

DIMENSIONAL CHANGES DURING HEAT TREATMENT AND THERMAL EXPANSION OF POLYCRYSTALLINE CARBONS AND GRAPHITE*

F. M. COLLINS†

Department of Physics, University of Buffalo, Buffalo, New York

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Measurements of irreversible changes of length during heat treatment of carbon from 1100°C–2800°C, and of the thermal expansion of the resultant graphite were made on rods within a furnace using two externally mounted short range telescopes. Extruded carbon rods made from Texas coke, Kendall coke, and a hard coke were investigated. A number of rods were prepared from each coke calcined to different temperatures. The dependence of both the changes of length during heat treatment and of the thermal expansion upon the coke calcination temperature and particle size were studied. Data concerning the influence of impregnation on the thermal expansion of rods made from Kendall coke were obtained.

I. INTRODUCTION

An interesting property of polycrystalline carbon which is not well understood is its thermal expansion. The volume thermal expansion of the polycrystalline substance is not only smaller than that of the single crystals of which it is composed, but varies greatly from one type of carbon to another.

The expansion coefficients for a single crystal of graphite as calculated from X-ray diffraction studies are, at room temperature, $- .5 \times 10^{-6}$ per °C in a direction within the graphite plane, and 28×10^{-6} normal to the plane, that is, about 27×10^{-6} for the volume coefficient¹. The volume expansion coefficients of polycrystalline carbons, however, are seldom reported larger than 18.5×10^{-6} ² and were found in some cases as low as 10×10^{-6} per °C.

The ultimate aim of this investigation is to discover the factors which are responsible for this wide variation in the thermal ex-

pansion among polycrystalline carbons. The resulting knowledge should prove useful for the production of carbons with definite properties and in their use as structural materials, and, in conjunction with the results of other experiments, should be valuable in identifying the structural characteristics of artificial carbons and graphites. To acquire this information, a systematic, controlled variation of the procedures used in fabricating carbon is necessary, together with studies of the resulting differences in the thermal expansion of the products. In this report results of some preliminary experiments are described, the experiments being designed to establish which stages of the manufacturing processes are most critical in this respect, and exactly how the variation of these procedures and heat treatments affect the thermal expansion of the product.

In order to determine the thermal expansion for all temperatures up to 2800°C, it is convenient to measure expansion in low- and high-temperature ranges with separate instruments. Only data in the high-temperature range have been taken until now. Using the high-temperature equipment (800°C–2800°C), it is possible to measure

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† Speer Carbon Company Fellow, 1955–1956.

¹ J. B. Nelson and D. P. Riley, Proc. Phys. Soc. **57**, 477 (1945).

² P. Hidnert, Journ. Res. Nat. B. Stand. **13**, 37 (1934).

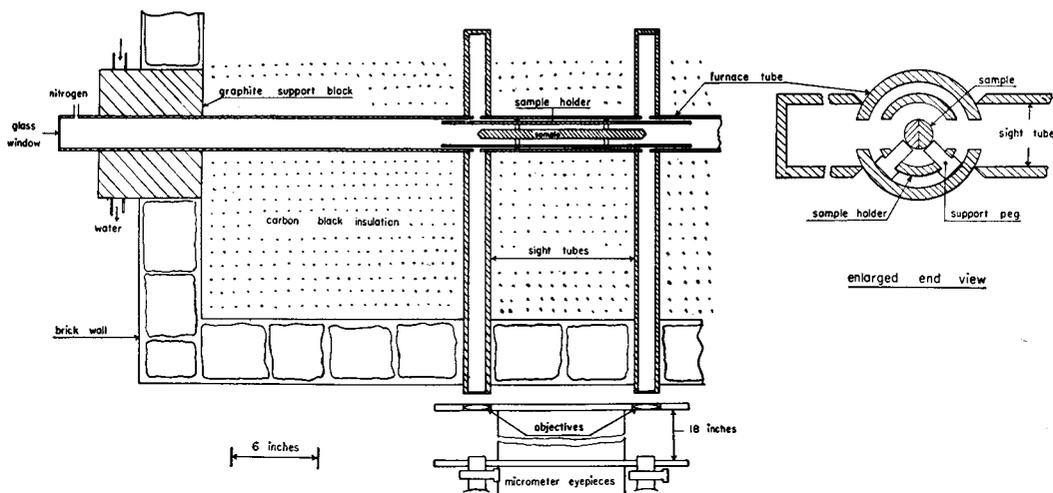


FIG. 1. Schematic diagram showing the arrangement of the furnace sample holder and telescopes.

not only the thermal expansion of graphites, but also the very interesting irreversible changes of length of carbon rods caused by the transformation of carbon to graphite during the heat treatment.

