

Compaction of Natural Graphite

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Three broad types of natural graphites are recognized: flake, vein, and amorphous. The compaction of graphite powders, representing these types, into coherent binderless artifacts at room temperature and pressures up to 125,000 psi has been studied. The graphite powders were characterized as to their particle size distributions, crystallinity, relative crystallite alignment, surface areas, and surface homogeneities. The compacts were characterized as to their surface area, density, pore size distributions, and compressive strengths. It is concluded that chemical bonding between atoms on a small fraction of adjacent particle surfaces is of primary importance in determining compact strength, with van der Waals attractive forces between basal plane surfaces also playing a role.

1. Introduction

Previous studies have been made on the compaction of finely ground natural ^{1),2)} and artificial graphite ^{3),4)} into artifacts without the use of binders. At comparable densities, the compressive strengths of the best artifacts are about 20-30% of the strengths of typical graphitized carbon bodies composed of filler and binder phases.¹⁾ The strengths of the artifacts are found to vary widely, however, depending upon molding pressure, heat treatment temperature of the graphite, and amount of moisture on the graphite surface. In this study, the production of artifacts from the compaction of three different natural graphites is examined.

2. Experimental

2.1. Natural Graphites

In the industry, natural graphite is considered, on the basis of the physical form of the particles, to be of three principal types: flake, vein, and amorphous.^{5),6)} In nature, flake graphites consist of isolated, flat, plate-like particles, which are usually found disseminated in layers, lenses, or pockets in metamorphic rocks. Vein graphites occur in fissures, fractures or cavities and form veins traversing igneous or metamorphic rocks. They are formed in masses of coarse plate-like intergrowths of acicular aggregates. Amorphous graphites are, in fact, microcrystalline graphites. The principal sources are metamor-

phosed carbonaceous sediments. In this study a principal source of each type of natural graphite was used, that is, Madagascar, Ceylon, and Mexican.

2.2. Treatment of Graphites

The graphites were compacted at 25,000 and 125,000 psi into cylindrical samples 1/2 in. in diameter and 1±1/16 in. in length, using a hardened steel mold and a Pasadena Hydraulic Press.¹⁾

Heat treating of the graphite powders or compacts was performed in an induction furnace in a flowing He atmosphere.

2.3. Property Measurements

2.3.1. Crystallinity - A 164° (2θ) General Electric X-ray diffractometer, XRD-3, was used to determine interlayer spacings and relative crystallite orientation in the graphite powders. Interlayer spacings were measured with an accuracy of ±0.0004Å, as previously described.⁷⁾ Crystallite orientation was measured as previously described.⁸⁾ The orientation is given by the so-called ω factor, that is, $(I_{0002}^R / I_{10\bar{1}0}^R) / (I_{0002}^T / I_{10\bar{1}0}^T)$ where I^R and I^T represent the maximum intensities (above background) of the (0002) and (10 $\bar{1}$ 0) diffraction peaks in reflection and transmission.

2.3.2. Surface areas - A standard volumetric apparatus⁹⁾ was employed to determine adsorption isotherms for N₂ at 78°K on the powders and molded samples. From the isotherms, specific surface areas were calculated using the BET equation.⁹⁾

2.3.3. Pore size distribution - A mercury porosimeter, capable of operating up to 30,000 psi, was

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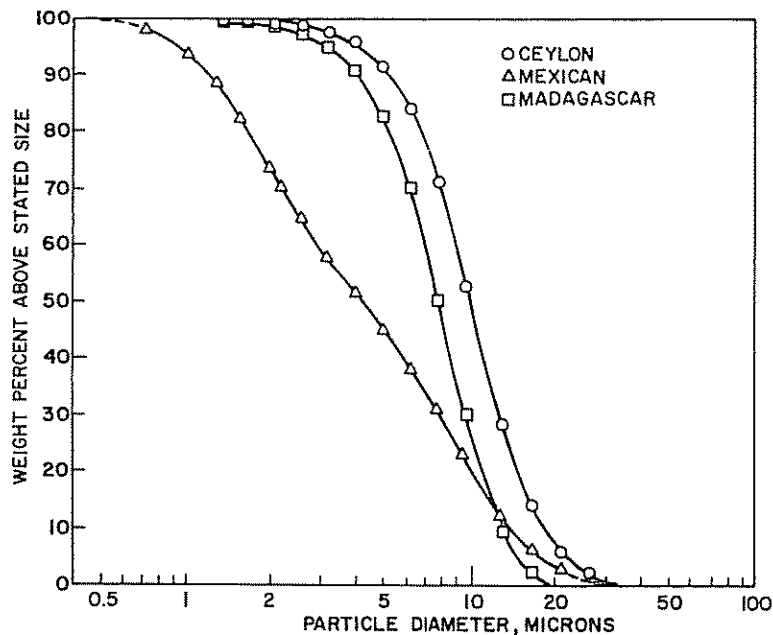


