JOURNAL OF MATERIALS SCIENCE LETTERS 6 (1987) 872–874

X-ray analysis of the effect of grinding on some heat-treated carbons

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The effects of grinding on the structure of natural graphite and graphitized polyvinyl chloride coke have been reported by Inagaku *et al.* [1]. In this letter, we report the effects of slight grinding on the crystal structure of heat-treated carbons of varying degrees of graphitization. An X-ray diffraction method has been used for the analysis. Details of sample preparation, heat treatment and other experimental details have been published elsewhere [2, 3]. The samples used for grinding include mesophase pitches heat treated at 2400 and 2700° C (HTT) for various residence times (RT). Values of the graphitization index, (GI), defined as $[I(10.0) + I(10.1)]/I(10.2)$, where I is the intensity of reflections, for the samples before grinding are listed in Table I. The samples were ground manually in an agate mortar. As the interest of this investigation was to analyse the effects of slight grinding, the grinding time was restricted to 10 min for all the samples. The effect of grinding on the crystal structure was analysed from values of the interplanar spacings, $d_{(00.2)}$, $d_{(11.0)}$, the half-value breadths, $b_{(00.2)}$, $b_{(11.0)}$ and the intensities of the reflections (1 0 . 0) and (1 0 . 1) estimated both before and after grinding.

The observed variation in the $d_{(00.2)}$ spacing with grinding is presented in Fig. 1. It is found that even slight grinding leads to a significant increase in the $d_{(00.2)}$ spacing of all the samples. It is also found that the increments in the $d_{(00.2)}$ spacings of samples heat treated at 2400° C are comparatively larger than those for samples heat treated at 2700° C. The gradual diminution in the separation between curves (iii) and (iv) in Fig. 1 further indicates that for samples heat treated at 2400° C, the effect of grinding decreased with increase in residence time. These features suggest that in heat-treated carbons, with GI values ranging from 12 to 69 (Table I), even slight mechanical grinding leads to destabilization of the stacking of the hexagonal planes along the crystallographic c-axis. The extent of destabilization seems to vary with the initial degree of graphitization of the sample. For samples characterized by low GI values, the extent of destabilization is low. This view is supported by the results obtained on commercially avialable ultra-F purity graphite characterized by a GI value of 5. It was found that in this sample, even 180 min grinding did not introduce any significant change in the $d_{(00.2)}$ spacing. Inagaku *et al.*'s results [1] also show that the change in the $d_{(00.2)}$ spacing was very slight after 30 h of grinding on natural graphite.

Comparison of the $d_{(11.0)}$ vaues of samples both before and after grinding showed that the basal plane parameter was not significantly altered by grinding. Even for samples characterized by comparatively high GI values, the change in $d_{(11.0)}$ value was not significant. The strikingly anisotropic variation of the d-spacings with grinding is understandably due to the weak Van der Waal's forces existing between the planes along the c-axis and the strong covalent bonds in the ab-plane.

TABLE I Graphitization index (GI) of samples before grinding

HTT (°C)	Residence time (min)	GI
2400	10	69
	60	31
	300	9
2700	10	49
	60	24
	150	12

Variations in the half-value breadths of the reflections (0 0 . 2) and (1 1 . 0) due to grinding are shown in Fig. 2a and b, respectively. Both the reflections exhibit broadening, indicting that grinding leads to introduction of microstrain and/or reduction in the crystallite dimensions. As in the case of the d-spacings, samples heat treated at 2400° C are found to manifest a higher broadening than those heat treated at 2700° C, indicating that the effects of grinding are larger for samples with large GI values.

In addition to the changes in the d-spacing and b values, grinding was also found to introduce variations

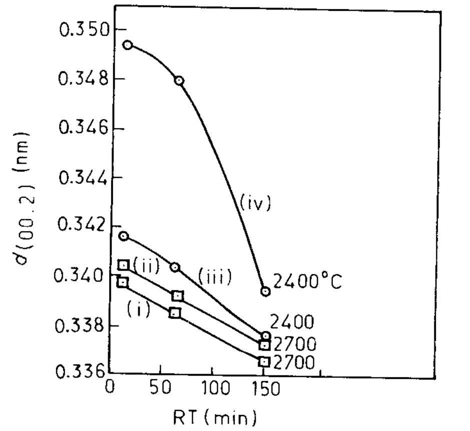

Figure 1 Variation of $d_{(00.2)}$ spacing with grinding. Curves (i) and (iii) correspond to values before grinding, and (ii) and (iv) to those after grinding.

