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INTERCALATED GRAPHITE ELECTRICAL CONDUCTORS

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For years NASA has wanted to reduce the weight of spacecraft and aircraft. It would certainly be advantageous to find a lightweight synthetic metal to replace copper. The subject of this paper, intercalated graphite, is such a material.

As shown in figure 1 intercalated graphite is made by heating petroleum or coal to remove the hydrogen and to form more covalent bonds, thus increasing the molecular weight. The coal or petroleum eventually turns to pitch, which can then be drawn into a fiber. With continued heating the pitch-based fiber releases hydrogen and forms a carbon fiber. The carbon fiber, if heated sufficiently, becomes more organized in parallel layers of hexagonally arranged carbon atoms in the form of graphite. Certain chemicals or dopants are introduced between the layers of this high-temperature-treated, highly oriented graphite fiber. These chemicals, called intercalants, react with the carbon to form a large molecule and are diffused into the graphite between its layers of carbon atoms. The intercalants affect the electron distribution of the carbon in a manner that increases its electrical conductivity. The conductivity in the A direction (in the planes) is substantially increased. In the C direction (perpendicular to the planes) it is not increased at all. A conductor of intercalated graphite is potentially useful for spacecraft or aircraft applications because of its low weight. These intercalated graphite fibers can be coated with various metals so that they can be soldered. With an appropriate fiber cable design, it may be possible to terminate them and treat them much like conventional conductors.

As shown in figure 2 the mass of a wire is equal to the density n times the area A times the length L . Resistance is $\rho L/A$, where ρ is resistivity. For a wire of a definite length that is to have a certain resistance, the resulting mass is proportional to the length squared, because the longer it is, the thicker it must be to have the same resistance. Density and resistivity can be varied in searching for the ideal conductor. Ideally, one wants to reduce the mass of conductor on an aircraft or a spacecraft by keeping its weight and resistance low.

Depending on the specific application, a variety of materials can be used (table I). Although copper is fairly dense compared to other materials, its resistivity is very low. Aluminum is slightly more resistive but substantially lighter, so that its product $n\rho$ is about half that of copper. Although that is good, aluminum suffers from some engineering termination difficulties that have tended to reduce its widespread replacement of copper conductors. Other materials are better than aluminum, such as sodium, which is even farther from being a practical wire material because of its reactivity. Graphite fibers are much lighter than aluminum but have extremely high resistivity ($250 \mu\Omega\text{-cm}$). However, if the graphite fibers are heat treated at high temperature, they become highly oriented and possess low resistivities (40 to $60 \mu\Omega\text{-cm}$) and will have densities that approach single-crystal densities of 2.26 g/cm^3 . The product $n\rho$ is still higher than that of copper by a factor of 4. However, intercalated highly oriented pyrolytic graphite (HOPG) has an $n\rho$ of $4.3 \mu\Omega\text{-cm}$ as compared with $15.1 \mu\Omega\text{-cm}$ for copper. The problem is that HOPG is not a fiber but a bulk material and so does not have

the characteristics suitable for fabrication of a wire. Intercalated graphite fibers have a slightly higher ρ of 8.1 $\mu\Omega$ -cm, which is still better than that of copper. There are practical problems that must be resolved. For example, arsenic pentafluoride is a very airreactive intercalant. There are many ways of treating the fibers or of using other intercalants so they will not be air reactive after intercalation.

Intercalation has other potential advantages, as shown in table II. Intercalated graphite fibers are extremely strong (250 000 psi compared with 40 000 psi for copper) and have a high strength-to-weight ratio. The expansion coefficient is much lower than that for copper. This might make them ideal for high-tension lines because they would not droop due to thermal expansion in the summer.

As shown in figure 3 when HOPG is intercalated, its normal resistivity ρ of 40 $\mu\Omega$ -cm is reduced by some constant k depending on the type of intercalant. For arsenic pentafluoride, $k = 24.2$. The mass of the conductor then is dependent on n , ρ , k , R , and L . The resistivity is dependent on two components. Resistance is offered in the conductors as a result of phonon interaction with the electrons and defects interacting with the electron transit. Phonon interaction is not changeable, but one can obtain relatively defect-free graphite.

Thus there are several factors that cannot be easily changed: the density of intercalated graphite does not vary much, the phonon term cannot be changed, length and resistance are prescribed. However, try to minimize the mass of the conductors, we can try to find graphite that is well organized and defect free and then search for the ideal intercalant by focusing on the terms outside the bracket in figure 3.

