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Authors

Kawamura, K.

Bragg, R.H.

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July 1985

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K. Kawamura* and R. H. Bragg

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*On leave from the Department of Chemistry, The National Defense
Academy, 1-10-20, Hashirimizu, Yokosuka 239, Japan.

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ABSTRACT

Studies of the average interlayer spacing, $\bar{d}_{002}$, strain parameter, ϵ , and fractional weight changes, $\Delta w/w$, were made of a pitch coke heat treated at temperatures in the range 1250 to 2300°C for periods up to 25 hours in inert atmosphere. Application of the superposition technique to the change in $\bar{d}_{002}$ gave an activation energy of 65 ± 5 kcal/mole between 1500°C and 2000°C and 220 ± 30 kcal/mole between 2000°C and 2300°C. The weight loss was thermally activated with an activation energy of about 100 ± 5 kcal/mole. The interlayer spacing decreases sharply at a critical value of weight loss, and this is attributed to removal of an interlayer chemical species, most likely interstitial carbon.

*On leave from the Department of Chemistry, The National Defense Academy, 1-20-20, Hashirimizu, Yokosuka 239, Japan.

1. INTRODUCTION

Carbons obtained from pyrolysis of hydrocarbons at temperatures in the range 1000 to 1500°C are generally assumed to be chemically pure, probably because the hydrogen content is a few percent or less, and in graphitized materials it is very small (10 to 100 ppm) [1]. Thus, hydrogen is usually considered to be benign in carbons; it has not been considered to affect the process of graphitization.

Recently, Bragg [2] advanced the hypothesis that hydrogen may play an important role in graphitization, suggesting, in fact, that some of the residual hydrogen is located between graphitic layers, thus forming what might be described as a graphite intercalation compound. The hypothesis was based on much indirect evidence, but the major points were that (i) hydrogen between layers might account for the increase in the interlayer spacing, d_{002} , from the 3.354Å of pristine graphite to the 3.44Å of fully turbostratic graphite, and its removal would produce intermediate interlayer spacings such as have been reported by Fischbach [3] and Pacault and co-workers [4], and (ii) hydrogen would act as a dopant and affect the electrical characteristics in a manner consistent with what is observed experimentally [4,5].

While interlayer hydrogen could play a role in the process of graphitization, it cannot provide the basis for a complete explanation. The known bond energies involving hydrogen and carbon are 104.2 kcal/mole for H-H bonds, and 98.8 kcal/mole for C-H bonds [6]. Furthermore, the diffusion of hydrogen in graphite occurs with

an activation energy of 98.4 ± 5.7 kcal/mole [7]. Thus, whatever the dominant mechanism the energy required to remove hydrogen from carbon is far less than the approximately 250 kcal/mole activation energy generally obtained for graphitization [3,4].

The suggestion that interlayer chemical species, akin to graphite intercalation compounds, are responsible for the intermediate interlayer spacings observed in graphitization is not new. Mering and Maire [8] proposed a model in which carbon atoms or CH groups are attached to individual layer planes. In this model, four structural states are possible involving interlayer spacings of 3.44Å, 3.40Å and 3.354Å. Chemical evidence in support of this model has been presented by Oberlin and Mering [9] but this line of investigation into the mechanism of graphitization has not been extensively pursued. Since graphitization involves the removal of defects both within and between graphitic layers, it is not obvious how one can design an investigation of either factor separately. However, one fruitful approach might be to focus attention on weight changes. The intent of the present work was to investigate the implication that removal of hydrogen is an important component of the mechanism of graphitization by measuring the thermally induced changes in weight during annealing of carbon in addition to changes in interlayer spacing, crystallite size and lattice strain perpendicular to the layer planes. Pitch coke was chosen as the model material because it graphitizes readily, the initial hydrogen

content is large and it appeared that weight losses during graphitization could be measured with reasonable accuracy.

