

MECHANICAL STRENGTH, THERMAL EXPANSION AND STRUCTURE OF COKES AND CARBONS*

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The relation between the mechanical strength, thermal expansion and the microcrystalline structure is considered for a broad class of solids, which starts from condensed polymeric organic solids (coals, raw cokes, resins, etc.), runs through carbonized organic substances like calcined cokes and polycrystalline graphite, up to essentially single crystals of graphite. The great anisotropy of single microcrystallites and the criss-cross hooking of the crystallites by C—C valence bonds leads, for polycrystalline materials, to: 1) a low thermal expansion and its strong dependence on the crystalline alignment, 2) the existence of unavoidable microscopic porosity at room temperature which is due to the difference in the volume contraction of single crystals and the bulk material, 3) the presence of large internal stresses which are created and frozen-in (absence of creep) during the cooling of the material. The reversible release of these stresses in heating is responsible for the increase of the mechanical strength of carbons with temperature. In the second part of this paper, the structure of cokes and its formation are discussed. Cokes are classed into soft and hard ones according to the high or low order in arrangement of crystallites on a microscopic scale (alignment in the form of platelets or in a disordered glassy state). The gradual growth of crystallites with temperature of heat treatment is mainly due to internal stresses created by the anisotropic thermal expansion of crystallites, the stresses being relieved by the growth and rearrangement of crystallites. Thus, no steady growth of crystallites is observed when carbons are held for a long time at high temperature. Some soft cokes show a streaky pattern and break up into needles in grinding. This structure is caused by a frozen-in flow pattern in the viscous fluid at the time of setting (solidification), the flow leading to an alignment of flat molecules with planes parallel to the direction of the flow. This alignment becomes more perfect with increase of temperature of heat treatment. Needle structures are present in all soft cokes; their occurrence is, however, dependent on conditions under which the coking was performed. In the third part, some of the complications introduced by the technological processes used in manufacture of carbons are pointed out and their influence on the physical characteristics of the final products indicated.

I. INTRODUCTION

In this paper a broad class of solids will be treated, solids which start from condensed polymeric organic solids (coals, raw cokes, resins, etc.), run through carbonized organic substances like calcined cokes, and polycrystalline graphites up to essentially single crystals of graphite. Any attempts at elucidation of the nature of correlations between the physical properties and struc-

ture for such materials encounter specific difficulties not found in other branches of the Physics of Solids. Although new obstacles are met, one discovers that some other difficulties are not present, thus leading in some respects to a considerable simplification of the problem. This is due to the characteristic structure of these substances which makes them unique in a number of respects. The characteristic distinctiveness of these substances will be illustrated in this paper by discussing the nature of the carbon structure and the

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resulting interesting mechanical and thermal behavior of such substances¹. The simultaneous presence of two factors is mainly responsible for this uniqueness: the very great anisotropy of the single crystallites on one hand, and the polymeric nature of the intercrystalline valence bonding on the other.

A single crystal of graphite or a micro-crystal of carbon (for the distinction between these two types of crystals, see below) is composed of a series of aromatic planes essentially built of a network of benzene rings in which neighboring atoms of carbon are held by valence forces, the planes being stacked on top of each other and held together by Van der Waals attractive forces. Valence forces are relatively strong; the plane benzene ring structures are therefore very rigid and thus the crystals have a very low compressibility and low thermal expansion in the direction parallel to the benzene planes (*a*-direction). On the other hand, Van der Waals forces are weak, consequently adjacent planes can be easily displaced parallel to each other or rotated around an axis perpendicular to the planes. Carbon crystallites being turbostratic are probably especially poorly resistant to such kinds of shears. Graphite crystals (of type I and II) having a preferential relative arrangement of benzene rings in adjacent planes, are probably somewhat stronger but their inability to support even small tangential stress is well known to experimenters. The weak Van der Waals attraction between planes is responsible for a high compressibility in the *c*-direction (perpendicular to the planes), also for a relatively high thermal expansion in the same direction. The volume compressibility of Ceylon graphite has been determined by Basset² up to 20,000 Kg/cm² and by Bridg-

man³ up to 25,000 Kg/cm². Basset found that the compressibility starts from the value 4.4×10^{-6} cm²/Kg at the lowest and decreases to somewhat below 2×10^{-6} at the highest pressures. Bridgman gives only an average value over the whole range of about 3×10^{-6} . The thermal expansion of graphite has been investigated by means of X-ray diffraction. In the *c*-direction, Backhurst⁴ gives a mean value between 0° and 900°C of $\alpha_c = 26.7 \times 10^{-6}$ per degree C. For high temperatures, Hirata⁵ finds an average between 0°C and 3500°C of $\alpha_c = 40 \times 10^{-6}$ (the temperature range was very poorly defined in these experiments). The best results are due to Nelson and Riley⁶. The variation of α_c with temperature as observed by Nelson and Riley in the range of 0°-800°C seems to be consistent with a value of at least 40×10^{-6} for temperatures around 2000°C. The coefficient of thermal expansion in the *a*-direction is in general very small ($|\alpha_a| < 1.5 \times 10^{-6}$) as expected for a valence bonding; at low temperatures, it is negative and above 383°C becomes positive.

The polymeric nature of carbons and polycrystalline graphites is due to the large number of free carbon valencies available on the peripheries of crystalline planes. Many of these, finding counterparts, become bonded either directly to peripheries of other microcrystals or indirectly through the intermediary of carbon atoms still remaining in the form of an intercrystalline disorganized phase, these carbon atoms being bonded either by tetrahedral-type linkages or by fractional double bonds. Thus, a carbon solid is essentially a three

³ P. W. Bridgman, Proc. Am. Ac. Arts and Sci. **76**, 9 (1945).

⁴ I. Backhurst, Proc. Roy. Soc. (London) **102**, 340 (1922).

⁵ M. Hirata, Sc. Pap. Inst. of Phys. and Chem. Res. Tokyo **15**, 219 (1931).

