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Author
Tidjani, M.

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DISCLAIMER

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M. TIDJANI, Jalil LACHTER, T.S. KABRE[*] and R. H. BRAGG

Materials and Molecular Research Division,
Lawrence Berkeley Laboratory,
and
Department of Materials Science and Mineral Engineering,
Hearst Mining Building,
University of California, Berkeley, CA, 94720

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[*] On leave from the Universite′ de Ouagadougou, Bourkina-Fasso.

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M. TIDJANI, Jalil LACHTER, T.S. KABRE[*] and R. H. BRAGG

Materials and Molecular Research Division,
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ABSTRACT

Grinding was performed at room temperature on a natural graphite with a perfectly ordered structure (c = 6.708 ± 0.002A), using both ceramic and steel ball-mills for periods up to 90 hours. The induced structural transformations were studied by X-ray diffraction. The interlayer spacing d_{002} was found to increase with grinding time, exhibiting plateaus around 3.375A and possibly 3.40A, and a limiting value of 3.434 ± 0.013A was reached in both ball-mills. The mean crystallite size decreased from 3000A to about 10A. The changes in d_{002} are attributed to the introduction into the initial pristine graphite structure of interstitial carbon atoms.

I - INTRODUCTION

When carbonaceous materials are annealed, a high temperature disorder-order transformation occurs above 2500C and the fully ordered material has the structure of natural graphite. This "*graphitization*" process is best characterized by diffraction experiments and what is observed is that the diffraction pattern of the disordered material consists of symmetrical *(00l)* reflections like those of graphite and, asymmetrical *(hk)* bands. This similarity to the patterns obtained from layer clays led to a model of *turbostratic* carbon [1] wherein the disorder is attributed to random layer stacking.

Both the hexagonal and rhombohedral forms of graphite are well known and the interlayer spacings of each are identical. Thus random layer stacking, which would only provide mixtures of the two phases, should not lead to an increase in the interlayer spacing d_{002}. In fact, mild grinding of hexagonal graphite leads to a partial transformation to rhombohedral graphite. The experimental finding however, is that in highly disordered synthetic carbons, d_{002}

is typically 3.44A but when the material is annealed at high temperature, d_{002} decreases ultimately reaching the 3.354A value of pristine graphite [2].

A possible explanation for the increase in d_{002} above 3.354A is that the disordered carbon, typically obtained by pyrolyzing a hydrocarbon precursor, contains hydrogen between the graphitic layers as in a graphite intercalation compound [3] and hence graphitization would consist of the thermal decomposition of an intercalation compound. This hypothesis has been the subject of a recent criticism by KAWAMURA and BRAGG [4]. These authors showed that removal of intercalated hydrogen could at most contribute a decrease of the order of 0.01A in the interlayer spacing. The decrease in the interlayer spacing encountered during the heat-treatment of pitch cokes was thought to be related to the annealing of point defects , i.e., vacancies and interstitial carbon atoms, previously present in the pitch coke structure.

While mild grinding does not alter the interlayer spacing in graphite [5], the effect of severe grinding has not been studied in detail. In this work, initially pristine graphite was

disordered by grinding in a vibratory ball-mill. Since the interlayer spacing can be increased by the formation of intercalation compounds [6], two kinds of ball-mills were used to determine the nature and quantity of the impurities introduced during the grinding and their effect, if any, on the interlayer spacing.

II. EXPERIMENTAL PROCEDURES

The grinding experiment was conducted on a natural polycrystalline graphite supplied by the Superior Graphite Company, (8500 graphite, c = 6.708A and a = 2.461A) for times up to 90 and 62 hours in ceramic and steel ball-mills respectively. The vibratory mill (Schutz O'Neil Co.) driven by a D.C. motor (General Electric, 1725 RPM) uses cylindrical ball-mills (base diameter 9cm, height 10cm) containing ceramic and steel balls 1.8cm to 2.5cm in diameter. The charge is constant and equals 14 gr.