2. EXPERIMENTAL PROCEDURE

A primary sample of pitch coke was prepared by the carbonization of coal-tar pitch at a heat treatment temperature (HTT) of 1000°C for one hour in argon atmosphere. The product was a porous, massive carbon whose chemical composition was C = 98.14%, H = 0.34% and N = 1.05% by weight (atomic ratio C : H : N = 8.17 : 0.337 : 0.075). The interlayer spacing, $\bar{d}_{002}$ was $3.44 \pm 0.01 \text{ \AA}$ and the crystallite size, $\bar{L}_c$, was about 20 Å. The chemical analyses* of the precursor material after carbonization at different HTT up to 1000°C are shown in Fig. 1. This pitch coke was cut into 1 to 2 g specimens and put into a closed pillbox-like graphite cylinder for heat treatments. The heat treatments were carried out in an Astro furnace which had been specially modified for kinetic studies. Prior to a run the specimens are positioned above the hot zone and the furnace hot zone is heated to the desired HTT. At the beginning of a run (time $t = 0$), they are quickly lowered into the hot zone, whereupon the temperature of the hot zone decreases sharply, as shown at point A in Fig. 2, but returns to its original value in less than 10 minutes. At the desired time, t , the furnace power is switched off, and the furnace

*Microcombustion analyses were done by the Analytical Center at Kyushu University. A few analyses were performed at the Lawrence Livermore Laboratory.

temperature decreases rapidly to room temperature. Heat treatments were carried out at 1250, 1500, 1750, 2000, 2200 and 2300°C for heat treatment times (HTt) from 1 hour up to 25 hours in extra pure helium (99.995%). Temperatures were measured with a disappearing filament optical pyrometer, which had been calibrated beforehand, and maintained to within $\pm 20^{\circ}\text{C}$ with an automatic controller. The changes in specimen weight were determined by the difference of the weights before and after a run from measurements made using an analytical balance, single pan, accurate to $\pm 1 \times 10^{-4}$ g. Samples were kept in a dessicator and errors due to losses during handling were found to be negligible. X-ray diffraction measurements were made on powder samples mixed with pure silicon powder as internal standard with a GE-XRD 5 diffractometer employing nickel filtered CuK_{α} radiation combined with a proportional counter and pulse height discrimination. The observed line profiles were corrected for absorption, Lorentz-polarization and atomic scattering factor variations [10]. An extrapolation technique was used to obtain an accurate value of the interlayer spacing $\bar{d}_{002}$ from the observed 002 and 004 reflections [11]. The widths, β of the corrected line profiles were used to calculate a number, ϵ , related to the lattice strain perpendicular to the layer planes from the slopes of graphs of $\beta \cos\theta$ versus ϵ^2 [12,13].

3. RESULTS

Interlayer Spacing, $\bar{d}_{002}$

The X-ray diffraction line profiles consisted of broad symmetrical (00 ℓ) interlayer reflections and diffuse asymmetrical (hk) bands. Analyses were restricted to the 002 and 004 interlayer reflections because higher orders were too weak to be observed, and typical graphs of extrapolations according to [11] are shown in Fig. 3. It can be seen that one hour heat treatments at different temperatures can produce markedly different slopes of the extrapolation graphs. That is, the slope is large at 1250°C and decreases as the HTT increases, but has not been reduced to zero even at 2300°C. Figure 4 shows the extrapolated interlayer spacing $\bar{d}_{002}$ versus HTt, and Fig. 5 shows the result of a superposition of these data for all HTT onto that for 1250°C according to the method described by Fischbach [3].

The shifts along the $\ln$ HTt axis necessary to obtain the superimposed master curve in Fig. 5 are shown in the Arrhenius plot in Fig. 6. The data indicate that there are relatively well defined temperature regions characterized by activation energies of $\Delta H = 65 \pm 5$ kcal/mole between 1500 and 2000°C, and $\Delta H = 220 \pm 30$ kcal/mole between 2000°C and 2300°C. In the region below 1500°C it is doubtful that a single activation energy is appropriate. In fact, the lower slope in this region indicates a much smaller activation energy, close to 10 kcal/mole.

