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Effective Debye–Waller parameter of carbons

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The effective Debye–Waller parameters, B_{eff}, were determined along the c- and a-axes on two kinds of coke and a thermal black with different heat-treatment temperatures. From B_{eff} values at room temperature and around 90 K, the dynamic component, B_{d}, and the Debye temperature, θ_{D}, for the thermal vibration of atoms, and the static component, B_{s}, due to static displacement of atoms, were determined separately. The development of graphite structure detected by the decreases in interlayer spacing, $\bar{d}_{002}$ and the growth of crystallites caused decreases in both B_{d} and B_{s}. The thermal black had a much larger B_{d} and B_{s}, which was probably caused from retention of its spherical particles even after heat-treatment at high temperatures. The Debye temperature for the in-plane vibration, $[\theta_{\mathrm{D}}]_a$, increased remarkably with the decrease in $\bar{d}_{002}$, and that for the out-of-plane vibration, $[\theta_{\mathrm{D}}]_c$, increased slightly, which corresponded to a remarkable increase in anisotropy with heat treatment. The Debye temperatures showed apparent dependences on B_{s} which could be extrapolated to the Debye temperatures along a- and c-axes for the single crystal graphite at $B_{\mathrm{s}} = 0$. The present results on Debye–Waller parameters agree with the results on structural studies obtained by X-ray diffraction and high resolution electron microscopy.

1. Introduction

The effective value of the Debye–Waller parameter, B_{eff}, is determined from observed diffraction intensities, $I_{\mathrm{obs}}(h\,k\,l)$, by using the following relation,

$$\ln[I_{\mathrm{obs}}(h\,k\,l)/I_{\mathrm{calc}}(h\,k\,l)] = \ln(k) - 2B_{\mathrm{eff}} \sin\theta^2/\lambda^2 \quad (1)$$

where $I_{\mathrm{calc}}(h\,k\,l)$ is the theoretical intensity of the $h\,k\,l$ line, k is the so-called scale factor depending on the apparatus and its conditions employed, θ is the diffraction angle of the $h\,k\,l$ line, and λ is the wavelength of the X-rays used.

It has been pointed out [1, 2] that the value of B_{eff} of a material is very different from sample to sample, depending mainly on the physical state of the sample. One of the present authors (M.I.) proposed the use of B_{eff} as one of the characterization parameters of powder materials, by showing its remarkable change with grinding and by relating it to the so-called lattice strain determined from the broadening of diffraction lines on various materials [2, 3].

The Debye–Waller parameter is theoretically related to the thermal vibration of the constituent atom [4] through the Debye temperature, θ_{D}, as follows;

$$B = (6h^2 T/mk\theta_{\mathrm{D}}^2)[\Phi(x) + (x/4)] \quad (2)$$

where

$$\Phi(x) = 1/x \int_0^x \varepsilon\mathrm{d}\varepsilon/(e^x - 1), \quad x = \theta_{\mathrm{D}}/T,$$

and where h is Planck's constant, m the mass, k the Boltzman constant, and T the ambient temperature. The Debye–Waller parameter is also related to the mean square displacement, $\langle u^2 \rangle$, of the atoms due to thermal vibration along a certain direction,

$$B = 8\pi^2\langle u^2 \rangle. \quad (3)$$

All of the results on experimental determination of B_{eff} vlaues on various materials, however, suggest that B_{eff} contains an excess component in addition to the component due to the thermal vibration of atoms, because values of B_{eff} depend strongly on the state of the materials, and θ_{D} calculated from the B_{eff} is always lower than that determined from the specific heat [1, 2, 5, 6]. The component due to the thermal vibration can be called the dynamic component of displacement. The excess component, on the other hand, is supposed to be due to the static displacement of atoms from their equilibrium positions in the crystal structure, associating with various defects including the surface.

In the previous paper [7], the B_{eff} values of palladium metal powders with different particle sizes were determined, and were successfully divided into two components B_{d} and B_{s}, the former, B_{d}, being due to thermal vibration and the latter, B_{s}, to static displacement of atoms.

The assumptions which underlay the procedure for the separation of B_{d} and B_{s} were that B_{eff} is a simple sum of two components, B_{d} and B_{s}, the dynamic component B_{d} is expressed by Equation 2, and the static component B_{s} is temperature independent.

A relation was observed between B_{s} and θ_{D}, which could be extrapolated to the θ_{D} value for the single crystal at $B_{\mathrm{s}} = 0$. These results suggested the importance of the static component B_{s} in B_{eff} for the characterization of structure perfection of polycrystalline materials, as well as for the evaluation of Debye temperature, θ_{D}, from X-ray intensities.