II. EXPERIMENTAL

A. High Temperature Measuring Apparatus

The positions of the ends of a sample rod within the furnace were determined using two rigidly connected telescopes equipped with micrometer eyepieces. The positions were recorded for different temperatures of the furnace, the temperature being determined with an optical pyrometer. A diagram of the equipment is given in Fig. 1.

The furnace consisted of an electrically heated, six-foot-long, $1\frac{1}{2}$ "-inside-diameter graphite tube mounted across a brick enclosure filled with carbon black for insulation. Current was supplied through large watercooled graphite blocks supporting the furnace tube at its ends. An atmosphere of nitrogen gas was maintained in the tube to prevent oxidation of samples.

Two parallel carbon sight tubes extended through the brick side-wall from and at right angles to the furnace tube. Another

pair of tubes with closed ends extended from the opposite side of the furnace tube to a cooler part of the furnace. The ends of the luminous sample rod mounted within the furnace tube were viewed through the sight tubes against a dark background provided by the second pair of tubes.

The telescopic objectives were fastened to a bar of steel which was placed at a distance of 18" from the sample; eyepieces were fastened to a second bar, and both of these were in turn secured to a single piece of brass which was mounted on a heavy frame. The telescopes produced a magnification equivalent to .0048 mms of the sample/micrometer scale unit. Readings could be reproduced to better than ± 2 scale units, or approximately $\pm .01$ mm, which is about 1% of the total length change for the twelve-inch-long sample heated from 1000°C to 2500°C.

Measurements with such an arrangement are primarily limited to temperatures at which the sample is luminous. However, using artificial illumination of the ends of the sample, measurements were made in some cases at or near room temperature, permitting an estimate of the average thermal expansion coefficient for the range

0°C–1000°C, but unfortunately with somewhat lower accuracy than for the coefficient in the range 1000°C. to 2500°C.

The sample rod was held concentric with the furnace tube in a device consisting of a smaller graphite tube having four radially directed graphite legs which also protruded into its interior. The sample was held in position by these legs; the surrounding tube fitted with appropriate observation holes acted as a thermal shield. The optical pyrometer was sighted on one of the legs from the end of the furnace tube. It was necessary to do that since there was a parabolic temperature distribution along the furnace tube at equilibrium and as a result there also was a temperature difference of about 50° between the center and the ends of the sample. The supporting pegs were located about halfway between the center and the end of the sample and their temperature represented quite closely the average temperature of the whole sample. The presence of the temperature gradient decreases the reliability of absolute values of expansion obtained but does not impair the comparison of the behavior of different carbons, which is of more direct interest at the present stage of investigation.

B. Preparation of Samples

The samples were $\frac{1}{2}$ "-diameter extruded rods prepared in the laboratory. The basic materials used were two types of petroleum soft cokes, Texas and Kendall, as designated by the type of crude oil from which they were made. The Texas coke was mixed with medium grade coal tar pitch as binder, and the Kendall coke with Portland Gas Company binder. In addition to these two soft cokes, a hard coke was made from a phenolbenzaldehyde resin and was mixed with the same resin as the binder.

The commercial soft cokes as received were raw, that is, heated in processing to only about 500°C. Different batches were

first heat treated or "calcined" to a number of higher temperatures before using, a process which results in both removal of most volatiles, and an increase in the real density of the coke. The calcination temperature of the coke, the maximum heat treatment the coke received before processing, is an experimental parameter which will hereafter be designated by the abbreviation C.T. After calcination, the coke was pulverized in a series of grinding operations and sorted into sizes by sieving.

The coke was mixed with binder for 45 minutes at a temperature at which the binder was fluid and the pliable mixture obtained extruded under pressure through a $\frac{1}{2}$ " die at a somewhat lower temperature. The same die was used in making all the samples used in this study but the electrical heating element was arranged differently in the early work, probably resulting in a slightly different temperature distribution along the die. This is mentioned here since it might be that the carbon structure is in some way affected by this distribution.

After extrusion, the so-called green rods were packed in a crucible with a sand-coke mixture and baked to 1100°C by slowly increasing the temperature in a three-day period. Following the baking the coked binder comprised about 15% of the rod's weight.

III. RESULTS

Data are first presented concerning the dependence of the longitudinal thermal expansion and length changes during heat treatment on a) variation of the coke calcination temperature, b) variation of the coke particle size, and c) impregnation of the rods with additional pitch. Later, the results of some preliminary measurements performed to determine the anisotropy of some of the Kendall coke graphite samples and also studies of their X-ray diffraction patterns are reported.

