PHYSICAL REVIEW B VOLUME 33, NUMBER 12 15 JUNE 1986

Interstitials in graphite and disordered carbons

Jalil Lachter and Robert H. Bragg
Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
and Department of Materials Science and Mineral Engineering, Hearst Mining Building,
University of California, Berkeley, California 94720
(Received 6 February 1986)

The steps in the interlayer spacing observed in annealing studies of artificial carbons on the one hand, and those seen in fast-neutron irradiation and grinding of graphite on the other hand, are shown to demonstrate the existence of interstitial carbon atoms between the aromatic planes of carbon atoms, sp^2 bonded as in the graphite-crystal structure. The steps are analogous to staging in graphite intercalation compounds.

The disorder-order transformation in which structurally imperfect carbonaceous materials are converted to perfectly ordered graphite by annealing at temperatures above 2000 °C, usually denoted as "graphitization," has been the subject of numerous investigations.[1,2] It is clear that the transformation must involve diffusion of defects, but a satisfactory explanation of the process is still lacking. In fact, there is some controversy concerning the experimental data, and there is no agreement on a model of the structure of disordered carbons. The situation is complicated by the fact that these materials are in polycrystalline form and so finely divided that the diffraction effects require considerable sophistication for their interpretation. Since the diffraction patterns resemble those of layer clays, Warren[3] proposed a model wherein carbon atoms are sp^2 bonded in layers as in the graphite structure, each layer assumed to be defect free. However, instead of the normal *ABABA* . . . stacking sequence of the layers characteristic of hexagonal graphite, the stacking is extensively and randomly faulted. This "turbostratic" model of disorder carbon leads to the prediction of diffraction patterns which are quantitatively in agreement with experiment, but even with refinements this model cannot fully account for the experimental observations. A critical flaw is that it does not predict interlayer spacings different from that of pristine graphite, whereas interlayer spacings ranging from 3.345 to 3.44 Å are observed experimentally. On the basis of extensive x-ray analysis, Maire and Mering[4] formulated a model in which interstitial carbon atoms are grafted on each side of imperfect layer planes. This model is an improvement of the turbostratic model in that it predicts different structural states and a range of interlayer spacings. Ruland's[5] and Ergun's[6] models also postulate the presence of interstitial carbon, but they emphasize layer plane defects and distortions and do not address the question of intermediate interlayer spacings.

This Rapid Communication presents direct evidence for the physical realty of a hierarchy of interstitial entities based on the interlayer spacings observed during annealing experiments, and on studies wherein initially perfect graphite is deliberately disordered by fast-neutron irradiation or severe mechanical grinding.

The most extensively studied among the intrinsic parameters of disordered carbons is the interlayer spacing d_{002}. Figure 1(a) shows isothermal annealing curves of d_{002} for petroleum cokes.[7] Superimposed curves of isothermal annealings of pyrocarbons and pitch cokes[1,2] are displayed on Fig. 1(b). The combined data clearly show steps involving

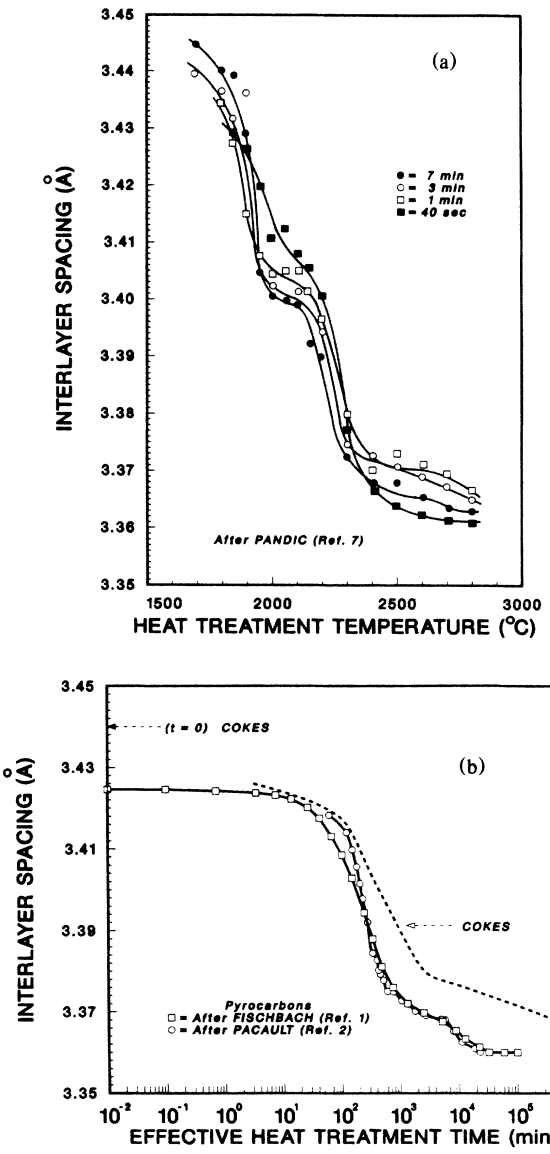

FIG. 1. (a) Interlayer spacing as a function of heat-treatment temperature in isochronal annealings of petrolium cokes (Ref. 7). (b) Superimposed annealing curves of interlayer spacing as function of heat treatment time for pyrocarbons and pitch cokes (Refs. 1 and 2).