For diffraction measurements, the dimensions of the samples (pressed pellets) were chosen according to the geometry of the incident beam and the absorption coefficient of the graphite to allow a maximum incident intensity on the sample surface and obtain a maximum diffracted intensity. The X-ray diffraction patterns were recorded with a Diano XRD-5 commercial diffractometer using CuK_α radiation and pulse height discrimination for partial monochromatization. Recording was done either continuously or by fixed counts at given angular increments. Major corrections were performed on the line profiles , i.e., low specimen absorption, Rachinger, instrumental broadening, Lorentz polarization factor and atomic scattering factor corrections. All possible interlayer reflections were recorded, (002), (004), (006), (008) except for the most severely ground samples where the higher order reflections became too weak to be recorded. In the extreme cases, only the (002) peak was observable.

The chemical analysis of each specimen including the initial material were carried out by combustion in oxygen at 950C using an elemental analyzer.

III. RESULTS

The Nelson and Riley extrapolation function was used for an accurate determination of d_{002} for each grinding time. The results shown on Figure 1 depict d_{002} versus grinding time for the ceramic and steel ball-mills. It can be seen that grinding in either ball-mill introduces an appreciable change in d_{002}. For both cases, d_{002} increased continously from 3.354A to a limiting value 3.434 ± 0.013A. A major point to be noted is the occurence, in both cases, of a plateau corresponding to a value of d_{002} around 3.37A. Moreover, there is some indication of a plateau for d_{002} at 3.40A in the data for the ceramic ball.

The nature and the quantity of impurities introduced during the grinding are shown in Table 1.

IV. DISCUSSION

In the early fifties, BACON [7] reported that grinding of graphite leads to a reduction of the crystalline perfection, and an increase of the interlayer spacing d_{002}. His interpretation of the results involves a model of misalignment of the layer planes. NAKAMIZO, HONDA and INAGAKI [8] found similar results, i.e., d_{002} increases with grinding time. On the basis of Raman spectroscopy measurements, these authors attributed the change observed in d_{002} to the introduction of structural defects whose nature is not discussed. BACON's data are not in quantitative agreement with the present results. However, NAKAMIZO, HONDA and INAGAKI obtained values of d_{002} which are in agreement with the present work when the time scale is adjusted appropriately. Indeeed, grinding rates may vary considerably according to the nature of the ball-mill, the speed and the type of vibration, the charge, etc....[9]. An adequate scale modification along the grinding time axis leads to a superimposed curve as shown on Figure 1.

It has been shown that light grinding of a perfectly ordered graphite crystal leads to creation of rhombohedral sequences which are characterized by the (012) and (015) lines in the X-ray diffraction pattern [7]. These lines are not observed even for the samples ground for very short times. Because of the severe grinding used to conduct the present investigations, the hexagonal-rhombohedral transformation

probably takes place at an early stage of the experiment i.e for grinding times shorter than 1 hour.

The results clearly show that severe grinding converts pristine graphite into a material structurally identical with the disordered material obtained in pyrolyzing hydocarbons, e.g. pitch coke. A surprising finding is that a plateau is also found at 3.37A, in addition to the plateau at 3.434A. In both studies of the annealing of artificial carbons via changes in the interlayer spacing and lattice parameters changes of graphite due to fast neutron irradiation, plateaus corresponding to the same values of d_{002} , i.e., 3.37A and 3.44A were reported [2,10]. In a recent paper, LACHTER and BRAGG [11] established the unequivocal correlation of the steps observed with interstitial carbon atoms. Thus disorder due to grinding or irradiation produces the same steps, and these are the same as those observed in annealing. The chemical analyses revealed the presence of iron in the samples ground in the steel ball-mill and silicon in the samples ground in the ceramic ball-mill. It is well known that many chemical species can be inserted between the layer planes in graphite to form graphite intercalation compounds [6]. One might then argue that an increase in the interlayer spacing of the ground samples could be due to the intercalation of either iron or silicon in the initial graphite structure. However, the random variation of iron and silicon content with grinding time on the one hand, and the superimposition of the data corresponding to two different ball-mills on the other hand, rule out the hypothesis of an intercalated compounds of these elements. Therefore, the steps observed in the interlayer spacing of the ground samples must be attributed to other interstitial species, namely carbon atoms.