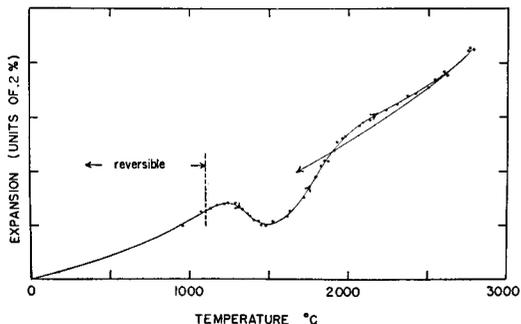


FIG. 2. Longitudinal dilatation of an extruded baked Kendall coke 1100 C.T. carbon rod as a function of the temperature during initial heat treatment, with all experimental points indicated.

A. Longitudinal Thermal Expansion of Graphites and Changes of Length During Heat Treatment

1. Illustrative Curve

Following baking, the rods were inserted into the high temperature furnace described previously, and heat treated (graphitized) to 2800°C. The type of results obtained on an individual samples are presented in Fig. 2. The relative expansion (increase in length over total length at 0°C) is plotted against the (successively larger) temperature of the sample. The curve can be divided into several distinctively different parts. The first part is a reversible expansion up to 1100°C, the maximum temperature to which the carbon was heated in baking. The crystallite structure of carbon changes continuously and irreversibly during its original heat treatment, but does not change during subsequent cooling or heating, being determined only by the maximum temperature to which the carbon was, originally or at any later time, heat treated. In heating the sample above 1100°C, the crystallites resume their "growth" and the rod starts again to exhibit irreversible changes in its dimensions. A shrinkage takes place from 1100°C up to about 1600°C, followed by a rapid increase in length in the range around 1850°C or in what is known as the puffing range, and

finally a less rapid increase in length or even a slight contraction occurs in the graphitization range 2000°C–2500°C. Such a curve as in Fig. 2 is representative of irreversible changes in structure, and therefore is not retraced when the sample is cooled from any temperature greater than 1100°C. When cooled, the sample contracts smoothly and reversibly, with a definite thermal expansion coefficient characteristic of its new crystallite structure, which was formed at the highest temperature reached by the sample. In this work samples were heat treated to either 2700°C or 2800°C and the variation of length of the rods was observed during the heating cycle (heat treatment curve) and on subsequent cooling. The thermal expansion coefficients reported in this paper were obtained from the smooth cooling curves by taking the average expansion in the ranges 0°–1000° and 1000°–2500°C.

2. Influence of the Temperature of Calcination of the Coke

a. *Kendall coke.* Batches of samples were made using Kendall coke calcined to different temperatures. Rods were made with 38 parts by weight of Portland Gas Company pitch as binder and a weight of coke such that it would amount to 100 parts after heat treatment to 1100°C. This means that proportionately larger quantities of the coke calcined to lower temperatures were used to compensate for their greater weight loss during baking to 1100°C, so that the final carbon would have identical ratios of binder coke to particle coke in every case. The heat treatment curves for these samples are shown in Fig. 3a where the origin for each curve has been arbitrarily shifted in the upward direction to avoid overlappings and crossing of the curves. The curves in Fig. 3a show that the shrinkage in the 1100–1600° range during heat treatment is strongly dependent on the C.T.; the lower the C.T. of the rod, the greater the shrinkage of the rod in this range. This is very

Apparently due to shape of particles in rods being a function of their C.T. Higher Temp. \rightarrow orientation of particles.