The orientation and number of defects are directly dependent on the process used to make the fibers (fig. 4(a)). Both the structures and the properties are affected by processing. If oil or coal is heated, it begins to increase in molecular weight and hydrogen is evolved. It goes through a liquid-crystal phase, called mesophase. As the process continues with increasing temperature (1000° to 2500° C), we eventually obtain carbon. Increasing temperature to 3000° C increases organization and graphitization to produce an ideal graphite-like structure.

In the liquid phase, where the pitch becomes a thick fluid, it initially is not very organized, that is, there is an isotropic orientation of hexagonal platelets. Within this sea of randomly organized, or disorganized, platelets, there develop droplets of the mesophase, or liquid-crystal phase. In this phase the platelets link up and gradually change direction, so there is very good organization within these spheres. They also coalesce as the material is heated (fig. 4(b)). Each hexagonal platelet touches the next and there is a gradual, smooth transition to a more complete liquid-crystal phase.

Figure 5 shows pitch coalescing under polarized light. Droplets of the mesophase liquid crystal are immiscible with the surrounding isotropic pitch and thus gradually get bigger as they coalesce. Figure 6 shows a polarized-light photomicrograph and a drawing based on interpretation of the orientation of the platelets in the polarized-light photomicrograph. The lines are drawn parallel to these platelets. The platelets follow each other in a continuous manner just as in a pneumatic liquid crystal in that there is a continual or gradual variation in orientation of these platelets. Extruding the mesophase liquid crystal with some of the globules that have coalesced in this sea of random changes in direction through spinnerettes provides further directional organization to these fibers (fig. 7). This spun mesophase pitch-based carbon fiber (fig. 8) is not necessarily a graphite fiber unless it is heat treated. Generally, spun carbon fibers are of the order of 10 μm in diameter, which is

ideal for a variety of engineering reasons. Figure 9 is an end view of such a fiber; it shows no semblance of graphite organization. It is simply a carbon fiber that has been extruded and is largely amorphous. It is not graphitic. It is a fiber of the type one might use for structural composites. However, by suitable processing and proper heat treatment, the fiber can be organized with an onionskin type of geometry (fig. 10), where the graphitic planes are organized circumferentially just like the skin of an onion. This type of fiber is very difficult to intercalate because intercalation occurs through the edges of the planes. Because there are very few edges present, it is difficult to intercalate radially. However, we can similarly fabricate a different type of fiber (fig. 11) in which the planes are radial. The wedge is caused by further shrinkage of the fiber due to hydrogen release, but this does not occur in all radially oriented fibers.

The radially oriented fiber is the ideal geometry to intercalate. Even with this orientation it is possible not to have an ideal geometry of AB,AB staggered orientation of hexagonal planes, but rather a geometry of parallel but rotated planes with respect to each other. This is called turbostratic graphite (fig. 12). Although it is disorientation of a lower importance, the defects causing poor conductivity must also be eliminated.

Figure 13 shows an internal void. These voids and surface defects all increase the resistivity of a fiber before intercalation and have a direct effect on the ultimate resistivity. Figure 14 shows an included particle, which is another defect to be avoided. Progress has been made by various types of treatment and processing to minimize the occurrence of these defects.

The molded graphite normally found in a machine shop (fig. 15) is polycrystalline and has fairly high resistivity and low density (table III). Extruded graphite is slightly more organized and has a higher density. Pyrolytic graphite exhibits both good organization and anisotropy. There are three orders of magnitude difference in the resistivity in the plane as opposed to through the plane. The highly oriented pyrolytic graphite (HOPG) exhibits the highest degree of organization and anisotropy. The most highly organized fiber, P100, which is commercially available, has a resistivity of 250 $\mu\Omega$ -cm. Pyrolytically deposited fibers have been made in which the fibers have been grown through decomposition of organic gases; these have properties that approach those of HOPG. Intercalation of these fibers would result in very high conductivity.

The intercalant used in figure 16 is potassium. Figure 16 shows a first-stage intercalation in that there is one carbon layer between each intercalant layer. The compound is actually C_8K . One can put various intercalant concentrations in materials. For example, you could have a first stage compound where it is between every carbon layer, or a second stage (between every other carbon layer). To obtain the higher conductivity per volume, a second or third stage would generally be optimal, although at least 10 stages have been identified. Stages of intercalation are shown in figure 17.

