CARBON—AN OLD BUT NEW MATERIAL*

P. L. WALKER, JR.
Department of Material Sciences, The Pennsylvania State University,
University Park, Pennsylvania 16802, U.S.A.

Abstract—Carbons of widely differing properties (properties approaching those of ideal graphite more or less closely) can be prepared by starting with different carbonaceous materials (in form of solids, liquids, and gases) and treating these materials in various ways. The variation in properties is a result, primarily, of a variation in carbon crystallite size and orientation and extent of cross-linking between trigonally bonded regions. Carbons of widely different structure and properties will be considered and their present and future applications in engineering and science discussed. Among those materials considered will be electrode carbons, glassy carbon, molecular sieve carbons, carbon blacks, pyrolytic graphite, stress recrystallized graphite and carbon fibers.

1. INTRODUCTION

Ten years ago this fall, I presented at a number of universities a Sigma Xi National Lecture on "*Carbon—An Old But New Material*". In that talk I attempted to review the structure of carbon, some of its interesting properties, and to consider some of the more important preparative procedures. The age of materials science was just upon us and it did not take a crystal ball to predict that carbon materials (what with the possibility of producing such varied and outstanding properties) would be of increasing importance and utilization in many facets of our civilization. Indeed, I concluded the talk saying that "Progress in the development of new carbon materials and in the improvement of old carbon materials will continue to be recorded—as a chapter in the over-all story of materials science".

I would like to devote this paper to two main areas. One, to discuss some of the advances which indeed have been made in carbon materials over the last ten years and, second, to predict some advances that may be made in the next ten years. I will not have space to consider all important past advances; and further I may, in some cases, prejudice my paper more towards our own work than normally would be the case. But I presume this is the prerogative of the Skakel Lecturer.

As we know, we produce carbons of various properties by starting with organic precursors, more or less complicated (oil, coal, natural gas, a polymer, an organic compound) and heating to sufficiently high temperatures to liberate H, O, N, S. Carbon–carbon bonds are broken, new carbon sites are produced which join together to give larger molecules and then crystallites.

As we further know, we have a choice of two major routes in converting the organic precursor to a carbonaceous solid: a low temperature route where the precursor is coked or charred and a higher temperature route where the precursor (in the form of a gas or vapor) is cracked. Major advances have been made in both of these areas in the past ten years, and my paper will dwell primarily on some of these advances.

2. CARBONS PRODUCED VIA A LOW TEMPERATURE ROUTE

2.1 *Petroleum cokes*

Organic precursors (petroleum and coal) are used to produce petroleum and coal cokes, which are of major industrial importance. Petroleum coke is in turn used to produce graphite, *ca.* 350,000 tons per year in the United States, with the major amount going into fabrication of electrodes for steel making, and baked anodes (2 million tons per year) primarily used to produce aluminum. These both are substantial growth markets. In addition, about 70 million tons per year of coal coke are used in the blast furnace to reduce iron ore.

The exciting thing, as we know, is that there are petroleum cokes and there are petroleum cokes. They vary much in their properties, depending upon the nature of the precursor and how the coking process is performed. For production of graphite electrodes and anodes, it is desired that we have a coke of good crystallite alignment, which will be highly graphitizable and give particles on grinding that are needle-like. The more needle-like, the more these particles can be aligned upon extrusion of the electrode. Hence, a lower electrical resistivity in the body will result.

Let us look briefly at what we have learned in this area in the past ten years. We knew ten years ago that we wanted to start with a relatively clean feed stock. We also knew that each organic precursor material carbonized differently and produced a coke of different morphology and graphitizability. We have learned how to produce better needle cokes and gained in our understanding of why.

We might look at several pictures showing petroleum coke. In Fig. 1 we see particles of different shapes. The particles on the left are a fluid coke produced in a fluid bed by the cracking of petroleum feed stock on to seed particles[1] Typically fluid coke particles approach closely a spherical shape, having a shape factor of close to 6. Layers of carbon are built up, as in an onion-shell-type structure. Because of this arrangement of layers, fluid coke shows a high resistance to oxidation[2] but also is not particularly graphitizable. By contrast, we also see particles of delayed coke. In this case, the organic precursor is heated to coking temperatures, under pressure, as it passes through a pipe furnace and then is discharged into an insulated drum, where coking proceeds at lower pressures[3]. The sample on the right is clearly needle-like in character and thus is a prime source of artificial graphite. As we proceed to more needle-like coke, the price of the material increases significantly. The sample in the middle is typical of a delayed coke used in the production of anodes, which in turn are used for aluminum production. In this case, premium needle coke is not required since the anodes are not graphitized at temperatures between 2500–2800°C. Rather, the coke is calcined between 1400–1800°C, the anode fabricated from the calcined coke and coal tar pitch, and then heat treated to 1000–1100°C. For this application, the use of graphite anodes would not be economical because of the large consumption of carbon in the reduction of aluminum oxide to aluminum. By contrast, the consumption of graphite electrodes in the electric steel furnace per ton of steel produced is negligible.

Figure 2 shows, at higher magnification, the characteristic texture of a needle-like petroleum coke particle. We see a distinct flow pattern, where the basal planes of the small crystallites (about 30 Å in diameter and consisting predominantly of carbon atoms showing trigonal bonding) align more or less closely to this flow pattern. We see distinct cracks of various sizes running parallel to the flow pattern. These cracks, in most cases, are produced by the differential thermal contraction of the material upon cooling from coking temperatures and are of considerable importance in determining the coefficient of thermal expansion of the filler
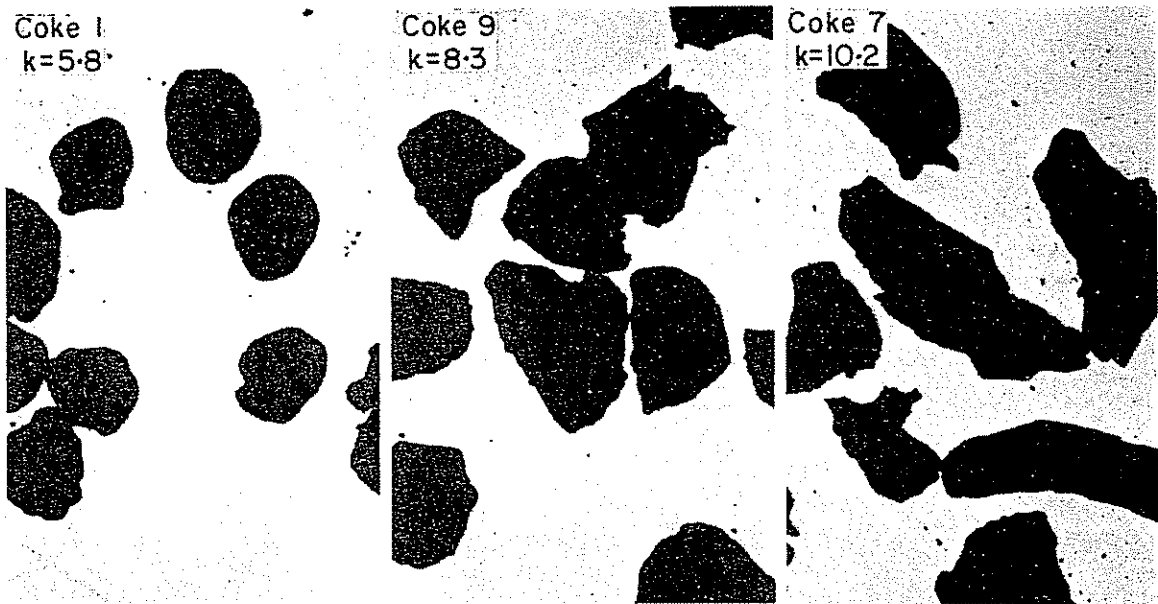
Fig. 1. Photomicrographs of selected petroleum cokes having different particle shapes. $k = 6.0$ for a spherical particle and increases with increasing particle asymmetry. $\times 45$
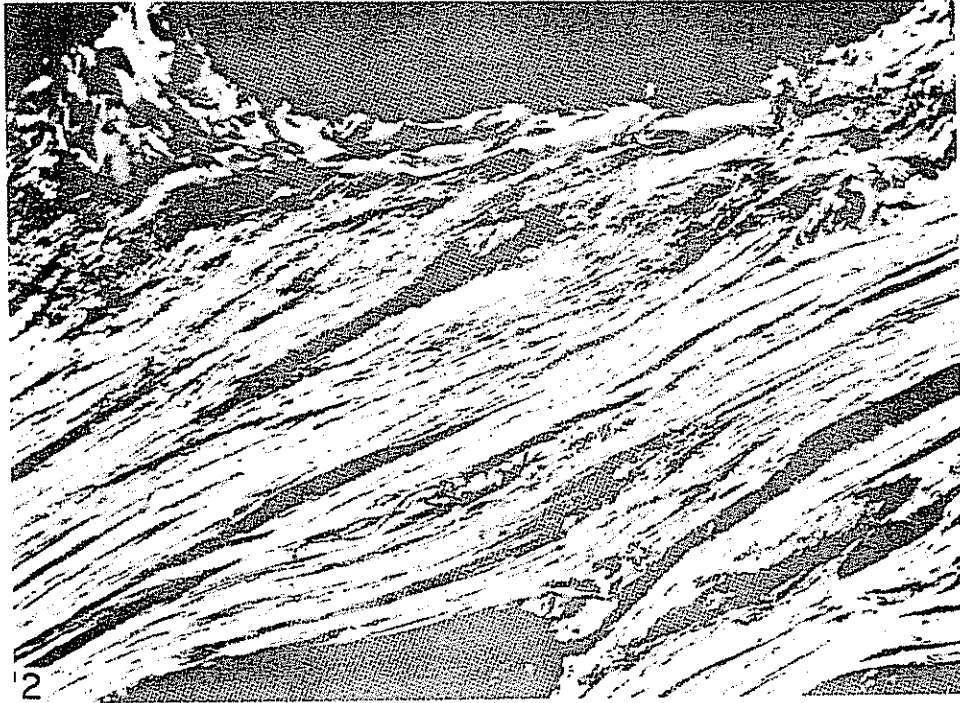
Fig. 2. Texture of a calcined needle-like petroleum coke particle, showing
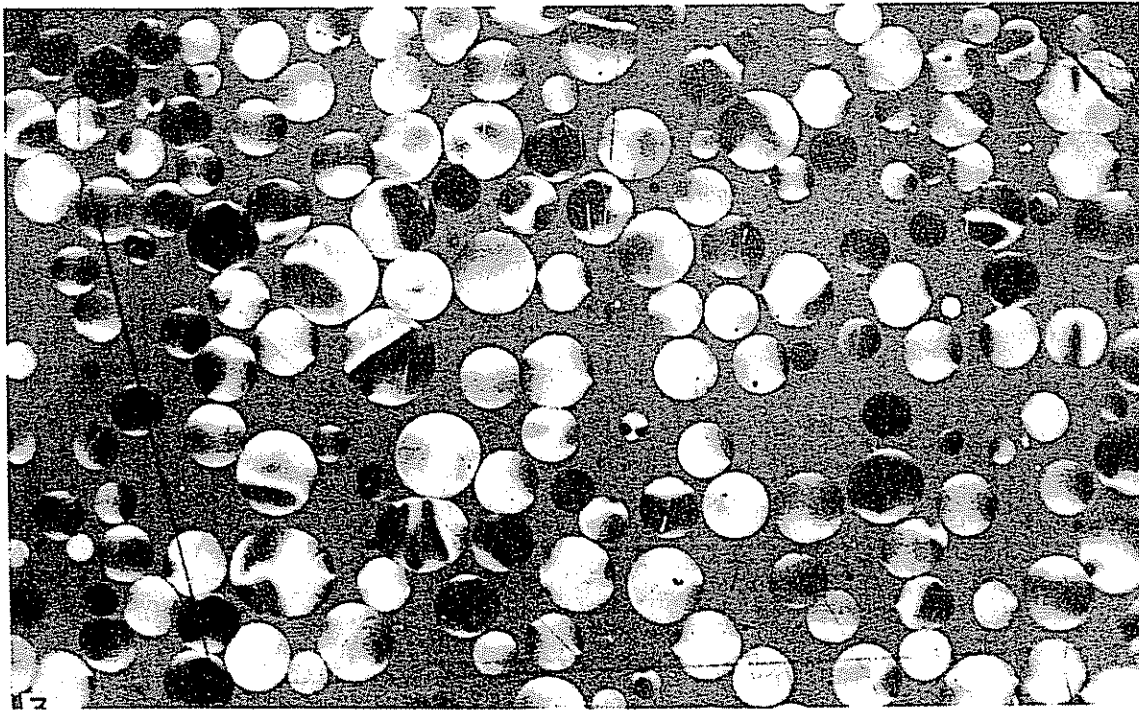typical flow patterns. ×80

