

FOREWORD

This report is a supplement to the thirteenth volume of WADD Technical Report series 61-72, describing various phases of research and development on advanced graphite materials conducted by National Carbon Company, a Division of Union Carbide Corporation, under USAF Contract No. AF 33(616)-6915.

The work covered in this report was conducted from September 1962 to May 1963 at the Advanced Materials Laboratory of National Carbon Company under the management of R. M. Bushong, Director of the Advanced Materials Project, and of R. C. Stroup, Manager of the Advanced Materials Laboratory.

The contract for this R&D program was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735002, "Refractory Inorganic Non-Metallic Materials; Graphitic;" Project No. 7381, "Materials Application," Task No. 738102, "Materials Processes," and Project No. 7-847, "Process Development for Graphite Materials." The work was administrated by the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command. Major R.H. Wilson, L.J. Conlon and W.P. Conrardy acted as project engineers.

Other volumes in this WADD Technical Report 61-72 series are:

- Volume I - Observations by Electron Microscopy of Dislocations in Graphite, by R. Sprague.
- Volume II - Applications of Anisotropic Elastic Continuum Theory to Dislocations in Graphite, by G. B. Spence.
- Volume III - Decoration of Dislocations and Low-Angle Grain Boundaries in Graphite Single Crystals, by R. Bacon and R. Sprague.
- Volume IV - Adaptation of Radiographic Principles to the Quality Control of Graphite, by R. W. Wallouch.
- Volume V - Analysis of Creep and Recovery Curves for ATJ Graphite, by E. J. Seldin and R. N. Draper.
- Volume VI - Creep of Carbons and Graphites in Flexure at High Temperature, by E. J. Seldin.
- Volume VII - High-Density Recrystallized Graphite by Hot-Forming, by E. A. Neel, A. A. Kellar and K. J. Zeitsch.

Contrails

- Supplement - High-Density Recrystallized Graphite by Hot-Forming,
by G. L. Rowe and M. B. Carter.
- Volume VIII - Electron Spin Resonance in Polycrystalline Graphite, by
L. S. Singer and G. Wagoner.
- Volume IX - Fabrication and Properties of Carbonized Cloth Com-
posites, by W. C. Beasley and E. L. Piper.
- Volume X- Thermal Reactivity of Aromatic Hydrocarbons, by I. C.
Lewis and T. Edstrom.
- Supplement - Thermal Reactivity of Aromatic Hydrocarbons, by I. C.
Lewis and T. Edstrom.
- Volume XI - Characterization of Binders Used in the Fabrication of
Graphite Bodies, by E. de Ruiter, A. Halleux, V. Sandor
and H. Tschamler.
- Supplement - Characterization of Binders used in the Fabrication of
Graphite Bodies, by E. de Ruiter, J.F.M. Oth, V.
Sandor and H. Tschamler.
- Volume XII - Development of an Improved Large-Diameter Fine-Grain
Graphite for Aerospace Applications, by C. W. Waters
and E. L. Piper.
- Supplement - Development of an Improved Large-Diameter Fine-Grain
Graphite for Aerospace Applications, by R. L. Racicot
and C. W. Waters.
- Volume XIII - Development of a Fine-Grain Isotropic Graphite for Struc-
tural and Substrate Applications, by R. A. Howard and
E. L. Piper.

ABSTRACT

This report covers the characterization of grade RVC graphite and describes process and blend variations which have been studied in the fabrication of substrate-type graphite since the publication of WADD Technical Report 61-72, Volume XIII. Present trials show that a forming pressure of 900 lbs./in.², instead of the 1000 lbs./in.² as used previously, would increase the yield of grade RVC and not significantly change the properties of the material. Furthermore, these trials show that various other blends will also produce a substrate graphite suitable for silicon carbide coating.

This report has been reviewed and is approved.



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1. INTRODUCTION

WADD Technical Report 61-72, Volume XIII, describes the development of a graphite, designated as grade RVC, which has nearly isotropic thermal expansion characteristics and whose thermal expansion is approximately the same as that of the silicon carbide coating for which it was developed. The present report, Supplement to Volume XIII, discusses the property evaluation of grade RVC graphite, and the process and blend variations which have been investigated for substrate graphites since the completion of the work covered in the previous report.

This supplemental report is divided into three parts. The first is a description of the mechanical and thermal properties of grade RVC graphite, both at room and at elevated temperatures. The second is an evaluation of forming variables studied in an effort to increase yields of RVC while still maintaining the desirable properties of the grade. The third is a study of the effect of mix formulation on processability and properties of various substrate graphites.

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2. PROPERTY CHARACTERIZATION OF GRADE RVC GRAPHITE

In a semiproduction run, described in Volume XIII of this series, 33 pieces in total of grade RVC, 18 inches indiameter by 15 inches in length, were fabricated and 16 of these pieces were free of flaws. Two of these flaw-free blocks were sampled for characterization of grade RVC. The results of physical properties measured at room temperature are presented in Table 1. The mechanical properties listed in Table 1 are of most concern if the coated graphite is to be used as a structural member. The flexural strength is 3215 and 2040 lbs/in² in the with-grain and across-grain directions, respectively. The compressive strength is approximately 11,000 lbs/in² in both directions, as compared to approximately 8500 lbs/in² for ATJ graphite. In addition to other properties, Table 1 shows the per cent thermal expansion from 20 to 100°C of 0.0295 and 0.0356 with and across grain, respectively, as compared to 0.0184 and 0.0280 for ATJ graphite. The former are relatively high thermal expansion values for graphite and are characteristic of grade RVC. Table 2 lists the high-temperature properties of grade RVC. Figure 1 shows the thermal expansion of grade RVC from room temperature to 2800°C. The RVC material from this semiproduction run, although not as isotropic with regard to thermal expansion as that made previously in smaller experimental quantities is sufficiently isotropic to maintain a protective silicon carbide coating upon repeated thermal cycling as discussed in Section 5 of this report.

