THE GRAPHITIZATION PROCESS

D.B. Fischbach

Department of Mining, Metallurgical and Ceramic Engineering, University of Washington, Seattle, Wash. 98105

Ordinary hexagonal graphite is generally agreed to be the thermodynamically stable crystalline form of carbon at ordinary pressures. All other forms of solid carbon are metastable and tend to transform to graphite at elevated temperatures. This transformation is called graphitization, and is one of the most fundamental processes in the science and technology of carbon. Over the last ten years or so studies on the carbonization process, the structure of carbons, and the kinetics of graphitization have led to a much better understanding of this complex process. This paper reviews current knowledge of the graphitization process as interpreted by the author. A more extensive review is in the process of publication (1).

The term graphitization is often misused to designate high temperature ($\geq 2500^\circ$C) treatment of carbons without regard for the structure developed. This is not correct. Graphitization is the development of the hexagonal graphite structure with a regular ABABAB layer stacking sequence from any of the other metastable forms of carbon. These metastable carbons include both crystalline forms (cubic and hexagonal diamond, rhombohedral graphite) and forms with poorly developed, disordered structures (cokes, pyrolytic carbons, carbon blacks, glassy carbons, etc.). There are then two general types of graphitization:

a) An order-order type involving the transformation of other crystalline forms of carbon to graphite,

b) The more common disorder-order type in which crystalline graphite is formed from an initially disordered carbon.

The order-order transformations are interesting but have less technological importance and have been studied less. This paper is concerned entirely with disorder-order transformations.

Disordered carbons vary widely in transformation behavior, from easily graphitizable cokes and pyrolytic carbons (PCs) through partially graphitizable carbon blacks to so-called "non-graphitizing" chars, glassy carbons, etc. These differences in behavior result from differences in microstructure which originate during the initial formation of the carbon from a carbonaceous precursor. Carbonization conditions which encourage formation of large aromatic layers in roughly parallel stacks produce graphitizing carbons (2). These conditions include:

1) Production of stable, planar radical intermediates during pyrolysis.
2) High molecular mobility (plastic, liquid or gas phase reaction).
3) Predominance of aromatic over aliphatic condensation and cross-linking.

Non-graphitizing carbons result when development of layer diameter and parallel stacking is inhibited by:

1) Production of unstable and/or non-planar radical intermediates.
2) Low molecular mobility (solid state reaction).
3) Conditions encouraging cross-linking and aliphatic condensation (presence of oxygen, sulphur, low H/C ratio, cross-linked precursor, etc.).

The structure produced during "low" temperature carbonization, which depends on both the nature of the carbon source material and the pyrolysis conditions, determines the subsequent high temperature graphitization behavior.

To understand graphitization, it is necessary to understand as completely as possible the structure of disordered carbons. Disordered structures are difficult to characterize in detail, and our understanding of them is still poor. After most of the residual hydrogen and other impurities have been driven off by calcining at 1200 - 1800°C, disordered carbons of many types have several features in common:

a) Hexagonal layers with $a_0 \approx 2.46$ Å, like graphite.

b) No regular layer stacking order.

c) Interlayer spacing $d$ larger than the graphite value.

d) Small apparent crystallite size and/or much lattice distortion.

These characteristics may be interpreted in various ways.

The oldest, best known and simplest interpretation is the turbostratic (rotated layer) model proposed by Warren and developed by Franklin, Bacon and others. In this model, layer stacking disorder is assumed to be the fundamental characteristic. $d$ is increased because the inter-
layer van der Waals bonding is weakened by the stacking disorder. A specific value of 3.44 Å is assigned to completely random stacking. The actual crystallite dimensions are assumed to be small, and imperfections in the layers are not considered important. Single layers and disorganized carbon (single carbon atoms or small clusters not included in the layer structure) are postulated to account for diffuse scattering. In this model, graphitization consists of growth of layers (by condensation of smaller segments and disorganized carbon), rearrangement in parallel stacks, and shear to achieve ABAB stacking sequences. This model is too simple, and it seems to be basically wrong.