Weight Loss, $\Delta w/w$

Data of the fractional weight loss, hereafter simply called weight loss, $\Delta w/w$, versus HTt for five different HTT are shown in Fig. 7. The data of Fig. 7 suggest that there are at least two processes characterized by quite different activation energies. Since the precision of the data is not high, and the overlap between different HTT is small (even missing for the region between 1250 and 1500°C) the data are clearly not well suited for a superposition analysis. The curve shown in Fig. 8 (which includes an extrapolation between 1250 and 1500°C) was obtained after considerable trial and error, and the shifts along the $\ln t$ axis required to obtain this master curve gave the Arrhenius plot in Fig. 9. The implication is that the weight loss is characterized by an activation energy of 100 ± 5 kcal/mole, but it seems likely that there is another process having a larger activation energy involved over the range of HTT in this study.

Lattice Strain Parameter, ϵ

Typical data of $\beta \cos \theta$ versus ℓ^2 are shown in Fig. 10. The slope of the lines are proportional to the (strain)² perpendicular to the layer planes, and the intercept gives λ/L_c , where λ is the wavelength and L_c is the mean crystallite height. This slope is hereafter designated as ϵ , a strain parameter. It should be noted that at 1250°C the strain parameter was reduced only slightly after 25 hours but the crystallite height increased from 50Å to 70Å.

Figure 10 also shows that the same general behavior occurs at each temperature up to and including 2300°C. That is, there is an abrupt change in strain parameter when the HTT is increased from one value to another, but little change thereafter at this temperature. Thus most of the strain is a non-kinetic function of the HTT. It should be noted that the strain parameter is largest at 1000°C, decreases monotonically with increasing HTT to a very small value at 2300°C. Graphs of ϵ versus HTT for one hour and for 25 hours are shown in Fig. 11.

Crystallite Size, $\bar{L}_c$

The crystallite sizes obtained from intercepts of the plots of $\beta \cos\theta$ versus λ^2 for 1 hour and 25 hours are shown in Fig. 12. As in the case of the strain parameter the data do not overlap. That is, the changes in $\bar{L}_c$ also appear to be non-kinetic. The value of $\bar{L}_c$ below 1000°C could not be determined because the 004 reflection was too weak to be measured.

Correlation of $\bar{d}_{002}$ and $\bar{L}_c$ with Strain

Figure 13 shows data of $\bar{d}_{002}$ and $\bar{L}_c$ versus strain parameter for 1 hour and 25 hours. In general, the strain parameter is largest for the largest average interlayer spacing and for the smallest crystallite sizes. That is, when $\bar{d}_{002}$ is near 3.43Å the interlayer spacing is little affected by a large decrease in strain parameter, but in a critical region the interlayer spacing decreases

precipitously with further decrease in strain parameter. Figure 13 also shows that at about the same critical region the crystallite size increases sharply as the strain parameter is decreased. A graph of $\bar{d}_{002}$ versus $\bar{L}_c$ on the other hand, Fig. 14, shows an almost linear relation between $\bar{d}_{002}$ and $\bar{L}_c$, when $\bar{L}_c$ is greater than about 300A. This figure also shows that at temperatures below 1750°C there is not a one-to-one correspondence between $\bar{d}_{002}$ and $\bar{L}_c$.

Correlation of $\bar{d}_{002}$ with Weight Loss, $\Delta w/w$

A graph of $\bar{d}_{002}$ versus $\Delta w/w$ is shown in Fig. 15. It appears that the interlayer spacing is relatively insensitive to weight loss up to about $\Delta w/w = 0.0125$, the region corresponding to HTT of 1250 and 1500°C. There is an intermediate region between 1750 and 2000°C wherein $\bar{d}_{002}$ begins to decrease more rapidly as $\Delta w/w$ increases from about 0.0125 to 0.0175, and a third region, between 2000 and 2300°C wherein $\bar{d}_{002}$ decreases precipitously for very small increases in $\Delta w/w$, from 0.0175 to about 0.020. There is no indication of a plateau, i.e., a discrete value of $\bar{d}_{002}$ either in Fig. 15 or in Fig. 5.