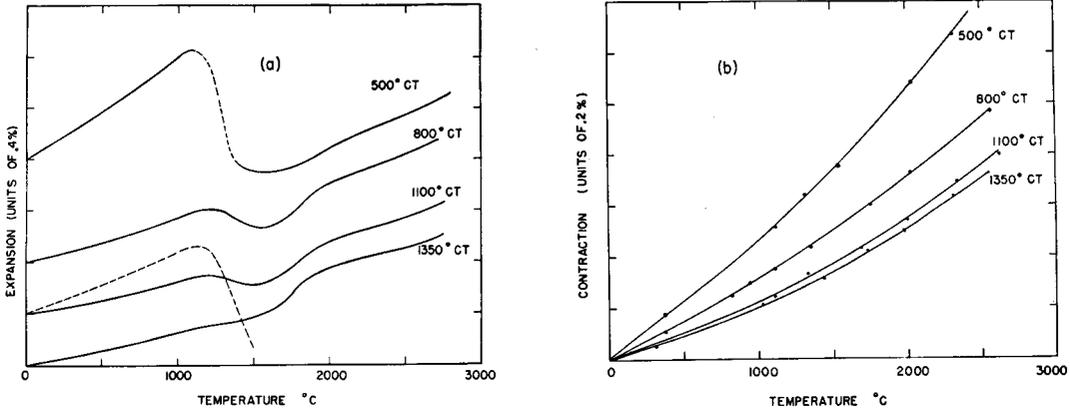


FIG. 3. Longitudinal dilation of Kendall coke carbon rod a) during heat treatment and b) during cooling. C.T. is the coke calcination temperature. Dotted curve in graph a represents the dilation in the transverse direction.

remarkable in view of the fact that at 1100°C all the samples with the exception of the 1350 C.T. rod consisted of identical relative amounts of originally the same materials, all of which had been heat treated to just 1100°C, with the only difference that the operations of grinding and mixing with binder were performed at different stages of calcination of the coke. The dotted line is a partially incomplete heat-treatment curve for the C.T. 1100°C carbon in the transverse direction, which was obtained with a sample prepared in a way to be described later.

Changes of length occurring in cooling for the same samples of Kendall coke rods are presented in Fig. 3b. The values of the longitudinal thermal expansion for the baked rods before and after graphitization are plotted in Fig. 7, where data obtained for other cokes are also included. The expansion coefficient also is seen to be markedly dependent on the C.T. of the rod, being larger for a lower C.T. In going from the baked to graphitic state the coefficient seems to decrease slightly in each case, a quantitative comparison not being warranted in view of the lower accuracy in the range 0-1000°C.

In order to give a more complete picture

of the physical characteristics of these rods, the values of their room-temperature diameters and apparent densities after various heat treatments are plotted in Figs. 4a and 4b. Although the temperature of the die during extrusion was kept the same in preparation of all these samples, the diameters of the rods (4a) differ for different C.T. even in the green (or unbaked) state, showing that the coke particles calcined to higher temperatures have greater elasticity. Also, one can see from the decrease in diameter of the 1100 and 1350 C.T. samples during baking that a contraction of the whole structure occurs which is due to the shrinkage of the binder coke alone. (The coke particles in the raw and 800 C.T. samples are also shrinking).

The rods lose weight with every heat treatment because of removal of volatiles and also due to a small amount of oxidation which takes place at each heating, which produces a small but, with each heat treatment, progressively larger deviation of the measured densities shown in Fig. 4b from the correct values for unoxidized material. The real density of the ground coke as found by an immersion technique after the various heat treatments is also given there. Since the real coke density

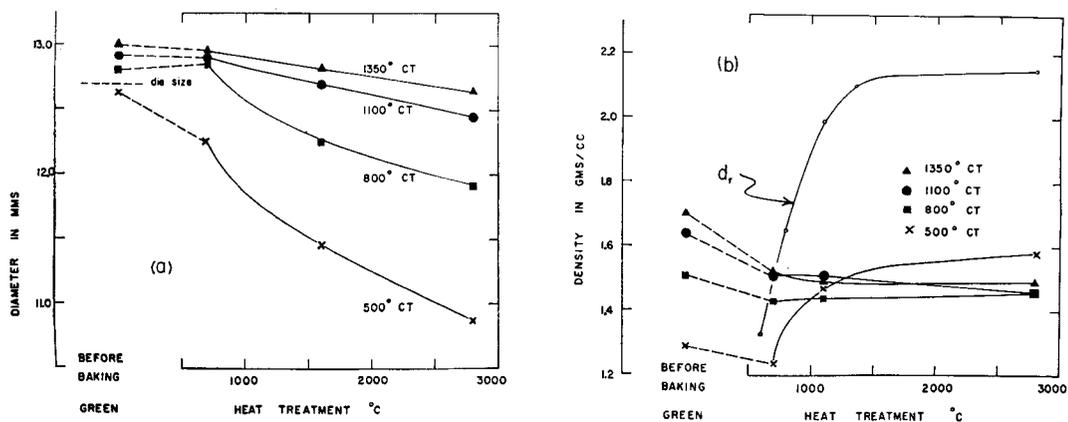


FIG. 4. Changes in a) diameter and b) in apparent density as a function of maximum heat treatment temperature for Kendall coke carbon rods of different C.T. as measured at room temperature. A curve giving the real density d_r of Kendall coke is included in graph b.