Some of the many intercalants include K, Br_2 , Cl_2 , Cs, Li, Na, F, Rb; N_2O_5 , SO_3 , CrO_2 ; IBr; ICl , $AlCl_3$, $CuCl_2$, $FeCl_3$, $NiCl_2$, $MnCl_2$, $ZnCl_2$, $SbCl_5$; $PdCl_2$, $MoCl_5$; CrO_2Cl_2 ; $Ba(NH_3)_2$; H_2SO_4 ; SbF_5 ; and AsF_5 . Many of the intercalants such as bromine are very air reactive. Some of them such as copper chloride are not air reactive. A reactive material can be introduced first as a wedge to pry apart the molecules so that another material can be introduced later. Figure 18 shows pyrolytic graphite strips that have been intercalated with bromine as well as virgin graphite. The intercalated graphite strips are wider (the outside two pieces). They were intercalated by immersing the graphite in bromine and as a result they became about 30 percent

thicker. They delaminated because this bromine wedge was driven in so fast that stresses exceeded the intralaminar bonding forces.

Figure 19 shows two pieces of pyrolytic graphite held by small C-clamps. The left one is not treated; the right one was intercalated with gaseous bromine and photographed using laser holography double exposures. The exposures were taken 30 seconds apart. The interference fringes indicate the intercalant is leaving from the edge. Thus, intercalation swells the graphite and, as it deintercalates to some residual compound, it actually gets thinner. The process occurs out the edges rather than through the face.

If intercalation is done too quickly, by immersion in liquid bromine, defects will be generated that can increase resistivity. Figure 20 shows pyrolytic graphite that was intercalated by liquid immersion rather than by vapor exposure. The intercalation was so rapid that it disrupted the surface structure of the graphite. Deintercalation occurred all over the surface not just from the edges - indicating structural damage to the surface.

Figure 21 illustrates what happens in real time with respect to resistance of pyrolytic graphite strips upon intercalating with bromine. The resistivity was reduced by a factor of 16.7 in 280 minutes. When the graphite was removed from the vapor, it began to deintercalate, so the resistivity increased again (fig. 22). However, it did not rise to the same level. There was a net reduction in resistivity of $4.3 \mu\Omega\text{-cm}$ in this particular experiment. Thus there was a net increase in conductivity.

Many engineering aspects pertinent to the practical application of intercalated graphite conductors need to be looked at. One is coating fibers to make them solderable. Figure 23 shows a fiber that was electroplated with copper. The coating is not uniform. One would like a very thin coating; one would like to be able to solder these fibers so that they could be treated like a conventional wire to at least some extent. One of the problems with the particular process used is shown in figure 24. As can be seen, some of the fibers have coalesced during electroplating and would be less flexible because the plating joins them and they fracture quite easily. NASA Lewis is looking at a variety of intercalants. Many engineering aspects must be considered before they can really compete with copper conductors, but there are many exciting opportunities. A suitable method of terminating a bundle of brittle fibers must be determined. The fibers have to be coated for soldering so that they can be used from a spool just like a conventional wire. A suitable insulation has to be derived for them that is intercalant resistant, with consideration given to limit fiber flexure. If you bend fibers over too small a radius of curvature, they will fracture because they are so thin, but coating with insulation should make them more pliable. At high current, intercalated graphite "wires" may get hot momentarily, which may affect the intercalant: it may deintercalate or it may go to a different stage in intercalation. Thus the residue intercalation compound has to be stable on exposure to air, moisture, salt, or vacuum. It must be stable under steadily applied dc and ac fields. Some of these concerns are not well understood at this point and they are subjects of current research activity.

BIBLIOGRAPHY

1. Singer, L. S.: Carbon Fibers from Mesophase Pitch. Fuel, vol. 60, Sept. 1981.
2. Hooley, J. G.: The Intercalation of Layered Structures. Carbon, vol. 18, 1980, pp. 82-92.