Fig. 3. Spheres of mesophase appearing during the carbonization of a toluene-soluble
fraction of coke-oven pitch [4]. × 320

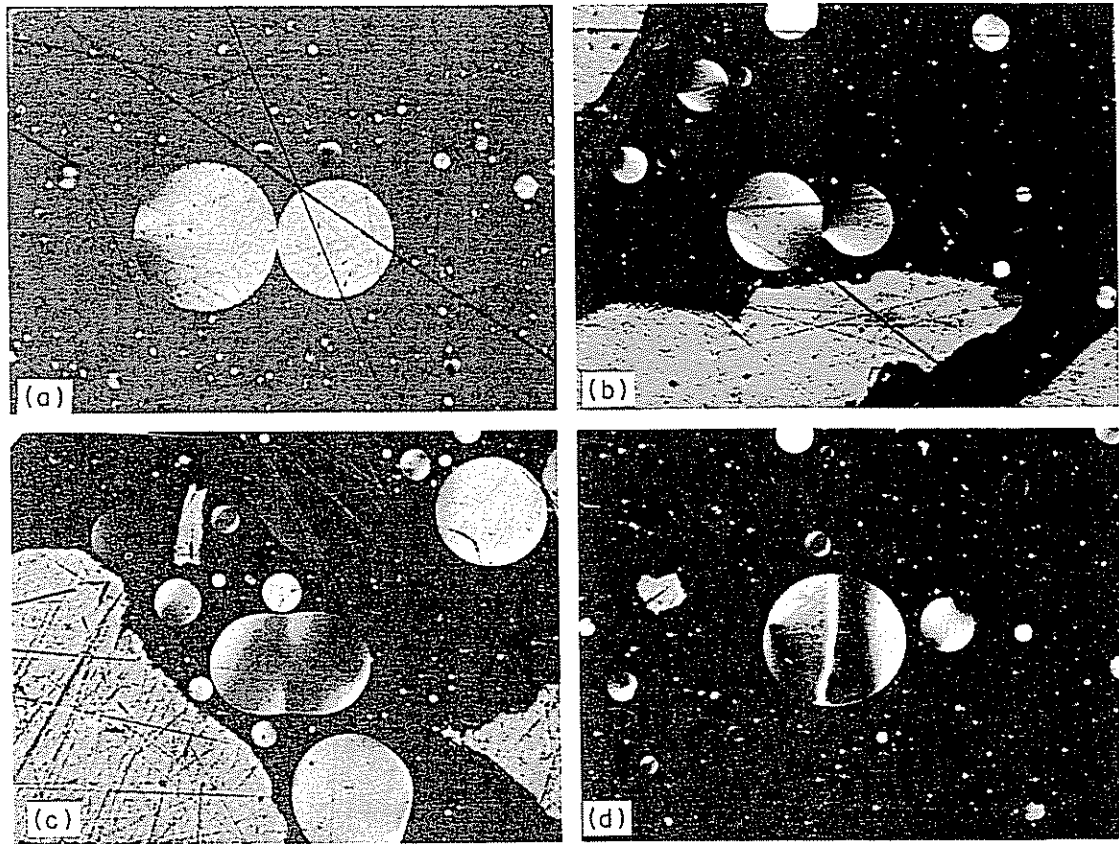Fig. 4. Stages in the coalescence of two spheres: (a) initial contact; (b), (c) coalescence; (d) contraction to form composite sphere [4]. × 300
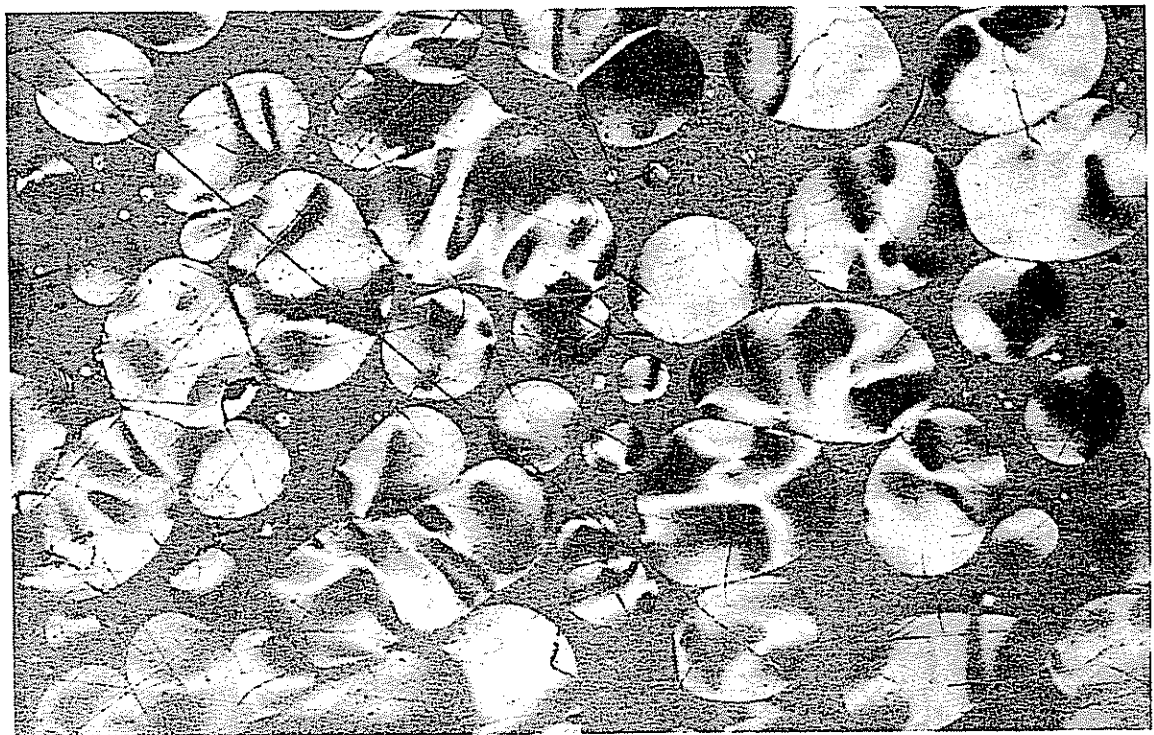

Fig. 5. Later stage than Fig. 3 in the carbonization sequence. The bodies are no longer spherical but have become distorted through mutual interference [4]. × 400
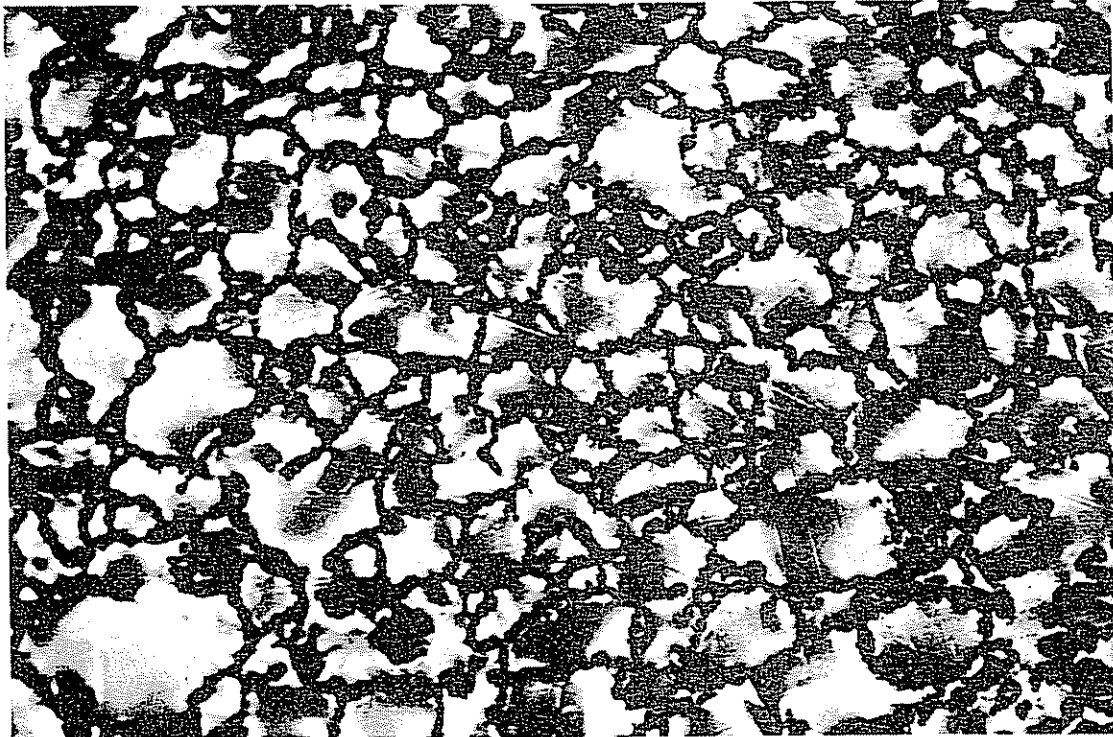
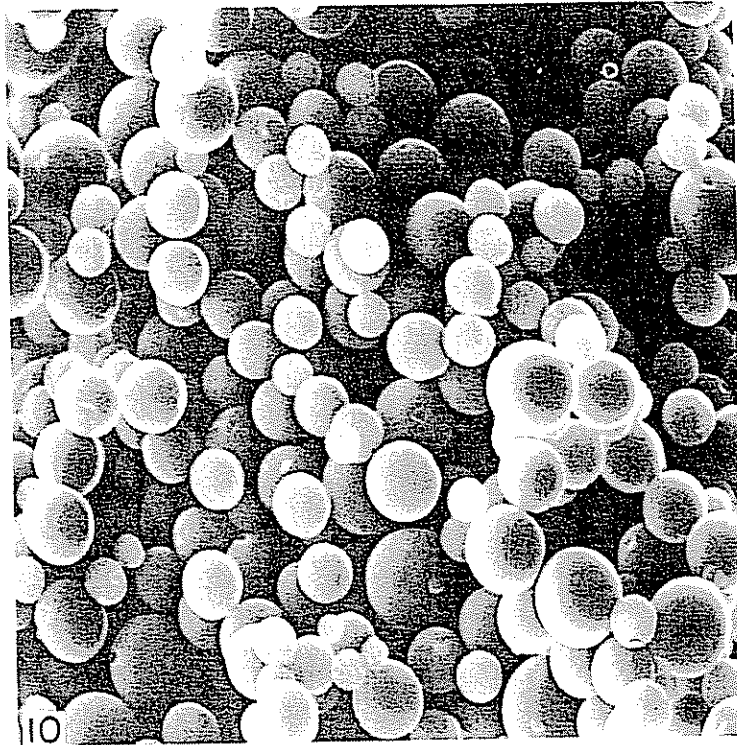Fig. 7. Three-dimensional network of insolubles in mesophase, which hinders formation of large mosaic regions [4]. × 400