In the present work, carbon materials were selected as samples. The structure of carbons had been well studied by different techniques, such as X-ray

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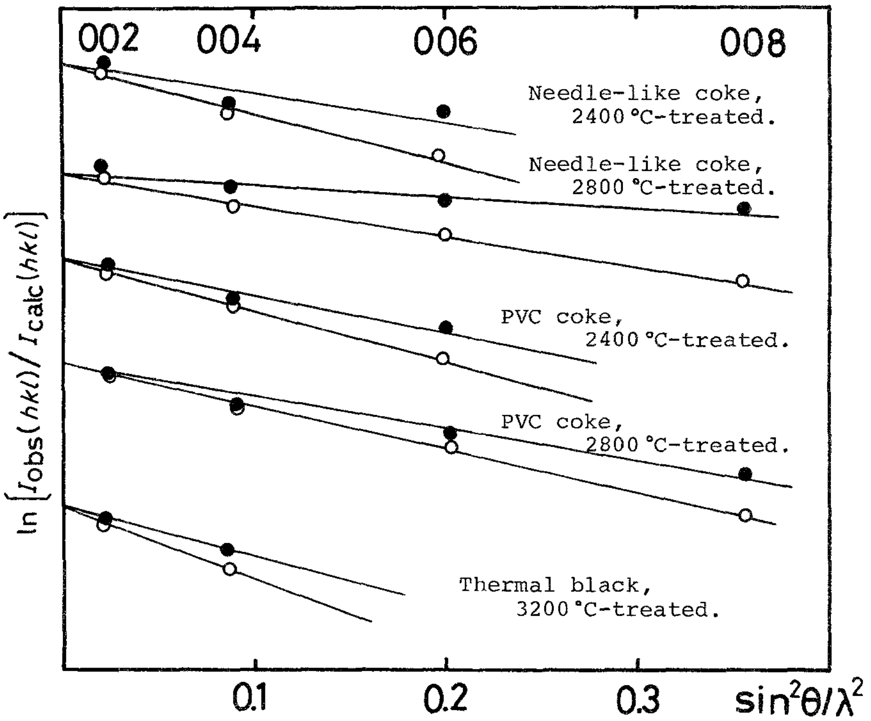

Figure 1 Plots of ln $[I_{\mathrm{obs}}(h\,k\,l)/I_{\mathrm{calc}}(h\,k\,l)]$ against sin θ^2/λ^2 on three carbon samples. ● ~90 K. ○ Room temperature.

diffraction [8], high resolution electron microscopy [9, 10], Raman spectroscopy [11], etc, and known to change with heat treatment. The elemental structural unit of these carbon materials is a graphite-like hexagonal network of carbon atoms (basal plane) with strong anisotropy. Therefore, it was necessary to evaluate Debye–Waller parameters along the c-axis of graphite (out-of-plane mode of displacement) and those along the a-axis (in-plane mode), separately.

2. Experimental techniques

2.1. Samples

Three kinds of carbons were used as starting materials; a coke prepared from polyvinylchloride by carbonizing to 700° C in the laboratory (PVC coke), a coke supplied from an industry (so-called needle-like coke) and a thermal black with a particle size of about 300 nm. The coke powders pulverized in advance under the 325 mesh sieve ($< 44\,\mu$m) were heat-treated at 2000, 2200, 2400, 2600, 2800 and 3000° C for 30 min in a flow of argon gas. The thermal black was heat-treated at 2700, 2900, and 3200° C for 30 min.

On each sample, the average interlayer spacing, $\bar{d}_{002}$, and crystallite thickness along the c-axis, L_c, were determined from 0 0 2 and 0 0 4 diffraction profiles which were measured by scanning the goniometer at a rate of $\frac{1}{4}$° min^{-1}. An internal standard of silicon was used.

2.2. Determination of B_{eff} along the c-axis

The integrated intensities of 0 0 l diffraction lines, I_{obs} (0 0 l), were measured at two ambient temperatures, room temperature and about 90 K, by a step-scanning technique with a step width of 0.05° in 2θ and a fixed time of 40 sec. The details of the determination of integrated intensisites were reported previously [7]. Nickel-filtered CuKα radiation and a scintillation counter were used.

From the slopes of the linear relations between $\ln[I_{\mathrm{obs}}(0\,0\,l)/I_{\mathrm{calc}}(0\,0\,l)]$, and $\sin\theta^2/\lambda^2$, the B_{eff} values were determined using Equation 1. Examples of plots of $\ln[I_{\mathrm{obs}}(0\,0\,l)/I_{\mathrm{calc}}(0\,0\,l)]$ against $\sin\theta^2/\lambda^2$ are shown in Fig. 1. On the coke samples heat-treated below 2400° C, the 0 0 8 diffraction line was too weak to be determined by the present technique and on the thermal black it was only possible to measure two lines at low diffraction angles.

