enough so that structural ordering could result from shrinkage of the resin around them -- which might be the case for particles of completely insoluble additives.

Each of the organometallic compounds was tested by dispersing or dissolving it in a standard furfuryl alcohol resin. The metal-doped resins were then cured and heat-treated to 2800°C. The effects of the additives on the structures of the resulting carbons were determined by optical and electron microscopy and by x-ray diffraction analysis. For some of the organometallics, the effects of additive concentration, of the presence of a filler material, and of an added curing catalyst were also examined. To test the generality of the effects of organometallic additives on other thermosetting resins, the carbons produced from an organometallic-doped phenolic resole were also investigated.

TABLE III
EFFECTS OF ADDITIVE CONCENTRATION ON THE STRUCTURES OF CARBONS
DERIVED FROM FURFURYL ALCOHOL RESINS

Additive ^a	Concentration %		Carbon Yield, % ^c	L _c , Å
	Compound	Metal ^b		
None	---	---	37	27
Maleic Anhydride	1	---	49	28
Maleic Anhydride	5	---	53	28
V	1	0.1	48	197
V	5	0.7	49	194
V	10	1.4	43	190
Fe	1	0.2	43	62
Fe	5	0.8	40	81
Fe	10	1.6	40	85
Zr	1	0.2	38	148
Zr	5	0.9	43	153
Ti	1	0.2	46	185
Ti	5	0.9	47	218

^aMetals added as organometallic compounds.

^bPercent metal in resin due to organometallic addition.

^cPercent of original resin remaining after heat-treatment to 2800°C.

The first part of the study was directed toward determining which of the variety of organometallic compounds available would promote graphitization of the carbon derived from a furfuryl alcohol resin when they were added to the resin prior to heat-treatment. For this purpose, 5% by weight of each of the organometallics were dissolved or dispersed in 10 g samples of a 400 cp, acid-polymerized furfuryl alcohol resin. The samples of metal-doped resin were then cured and heat-treated to 2800°C. Crystallite sizes of the heat-treated carbon specimens, measured by x-ray diffraction, are listed in Table II, together with other pertinent experimental data. These results show that several of the carbons derived from metal-doped resins had more highly developed structures than did those obtained from the resin alone or from the resin catalyzed only by the addition of maleic anhydride. In particular, additions of vanadium, zirconium, and titanium organometallics resulted in relatively

well-developed graphite structures -- with crystallite sizes of 194, 153, and 218 Å respectively. Carbons derived from resins doped with cobalt, iron, and nickel organometallic compounds had moderately developed structures. The other additives tried had little or no effect on structure, yielding carbons which remained highly disorganized even after heat-treatment to 2800°C.

Optical and electron microscopy showed that the graphitic carbons derived from resins doped with vanadium, zirconium or titanium additives had uniform, smooth-textured microstructures composed of small, randomly oriented optical domains. A small metal-carbide particle could occasionally be detected in the structures of these carbons.

Carbons derived from resins containing cobalt, iron or nickel organometallic additions were also found to be uniform in structure and relatively smooth in texture. However, in these samples the graphite structures were

too poorly developed to be observed microscopically. X-ray diffraction indicated that carbon samples from resins doped with either iron or nickel contained small amounts of a phase which was more highly graphitic than the major phase present. The iron-doped sample was found microscopically to contain spherical pocks, up to about 15 μ diameter, scattered throughout the carbon matrix. These were composed of a carbon which was coarser-grained than the matrix material.

Several of the additives were investigated in concentrations ranging from 1% to as high as 10% of the resin, with the results listed in Table III. It is of interest that even 1% by weight of the organometallic additive, representing as little as 0.1% of metal, is usually sufficient to promote graphitization of the carbon residue. There seems to be little advantage in increasing the proportion of organometallic to 5% or 10%.

