

# EXPERIMENTS ON THE COMPACTION OF GRAPHITE

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The bonding of synthetic graphite and chemically purified Ceylon graphite was studied at pressures ranging from 20,000 psi. to 80,000 psi. It was found that densities of the order of 2.06 g/cm<sup>3</sup> could be attained by cold compaction of the purified naturally occurring material, whereas the synthetic graphite failed to show any bonding tendency.

Oxidation of both graphite types to various extents by means of Brodie's mixture produced pronounced increases in the *c*-spacing with a corresponding reduction of crystallite diameters perpendicular to the *c*-direction. This suggested the formation of broken C—C bonds and development of fresh edges, so that pressing of partially wet oxidized synthetic graphite enabled compacts to be produced at 80,000 psi. having a density of 1.9 g/cm<sup>3</sup>.

Heat treatment of partly wet oxidized graphite to 2600°C in a helium atmosphere resulted in a weight loss of 13%–14% and a density decrease. Hot pressing, however, yielded a final density of 1.93 g/cm<sup>3</sup>.

## I. INTRODUCTION

Preliminary investigations into the production of a dense graphite of high purity were carried out using a synthetic electrode graphite (National Carbon Grade AGX) ground to pass a 200 mesh sieve which was bonded with various proportions of a 300°F pitch. Using a pressure of 10,000 psi. and a temperature of 170°C., specimens 2.55 cm. diameter and 0.5 cm. thick were pressed from a range of compositions after which the compacts were broken, ground to pass a 100 mesh sieve and subsequently re-pressed under the same conditions. This yielded compacts of greater density than could be achieved by a single pressing operation within the range of pressures used as shown in Fig. 1.

Blends containing between 12% and 16% pitch yielded the optimum pressed densities ranging from 2.025 g/cm<sup>3</sup> to 2.029 g/cm<sup>3</sup>. Heat treatment of specimens falling within this range of density to 1000°C embedded in lamp black, produced a density decrease as

anticipated to the order of 1.44 g/cm<sup>3</sup> but by hot pressing compacts containing 12% pitch to 2200°C in an induction furnace at 1000 psi and 5000 psi, specimens were obtained having densities of 1.907 g/cm<sup>3</sup> and 1.940 g/cm<sup>3</sup>, respectively.

Calculations by Mrozowski<sup>1</sup> taking into consideration the strongly anisotropic thermal expansion and cross linking characteristics of graphite have indicated that for polycrystalline graphite a density of the order of 2.1 g/cm<sup>3</sup> is the maximum likely to be achieved by industrial graphitization. The most promising method whereby high densities might be achieved appeared to involve the elimination of bonding materials having considerable weight loss when heated, and attention was therefore directed to the bonding properties of synthetic and naturally occurring graphite under pressure.

## II. BONDING OF PURIFIED CEYLON GRAPHITE

As a source of natural graphite, Ceylon flake containing 11.9% ash was selected and purification effected by milling in alcohol

\* Now at North American Refractories Co., Cleveland, Ohio.

<sup>1</sup> S. Mrozowski, This volume, page 31.

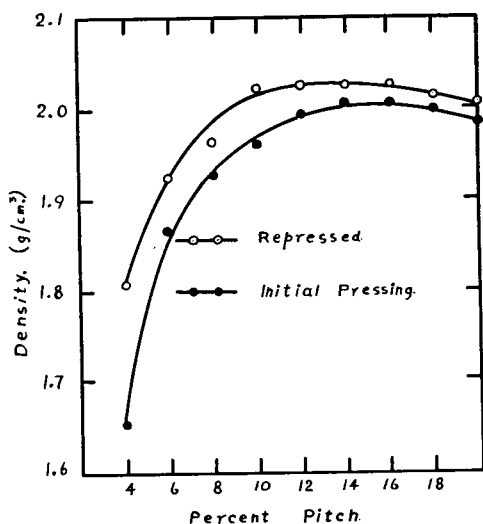


FIG. 1. Density of pitch-bonded synthetic graphite compacted at 10,000 psi.

for 72 hours, sieving through a 200 mesh followed by drying and digestion with hydrofluoric and sulfuric acids to decompose silicates. Conversion to chlorides and subsequent washing out of soluble salts completed the process whereby a graphite containing 0.4% ash resulted.