Table 1. Summary of Room Temperature Properties for RVC Graphite, 18-Inch Diameter by 15-Inch Length

| Property | With Grain | | | | Across Grain | | | | | |
|--|------------|----------|--------------------|---------------|---------------|----------|--------|--------------------|---|---------------|
| | Ave. | σ | n | No. of Blocks | Ave. | σ | n | No. of Blocks | | |
| Bulk Density, g/cc | 1.84 | .01 | 40 | 2 | - | - | - | - | | |
| Specific Resistance, 10^{-4} ohm-cm | 13.08 | .48 | 20 | 2 | 16.44 | .83 | 20 | 2 | | |
| Young's Modulus, 10^6 lbs/in ² | 1.77 | .06 | 20 | 2 | 1.38 | .08 | 20 | 2 | | |
| Flexural Strength, lbs/in ² | 3215 | 206 | 10 | 2 | 2040 | 270 | 10 | 2 | | |
| Compressive Strength*, lbs/in ² | 11160 | 660 | 20 | 2 | 10940 | 890 | 20 | 2 | | |
| Compressive Strength**, lbs/in ² | 10920 | 1143 | 9 | 1 | 11215 | 779 | 9 | 1 | | |
| Tensile Strength, lbs/in ² | 2730 | 185 | 11 | 1 | 1300 | 236 | 10 | 1 | | |
| Shear Strength, lbs/in ² | 2455 | 254 | 10 | 1 | 2125 | 169 | 10 | 1 | | |
| ----- | | | | | | | | | | |
| | Max. | Min. | Ave. | n | No. of Blocks | Max. | Min. | Ave. | n | No. of Blocks |
| Per Cent Thermal Expansion, 20-100°C | 0.0300 | 0.0292 | 0.0295 | 6 | 2 | 0.0360 | 0.0341 | 0.0356 | 6 | 1 |
| Thermal Conductivity, $\frac{\text{cal-cm}}{\text{sec cm}^2\text{°K}}$ | 0.280 | 0.260 | 0.268 | 6 | 2 | 0.259 | 0.225 | 0.236 | 6 | 2 |
| Permeability, 10^{-3} darcy's | 1.27 | 0.40 | 0.72 | 4 | 1 | 0.56 | 0.23 | 0.36 | 4 | 1 |
| Admittance, cm ² /sec | - | - | 2×10^{-2} | 1 | 1 | - | - | 1×10^{-2} | 1 | 1 |
| Ash, per cent | 0.266 | 0.226 | 0.238 | 4 | 1 | - | - | - | - | - |

*Specimen size, 1- by 1- by 1-inch cube

**Specimen size 1/2-inch diameter by 1/2-inch length

Table 2. Summary of High-Temperature Properties for RVC Graphite, 18-Inch Diameter by 15-Inch Length

| Properties | Temp. °C | With Grain | | | | Across Grain | | | | | |
|---|---|-------------|-------|-------|---|------------------|-------|-------|-------|---|------------------|
| | | Max. | Min. | Ave. | n | No. of Blocks | Max. | Min. | Ave. | n | No. of Blocks |
| Per Cent Thermal Expansion $\frac{\Delta l}{L} \times 100$ | 20 | - | - | 0 | - | - | - | - | 0 | - | - |
| | 500 | 0.208 | 0.171 | 0.195 | 6 | 2 | 0.246 | 0.220 | 0.234 | 6 | 2 |
| | 1000 | 0.464 | 0.417 | 0.450 | 6 | 2 | 0.538 | 0.508 | 0.529 | 6 | 2 |
| | 1500 | 0.782 | 0.743 | 0.770 | 6 | 2 | 0.843 | 0.868 | 0.883 | 6 | 2 |
| | 2000 | 1.172 | 1.097 | 1.132 | 6 | 2 | 1.328 | 1.281 | 1.296 | 6 | 2 |
| | 2400 | 1.488 | 1.412 | 1.453 | 6 | 2 | 1.680 | 1.628 | 1.663 | 6 | 2 |
| | 2800 | 1.809 | 1.720 | 1.760 | 6 | 2 | 2.047 | 1.971 | 2.011 | 6 | 2 |
| Young's Modulus, 10^6 lbs/in ² | RT | 1.92 | 1.72 | 1.85 | 3 | 1 | 1.58 | 1.49 | 1.53 | 3 | 1 |
| | 500 | 2.02 | 1.82 | 1.94 | 3 | 1 | 1.66 | 1.56 | 1.59 | 3 | 1 |
| | 1200 | 2.25 | 1.93 | 2.14 | 3 | 1 | 1.57 | 1.67 | 1.71 | 3 | 1 |
| | 1600 | 2.43 | 2.25 | 2.32 | 3 | 1 | 1.89 | 1.87 | 1.88 | 3 | 1 |
| | 1800 | 2.43 | 2.22 | 2.31 | 3 | 1 | - | - | - | - | - |
| | 2000 | 2.44 | 2.20 | 2.30 | 3 | 1 | 1.93 | 1.89 | 1.91 | 3 | 1 |
| | 2400 | 2.29 | 2.11 | 2.19 | 3 | 1 | 1.78 | 1.72 | 1.75 | 3 | 1 |
| Tensile Strength, lbs/in ² | 2800 | 2.12 | 1.85 | 1.99 | 3 | 1 | 1.62 | 1.54 | 1.58 | 3 | 1 |
| | 1000 | 4180 | 2730 | 3285 | 3 | 1 | - | - | 1870 | 1 | 1 |
| | 1500 | - | - | 3190 | 1 | 1 | - | - | 2420 | 1 | 1 |
| | 2000 | 4550 | 3830 | 4190 | 2 | 1 | - | - | 2260 | 1 | 1 |
| | 2500 | 5610 | 5190 | 5375 | 3 | 1 | 4985 | 3265 | 4125 | 2 | 1 |
| | 2700 | 5170 | 2600 | 4285 | 3 | 1 | 3550 | 2540 | 3045 | 2 | 1 |
| | Compressive Strength* | | | | | | | | | | |
| Compressive Strength*, lbs/in ² | 1000 | - | - | 11180 | 1 | 1 | - | - | 11160 | 1 | 1 |
| | 1500 | - | - | 12680 | 1 | 1 | - | - | 13590 | 1 | 1 |
| | 1700 | - | - | - | 1 | 1 | - | - | 13950 | 1 | 1 |
| | 2000 | - | - | 17470 | 1 | 1 | 14205 | 13240 | 13720 | 2 | 1 |
| | 2500 | - | - | 20140 | 1 | 1 | 21490 | 18970 | 20230 | 2 | 1 |
| | 2700 | No break at | 30680 | 4 | 1 | 1 | 23225 | 16740 | 19980 | 2 | 1 |
| | Apparent Shear Strength, lbs/in ² | | | | | | | | | | |
| Apparent Shear Strength, lbs/in ² | 1000 | - | - | 2620 | 1 | 1 | - | - | 3745 | 1 | 1 |
| | 1500 | - | - | 3840 | 1 | 1 | - | - | 3735 | 1 | 1 |
| | 2000 | - | - | 3820 | 1 | 1 | - | - | 4005 | 1 | 1 |
| | 2500 | - | - | 5870 | 1 | 1 | - | - | 5120 | 1 | 1 |
| | 2700 | - | - | 6520 | 1 | 1 | - | - | 5335 | 1 | 1 |

