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PRODUCTION OF GRAPHITE SINGLE CRYSTALS BY THE THERMAL DECOMPOSITION OF ALUMINUM CARBIDE

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Abstract

Aluminum carbide, Al_4C_3, dissociates in the vicinity of 2200–2500° C., at atmospheric pressure, to aluminum vapor and graphitic carbon. Under suitable geometry and heating conditions large, pure, single crystals of graphite can be produced. The crystals have an unusual morphology. In no case is the macroscopic hexagonal symmetry evident. All crystals show growth lines and steps that presumably carry over from the carbide precursor. Twinning and cleavage are common but less frequent than in graphite from other sources. An interlayer spacing of 3.3545 ± 0.0005 Å at 25° C. was measured.

Introduction

Graphite exhibits a number of interesting properties that are associated with the high degree of anisotropy in directions parallel and perpendicular to the *c*-axis. This anisotropy is associated with a unique distribution of electrons, which are more-or-less free to move through the carbon net parallel to the basal plane, but are constrained from movement from one net to another. The graphite lattice has strongly bonded carbons at essentially the closest possible distance of approach (1.42 Å) in the carbon net, but adjacent nets are bonded by only coulombic attraction, and are about 3.35 Å apart.

The anisotropy of graphite can best be investigated on single crystals. The inaccessible melting point and the extremely low sublimation pressure preclude the preparation of large crystals by conventional techniques.

Most carbonaceous material graphitizes at temperatures above 1500° C., more completely the higher the temperature. The crystallite size is very small, however, and the interlayer spacing of the classical graphite lattice is approached only at the highest accessible temperature.

Fairly large (a few millimeters) graphite crystals can be grown from an iron melt saturated with carbon. Cooling the surface of such a melt by a stream of gas (1), or rapidly cooling the liquid by plunging a cold object into it, causes precipitation of single crystals that float to the surface. Graphite produced in this way is invariably contaminated with iron. Crystals prepared by the authors contained approximately 10% iron by weight, and were magnetic. Undoubtedly, most of the iron is mechanical contamination and its removal by acid treatment should not affect the structure of the graphite crystals. It is questionable, however, whether all of the iron is mechanically occluded, and whether iron removal treatments, such as high temperature chlorination, could remove it completely without affecting the crystal.

By far, the greater number of measurements on crystalline graphite have employed flakes of natural graphite, cleaved from pieces that had been separated from the matrix of limestone and other material where they occur.

Dutta (2) reported electrical measurements on natural, single crystals of Ceylon graphite that were one to two centimeters on a side, and about a half millimeter thick. They were cut from a larger crystal that was stated to be free of impurities, and showed no twinning or strains. It would be remarkable if a crystal of that size and perfection could be found in the natural state free of the profusion of impurities that ordinarily accompany natural graphite. Possibly, the examination of the specimens was only of a cursory nature. More frequently, natural graphite that can be considered as single crystals by most criteria is in the form of tiny flakes, two or three millimeters in the largest dimension, such as described by Palache (3), and Primak and Fuchs (4).

It would be expected that the carbides of all but the most refractory metals should yield graphite at temperatures where the compounds dissociate and the metal is volatilized. To the writers' knowledge, the various possibilities have not been explored.

Aluminum carbide, Al_4C_3, is an attractive starting material because it can be grown in large single crystals, and considerable is known about its chemical stability. Thermal data on aluminum carbide are sparse. Gross* determined the heat of formation at 900° C. as -32 kcal./mole. From known heat capacities of aluminum and carbon, and an approximation for that of aluminum carbide, it is calculated that the free energy of formation at 2000° C. is -24 kcal./mole., corresponding to an aluminum dissociation pressure of about 30 mm. This must be considered very approximate. At the same temperature, the sublimation pressure of carbon is negligible.

This paper describes the preparation of large, pure, single crystals of graphite by the thermal decomposition of pure aluminum carbide at temperatures in excess of 2000° C.