It is now known that imperfections within and perhaps between the layers are very important. Mering and Maire (3) have proposed a model based entirely on one kind of layer imperfection -- interstitial carbon atoms attached to each side of each layer. These thick, imperfect layers cause increased $d$, stacking disorder, distortion, etc. Variations between carbons are caused by different concentrations of interstitials. In this model, graphitization occurs in three stages: First, the disordered interstitials take up an ordered arrangement relative to the regular structure within the layer. Then the interstitials are removed from first one side and then the other of each layer. This model also seems much too simple, but it correctly emphasizes the importance of imperfect layers.

Extensive studies by Ruland (4), Strong (5) and others have suggested a much more general and, I believe, more realistic interpretation. Disordered carbons of all types can be considered as very defective graphites. There are many types of defect which contribute to the disorder, including holes in the layers, interstitial carbon atoms, distorted or cross-link bonds, layer curvature, etc. These defects, all together, produce the characteristics of the disordered structure. Supposedly, the predominant types of defect and the concentration and distribution of defects varies with the type of carbon and the degree of disorder present. Layer curvature may be an especially important type of defect, $L_a$ is actually a measure of the mean dimension of defect-free, flat layer regions, not the size of the whole layer. Therefore, $L_a$ is reduced by layer curvature, holes in layers, etc. Stacking disorder results directly from the shear strain produced by bending stacks of parallel layers. This helps explain the well-established empirical correlation between layer stacking order and $L_a$ illustrated in Fig. 1 (6, 7). Furthermore, Ruland found that the mean interlayer spacing is a linear function of the mean shear displacement of the layers, so $d$ itself is a good measure of the degree of graphitization. However, there is a broad distribution of interlayer spacing values around $d$ that contributes importantly to the breadth of the (001) diffraction peaks. Therefore, $L_c$ is more a measure of distortion than of layer stack height in very disordered carbons.

A general description of the graphitization process can be formulated from these concepts. Graphitizing carbons have large but very imperfect layers with substantial near-parallel stacking. High temperature heat treatment improves and perfects this intrinsic graphitic structure toward that of perfect graphite by removing the defects. Graphitization is therefore a sort of generalized disorder-order transformation* that proceeds by a process of annealing. In non-graphitizing carbons the actual layer diameter is small and parallel stacking is not well developed. Distorted or cross-link bond along the layer edges are a significant fraction of the material and inhibit layer ordering. This type of material cannot be converted to graphite by annealing out defects within or between the layers because the intrinsic graphitic structure is not sufficiently well developed. A much more complete reorganization of the structure is required. Carbon does not appear to recrystallize (nucleate and grow new perfect crystals in the solid state) at ordinary pressures as metals do, probably

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* This term is used here in the general sense relating to lattice perfection. It should not be confused with the configurational short- or long-range order-disorder phenomena observed in many metal alloy systems and in some graphite interlaminar compounds.
because of the anisotropic structure. Therefore, the disordered structure is quite stable in these non-graphitizing carbons. In powder form, a small amount (≤10%) can transform to graphite or graphitized carbon (two or three phase graphitization) by a sudden martensitic-type of transformation that is evidently induced by high thermally-induced internal stresses. But the bulk of the material can be graphitized at ordinary pressures only by melting, solution in and precipitation from a suitable solvent, and similar processes which provide enough mobility for complete reorganization of the structure.

**Fig. 2** Typical isothermal graphitization curves for a substrate-nucleated pyrolytic carbon (PC-A) (1).

**Fig. 3** Typical isothermal graphitization curves for a petroleum coke (pre-treated 15 minutes at 2000°C) (1).

This model of graphitization as a disorder-order process involving annealing out of defects is generally consistent with graphitization kinetic behavior. Kinetic studies provide additional insight into the detailed nature of the process. The graphitization of cokes, PCs and carbon blacks is a time and temperature dependent thermally activated rate process. See Figs. 2 and 3. The effective rate constant is characterized by an activation energy \( \Delta H \) and a pre-exponential factor \( k_0 \): 
\[
 k = k_0 \exp \left( -\frac{\Delta H}{RT} \right)
\]

The different ranges must be considered:

a) The pre-graphitization range, at temperatures below about 2000 ± 200°C, in which residual impurities and non-equilibrium concentrations of point defects in the carbon may be important. In this range, \( L_a \) growth is important, the \( d \) decrease is small, and layer stacking order is not observed.

b) The graphitization range, above about 2000°C, in which hydrogen and other impurities have largely evaporated and, perhaps, cross-link bonds have been broken down. \( L_a \) growth continues, the \( d \) decrease is significant, and layer stacking order develops. Important changes in preferred orientation texture and visible microstructure may also occur. The behavior described is characteristic of cokes and variations are often observed in different carbons.