⁶ J. B. Nelson and D. P. Riley, Proc. Phys. Soc. **57**, 477 (1945) and D. P. Riley, Proc. Phys. Soc. **57**, 486 (1945).

¹ Some of these results were presented at a meeting of the American Physical Society; see S. Mrozowski, Phys. Rev. **86**, 622 (1952).

² J. Basset, C. R. Ac. Sc. Paris **213**, 829 (1941).

dimensional network of crystallites held rigidly by a complicated system of criss-cross valence bonds which stabilize the structure to such an extent that parallel shifts of planes in crystallites can occur only under forces sufficient to break the peripheral C—C bonds. The valence bond once broken will not be restored if the temperature is not high enough for the peripheral carbon atoms to migrate into new positions compatible with the directional properties of carbon valencies and the new relative positions of the crystallite boundaries. Thus, carbons should fail by brittle fracture and no viscous creep is expected to occur for them up to temperature above 1700°C (where diamond structure begins to transform into a graphitic one, showing that some tetrahedral bonds are broken by temperature motion as a preliminary to this transformation). In fact, experiments performed at National Bureau of Standards and at North American Aviation⁷ have shown that viscous creep is detectable in polycrystalline graphites at temperatures not lower than 2000°C⁸. Furthermore, it has been found that diffusion of carbon atoms through the material is also negligible at temperatures below 1800°C⁹.

II. THERMAL EXPANSION, INTERNAL POROSITY AND FROZEN-IN STRESSES

A. Thermal Expansion

The great rigidity of the carbon structure in conjunction with the anisotropy of crystallites is responsible for three remarkable features of these materials—features

⁷ C. Malmstrom, R. Keen and L. Green, Jr., *J. App. Phys.* **22**, 593 (1951).

⁸ A slight permanent set observed when carbon rods or tubes are bent at room temperature is probably due to internal shifts (dislocations) of the material around microcracks and locking in the new position due to friction.

⁹ M. H. Feldman, M. V. Goeddel, G. J. Dienes and W. Gossen, *J. App. Phys.* **23**, 120 (1952).

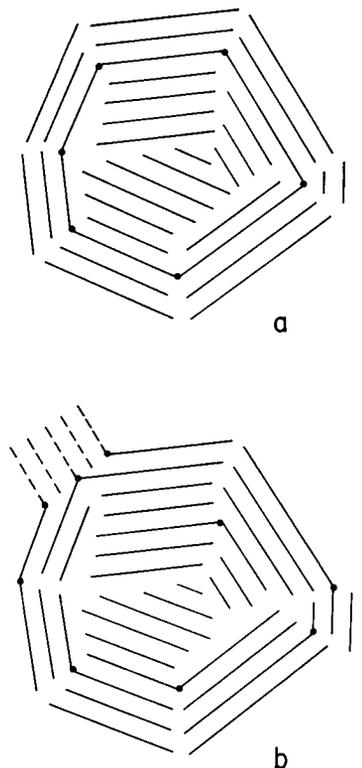


FIG. 1. Microcrystals of carbon linked by valence bonds. a) Closed ring arrangement. b) Random ring-like linkage.

which will be considered in succession. First is the exceptionally low thermal expansion and its wide variation and great structure sensitiveness. Fig. 1a shows a system of crystallites which are all bonded at the peripheries directly or indirectly through a disorganized phase (the single crystallites in Fig. 1 might represent whole groups of crystals as they appear in platelets, see further below). It is clear that such a unit as given in Fig. 1a would show an expansion in any direction equal to the expansion of a single crystal in the a -direction (α_a), that is, a contraction at lower and slight expansion at higher temperatures. Such a bonding as is assumed in Fig. 1a seems to be quite artificial and in Fig. 1b, a bonding distributed more at random is given. In this case, the unit will exhibit a slightly larger expansion in the plane of the

paper due to the contribution of the expansion in the c -direction but still an expansion α_a in the direction perpendicular to the paper. In actual materials, the system of crisscross bonding is tridimensional and the contribution of α_c will be felt in all three directions. Thus, for a particular direction, the expansion coefficient will be $\alpha = (1 - x)\alpha_a + x\alpha_c$ where x represents the fractional contribution of the α_c in the given direction. In fact, the values for α found for carbons and polycrystalline graphite at room temperature are known to be in the range 1 to 5×10^{-6} . Taking $\alpha_a = -1.5 \times 10^{-6}$ at 0°C , one finds $0.08 < x < 0.2$, which is considerably less than the value $\frac{1}{3}$ for x expected for a loose randomly arranged heap of crystals. The low value of x emphasizes the rigidity of the structure. Moreover, the contribution x is very strongly structure sensitive; an alignment of crystallites and a less random distribution of the intercrystalline bonds (Fig. 1a) will strongly affect the expansion coefficient in different directions. This great sensitivity is probably the reason that until now no sufficiently general direct correlation has been found between the value of thermal expansion coefficient and other physical properties of carbon.

B. Unavoidable Porosity

The second feature of the carbon structure at room temperature is the unavoidable presence of intercrystalline pores. The structure is formed by heat treatment at high temperature; even if at the highest heat treatment temperature the carbon material should happen to be perfectly dense, as it cools voids will be formed; crystals shrinking in the c -direction and rigidly held as in Fig. 1 will open voids in the center of the ring structures. The unavoidable formation of a porosity can be seen directly from the difference in bulk contraction of a single crystal and of the polycrystalline material, and its magnitude can be easily

estimated. For a carbon with a low thermal expansion coefficient of about 2×10^{-6} at room temperature, assuming an average expansion coefficient between the limits from 0°C to 2500°C equal to 3×10^{-6} (the expansion coefficient is known to increase with temperature¹⁰ but studies were made only up to 1000°C ; by assuming a double value for 2500°C the increase is probably overestimated), one gets an average bulk expansion of 9×10^{-6} . On the other hand, the bulk expansion for a single crystallite in the same limits is $2\alpha_a + \alpha_c = 2 \times 10^{-6} + 35 \times 10^{-6} = 37 \times 10^{-6}$ (35×10^{-6} is the average between 27×10^{-6} for 0°C and about 43×10^{-6} for 2500°C). Thus the difference of the two bulk expansions is equal to 28×10^{-6} per $^\circ\text{C}$; for such a carbon heat treated to 3000°C and cooled to room temperature, this will lead to 8.4% porosity and for a carbon treated to 2500°C to 7%. The density of a graphite crystal being 2.26, the density of a polycrystalline graphite will be therefore at room temperature 2.08 for a 3000°C heat treatment and 2.11 for 2500°C treatment.