FIGURE 1 PARTICLE SIZE DISTRIBUTION CURVES FOR THE THREE GRAPHITE POWDERS

used to obtain pore size distributions on the molded samples. The design and operation of this apparatus has been previously given.¹⁰⁾

2.3.4. Compressive strength - Strengths were measured on the artifacts using a Baldwin Southwark Universal Testing machine.¹⁾ Strengths were measured on between five and ten compacts, prepared under each condition.

3. Results

The ash contents of the as-received graphites were: Ceylon, 1.8%; Madagascar, 0.1%; and Mexican, 13.3%. The majority of the mineral matter in Ceylon graphite is quartz.⁶⁾ The mineral impurities in Mexican graphite are finely dispersed in the carbon matrix, which makes beneficiation difficult; the major mineral is kaolinite.

3.1. Particle Size Distribution

Figure 1 presents particle size distributions for the graphites, as measured by the Coulter Counter.¹¹⁾ The Ceylon and Madagascar graphites have reasonably narrow particle size distributions, with 50% of their particles less than 10 and 7.8 microns in diameter respectively. The Mexican graphite has a broader distribution, with 50% of its particles less than 4.2 microns in diameter. These distributions are typical of the finely ground materials available today in the natural graphite industry.

3.2. Crystallinity

Values for the interlayer spacings (15°C) and relative crystallite orientations of the graphites are given in Table

1. The spacing for Ceylon graphite is in excellent agreement with that previously reported.^{12),13)} Ceylon graphite has been taken as having complete three-dimensional graphite structure.¹⁴⁾ The interlayer spacing of the Madagascar graphite is significantly, but only slightly, higher than that of the Ceylon graphites, indicating that the latter has a larger average crystallite diameter.¹⁵⁾ The Mexican graphite has an inter-layer spacing comparable to that in some of the best artificial needle graphites. In this sense, its geological designation as an amorphous graphite is a misnomer. As expected from the interlayer spacing results, the Ceylon graphite shows the highest degree of crystallite alignment and Mexican the least.

Table 1. Crystallographic Data on Natural Graphites

Graphite	Interlayer Spacing A (15°C)	Orientation Factor, ω
Ceylon	3.3540	37
Madagascar	3.3549	22
Mexican	3.3585	10

3.3. Surface Areas

Table 2 summarizes surface area results on the graphite powders and compacts, as measured by N₂ adsorption at 78°K. As expected, the powders have different surface areas. However, the differences are greater than would be predicted from particle size distribution data and suggest that as we go from Ceylon to Madagascar to Mexican the degree of surface roughness (in the basal plane)

and internal porosity increase. As previously reported,¹⁵⁾ molding up to 125,000 psi at room temperature has a negligible effect on reducing graphite surface area. This means that N_2 is still accessible to the particle surface or that an insignificant fraction of the surfaces of adjacent particles approaches within a distance of about 5A or less.¹⁶⁾

Table 2. Surface Areas of Natural Graphite Powders and Compacts

	Surface Area, m ² /gm		
	Ceylon	Madagascar	Mexican
Powder	5.8	9.4	25
Compact (25,000 psi)	6.4	9.0	25
Compact (125,000 psi)	5.8	9.0	27

Portions of the Ceylon and Madagascar graphite powders were heated at temperatures up to 3000°C. No significant change in surface areas resulted. Also, Kr adsorption was measured at 70°K on these heat treated graphite powders. For the Ceylon graphite, three vertical steps in the isotherm were found, which is indicative of a very high degree of surface homogeneity.¹⁷⁾ For the Madagascar graphite, two vertical steps were found; the third step at a relative pressure of about 0.5 was not vertical. This means that the surface of the Madagascar graphite was not as homogeneous as that of the Ceylon graphite, which was expected from the crystallographic data.