From B_{eff} values at the two different temperatures, the Debye temperature along the direction of the c-axis, $[\theta_{\mathrm{D}}]_c$, and consequently the dynamic component $[B_{\mathrm{d}}]_c$ and the static component $[B_{\mathrm{s}}]_c$ in B_{eff} were calculated by using the same procedure as reported previously [7].

The accuracy of the B_{eff} value seemed to be less than 0.001 nm^2 and that of the θ_{D} value calculated from B_{eff} was about 60°. The values for thermal black had a much lower accuracy because only two diffraction lines were able to be used.

2.3. Determination of Debye temperature along the a-axis

Only the 1 1 0 diffraction line was employed, because the 1 0 0 diffraction line overlapped the 1 0 1 line. Therefore, the value of B_{eff} along the a-axis could not be determined. However, the ratio between the intensities of the 1 1 0 diffraction line measured at two different temperatures, T_{a} and T_{b}, is related to the difference in B_{eff} values, and therefore to that in B_{d} values as follows,

$$\begin{aligned}\left(\frac{\lambda^2}{\sin^2\theta}\right)\left[\frac{I_{\mathrm{obs}}(T_{\mathrm{a}})}{I_{\mathrm{calc}}(T_{\mathrm{b}})}\right] &= B_{\mathrm{eff}}(T_{\mathrm{a}}) - B_{\mathrm{eff}}(T_{\mathrm{b}}) \\ &= B_{\mathrm{d}}(T_{\mathrm{a}}) - B_{\mathrm{d}}(T_{\mathrm{b}}) \qquad (4)\end{aligned}$$

because of the assumption that B_{s} is temperature independent.

By the same procedure used for along the c-axis, the Debye temperature along the a-axis, $[\theta_{\mathrm{D}}]_a$, was determined numerically. From the θ_{D} values thus determined, the values of B_{d} along the direction of the