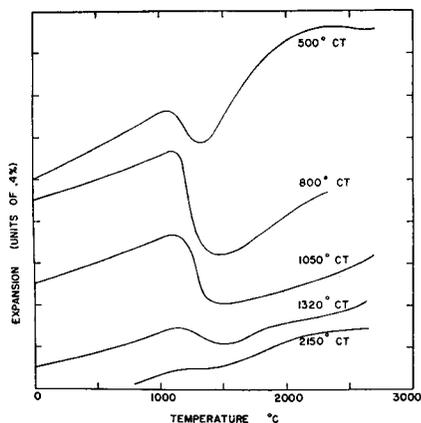


FIG. 5. Longitudinal dilation during heat treatment of Texas coke carbon rods with different C.T.

increases with heat treatment much faster than the apparent densities of the rods, it is clear that a greater porosity results from higher heat treatment of these materials.

b. Texas coke. A series of rods was made from through-200-mesh Texas coke calcined to 2150°C, 1320°C, 1050°C, 800°C and raw, using 45 parts by weight coal tar pitch per quantity of coke which will reduce to 100 parts after heat treatment to 1100°C. The changes of length of these rods during heat treatment are plotted in Fig. 5 (again the curves being shifted in an upward direction) and the values of the

average expansion coefficients after baking and after graphitization are given in Fig. 7. With the exception of the raw coke rod this group qualitatively resembles the Kendall coke series in its dependence on C.T. of both the shrinkage in the 1100°C–1600°C region, and of the expansion coefficients. For each definite C.T. however, the amount of shrinkage and the expansion coefficients of the Texas coke rods are considerably greater than the corresponding values for the Kendall coke rods. The Texas raw coke rods behave anomalously; this was confirmed by running a second sample of this type. During heat treatment they show little shrinkage but an excessive puffing, and consequently in the range 1100–1600°C the minimum occurs at a lower temperature than it does in the other Texas samples. From Fig. 7 it is apparent also that the expansion coefficient decreases far more during heat treatment (~25%) than those of samples of higher calcination temperature.

c. Phenol-benzaldehyde coke. Two rods were made from phenol-benzaldehyde resin coked to 400°C and 1100°C respectively. 50 parts 65/100-mesh and 50 parts 150/200-mesh particle sizes of this coke were mixed with an amount of binder equivalent to 45

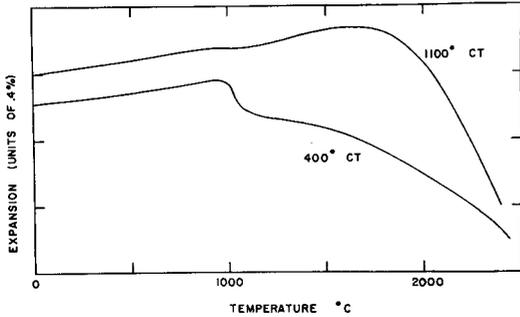


FIG. 6. Longitudinal dilation during heat treatment of two phenol-benzaldehyde resin carbon rods with different C.T.

parts per 100 parts coke heat treated to 1100°C, using as binder the same resin from which the coke was made. The changes of length of the rods using heat treatment given in Fig. 6 show a contraction throughout the whole heating range for the 400 C.T. sample, whereas the 1100°C C.T. sample shows no contraction below 2000°C but a much faster one above 2000°C. This is a striking difference in behavior; it should be again recalled that both these samples were made from the same materials and differ only in the sequence of the heat treatment of the coke to 1100°C and combining it with the binder.

The hard coke rods are the only ones for which an appreciable shrinkage was found

at temperatures beyond 2000°C. As can be seen from Fig. 7, the expansion coefficients of the hard coke rods after baking to 1100°C were both exceedingly low (1.7×10^{-6}) in comparison to those for soft cokes, and independent of the C.T. However, after heat treatment to 2700°C, the thermal expansion of both PB rods became much greater (5.3×10^{-6}), a behavior opposite to soft cokes, for which a slight decrease is observed with graphitization.

3. Dependence on Particle Size

Several rods were made from Texas coke calcined to 1320°C, varying the particle size to which the coke was ground in each case. The samples were made as nearly identical as possible. It turned out, however, that the larger-particle-size mixes required much higher pressures for extrusion than did the smaller-sized ones, although they appeared much wetter for the same pitch content. As can be seen from Fig. 8a, the samples differ considerably as to the amount of puffing they exhibit during heat treatment.

