BNWL-SA-

Conf-661003-2

JUN 23 1966

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Graphite: Advantages, Limitations, and Applications (a)

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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[redacted]

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(a) WORK PERFORMED UNDER CONTRACT NO. AT(45-1)-1830
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INTRODUCTION

Graphite is being used in several forms and in combination with a variety of materials in high-temperature nuclear reactors. Historically, the first application was as a moderator, where it is used in the form of large bars of polycrystalline artificial graphite. The moderator bars are made by the process used for graphite electrodes, with special attention given to selection of pure raw materials. A special halogen purification was developed to attain the puritv required in the early natural-uranium plutonium production piles. Improvements have been made in the moderator graphites especially with regard to radiation stability.

In recent years graphite has been employed in the fuel elements of high-temperature reactors, either as a fuel-particle coating, as a matrix for the fuel particles, or for both. In this paper, I will review the properties of graphite, pointing out some of the advantages and limitations in the use of graphite in high-temperature nuclear applications. In the papers to follow, some specific applications will be discussed.

FABRICATION OF CARBONS AND GRAPHITE

To the non-specialist "graphite" usually means one thing - the most common crystalline form of carbon. Yet the term is loosely used today to refer to a wide variety of materials made from carbon that may have very different properties. In some forms graphite is used because it is a good thermal conductor, whereas in other forms, graphite (more properly called carbon) is used as a thermal insulator. Other properties may also vary widely. It can be made as a dense or as a very light body; as a highly anisotropic, or as an isotropic material; as a high-purity neutron moderator, or (by addition of a little boron) as a control-rod or shield material; as a lubricant, or an abrasive; as an extremely low permeability gas barrier (comparable to glass) or as a highly porous filter.

The flexibility offered to the designer by this wide range of properties is very valuable. However, it does not come without some penalty. It also means that it may be very difficult to obtain specified properties within narrow limits that are consistent from batch to batch. For new grades the properties of interest and their variation may not be known. These are some of the most serious problems with the use of graphite today. Improvements will only come as we are able to better understand and control the fabrication process and provide reliable design information.

The wide range of properties can ultimately be traced back to the crystal structure of graphite; this will be examined more closely in a later section. But first, we will consider some of the methods of making graphites.

Although the detailed methods used for a given grade of graphite are usually highly proprietary, the general method of manufacturing polycrystalline materials has been fully described.[1-3] Raw petroleum coke is calcined at 1300°C, milled, sized, and mixed at about 165°C with a coal-tar pitch. This mixture is then cooled to about 110°C and extruded. Upon cooling to room temperature the "green" body is rigid enough to be supported in a baking furnace by a permeable pack of sand and carbon. During baking to 800°C, a large volume of gas is volatilized by pyrolysis of the pitch, and the carbon body shrinks about 5 vol.% during baking. It can then be "graphitized" in an Acheson electric furnace to 2500°C to 3000°C. During graphitization some further gas is evolved, but the principal change is to transform the amorphous carbon into crystalline graphite.

There are many variations to this process that can markedly affect the final properties. Large changes are observed with different starting materials. The baked carbon is often impregnated with pitch before graphitization to improve density and strength; the graphitized body may also be heated in a halogen-containing gas to remove trace impurities. Different methods of forming, such as molding, are sometimes used.

High-purity graphite made by this process is a relatively inexpensive material. Currently, unmachined grades cost \$0.50 to \$0.75 per pound in several-hundred-ton quantities. Machining adds \$0.25 to \$0.50 per pound to the cost. Very large bars can now be produced. For example, the core of the Experimental Gas-Cooled Reactor shown in Figure 1 was assembled from monolithic columns 16-in. in cross section and 20-ft. long.

The conventional process must be modified if fuel particles are incorporated in the mix. A thermo-setting resin is usually employed as the binder and the final heat-treatment temperature must be limited to about 2000°C to prevent excessive reaction and diffusion of the uranium fuel. The process used for the UHTREX fuel is described in a following paper.

The manufacture of boronated graphite for fast-reactor shields or control rods generally follows the conventional method. Boron-carbide particles are added to the original mix. The final heat-treatment is again limited to prevent excessive loss of boron. Temperatures up to the melting point of boron carbide (∿2450°C) and above can be used, although if this temperature is exceeded, extensive recrystallization of the graphite and dispersion of the boron occurs, and radiation effects in the material are much larger.[6]

Interest in pyrolytic carbons and graphites has increased greatly in the last 10 years, first for rocket nozzles and re-entry shields, and more recently as a coating for fuel particles. The carbon is made by pyrolytic decomposition of hydrocarbon gases.[7,8] For free-standing bodies, the carbon is usually deposited on a graphite substrate at temperatures of 1400 to 2400°C. The preferred orientation, density, and other properties can be varied widely by changes in gas pressure, temperature, and other conditions. Subsequent heat-treatment to higher temperatures improves the crystallinity. Small samples (1 to 5 mm) that have been heated to very high temperatures (3000° - 3600°C) exhibit electrical properties very close to those of single crystals.[9] Larger samples suitable for physical property measurements and irradiation tests with near-single-crystal properties can be made by heating pyrolytic graphite above 2500°C while under a compressive stress.