Correlation of Strain with $\Delta w/w$

In Fig. 16 a graph of strain versus $\Delta w/w$ is shown. The general trend of the data is linear, but in contrast with the correlation of $\bar{d}_{002}$ with $\Delta w/w$, a one-to-one association of strain parameter with $\Delta w/w$, independent of the time, is not observed. Thus, as in the case

of $\bar{d}_{002}$ versus $\bar{L}_c$, there is not a unique correlation between strain parameter and weight loss.

4. DISCUSSION

$\bar{d}_{002}$

Although the graphitization of pitch cokes has been extensively studied, the literature contains little information concerning kinetic aspects in the temperature range investigated here. Fischbach's review [3] shows clearly that there is a high temperature process ($HTT > \sim 2000^\circ\text{C}$) characterized by an activation energy of about 250 kcal/mole, whereas lower activation energies (typically ≤ 175 kcal/mole) are generally found below 2000°C . The authors believe that the 220 ± 30 kcal/mole energy found in this work is to be associated with the high temperature process and is numerically the same within experimental error.

Mizushima [14] obtained activation energies ranging from about 75 to 200 kcal/mole from measurements of the electrical and thermal conductivities and the crystallite size of a 700°C petroleum coke as a function of heat treatment over the range 900 to 2500°C . Two major thermally activated processes were inferred: One with $\Delta H \sim 100$ kcal/mole around 1400°C , and another with $\Delta H \sim 200$ kcal/mole around 2200°C . More recently, Fitzer and Weisenburger [15] made in-situ d_{002} studies of the graphitization of a petroleum coke between 1700 and 2500°C . They found that the non-isothermal kinetic behavior

during heat-up (20-30 seconds) was characterized by an activation energy of about 10 kcal/mole, and they obtained a value of approximately 65 kcal/mole for the first minute of isothermal treatment. For longer times, energies of 220 to 270 kcal/mole were found. They attributed the 10 kcal/mole value to the elimination of mobile single interstitial atoms or loops. Their model for the 65 kcal/mole process is not entirely clear from the text, but the critical process seems to require migration of interstitials. Bose and Bragg [16] obtained an activation energy of 64 ± 10 kcal/mole for the annealing of specific surface area in glassy carbon between 2000 and 2700°C; and Henry [17] found a value of 76 ± 4 kcal/mole for pore growth in the same material and temperature range.

The present authors suggest that all three activation energy regions (≤ 10 , $\sim 60-80$, and ≥ 220 kcal/mole) observed in this work and reported in the literature can be understood in terms of a simple model wherein interlayer spacings greater than $3.35\text{\AA}$ are attributed to interstitial carbon atoms, according to the model of Maire and Mering [8]. It is assumed that the starting pitch coke contains excess (non-equilibrium) vacancies as well as interstitials, and that the latter are present in both mobile and immobile (bound) states [18,19]. Mobile interstitials (or bound interstitial-vacancy close pairs) disappear quickly with a low activation energy (the migration energy of mobile interstitials is ≤ 2 kcal/mole [18]), causing an initial small decrease in $\bar{d}_{002}$. Further graphitization requires the removal of the much more stable bound interstitials that are not

adjacent to vacancies. According to recent theoretical calculations of Abrahamsen and MacLagan [20], migration energies for di-interstitials (C_2 molecules) are about 100 and 140 kcal/mole, and about 200, 231 and 281 kcal/mole for bound single interstitials. It is proposed that these bound interstitials are substantially immobile below 2000°C, but that a portion of them are annihilated in the 1500-2000°C range by the excess vacancies, which diffuse to them. The literature value for the vacancy migration energy parallel to the layer planes is about 72 kcal/mole [18]. When the supply of excess vacancies is depleted, removal of the remaining interstitials and further decrease in $\bar{d}_{002}$ above 2000°C is accomplished by combination with migrating thermal equilibrium vacancies, giving an activation energy of about 245 kcal/mole (173 for vacancy formation energy plus 72 for vacancy migration energy); or by the migration of single interstitials to sinks.