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TABLE I. - CHARACTERISTICS OF MATERIALS

Material	Density, n_s g/cm ³	Resistivity, ρ_s $\mu\Omega$ -cm	$n_x \rho_s$, $\mu\Omega$ -g/cm ²
Copper	8.9		15.1
Magnesium	1.74	4.4	7.7
Aluminum	2.7	2.8	7.6
Sodium	.97	4.8	4.6
Calcium	1.55	3.4	5.2
Graphite fibers	2.15	250.0	537.5
Highly oriented pyrolytic graphite (HOPG)	2.26	40.0	90.4
Intercalated graphite fibers (AsF ₅)	2.7	3.0	8.1
Intercalated.HOPG (AsF ₅)	2.7	1.6	4.3

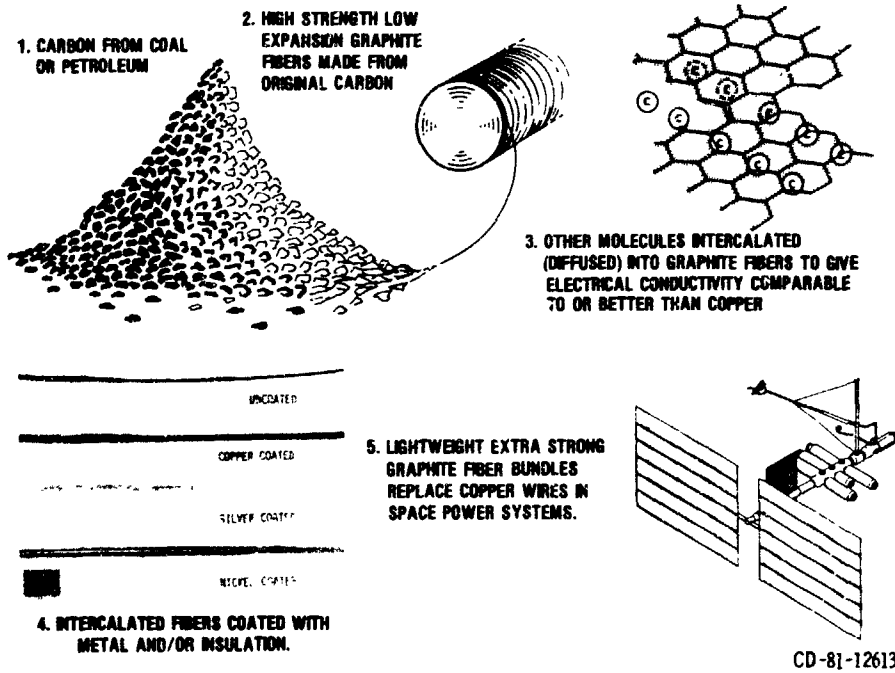
TABLE II. COMPARISON OF INTERCALATED GRAPHITE FIBERS WITH METALS

Material	Tensile strength, psi	Strength to weight ratio, psi cm ² /g	Thermal expansion coefficient, 1/C°
Copper	40 000	4 490	16x10 ⁻⁶
Aluminum	80 000	29 600	14
Steel	400 000	50 600	7
Intercalated graphite fibers	250 000	147 000	1

TABLE III. - CHARACTERISTICS OF MOLDED GRAPHITE

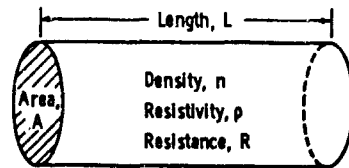
	Resistivity, $\mu\Omega$	Density, m ³
Bulk carbon		
Molded polycrystalline graphite	1 400	1.75
Extruded polycrystalline graphite	900	1.77
Pyrolytic graphite		
A	250	2.20
C	300 000	
Highly oriented pyrolytic graphite		
A	40	2.26
C	200 000	
Carbon fibers		
Thornel 300 (450 ksi tensile)	1 800	1.75
Thornel 50 (pan)	750	2.02
Thornel P100 (pitch)	250	2.15
Pyrolytically deposited (endo)	59	----

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Figure 1. - Graphite intercalated conductor.



Mass of conductor = nAL

$$R = \frac{\rho L}{A} \text{ or } A = \frac{\rho L}{R}$$

$$\text{Mass of conductor} = \frac{n\rho L^2}{R}$$

Figure 2 - Characteristics of conductors.