Pyrolytic-carbon coatings on fuel particles are applied in a fluidized bed. Fuel particles on the order of 150-200μ diameter may be thorium or uranium carbides or oxides. The carbon coatings are usually applied to a thickness of about 100μ. A great deal of work has been reported on the preparation, properties, and structure of coated fuel particles,[10] and several of the papers in this session will deal with this topic in considerable detail.

Another class of interesting materials is carbon and graphite fibers and fabrics.[11,12] They are manufactured by pyrolysis of rayon or cellulose yarn or woven cloth to a non-melting-char. Heating to 1400°C yields a carbonaceous product and further heating to 2700°C imparts a more graphitic structure. These products are now offered commercially in the form of cloth, felt, braided yarn, and chopped fibers in a variety of grades. Carbon fibers are also promising reinforcements for metals composites.

A "glassy" carbon has been described that has some rather interesting properties.[13-15] Although the method of manufacture has not been described in much detail, it is believed to be formed by carefully heating certain resins. The trick is to decompose the material without forming cracks when the large volume of gases are evolved and the body shrinks.

You will see from this brief review that there are many ways to make pure carbon materials. Some of these materials are illustrated in Figure 2. I would like now to describe the structure and properties of these materials and indicate some of their nuclear applications.

STRUCTURE AND MORPHOLOGY

CRYSTAL STRUCTURE

The crystal structure of graphite is shown in Figure 3. In the most common form of graphite the layer planes are stacked ABAB... producing a hexagonal crystal structure. A much less common form is the rhombohedral structure in which the layer planes are stacked ABCABC.... The properties of these two forms are almost identical.

Two important features of the crystal are ultimately responsible for many of the unique properties of graphite: (1) the system of strong chemical bonds forming large sheets of hexagonal rings in which the electrons are quite mobile; and (2) the large spacing and weak bonding between the layer planes. The former accounts for the high strength and good electrical and thermal conductivity of graphite in the <u>a</u> direction. The latter accounts for the low shear strength in the <u>a</u> direction and low conductivities in the c direction. The high anisotropy, good lubricity, and some of the radiation effects are also readily explained in terms of the structure.

POLYCRYSTALLINE GRAPHITE

If the properties of perfect single crystals are predictable and easily understood, quite the opposite is true of non-perfect polycrystalline graphite. All graphites used industrially have a variety of crystal defects that change the properties of the crystals; but, perhaps more importantly, the coke particles (containing oriented crystallites) are almost randomly arranged and held together by a less well ordered binder phase. Figure 4 shows the morphology of a typical nuclear graphite at several magnifications. Filler particles in the original mix can be often identified, which, after graphitization, consist of many crystals generally oriented in a perferred direction. These are held together by the graphitized pitch binder, which is composed of smaller crystallites with more random orientation. If carbon blacks are added to the mix, as is sometimes done to increase density and strength, these can generally be identified in the electron microscope.[16]

The columnar and gas-nucleated structures of pyrolytic graphite are shown in Figure 5. Both materials are very dense, but the crystals are not perfect. The layer planes are buckled and warped, although the preferred orientation is very high. Stress annealing above 2500°C tends to straighten the planes and produces a material with properties as near to those of a single crystal as is presently available.

The crystallites in "glassy" carbon are very small and randomly oriented. Figure 6a is a micrograph of Grade GC-30 manufactured by Tokai Electrode. This material, which has been heat-treated to 3000°C, has an extremely fine-grain structure; in fact no texture at all is seen by bright field, sensitive tint, or polarized light at a magnification of 75X. The resins used to produce glassy carbon do not graphitize well even at 3000°C.

In Figure 6b the structure of stress-annealed pyrolytic is shown. This material, which is probably the most crystalline of all synthetic graphites, was made by compressing pyrolytic graphite at about 4000 psi at 2800°C. The very fine texture observed is seen only under polarized light very near the extinction angle. The misorientation of the fine platelets is very small and cannot be observed by sensitive-tint illumination. The contrast produced by platelets near the edge that were deformed by machining of the sample illustrate the high degree of preferred alignment within the bulk of the specimen.

As might be expected from the extremely anisotropic nature of graphite crystals, most graphite bodies are anisotropic. The starting coke particles have a flake or needle shape to varying degrees, and these are oriented during molding or extrusion to produce a body with preferred orientation. Special starting materials and processes can be used to make an almost completely isotropic material.

Pyrolytic graphite is the most anisotropic of the graphites used in nuclear applications, but again, variations in deposition conditions can be used to change the anisotropy. Glassy carbon is quite isotropic.