At this point it was natural to speculate concerning the mechanism by which graphitization of the resin-derived carbons was promoted. Two possibilities occurred to us. One was that the organometallic had little effect on the initial formation of amorphous carbon during pyrolysis, but that, during higher-temperature heat-treatment, the dispersed metal derived from it was converted to metal-carbide particles which then "catalyzed" graphitization in the manner postulated by Fitzer *et al.* and by Gillot *et al.* A second possible mechanism was conceived on the basis of a correlation observed in the data of Table II. Only those organometallic additives which were soluble in the precursor resin were effective in promoting graphitization of the carbon residue. The criterion of additive solubility suggested that the metals might be interacting chemically with the precursor resin prior to carbonization in such a way as to hinder or even prevent crosslinking of the resin. A resin which has been crosslinked to a lesser degree than normal might be expected to yield a more graphitic carbon when heat-treated. Subsequent experiments were designed to make possible a choice between these two mechanistic possibilities.

The effect of incorporating a curing catalyst (maleic anhydride) into the precursor resin together with 5% additions of the organometallic compounds was then studied.

The various catalyst-additive combinations investigated are listed in Table IV, together with carbon yields and the crystallite sizes of the graphitized carbon residues. It is evident that the degree to which graphitization of the carbon is enhanced is not appreciably different for resins containing both maleic anhydride and the organometallic additive than for resins containing only the organometallic. This observed lack of dependence of crystallite size on the presence or absence of the maleic anhydride catalyst tends to rule against a mechanism in which the metallic additive interferes chemically with crosslinking of the resin.

The usual function of a curing catalyst such as maleic anhydride is to aid in the rapid development of a completely crosslinked resin structure before the molecular scissioning and rearrangements accompanying resin carbonization begin. In the absence of curing catalysts, thermal processes alone result in the slower development of a system of crosslinks, which may therefore be incomplete. The result is that a relatively large proportion of the resin structure is left loosely bound, and therefore is more easily lost as volatile material during carbonization. This is illustrated in Table II by the fact that the addition of the curing catalyst to the precursor resin increased carbon yield from 37% to 53%. If the observed increase in the graphitizing tendency of the resin carbon from the metallic addition were related to chemical modification of the degree of resin crosslinking, it would be expected that addition of a curing catalyst to an organometallic-doped resin would sufficiently enhance the crosslinking tendency so that the metallic additive would be less effective than when no catalyst was used. This was not the case, and so it is doubtful that an organometallic addition has a significant effect on resin crosslinking.

One useful observation of a practical nature does emerge from the data presented in Table IV. Carbon yields of the metal-doped resins, which were previously (Tables II and III) rather low, have been increased to quite respectable levels by the addition of a curing catalyst, without significantly altering the degree of graphitization of their heat-treated carbon residues.

TABLE IV
EFFECTS OF ADDITIONAL CATALYST ON STRUCTURES OF CARBONS
DERIVED FROM FURFURYL ALCOHOL RESINS CONTAINING 5% ORGANOMETALLIC ADDITIONS

<u>Metal</u> <u>Additive^a</u>	<u>Maleic</u> <u>Anhydride, %</u>	<u>Carbon</u> <u>Yield, %^b</u>	<u>L_c, Å</u>
None	0	37	27
None	5	53	28
V	0	49	194
V	5	48	158
Ti	0	47	218
Ti	2.5	55	205
Ti	5	53	240
Zn	0	37	27
Zn	2.5	48	29
Zn	5	48	25
Co	0	41	83
Co	5	50	67

^a Added as an organometallic compound.

^b Percent of original resin remaining after heat-treatment to 2800°C.

In another part of this study we examined the behavior of organometallic-doped furfuryl alcohol resins when they were used as binders for glass-like carbon filler materials. The results of this investigation also tend to favor the "catalytic graphitization" mechanism alluded to above.

In the presence of a particulate filler, furfuryl alcohol resin binders are known to yield relatively graphitizable carbons, presumably as a result of the structural alignment which occurs within the resin as it shrinks around an essentially incompressible filler particle. Thus, when the filler is a glass-like carbon, the carbon residue from the binder resin will in general develop a better-organized graphite structure during high-temperature heat-treatment than does the nearly amorphous glass-like filler. For thermodynamic reasons (which are amply discussed by the investigators referred to above), the process of catalytic graphitization would be expected to reorganize the glass-like filler material in preference to the moderately graphitic binder residue.