Specimen size 1/2-inch diameter by 1/2" length

*Specimen size 1/2-inch diameter by 1/2" length

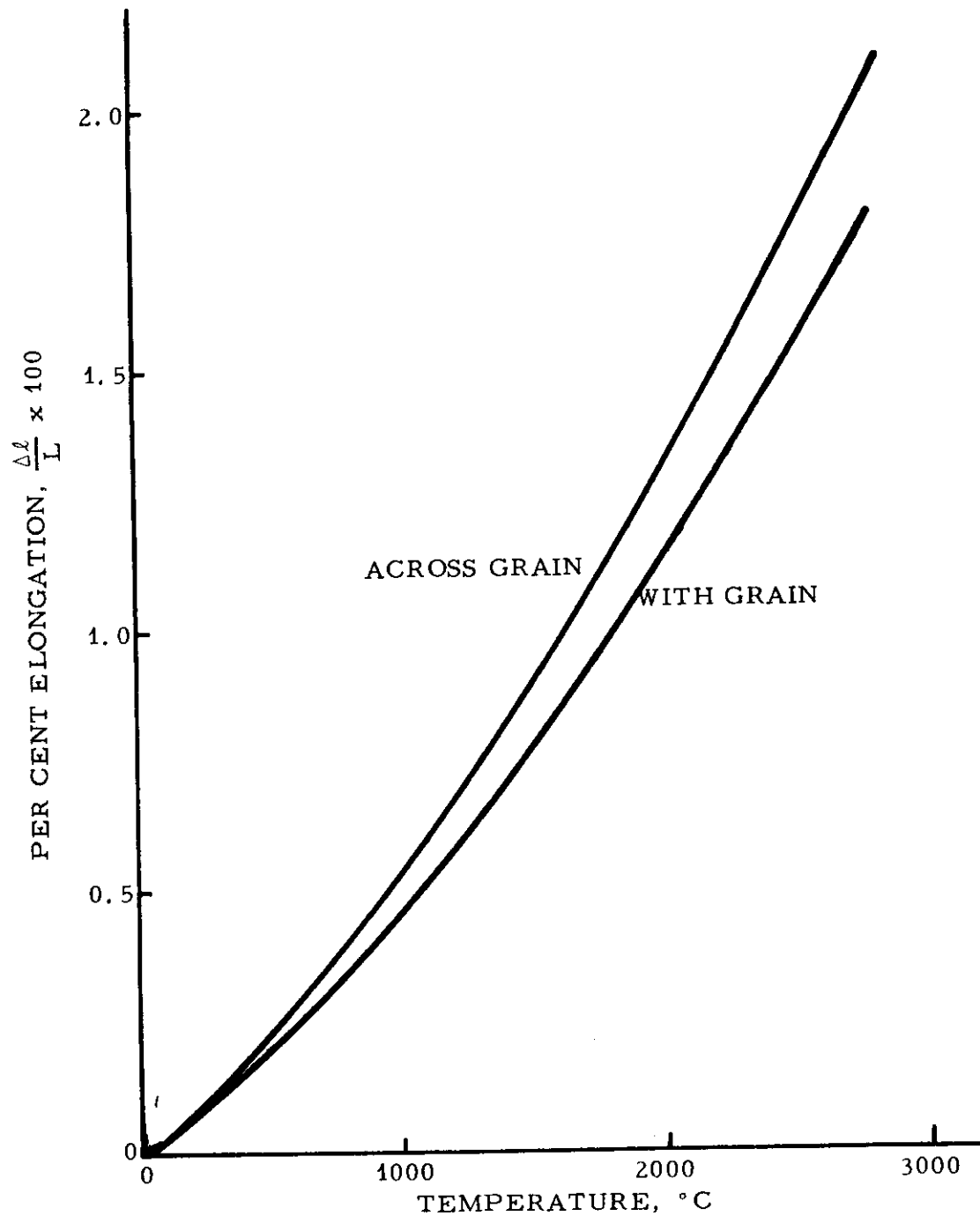


Figure 1. Thermal Expansion of Grade RVC Graphite

3. PROCESS IMPROVEMENTS OF GRADE RVC GRAPHITE

An examination of the grade RVC graphite billets produced in this semiproduction run showed that most of the scrap was caused by a mechanically weak area near the center of the piece, a condition usually indicated by low across-grain flexural strengths. At times a small flaw was found and, in the extreme cases, the billet was broken into two pieces. In every case the cracks or flaws were perpendicular to the axis of the stock and near the center. In an attempt to alleviate the cracking problem and otherwise to improve the quality of grade RVC, a number of changes was made in the process techniques.