PROPERTIES

NUCLEAR PROPERTIES

Because carbon is a relatively light atom, graphite is an efficient moderator. A figure of merit sometimes applied to moderators is the slowing-down power. It is the average logarithmic energy change of a neutron when it collides with a moderator atom divided by the mean free path between collisions. For nuclear graphite with a density of 1.65 g/cm^3 the slowing-down power is 0.063 cm^{-1}. Light water has the highest slowing-down power (1.5 cm^{-1}) and several other materials (Be, BeO, and D_2O) rank higher than graphite. A second requirement is that a moderator must not absorb many thermal neutrons. On this score, graphite is very good, being outranked only by D_2O.

Graphite is also used as a combined moderator and neutron absorber to shield fast reactors, in which case a nuclear poison such as boron is added to the graphite mix. The carbon atoms moderate the fast neutrons, which can then be captured by the boron.

STRENGTH

At low temperatures graphite is relatively weak when compared with other structural materials. This was not a serious problem a few years ago when graphite was used exclusively as a moderator and only needed to have a compressive strength of a few thousand pounds per square inch. However, in recent years, much more is being asked of graphite, and good consistent strength is needed.

One of the outstanding properties of graphite is its high-temperature strength. In contrast to most materials, strength increases with temperature to very high temperatures, reaching a maximum at about 2500°C. A typical polycrystalline nuclear graphite with a tensile strength of 2000 psi at room temperature would have a strength at 2500°C of about 4000 psi. Because graphite is a light material, its strength-to-weight ratio is also outstanding, and in fact is better than any known material above about 1500°C. The very good high-temperature strength, good nuclear properties, and low cost are the three major reasons for its extensive use in high-temperature gas-cooled and nuclear propulsion reactors.

THERMAL CONDUCTIVITY

The thermal conductivity of graphite can be varied widely as shown in Table I.

TABLE I

Typical Values of Thermal Conductivity at Room Temperature

		cal/cm-sec-°C	BTU/hr-ft-°F	Ref.
Moderator Graphite	(w.g.)*	0.40	97	(17)
(Type CSF)	(a.g.)	0.26	63	
Pyrolytic Graphite	(w.g.)	3.8	920	(18)
(Annealed at 3300°C)	(a.g.)	0.018	4.3	
Pyrolytic Graphite	(w.g.)	2.6	628	(18)
(Annealed at 2900°C)	(a.g.)	-		
Low Density Carbon	(w.g.)	0.0015	0.36	(19)
($\rho = 0.73$ g/cm^3)	(a.g.)			
Boronated Graphite	(w.g.)	0.202	48.9	(20)
(7 wt% B_4C)	(a.g.)	0.142	34.4	
Carbon Felt		8.6×10^{-5}	0.021	(11)
Glassy Carbon (Grade GC-20)		0.021	5.0	(21)

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

The thermal conductivity above room temperature does not change drastically with temperature because, except in the case of extremely crystalline graphite, the mean free path of lattice waves carrying the heat is limited by temperature-independent scattering at crystal boundaries. The temperature dependence of thermal conductivity for several materials is shown in Figure 7.

CHEMICAL PROPERTIES

At low temperature, graphite is inert to all but the strongest oxidizing agents. However, its reaction proceeds at a measurable rate (10^{-6} hr^{-1}) with oxygen at 380°C, water vapor at 625°C, and carbon dioxide and hydrogen at about 750°C when any of these gases are present at atmospheric pressure. A great deal of work has been published on these reactions.[22] Traces of certain impurities such as vanadium and iron can cause accelerated attack. Certain gases such as carbon monoxide[23] and hydrogen[24] will inhibit the oxidation by gases to some degree, but in general it is necessary to use graphite in an inert atmosphere or coat it with a suitable material. Carbides of silicon, tantalum, zirconium, and niobium have been used with varying degrees of success as coating on graphite.

Graphite is compatible with several liquid metals, notably bismuth, lead, tin, magnesium, and aluminum. Sodium and the other alkali metals react rapidly with graphite, causing it to swell.

Copper is one of the least reactive metals with graphite. It does not form a carbide and the solubility in graphite is immeasurably small. Nickel, like copper, does not form a carbide, but dissolves 0.65 wt.% carbon at the eutectic temperature (1316°C).

Much work has been done on the compatibility of iron-chromium and iron-chromium-aluminum alloys with graphite.[25] Although carbide formation occurs to varying degrees, these alloys are generally useful to about 800°C. The high solubility of carbon in austenite gives the austenitic steels a relatively low resistance to carburization.

MISCELLANEOUS PROPERTIES

Graphite is easily machined; however, if it contains non-graphitic carbon or hard particles such as carbides, tool wear is rapid.

Moderator graphites are usually quite porous, having a total pore volume of about 25% and a permeability of 10^{-2} to 10^{-3} cm^2/sec. The permeability can be reduced to 10^{-6} - 10^{-7} cm^2/sec. in a fine-grained base stock by multiple impregnation and carbonization.

If free of cracks, pyrolytic graphite and glassy carbon are practically impermeable, having permeabilities comparable to ordinary glass.