Making allowance for the fact that small errors in temperature measurement, and small amounts of oxidizers in the heat treatment atmosphere can have a large effect on the results, it seems likely that there is a single effective high temperature activation energy of about 250 ± 40 kcal/mole for the graphitization of all types of graphitizing carbons. See Fig. 4. The same activation energy also seems to apply to the thermally activated high temperature plastic deformation behavior. The fundamental thermally activated process seems to be the same for all graphitizing carbons. The activation energy value is appropriate for self-diffusion in a graphitic lattice by a vacancy mechanism parallel to the layers or, perhaps, by an interstitial mechanism perpendicular to the layers. It appears therefore that self-diffusion is the rate determining process in graphitization. This is consistent with a mechanism of annealing out of defects.

In the pre-graphitization range, the effective activation energy seems to be much smaller, around 140 ± 30 kcal/mole (Fig. 4). The reasons for this are not clear. It might result from the presence of impurities; or from the presence of large numbers of vacancies and interstitials in the structure. The increase of activation energy measured at 1800 - 2360°C (a sort of transition temperature range) due to pre-treatment at 1500 - 2060°C reported by Inagaki, Murase and Noda (10) would be consistent with either hypothesis.

Although the high temperature \( \Delta H \) appears to be the same for many types of carbon, the rate of graphitization and the shape of the graphitiz-
Fig. 4 Arrhenius plots for several types of carbon, as analyzed by the author.

1) Substrate-nucleated pyrolytic carbon A, deposited at 2100 °C; 2) Petroleum coke (pre-treated at 2000 °C); 3) Pitch coke (calcined at 1100 °C) (8); 4) Carbon black (9). High temperature $\Delta H \approx 260$ kcal/mole, low temperature $\Delta H \approx 150$ kcal/mole.

Fig. 5 Comparison of the isothermal graphitization behavior at 2500 °C of several carbons (superimposed master curves). Substrate-nucleated pyrolytic carbons A (La \approx 240 A) and B (La \approx 340 A); regeneratively nucleated pyrolytic carbon F; petroleum coke (pre-treated at 2000 °C).

Fig. 6 Schematic representation of the first-order rate constant distributions for three of the carbons in Fig. 5.

is a first order rate process, then we can write:

$$d = d_f + \int_{d_0}^{d_f} w(\ln k) \exp(-kt) d\ln k$$

where $d$, $d_0$, and $d_f$ are the instantaneous, initial and final interlayer spacing values respectively, $k$ is the rate constant, and $w(\ln k)$ is a distribution function. Some typical rate constant distributions are shown in Fig. 6. Since $\Delta H$ is constant, these $k$ distributions are really distributions of pre-exponential factors. These different pre-exponential factors may be related......
to the amount of diffusion required to anneal out the defects in the disordered carbon. This would depend on the type, concentration and distribution of the defects and of the sources and sinks of vacancies and interstitials. Therefore, the rate and shape of the graphitization curves should depend on the microstructure.