3.1. Precompaction Trials

A technique for forming graphite, called the precompaction-particle-envelope method, was developed for use with the pressure-curing process during the grade RVA graphite trials.⁽¹⁾ In this method, the blended materials are placed under pressure in a mold and heated by electrical resistance to temperatures sufficient to plasticize the binder without initiating the polymerization reaction. The precompacted plug is then removed from the mold and its diameter is machined to allow annular space in the same mold for a particle envelope. The piece is returned to the mold and surrounded by particles prior to the curing operation. It was found in the work on grade RVA that the major portion of the slump, which would otherwise occur in the curing operation, is achieved during the precompaction period, thereby reducing sidewall friction in the curing operation. The precompaction method was used for the fabrication of grade RVC, but the binder level had to be increased from 19.5 to 22 parts per hundred of the filler by weight in order to facilitate precompaction. Of 13 pieces formed by this method, X-radiographic examination after baking showed that 11 contained the typical internal flaw. The other two pieces developed similar flaws during the graphitizing operation. A strength traverse was made on one of the graphitized pieces and the results are given in Table 3. The values show that the precompacted material contained low strength centers much the same as the stock formed using the particle envelope without precompaction. Figure 2 shows that a higher binder level and/or the precompaction method results in a material having higher thermal expansion than material made by pressure curing without precompaction.

(1) WADD Technical Report 61-72, Volume XII, "Development of an Improved Large-Diameter, Fine-Grain Graphite for Aerospace Applications," by C. W. Waters and E. L. Piper.

Table 3. Flexural Strength of Grade RVC
Made by Precompaction Method

| Sample No. | | Flexural Strength lbs/in ² | |
|------------|--|---------------------------------------|-------------------------|
| | | w. g. * (top to bottom) | a. g. ** (side to side) |
| 1 | Edge | 3769 | 2991 |
| 2 | <div style="display: flex; align-items: center; justify-content: center;"> <div style="width: 10px; height: 100px; border-left: 1px solid black; margin-right: 5px;"></div> <div style="writing-mode: vertical-rl; transform: rotate(180deg);">Center</div> </div> | 3745 | 2131 |
| 3 | | 2743 | 2321 |
| 4 | | 2930 | 2142 |
| 5 | | 3685 | 1721 |
| 6 | | 3304 | 1838 |
| 7 | | 3372 | 1739 |
| 8 | | 3507 | 1478 |
| 9 | | 3521 | 2046 |
| 10 | | - | 2563 |
| 11 | Edge | - | 2743 |
| Ave. | | 3397 | 2169 |

* w. g. = with grain
** a. g. = across grain

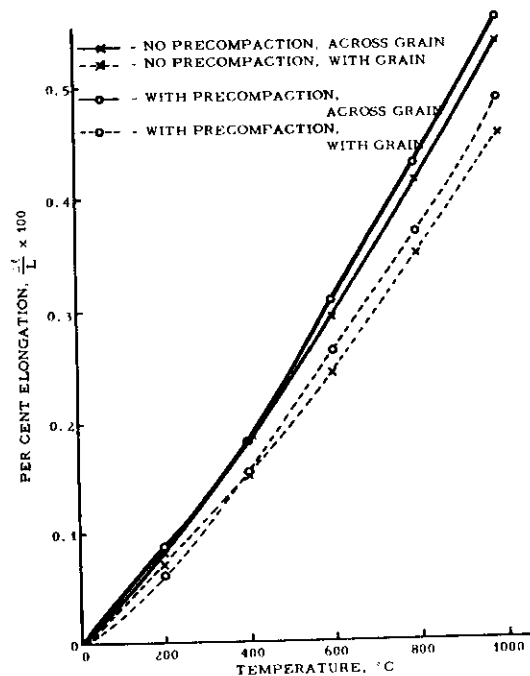


Figure 2. Thermal Expansion of Grade RVC Formed
With and Without Precompaction

The processing time for grade RVC is such that approximately three months had elapsed between the time 18-inch diameter billets were formed and the finished product could be examined. Thus, in the development of this graphite, a three-month period was required to fully evaluate the effect of any change in forming parameters. To reduce this time lag, a method was sought for analyzing the cured stock and predicting the structural integrity of the finished article. Since electrical resistivity is sensitive to the presence of microflaws, it was felt that this property should be useful in detecting flaws in the centers of blocks. Electrical resistance profiles, therefore, were made in the across-grain direction of the cured blocks. Figure 3 shows the resistivity profile obtained from

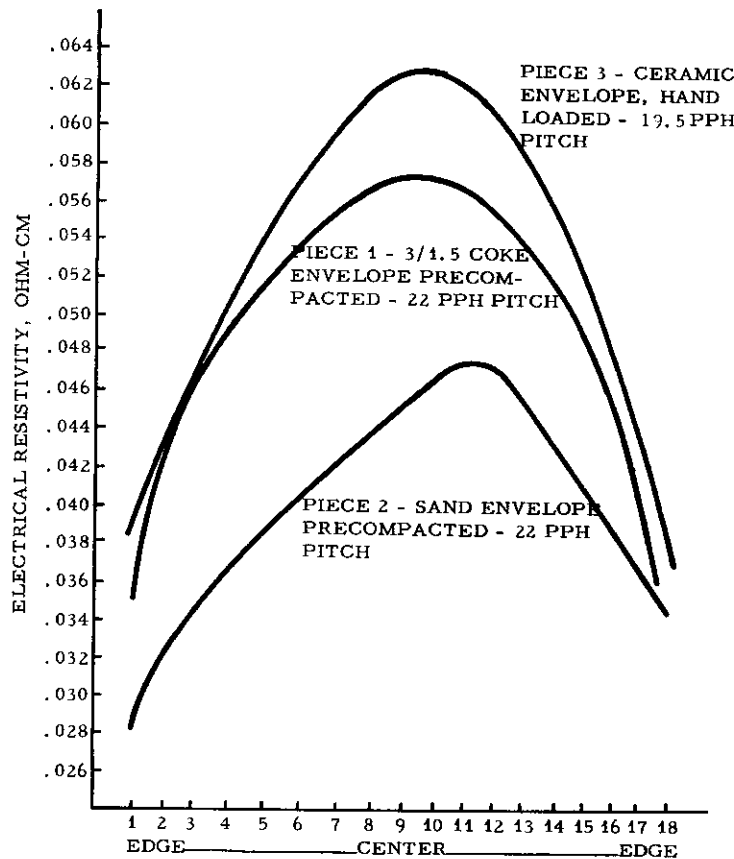


Figure 3. Electrical Resistivity Gradient Along Diameter of Cured RVC, Formed at 1000 lbs/in²