EXPERIMENTAL

Preparation of Aluminum Carbide

At moderate temperatures, aluminum should react to completion in the presence of excess carbon to form aluminum carbide. When the amount of exposed carbon surface is limited, however, the layer of carbide that forms at the carbon-aluminum interface inhibits further reac-

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* Gross, P., Private communication.

tion, and the solution appears to be stable. Figure 1 shows a section through aluminum that had been held at about 1800° C. in a graphite crucible. The precipitated yellow carbide plates that appear separated in the illustration actually communicate in the three-dimensional piece, and the mass exhibits a brittle fracture, although it consists predominantly of ductile aluminum.

Under no conditions will free carbon precipitate from an aluminum-aluminum carbide solution. If a mixture, such as that shown in Fig. 1, is heated in vacuum, the excess aluminum vaporizes readily at about 1800° C., to leave a residue of large, single crystals of aluminum carbide.

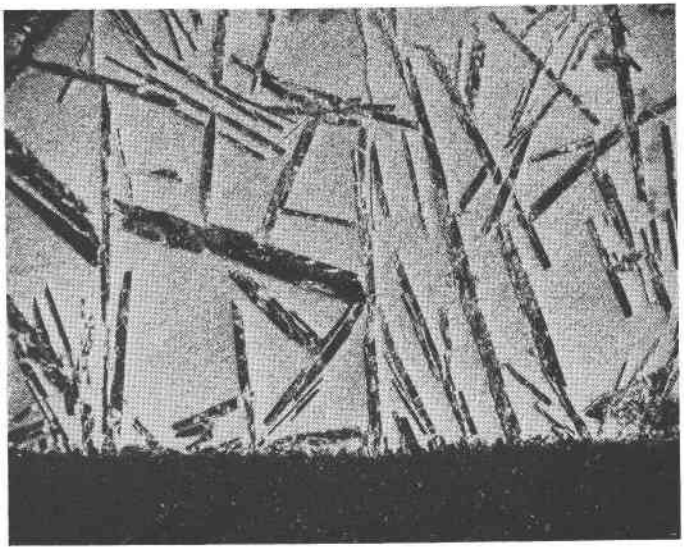

FIG. 1. Polished section of aluminum that had been held at 1800° C. in a graphite crucible. The plates that appear black are yellow transparent aluminum carbide. Mag. 19×.

This method of preparation is troublesome, because large quantities of aluminum condense in the lining and insulation of the furnace. A more satisfactory synthesis consists of heating lampblack and atomized aluminum powder in the stoichiometric ratio to make aluminum carbide. Complete reaction is obtained when the ball-milled mixture is held at 1850° C. in an argon atmosphere for approximately two hours. The product is yellow-orange and, though partially sintered, it can be crumbled readily by hand. The crystal size varies, depending on the heating conditions, but 0.1 to 1 mm. is a typical range.

The product is shown to be pure, stoichiometric aluminum carbide by *x*-ray examination, and by methane evolution in hydrochloric acid.

Preparation of Graphite Crystals

Aluminum carbide converts readily to graphite on heating above 2000° C. in vacuum, or to somewhat higher temperatures in inert atmospheres. However, in order to grow large crystals, it is necessary that the geometry of the charge and the heating conditions be such as to grow large carbide crystals first. Although large carbide crystals are necessary precursors, they do not assure large graphite crystals. In one experiment where large, perfect carbide crystals, contained loosely in an open graphite crucible, were heated in high vacuum to 2500° C., the graphite product was microcrystalline. The best product was obtained when the optimum geometry for growth of the carbide crystals was maintained during further heating to the dissociation temperature.

The following procedure gave the best graphite crystals. Aluminum carbide was ground to −325 mesh. A rough cylinder, approximately 4 cm. in diameter by 8 cm. long, was hydrostatically pressed at about 60,000 psi in a high pressure, oil-filled bomb. The fine particle size was necessary to give adequate green strength to the pressed body. A 1-cm. hole was drilled axially through the cylinder. The cylinder was placed in a loose-fitting, graphite tube in a horizontal induction-heated furnace that was equipped with graphite radiation shields at either end. The charge was heated slowly so that it reached about 2400° C. in 4 hours. It was held at that temperature for an additional 2 hours, then slowly cooled by reducing the power to the induction coil. Purified argon was passed through the unit at atmospheric pressure at approximately 40 ml./minute throughout the entire heating cycle.