One can see, therefore that for a given carbon with a definite type of random structure there exists a limit for the density which will be impossible to surpass unless a new process for preparation of the polycrystalline material is found which proceeds wholly at lower temperature¹¹. These remarks vindicate to some extent the slow progress of the technology towards development of carbons with higher densities,

¹⁰ P. Hidnert, J. Res. Nat. Bur. Standards **13**, 37 (1934).

¹¹ P. W. Bridgman, J. Chem. Phys. **15**, 92 (1947), has obtained a dense material (2.25) from polycrystalline graphite of density 1.9 by applying a very high pressure at a temperature of about 2500°C . Evidently a considerable amount of plastic flow has occurred in this process which led to an alignment of crystallites with the c -axis parallel to the main direction of the compression and in consequence practically no pores were formed in the cooling process.

showing that the industrial processes leading to densities of 1.7 and in exceptional cases up to 1.9 are not so far off from the theoretical limit as it is generally believed. When a carbon with a low expansion coefficient is required, one selects automatically a material for which a theoretical density limit is lower, thus the two requirements are essentially contradictory. If, until now, simultaneous advancement in both directions was possible, this was due to the fact that carbons as made have densities still way below the theoretical limit and advancement is made by decreasing the regular porosity but making this more difficult by selecting materials with a lower maximum density limit. By regular porosity is meant here the porosity which remains at the highest heat-treatment temperature and which consequently could be eliminated by some manufacturing operation. This regular porosity is responsible for the apparent disagreement of the results of our density calculations with common experience. It is known that a polycrystalline graphite heat treated to 3000°C is slightly denser than the one heat treated to 2500°C, but this is due to the permanent shrinkage of the whole solid piece at the expense of the regular porosity, this effect over-balancing the effect of the increase in unavoidable microscopic porosity.

C. Frozen-in Stresses

The third feature of the carbon structures, closely related to the other two, is the unavoidable presence of large frozen-in stresses in the material. If one considers the groups of microcrystallites hooked together in Fig. 1, it is clear that in the case a) of a closed ring of hooked-together planes, no stresses will be created; on the contrary, in case b) a gradual deformation of the shape of the open ring will occur, thus creating angular and shearing stresses located at the joints. Furthermore, large compressional and tensile stresses are

created in carbons. This is well evident especially when the hooking of microcrystals in three dimensions is considered but it can be seen also in Fig. 1b to occur for a microcrystal hooked on the side to the main ring (dashed lines). The largest stresses will be created when the hooked edge of the microcrystallites is not perpendicular to the *c*-axis of both crystals (twisted hooking). Considerable stresses caused by the anisotropy of thermal contraction of single crystals are known to exist in polycrystalline metallic materials¹². However, in metals the anisotropy is very small in comparison not only to the anisotropy of a single crystallite of graphite, but even to the anisotropy of regions containing large numbers of partly oriented microcrystallites of carbon. Furthermore, stresses created in metals by the anisotropic contraction are partly relieved by a viscous flow of the grain boundaries during the cooling process. In carbons, as pointed out before, viscous creep is present only at very high temperatures; as a result, stresses will be relieved by creep in cooling, but only as long as the creep relief is fast enough in comparison to the speed of the cooling process (above what is here-in called the freezing temperature range). Under laboratory and industrial conditions, this will be true above 2300°C–2500°C. Below this range no relief mechanism will be operating, consequently stresses built up in the cooling process from this temperature range down will remain locked in the material and can be only released by heating the material again. The existence of these frozen-in stresses reoccurring reversibly at each cooling and disappearing in heating is responsible for the peculiar temperature dependence of the mechanical strength as is observed for carbons^{7, 13}. Essentially, the short-time ten-

¹² F. P. Bowden, Symposium on Internal Stresses in Metals, Institute of Metals, London (1948).

¹³ L. Green, Jr., J. Appl. Mech. **20**, 283 (1953).

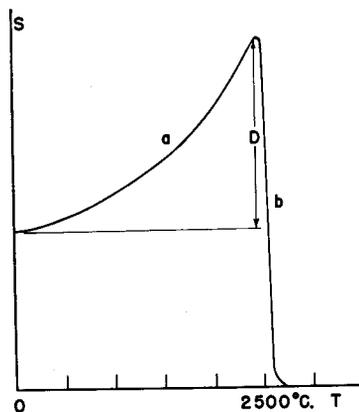


FIG. 2. Variation of mechanical strength S with temperature T for polycrystalline graphite (heat treated to above 2500°C). a) Frozen in stress range. b) Plastic failure range. D is the total decrease in strength from the relaxed state down to room temperature.

sile and compressive strength of these materials increases with temperature up to around 2500°C and after that quickly drops to zero (Fig. 2). The increase of strength with temperature is due to the gradual release of frozen-in stresses as explained above. The subsequent drop appears in the region where the viscous creep becomes so fast that the mechanical failure occurs not through a brittle fracture but through a plastic deformation.