Fig. 10. Scanning electron micrograph of un-coalesced spheres produced during extensive carbonization of anthracene at 600°C and 10,000 psi. × 800
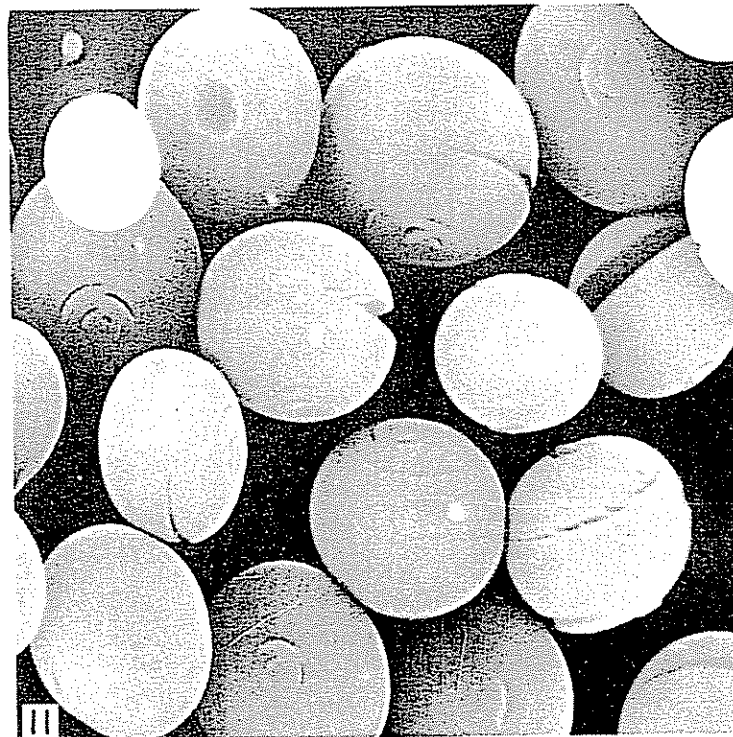