a cured block made by the precompaction-particle-envelope technique, and compares it with those of two other pieces made by variations of this technique. Both of the latter pieces were cured in insulating liner materials, one in sand and one in a solid ceramic liner, and were made in a deliberate attempt to divert more of the current to the center of the piece

during curing, thereby causing the temperature at that point to be significantly higher than at the periphery. The usual result of high temperatures in the center of any pressure-cured article is to create flaws on the surface of the piece rather than near the center. The higher resistance values for the centers of the blocks, shown in Figure 3, nevertheless indicate the presence of microflaws at the centers of all three cured blocks. These results showed that the flaws were present in the stock regardless of the degree of uniformity in curing temperature and, consequently, another cause was sought.

3.2. Forming Pressure Trials

It was reasoned that, if forming pressures were sufficiently high, the spherical particles in grade RVC would be elastically deformed and held in this state by the thermoset binder. The stresses induced by this deforming could be relieved during coking of the binder in the baking operation and the deformed particles would spring back, giving rise to horizontal microflaws.

Examination of the blocks of grade RVC produced in the semiproduction run indicated an increase in length exceeding 0.5 per cent from the cured to the baked state. This expansion in length during the baking operation could be accounted for by the relief of internal stresses and indicated that curing pressures of 1000 lbs/in² may have been excessive. The majority of the scrap in the semiproduction run was caused by cracks near the centers of the blocks perpendicular to the direction of application of forming pressure. To determine the effect of lower curing pressures, stock was prepared at pressures ranging from 500 to 1000 lbs/in², using the typical grade RVC blend formulation listed in Table 4. The same pres-

Table 4. Composition of Grade RVC Graphite

| | Per Cent by Weight |
|--|-----------------------|
| Fluid Coke Particles, through 35-Mesh Screen | 12.1 |
| Gilsonite Particles, through 10- on 30-Mesh Screen | 20.3 |
| Gilsonite Flour | 31.4 |
| Petroleum Coke-Base Graphite Flour | 10.4 |
| Thermatomic Black | 6.7 |
| 175°C-mp Coal-Tar Pitch | 15.8 |
| Sulfur | 3.3 |

sure curing techniques were used throughout the evaluation with curing

pressure the only variable. In addition to the normal 1000 lbs/in², trials were made using each of the following pressures. All pressures are expressed in lbs/in².

- 1) 1000 reduced to 500 after the slumping period
- 2) 1000 reduced to 750 after the slumping period
- 3) 1000 reduced to 875 after the slumping period
- 4) 1000 reduced to 925 after the slumping period
- 5) 750
- 6) 900

The forming pressure of 1000 lbs/in², used during that portion of the cycle when the binder becomes plastic, insured maximum compaction of the charge. After maximum compaction, and prior to the thermo-setting reaction, the pressure was reduced to allow stress relief within the particles.

Blocks 18 inches in diameter by 15 inches in length were cured using the indicated pressures. After curing, the surfaces of the blocks were machined to permit accurate measurements. The blocks were measured before and after baking (750°C) and the linear changes were calculated (see Table 5). These results showed that the blocks cured at 900 lbs/in² and those cured at 1000 reduced to 875 lbs/in² produced no change in length during the bake. All blocks were subjected to careful examination by X-ray (4 to 8 X-rays per block at each processing stage) and physical properties were measured rather extensively on each graphitized block.

Table 5. Linear Shrinkage of Baked RVC
Blocks, Cured at Various Pressures

| Curing Pressure, lbs/in ² | Cured Length, cm | Baked Length cm | Change in Length*, per cent |
|---|---------------------|--------------------|--------------------------------|
| 1000-500 | 40.8 | 40.6 | -0.490 |
| 750 | 37.7 | 37.6 | -0.265 |
| 1000-750 | 39.3 | 39.2 | -0.254 |
| 1000-875 | 43.0 | 43.0 | 0 |
| 900 | 41.2 | 41.2 | 0 |
| 1000-925 | 40.5 | 40.7 | +0.494 |
| 1000 | 39.7 | 39.9 | +0.504 |

* - = Shrinkage
+ = Expansion

The process methods which appeared to produce the best graphite were the 900 lbs/in² cure and the 1000 reduced to 875 lbs/in² cure. Three 18-inch diameter blocks were made at 900 lbs/in² and two of these were considered as completely satisfactory in every way. Two blocks of the same size were produced at 1000 reduced to 875 lbs/in² and one of these was completely satisfactory. Although the number of blocks was limited, it was felt that the yields indicated for the two methods (67 and 50 per cent) were reliable minimums because of the very exacting restrictions imposed on the quality by the evaluation methods discussed above. Blocks made at other pressures had lower indicated yields than those made at these two pressures.

The physical properties of the graphite billets cured at various pressures are compared with those of conventional RVC graphite in Table 6. Young's modulus, flexural strength, and specific resistance for all stock made at lower pressures were nearly the same as for standard grade RVC. The density was affected very little by the lower pressures and did not go below 1.80 g/cc except in the case where the block was cured at 1000 reduced to 500 lbs/in². The thermal expansion was within the range required for coating with silicon carbide. The graphite also was as isotropic in regard to thermal expansion as grade RVC previously produced. Inspection of yields and properties indicated that blocks cured at 900 lbs/in² were generally superior to those cured at 1000 lbs/in².