Graphites can be made with a wide range of densities. Typical values are shown in Table II. By far the most common values for all but the "specialty" materials range from 1.5 - 1.6 g/cm^3.

TABLE II. Typical Densities of Carbons and Graphites

Material	Bulk Density, g/cm^3
Single Crystals (theoretical density)	2.26
Moderator Graphite	1.5 - 1.7
Special Polycrystalline Graphites	1.0 - 1.9
Pyrolytic Carbon and Graphite	1.2 - 2.2
Carbon Felt	0.08 - 0.17
Glassy Carbon	1.5
Porous Carbon and Graphite	0.6 - 1.3

NUCLEAR APPLICATIONS

MODERATOR

Graphite has found most use as a moderator material. In 1962 about 80,000 tons of graphite were in use in the United States, England, and France, and a large additional amount of less pure material was being used in reflectors.

Recently completed graphite reactors in the United States include: Hanford N-Reactor; Hallam Sodium-Cooled Reactor; Experimental Gas-Cooled Reactor (EGCR); Peach Bottom High-Temperature Gas-Cooled Reactor (HTGR); Ultra-High-Temperature Reactor Experiment (UHTREX); Molten-Salt Reactor Experiment (MSRE); and the nuclear propulsion reactors (KIWI and NERVA).

In addition to projects in the United States, reactor development in England and France has concentrated heavily on graphite-moderated gas-cooled reactors and a number of large power reactors have been and are now being built.

Properties of most interest for moderator applications are purity, chemical reactivity, strength, thermal conductivity, radiation-induced creep, and dimensional stability. The latter problem has resulted in a great deal of research to develop more stable materials. In the United States the work has concentrated on radiation effects at 500 - 1200°C, whereas, most interest in England is in the range 350 - 650°C. One of the papers [26] in this symposium will consider the problems of radiation effects in graphite.

For high-temperature gas-cooled reactor applications in the United States, much more information is needed on the dimensional stability and creep rates at 800°C and above at exposures in the range 10^{21} - 10^{23} neutrons/cm^2. Isotropic graphites with good crystallinity appear to be the most promising.

MATRIX MATERIALS

As discussed in much detail at this symposium, graphite is used as a matrix for fuel particles. Currently, these materials are used in the UHTREX, Peach Bottom, and NERVA reactors. Most effort has been directed to development of fuel particles that will retain fission gases. The progress on coated particles in the last few years has made it unnecessary to use low-permeability graphite fuel cans.

Poisoned graphite is used as a neutron shield in the FERMI Reactor and fast-reactors in Europe and will certainly be a candidate for future fast reactors. The shield in FERMI is a matrix of B_4C particles (5 - 7 wt% boron) in graphite. The limited amount of data on this material indicates that it has poorer dimensional stability than non-boronated material.[6] However, it will also be exposed to a much lower neutron dose.

OTHER APPLICATIONS

There are a number of special nuclear applications of graphite that take advantage of one or more of its properties. In UHTREX, porous carbon is used as a high-temperature thermal insulator. Graphite containing boron carbide is also used as control rods in several reactors. In future high-temperature reactors, graphite will probably be used to contain loose fuel particles. The nuclear propulsion reactors contain many parts made from carbons and graphites to serve special needs, and we can expect that such specialty applications will find more use as the trend to higher temperature continues in other reactors.

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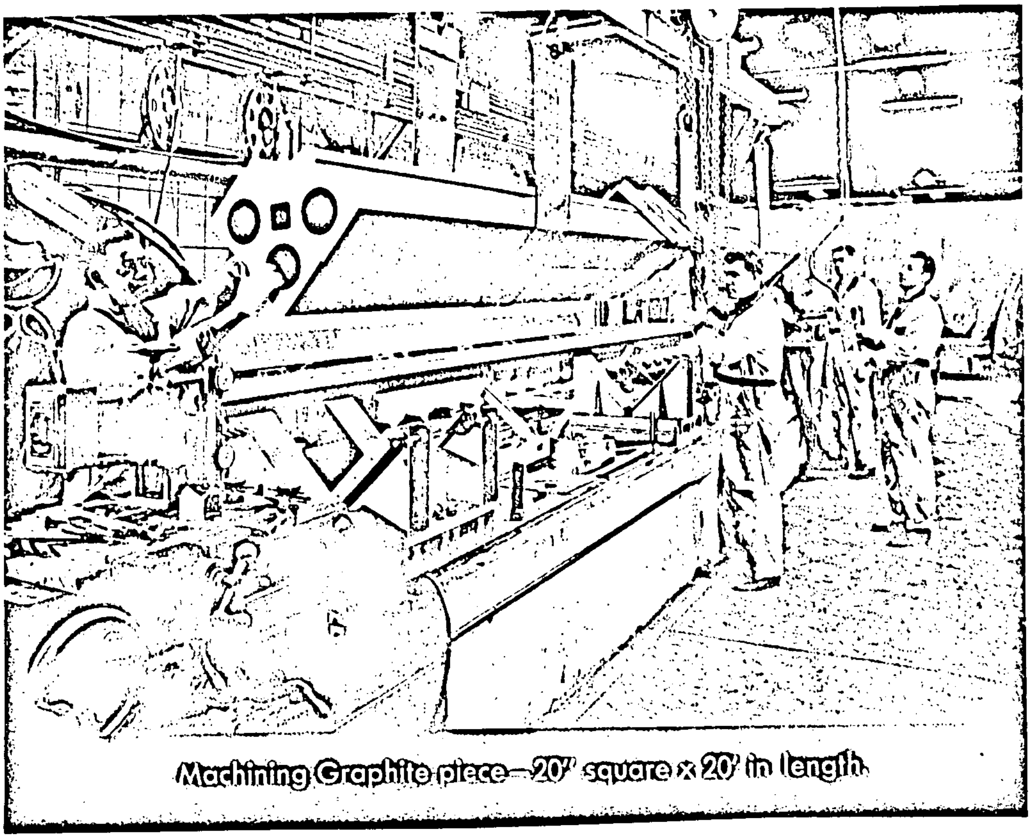