The temperature was measured at the hottest part of the charge that could be seen through axial holes in the radiation shields. Undoubtedly, part of the charge that was hidden from view was at a higher temperature. However, previous experience with the furnace had indicated that temperature differentials exceeding 100° C. were unlikely.

On occasions, part of the charge appeared to melt. Since aluminum carbide probably does not melt, per se, it is assumed that in those cases aluminum vaporized from the hottest part of the charge, condensed onto the cooler parts, and dissolved the carbide to produce the liquid phase.

The largest graphite crystals were found growing into the axial hole in the charge and into voids throughout the charge that had resulted from shrinkage or cracking during the heating period. Those are the places where the largest carbide crystals would have been found had the heating been interrupted before the dissociation temperature was reached.

Figure 2 shows transparent, yellow aluminum carbide plates before

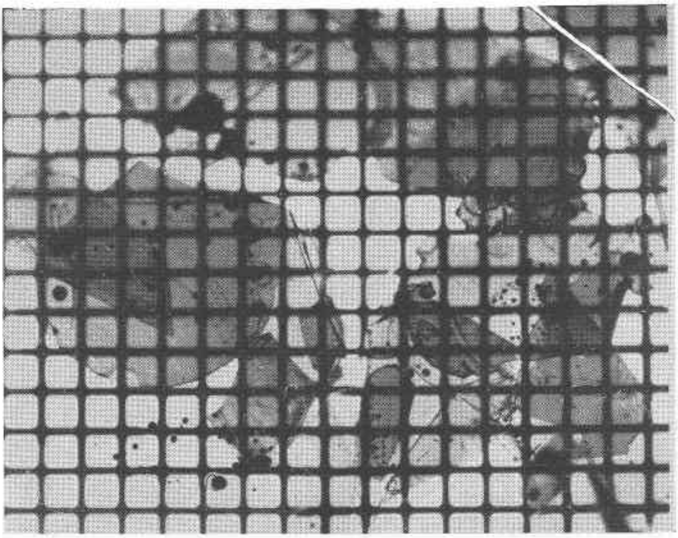

FIG. 2. Single crystals of aluminum carbide supported on a fine mesh screen to show their transparency. The small black dots are droplets of metallic aluminum that condensed on the crystals during cooling. Mag. 14×.

their conversion to graphite. Figure 3 shows a charge and the containing graphite tube broken open after completion of the graphitization. The largest graphite crystals are seen in the center.

PROPERTIES OF GRAPHITE CRYSTALS

Purity

The most likely impurities in the graphite would be free aluminum and unreacted aluminum carbide. Because of the temperature gradients, the charge was seldom completely converted to graphite throughout. Moreover, aluminum carbide was everywhere in the furnace, either blown about mechanically by the argon stream, or formed by reaction of the vaporized aluminum with the carbon furnace parts. There was never complete assurance, therefore, that a large enough sample of graphite for analysis could be recovered without the possibility of mechanical inclusion of aluminum or aluminum carbide.

Purity was established on a sample of approximately 0.075 g. of the cleanest appearing crystals that had been leached free of occluded aluminum carbide with dilute hydrochloric acid. The crystals were not visibly altered during this treatment, and it is likely that the acid removed only the admixed carbide and aluminum that had been visible as tiny particles under the microscope.

The crystals exhibited amazing retention of the acid. Repeated washing over a three-week period did not completely remove the hydrogen ion. This treatment would not be expected to produce lamellar or residual compounds, so perhaps the acid was only mechanically entrapped.

Ignition of the sample at 800° C. left no residual ash within the weighing precision of an ordinary analytical balance. Furthermore, microscopic examination of the platinum ashing crucible showed no residue that could be attributed to the graphite.