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ρ_1 - Resistivity after intercalation

k - Constant for each intercalant ≈ 24.2 for AsF_5 ; 12.7 for HNO_3 ; 3.5 for Rb

$$\rho_1 = \frac{\rho}{k}$$

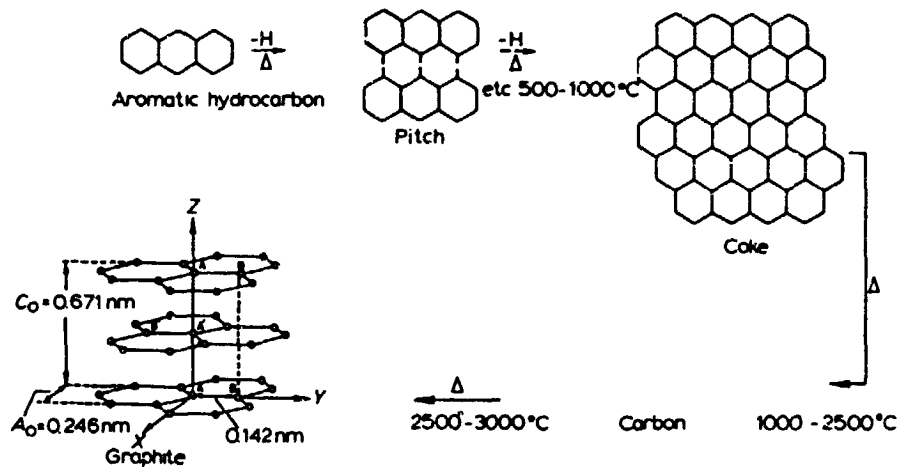
$$\text{Mass of conductor} = \frac{n\rho L^2}{kR}$$

$$\text{where } \rho = \frac{\rho_{\text{phonon}} \rho_{\text{defect}}}{\rho_{\text{phonon}} + \rho_{\text{defect}}}$$

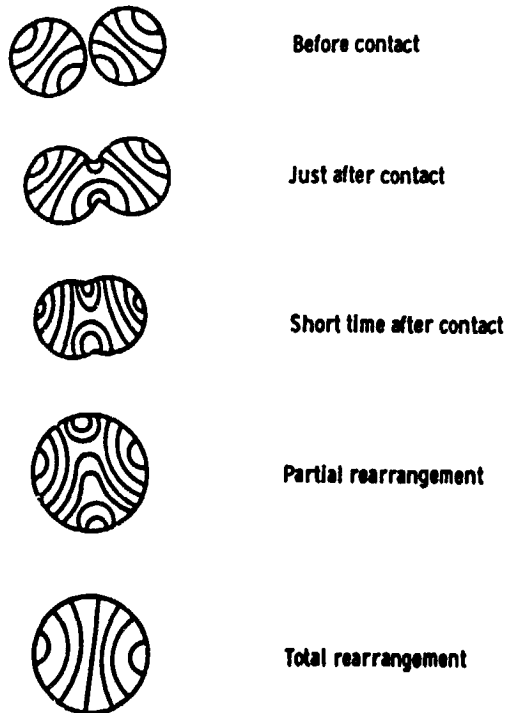
$$\text{Mass of conductor} = \frac{\rho_{\text{defect}}}{k} \left[\left(\frac{n\rho_{\text{phonon}} L^2}{\rho_{\text{phonon}} + \rho_{\text{defect}}} \right) \frac{L^2}{R} \right]$$

Figure 3. - Intercalated graphite conductors.

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(a) Dependent on manufacturing process.



(b) Arrangement of hexagonal platelets.

Figure 4. - Orientation and number of defects.

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Figure 5. - Polarization of pitch under polarized light.

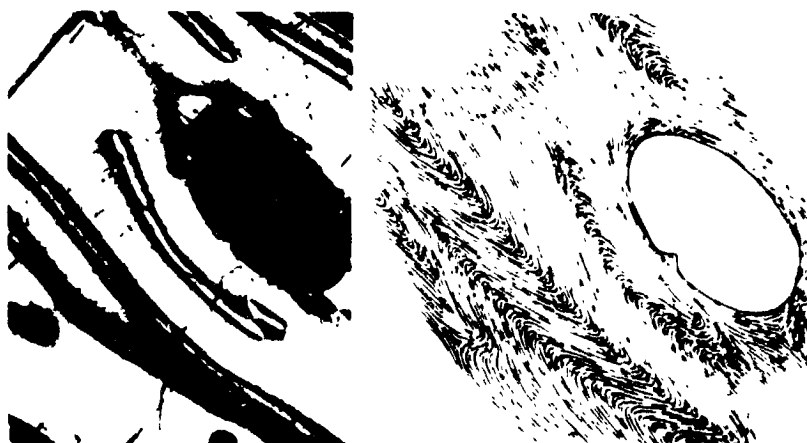


Figure 6. - Polarized-light photomicrograph and drawing based on orientation of platelets in photomicrograph.