Machining Graphite piece—20" square x 20' in length.

FIGURE 1

Monolithic Graphite Moderator Blocks for the Experimental Gas-Cooled Reactor.

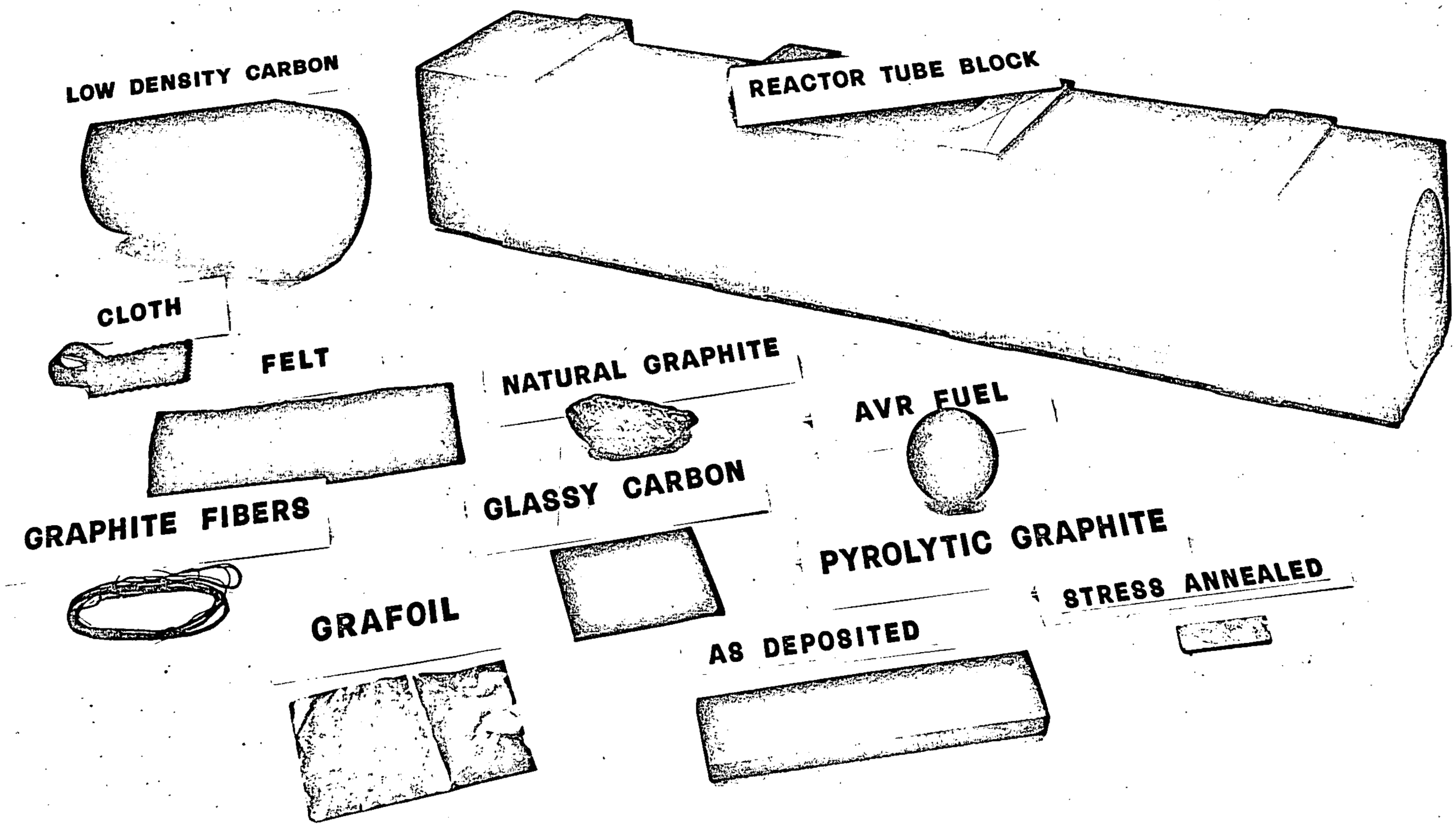
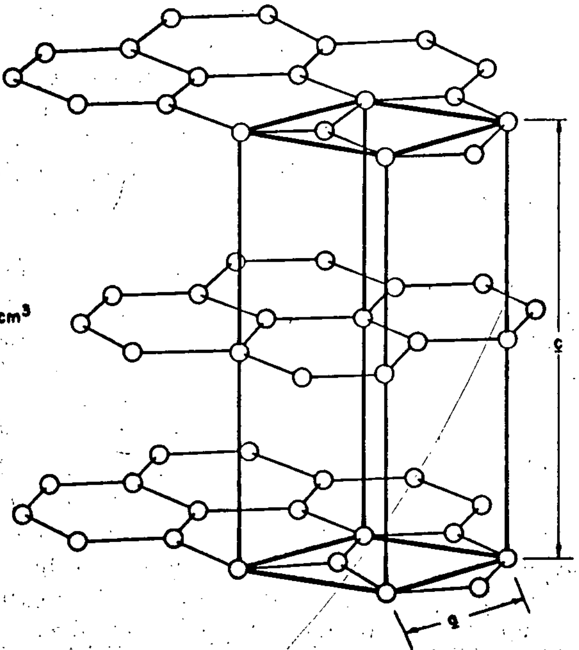