In a series of heat-treated samples which originally contained 50% by weight of glass-like carbon filler and 50% furfuryl alcohol resin doped with either 1% or 5% of an organometallic compound, this was evidently the case. Microstructural examination indicated that the filler material was reorganized in preference to the binder carbon residue.

Because of the accompanying reorganization of the filler, it was not possible in these experiments to assess quantitatively the degree to which either the binder carbon or the filler material, individually, had been graphitized. However, in all samples examined, the glass-like carbon filler appeared to have developed more highly ordered structures than had the binder-carbon residues. In most cases there was evidence that the binder residue had been reorganized only in regions which were relatively remote from filler particles and within which strain-induced ordering had therefore not previously developed.

As might be expected, the organometallic additives which were most effective in promoting graphitization of the carbon residues from unfilled precursor resins -- compounds of vanadium, zirconium, and titanium -- tended also to be the most effective reorganizers of the filler material. The extent to which reorganization of the glass-like filler occurred was found to depend somewhat on additive concentration. With lower organometallic concentration, incomplete reorganization was observed more frequently.

In the presence of a glass-like carbon filler, then, we were unable by the use of organometallic additions to enhance the graphitization of the already reasonably well-ordered carbon residue of a furfuryl alcohol resin binder. We would, however, expect to be able to do so when a normally graphitizable filler material was used instead of a glass-like carbon filler. In this case, the more disorganized phase present would ordinarily be the binder-carbon residue, and we would expect it to be reorganized by the high-temperature processes in preference to the initially better-ordered filler material. Experimentally, it will be difficult to assign quantitative values to the degree to which ordering has occurred in the two types of material. Even relatively large changes in the degree of graphitization of the binder-carbon residue are not easily detected when a large proportion of highly graphitic filler material is also present. Physical-property measurements instead of x-ray parameters may, therefore, provide better indications of the effects and usefulness of organometallic additions to the binder in a normal filler-binder system.

Implicit in the thermodynamic explanation of the high-temperature catalytic graphitization of disordered carbons is the expectation that, in the presence of an effective metal catalyst, any such carbon -- whatever its origin -- should be reorganized during high-temperature heat-treatment. To test this, we dispersed 5% by weight of the vanadium, zirconium and titanium organometallic compounds, individually, into samples of a 2000 cp phenolic resole, and subsequently examined the heat-treated carbon residues. The crystallite sizes of these heat-treated residues, listed in Table V, indicate that the

TABLE V
EFFECTS OF ORGANOMETALLIC ADDITIVES
ON THE STRUCTURES OF CARBONS
DERIVED FROM A PHENOLIC RESOLE

Additive	% Metal	$L_c, \text{\AA}$
None	---	26
Vanadium Acetylacetonate	0.7	206
Zirconium Acetylacetonate	0.9	150
Titanium Oxyacetylacetonate	0.9	250

organometallic additions have increased the graphitizability of the normally disordered carbon residue of the phenolic resin to a degree comparable to that observed for furfuryl alcohol resins. It is probably safe to conclude that the addition of these same organometallic compounds to any other polymeric precursor which normally yields "hard" or glass-like carbons will also result in the reorganization of that carbon during high-temperature heat-treatment to a higher degree of structural order.

III. FABRICATION

A. Soaking-in of the Binder (H. D. Lewis)

An investigation of the effect of storing blended, resin-bonded mixes for various periods of time before extruding them was described in Report No. 20 in this series. The results of that investigation indicated that optimal "soaking" times were about two and about eight days, and that intermediate soaking times resulted in reduced bulk density of the finished graphite.