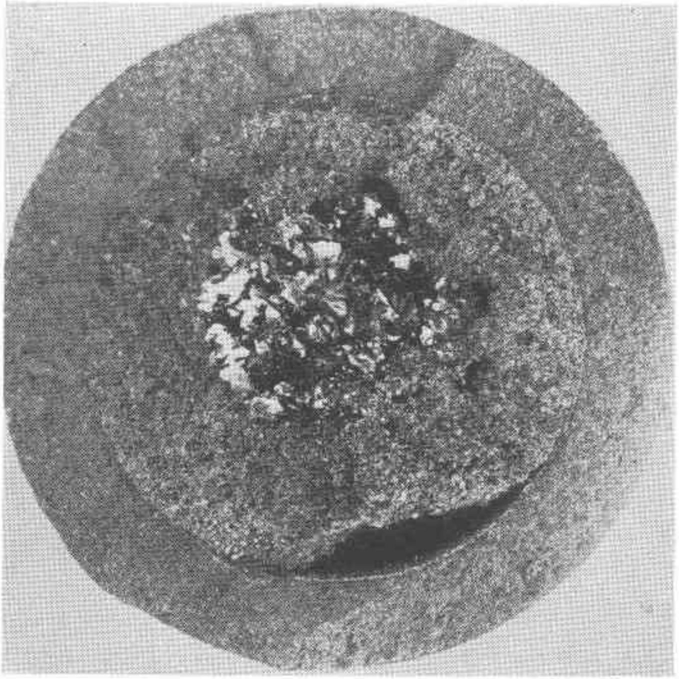

FIG. 3. Graphite crystals formed in the center of a charge of aluminum carbide that had been held at 2400° C. Mag. 2×.

X-RAY PROPERTIES

The interlayer spacing was measured on a Norelco diffractometer. The spacing was obtained by extrapolating to zero ($\theta = 90°$) the plot of d-values, calculated from the 002, 004, 006, and 008 reflections, versus $\cos\theta \cos^2\theta$. The crystals were oriented with the basal planes parallel to accentuate those reflections. An interlayer spacing of 3.3545 ± 0.0005 Å at 25° C. was determined on one lot of particularly fine crystals.

A number of Laue patterns were made of carefully selected crystals.

In only one instance was a pattern obtained that showed simple sixfold symmetry of a single individual. More frequently, the spots indicated two or more individuals with common *c*-axes, rotated slightly with respect to one another. The persistent rotation between two individuals of $2\frac{1}{2}°$, that was reported by Lukesh (5), generally was not observed.

Powder patterns of finely ground crystals showed extra lines corresponding to a few per cent of the rhombohedral modification, which was first reported by Lipson and Stokes (6). Although the source of these extra lines was controversial a few years ago, it now appears that the phenomenon can be adequately described by the alternative stacking sequence of ABCABC, in the rhombohedral modification, rather than the ABABAB stacking for the usual hexagonal form. This situation has been well described by Laves and Baskin (7), and others, and will not be discussed here. It was not established whether the rhombohedral modification existed in the single crystals or was produced by grinding for the powder patterns.

TWINNING

Twinning, of the type described by Palache (3), and Laves and Baskin (7), could easily be observed, although growth twins were infrequent. Perhaps only one out of ten crystals from a good lot showed twins that could be detected by light reflection under a microscope, if they were carefully handled so as not to induce mechanical twinning. Mechanical twinning could be induced very easily by pressing a sharp point into the flat surface of a crystal. Such a twin could be led over the crystal in a striking manner by drawing the point along the surface.

MORPHOLOGY

The most striking characteristic of the graphite crystals is the unusual crystal form. This is best illustrated by Figs. 4–7. In contrast to crystals grown from iron (Fig. 8), which clearly show the hexagonal symmetry, crystals from the decomposition of aluminum carbide in no instance showed a straight edge or a well-defined angle. On the other hand, growth lines and steps that are indistinct or absent in graphite from other sources were most pronounced in all of the specimens of carbide graphite that were examined. Similar growth lines can be seen in most aluminum carbide crystals and it is assumed that these carry over in some fashion to the graphite. In addition to growth lines, however, most carbide crystals show one or more hexagonal angles. Figures 4A and B show typical graphite crystals. No twinning is apparent. The spallation in the center of the crystal of Fig. 4A is a typical defect resulting from cleavage of a thin layer off the surface of the crystal. This might have been caused by