3.4. Pore Size Distribution in Compacted Samples

Figures 2 and 3 present pore size distribution curves for the graphites compacted at 25,000 and 125,000 psi. The total specific pore volume for the compacts was calculated knowing the compact density, the density of the graphite crystallites, the weight per cent carbon and mineral matter in the compact, and the mineral matter density. The mineral matter density was taken as 2.7 g/cc,¹⁸⁾ from studies on coal. This value is thought to be the best approximation of mineral matter density in the case of the Mexican graphite. Since the mineral matter content in the other two graphites is low, however, slight errors in their densities will have little effect on pore volume calculations.

The pore volume distributions in the compacts from the Ceylon and Madagascar graphites are very similar. For the samples compacted at 25,000 psi, negligible pore volume is present in pores greater than 1000A in radius. In both samples, the majority of the pore volume is located in pores between 100-1000A. For the samples compacted at 125,000 psi, negligible pore volume is present in pores greater than 200A in radius, and the majority of the pore volume is located in pores between 50-200A. Compacts from the Mexican graphite have substantially higher pore volumes for both compaction pressures. As expected from the relatively broad particle size distribution for the Mexican graphite, the pore size range over which significant pore volume is present is greater than for the Ceylon or Madagascar compacts.

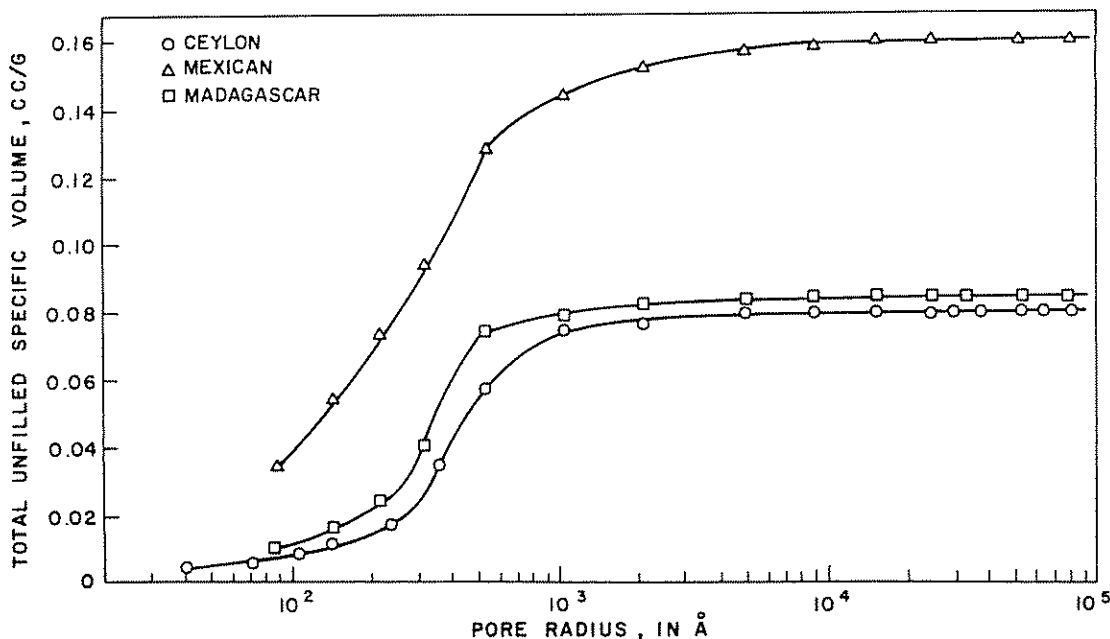


FIGURE 2 SIZE DISTRIBUTION CURVES FOR THE THREE GRAPHITES MOLDED AT 25,000 psi

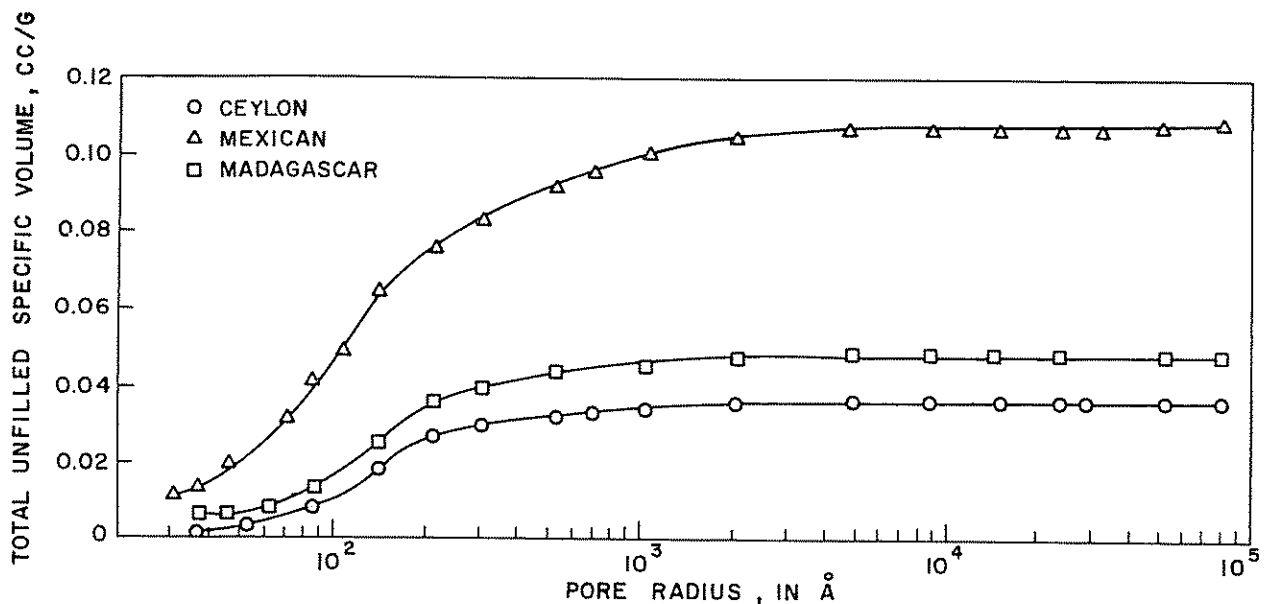


FIGURE 3 SIZE DISTRIBUTION CURVES FOR THE THREE GRAPHITES MOLDED AT 125,000psi

Table 3. Crushing Strengths and Apparent Densities for Graphite Compacts

Pelletizing Pressure, psi	Ceylon		Madagascar		Mexican	
	Strength, psi	Density, g/cc	Strength, psi	Density, g/cc	Strength, psi	Density, g/cc