Since the frozen-in stresses are proportional to the total contraction of the material from the freezing temperature down, the slope of the curve in Fig. 2 should be roughly proportional at each point to the value of the thermal expansion coefficient (more exactly to the local differences of coefficients in two directions). The experimentally-found drop D (Fig. 2) in mechanical strength is about 3000 lbs./inch^2 .⁷ In order to have such large frozen-in stresses in carbon material the local difference in average thermal expansion in two directions has to be about 2×10^{-6} per degree. This number is calculated from an elementary formula for the average stress¹⁴

¹⁴ This formula is derived by considering two rigidly connected rods of unit cross-sectional areas. When their temperature is changed by

$$P = (\alpha_1 - \alpha_2) \cdot \Delta T / (K_1 + K_2)$$

by taking $\Delta T = 2500^{\circ}\text{C}$ and putting, instead of the sum of compressibilities $K_1 + K_2$ an average $2\bar{K} = 2/E$, where E is the average modulus for a carbon ($E = 1.2 \times 10^6 \text{ lbs./inch}^2$). An anisotropy of this order is well known to exist in carbon materials as evidenced by the difference of coefficients parallel and perpendicular to the extrusion direction. The anisotropy calculated here, however, is not the one which is evidenced in the form of the external anisotropy of the large solid piece but is the part of the anisotropy of the relatively small regions of the material which is averaged out in the larger piece. The part of the anisotropy which, due to an alignment of the elementary small regions in viscous flow (extrusion or other processes), becomes observable in the large piece does not contribute to the formation of frozen-in stresses.

Actually the frozen-in stresses on the microcrystalline scale are much larger than those required for this explanation: taking the most exaggerated case of a perpendicular hooking of two graphite crystals one has $\alpha_c - \alpha_a = 35 \times 10^{-6}$ and $K_c = 45 \times 10^{13} \text{ cm}^2/\text{dyne}$, thus $P \cong 2 \times 10^5 \text{ lbs./inch}^2$, that is, tremendous stresses which are mainly sustained by the peripheral valence bonds. As a result, probably many of these bonds which have been established in the heat treatment at high temperature break under stress in the first cooling process.

As mentioned in the beginning, the polymeric nature of the carbon structure in conjunction with the great anisotropy of crystallites leads to the low values and large variety of thermal expansion coefficients for different carbons, to the existence of un-

ΔT , the differential expansion $(\alpha_1 - \alpha_2)\Delta T$ due to rigidity of the connection leads to elastic strains $K_1 P$ in one rod and $-K_2 P$ in the other. Since $P = 3000 \text{ lbs./in}^2$ is the average internal stress for a regular porous material, the value substituted for E has to be taken for the same kind of material, the two porosity factors cancelling each other in the formula.

avoidable internal pores, and to the existence of frozen-in stresses. It is clear that if there is any alignment of the crystallites (order) then this anisotropy will show up in the expansion coefficient and the distribution and shape of the voids and the distribution of frozen-in stresses as well. The interrelation between these physical quantities is, however, not simple and does not permit one to make general statements without more thorough analysis of the situation. For instance, Fig. 1a shows that the existence of large unavoidable porosity (low expansion coefficient) does not necessarily have to lead to the existence of large internal stresses. It is the character and the distribution of bonds which will determine this exact interrelation. Thus, although one would be tempted to make a sweeping statement that carbons having a lower bulk expansion should show a larger variation in the mechanical strength with temperature, this might not in general be true. The randomness of the crystalline growth, however, makes it probable that when looked upon statistically carbons with higher expansion coefficients should show less temperature variation in mechanical strength. No simple direct correlation of the mechanical strength for different carbons at room temperature with the type of their crystalline structure is to be expected, unless there should exist a general relation for all carbons between the strength in the relaxed state and the amount of frozen-in stresses. No experimental evidence as to the existence of such a relation is at present available, the whole problem being complicated in the case of manufactured carbons by the presence of porosity and structure introduced in the process of preparation of the materials (See Part III).

III. STRUCTURE OF COKES AND ITS FORMATION

A. *Soft and Hard Cokes*

Soft carbons are formed from organic materials which melt at heating and then

solidify at temperatures above 400°C. Polymeric solids thus formed are composed of organic molecules crosslinked in a complicated pattern. A great proportion of these molecules is made up of large condensed ring systems, the remaining part being organic molecules of different types interspersed between them and forming the so-called disorganized phase. At temperatures around and somewhat above 800°C, these substances having gradually lost most of the atoms other than carbon by evolution of gases, become calcined or baked carbons. At this stage, these carbons are composed of small turbostratic crystallites of about 30Å diameter, built of disordered stacks of parallel equidistant planes of condensed benzene rings, and of the disorganized carbon phase forming a matrix which surrounds these crystallites. The crystallites grow as the temperature is increased, mainly at the expense of the disorganized phase at first, and when this is exhausted (which happens around 1300°C, see below, discussion of Fig. 5) further growth continues at the expense of the smaller and less advantageously located crystallites. Around 2100°C carbon crystallites, having reached sizes of about 150Å in the *a*-direction, begin to change into crystallites of graphite by rotation and relative shifts of the benzene ring planes^{15, 16}. Further increase of heat treatment temperature results in a rapid growth of graphitic crystallites.

The so-called hard carbons form a broad class covering all the substances obtained from organic materials which do not melt at all (polymers) or which solidify at low temperatures. The early stabilization of the structure by intermolecular bonding hampers the condensation process, thus such carbons show a slower increase in size of carbon crystallites. They do lose, however, the light fractions in the same tem-

¹⁵ R. Franklin, Proc. Roy. Soc. (London) **209**, 196 (1951).

¹⁶ H. T. Pinnick, J. Chem. Phys. **20**, 657 (1952).

perature range as the soft carbons and become preponderantly carbon materials at above 800°C. The hard carbons form a wide variety of types starting from borderline cases more similar to soft cokes and ending with materials almost amorphous with glassy appearance.

There is a very distinctive characteristic of the soft cokes which makes it possible to differentiate them from any coke of a hard type. When cokes are ground to a size of the order of 1μ or smaller and investigated under an electron microscope, one finds that all soft cokes show a platelike structure¹⁷. Thus, on a microscopic scale soft cokes possess a very characteristic and regular structure which forms at the time the substance is solidifying: swarms of stacks of flat molecules or crystallites—all well packed into a thin layer. In hard cokes the structure has been set at the time when little motion was allowed to the molecules; subsequently the criss-cross bonding holding the latter ones rigidly in place did not create conditions under which such structure could develop. Consequently, hard cokes, when ground break up into jagged pieces without indications of any finer structure. Due to the random valence interlinkage more voids remain between disaligned molecules in hard carbons and as a result hard carbons have lower real densities (as determined by liquid immersion method).