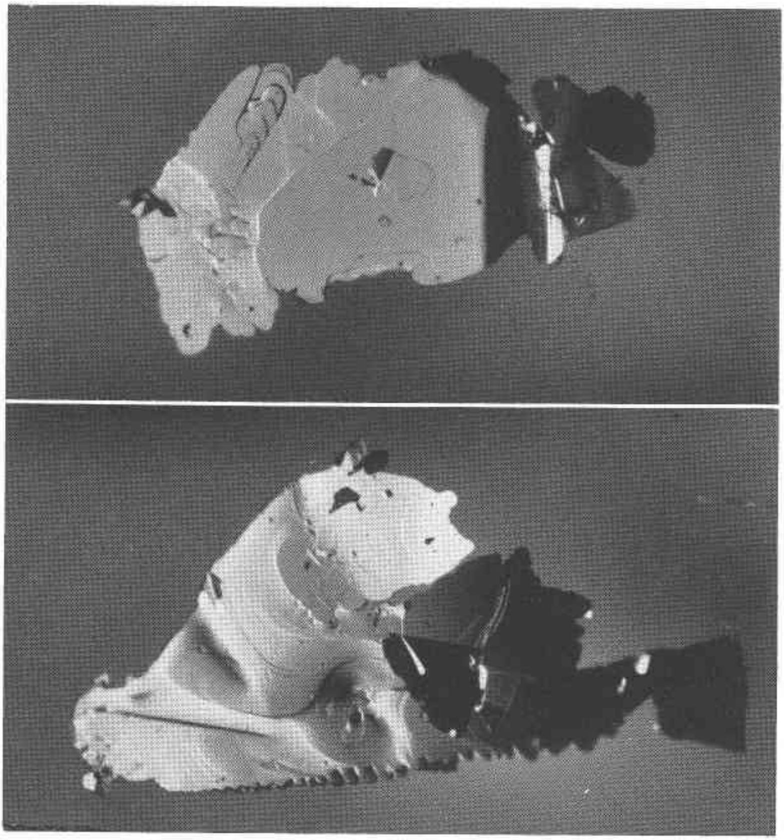

FIG. 4. Typical crystals of graphite produced by thermal decomposition of aluminum carbide. Mag. 25×.

handling the crystal after it was prepared. Figure 5 shows twinned crystals. Figure 5A shows profuse twinning. This was rare in the samples under study, although it is characteristic of natural graphite crystals. Figure 5B shows a crystal that was untwinned initially, but was mechanically twinned by pressing the point of a pencil into the surface at the position where the twin lines originate. Figure 6 is the largest crystal showing no twinning or cleavage that was found in a cursory examination of several hundred specimens. This crystal is approximately $\frac{1}{4}$ inch long.

Figure 7 shows a crystal with two pronounced twin lines, one showing as a dark, black shadow and the other as a light band. These twins are seen to go through the growth rings uninterrupted and without change of direction.