To verify the effect of intermediate soaking times, two additional extruded graphites were manufactured from the same mix composition previously used: graphite ADK15, which was soaked for 120 hours (5 days) between blending and extrusion, and graphite ADK16, which was soaked for 96 hours (4 days). Manufacturing conditions and measured properties are summarized in Tables VI and VII. Both mixes were difficult to extrude. The mix for ADK16, soaked for 4 days, could not be extruded without forming longitudinal surface cracks, although graphitized density was relatively high.

TABLE VI
EXTRUSION CONDITIONS, ADK GRAPHITES

Specimen Number	Soaking Time		Pressure psi	Velocity in./min	Vacuum Torr	Temperature, °C		Green Dia, in.
	Days	Hours				Mix	Chamber	
ADK15	5	120	~ 12,000	166	400	50	48	0.503
ADK16	4	96	~ 9,000	163	400	50	45	0.505

TABLE VII
PROPERTIES OF ADK GRAPHITES

Specimen Number	Soaking Time		Bulk Density g/cm ³	Binder Carbon Residue, %	Electrical Resistivity μΩ cm
	Days	Hours			
ADK15	5	120	1.892 ± 0.006 ^b	50.7 ± 0.6	1140 ± 12
ADK9 ^a	6-5/6	164	1.894 ± 0.002	46.2 ± 0.2	1154 ± 8
ADK16	4	96	1.873 ± 0.010	48.8 ± 2.7	1176 ± 12
ADK4 ^a	4	96	1.876 ± 0.001	48.6 ± 0.3	1169 ± 16

^aPreviously reported.

^bVariability in seven rods, reported as ± one standard deviation.

The measured properties of graphites ADK4 and ADK9, which were previously reported, are included in Table VII for comparison. Results on ADK15 and ADK16 are in good agreement with those of the original experiment, and again indicate that less-than-optimum properties can be expected if graphite mixes of this type are stored for more than two but less than eight days prior to extrusion.

B. Phenolic-Bonded Extrusions (H. D. Lewis, E. M. Wewerka, R. J. Imprescia)

A series of extrusions has been made to investigate the general usefulness of phenolic resin binders for the manufacture of polycrystalline graphites. The immediate objectives of the initial investigation were: (1) To determine the mix compositions and extrusion conditions required to produce "standard" 0.5-in. diam phenolic-resin-bonded rods, which might later be scaled up to larger diameters; (2) To investigate the behavior of phenolic-bonded artifacts during curing, baking, and graphitization; (3) To compare the behaviors of several different phenolic resins synthesized in CMB-13; (4) To

compare the properties of extruded phenolic-bonded graphites with those of otherwise similar graphites bonded with furfuryl alcohol resins.

The first two extrusion mixes prepared, Lots ADM1 and ADM2, both contained 85 parts by weight of Great Lakes grade 1008-S graphite flour and 15 parts of Thermax carbon black. Resin PR-6, a resol, was used in mix ADM1 and resin PR-10, a novolac, was used in mix ADM2. Both resins were synthesized by E. M. Wewerka in the course of preliminary studies of problems involved in the batch synthesis of phenolic resins suitable for use as graphite binders. Because of the small amount of material in each batch, viscosities of the two resins were not measured. However, comparisons of their flow characteristics with those of other resins of known viscosity indicated that the room-temperature viscosity of resin PR-6 was approximately 2500 cp and that of PR-10 was about 8000 to 10,000 cp.

Mix ADM1 contained 26.3 pph of the resol resin, PR-6. The resin was diluted with acetone to reduce its viscosity, hand-mixed with the filler and carbon black,