25,000	1397± 94	1.96	1256± 44	1.91	550± 74	1.64
125,000	2348±149	2.10	1934±464	2.08	1203±445	1.83

3.5. Compressive Strengths of Compacts

Strength data are summarized in Table 3, with 95% confidence limits given. Strengths measured on samples compacted at 25,000 psi were more reproducible. This was expected on the basis of our experiences during compaction. That is, the graphites could be easily compacted at 25,000 psi and separated from the mold to yield a cylindrical sample with flat ends. However, following compaction at 125,000 psi the pellets tended to stick to the end of the plunger. This made it difficult to maintain flat ends on the samples, since they often broke unevenly in the process of being separated from the plunger. Similar difficulties in compaction of solids under high pressure have been noted.¹⁹⁾ Suffice it to say that an increase in molding pressure produced an increase in compact density and strength, as expected and as previously reported.^{1),3)} The strongest compacts were produced from Ceylon graphite at both molding pressures; compacts from the Mexican graphite were the weakest.

The possible effect of certain variables on the strength of compacts from Ceylon graphite was studied in more detail. Results are summarized in Table 4 for samples molded at 25,000 psi. First, this as-received

graphite was kept in a desiccator over magnesium perchlorate for varying periods of time up to 96 hr prior to molding for the possibility of reducing the amount of physically adsorbed water on the surface. No subsequent effect on compact strength was found. May previously observed that the deliberate addition of between 0.7-4.0% moisture to artificial graphite powder resulted in a decrease in strength of molded, binderless pellets produced therefrom. In our study the as-received graphite contained less than 0.1% water. Therefore, it is possible that our measurements were not sensitive enough to see an effect of a small change in water concentration on compact strength.