It would seem that hard carbons possessing stiffer structures should exhibit lower thermal expansion. Franklin¹⁵ mentions one of the soft carbons (coking coal) investigated by her having a double expansion of that of a low rank coal coke (hard). This, however, is not in general true—the lowest expansions being found frequently for soft cokes; it might be that this phenomenon is associated with the presence of the needle structure (see Part III, C) in these cokes,

but this problem has not yet been studied in a systematic manner.

B. Mechanism of Crystalline Growth

The very gradual growth of crystallites when a carbon is heat-treated seems to be a process with an essentially different mechanism from the growth of crystallites as observed in other materials. The crystallite size appears to be primarily dependent on the highest temperature of heat treatment the carbon has been subjected to. For soft carbons below 1300°C the growth occurs by incorporation of the disorganized phase; above 1300°C at the expense of other crystallites. In both cases, it is hard to see why the growth does stop when a definite size is reached. As a result of a detailed discussion of this problem Franklin¹⁵ came to the conclusion that growth occurs by a displacement of whole layer planes; thus as the size of the planes increases higher temperatures are required to provide sufficient energy to displace them. It can be seen, however, that the temperature motion cannot be the only driving force in this process. If it would, the growth would practically stop at a given temperature when the Boltzmann factor $e^{-\Delta E/kT}$ becomes small enough (here ΔE is the activation energy for moving of the planes). In other words, ΔE would be proportional to the highest heat-treatment temperature; but the work of moving a plane is at least equal to the work of breaking the circumferential bonds holding the plane in position (total work proportional to the diameter of the planes d) plus the work against the Van der Waals attraction between neighboring planes (proportional to the square of the diameter d). Thus ΔE is proportional at least to the diameter d if not to a higher power of d ; consequently d could not increase faster than proportionally to heat treatment temperature T . The observed growth of turbostratic crystallites in carbon is considerably faster

¹⁷ E. A. Kmetko, This volume, page 21.

Expansion
1/2 - 2/3

than that. For instance, at 1000°C, $d \cong 30\text{\AA}$ and at 2100°C, $d \cong 150\text{\AA}$, the growth at higher temperatures becoming even faster.

It has been established by a series of experiments¹⁸ that the electric resistivity and the real density (as determined by an immersion method) of a baked (calcined) carbon does depend somewhat on the heating rate (markedly only for very high heating rates) but mainly on the highest temperature of the heat-treatment and time of soaking (holding time at maximum temperature). As the soaking time is increased, the resistivity decreases and the density increases. However, most of the change occurs in the first fifteen minutes of holding (the process occurs at a faster rate for higher temperatures). After that a very slow change is observed towards a limiting value. It seems then that there is a driving force present which by causing the crystallites to grow spends itself in the process. Evidently this must be the anisotropic expansion of carbon crystallites which leads to the creation of large local stresses, the stresses leading to and becoming relieved by the growth and rearrangement of crystallites. Thus, the main driving force is possibly due to the thermal stresses, naturally with an assistance from the energy of the thermal motion. If this is true, absence of such stresses should cut down considerably the rate of crystallite growth. Experiments were performed¹⁸ by grinding some of the calcined (1000°C) coke to a fine powder before heat treatment and the other part after heat treatment (to about 2100°C) to about the same particle size. Comparison of the two samples showed a considerably higher electrical resistance for the sample ground first but later heat-treated to the same temperature (2100°C). This has been repeated for a number of temperatures and

also done for a hard carbon with the same result (the oxygen layers formed in grinding were removed in all cases by additional heating to 1000°C). The particle size, being of the order of 1μ , could not impose a limitation on the crystallite growth; thus one might conclude that the reduction in size decreases the thermal stresses and by that affected the growth of crystallites. There are other features, however, which make this whole effect not so simple as described, and no definite conclusions can be drawn from these results without further investigation.

The partial release and unbalancing of frozen-in stresses by grinding might be responsible for shifts in relative positions of graphite layers and thus explain the increase in proportion of graphite II in the powdered material, as observed by Bacon¹⁹.

The graphitization process for hard carbons seems to be, at least in most cases, more complicated than for soft cokes. Franklin¹⁵ has found that although the bulk of a hard carbon resists graphitization up to quite high temperatures, small amounts ($\sim 2\%$) of other phases are present which graphitize as easily as soft cokes. This Franklin ascribes to the existence of sufficiently large thermal stresses in hard carbons which lead to local crystallization under high pressure. Recently Loebner²⁰ has shown that in a phenol-benzaldehyde resin coke, graphitization occurs in two distinct stages: around 1800–2100°C some 12% of the coke forms tall stacks of planes and it is only at about 2800°C that the rest of the material starts to graphitize rapidly. Too few studies have been made on hard carbons to permit more general conclusions. The case of the phenol-benzaldehyde coke seems to show, however, that the effect of local thermal stresses might be insufficient to explain the whole phenomenon.

¹⁸ S. Mrozowski and H. T. Pinnick, unpublished results.

¹⁹ G. E. Bacon, *Acta Cryst.* **3**, 320 (1950).

²⁰ E. E. Loebner, *Phys. Rev.*, April (1956).

