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January 1986

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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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.

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ABSTRACT

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 analagous 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 2000C, 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 disordered 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 3.345A to 3.44A 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 on 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 note 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 Figure 1(b). The combined data clearly show steps involving interlayer spacings of 3.36A, 3.37A, 3.40A, 3.425A and 3.44A. 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 parameters 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 3.36A, 3.37A, 3.40A, 3.425A and 3.44A. 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. Once again, intermediate steps in d_{002} around 3.37A and possibly 3.40A are apparent and the data tend towards a limiting value about 3.44A. 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 parameters changes in irradiated graphites have been interpreted in terms of a variety of defects including vacancies, interstitials, vacancy lines and loops, 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 (Figures 2 and 3) is that plateaus in d_{002} are found at 3.37A and 3.44A, possibly 3.40A , 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 behaviour with plateaus at the same interlayer spacings. Comparison of the data in Table 1 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 3.44A observed in irradiation studies could be attributed indeed to more complex imperfections , i.e., loops and lines of vacancies and interstitials, probably non existant 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 3.36A, 3.37A, 3.40A and 3.44A 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 in characterized by several activation energies.

Other indirect evidence can be obtained from

theoretical 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 note 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 artificial carbons as well as the activation energies involved will be discussed [14].

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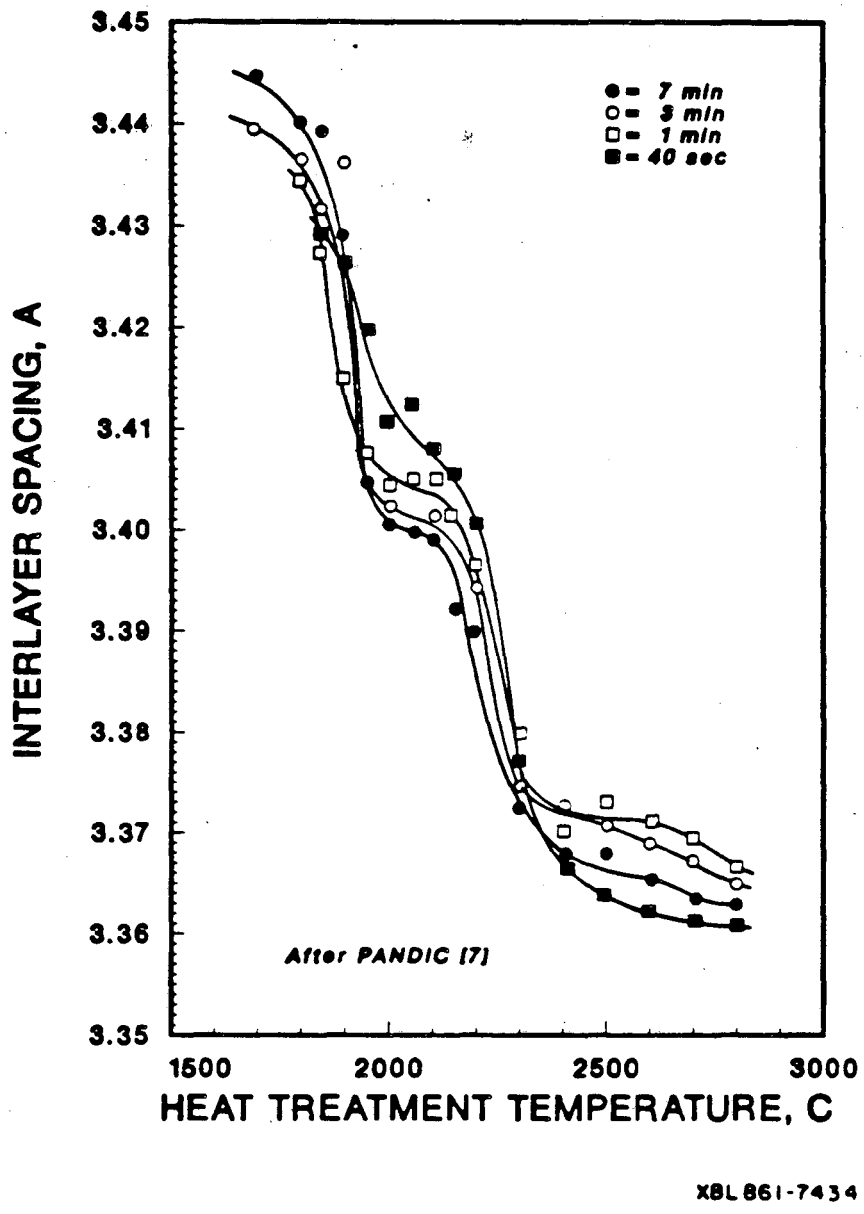

FIGURE 1(a) : Interlayer spacing as a function of heat treatment temperature in isochronal annealings of petrolium cokes [7].