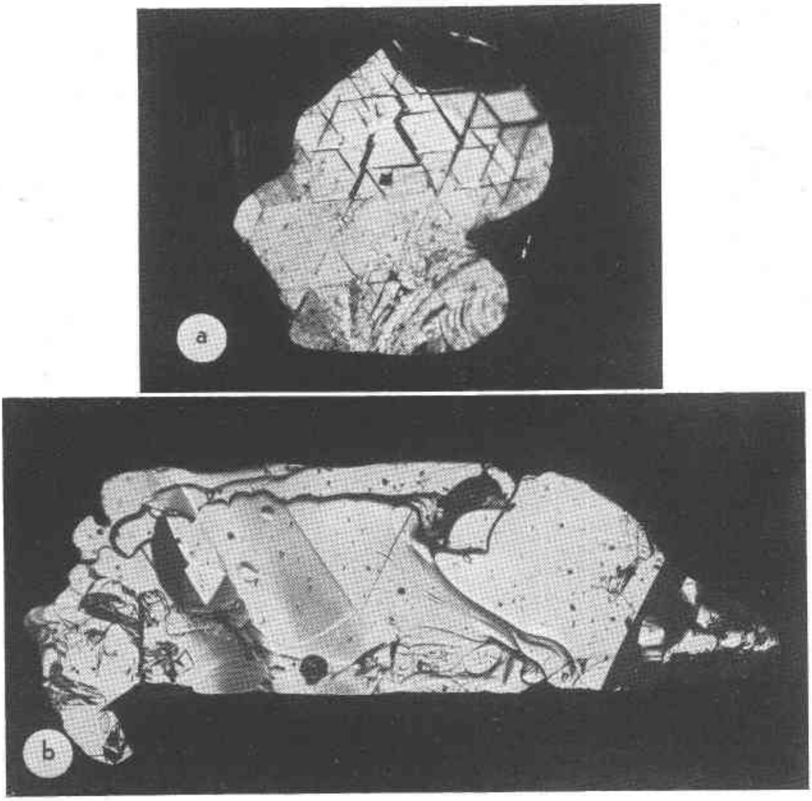

FIG. 5. (a) Graphite crystal showing extensive twinning. (b) Graphite crystal showing mechanical twinning. Mag. 25×.

DISCUSSION

It is possible that aluminum carbide is unique among the metal carbides in its ability to form large single graphite crystals by volatilization of the metal cation. The temperature where the conversion to graphite occurs is much lower than the temperature where amorphous or microcrystalline carbon would be expected to become ordered to give the near-classical *c*-spacing. It appears then, that the conversion must entail a systematic diffusion of aluminum atoms and contraction of the carbon lattice.

The Group III metals are the least electropositive elements that form salt-like carbides, where the lattice is determined by packing of the carbon atoms. The Group IV, V, and VI metals are too large to fit in the interstices between carbons, and the structure is determined by the metal atom packing. These latter carbides are usually referred to as interstitial carbides.

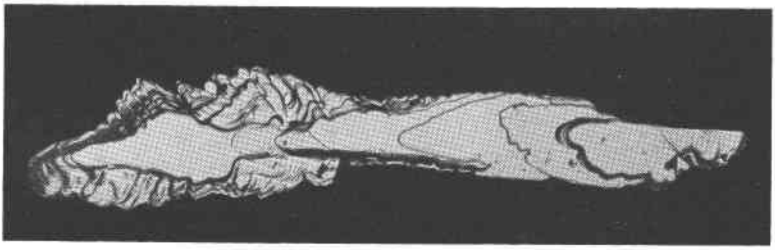

FIG. 6. Large graphite crystal free of cleavage and twinning. Mag. 15×.

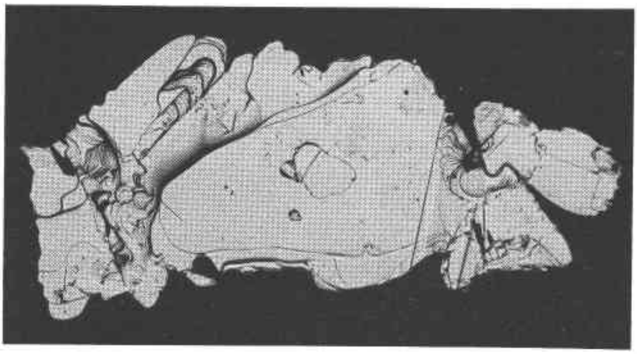

FIG. 7. Graphite crystal showing two parallel twin lines that extend through growth lines. Mag. 12×.

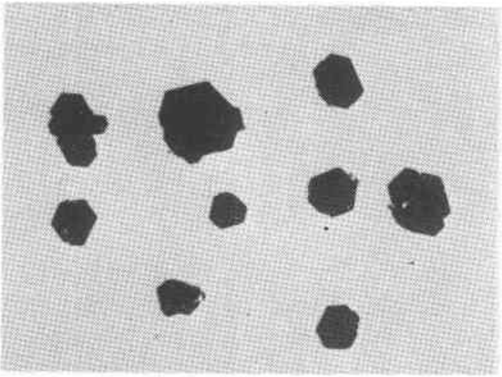

FIG. 8. Graphite crystallites grown from an iron-carbon melt. Mag. 25×.