C. Macrostructure of Soft Cokes and its Formation

The variety of appearance of soft cokes under casual observation is due to the type of macroscopic porosity (sizes from about 0.1 mm up) which in turn is a function of the conditions under which the coking has proceeded. When pitch is coked in a container, a dense shell is formed on the outside where the coking process is the fastest. Toward the center, the porosity which is

due to entrapped bubbles and open paths for escape of evolving gases, becomes quite considerable. The distribution in pore sizes is a function of the depth below the surface (pressure) and of the viscosity of the pitch at the setting conditions. Thus, it depends on the dimensions of the container and applied heating rate. There are great differences, however, also in the appearance of the dense parts of the coke itself. Some surfaces look under a low power microscope smooth and dense; others show streaks reminding one of a frozen-flow pattern. Two typical cases are seen in Fig. 3 which are photographs of polished surfaces. Cokes

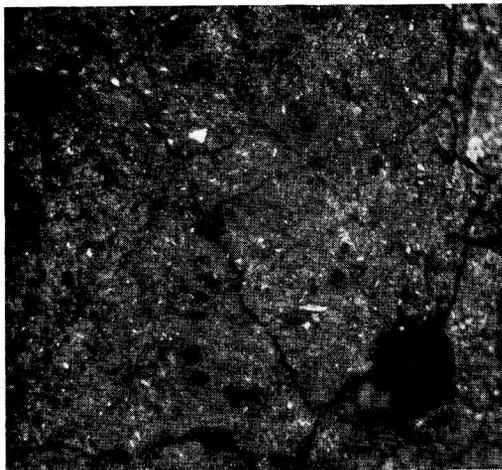


FIG. 3a

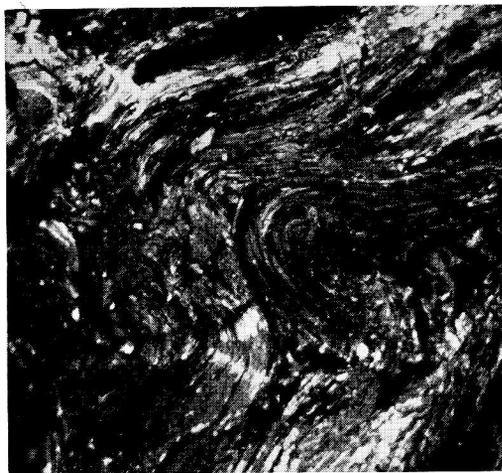


FIG. 3b

FIG. 3. Polished surfaces of calcined cokes. Magnification $\times 65$. a) Outside dense shell of Dominion Tar and Chemical Company pitch coke. b) Kendall petroleum coke.

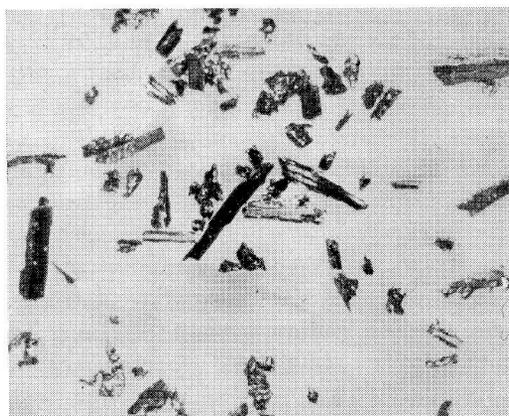


FIG. 4. Typical shapes of particles obtained by grinding a section of calcined Kendall coke with a strong needle structure. Magnification $\times 20$.

with a streaky appearance, when ground to a size of the order of 1 mm, break up into elongated pieces in which the streaks always run lengthwise (See Fig. 4). Evidently, the streaks are indications of a low mechanical strength along their direction which lead in grinding to these needle-like shapes of coke particles. When such a single needle is investigated by means of X-ray diffraction, it is found that the microcrystals of carbons are well aligned with planes parallel to the long axis of the needle. This alignment is similar to the

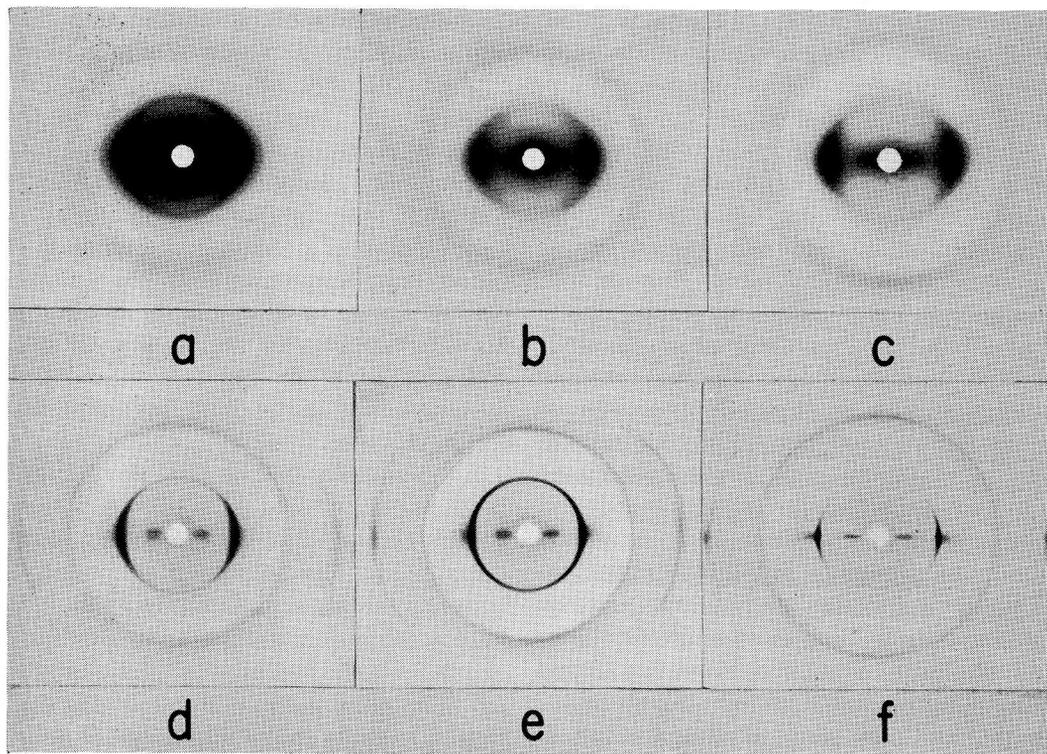


Fig. 5. X-ray diffraction patterns showing the alignment of carbon microcrystallites in needles of Kendall coke. The temperatures to which the cokes have been heat treated are the following: a) raw coke, b) 800°C, c) 1100°C, d) 1600°C, e) 2000°C, and f) 2800°C.