TABLE VIII
EXTRUSION CONDITIONS, ADM GRAPHITES

Rod Numbers	Binders	Pressure psi	Velocity in./min	Vacuum Torr	Temperature, °C		Green Dia, in.
					Mix	Chamber	
ADM1-1, ADM1-2	PR-6, 26.3 pph	10,670	13.7	400	48	25	0.501
ADM1-3 thru ADM1-8	PR-6, 26.3 pph	9,440	11.7	400	48	25	0.502
ADM2-1 thru ADM2-4	PR-10, 27.6 pph	22,500	~1.0	400	80	42	0.501

and the wet mix was then twin-shell blended for 15 minutes and passed through the food-chopper five times. The conditioned mix was then extruded as 0.5-in. diam rod at 167 in./min, an extrusion velocity equivalent to that normally used for furfuryl-alcohol-resin bonded mixes. At this rate, the phenolic-bonded ADM1 mix issued from the extrusion die in short lumps containing many cracks. The extruded mix was chopped twice and re-extruded at about one tenth of the original rate, which produced a coherent rod. This rod was chopped twice, and extruded a third time, using two different speeds: 13.7 in./min for the first 30 inches, at an extrusion pressure of 10,670 psi; and 11.7 in./min for the last 46 inches, at a pressure of 9440 psi. This reduction in extrusion velocity slightly improved the qualitative appearance of the green rod. However both rates are very low, and it is evident that future experiments must include attempts to increase extrusion velocity while still maintaining integrity of the rod.

Final extrusion conditions for the ADM1 mix are summarized in Table VIII. Extrusion pressures, as indicated by the record of pressure vs ram travel, were extremely uniform at both extrusion velocities compared with pressures recorded during extrusion of typical furfuryl-alcohol-resin bonded mixes. The ADM1 extrusions had very smooth, dense-appearing surfaces. Rod diameter was 0.501 in. for the first portion of the extrusion and 0.502 in. for the last. Rods 8-in. long were cut from the green extrusion for separate heat-treatments. Rods ADM1-1 and ADM1-2 were taken from the section extruded at 13.7 in./min, and rods ADM1-3 through ADM1-8 were cut from the section extruded at 11.7 in./min.

All eight of the ADM1 extruded rods were cured to 200°C in a "standard" 66-hour cycle developed for furfuryl-alcohol-resin bonded graphites, which appeared also to be satisfactory for the phenolic-bonded mix. Rods ADM1-6 and ADM1-7 were then baked in a relatively fast cycle, involving a constant rate of temperature rise to 900°C over a period of 24 hours, as a preliminary indication of the feasibility of producing much thicker sections of phenolic-bonded graphites. Rods ADM1-2, -3, and -8 were baked in 44-hour linear cycles to 900°C, and rods ADM1-1, -4, and -5 in 90-hour linear cycles to 900°C. All baking was done in a flowing argon atmosphere. All rods were graphitized together in a "standard" heat-treatment to approximately 2825°C. Visual examination revealed no surface defects in any of the graphitized rods.

Properties of these graphites so far determined are listed in Table IX. Bulk densities and binder-carbon residues are somewhat lower than for well-made furfuryl-alcohol-resin bonded graphites containing the same filler mix, in spite of which electrical resistivity is slightly lower and Young's modulus is significantly higher for the phenolic-bonded graphites. Although there is no strong trend of properties with extrusion speed or baking rate, it appears that the lower speed and longer heating cycle may improve properties slightly. X-ray diffraction measurements on specimen ADM1-5 indicate that the binder carbon has graphitized reasonably well.

Microscopic examination of ADM1 graphites after various stages of heat-treatment showed about the same degree of microcracking at all stages, indicating that the few microcracks observed were probably formed during extrusion. The structure appeared very dense,

TABLE IX
PROPERTIES OF ADM GRAPHITES

Specimen Number	Baking Cycle, hr	Density g/cm ³	Binder-Carbon Residue, %	Electrical Resistivity $\mu \Omega \text{ cm}$	Young's Modulus 10 ⁶ psi	X-Ray Parameters, Å	
						L _c	d ₀₀₂
ADM1-1	90	1.795	45.3	1128	2.38	---	---
ADM1-2	44	1.781	43.0	1152	2.33	---	---
ADM1-4	90	1.831	46.2	1093	2.58	---	---
ADM1-5	90	1.835	46.0	1091	2.60	460Å	3.361Å
ADM1-3	44	1.802	44.3	1123	2.49	---	---
ADM1-8	44	1.794	45.9	1100	2.48	---	---
ADM1-6	24	1.793	46.1	1096	2.48	---	---
ADM1-7	24	1.790	46.1	1098	2.47	---	---
ADM2-4 (Average)	90	1.81 ^a	48.78	---	---	---	---

^a All rods were bowed or warped as much as 1/8 to 3/16 inch, making length measurements and density calculations uncertain.

and there were almost no filler-binder interface cracks, which are a common defect in resin-bonded graphites.