Of the metals that form salt-like carbides, only beryllium and aluminum are sufficiently small to be contained in the equivalent tetrahedral cavities between the carbons in the number required to satisfy their normal chemical valence. This results in hexagonal, lamellar crystals that exhibit cleavage through the planes that separate stoichiometric units. This lamellar character might well be a requirement for any crystal to dissociate to a lamellar product.

Beryllium carbide emerges as the only crystal, besides aluminum carbide, that would be expected to dissociate to the free metal and macrocrystalline graphite. However, the lower vapor pressure of beryllium would necessitate a higher dissociation temperature to effect the complete removal of beryllium from the product.

The structure of aluminum carbide was determined by Stackelberg and Schnorrenberg (8). The crystal is hexagonal with a layer lattice. Each layer consists of four aluminum and three carbon atom planes. The four aluminum planes lie over one another in what would be cubic close packing, except for the interposed carbon planes. The cubic packing is disrupted at the boundary of a layer in such a way that two outer aluminum planes in one layer and the first aluminum plane in an adjacent layer are hexagonally close packed. Between the aluminum planes lie three carbon planes, one of which forms the middle plane of the layer. This C_{I} plane is flanked on each side by an Al_{I} plane. These are followed by C_{II} planes, and finally on each side by an Al_{II} plane, which terminates the layer. The next layer begins with an Al_{II} plane. Each layer thus has the stoichiometric Al_4C_3 composition with saturated valences, and the boundary of the layer constitutes the cleavage plane along the horizontal base. The arrangement of the carbon planes is somewhat similar to that of the aluminum planes. That is, the packing is hexagonal across the layer boundary and cubic within the layer.

It is interesting to speculate how these carbon layers can transform to the graphite structure. In the carbon planes of aluminum carbide there are approximately 0.105 carbons/Å², compared to 0.382 carbons/Å² in the graphite carbon net. This suggests a condensation of the three carbon planes of a carbide layer to form one carbon net of approximately three times the carbon density. Two adjacent planes, merging along the *c*-axis, produce an open-center, carbon net. The C—C distance is 1.92 Å, $(\frac{1}{3}\sqrt{3}a)$, however, and appreciable contraction would be required to reach the 1.42 Å spacing in the graphite net. If the third carbon plane compresses along the *c*-axis, without rotation, the atoms go into the center of the open net formed by the previous two, to give full hexagonal symmetry with one atom in the center of a hexagon whose side is still 1.92 Å. There is no obvious way that this layer could transform to the open carbon net of graphite with a C—C distance of 1.42 Å, without appreciable atom shift and the loss, momentarily, of the hexagonal symmetry. The complete absence of straight sides and well-defined angles in the graphite crystals suggest that considerable atom shift or rotation of carbon planes does take place during the transformation. It is reasonable that, at the high temperature the loss of aluminum by diffusion, and the compression and reorientation of carbon planes, takes place simultaneously in a reaction zone or front that progresses across the crystal with the thermal gradient.

The smallest *c*-spacing found experimentally on graphite crystals is not well identified in published reports. The value of 6.696 Å appears frequently. Lukesh (6), however, cites the same value in kx units (6.696 kx units = 6.709 Å). The best value that was found in a cursory examination of the literature was the interlayer spacing of 3.3538 ±0.0005 Å, at room temperature, for a single crystal of natural graphite, that was determined by Baskin and Meyer by an extrapolation method (9). The same authors found 3.3542 Å for natural graphite powder, and 3.3600 Å for artificial graphite powder.

It appears that the interlayer spacing in the graphite crystals produced from aluminum carbide is acceptably low, and might well be comparable to the lowest spacing ever reported. It would be interesting to see if a higher dissociation temperature would result in an even smaller spacing.

The low *c*-spacing, combined with chemical purity, large size, and general absence of cleavage and twinning, make these crystals attractive for more precise investigation of the properties of graphite. The authors feel that with larger furnace equipment, capable of going to higher temperatures, crystals at least ½ inch across could be prepared.

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