fiber-like alignment occurring in carbon filaments formed in the process of thermal cracking of organic vapors and investigated by Riley and his associates²¹. Franklin¹⁵ has found pieces which might have been needle-like structures (she considered it to be a plate-like arrangement) but by far not as perfect as they were found by the author to be present in such materials as the Kendall, Cleves, Lima or even Texas coke. Typical X-ray diffraction pictures for needles broken off from pieces of Kendall coke are given in Fig. 5. By looking at the (002) diffraction ring, it is evident that the alignment is already formed at the setting temperature and persists up to the highest heat treatments, gradually becoming even more and more ordered relative to the axis

²¹ J. Gibson, H. L. Riley and J. Taylor, *Nature* **154**, 544 (1944).

of the needle. By making a series of pictures for different positions of a needle rotated around its axis, one can show that crystallites are not all parallel to each other in a needle, but are arranged with normals to the planes distributed in all directions, approximately around a plane perpendicular to the axis of a needle. Only in a few exceptional cases an intensity difference between the two (002) diffraction spots has been noticed. Thus the arrangement of crystallites might, in some cases, be platelet-like (parallel platelets in a larger platelet) and in others might possibly look, when viewed along the direction of the axis of the needle, similar to the schematic drawing in Fig. 1 (since as Kmetko's work¹⁷ has shown, the soft cokes are composed of platelets, these are really the whole platelets and not single microcrystallites which are arranged

in the manner of Fig. 1). All possible intermediate cases should be, however, the most frequent in the needles. The intensity distribution in all other diffraction rings for the cokes is compatible with the assumed distribution of crystallite positions in needles.

For the raw Kendall coke the (002) ring appears to be quite sharp, showing the presence of large stacks of parallel molecules. This highly ordered arrangement is to a great extent destroyed in the process of evolution of gases and shrinkage of the material, the (002) ring becoming quite diffuse. It is only at much higher heat treatments that larger stacks of aromatic planes (turbostratic crystallites) are formed and the ring regains and then surpasses its original sharpness. The continuous isotropic low-angle scattering which is due to the disorganized phase and is visible around and close to the shade of the absorbing center pin disappears at temperatures of heat treatment around 1300°C. Some kind of non-isotropic continuous scattering (bow-tie-like pattern) persists, however, up to graphitization and indicates probably an existence of small plate-like voids between not exactly parallel microcrystals. The bow-

tie pattern does not extend to very low diffraction angles; also its abrupt termination on the high angle side is quite remarkable. On the high angle side of the (002) diffraction spots an additional continuum with structure is observed. In order to ascertain if these features are characteristic of polycrystalline graphite in general platelets broken off from highly purified (as pure as can be made) ceylon graphite lumps were investigated. Fig. 6 shows that the bow-like pattern and high angle extension of the (002) line are present also in this case.

A visual examination of ground soft cokes has shown that in almost all of them needles can be found (as checked by X-ray diffraction). The frequency of occurrence varies, however, in wide limits some cokes have a preponderantly needle structure and in some others hundreds of particles have to be inspected before a needle is identified. One can ask what the conditions are which lead to formation of such needle structures. It seems as if the presence of more advanced condensation of molecules is necessary. Needles are formed if large amounts of pitch are coked; they can not be found if coking was done fast using a small quantity of pitch. Therefore, one suspects that the presence of higher pressures driving the gas bubbles through the stiffening fluid mass creates a viscous flow in the fluid which in turn leads to an alignment of the large flat aromatic molecules with surfaces parallel to the direction of flow. Telescopic flow will lead to an alignment similar to Fig. 1 (fibers). The flow pattern becomes frozen-in as the fluid mass sets. When fine solid particles are present, the flow pattern becomes disturbed and in the average over volumes larger than these particles no preferential molecular alignment is detectable. In microscopic regions, however, the alignment will still be present, thus leading in all cases to plate-like structures.

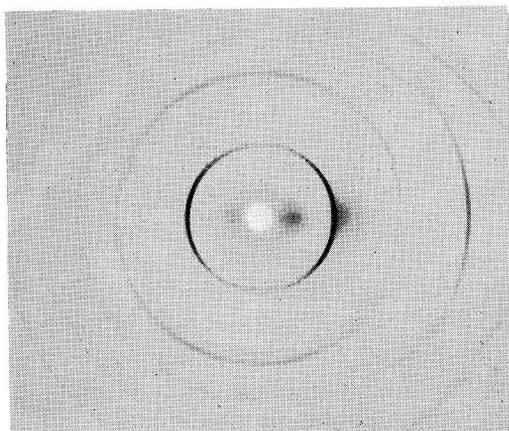


FIG. 6. X-ray diffraction pattern of a purified Ceylon graphite flake. Note the presence of the bow-tie like scattering similar to the one in cokes (Fig. 5).

IV. MECHANICAL STRENGTH OF MANUFACTURED MATERIALS

Until now, we have considered the mechanical properties and structure of the dense parts of the cokes, that is, carbons which are as dense as can be made directly by carbonization of organic materials. Cokes have a macroscopic porosity, however, which makes them mechanically very weak and unsuitable for applications. Thus, in the manufacture of carbons, cokes are ground to such sizes that most of the macro-porosity is gone, binder in the form of a pitch is added, the mix compressed or extruded and then the so-called green carbon put through a baking or further also through a graphitizing heat-treatment cycle. By grinding the coke to a definite range of sizes, such carbons are made with a controlled macroscopic porosity, thus a high macroscopic uniformity of the material is achieved. For such materials with a uniform density of coke particles bound together into a solid piece by bridges formed by the binder coked between the particles, interesting quantitative relations can be derived for the dependence of different physical properties on the density of particles (compression factor) and amount of binder coke. The relations are well supported by experiments²². It might be of interest to mention here that the empirically established linear relation between mechanical strength and density for different parts of a larger piece of carbon material⁷ turns out to be a special case of the application of these formulas. In interpreting the results of any experiments with artificial carbon materials, however, one has to take into consideration in addition the microscopic structure of the component substances used in the process and the changes brought about in the course of manufacture.