Fig. 11. Scanning electron micrograph of un-coalesced particles produced during extensive carbonization of anthracene at 980°C and 30,000 psi. Note appearance of some shrinkage cracks. × 2400
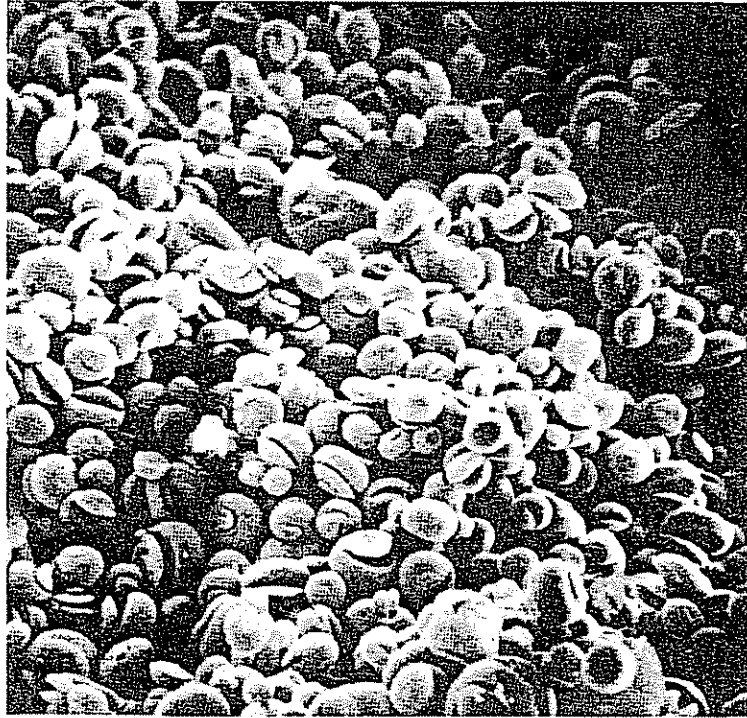
Fig. 12. Scanning electron micrograph of un-coalesced particles obtained by heat treating anthracene coke (produced at 550°C and 30,000 psi) to 2800°C [11]. × 450
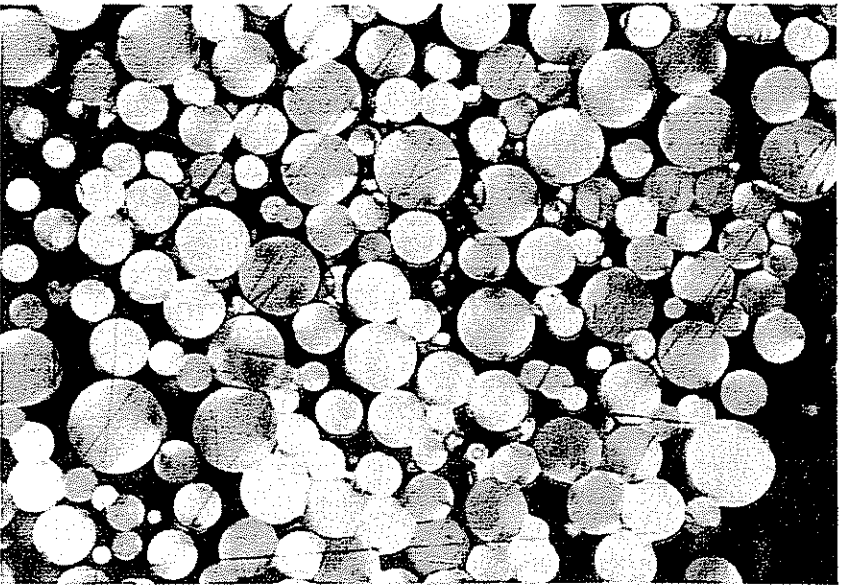
Fig. 13. Optical micrograph (using polarized light) of polished surfaces of spheres obtained by extensive carbonization of anthracene at 550°C and 13,200 psi. ×400
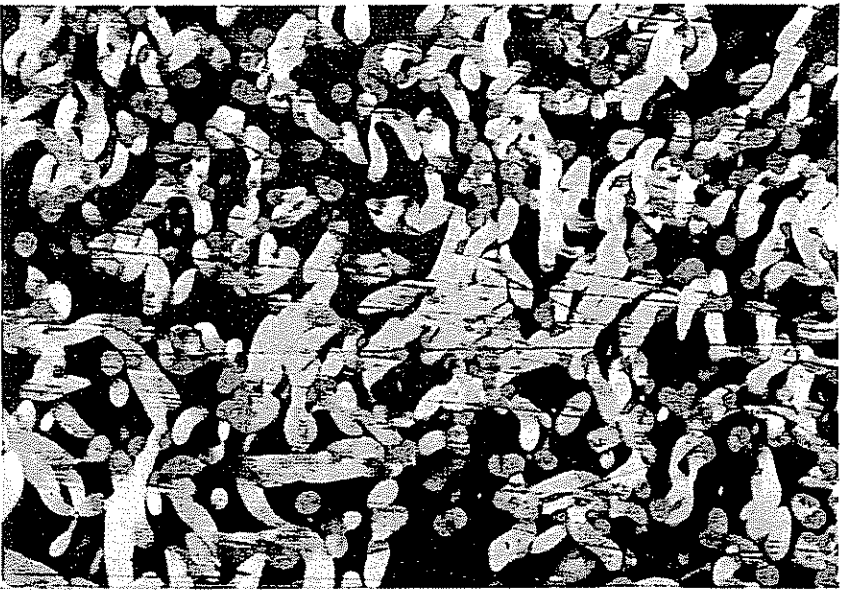
Fig. 14. Optical micrograph (using polarized light) of particles obtained by extensive carbonization of anthracene at 496°C and 37,000 psi. ×400
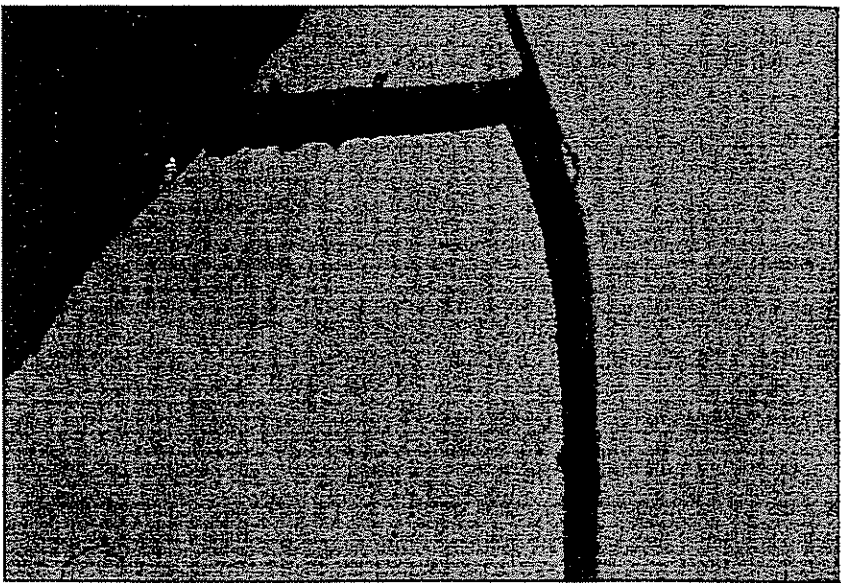
Fig. 15. Optical micrograph (using polarized light) of a sample produced by extensive carbonization of biphenyl at 600°C and 31,500 psi. ×400
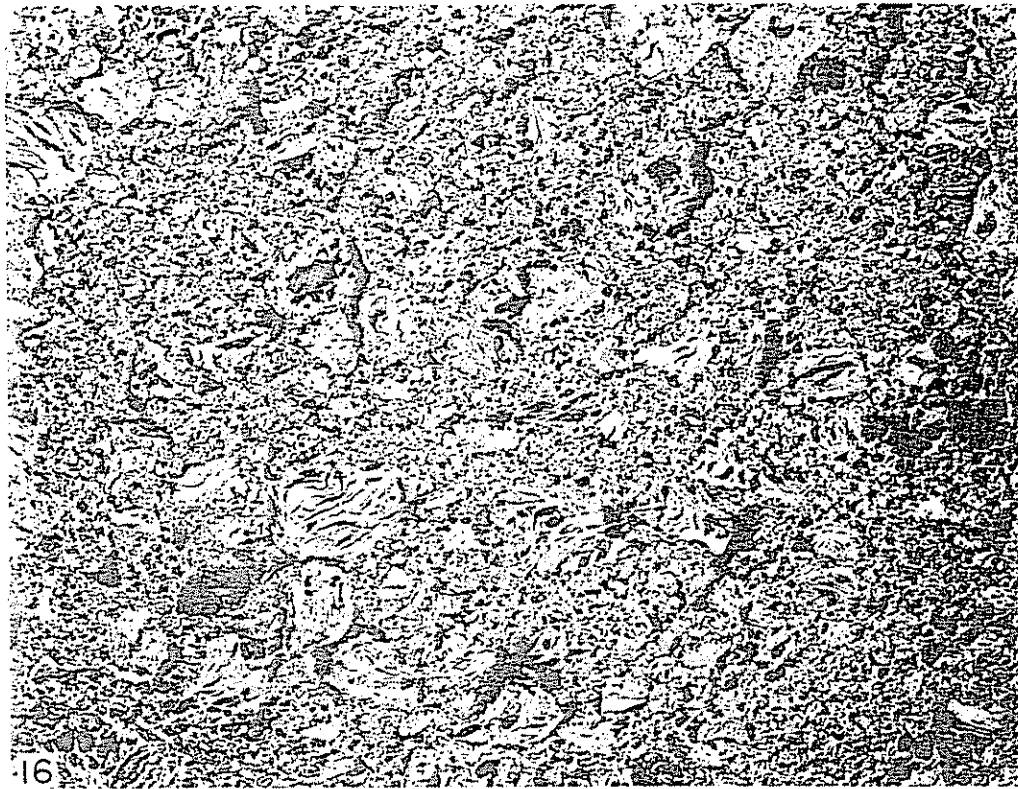
Fig. 16. Photomicrograph of a section of a composite containing non-needle-like petroleum coke. Significant porosity is in evidence. × 12
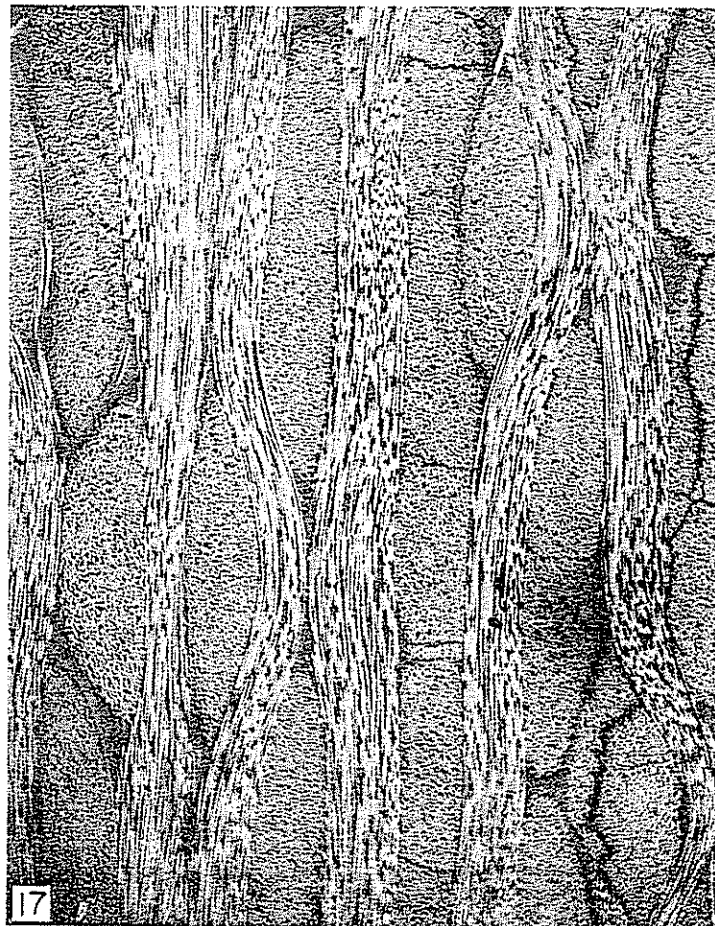
Fig. 17. Photomicrograph of a cross-section of a first generation composite containing carbon fibers bonded by an organic resin[13].
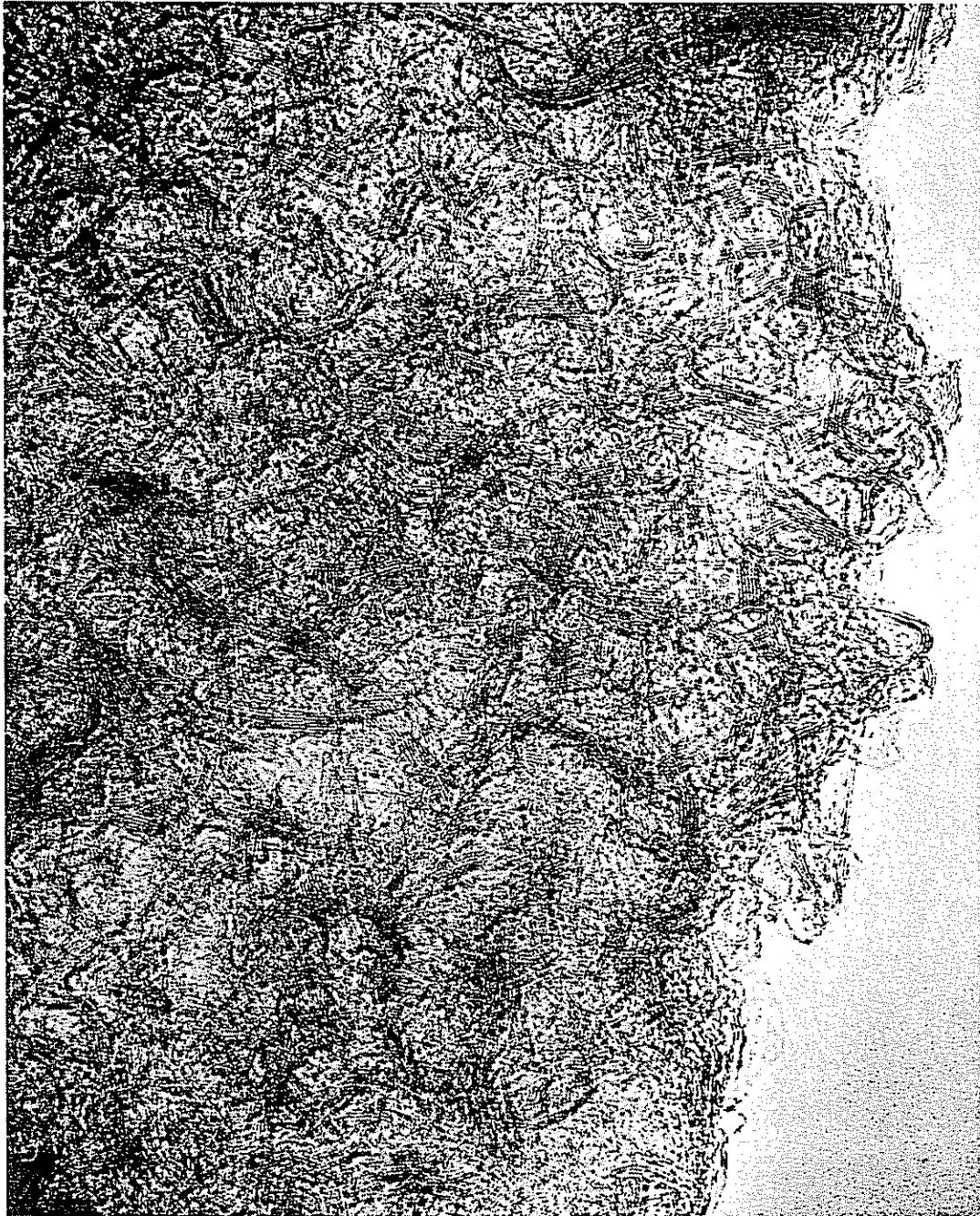
Fig. 19. Microstructure of glassy carbon produced by the heat treatment of phenolic resin to 2700°C [17]. Large distorted layers are evident. × 900,000
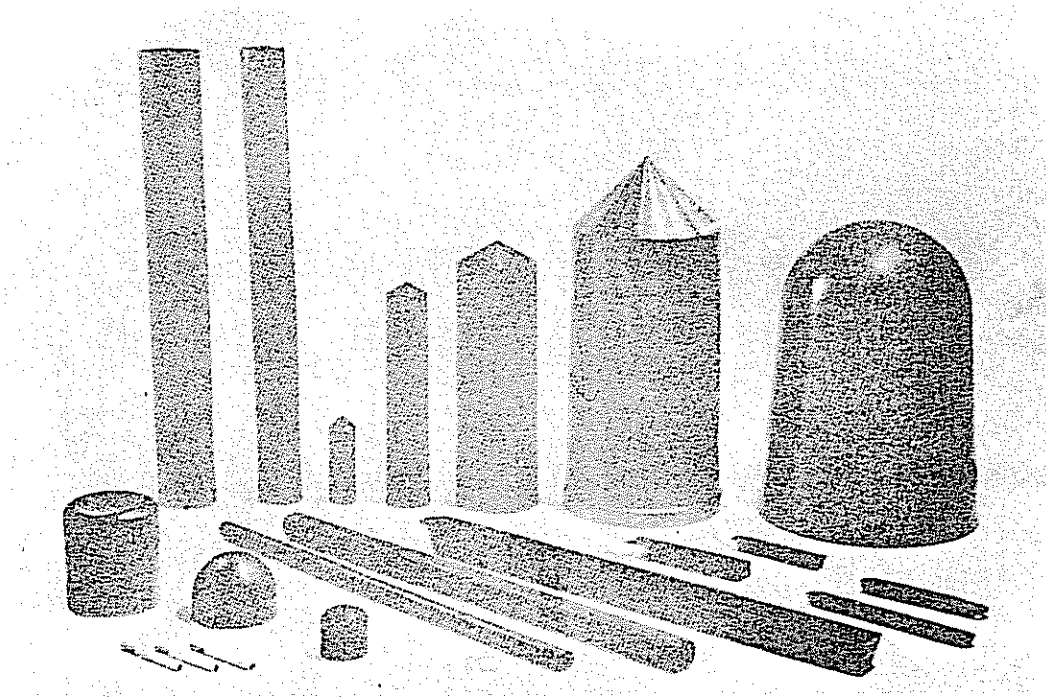
Fig. 20. Typical artifacts made from glassy carbon.