FIGURE 2

Materials and Shapes Made Entirely of Carbon.



Space Group: C6/mc(D_{6h}^{4})
Unit cell:
a = 2.4612 ± 0.0001 A
c = 6.7079 ± 0.0007 A
Volume = 35.190 A^3
Atoms per unit cell = 4
Crystal density = 2.266 g/cm^3

FIGURE 3

Crystal Structure of Graphite.

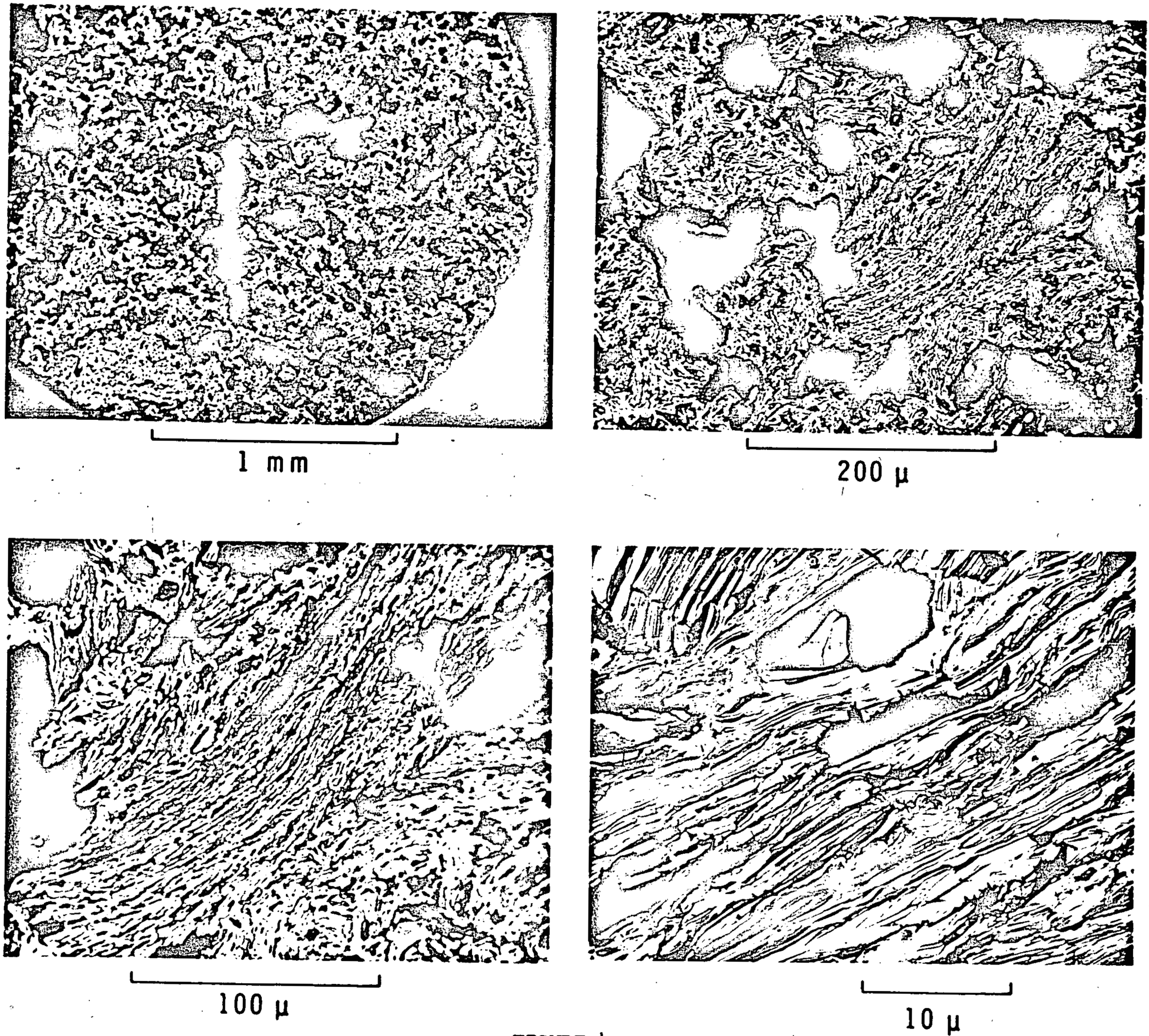