Weight Loss, $\Delta w/w$

The activation energy found for the weight loss, 100 ± 5 Kcal/mole is close to the known values for H-H and C-H bond energies, 104.2 and 98.8 kcal/mole, respectively [6]. Causey, et al. [7] measured the diffusion of tritium in pyrocarbon in the range 900 to 1500°C and found an activation energy of 98.4 ± 5.7 kcal/mole, and this value should be reasonably correct for hydrogen diffusion. Thus the kinetics of the weight loss are consistent with mechanisms involving hydrogen liberation from carbon. However, the absolute

values of the weight losses are too large to be attributed to loss of hydrogen alone. As noted in EXPERIMENTAL PROCEDURE the initial hydrogen content prior to heat treatment at 1250°C was about 0.34 percent. Thus, since the maximum weight loss found for 25 hours heat treatment at 2300°C was about 2.0 percent, the observed weight loss is too large by a factor of about 5 or more.

While the magnitude of the discrepancy noted above may be in error, there is little doubt that there is a discrepancy. Meyer, et al. measured the hydrogen content of several different carbons, generally regarded as commercially pure [1]. Their results shown in Fig. 17, suggest that carbons heat treated around 1000°C would have a hydrogen content of about 0.14 percent. This value is comparable to the solubility of hydrogen in pyrocarbon. Causey, et al. [7] found that deuterium dissolves in pyrocarbon as atomic deuterium with a heat of solution of -33.3 ± 5.1 kcal/mole, and about 0.027 deuterium atoms per carbon atom will dissolve at 1000°C at one atmosphere pressure. This indicates that about 0.22 weight percent of hydrogen would be dissolved at 1000°C. The considerations above indicate that the hydrogen content of the pitch coke was probably measured correctly, and that in the initial pitch coke there may have been a 50 percent excess of hydrogen above the solubility limit.

Other chemical species in conjunction with hydrogen could be responsible for the weight loss. Meyer, et al. also noted that in addition to hydrogen various hydrocarbons are evolved during high temperature annealing [1]. One might even consider the possibility

that the weight loss is due to hydrogen and nitrogen, but even in this case the maximum weight loss would be around 1.4 percent. However, microcombustion analyses, done at the Lawrence Livermore Laboratory, showed that the pitch coke annealed 25 hours at 2300°C contained less than 0.01 percent (100 ppm) of hydrogen and about 0.25 percent nitrogen so even in this case the discrepancy is a factor of 2. However, as pointed out in RESULTS it seems likely that there are at least two processes involved in the weight loss. Thus the data can be explained by the loss of hydrogen and interstitial carbon during annealing. It does not appear that nitrogen plays any essential role in the process.

Correlation of $\bar{d}_{002}$ with $\Delta w/w$

The correlation between $\bar{d}_{002}$ and $\Delta w/w$ shown in Fig. 15 is striking. It should be noted that the sharp drop occurs about where the HTT increases from 1750 to 2000°C, where it is suggested that the rate controlling mechanism changes from vacancy migration to vacancy formation plus vacancy migration. Figure 15 suggests that at a critical amount of removal of interstitial carbon the interlayer spacing reduces drastically from 3.425Å to 3.38Å. However, since $\bar{d}_{002}$ barely decreases below 3.38Å some interstitial carbon remains.