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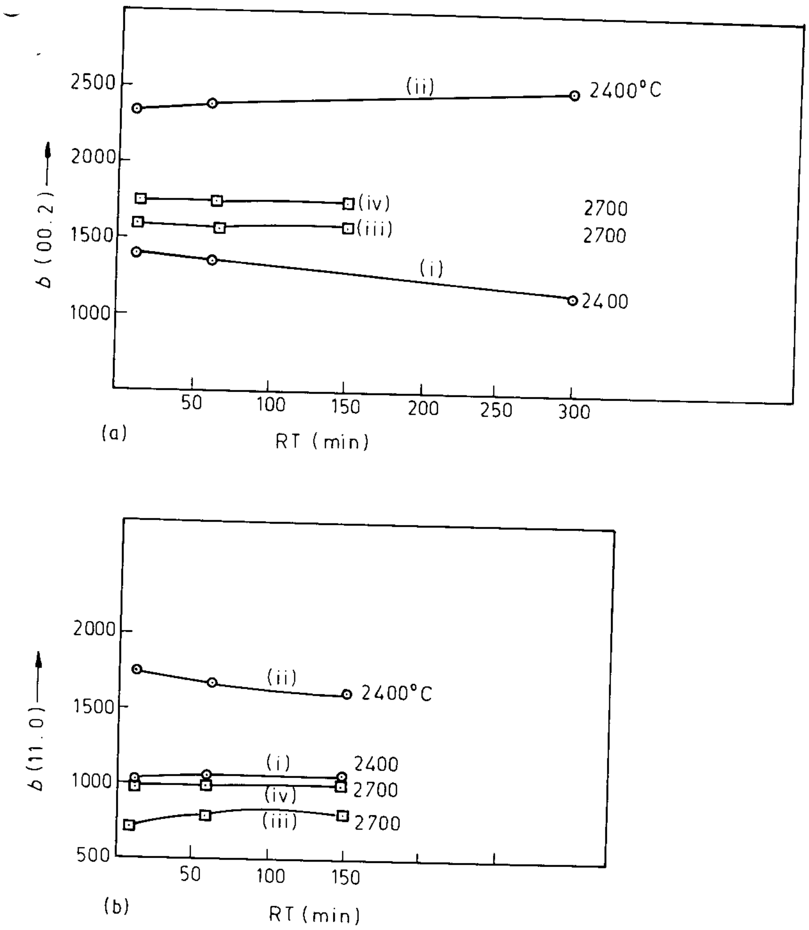

Figure 2 Variation in the half-value breadth, b, of the reflections (a) (0 0 . 2) and (b) (1 1 . 0). The b values are on an arbitrary scale. Curves (i) and (iii) correspond to the before grinding state and (ii) and (iv) to the after grinding state, respectively.

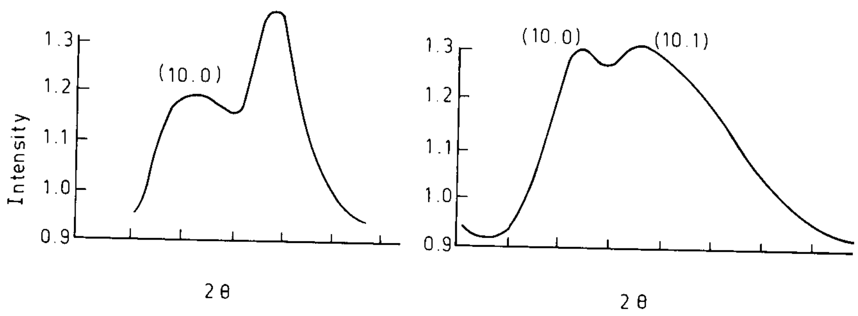

Figure 3 Intensity distribution of the reflection (1 0 . 0) and (1 0 . 1) (a) before and (b) after grinding. The intensities are on an arbitrary scale.

in the intensity distributions of the (1 0 . 0) and (1 0 . 1) reflections. A typical example of the observed variation is shown in Fig. 3. It may be pointed out that for the ultra-F purity graphite, I(1 0 . 1) > I(1 0 . 0) (Fig. 4) and in poorly graphitized or turbostatic structures, I(1 0 . 1) ≤ I(1 0 . 0) [4]. The observed reduction in the peak intensity of the (1 0 . 1) reflection may, therefore, be interpreted as a transition from a "more-ordered" to a "less-ordered" state, induced by grinding.

Based on these results it may be concluded that mechanical grinding leads to (i) destabilization of the stacking of the hexagonal planes and a consequent reduction in the three-dimensional order and (ii) introduction of microstrain and/or reduction in

Figure 4 Portion of the X-ray diffraction pattern from ultra-F purity graphite.

crystallite dimensions. These effects are less for samples with an initially high degree of graphitization.

Acknowledgement

The authors thank Dr B. C. Pai for supplying the mesophase carbons, M/s Graphite India, Bangalore, for heating the specimens, and also Dr A. K. Singh for providing the ultra-F purity sample.

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Received 29 January and accepted 4 March 1987