As seen in Fig. 8b, the longitudinal thermal expansion coefficient of the rod composed of the smallest particles, through-325-mesh size, is about 20% lower than that of the rod made of largest coke particle sizes, 65/100 mesh. It might be worth

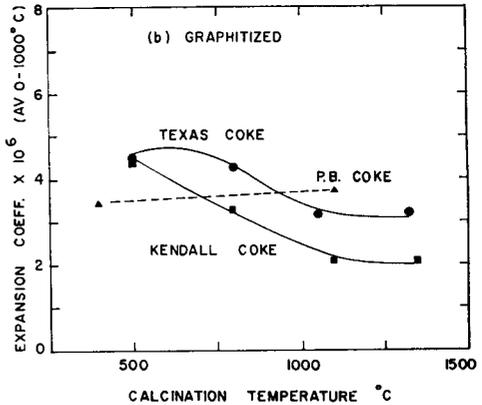
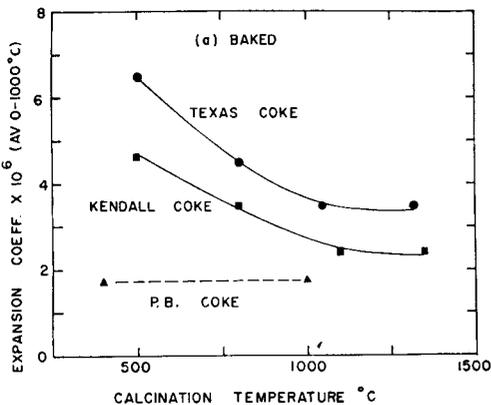


FIG. 7. Longitudinal thermal expansion coefficient for different carbon rods as a function of calcination temperature of the coke. a) baked rods, b) graphitized. PB—phenolbenzaldehyde resin carbon.

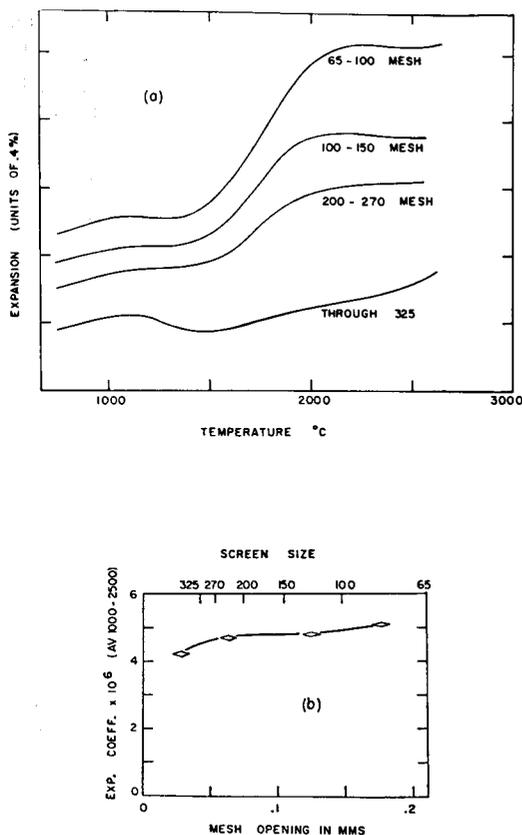


FIG. 8. Dependence of a) longitudinal dilation during heat treatment and b) longitudinal thermal expansion coefficient, both as a function of coke particle size.

mentioning that no significant difference was observed in the expansion coefficient of two rods made from the Texas raw coke, one with 65/100 mesh sizes and the other with through-200-mesh sizes, although the puffing was somewhat greater for the 65/100 mesh rod.

The puffing in the temperature range around 1850°C is generally believed to be related to the concurrent evolution of sulphurous gases. However, for both the Texas series (2b) and variable coke size series (3) large differences are found in the amount of puffing between samples made from mixes containing the same materials in the same ratios. Although sulphur may be the agent responsible for puffing there

certainly are additional controlling factors involved in this complicated process.

4. Effect of Impregnation

Impregnation of a carbon with pitch is a process for reducing the porosity of carbon and increasing its strength and density by widening the binder coke bridges between the particles. In order to impregnate rods they were placed in a vacuum chamber partly filled with molten Resin C pitch binder; after the chamber was evacuated the rods were submerged in the hot molten pitch. The container was then opened to the air, the atmospheric pressure forcing additional pitch into the pores of the carbon. The so-impregnated rods were rebaked in order to coke the impregnant. Such a process can be repeated a number of times, but each successive time with decreasing effectiveness. In this work only two successive impregnations were used.