Extrusion mix ADM2 was made from the same filler-carbon black mix but with 27.6 pph of the PR-10 phenolic novolac binder, diluted with acetone to reduce its viscosity and catalyzed with 4.8 wt % of hexamethylenetetramine. It was hand-mixed, twin-shell blended, and chopped by the same procedures used for ADM1. However, the mix was very stiff and sticky, and at the maximum ram pressure (22,500 psi) the extrusion speed was only about 1 in./min. It was extruded only once, and contained obvious surface cracks and a centrally located axial crack along the entire length of the rod. However, because of the danger of jamming the press, repeated extrusion was not attempted. Although the extrusion produced was obviously of poor quality, four rods were cut from it and heat-treated, to determine bulk density and carbon residue. Graphitized density was about the same as that of the ADM1 rods, and carbon residue was slightly higher. No other properties were measured.

Although the novolac type of phenolic binder does not appear promising at this very early stage of the investigation, its behavior can undoubtedly be improved --

perhaps simple by reducing its viscosity. The phenolic resol binder appears very interesting, and will be investigated further.

C. Ablation Specimens (R. J. Imprescia)

Six hot-molded graphites have been manufactured for ablation studies, machined into models, and shipped to the NASA-Ames Research Center for testing. Mix compositions and graphitized densities of these specimens are listed in Table X.

In all cases, the principal filler material used was a Union Carbide Corporation non-needle petroleum coke, CMB-13 Lot CNN-1. In five of the graphites the coke was mixed either with Thermax carbon black (CMB-13 Lot T-1), a coarse thermal black, or with Carbolac 1 (CMB-13 Lot T-3), a very fine channel black. Specimen 63H-1 was made with Carbolac 1 which had been calcined to 1820°C. All other graphites were made from as-received raw materials. In all cases the binder used was Allied grade 30M coal-tar pitch.

Standard solvent-blending and hot-mixing methods were used to prepare and condition the raw mixes. The models were molded to nearly their finished shape by our standard hot-molding (pressure-baking) process, using

TABLE X
GRAPHITES FOR ABLATION TESTING

Model No.	Filler Composition, wt % ^a			Graphitized Density, g/cm ³
	CNN-1	T-1	T-3	
83 A-1	100	---	---	1.86
83 B-1	95	5	---	1.85
83 C-1	90	10	---	1.86
83 D-1	80	20	---	1.86
83 E-1	98	---	2	1.88
83 H-1	96	---	4 ^b	1.89

^a Raw Materials: CNN-1 --- Non-needle petroleum coke, Union Carbide Corp.
T-1 --- Thermax carbon black, Thermatomic Carbon Co.
T-3 --- Carbolac 1, Cabot Corp.

^b Heat-treated to 1815°C prior to use.

graphite dies, a pressure of approximately 6000 psi, and a heating rate of 50°C/hr to 900°C. Graphitization was in flowing helium to 2800°C, in a 10-hour cycle. Because of the relatively high molding pressure used, densities of these specimens are somewhat higher than usual for graphites of this type.

In previous experiments Carbolac 1 has proved to be a useful additive for improving the properties of hot-molded graphites, but a difficult material to work with. In particular, additions of more than about 2% of as-received Carbolac 1 to the filler have usually resulted in extensive microcracking. Prior heat-treatment of the Carbolac 1 to about 1800°C seems to have eliminated the microcracking problem.

The ablation models listed in Table X have been finish-machined and shipped to NASA-Ames Research center for ablation testing.

IV. PUBLICATIONS RELATING TO CARBONS

AND GRAPHITES

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