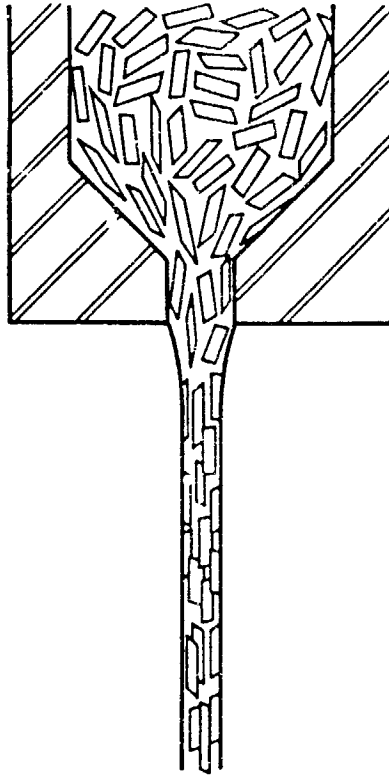


Figure 7. - Extrusion through spinnerette.



Figure 8. - Spun meso-phase pitch-based carbon fiber.

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Figure 9. - End view of spun meso-phase pitch-based carbon fiber.



Figure 10. - Onion-skin fiber geometry.

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Figure 11. - Radial fiber geometry.

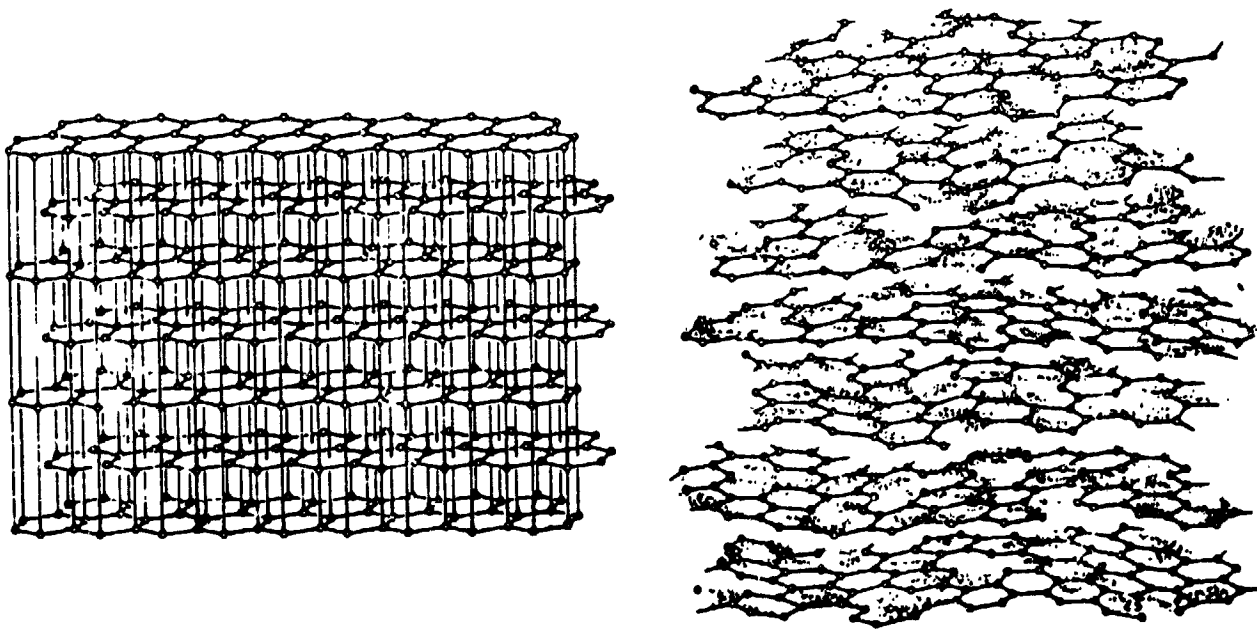


Figure 12. - Orientation of turbostratic graphite.

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Figure 13. - Internal void.



Figure 14. - Included particle.

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↑ ↑ ↑ ↑
0 1 2 3 cm

Figure 15. - Polycrystalline graphite.