The results reported herein are in agreement with results reported in the excellent review of Oberlin on carbonization and graphitization [21]. There it is shown that pitch coke evolves from basic structural units which can be described as layer stacks of

fused benzene rings having dimensions of the order of $10\text{\AA}$. In lattice images of 002 reflections the layers are seen edge-on as being wrinkled, having irregular thicknesses and a distribution of interlayer spacings. On the present model the irregular thicknesses could be attributed to carbon interstitials adsorbed on surfaces. As the annealing proceeds the basic structural units are associated into distorted columns where they pile up much like bricks thrown into a heap. The bricks approach each other more closely when heteroatoms (hydrogens, Fig. 1) are released around 800°C , and L_c , the mean coherence distance, increases. However, misoriented individual structural units trapped between columns prevent the rapid increase in L_c . Above 1500°C adjacent columns merge and both L_c and L_a , the mean defect free distance in the layer planes, increase. In the range 1500 to 1900°C , L_c increases very rapidly but the diameters of the wrinkled layers do not, being hindered by in-plane defects at the layer plane boundaries. Above 1700°C pairs of layers having the graphitic order are formed and above 1900°C the layers begin dewrinkling, and in the range 1900 to 2100°C dewrinkling occurs rapidly and the turbostratic structure disappears. Above 2100°C the in-plane defects are wiped out and the elemental domains improve in size and crystalline order.

It can be seen that the data of the present study tally well with the above description. Figure 12 accords well with Oberlin's description of the general dependence of L_c on HTT. The data of

ϵ versus HTT (Figs. 11, 13 and 16) are a combined manifestation of wrinkling and interlayer heteroatoms.

Critique of Bragg's Hypothesis of Intercalated Hydrogen

A major point of Bragg's model [2] was that interlayer (or intercalated) hydrogen is the source of increases in $\bar{d}_{002}$ above 3.354Å in graphitic carbons. However, since most of the hydrogen has been removed before $\bar{d}_{002}$ decreases below about 3.42Å, it cannot play an essential role in the graphitization process.

It is well known that the Hall coefficient changes from negative to positive somewhere in the region between 1700 and 1900°C during the annealing of both hard [22] and soft carbons [5]. Bragg's second major point was that the observed change in the sign of the Hall coefficient from negative to positive in the region of HTT around 1700 to 1900°C is due to the removal of hydrogen. That is, hydrogen would act as a chemical dopant, converting the material to n-type. To obtain an estimate of the orders of magnitude involved assume that each hydrogen atom, known to dissolve as atomic hydrogen [7], ionizes and supplies about one charge carrier to the conduction band. Then since the density of the pitch coke is approximately 2.0 g/cm³ and the weight fraction of hydrogen for 1000°C HTT is 0.0034 g H/g sample, the initial concentration of carriers due to hydrogen would be about 10²¹/cm³. While hydrogen analyses were not made on the pitch cokes between 1250°C and 2300°C, Fig. 17 indicates that at 1750°C the hydrogen concentration is only about 150 ppm, or less. In

fact, using the solubility data of Causey et al. [7], the solubility of hydrogen in carbon is calculated to be closer to about 20 ppm. From this one calculates that the hydrogen concentration and hence the electron contribution to the carrier concentration would be about $10^{18}/\text{cm}^3$ at 1750°C HTT. Thus the electron concentration due to hydrogen is about $10^{21}/\text{cm}^3$ at 1000°C HTT but decreases to below $10^{18}/\text{cm}^3$ in the region of HTT where the Hall coefficient changes sign.