In carrying out the purification process on a quantitative basis several samples containing 11.6% ash were purified to an ash content of 0.1% by heating to remove  $\text{SO}_3$  fumes prior to conversion to the chlorides. A weight loss of 12.6% was recorded and during the latter stage of the removal of  $\text{SO}_3$ , a black tarry material was observed to distil off. Up to the present time, this discrepancy between the weight loss and ash contents has not been investigated.

Using carbon tetrachloride as the liquid medium, graphite containing 0.4% ash was found to have a pycnometer density of 2.23 g/cm<sup>3</sup>, the original value for the impure material being 2.31 g/cm<sup>3</sup>.

Attempts to press purified graphite into compacts 2.86 cm. diameter and 1 cm. thick resulted in laminated specimens but by mixing the material to a paste with alcohol

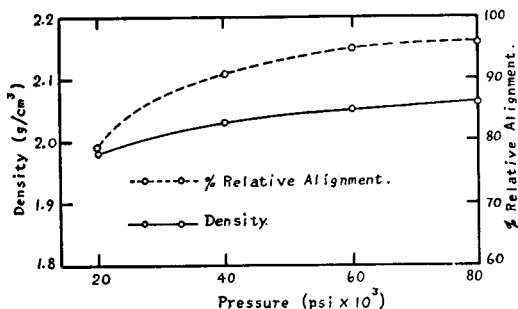


FIG. 2. Relationship between the applied pressure, density, and relative alignment of graphite crystallites in purified Ceylon graphite compacts.

TABLE I

*Relationship Between the Applied Pressure, Density, and the Relative Alignment of Graphite Crystallites in Purified Ceylon Graphite Compacts*

Applied Pressure	Density	Per Cent Relative Alignment
psi	g/cm <sup>3</sup>	
20,000	1.98	79
40,000	2.03	91
60,000	2.05	95
80,000	2.06	96

or ether to displace air, driving out almost all the volatile material in a heated mould and subsequently pressing, specimens free from laminations were obtained at pressures ranging from 20,000 psi to 80,000 psi. In Fig. 2 and Table I, the relationships between the compacting pressure and the density and relative alignment of the graphite crystallites are shown.

Determinations of the degree of alignment of the graphite crystallites in pressed specimens were made on cut and sand blasted sections, by measuring the intensity of the 002 reflection of x-ray diffraction patterns using a General Electric X-ray spectrometer and filtered copper radiation, according to the method of A. E. Austin<sup>2</sup>. Values of alignment were calculated using the expression:

<sup>2</sup> A. E. Austin, Batelle Memorial Institute, Columbus, Ohio. Private communication.

$$\% \text{ relative alignment} = \frac{I_1 - I_2}{I_1} \times 100$$

where  $I_1$  is the intensity of the 002 reflection of a face normal to the direction of the applied moulding pressure and  $I_2$  is the intensity of the 002 reflection of a face parallel to the direction of applied pressure.

The two surfaces studied were equal in area, the line intensity being determined by the difference between the background intensity and the peak intensity of the line. The greatest density obtained was 2.06 g/cm<sup>3</sup> under a pressure of 80,000 psi., this specimen showing a 96 % relative alignment of the basal plane.

### III. WET OXIDATION OF SYNTHETIC GRAPHITE

Similar attempts to press synthetic graphite compacts from electrode graphite ground and passed through a 200 mesh sieve failed to produce any bonding effect whatever within the same pressure range, but by oxidation of the material using Brodie's reaction, bonding was achieved.