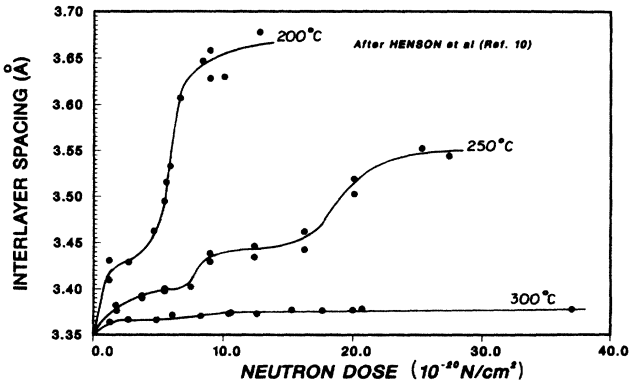

FIG. 2. Interlayer spacing of graphite as function of neutron-irradiation dose (Ref. 10).

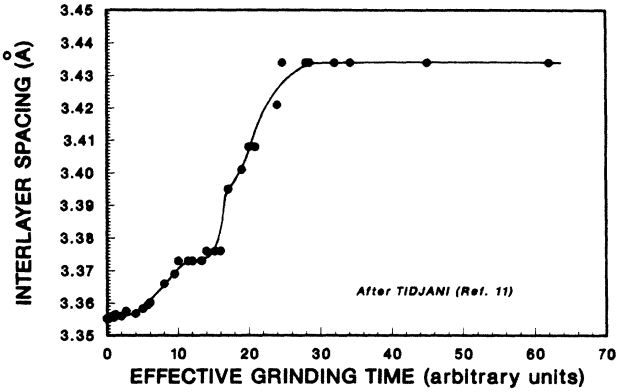

FIG. 3. Interlayer spacing of graphite as function of grinding time (Ref. 11).

interlayer spacings of 3.36, 3.37, 3.40, 3.425, and 3.44 Å. These materials initially contain small amounts of hydrogen as the major impurity.

Because of its use as a moderator, graphite has been subjected to extensive studies of damage introduced by fast-neutron irradiation.[8,9] The resulting lattice-parameter changes have been reported by several investigators. Figure 2 depicts isothermal[10] curves of d_{002} as a function of the irradiation dose for graphite. Once again, the data exhibit plateaus at interlayer spacings around 3.36, 3.37, 3.40, 3.425, and 3.44 Å. In this case there are no significant impurities, only carbon interstitials and vacancies.

Grinding experiments have been performed in order to induce disorder into initially highly perfect graphite material.[11,12] Figure 3 shows d_{002} as a function of the grinding time for a graphite powder.[11] Once again, intermediate steps in d_{002} around 3.37 Å and possibly 3.40 Å are apparent and the data tend toward a limiting value about 3.44 Å. An important finding in this work was that significant amounts of impurities introduced during the grinding did not affect the interlayer spacings produced. As in the case of neutron irradiation there are no significant impurities in the starting material.

Lattice-parameter changes in irradiated graphites have been interpreted in terms of a variety of defects including vacancies, interstitials, vacancy lines and loops, and interstitial loops.[8] The different steps observed in the interlayer spacing as a function of the irradiation dose led authors to conclude that the introduction of defects must occur in stages whose interpretation has not reached a level of consensus.[8,10,13] Grinding, on the other hand, might be expected to introduce distributions of defects different from those created by irradiation. However, the most striking feature of the experimental data (Figs. 2 and 3) is that plateaus in d_{002} are found at 3.37 and 3.44 Å, irrespective of the means of introducing the disorder. Equally striking is the fact that investigations of changes in d_{002} during isochronal and isothermal annealings of disordered carbons containing impurities show similar stepwise behavior with plateaus at the same interlayer spacings. Comparison of the data in Table I suggests that the defects responsible for the steps in the interlayer spacing found during annealing are essentially the same type of defects produced by irradiation, i.e., vacancies and carbon interstitials. It seems likely that failure to observe a particular spacing is an artifact of the specific experimental conditions or procedure.

It has been argued[4] that the defects introduced by irradiation differ fundamentally from those assumed to be intrinsic to artificial carbons. The activation energies derived from analyses of the fast-neutron-irradiation experiments and those derived from annealing of synthetic carbons do not support this argument. This point will be discussed in more detail in a review article on graphitization.[14] However, the interlayer spacings higher than 3.44 Å observed in irradiation studies could be attributed indeed to more complex imperfections, i.e., loops and lines of vacancies and interstitials, probably nonexistant in artificial carbons.