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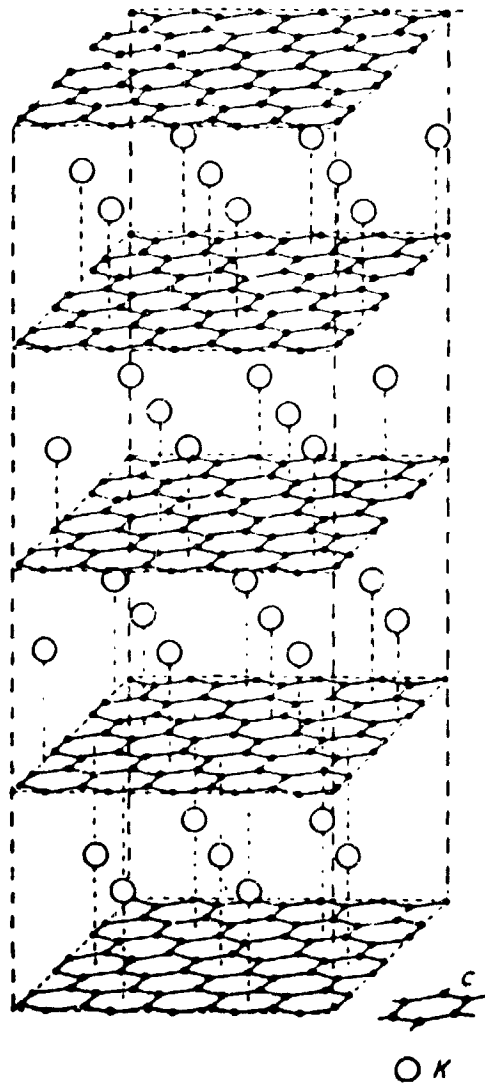


Figure 16. - First-stage intercalation.

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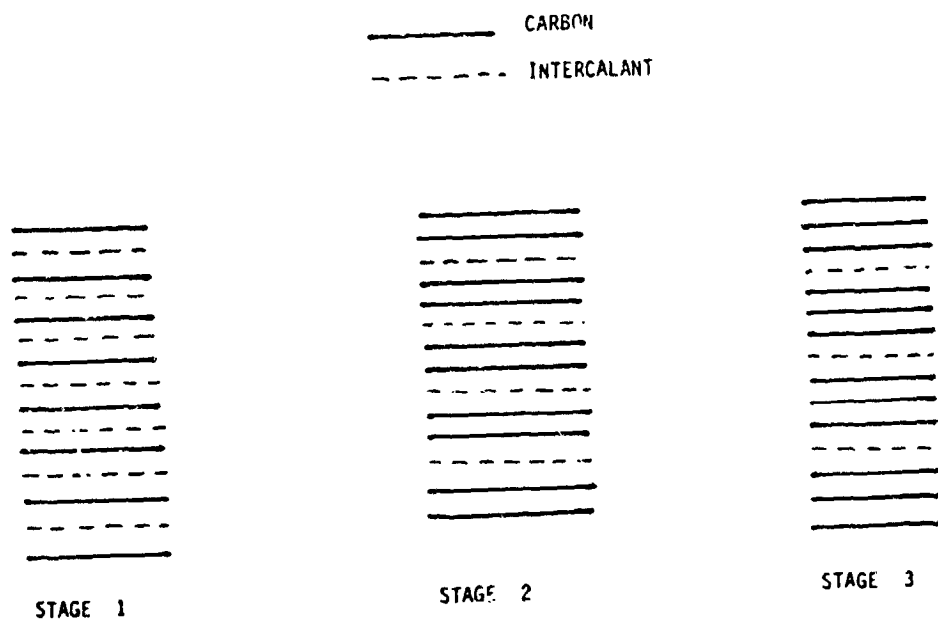


Figure 17. - Stages of intercalation.

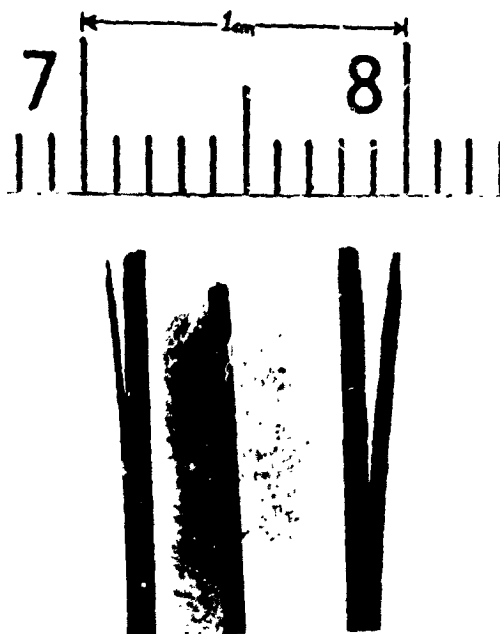


Figure 18. - Graphite strips intercalated with bromine.