In conducting the wet oxidation, 2.5 ml of fuming nitric acid were added per gram of graphite and the whole heated to 50°C

when a suitable amount of finely ground potassium chlorate was added in small increments, the quantity of chlorate being determined by the degree of oxidation desired. Digestion for 1 hour at 50°C was followed by a period of 20 hours at room temperature after which the green colored oxidation product was washed free from nitrates and chlorides, and the degree of oxidation studied by weight gain and x-ray analysis. The available oxygen content of the material was determined by reduction with standard ferrous ammonium sulfate solution under controlled conditions, and subsequent titration with potassium permanganate. This reduction produced an amorphous material showing diffuse bands in the x-ray diffraction pattern.

X-ray diffraction spectrometer measurements showed a distinct decrease in the intensity of the 002 reflection of graphite observed at 3.36 Å with increasing amounts of oxidation, and the development of a new reflection within the range of 6.4 Å-6.8 Å. for oxidized synthetic graphite, and 5.8 Å-6.3 Å for oxidized Ceylon graphite. This effect for natural graphite is shown in Fig. 3.

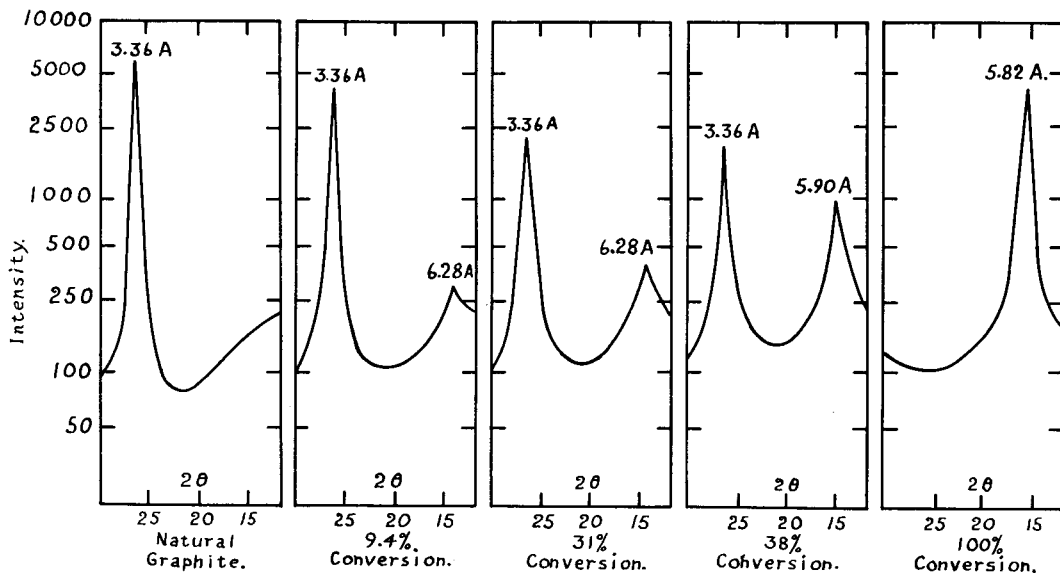


FIG. 3. Development of a new reflection and reduction of the 002 intensity upon oxidation of natural graphite with Brodie's mixture.

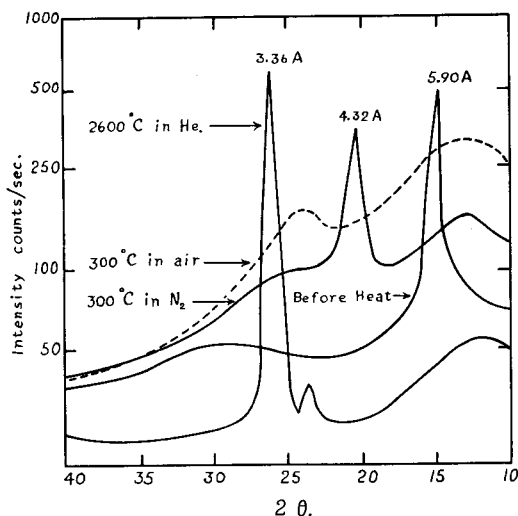


FIG. 4. Effect of heating oxidized synthetic graphite in various atmospheres.