In the process of extrusion (or molding) a preferential alignment of the coke particles

takes place relative to a certain direction, the degree of which depends on the amount of binder present (also its viscosity, driving pressure etc.). The result will depend on the size of the particles used; if the particles are large, they are about isotropic, small particles will have needle structure and very fine dust (fine flour) a platelet structure (by particles, it will be meant particles and flour). There is no reason to expect that the binder will set (carbonize) with crystals having any preferential arrangement; at the setting temperature in the baking process, there are no ordering forces, except in the very thin layers adjacent to the surface of the particle where the crystallization might be affected by the alignment in the substrate. Thus, a substance is obtained which is composed of aligned particles with carbon crystallites aligned in them but coated and bound together by bridges of binder coke which does not have aligned microcrystals. The resulting anisotropy of physical properties of the material is commonly but incorrectly explained as being due to the alignment of crystallites. In fact, the anisotropy is due to two causes, one of which is the crystallite alignment in the particles and the other is of a purely geometrical nature. For instance, grinding a perfectly isotropic coke (for instance, one of the hard cokes) will lead to particles of a variety of shapes (random). In the extrusion, however, all these particles will align with their longer axes parallel to the direction of the extrusion. Consequently, in the finished product an anisotropy will be created which is due to the relative frequency of binder bridges per unit path in different directions (Fig. 7). The relative contributions of the two causes depend on the type of physical property which is investigated. In case of mechanical failure, which as will be shown below, occurs mainly through the binder coke, the anisotropy is probably purely of the geometric origin.

²² S. Mrozowski, This volume, page 195.

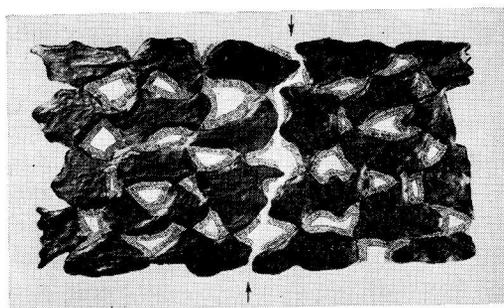


FIG. 7. Anisotropy of an extruded carbon caused by a purely geometrical effect (alignment of isotropic particles). Arrows indicate the line along which a mechanical failure might probably occur.

It is well known that raw cokes shrink very much when heat treated to or above 900°C ; some of them show a linear shrinkage as large as 15%. Particles which are coated with binder usually have been calcined to temperatures in excess of 1000°C —thus in baking above the setting temperature of the binder a situation is created in which the shrinking binder layer can decrease its volume only by way of opening cracks perpendicular to the surface of the particle. The stresses developed during the shrinking of the binder are very large and there can be no doubt that such cracks are formed. We have not been able to get electron micrographs of such surfaces yet, but arrays of cracks on the average $\frac{1}{2}\mu$ apart of a similar origin are observed on the surfaces of dense pieces of coke. Not all stresses are relieved by the formation of cracks; those which are left might relax in the process of graphitization. However, in cooling, new frozen-in stresses will be developed (in addition to the ones discussed on page 37) which are due to the thermal contraction of the binder coke being different from the anisotropic contraction of the particles. Thus, the binder coke even if made from the same original organic material as the particles will therefore be in an essentially different state: material full of cracks with high stress concentrations.

When a mechanical failure occurs, the break goes through the binder bridges (see arrows in Fig. 7) not only because this is the path of a minimum cross section but because the material is the weakest there. It is easy to see under a magnifying glass the needles protruding from a surface of a broken piece and the corresponding pits in the complementary surface. The surface of fracture has, therefore, always an appearance as if brittle fracture occurred, even if at high temperatures the failure is of a plastic nature; the volume of material which fails (binder coke) is very small in comparison to the total volume of the carbon and the possible change in structure brought about by the plastic deformation would be difficult to detect. Since the failure occurs through the binder and the frozen-in stresses there are due to the thermal contraction of the binder in the first place (and of the differential contraction of binder coke and particles in the second), the shape of the curve Fig. 2 for artificial carbons might not be in any simple relation to the thermal expansion of the carbon article as a whole. It should also be realized that creep as observed in experiments at high temperature is due mainly to deformation of bridges—thus the rate of the real creep in the carbon material is much larger than measured as an average for the whole piece. Due to this localization of the creeping area the third region of creep is likely to escape observation.

Two other effects of major importance which are due to the addition of the fluid binder to the solid carbon particles should be mentioned here. It is a common experience that as the duration of mixing is lengthened, the stiffness of the mix increases. Partly, this is due to an advancing polymerization of the binder, but is also connected with the gradual soaking up of particles with the lighter fraction from the binder. We have found in the case of a hard coke that under certain conditions

the presence of the light fraction which penetrated the particles disturbed the crystallite growth so much that when graphitized it resulted in a change in structure which was easily seen on X-ray diffraction photographs. Thus, one has to keep in mind that the structure of the heat-treated particles when soaked with binder might not be the same as that of the directly heat-treated coke.

The second effect to be considered is the compatibility of the binder coke with particles. If both cokes are essentially of a different type (hard-soft) a very poor bond might be established due to the inability of the microcrystallites to grow across the surface of the contact. As a result, a failure will occur not through the binder, but between the binder and the particles. We have found that binders which give a great strength when used with a coke of the same origin lead to relatively weaker pieces when

combined with a coke of an essentially different structure²². A quite striking example, however, of the absence of growth of microcrystals across the surfaces is met in the case of thermal carbon blacks which, surrounded by the binder, retain their individuality up to graphitization¹⁷.

The number of factors to be considered in order to understand the relation of the mechanical strength of carbon materials to their structure is very large. A great caution is required in interpreting results of experiments. It was tried in this paper to bring into the discussion most of the important ones, but it seems that with such a fragmentary knowledge of carbons as one has today, a number of them is possibly being overlooked. Future experiments must establish the extent to which each of these factors, acting in combination with the others influences the properties of the final material.