FIGURE 4

Morphology of a Typical Nuclear Graphite at Several Magnifications.

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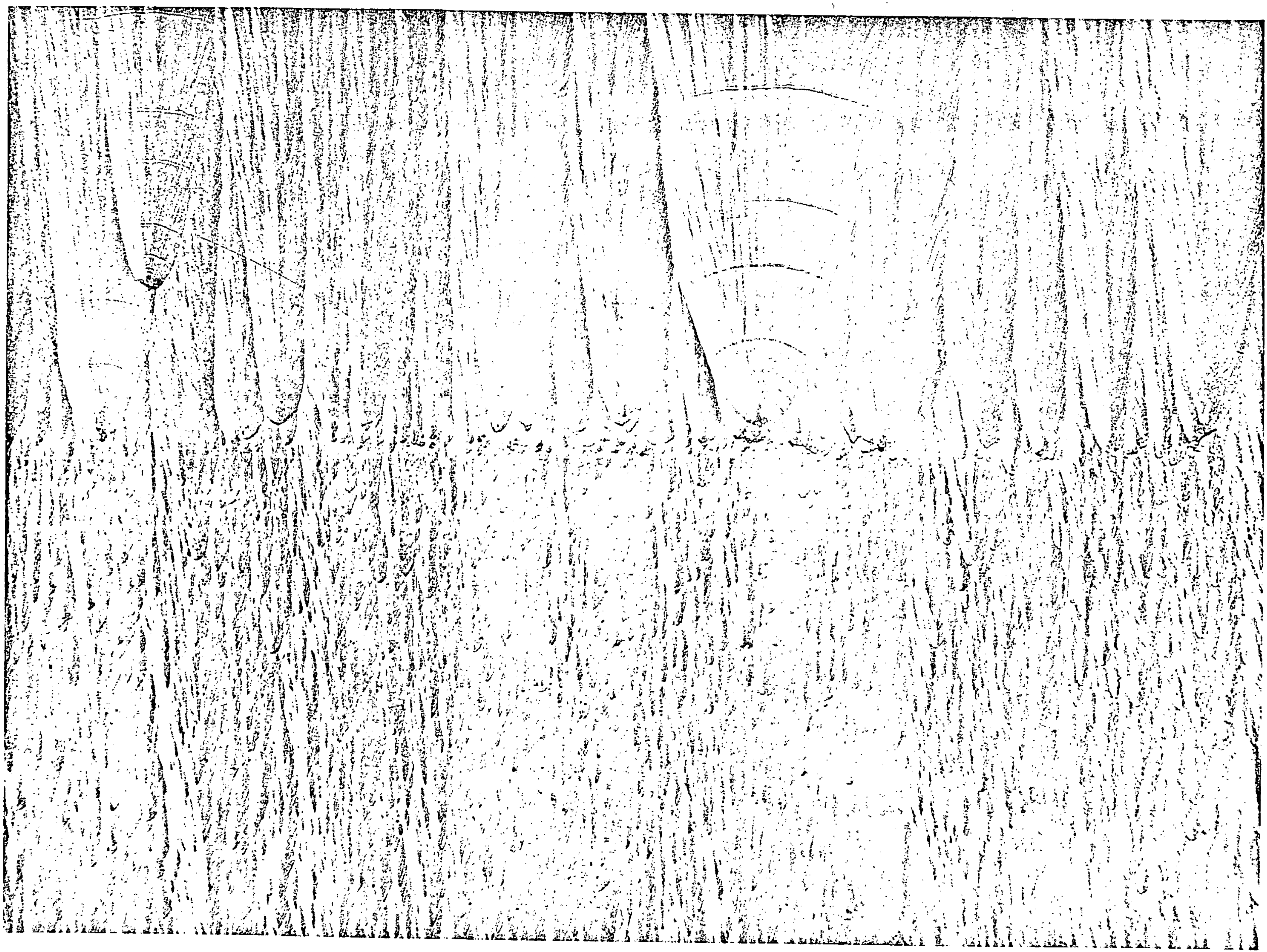

FIGURE 5

Morphology of Substrated-Nucleated and Gas-Phase Nucleated Pyrolytic Graphite.