Several different Kendall coke rods were subjected to this treatment and the results obtained for their thermal expansion coefficient are tabulated below in Table I. In some cases the rods were impregnated before, and in other cases, after graphitization.

The history of the sample is given in the first three columns; namely, the C.T. of the coke, the heat treatment the rod received

TABLE I

Effect of the Impregnation on the Thermal Expansion of Kendall Rods

Calcination Temperature of Coke	Heat Treatment before Impregnation	Number of Impregnations	Expansion Coefficient	Total % Change	Total % Increase in Density
°C	°C		×10 ⁻⁶		
800	800	None	4.26	—	—
800	800	One	4.37	+2.6 ± 2%	4.7
1100	1100	None	3.46	—	—
1100	1100	One	3.73	+7.4 ± 2%	6.8
1100	1100	Two	3.95	+13.3 ± 2%	16.3
1350	2800	None	3.35	—	—
1350	2800	One	3.50	+4.5 ± 1%	6.63
1350	2800	Two	3.58	+6.5 ± 1%	11.1

before it was impregnated, and the number of impregnations. The expansion coefficient for each sample after the sample was finally graphitized is given in the fourth column. The impregnated samples are seen to have higher expansion coefficients than the corresponding unimpregnated samples; the per cent increase is given in the fifth column. In the sixth and last column the relative increases in density resulting from impregnations are listed.

B. Anisotropy of Carbon Samples

Carbon is known to have anisotropic properties in directions parallel and perpendicular to the direction of extrusion. This arises from the great anisotropy of the single crystallites, through the alignment of crystallites within coke particles, which in turn during the process of extrusion become aligned in the mix³. In order to determine the anisotropy of the thermal expansion (α_L/α_T) of two Kendall coke samples, the expansion in the transverse direction was directly measured. A sample was made from discs cut from the rod whose longitudinal expansion was known, the discs being joined together by graphite pegs with a lower expansion coefficient. Reasonably reproducible results were obtained with such samples.

The magnetic susceptibility of the carbon has a directional dependence also. Small cubes cut out from the rods were suspended in an inhomogeneous magnetic field, and the decrease in their apparent weight as a function of magnetic field was determined for two orientations, one with the extrusion axis parallel and the other transverse to the field direction. The anisotropy of susceptibility (χ_L/χ_T) was found from the ratio of weight losses for each position. The anisotropies found for both physical properties as well as the longitudinal expansion coefficients are given in Table II for Kendall

TABLE II
Anisotropy of Graphitized Kendall Coke Rods
(2800°C)

Coke Calcination Temperature	Longitudinal Expansion Coefficient (per °C)	Anisotropy		Volume Expansion Coefficient (per °C)	
		I $\frac{\chi_L}{\chi_T}$	II $\frac{\alpha_L}{\alpha_T}$	I	II
	$\times 10^{-6}$			$\times 10^{-6}$	$\times 10^{-6}$
Raw (~500°C)	6.15	.78	.82	22.0	21.0
800°C	4.25	.64	—	17.5	—
1100°C	3.55	.57	.61	16.0	15.3

coke graphites of different C.T. The anisotropy of the magnetic susceptibility appears to be about equal to that for the thermal expansion. If this relation should happen to be general, one could predict at least approximately transverse thermal expansions from longitudinal ones, using magnetic determinations of anisotropy. The volume expansion coefficients calculated using the magnetic anisotropy as suggested above and those obtained from a direct determination of expansion coefficients are also given for the same three samples of different C.T.

The great difference in longitudinal expansion coefficients of these samples as a function of C.T. is probably due to the different degree of alignment of the coke particles in each case, the coke particles calcined to lower temperature being less anisotropic and less alignable⁴. The volume expansion coefficients are definitely dependent on the C.T. of the coke, however. Furthermore the carbons are anisotropic not only with respect to thermal expansion but also with respect to the dimensional changes during heat treatment, as can be seen in Fig. 3 from the heat treatment curve obtained for a transverse 1100° C.T. sample which shows in the range 1100–1600°C a very large shrinkage in the transverse direction.

³ S. Mrozowski, This volume, page 31.

⁴ E. A. Kmetko, This volume, page 21.

C. X-ray diffraction Measurements

X-ray diffraction measurements were made with a Norelco Spectrometer Goniometer for powdered Kendall coke graphite samples packed in a standard specimen holder. The diffraction pattern for the 1100° C.T. sample was found to have a greater intensity of the 002, 004, 006 lines, relative to the 110 line than that for the raw coke samples, the 800°C C.T. sample being intermediate. The difference in their X-ray patterns was found to be due to a varying degree of alignment of the powder particles under the same packing pressure. The alignment effect was conclusively demonstrated by obtaining identical patterns from all samples when they were held in a thin cellulose holder which required no packing pressure.