Fig. 25. Electron micrograph showing alignment of basal planes in surface of a polyhedral shaped thermal carbon black particle heat treated to 2700°C [24]. × 900,000
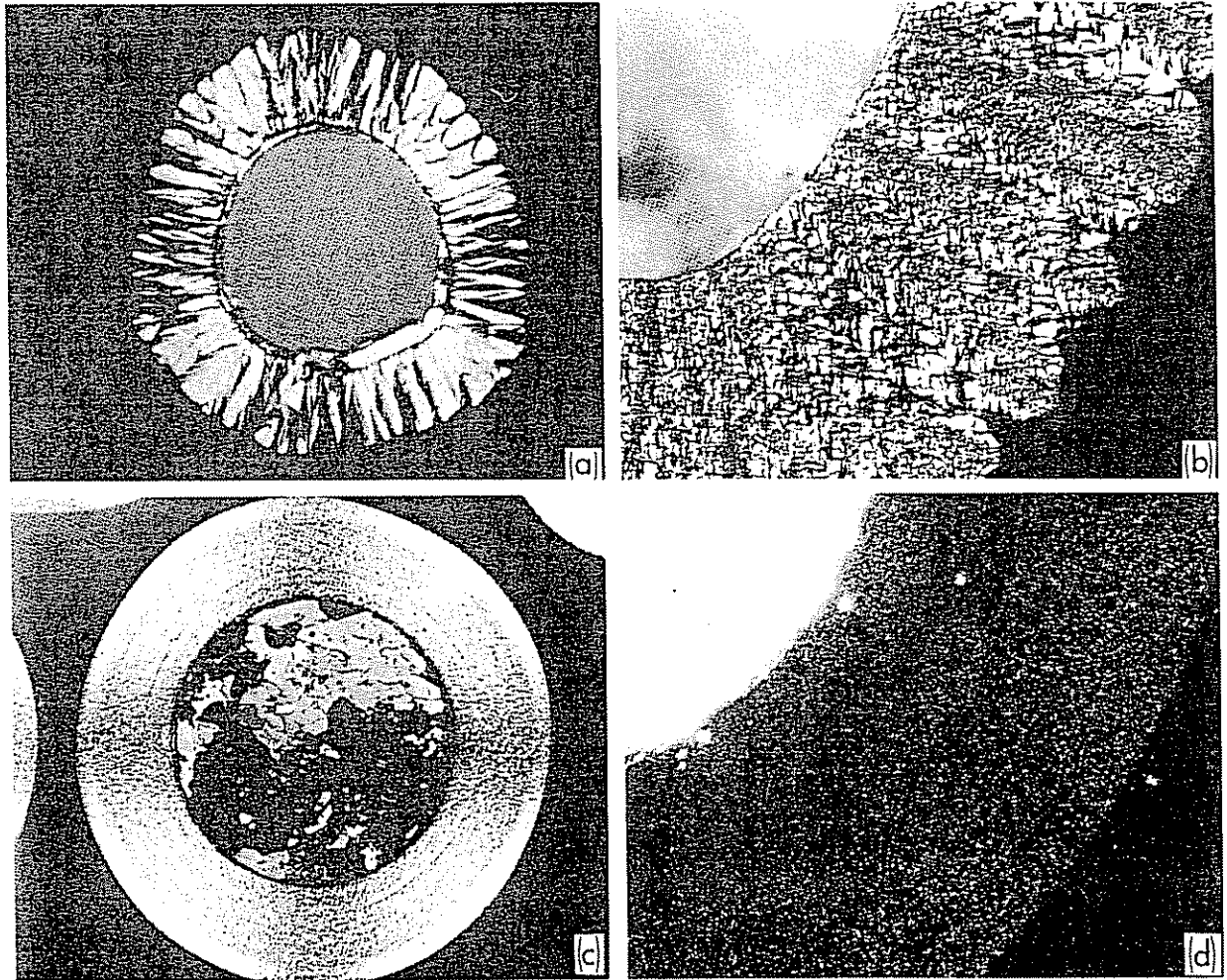
Fig. 27. Microstructure most commonly encountered in pyrolytic carbons deposited in fluid beds: (a) columnar, $\times 240$; (b) granular, $\times 160$; (c) laminar, $\times 72$; and (d) isotropic, $\times 160$. Polarized light used [26].
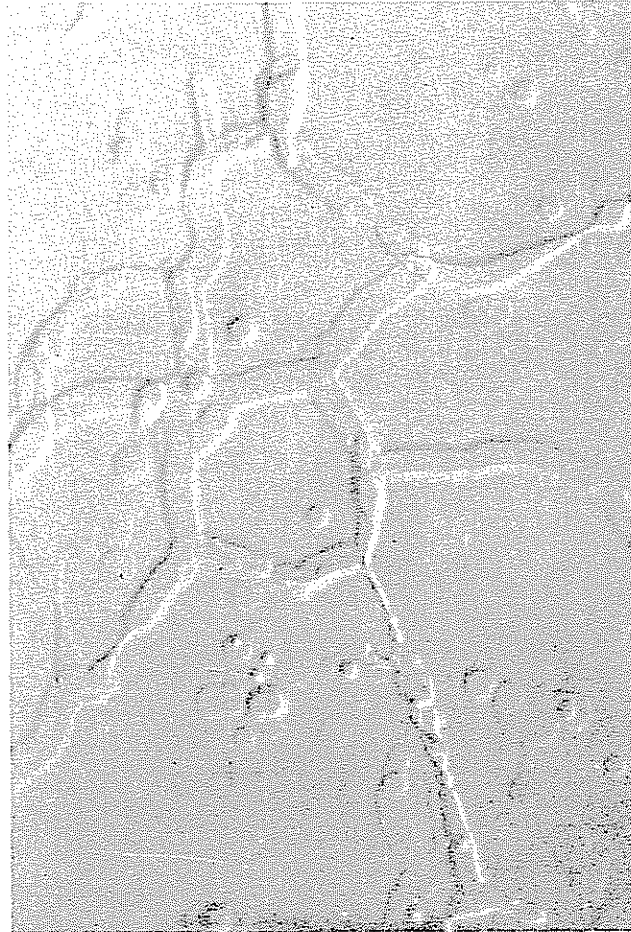
Fig. 29. Micrograph of surface of stress recrystal-
lized pyrolytic graphite following O_2 etch to 1 per
cent burn-off at 750°C. Crystallite boundaries are
preferentially etched and, thus, demarcated.
×675

carbon and, hence, the electrode produced. That is, much of the high thermal expansion which takes place perpendicular to the basal planes within the crystallites is accommodated within these cracks, resulting in a much reduced expansion of the filler particles and, therefore, the graphite electrode. A low thermal expansion in the electrode results in a body of significantly better thermal shock resistance and, hence, less possibility of electrode loss due to spalling.

2.2 Mesophase formation during coking

One of the major contributions to our understanding of the coking of organic materials over the last ten years was made by Brooks and Taylor[4]. They studied the early stages of carbonization of organic precursors like coal tar pitch, using light microscopy and electron diffraction. In the initial stage of carbonization, the organic melts, producing an isotropic medium. With increasing temperature and time of carbonization, Brooks and Taylor show, in the case of graphitizable precursors, that spherical mesophase* particles appear in the isotropic medium. See Fig. 3. These particles continue to increase in size and at about 50 volume per cent begin coalescence and the formation of a mosaic structure. In Fig. 4 we see four pictures, showing the various stages of mesophase coalescence into one particle. In Fig. 5, we see a more advanced stage of coalescence of the material. Schematically, Fig. 6 shows what is happening. That is, in the individual mesophase spheres the platelets (or flat aromatic molecules) are aligned so that the edges of the platelets intersect the surface of the sphere at right angles. (This is in marked contrast to the onion-shell structure of the fluid coke spheres which we have just discussed.)

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*The term 'mesophase' (Greek mesos = intermediate) is used for the substance of which the spheres and the mosaic (before solidification) are formed.

Before contact

Just after contact

Short time after contact

Type of complex internal structure formed when composite of two or more spheres contracts to one large sphere
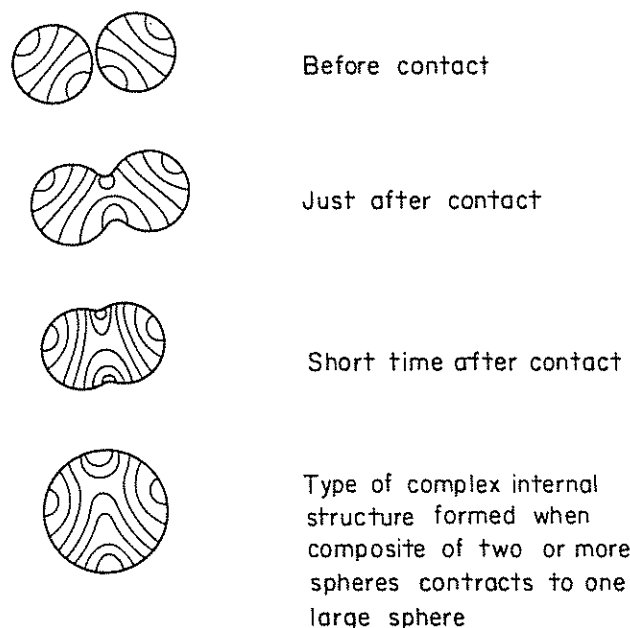
Fig. 6. Rearrangements which appear to occur when two spheres coalesce[4].

Upon coalescence, it is important that the small planar regions grow as well together in alignment as possible if large mosaic regions of well aligned crystallites are to be obtained. It has been known for some time that the solids content of the precursor should be low if the coke produced is to be highly graphitizable[5]. One previous explanation of this fact was that the solid material acts as nucleating centers on which coking of the organic precursors occurs[6]. The more nucleating sites, the greater the number of mesophase particles formed at any stage of coking and the lower the probability of forming extended mosaic regions upon coalescence of mesophase spheres. However, Brooks and Taylor have shown rather clearly that the main effect of the solids is that they reside at the surface of the mesophase particles (Fig. 7) and, thus, hinder the orderly coalescence of these particles producing well aligned large mosaic regions. This further supports the present thinking that the mesophase spheres are a type of organic liquid crystal. That is, their formation is not a result of nucleating centers but a result of three factors—(1) the increasing presence of

aromatic molecules of larger sizes as de-hydrogenation and condensation reactions occur[7]; (2) increasing mobility of planar molecules with increasing temperature permitting the possibility of their alignment; and, (3) an increasing probability of alignment as the planar molecules increase in size, and, hence, van der Waals attraction.

2.3 Carbons produced from known organic precursors

The usual organic precursors derived from petroleum and coal, which are used commercially for production of carbons, are composed of a complex mixture of compounds. Therefore, it is difficult to obtain correlations between structure of the precursor and structure of the carbon ultimately produced. Kinney, however, showed some years ago that indeed the graphitizability of cokes is markedly dependent upon the nature of the starting organic compound[8].

I would like to consider some of our results on carbonization of known organic compounds which we feel have significance. For example, we have looked at the carbonization of anthracene, phenanthrene and biphenyl. Anthracene and the isomer phenanthrene ($C_{14}H_{10}$) consist of three condensed benzene rings and are planar species. They lead to cokes which are highly graphitizable. On the other hand, biphenyl ($C_{12}H_{10}$) contains two benzene rings, which can rotate around the connecting carbon–carbon bond; it is a precursor of a coke which is poorl ' graphitizable. We were interested then in carbonizing mixtures of these compounds, which are mutually soluble, in an attempt to produce carbons of variable properties. Carbonization was performed at relatively low pressures, that is less than 1500 psi in a pressure vessel; heating up was at a rate of about 1°C min⁻¹ to 550°C, where coking was continued for various periods of time. More details on sample preparation are given elsewhere[9].