V - CONCLUSION

In conclusion, it has been shown that interlayer spacings of pristine graphite (d_{002} = 3.354A) ground in different ceramic and steel mill-balls increases stepwise and by appropriate time scaling superimpose on a single curve displaying plateaus corresponding to interplanar distances of 3.37A and 3.44A, and possibly 3.40A. These plateaus are attributed to the introduction into the structure of the initial material of interstitial carbon atoms. The phenomenon of stepwise increases during disordering or stepwise decreases during ordering bears a strong resemblance to staging in graphite intercalation compounds.

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IMPURITIES CONCENTRATION		
-	STEEL BALL-MILL	CERAMIC BALL-MILL
GRINDING TIME [HOURS]	IRON [%]	SILICON [%]
0	0.012	-
12	0.379	-
16	0.602	-
20	0.411	-
24	1.210	-
28	1.870	-
30	-	0.0659
32	1.320	-
35	-	0.0170
45	1.850	0.0782
50	-	0.0890
55	-	0.1830
62	4.160	-
65	-	0.2830
75	-	0.1060
90	-	0.1010

TABLE 1
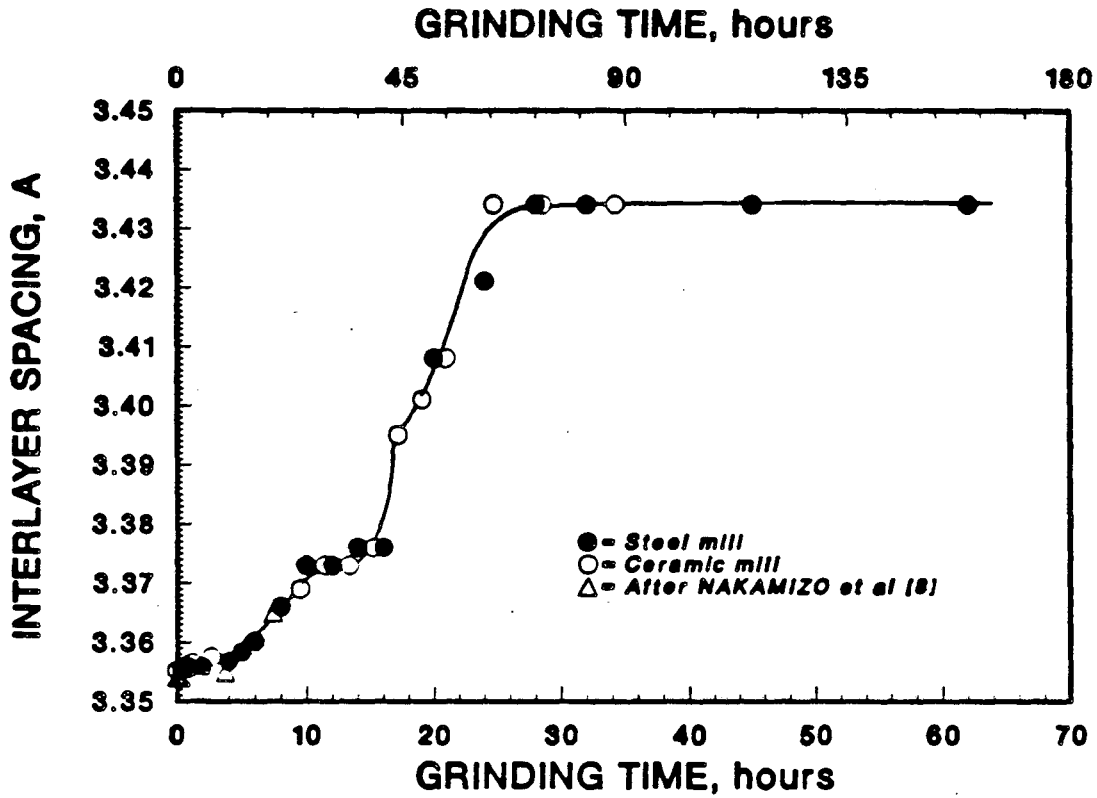
GRINDING TIME, hours

FIGURE 1 : Interlayer spacing d_{002} as a function of grinding time for ceramic ball-mill (a), steel ball-mill (b), and after NAKAMIZO's et al [7] (c).

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