IV. DISCUSSION

It has been shown in this work that the thermal expansion of a carbon and its behavior during heat treatment depend on a) the calcination temperature of the coke used, b) the particle size to which the coke was ground, and c) on whether or not the carbon was impregnated, and if so, at what heat-treatment stage of the sample the impregnant was introduced.

The volume expansion coefficient for polycrystalline carbons is always found to be lower than that of a single crystal. This characteristic is a consequence of the existence of rigid carbon-carbon bond networks which extend through the aggregate of crystallites and suppress the large expansion of the crystallites in the direction perpendicular to the graphitic plane³. Exactly how much smaller the expansion of the macrostructure is, and how strongly it depends on factors a, b and c listed above is determined by the relative arrangement of individual crystallites and the number and distribution of intercrystallite bonds.

No differences were noticeable in the X-ray diffraction patterns of samples made

from cokes with various calcination temperatures. Since the differences in structure responsible for variation in expansion coefficients are too slight to be detectable by the X-ray method, studies of the thermal expansion and of the changes occurring in heat treatment are a very useful and extremely sensitive method of investigating structural changes of carbons.

Although no explanation of the influence of each operation and the order in which they are performed in the preparation of the carbon on its final properties can be given, especially in view of the limited number of results obtained to date, it might be worthwhile to point out two possible reasons for carbons being sensitive to such variables. The first of these is the inevitable presence of internal stresses, which originate in one or more of the following ways³: a) stresses are formed during heating of an initially unstressed aggregate of anisotropic crystallites, or during cooling of such an aggregate from temperatures at which stresses have been relieved by creep, as happens in carbons heated to a temperature higher than about 2000°C, b) complicated stresses are formed when a carbon is cooled from a temperature below 2000°C when stresses created during heating are only partly relieved by processes other than creep, for instance by crystal growth, and c) additional stresses on more of a macroscale are formed for a two-component mixture of carbons with different microcrystalline structure, such as binder coke and particle coke. Large stresses are present for the last reason as the result of the baking operation when the binder coke shrinks irreversibly and calcined coke particles expand reversibly. Stresses created in this manner are not so large in samples prepared from raw coke particles, which shrink along with the binder during baking. The strong dependence of thermal expansion on coke calcination temperature might be due to such stresses directly or to the structural differences brought about by their

presence. Even in cooling after graphitization, after all stresses are relaxed by creep above 2000°C, the two dissimilar-in-structure components are shrinking at unequal rates and as a result stresses develop.

It seems probable that when carbons are heated (or cooled) their expansion is dependent on the magnitude of internal stresses created (or relieved) in a manner that is determined by the microcrystalline structure. However, there is a limit to the internal stress which the carbon can sustain without microfracture or without other irreversible changes in its structure being induced. Structural alterations resulting from the relief of thermal stresses, including forced crystallite growth³ are undoubtedly responsible for the irreversible features of the heat-treatment process.

In the two particular cases of greatest irreversible length changes during heat treatment, namely, in the puffing of the Texas raw coke and in the shrinkage of the hard coke rods, the thermal expansion was found to be greatly changed. An interrelation between the behavior during the heat treatment and the changes in the thermal expansion was not surprising, as both are dependent on structural modifications.

A second reason for the diversity in behavior of carbons is that the binder not only contributes directly to the expansion of the material by its presence between the coke particles, but also interacts with and changes the thermal expansion of the coke particles which it surrounds. Depending on the extent to which binder (especially the light fractions³) penetrates the coke micro-

structure, when solidified it might more or less affect the structure and the further growth of individual crystallites.

The variation of thermal expansion with variation of C.T. and as a result of impregnation seem to be caused by the influence of the binder on the structure of the coke. This would explain why the influence of the binder depends on the maximum heat treatment the carbon structure has received before the binder has been introduced into it; that is, on how much opportunity the structure may have had to develop before the disturbing agent was introduced.

The variation of thermal expansion with coke particle-size might also be due to the influence of binder. Smaller particles expose relatively greater surface to the binder and the binder penetrates them more easily. On the other hand, grinding releases some stresses in the coke and changes its structure even before the binder is introduced. Both factors might be of importance.

The action of the binder absorbed in the coke might be by way of changing the distribution of crystallites and their interlinkages or might be direct by modification of internal stresses. Further work is in progress in which an attempt is being made to isolate the action of the binder in the thermal expansion of the whole structure.

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