What microstructural parameters are important? It is well known that highly textured cokes graphitize better than isotropic cokes do. Therefore, layer plane preferred orientation texture might affect the pre-exponential factor, as suggested by Murty, Biederman and Heintz (11). However, since petroleum coke graphitizes more rapidly than pyrolytic carbons, structure parameters other than texture must dominate the behavior. The graphitization rate of substrate-nucleated PCs can be ranked in inverse order of the as-deposited value. The smaller the value, the faster the initial graphitization rate (for PC-A, \( L_a \approx 240 \text{ Å} \); for PC-B, \( L_a \approx 340 \text{ Å} \) in Fig. 5). This suggests that layer perfection is important in determining the rate. The larger the mean distance between imperfections (\( L_a \)), the longer the diffusion path required to anneal out the remaining defects and establish ordered stacking. In substrate-nucleated PCs with as-deposited \( L_a \approx 200 \text{ Å} \), the initial graphitization stage (\( \mathcal{g} \approx 3.37 \text{ Å} \)) occurs at approximately constant value. This corresponds to the large narrow peak in the \( \ln k \) distribution for this type of carbon (Fig. 6). During this stage the preferred orientation increases slowly, but considerable layer curvature evidently persists since the as-deposited growth cone structure doesn’t change much. However, very large values of \( L_a \) are required for good graphite and in the later stages of PC graphitization both \( L_a \) and stacking order increase together, and the growth cone structure gradually coarsens and disappears. The graphitization behavior of cokes is also consistent with a strong dependence on value. In petroleum cokes, the initial mean value is generally smaller (\( \approx 150 \text{ Å} \)) and the distribution of \( L_a \) values is possibly much broader than in PCs. Therefore, the initial graphitization rate is faster, but the curve is broader, \( L_a \) and stacking order increase together so the rate decreases as graphitization proceeds. In the region where the coke and PC curves converge (\( \mathcal{g} \approx 3.37 \text{ Å} \)) both types of carbon seem to have similar \( L_a \) values (\( \approx 500 \text{ Å} \)).

Internal stresses probably influence the graphitization behavior too, but it is difficult to separate such effects from the effects of microstructure in an anisotropic material like graphite. For example, differential thermal expansion stresses seem to be the cause of the preferred orientation increase which occurs during the graphitization of PC, especially during the later stages. This stress-induced texture change results in irreversible changes in macroscopic dimensions (expansion parallel and contraction perpendicular to the substrate orientation) and probably helps \( L_a \) growth. However, it has been found that the graphitization behavior of solid and of powdered samples of PC is the same within experimental error. Since powdering would be expected to relieve long-range (\( \approx 100 \text{ μm} \)) stresses, evidently only short-range internal stresses have a significant influence on graphitization. Whatever effect stress has must also be on the pre-exponential factor. Neither internal nor externally applied stresses seem to affect the activation energy. Much remains to be learned about the detailed influence of stresses and microstructure on graphitization behavior.

The important features of the description of the graphitization process discussed here can be summarized as follows:

1. Graphitization of graphitizing carbons is a disorder-order process by which the existing structure is improved toward the ideal graphite structure.
2. This improvement occurs by annealing out the structural defects which produce and stabilize the disorder.
3. This annealing is a thermally activated process.
4. The activation energy is constant (at high temperatures) and appropriate for a process of self-diffusion by a point-defect mechanism.
5. The graphitization pre-exponential factors vary with carbon type and generally involve distributions of values.
6. Differences in pre-exponential factor distributions are responsible for differences in graphitization rate and curve shape.
7. The effective pre-exponential factors are determined by the detailed microstructure of the carbon.
8. The structure of non-graphitizing carbons is not well enough developed to be transformed to graphite by an annealing process. More extensive reorganization of the structure is required.

There are a number of treatment conditions that can modify the graphitization behavior and affect the graphitization rate. For many carbons, graphitization can be accelerated by high temperature plastic deformation; moderately high pressures (\( \approx 10 \text{ kbar} \)); oxidizing atmospheres or additions; and various types of catalyst. An understanding of the effects of these treatments can be sought by considering their influence on the various aspects of the graphitization process listed above. For graphitizing carbons, any
treatment which helps to remove the defects in
the structure will accelerate graphitization: For
example, an increase in diffusion rate (boron
additions may accomplish this), or non-diffusive
breakdown or removal of defects (oxidation,
plastic deformation and, perhaps, high
pressure). The effect of these treatments on
non-graphitizing carbons is often rather different
because the basic graphitization process in these
carbons is different. Thus, plastic deformation
seems to be effective in glassy carbons only
during the carbonization process. Solution/
precipitation or compound-formation/decom-
position reactions involving metal carbides
appear to especially effective catalysts for non-
graphitizing carbons. The discontinuous two and
three phase graphitization processes are es-
pecially important under high pressures and
deserve further study.

The explanation of the graphitization process
presented here contains some speculative and
controversial features. However, it seems to
account for enough of the observed behavior to
make it a useful working hypothesis. Much more
must be learned about diffusion, the nature of the
defects, and the detailed structure of disordered
carbons and imperfect graphites before the com-
plex graphitization transformation can be under-
stood in detail.

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