Table 6. Typical Physical Properties of Grade RVC
Graphite Cured at Various Pressures

| Properties | 1000 lbs/in ² Standard RVC | | | 1000-500 lbs/in ² | | | 750 lbs/in ² | | | 1000-750 lbs/in ² | | | 1000-875 lbs/in ² | | | 900 lbs/in ² | | | 1000-925 lbs/in ² | | |
|---|--|--------|-------|------------------------------|--------|------|-------------------------|--------|------|------------------------------|--------|------|------------------------------|--------|------|-------------------------|--------|------|------------------------------|--------|------|
| | n | Ave. | σ | n | Ave. | σ | n | Ave. | σ | n | Ave. | σ | n | Ave. | σ | n | Ave. | σ | n | Ave. | σ |
| | | | | | | | | | | | | | | | | | | | | | |
| Bulk Density, g/cc | 40 | 1.84 | 0.010 | 26 | 1.79 | 0.01 | 24 | 1.82 | 0.02 | 25 | 1.84 | 0.02 | 21 | 1.81 | 0.01 | 23 | 1.83 | 0.01 | 20 | 1.83 | 0.01 |
| Specific Resistance, 10 ⁻⁴ ohm-cm | 20 | 13.98 | 0.48 | 12 | 14.53 | 0.50 | 11 | 15.48 | 0.60 | 11 | 13.00 | 0.70 | 10 | 14.15 | 0.83 | 11 | 13.83 | 0.23 | 10 | 13.31 | 0.19 |
| w. g. * | 20 | 16.41 | 0.83 | 14 | 19.37 | 0.80 | 13 | 17.67 | 0.90 | 14 | 15.46 | 0.30 | 11 | 16.60 | 0.25 | 12 | 15.80 | 0.29 | 10 | 15.93 | 0.24 |
| a. g. * | | | | | | | | | | | | | | | | | | | | | |
| Young's Modulus, 10 ⁶ lbs/in ² | 20 | 1.77 | 0.06 | 12 | 1.64 | 0.04 | 11 | 1.90 | 0.04 | 11 | 1.68 | 0.12 | 10 | 1.70 | 0.13 | 11 | 1.76 | 0.05 | 10 | 1.77 | 0.03 |
| w. g. | 20 | 1.38 | 0.08 | 12 | 1.45 | 0.08 | 13 | 1.53 | 0.07 | 14 | 1.30 | 0.14 | 11 | 1.44 | 0.04 | 12 | 1.47 | 0.04 | 10 | 1.42 | 0.03 |
| a. g. | | | | | | | | | | | | | | | | | | | | | |
| Flexural Strength lbs/in ² | 10 | 3215 | 206 | 12 | 3573 | 184 | 11 | 3678 | 250 | 11 | 2800 | 209 | 10 | 3142 | 190 | 11 | 3403 | 155 | 10 | 3490 | 260 |
| w. g. | 10 | 2040 | 270 | 14 | 3222 | 196 | 13 | 3047 | 325 | 14 | 2530 | 270 | 11 | 2304 | 450 | 12 | 2586 | 484 | 10 | 2157 | 122 |
| a. g. | | | | | | | | | | | | | | | | | | | | | |
| Per Cent Thermal Expansion, 20-100°C | 4 | 0.0295 | - | 2 | 0.0294 | - | 2 | 0.0283 | - | 2 | 0.0275 | - | 2 | 0.0294 | - | 2 | 0.0289 | - | 2 | 0.0293 | - |
| w. g. | 4 | 0.0356 | - | 2 | 0.0331 | - | 2 | 0.0346 | - | 2 | 0.0338 | - | 2 | 0.0355 | - | 2 | 0.0338 | - | 2 | 0.0356 | - |
| a. g. | | | | | | | | | | | | | | | | | | | | | |

* w. g. = With Grain
a. g. = Across Grain

4. EVALUATION OF THE EFFECT OF BLEND VARIATIONS

Several blend formulations were evaluated using essentially the same raw materials as for the RVC graphite previously produced. The evaluation of these blends covered three areas. First, an attempt was made to produce a graphite with the same isotropic characteristics as standard grade RVC, but which would be easier to process. Second, an investigation was made to determine a composition more amenable to scale-up. Third, an effort was made to produce a graphite with an isotropic thermal expansion higher than conventional grade RVC.

The various blends evaluated, as well as the standard RVC blend, are given in Table 7. The description of the raw materials listed

Table 7. Experimental Blends for Producing Substrate Graphite

| | <u>RVC Blend</u> | <u>Blend 1</u> | <u>Blend 2</u> | <u>Blend 3</u> | <u>Blend 4</u> | <u>Blend 5</u> |
|---|------------------|----------------|----------------|----------------|----------------|----------------|
| Graphitized Fluid Coke Particles, through 35-Mesh Screen | 12.1 | 11.9 | 0 | 0 | 0 | 0 |
| Calcined Gilsonite Particles, through 10- on 30-Mesh Screen | 20.3 | 0 | 0 | 0 | 31.87 | 28.57 |
| Graphitized Gilsonite Particles, through 10- on 30-Mesh Screen | 0 | 19.84 | 31.75 | 32.00 | 0 | 0 |
| Calcined Gilsonite Flour | 31.4 | 0 | 0 | 41.38 | 0 | 38.70 |
| Graphitized Gilsonite Flour | 0 | 30.79 | 23.95 | 0 | 41.22 | 0 |
| Petroleum Coke-Base Graphite Flour | 10.4 | 10.26 | 17.10 | 0 | 0 | 7.03 |
| Thermatomic Black | 6.7 | 12.56 | 6.56 | 6.62 | 6.59 | 7.32 |
| 175°C-mp Coal-Tar Pitch | 15.8 | 17.46 | 17.46 | 16.80 | 17.13 | 15.10 |
| Sulfur | 3.3 | 3.19 | 3.18 | 3.20 | 3.19 | 3.28 |