In the case of the anthracene–biphenyl system, it was noted from X-ray diffraction studies that the carbon produced upon heating the coke to 2800°C was a two-phase material, a well graphitized fraction produced from the anthracene and a poorly graphitized fraction produced from the biphenyl. The significant point here, we feel, is that the carbonization rate of anthracene is about 1200 times that of the biphenyl[10]; and therefore, carbonization of the anthracene is essentially completed before any significant carbonization of the biphenyl has taken place. Hence, the biphenyl intermediates (radicals) have little opportunity to cross-link the anthracene intermediates and to decrease its graphitizability. Thus, a two-phase carbon is produced.

On the other hand, in the case of the phenanthrene–biphenyl system, phenanthrene has a carbonization rate of only three times that of biphenyl[10]. Intermediates from both species are being produced concurrently. The result is a one-phase carbon upon heat treatment to 2800°C. Figure 8, for example, shows the effect of biphenyl addition to phenanthrene on the crystallinity of the carbons produced. We see that relatively small amounts of biphenyl markedly decrease crystallite growth. This possibility of produc-
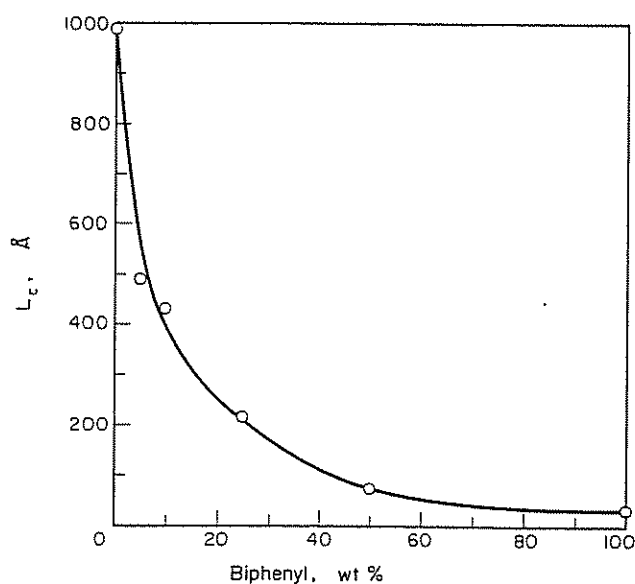

Fig. 8. Change in average crystallite height of the 2800°C carbons produced from different starting compositions of phenanthrene–biphenyl mixtures.

ing carbons of variable crystallite size enables us, in turn, to produce materials of different properties, depending on the relative amounts of phenanthrene and biphenyl used [9]. In Fig. 9 we observe the wide range of helium densities in the carbons produced. The phenanthrene carbon has a relatively high density of about 2.16 g cm^{-3}, because of the good crystallite alignment present and, therefore, the small amount of closed pore volume (to helium) present[2]. As we add biphenyl, the helium density progressively decreases until the biphenyl carbon has a helium density of only about 1.74 g cm^{-3}. This is equivalent to the carbon having about 20 per cent of its total volume closed to helium. This is a glassy carbon type of material which we will be discussing in more detail shortly. Also shown in Fig. 9 is the change in helium density of the coke samples heated to 950°C. It is interesting that at this stage of development the phenanthrene coke has a lower

density (more closed pore volume) than does the biphenyl coke.

2.4 Carbonization under moderately high pressures

Recently, we have been studying the effect of carbonizing selected compounds under high pressures on the nature of the carbons produced. We have again used anthracene, phenanthrene, and biphenyl as precursors. Small samples are sealed in gold tubes under nitrogen and placed in a hydrothermal apparatus. Pressure is applied to the gold tubes via the medium of water. More details on the experimental approach are presented elsewhere[11].

Let us consider our studies using anthracene. We find that for carbonization pressures up to 5000 psi, mesophase spheres form and ultimately coalesce, as we have previously discussed. However, when we go to higher pressures we find the interesting phenomenon that mesophase spheres form but do not coalesce as carbonization proceeds to completion. For example, Fig. 10 shows results upon heating anthracene to 600°C at about 2°C min^{-1}, soaking for 1 hr, all at a pressure of 10,000 psi. The scanning electron micrograph shows the presence of spheres ranging from about 3 to 15 μm in diameter. It is interesting that if we increase our carbonization temperature to 980°C, in this case under a pressure of 30,000 psi, we see again unagglomerated spheres but we also see the appearance of some shrinkage cracks in the particles produced by differential contraction of the particles (Fig. 11). The cracks run essentially parallel to the basal plane direction of the small crystallites which are about 30A in diameter. Subsequent heat treatment of the anthracene coke to 2800°C only results in a change in shape of the particles from spherical to oblate and the clear appearance of cracks in most every particle (Fig. 12). In Fig. 13 we see a light micrograph of a polished section in polarized light. The spheres were produced by the carbonization of anthracene at 550°C and 13,200 psi. Clearly
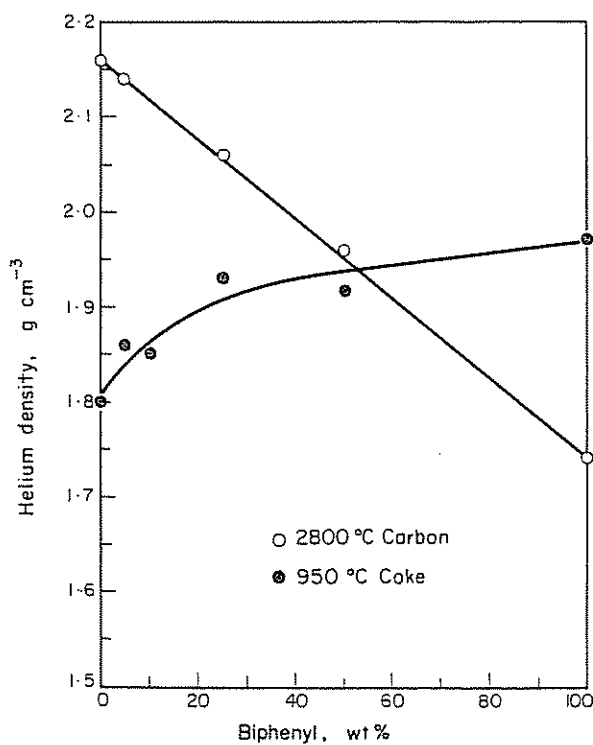
Fig. 9. Changes in helium density of 950°C coke and 2800°C carbon produced from different starting compositions of phenanthrene–biphenyl mixtures[9].

the particles are anisotropic, as seen by the difference in colors.

We are able to produce a different morphology from anthracene if carbonization is conducted at about 500°C. Figure 14 shows the result of carbonization at a pressure of 37,000 psi. The resultant coke now is in a 'spaghetti-like' form.

In the case of phenanthrene, we have also been able to produce cokes consisting of unagglomerated mesophase spheres similar to those produced from anthracene. In the case of biphenyl, a non-graphitizable precursor, there is little or no mesophase appearance even for carbonization pressures as high as 45,000 psi. Figure 15 shows a biphenyl coke, with its characteristic isotropic appearance, produced at 600°C and a pressure of 31,500 psi.

We think that our carbonization results at high pressures may have some practical significance. They suggest the possibility of producing carbons of a different morphology, that is spherical particles which will not be aligned during molding or extrusion but particles in which crystallite growth is reasonably good. Further, because some edges of crystallites are exposed in the surface, enhanced bonding to a second phase should be possible. This has been one of the limitations of using spherical particles of fluid coke. That is, bonding to a second phase is relatively poor because of the onion-shell nature of the particle.

2.5 Carbon composites

It is well to remind ourselves of the broad differences in carbon composites which can be produced as a result of varying the nature of the filler material. Figure 16 shows a composite containing a non-needle-like delayed petroleum coke filler bonded together with coal tar pitch coke. Obviously the body will be almost isotropic in its properties. It has a porosity of about 30 per cent, most of it located between particles but some also within the particles of petroleum coke.

On the other hand, as has been shown over the last ten years, if we want a highly anisotropic composite material we can select carbon fibers as the filler material. As we know, much work has been done in this area [12], but I will not attempt to go into detail in these studies in this paper. Figure 17 shows for comparison, however, a first-generation composite of fibers produced from a cellulosic precursor bound by phenol–formaldehyde [13]. The basal planes in the carbon crystallites run closely parallel to the fiber axis and, hence, impart to the composite properties that are highly dependent on the direction of measurement. The extent to which the high strength of the fibers along their axis is imparted to the composite depends strongly upon the bond between the fibers and the resin phase. It should be remembered that the carbon industry has long been concerned about this important problem in the production of electrode and anode composites. Much can be learned from their experiences.

2.6 Glassy carbon

Another area of interest in recent years has been the production of disordered carbons starting with thermosetting resins. These materials have been termed glassy carbons and vitreous carbons. Significant achievements have been made by the Japanese, British, French, and, more recently, the Americans [14]. The main objective has been to produce a material which is impermeable to gases and liquids. The material is usually referred to as a glassy carbon because of its shiny appearance, its conchoidal fracture, and its impermeability. Thermosetting resins like phenol–formaldehyde, furfuryl alcohol, and divinyl benzene have been used as precursors. They are cured, carbonized very slowly, and then heated to elevate temperatures. A structure is produced containing a significant volume of closed voids — about 30 per cent. The material is a cavity-aperture system, with the cavities being as large as 35A

in diameter [15]. Crystal growth is quite small. Recently Jenkins and Kawamura[16] have proposed a structure for glassy carbon, shown in Fig. 18. They suggest that such carbons consist of long microfibrils, a string comprising up to ten stacked graphite ribbons. The microfibrils twist, bend, and warp with ease to form stable entities which are bonded together with strong inter-fibrillar bonds. In glass-like carbons, these microfibrils are randomly oriented. In carbon fibers, Jenkins and Kawamura suggest that they are also present but oriented closely parallel to the fiber axis. Ban and Hess have recently confirmed the structure of glassy carbon by high resolution electron microscopy, as seen in Fig. 19 [17].
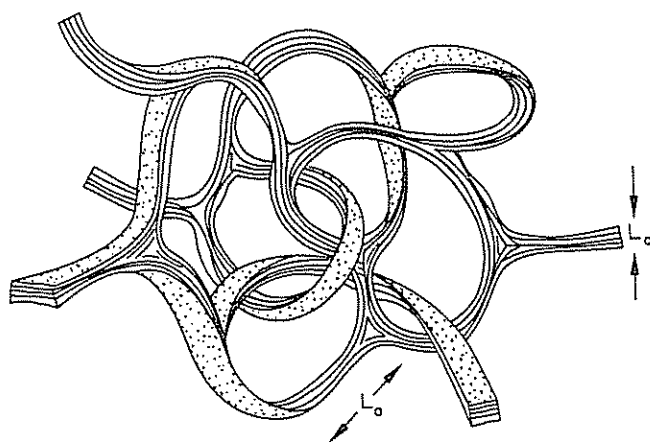

Fig. 18. A schematic structural model for glassy carbon [16]. L_c and L_a represent average crystallite height and diameter which would be measured by X-ray diffraction.