TABLE II

*Relationship Between the Degree of Oxidation of Ceylon Graphite and the Density of Compacts Formed at Various Pressures*

Per Cent Conversion To Graphitic Oxide	Per Cent Available Oxygen	Density, g/cm <sup>3</sup>				
		20,000 psi	40,000 psi	60,000 psi	80,000 psi	100,000 psi
Nil	Nil	1.98	2.03	2.05	2.06	—
9	1.13	1.96	2.05	2.07	2.08	2.08
31	3.11	1.93	1.97	1.99	1.99	—
38	4.73	1.90	1.93	1.94	1.95	1.95

With complete oxidation, the 002 reflection at 3.36 Å disappeared entirely, and as oxidation proceeded a decrease in the crystallite diameter normal to the *c*-direction was found which suggested the formation of broken C—C bonds and the development of fresh edges.

Complete oxidation of Ceylon graphite was accompanied by a weight gain of 46.8% and yielded a product having 13.6% oxygen capable of reacting with ferrous ammonium sulfate. Likewise, in the case of the synthetic material, a weight gain of 40.8% and 12.8% available oxygen resulted from complete oxidation. The per cent conversion to "graphitic oxide" was always greater in the

case of the Ceylon graphite than the synthetic material under identical conditions.

When subjected to heat, completely oxidized synthetic graphite exhibited very marked deflagration at 210°C in air at which temperature thermal analysis curves showed a distinct peak. Heating in nitro- to 300°C failed to produce this disruption but the peak at 5.9 Å disappeared and was replaced by a new one at 4.32 Å, as indicated in Fig. 4.

#### IV PRESSED OXIDIZED SYNTHETIC AND CEYLON GRAPHITES

Upon compacting Ceylon graphite oxidized to various extents, it was found that at conversions to "graphitic oxide" in excess of 31% where the available oxygen content exceeded 3.11%, densities were less than those obtained from non-oxidized material but at 9% conversion corresponding to an available oxygen content of 11.3%, densities were slightly greater than those pertaining to the unoxidized material, the highest value being 2.08 g/cm<sup>3</sup> compared with 2.06 g/cm<sup>3</sup> for unoxidized graphite. Results recorded in Table II and Fig. 5 show the relationships between the extent of oxidation and the densities achieved at various compacting pressures.

Similar treatment of oxidized synthetic graphite results of which are shown in Table III and Fig. 6, produced compacts which bonded quite strongly. Material having a 20% conversion to "graphitic oxide" and 1.44% available oxygen produced compacts of the greatest density for any given pressure, the highest value being 1.91 g/cm<sup>3</sup> at 60,000 psi.

Compacts pressed at 80,000 psi from synthetic graphite with a 20% conversion to "graphitic oxide" having a density of 1.91 g/cm<sup>3</sup> were heat treated to 300°C in air or nitrogen. No dimensional change occurred in either specimen but a decrease in density to 1.74 g/cm<sup>3</sup> took place in both instances.

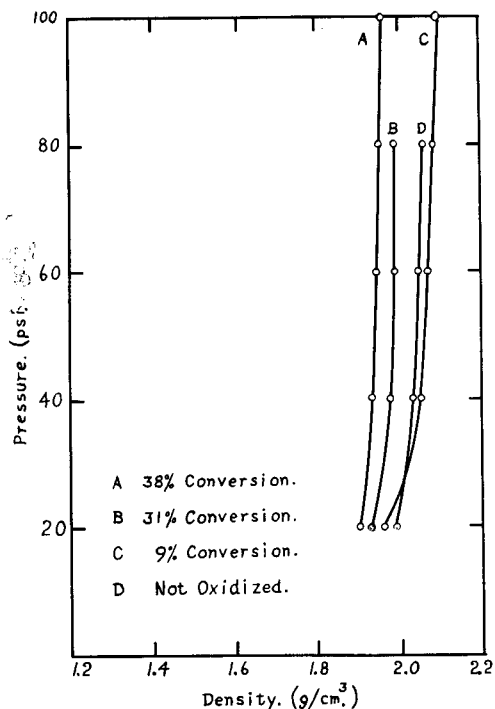


FIG. 5. Effect of the extent of oxidation on the density of oxidized Ceylon graphite compacts formed at various pressures.