* All values are expressed in weight per cent.

in Table 7 was given in Volume XIII of this report series with the exception of graphitized gilsonite particles and graphitized gilsonite flour. The latter two materials correspond to calcined gilsonite particles and calcined gilsonite flour (given in Volume XIII) except that the graphitized materials were heated to 2800°C before being incorporated into the blend. Calcined gilsonite shrinks about 10 per cent volumetrically when it is graphitized. If the gilsonite is not graphitized before it is incorporated into the blend,

this shrinkage takes place in the formed billet, increasing the incidence of flaws in the graphitized stock. Therefore, the use of graphitized gilsonite increases the processability of the blocks. Because of the limited quantity of experimental raw material, graphitizing of the gilsonite made it desirable to do some of the evaluation in smaller size blocks. In some cases the blocks were 10 inches in diameter by 10 inches in length; in other cases, where more material was available, blocks 18 inches in diameter by 15 inches in length were produced.

In the previously mentioned report on RVC graphite it was explained that graphitized fluid coke has a relatively low thermal expansion whereas calcined gilsonite has a rather high thermal expansion. Graphitizing the gilsonite raw material reduced its 400 to 1000°C thermal expansion from 0.330 to about 0.270 per cent. The use of graphitized gilsonite, which has a lower thermal expansion, eliminates the need for graphitized fluid coke in the RVC blend since the fluid coke had been added to reduce the thermal expansion of grade RVC.

From Table 7 it will be noted that Blend 1 used both graphitized fluid coke and graphitized gilsonite. This combination produced per cent thermal expansion values up to 0.306 per cent (400 to 1000°C), as shown in Table 8. Blend 2 used graphitized gilsonite without fluid coke and pro-

Table 8. Per Cent Thermal Expansion for
Graphite from Experimental Blends

| | RVC | Blend 1 | Blend 2 | Blend 3 | Blend 4 | Blend 5 |
|--|--------|---------|----------|---------|---------|---------|
| Per Cent Thermal Expansion, 20-100°C | | | | | | |
| w. g. * | 0.0295 | 0.0258 | 0.0233** | 0.0310 | 0.0290 | 0.0316 |
| a. g. * | 0.0356 | 0.0324 | 0.0302 | 0.0358 | 0.0362 | 0.0366 |
| Per Cent Thermal Expansion, 400-1000°C | | | | | | |
| w. g. | 0.300 | 0.270** | 0.288** | - | - | 0.312** |
| a. g. | 0.350 | 0.306** | 0.300** | - | - | 0.360** |

* w. g. = With Grain; a. g. = Across Grain.

** Indicates samples from blocks 10 inches in diameter by 10 inches in length. All other samples from blocks 18 inches in diameter by 15 inches in length.

duced stock having thermal expansion values in the range from 0.288 to

0.300 per cent (400 to 1000°C). While the stock from Blend 2 was being processed, it was suspected that it might have per cent thermal expansion values less than the desired 0.300 per cent (400 to 1000°C). Accordingly, blends 3 and 4 were formed. Blend 3 contained calcined gilsonite flour and graphitized gilsonite particles. In Blend 4 the gilsonite flour was graphitized and the particles remained in the calcined form. In both Blends 3 and 4, the petroleum coke-base graphite flour was eliminated because experience with Blends 1 and 2 had shown that if enough of the other components, by weight, were graphitized this graphite flour was not required to give an even heat distribution during the curing operation. Both Blends 3 and 4 were difficult to process because of shrinkage of the calcined component, and the thermal expansion (Table 8) was higher than desired.

Blend 5 was tried as a method of producing a high thermal expansion substrate which might be used for coatings such as MoSi_2 , TiN , TiC , and others with thermal expansion higher than that of SiC . This blend contained no low thermal expansion fluid coke and all the gilsonite was calcined. Enough petroleum coke-base graphite was added to give reasonably good heat distribution in the curing operation.

Because of its large volumetric shrinkage (8 to 10 per cent), stock made with a high per cent of calcined gilsonite is difficult to process. It was intended, therefore, to produce only small pieces from Blend 5. Even in a block as small as 10 inches in diameter by 10 inches in length, one crack was formed because of shrinkage. In the larger size blocks, many cracks were noted. In addition, the thermal expansion of stock made from Blend 5 was not sufficiently high to permit coating with refractories having thermal expansion values greater than about 0.360 per cent at 400 to 1000°C.

The properties of stock made from the five blends evaluated are given in Table 9. A comparison of these properties with those of RVC, shown in Table 1, indicates noticeable similarities. Blends 3 and 4 gave lower flexural strengths in the across-grain direction, probably because of flaws arising from shrinkage during graphitization of the calcined gilsonite. The samples used to evaluate Blend 5 were taken from flaw-free portions of the cracked blocks.

The thermal expansion measurements and other properties indicate that the use of Blend 2, or slight modification thereof, may permit larger sections of isotropic substrate graphite to be produced with higher yields and without significantly affecting the desirable characteristics of grade RVC graphite.