Figure 20 shows some of the types of objects that have been made from glassy carbon, that is, boats, crucibles, bars, tubes, and plates. The limit on wall thickness is about $\frac{1}{8}$ in. and is dictated by the necessity of liberating gaseous products during curing and carbonization. Formation of cracks in the artifacts cannot be tolerated. In Table 1 we compare some typical properties of glassy carbons with those of an artificial graphitic electrode. The apparent density of glassy carbon is smaller; however, its gas permeability is also markedly less because its porosity is closed. The tensile and compressive strengths of the glassy carbons are typically higher than the electrode graphite. Its electrical resistivity is higher and its thermal conductivity lower. Its coefficient of thermal expansion is comparable to artificial graphite. Its oxidation rate in air is significantly lower, probably because of its very small available surface area and its higher purity. It is harder than artificial graphite.

2.7 Molecular sieve carbons

We have been most interested in the fact that the same organic precursors which can be used to produce glassy carbons can also be used to produce molecular sieve carbons upon heating to appropriate temperatures. That is, typically, when a thermosetting pre-

Table 1. Comparison of properties of glassy carbon (3000°C) with artificial graphite

Property	Glassy carbon	Artificial graphite
Apparent density (g cm³)	1.45	1.60
Gas permeability (cm² sec⁻¹)	10^{-8}	10^{-2}
Tensile strength (kg cm⁻²)	420	50
Compressive strength (kg cm⁻²)	950	200
Electrical resistivity (Ω cm)	$(35-40) \times 10^{-4}$	7×10^{-4}
Thermal conductivity (cal cm⁻¹ sec⁻¹ °C⁻¹)	0.04	0.3–0.4
CTE (°C⁻¹)	$(2.0-2.2) \times 10^{-6}$	$(1-3) \times 10^{-6}$
Oxidation rate, air at 800°C	$\frac{1}{5}$ that of graphite	
Shore hardness	70–80	30–60

cursor is heated, the accessible surface area and pore volume of the material go through a maximum with increasing heat treatment temperature. For appropriate heat treatment temperatures (which varies for each precursor), the material can have quite a significant surface area and pore volume in voids of molecular dimensions. Further heating to higher temperatures closes up these voids, or probably the apertures, resulting in a glassy carbon.

Figure 21, for example, shows the effect of heat treatment of polyvinylidene chloride (PVDC) on the surface area of the carbons produced[18]. We are using four molecules of varying size, the smallest carbon dioxide and the largest neopentane, to probe the pores of the material. We see that for heat treatment temperatures between about 800 and 1200°C the surface area accessible to all adsorbates is high and molecular sieving
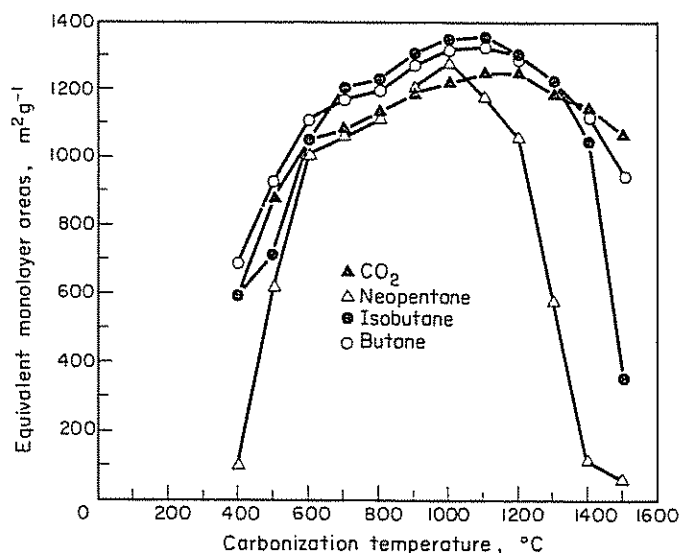

Fig. 21. Surface areas of polyvinylidene chloride carbons heated to different temperatures as measured by molecular probes of various sizes. CO_2 uptake at −77°C. Hydrocarbon uptake at 0°C[18].

is negligible. When we then heat to higher temperatures, we begin to close up the pore system sufficiently to first screen out neopentane at about 1400°C and then isobutane at about 1500°C. Heat treatment to still

higher temperatures would undoubtedly also screen out smaller molecules.

Recently, molecular sieve carbons produced by the carbonization of Saran, which is a commercial material containing about 85 per cent PVDC and 15 per cent polyvinyl chloride, have been of interest for the dynamic separation of organic molecules. In Fig. 22, for example, we see the effectiveness of pellets of carbonized Saran in separating n-heptane from isooctane[18]. The pellets were produced from Saran as the filler and either lignite pitch or methyl cellulose as the binder. The whole pellet was carbonized prior to its use, as described elsewhere[18]. The hydrocarbons were added to a helium carrier stream and passed through a bed of ⅛ in. pellets at about 30°C. The concentration of the hydrocarbons in the outlet stream was monitored as a function of time. If the hydrocarbons have little accessibility to the internal surface of the sieve, they quickly pass through the column, with their outlet concentration equal to their inlet

Fig. 22. Breakthrough plots for the system n-heptane (O) and iso-octane (⊛) entrained in helium when passed through packed beds of Saran carbon, Linde 5A zeolite, and a Pittsburgh activated carbon at 34°C[18]. The Saran samples were formed from 80 parts Saran char and 20 parts lignite pitch. Following carbonization, they were reacted with CO_2 to either 2.2 or 2.4 per cent weight loss to open up the pitch binder carbon slightly.

concentration. On the other hand, if the compound is taken up to a significant extent on the sieve, there is a significant time lapse before breakthrough of the compound into the outlet stream occurs. We note in the upper two plots the rapid breakthrough of isooctane, denoted by the solid circles, and the high capacity of the Saran sieves for n-heptane. By comparison, we show the 5A Linde zeolite, which is now used commercially to separate straight from branched hydrocarbons. It also shows good separation. The lower plot shows a commercial activated carbon. Here the pores are sufficiently large so that both hydrocarbons are taken up to a large extent and no molecular sieving is apparent.

We have concluded from our studies that we have an aperture-cavity system in these carbon sieves with the aperture being slit-shaped[19]. That is, the sieves have the ability to take up large, flat molecules which are able to align themselves with their thin dimension parallel to the thin dimension of the slit. Consequently, these sieves show promise in separating flat molecules varying slightly in thickness. For example, in Fig. 23 we show the separation of cyclohexane from benzene. The cyclohexane, which is about 1.1A thicker than benzene (but about 0.2A shorter), is not taken up by the carbon sieve but breaks through the column rapidly. We also see in Fig. 23 the behavior of a commercial 10X Linde zeolite and an activated carbon. Both of these materials have significant capacity for both hydrocarbons. An additional behavior is also noted on these two materials. Because of the higher heat of adsorption of benzene than cyclohexane, benzene displaced cyclohexane, which was adsorbed in the beginning of the run, from the carbon. This is particularly noticeable on the 10X zeolite.

We have also recently looked at the possibility of introducing metals into molecular sieve carbons with the idea of using these materials as selective catalysts. For example, it is possible, starting with polyfurfuryl
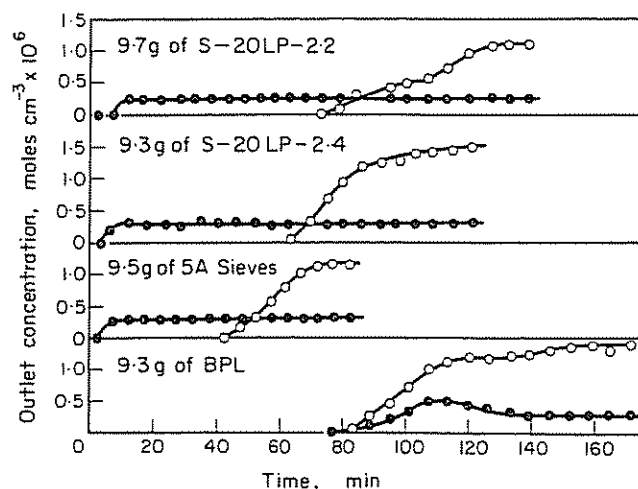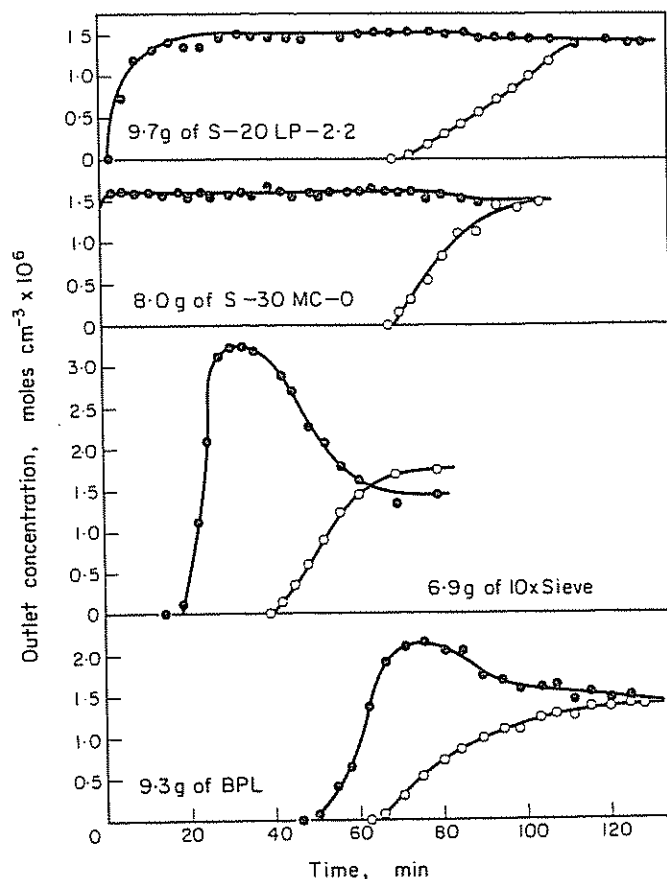

Fig. 23. Breakthrough plots for the system benzene (○) and cyclohexane (◉) entrained in helium when passed through packed beds of Saran carbon, Linde 10X zeolite, and a Pittsburgh activated carbon at 34°C[18]. The Saran samples were formed from Saran char and either lignite pitch or methyl cellulose, as designated.

alcohol, to introduce platinum and to obtain a material which shows selectivity for the hydrogenation of olefins[20]. For example, 1-butene can be selectively hydrogenated in a stream of 1-butene and 3-methyl-1-butene, as shown in Fig. 24. Only 1-butene has accessibility into the voids of the sieve structure and, hence, to the platinum sites. When the system platinum supported on a typical activated carbon is used as a catalyst, both hydrocarbons are rapidly hydrogenated.