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(a) Untreated

(b) Intercalated with gaseous
bromine.

Figure 19. - Two pieces of pyrolytic graphite.

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Figure 20. - Pyrolytic graphite intercalated by liquid immersion.

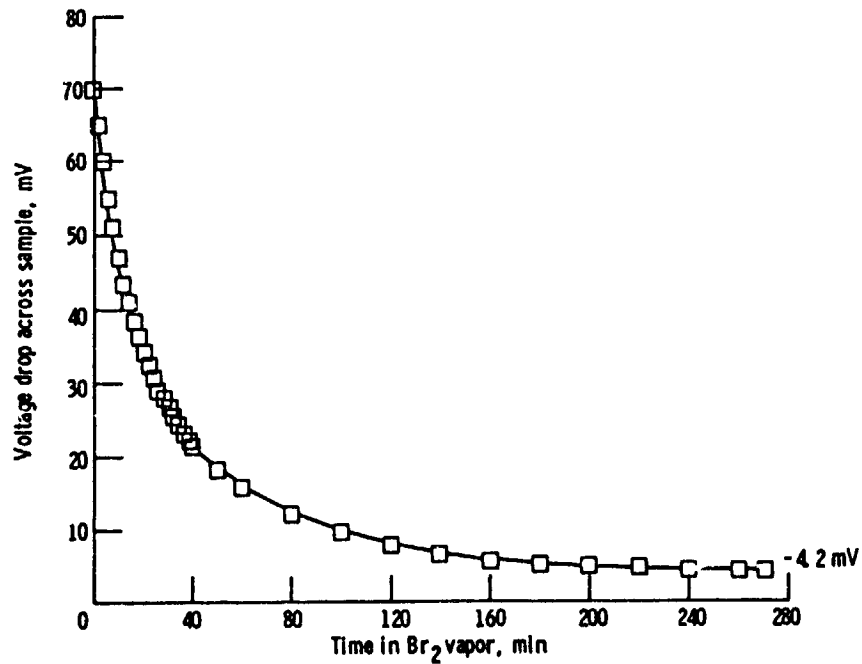


Figure 21. - Voltage drop across sample as a function of time in bromine vapor.

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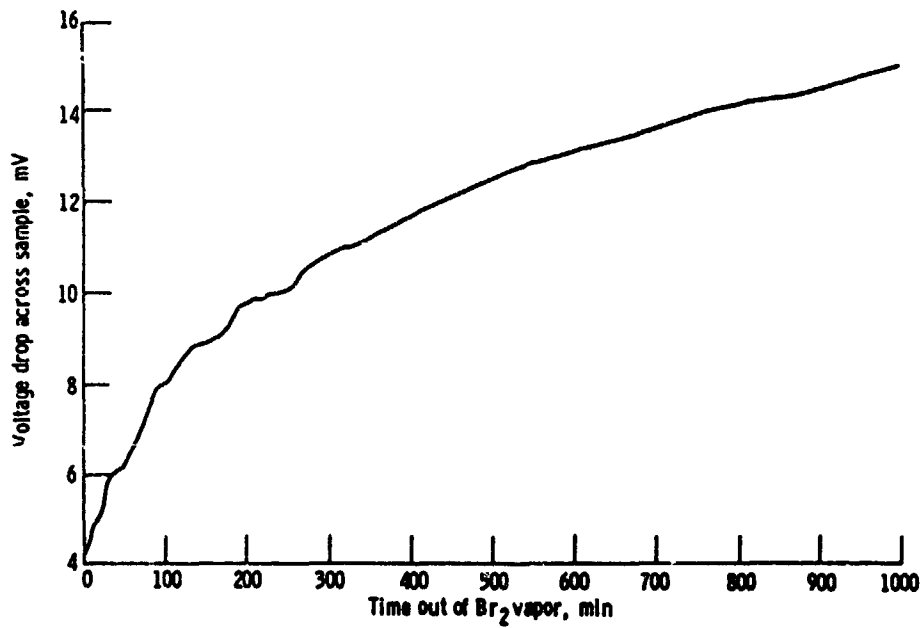


Figure 22. - Voltage drop across sample as a function of time out bromine vapor.

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Figure 23. - Fiber electroplated with copper.



Figure 24. - Fibers coalesced during electroplating.