Table 9. Typical Physical Properties of Graphite
from Experimental Blends

| Properties | Blend 1 | | | Blend 2 | | | Blend 3 | | | Blend 4 | | | Blend 5 | | |
|--|---------|-------|----------|---------|--------|----------|---------|-------|----------|---------|-------|----------|---------|-------|----------|
| | n | Ave. | σ | n | Ave. | σ | n | Ave. | σ | n | Ave. | σ | n | Ave. | σ |
| Bulk Density, g/cc | 23 | 1.87 | 0.01 | 20 | 1.84* | 0.003 | 22 | 1.89 | 0.01 | 19 | 1.82 | 0.02 | 21 | 1.87 | 0.01 |
| Specific Resistance, 10 ⁻⁴ ohm-cm | | | | | | | | | | | | | | | |
| w. g. ** | 10 | 12.57 | 0.06 | 8 | 12.55* | 0.17 | 10 | 12.66 | 0.46 | 10 | 12.92 | 0.22 | 10 | 13.13 | 0.13 |
| a. g. | 13 | 15.77 | 0.12 | 12 | 15.52 | 0.21 | 12 | 14.89 | 0.32 | 9 | 16.02 | 0.49 | 11 | 15.90 | 0.28 |
| Young's Modulus 10 ⁶ lbs/in ² | | | | | | | | | | | | | | | |
| w. g. | 10 | 1.75 | 0.05 | 8 | 1.51* | 0.03 | 10 | 1.91 | 0.06 | 10 | 1.74 | 0.05 | 10 | 1.99 | 0.05 |
| a. g. | 13 | 1.32 | 0.02 | 12 | 1.17 | 0.02 | 12 | 1.43 | 0.05 | 9 | 1.29 | 0.04 | 11 | 1.58 | 0.06 |
| Flexural Strength, lbs/in ² | | | | | | | | | | | | | | | |
| w. g. | 7 | 3452 | 201 | 8 | 2701* | 181 | 10 | 3492 | 175 | 10 | 3025 | 256 | 10 | 3904 | 190 |
| a. g. | 13 | 2622 | 153 | 12 | 2317 | 120 | 12 | 1882 | 260 | 9 | 1594 | 137 | 11 | 2045 | 178 |

* Properties from 10-inch diameter by 10-inch length blocks; all others from 18-inch diameter by 15-inch length blocks.

** w. g. = With Grain; a. g. = Across Grain.

5. OXIDATION AND THERMAL CYCLING TESTS ON COATED MATERIALS

Bars (1 by 1½ by 8 inches) cut from blocks made from Blends 1, 2 and 5 as well as standard RVC blend were coated with silicon carbide and subjected to oxidation tests. In these tests, the samples were placed in a furnace, preheated to 1000°C for one hour, removed and allowed to cool to room temperature, and weighed to determine weight loss or gain through oxidation. The cycle was repeated 7 times on these samples. There was no weight loss found on any sample, thus indicating no failure of the coating. There was a maximum of 0.19 per cent weight increase due to oxidation of excess silicon in the coating to SiO₂. A plot of weight change versus time is presented in Figure 4.

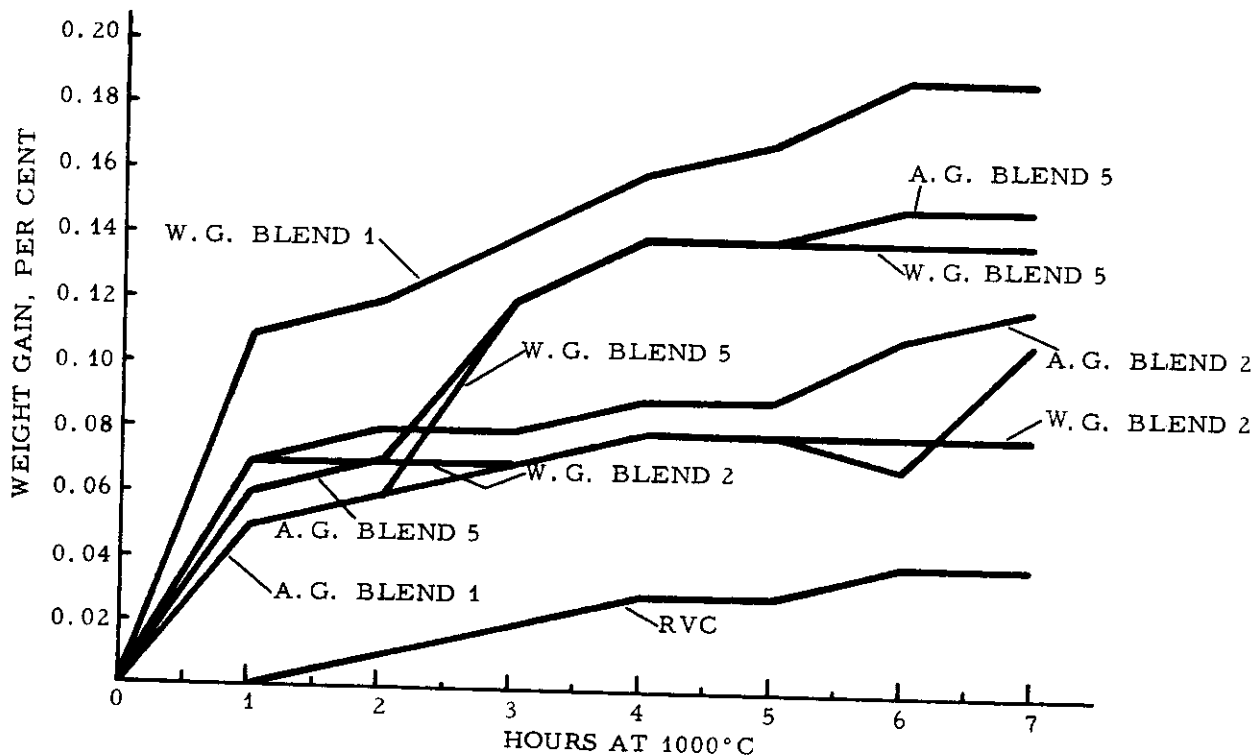


Figure 4. Weight Change Versus Time at Temperature,
SiC Coating on Various Graphites

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6. CONCLUSIONS

On the basis of this study, the following conclusions can be made:

- 1) Curing the grade RVC blend at 900 lbs/in² improves the yield without significantly changing the finished graphite.
- 2) A variation of the RVC blend, using graphitized gilsonite instead of calcined gilsonite, and eliminating other components will provide stock which is easier to process and which will have properties similar to grade RVC.
- 3) Blocks made from a calcined gilsonite blend do not have thermal expansion values sufficiently high to permit coating with refractories having a per cent thermal expansion, measured at 400 to 1000°C, in excess of about 0.360.