Strengths were normally measured within 24 hr after sample compaction. It is seen from Table 4 that aging the Ceylon compacts up to 20 days had no significant effect on their strength or density.

Some compacts were heated at temperatures up to 2320°C in He prior to strength measurements. Between 1400-2320°C, the heating-up rate was maintained between 20-32°C/min. The total time required to reach 2320°C was about 1 hr. There was no soak time at maximum temperature. Table 5 summarizes the weight loss and dimensional changes incurred upon heat treatment of the pellets. The

Table 4. Crushing Strength of Ceylon Graphite Compacts Following Various Treatments

Treatment	Strength, psi	Density, g/cc
Powder Dried 24 hr	1336 ± 172	1.96
	1277 ± 85	1.96
	1319 ± 148	1.96
	1335 ± 167	1.95
Compact Aged 24 hr	1358 ± 143	1.96
	1261 ± 93	1.96
	1345 ± 140	1.96
Compact Heated, 1405°C	996 ± 80	1.88
	875 ± 70	1.86
	862 ± 87	1.83
	867 ± 90	1.83
	728 ± 68	1.78
Powder Heated, 1395°C	778 ± 126	1.94
	468 ± 76	1.90

Table 5. Weight Loss and Dimensional Changes of Ceylon Graphite Compacts Upon Heat Treatment

Temperature, °C	Wt. Loss, %	Expansion, %	
		Length	Diameter
1405	0.72	2.09	0.52
1600	1.57	2.52	0.54
1795	1.96	3.13	0.72
1990	2.07	3.55	0.79
2320	2.38	5.02	1.11

weight loss increased progressively with increasing HTT; at 2320°C it is somewhat greater than the ash content of the Ceylon graphite (1.8%). Upon heat treatment, the mineral matter will first be reduced by the carbon. Weight loss will then be caused by volatilization of the metals and loss of CO and CO₂. To check that a negligible weight loss occurred due to carbon gasification by possible traces of oxidizing gases in the He atmosphere, molded samples of SP-1 spectroscopic graphite were heated to 1400°C in He. No weight loss was detected. Also in Table 5 it is seen that the compacts continued to expand with increasing HTT. Expansion in the longitudinal direction of the cylindrical samples was substantially greater than in the radial direction. As seen in Table 4, with increasing HTT there is a progressive decrease in sample density and strength. The compact heated to 2320°C has roughly half the strength of the unheated compact.

Ceylon graphite powder was also heated to 1395 and 2320°C prior to molding at room temperature. As seen in

Table 4, this heat treatment significantly decreased the density and strength of the pellets subsequently produced. This effect was previously reported by May³⁾ and Livey et al.⁴⁾ for artificial graphite powder.

4. Discussion

It is of interest to consider what we know and can conclude about the factors which determine the strength of binderless graphite compacts. For convenience, these compacts were caused to fail by the application of a compressive force. It is clear, however, that failure occurred in shear and/or tension—probably primarily in the former.

Generally, the higher the density of a body the greater is its strength. May attributes the ability to produce cohesive bodies by the cold molding of graphite powder to its lubricity which facilitates interparticle slippage, closer packing, and, hence, higher densities.³⁾ Closer packing of flake-like natural graphite particles can only mean a closer average approach of the basal plane surfaces which compose most of the geometric surface area. The closer the packing the greater the orientation of the particles with their basal planes aligned more closely parallel to the top and bottom surfaces of the cylindrical samples. Grosewald studied by X-ray diffraction the relative alignment of basal planes in compacts of Madagascar graphite produced by molding at 100,000 psi.²⁰⁾ Orientation could be expressed using the normalized orientation density function²¹⁾ $I(\delta)/I(0) = \cos^m \delta$, where δ is the angle of inclination which the basal plane makes with the top surface. From Grosewald's studies, $m = 8$, which means that 50% of the basal planes makes an angle of inclination of less than about 23° with the top surface.²¹⁾ This is not a high degree of alignment and is similar to that found in as-deposited pyrolytic carbon.²¹⁾ We feel that this approximates the degree of alignment found in our Ceylon and Madagascar samples compacted at 125,000 psi; samples compacted at 25,000 psi would have a smaller degree of alignment as reflected in their lower densities. Because of the degree of alignment found, it is concluded that the majority of points of closest contact between graphite particles in the compacts consists of a prismatic surface of one particle approaching a basal surface of a second particle. From surface area and pore size distribution results, it is clear that the fraction of these surfaces which approach each other within 2A (or within the range where chemical bonding is important) is very small.