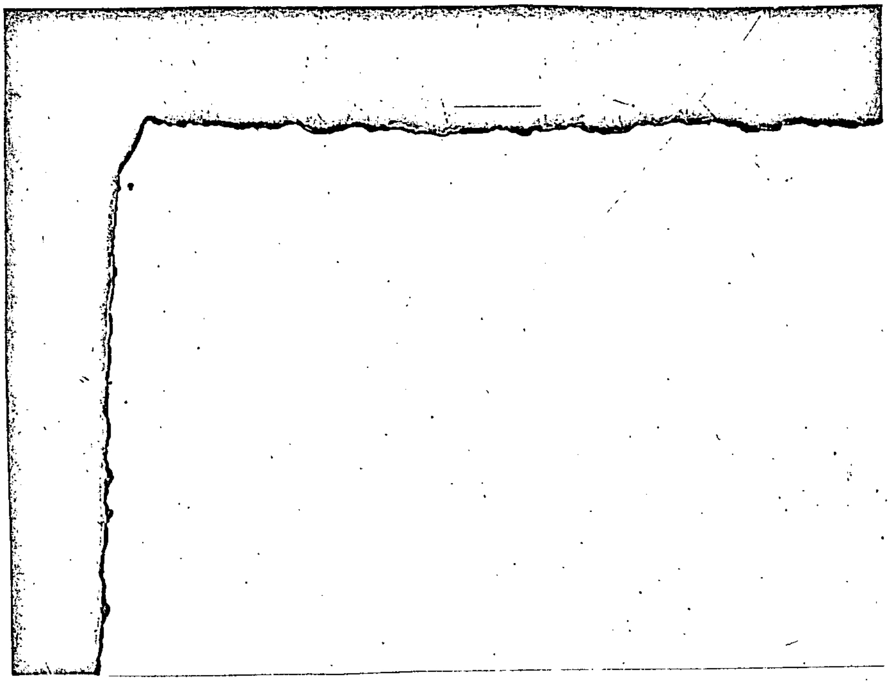

FIGURE 6a

Texture of "glassy" carbon manufactured by Tokai Electrode (Grade GC-30). Bright-field illumination at 75X.

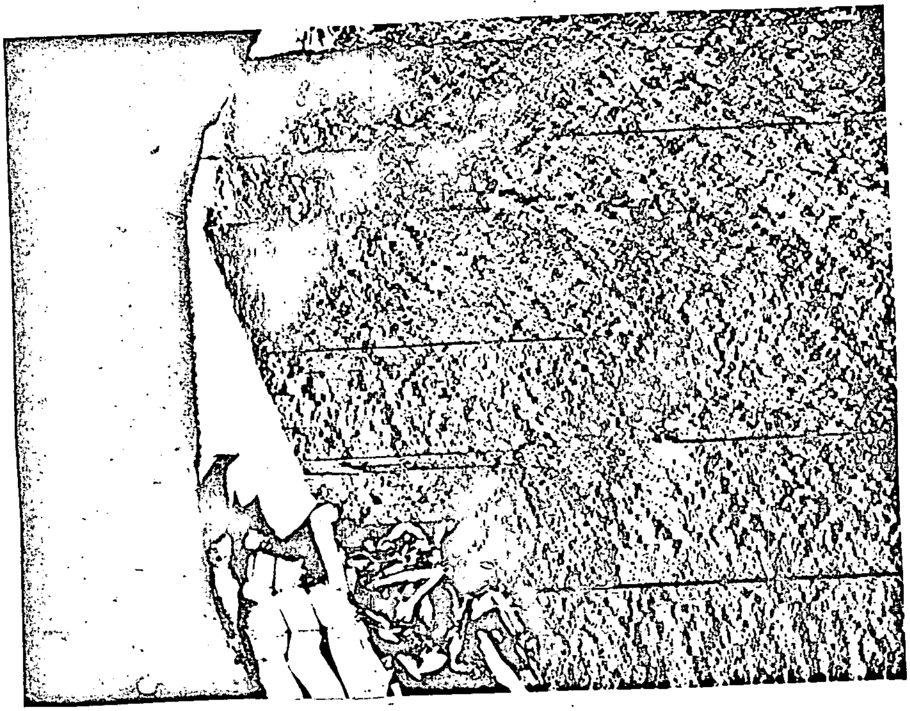

FIGURE 6b

Stress-annealed pyrolytic graphite. Polarized-light illumination at 75X.

FIGURE 7. Thermal Conductivity of Several Carbons and Graphites as a Function of Temperature.

TSX - Anisotropic, crystalline nuclear graphite

CSF - Conventional nuclear graphite

P.G. - Pyrolytic graphite

Carbon - Low-density, isotropic carbon