TABLE III

*Relationship Between the Degree of Oxidation of Synthetic Graphite (National Carbon AGX) and the Density of Compacts Formed at Various Pressures*

Per Cent Conversion To Graphitic Oxide	Per Cent Available Oxygen	Density, g/cm <sup>3</sup>				
		20,000 psi	40,000 psi	60,000 psi	80,000 psi	100,000 psi
Nil	Nil	No bonding				
11	1.11	1.73	1.79	1.82	1.86	1.86
20	1.44	1.76	1.87	1.91	1.91	1.91
32	2.81	1.68	1.46	1.80	1.81	1.84
100	12.96		1.26	1.36	1.38	1.60

Subsequent heat treatment to 2600°C in a vacuum atmosphere extended the drop in density to 1.66 g/cm<sup>3</sup> but again no significant change in dimensions could be detected. Hot pressing of a compact of the same material having an initial density of 1.91 g/cm<sup>3</sup> to 2600°C at 5000 psi produced a specimen having a density of 1.93 g/cm<sup>3</sup>.

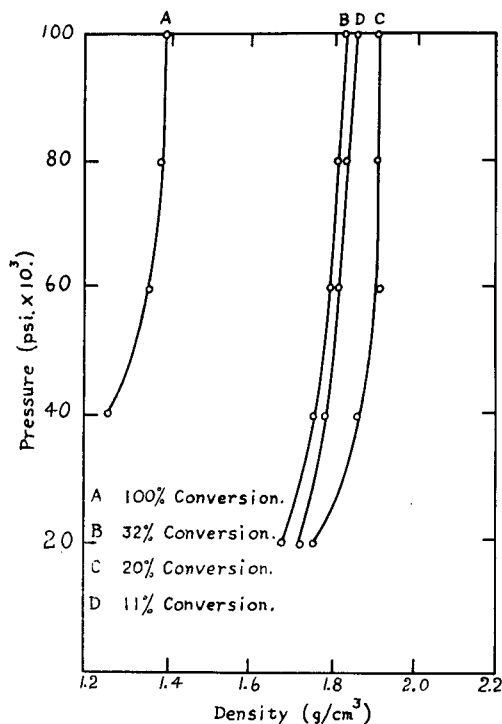


FIG. 6. Effect of the extent of oxidation on the density of oxidized synthetic graphite compacts formed at various pressures.

## V. CONCLUSIONS

In general, it may be concluded that synthetic graphite can be bonded under pressure without the addition of a binding agent if the material is partially wet oxidized. Similar treatment of Ceylon graphite does not appear to offer any outstanding advantage.

The deflagration of oxidized synthetic graphite when heated in air, and the lack of volume change on heating compacts of the same material may be associated with the rate of heating since Hennig<sup>3</sup> has reported that wet oxidized graphite fails to deflagrate if heated sufficiently slowly in air.

No attempt has been made to investigate the composition of the oxidation products in

<sup>3</sup> G. R. Hennig, Chemistry Division, Argonne National Laboratory, Lemont, Illinois. Private communication.

any detail since this was not within the scope of the present work. According to Thiele<sup>4</sup>, however, the oxidation product is capable of cation exchange reactions, and investigations of the ion exchange capacity of slightly oxidized graphites are being

<sup>4</sup> H. Thiele, Salt Formation and Base Exchange of Graphitic Acid. *Kolloid Z.* **80**, 1 (1934).

made with a view to developing casting slips along the lines of the conventional methods used in the ceramics field.

#### ACKNOWLEDGEMENT

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