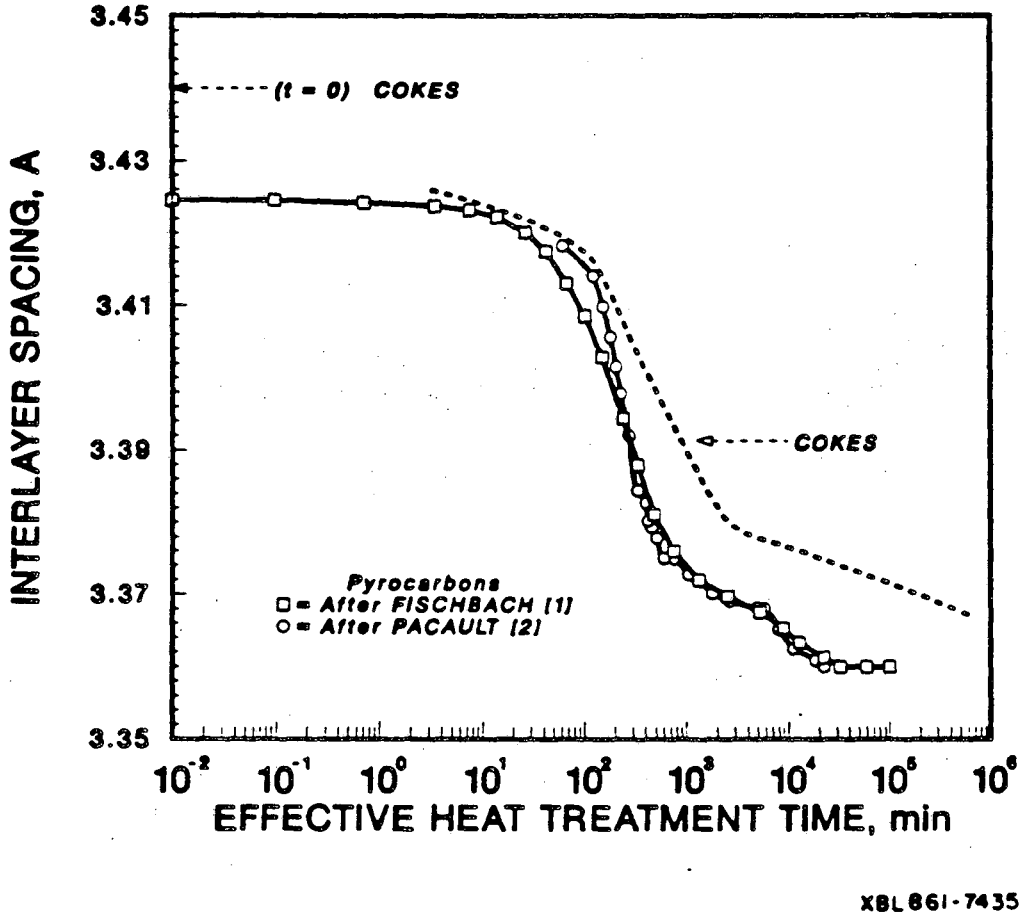

FIGURE 1(b) : Superimposed annealing curves of interlayer spacing as a function of heat treatment time for pyrocarbons and pitch cokes [1,2].