The calculations of Abrahamson and MacLagan indicate that the C_2 interstitial would have a net negative charge of about 0.3 electrons. Thus the effect of C_2 interstitials alone would be to make the material p-type. However, the maximum interstitial content appears to be about 2 percent, so that the concentration of holes in the valence band would be about $3 \times 10^{20}/\text{cm}^3$. Thus the initial sign of the Hall coefficient would be negative as is observed. As annealing proceeds, the concentration of hydrogen decreases faster than the concentration of carbon interstitials and the Hall coefficient will change sign from minus to plus. The C interstitial on the other hand carries a slight positive sign, which would tend to make the material n-type, i.e., the Hall coefficient again negative. One can imagine an initial distribution of C and C_2 interstitials such that the sign of the Hall coefficient could have either sign. However, since the C_2 interstitials diffuse more rapidly than the C interstitials, it seems unlikely that a material, initially n-type, would convert to p-type during annealing. Thus the more likely explanation is that

hydrogen is responsible for the initially negative Hall coefficient, and its removal is responsible for the change in sign from minus to plus. However, this is conjecture and what is needed is experimental data correlating electrical properties with chemical species in carbons.

5. SUMMARY AND CONCLUSIONS

The present work has shown that Bragg's hypothesis of a graphite intercalation compound of hydrogen is not in agreement with experiment; it cannot account for increases in the interlayer spacing of graphite above 3.354Å to 3.44Å. On the other hand, hydrogen may be the source of the negative Hall coefficient observed in pitch coke and hard carbons below about 1900°C. The observed increases in $\bar{d}_{002}$ above 3.354Å are most likely due to interstitial carbon. The results indicate that in addition to the fast diffusing interstitials, which migrate with an activation energy of 0.5-2.0 kcal/mole, carbonized pitch coke contains relatively immobile carbon interstitials which migrate with an activation energy around 100 kcal/mole and higher. At temperatures above 2000°C the decrease in interlayer spacing is attributed to the removal of the relatively immobile carbon interstitials.

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XBL 853-5959

Fig. 1. Chemical analysis data for pitch coke heat treated at various temperatures below 1000°C for one hour.

XBL 853-5947

Fig. 2. Hot zone temperature versus time. Sample holder was inserted at time A.

XBL853-5948

Fig. 3. Extrapolation graph of d_{002} for one hour heat treatment at different heat treatment temperatures (HTT).

XBL853-5950

Fig. 4. Extrapolated interlayer spacing, $\bar{d}_{002}$ versus HTt for various HTT .

XBL 857-6452

Fig. 5. Superimposed master curve of $\bar{d}_{002}$ versus $\ln HTt$ using 1250°C data as basis.

XBL 857-6453

Fig. 6. Arrhenius plot of effective rate constants obtained by superposition of data in Fig. 5.

XBL 853-5953

Fig. 7. Sample weight loss ($\Delta w/w$) versus HTt for different HTT.

XBL 857-6448

Fig. 8. Master curve of weight loss ($\Delta w/w$) superimposed onto weight loss data for 1250°C.

XBL 857- 6449

Fig. 9. Arrhenius plot of effective rate constants obtained by superposition of data in Fig. 8.

XBL 856-6323

Fig. 10. $\beta \cos \theta$ versus l^2 . [Plot to determine $\lambda/\bar{L}_c$ (intercept) and lattice strain parameter ϵ (slope) from corrected 002 linewidths β .]

XBL856-6353

Fig. 11. Change in lattice strain parameter (ϵ) with HTT.

XBL 856-6325

Fig. 12. Change in crystallite size ($\bar{L}_c$) with HTT).

XBL 856-6324

Fig. 13. Correlation of $\bar{d}_{002}$ and $\bar{L}_c$ with lattice strain parameter (ϵ).

XBL 856-6322

Fig. 14. Correlation of $\bar{d}_{002}$ with $\bar{L}_c$.

XBL 857-6450

Fig. 15. Correlation of $\bar{d}_{002}$ with weight loss ($\Delta w/w$).

XBL 857-645I

Fig. 16. Lattice strain parameter (ϵ) versus weight loss ($\Delta w/w$).

XBL 853-5960

Fig. 17. Residual hydrogen content and $\bar{d}_{002}$ versus HTT in carbons and graphite (data from [1]).

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*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*