Attractive forces between graphite particles in the compacts is expected to be of two main types: i) a van der Waals attraction between basal plane surfaces and ii) a

chemical attraction between atoms in a prismatic surface and a basal plane surface. Because it is concluded that the basal planes on adjacent particle surfaces, on the average, do not approach each other closely, the van der Waals attraction energy per unit basal plane area is expected to be small.²²⁾ However, this overall attraction is still significant because most of the geometric area of the graphite particles is basal plane area.²⁾ The chemical attractive energy can involve bonding between carbon and/or oxygen atoms (which have unpaired electrons) located in a prismatic surface and at defects (such as vacancies and steps) in the basal plane surface. In fact, the latter atoms are also located at prismatic surfaces.

Heat treatment of the graphite in He prior to their molding markedly lowers compact strength. Heat treatment up to 2320°C would remove most of the oxygen complex from prismatic surfaces, which was chemisorbed during and immediately after fine grinding of the natural graphites. Removal of oxygen will reduce the number of hydrophilic sites on which physical adsorption of water can take place.²³⁾ Since it is known that the lubricity of graphite decreases rapidly with decreasing water adsorption,²⁴⁾ it might be argued that heat treated graphite powders would not compact to as high a density as would the as-received graphite. However, in a key experiment May showed that artificial graphites, both as ground and after heating to 2400°C in Ar, compressed to the same extent.³⁾ May found that the resulting lower density of the compact produced from the heat treated graphite was caused by its much greater expansion after release of the molding pressure. If attractive forces between graphite particles were primarily of the van der Waals type and if equal compact density (under pressure) means equal average approach distance of the basal plane surfaces to each other, the compacts would have been expected to expand a similar amount after pressure release. Therefore, it is concluded that specific chemical bonding is a significant factor in the attraction between particles. It would appear that this bonding is optimum when the prismatic carbon atoms are covered with dissociatively chemisorbed oxygen. As expected, and as shown by May,³⁾ significant coverage of this oxygen by physically adsorbed water decreases pellet strength.

Further strengthening this argument of the importance of specific chemical bonding is May's finding that if the graphite was not ground to a sufficiently fine size, coherent compacts could not be formed. Finer grinding would produce more prismatic surface and more oxygen chemisorption. In this light it is interesting then that our pellets produced from Mexican graphite powder, which was more highly ground than the Ceylon or Madagascar, were the

weakest. From surface area results, it was concluded that the Mexican graphite had the highest degree of surface roughness. The extent of this roughness appears to be another factor of importance in determining ultimate pellet strength. Much of this roughness could be steps on the basal plane surfaces; these steps could inhibit interparticle slippage and densification.

Our finding that a subsequent heat treating of graphite compacts formed at room temperature decreases strength is expected. Sintering of graphite particles at atmospheric pressure and at temperatures up to 2320°C has never been reported. The fact that heating the graphite powders to 3000°C produced no significant decrease in their surface areas confirms this point. When the compacts are heated, they will expand. Because of some basal plane preferred orientation and anisotropy in the coefficient of thermal expansion in different crystallographic directions, the cylindrical samples will expand more in the longitudinal direction than the radial direction. If heat treatment did not affect the chemical bonding between particles, the compacts would be expected to return essentially to their original dimensions upon cooling to room temperatures. However, heat treatment results in removal of oxygen complex as CO and CO₂. This will result in the breakage of chemical bonds between adjacent particles and an increase in distance between the new surface carbon atoms. Without further application of pressure, these atoms will not be brought sufficiently close together to reform a new chemical bond. As a consequence, upon cooling to room temperature the compacts do not return to their original dimensions. As expected, the per cent residual expansion is greater in the longitudinal direction.

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