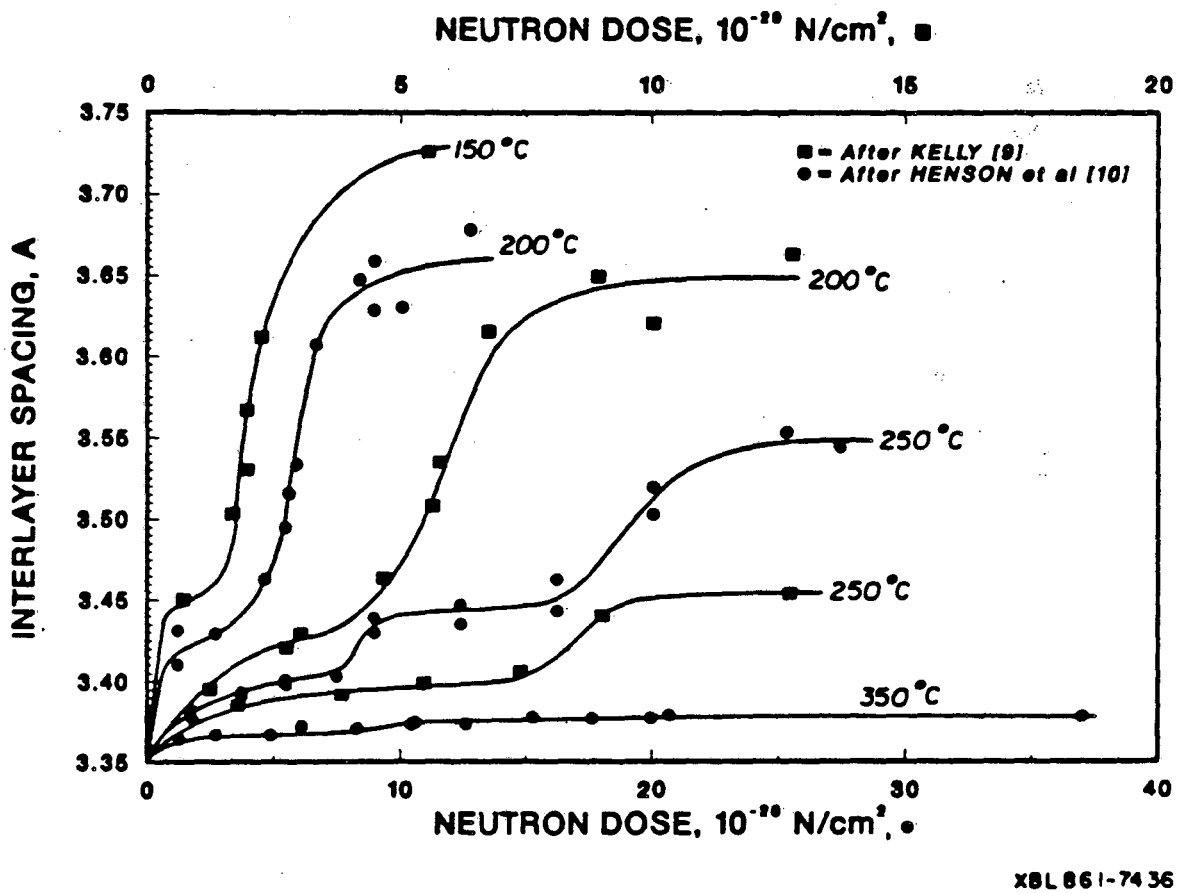

FIGURE 2 : Interlayer spacing of graphite as a function of neutron irradiation dose [9,10].

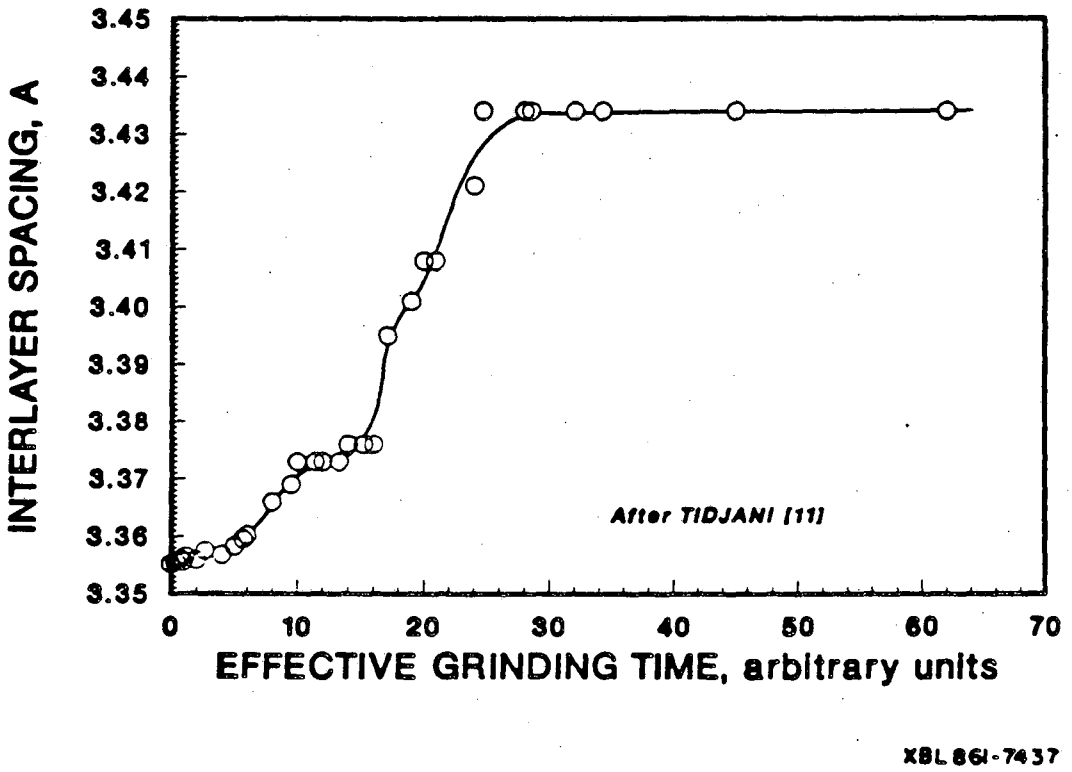

FIGURE 3 : Interlayer spacing of graphite as a function of grinding time [11].

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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