3. CARBONS PRODUCED VIA A HIGH TEMPERATURE ROUTE

3.1 Carbon blacks

Now let us turn, somewhat more briefly, to several of the interesting advances which
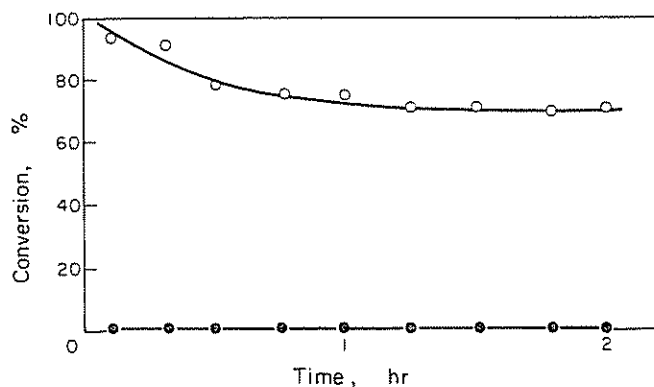
Fig. 24. Competitive hydrogenation of 1-butene (O) and 3-methyl-1-butene (⊜) over a carbon molecular sieve support containing 1 per cent platinum. $H_2:1-C_4H_8:3$-methyl-1-butene equals 40:4:1. Residence time, 1.8 sec. Temperature, 150°C [20].

have been made in the production of carbons by the cracking of gases or vapors at higher temperatures. The major commercial market here is the production of carbon black. Roughly 1.5 million tons of carbon black were produced in the United States last year. It was mostly used in the reinforcement of rubber [21]. Back in 1962 in my Sigma Xi paper [22] I discussed the interesting change in morphology of carbon black particles as they are heat treated to temperatures up to 2700°C in the absence of oxidizing gases. With increasing heat treatment temperature, we find that the particle surfaces become progressively more homogeneous. Surface chemists, for example, have used graphitized carbon blacks for some years for adsorption studies. They conclude, because of sharp steps in their isotherms and the nature of the variation of the heat of adsorption with coverage, that the surface is composed predominantly of just one crystallographic plane, probably the basal plane.

Indeed, one of Professor Mrozowski's colleagues some years ago [23] produced electron micrographs which suggested that the particles heated to elevate temperatures were polyhedral in shape. It was not until just recently, however, that Ban and Hess showed by very high magnification electron microscopy that indeed the surface of heat treated carbon blacks are composed of basal planes [24]. In Fig. 25, we see this clearly, as well as being able to see individual basal planes separated by about 3.4A. We also see the intersection of two polyhedral surfaces with the planes bending around at this intersection.

More recently, there have been indications that heat treated carbon blacks show good stability to neutron irradiation at high temperatures. Thus, the material may well have applications in high temperature gas cooled thermal reactors and molten salt breeder reactors.

3.2 Pyrolytic carbon

Back in 1961 there was much research and development in progress in the area of producing massive shapes of pyrolytic carbon by the cracking of hydrocarbons over and the deposition of carbon on various substrates. This work had been stimulated by the studies of Watt and coworkers some 5 to 10 years earlier [25]. I think what has been particularly interesting in the past 10 years has been the spin-off from the military and space applications of pyrolytic carbon to potentially important civilian applications. For example, it has been shown by Bokros and his group, and others, that we can coat uranium and thorium carbide fuel particles with pyrolytic carbon and thereby produce material which can retain undesirable gaseous fission products at elevated temperatures [26]. Figure 26 shows a typical fluid bed apparatus which can be used for the coating. The temperature and partial pressure of the hydrocarbon are adjusted depending upon the structure of the pyrolytic carbon desired. The bed is operated at a total pressure of atmospheric. The gas which appears to be most preferable for the coating is propylene. Because it is less stable than methane, carbon can be formed at a lower and, thus, more convenient temperature (about 1200°C). The fuel particles in the fluid bed are thus coated to the desired thickness with pyrolytic carbon, with
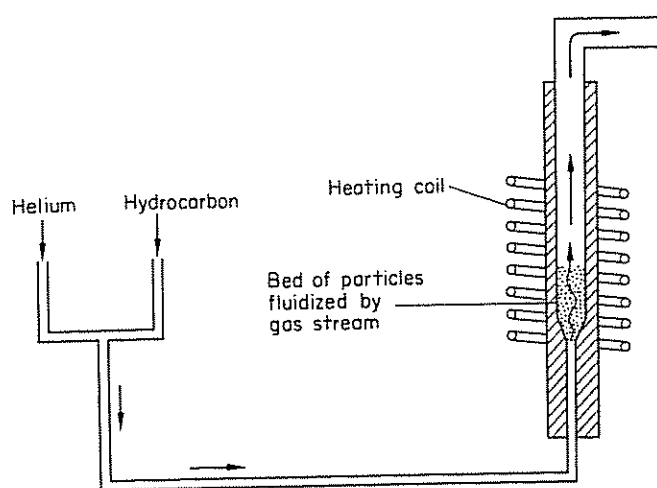
Fig. 26. Schematic diagram showing particles being coated with carbon in a fluidized bed[26].

the nature of the coating being changed with thickness if desired.

Figure 27 shows some of the coatings which have been produced. Ideally the coating next to the fuel particles is somewhat porous so that the fission gases produced can be taken up. There is then an outer coating which is impermeable to the gases.

Another most interesting spin-off in the pyrolytic carbon area is the recognition that it is one of the very best biomaterials[26]. That is, it can be used for such things as heart valves because its interaction with the blood is very small; and, therefore, the extent to which it promotes coagulation of the blood, low. It also shows unusual promise in artificial joints, since it is strong but at the same time has some lubricity so that the joints will not seize as in the case with metals.

3.3 Stress recrystallized pyrolytic-graphite

In the last 10 years there has been significant progress made in the taking of as-formed pyrolytic carbon to elevated temperatures (as high as 3400°C) and placing it under stress to enhance crystallite alignment and growth[27]. So-called stress recrystallized pyrolytic graphite is formed, which has some interesting commercial applications as X-ray monochromators[28].

From the standpoint of basic research, we feel that this material lends itself very well to studies which will lead to a better understanding of structure–property relationships. That is, the material can be produced in different crystallite sizes, containing varying amounts and types of defects. The material can be conveniently characterized using, for example, the Hennig etch decoration technique[29]. One of the groups which pioneered the structure–property relationship of this material was the 'Ubbelohde School' at Imperial College. They produced their own materials and studied primarily electronic and thermal properties.

Figure 28, for example, is a plot of the mean carrier mobility vs. temperature for a number of samples, as determined from magnetoresistance measurements[30].
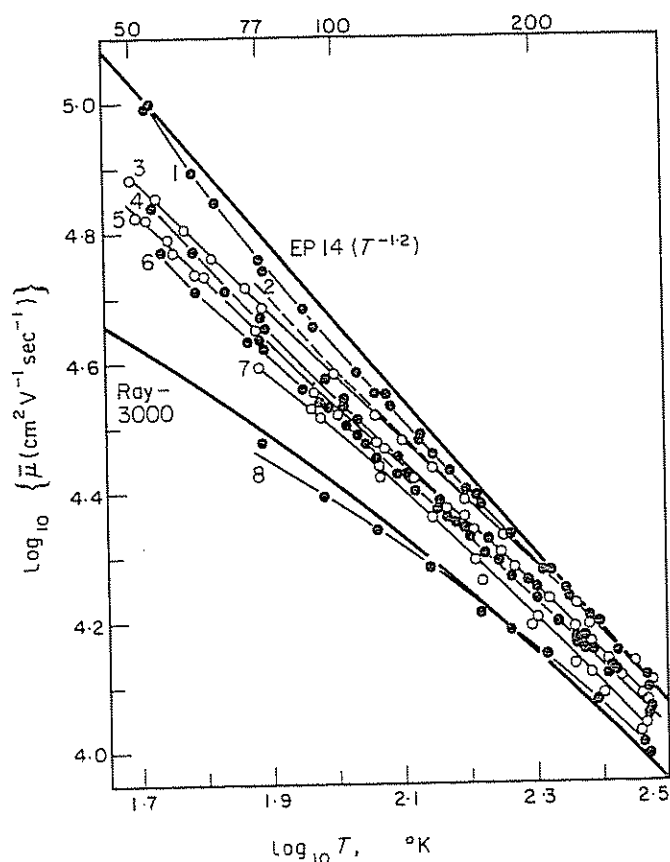

Fig. 28. Logarithm of the mean mobility, $\bar{\mu}$, measured at 3 kG vs. temperature plotted for a range of stress-recrystallized pyrolytic materials. Limiting curves for a natural graphite EP14[31] and a pyrolytic graphite, RAY 3000, annealed at 3000°C[32] are also shown[30].

It is seen that the mobility approaches more or less closely that of the single crystal EP14 on which Soule did pioneering studies[31]. Ubbelohde and coworkers were able to estimate average crystallite diameters from the mobility measurements and found that agreement with crystallite diameters estimated from microscopic studies was good.

More recently, we have been interested in using the stress recrystallized material to study the carbon–oxygen and carbon–carbon dioxide reactions. Oxygen attacks the graphite preferentially at crystallite boundaries and at the sample edges. A burn-off in oxygen of only about 1 per cent at 750°C is sufficient to demarcate these boundaries by light microscopy, as is shown in Fig. 29. Some additional attack is noted within crystallite regions at defects. Suffice it to say, we think this material lends itself very well to gaining a basic understanding of the gas reactions of carbon.

4. OTHER PERTINENT RECENT DEVELOPMENTS IN THE MATERIALS SCIENCE OF CARBON

As I indicated at the beginning of this paper, in the limited space available I would not be able to touch on all of the interesting developments, over the last ten years, in the materials science of carbon and graphite. However, let me briefly list some of the other highlights.

(1) The production of more perfect and larger synthetic diamonds and, in some cases, those having semiconductor properties[33].

(2) The achievement of improved control in producing activated carbons of desired pore spectra and surface properties[34].

(3) Production of a new allotropic modification of carbon, that is, the so-called linear carbon having retained the polyyne or the cumulene structure[35].

(4) Growth of thin films of carbon using sputtering and vaporization techniques where the deposited species may be neutral or charged[36].

(5) Production of very low density carbons, such as carbon foams and hollow carbon spheres[37].

(6) Artifacts produced by the impregnation of porous bodies with pyrolytic carbon [38].

(7) The application of lamellar compounds of graphite, for example the intercalation by potassium, to obtain an active catalyst for polymerization reactions[39].

5. WHAT THE FUTURE MAY HOLD

Lastly, I would like to make some predictions for advances over the next 10 years in the area of carbon and graphite. These include:

(1) Much expanded studies on metal-carbon composites and cermets, with the carbon not necessarily being in the form of a fiber.

(2) Use of carbon composites in land-based construction and aerospace applications becomes significant.

(3) Carbon molecular sieves come of age.

(4) Glassy carbons are modified extensively by the addition of carbon and metal additives.

(5) Carbon films are found to have interesting electronic uses.

(6) Expanded use of carbon as a catalyst support and as a catalyst.

(7) Use of extracted coal, in which the mineral matter has been essentially removed, as a source of coke for anode and electrode production.

(8) Expanded use of pyrolytic carbon to densify carbon bodies and, in some cases, to serve as the binder phase.

(9) The use of carbon fibers, produced from coal tar and petroleum pitches, in the fabrication of graphite electrodes.

(10) Much better understanding of the conversion of organic precursors to

carbon. Understanding the relation between polymer morphology and carbon morphology. That is, the new materials science of carbon and graphite (from benzene to graphite) will be developed; and, as a consequence, much more interest and recognition will be seen in universities in this field. Indeed, the new materials science of organic materials will take its place along side of the fields of metallurgy and ceramic science as an important area.

In any case, I think we would settle for the next ten years being as exciting and dynamic in the carbon field as the last ten years have been.

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