Indirect evidence of interstitials is provided by chemical oxydation kinetics of soft carbons. Oberlin and Mering[15] detected the presence of four structural forms whose defects and distortions have been studied in detail.[16] The same technique of oxydation applied to irradiated graphites led other workers[17] to conclude that, depending upon the temperature and the dose of irradiation, two or three structural forms can be identified. In both studies, interlayer spacings of 3.36, 3.37, and 3.44 Å are involved.

In a recent paper, Kawamura and Bragg[18] showed that the weight loss observed during kinetics studies of pitch cokes is much too large to be attributed solely to the exodiffusion of hydrogen and nitrogen impurities, and analyses of the kinetics of the interlayer spacing decreases showed that this process is characterized by several activation energies.

Other indirect evidence can be obtained from theoretical

TABLE I. Interlayer spacing d_{002} (Å).

Artificial Carbons			Graphite	
	Thermal annealing		Neutron irradiation	Grinding
Pandic[a]	Fischbach[b]	Pacault[c]	Henson[d]	Tidjani[e]
3.44	3.44[f]	3.44[f]	3.44	3.435
· · ·	3.425	3.42	3.425?	· · ·
3.40	· · ·	· · ·	3.40	3.40
3.37	3.37	3.37	3.37	3.375
3.36	3.36	3.36	3.36	3.36

[a]Reference 7.
[b]Reference 1.
[c]Reference 2.
[d]Reference 10.
[e]Reference 11.
[f]Corresponds to the initial d_{002} value of pitch cokes.

studies of interstitials in graphite. Abrahamson and Maclagan[19] calculated the energies for the different possible mechanisms of migration for several assumed configurations of interstitials in graphite. The most important finding was that the most stable configuration was a C_1 interstitial grafted onto a layer plane, either side, and the next was C_2 interstitials in dipolar juxtaposition from adjacent layers. Activation energies for the motion of C_1 and C_2 interstitials are in essential agreement with those found in the literature, in both annealing and irradiation studies.

In summary, this Rapid Communication points out the unequivocal correlation between the steps observed in both irradiation and annealing studies with structural imperfections, i.e., interstitial species. Since the concentration of vacancies in the cokes and pyrocarbons is negligible, these interstitial species must be carbon atoms. Depending upon concentration, they are arranged in configurations analagous to staging in graphite intercalation compounds. The different mechanisms leading to graphitization of artifical carbons as well as the activation energies involved will be discussed in a review article.[4]

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

[1]D. B. Fischbach, in *Chemistry and Physics of Carbon,* edited by P. L. Walker (Dekker, New York, 1971), Vol. 7, pp. 1–105.
[2]A. Pacault, in *Chemistry and Physics of Carbon,* edited by P. L. Walker (Dekker, New York, 1971), Vol. 7, pp. 107–154.
[3]B. E. Warren, Phys. Rev. **59**, 693 (1941).
[4]J. Maire and J. Mering, J. Chem. Phys. **57**, 803 (1960).
[5]W. Ruland, in *Chemistry and Physics of Carbon,* edited by P. L. Walker (Dekker, New York, 1968), Vol. 4, pp. 1–84.
[6]S. Ergun, in *Chemistry and Physics of Carbon,* edited by P. L. Walker (Dekker, New York, 1968), Vol. 3, pp. 211–288.
[7]B. Pandic, in *Proceedings of the Second Conference on Industrial Carbons and Graphite,* Society of Chemical Industry, 1966 (Gordon and Breach, New York, 1966), p. 439.
[8]B. T. Kelly, *Physics of Graphite* (Applied Science, Essex, England, 1981).
[9]B. T. Kelly, Charles E. Pettinos Award Lecture, Fifteenth Biennal Conference on Carbon, Philadelphia, Pennsylvania, June 1981 (unpublished).
[10]R. W. Henson and W. N. Reynolds, Carbon **3**, 277 (1965).
[11]M. Tidjani, Jalil Lachter, T. S. Kabre, and R. H. Bragg, Carbon (to be published).
[12]G. E. Bacon, Acta Crystallogr. **3**, 320 (1950).
[13]P. A. Platonov, E. I. Trofimchuk, O. K. Chusunov, V. I. Karpukhin, Y. P. Tumanov, and S. I. Alekseev, Radiat. Eff. **25**, 105 (1975).
[14]Jalil Lachter and R. H. Bragg (unpublished).
[15]M. Oberlin and J. Mering, Carbon **1**, 471 (1964).
[16]A. Bouraoui, Bull. Soc. Fr. Mineral. Cristallogr. **88**, 663 (1965).
[17]M. Oberlin, J. Rappeneau, and M. Yvars, Carbon **1**, 481 (1964).
[18]K. Kawamura and R. H. Bragg, Carbon (to be published).
[19]J. Abrahamson and R. G. A. R. Maclagan, Carbon **22**, 291 (1984).