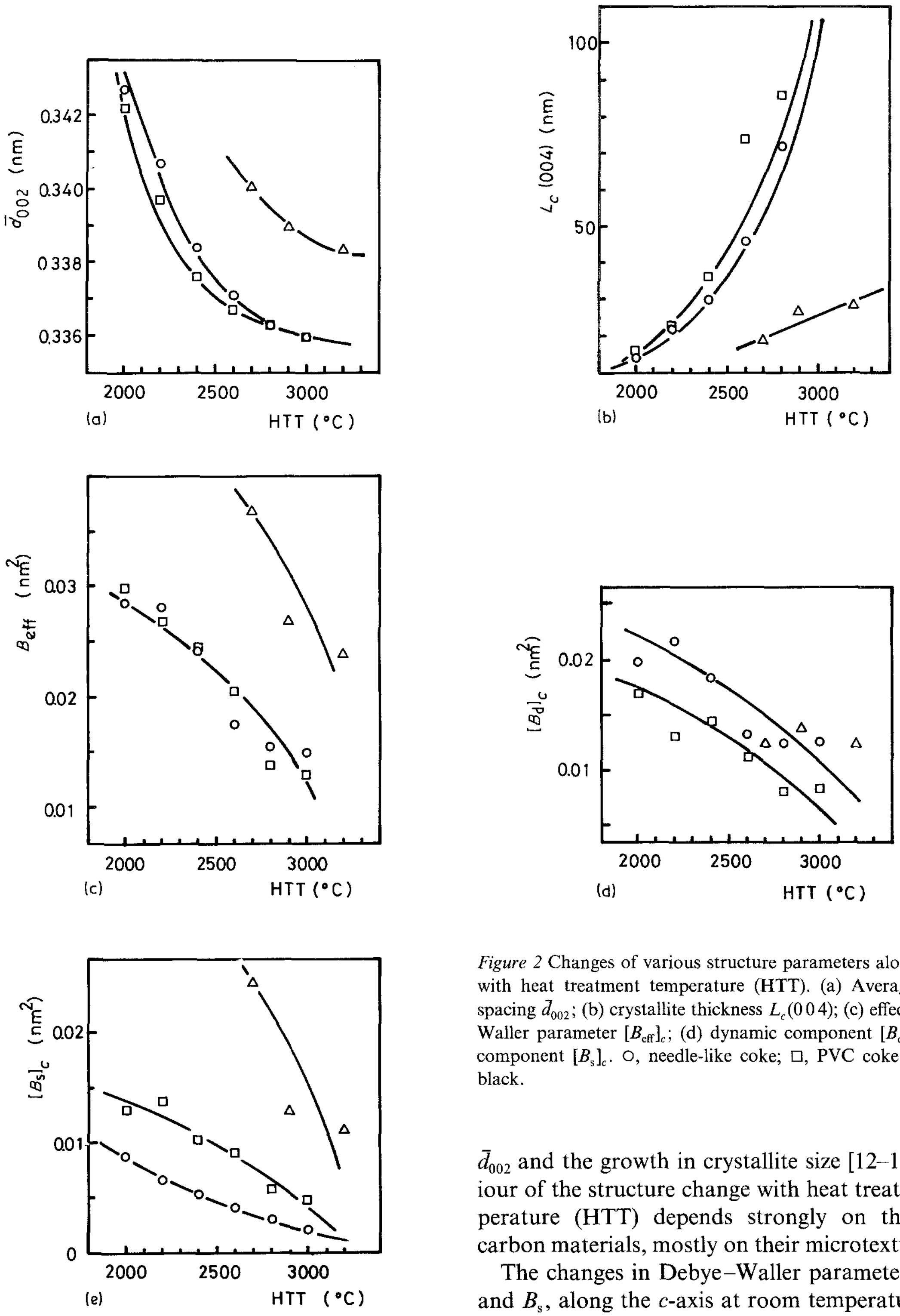

Figure 2 Changes of various structure parameters along the c-axis with heat treatment temperature (HTT). (a) Average interlayer spacing $\bar{d}_{002}$; (b) crystallite thickness $L_c(0\,0\,4)$; (c) effective Debye–Waller parameter $[B_{eff}]_c$; (d) dynamic component $[B_d]_c$; (e) static component $[B_s]_c$. ○, needle-like coke; □, PVC coke; △, thermal black.

a-axis, $[B_d]_a$, at different temperatures were calculated. The values of B_s could not be determined because B_{eff} values were not measured along the a-axis.

The relative error in the $[\theta_D]_a$ determination from the observed intensities reached 20 to 25% and strongly depended on the absolute value of θ_D. So, the accuracy in $[\theta_D]_a$ was about ±100° at θ_D of 400 K, but about 200 to 250° above 1000K.

3. Results

3.1. Changes in Debye–Waller parameters with heat treatment

The structure of carbons approaches that of graphite on heat treatment at high temperatures, being usually detected as the decrease in average interlayer spacing, $\bar{d}_{002}$ and the growth in crystallite size [12–14]. Behaviour of the structure change with heat treatment temperature (HTT) depends strongly on the starting carbon materials, mostly on their microtexture [9, 10].

The changes in Debye–Waller parameters, B_{eff}, B_d and B_s, along the c-axis at room temperature as well as in $\bar{d}_{002}$ and $L_c(0\,0\,4)$ with HTT are shown for three samples in Figs. 2a to e.

The decrease in $\bar{d}_{002}$ to the graphite value 0.3354 nm is strongly depressed in the thermal black in comparison with the cokes used, and consequently the growth of crystallite thickness, $L_c(0\,0\,4)$, is also constrained in the thermal black, as pointed out by different authors [12, 13].

The difference in structural development with HTT between the thermal black and the cokes is reflected in the changes in Debye–Waller parameters with HTT. The B_{eff} value for the thermal black is much larger than those for the cokes, which mainly stems from the large value of the static components B_s. A large value of $[B_s]_c$ (in other words, a high amount of static out-of-plane displacement) is probably due to small

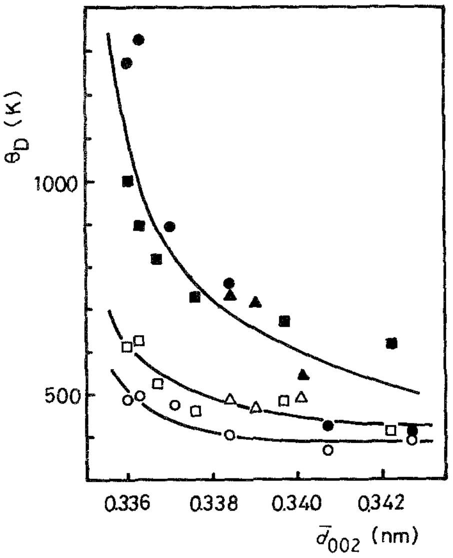

Figure 3 Changes of Debye temperatures along the *c*- and *a*-axes, $[\theta_D]_c$ and $[\theta_D]_a$, with average interlayer spacing $\bar{d}_{002}$. $[\theta_D]_c$: ○, needle-like coke; □, PVC coke; △, thermal black. $[\theta_D]_a$: ●, needle-like coke; ■, PVC coke; ▲, thermal black.

basal planes and also to retention of minute spherical particles [13, 14].

Only small differences are detected in $\bar{d}_{002}$ and $L_c(004)$, between two cokes, needle-like and PVC cokes, the latter having a slightly smaller $\bar{d}_{002}$ and larger L_c. Although both have almost the same B_{eff} value, however, the components of this value are quite different, the needle-like coke having an appreciably higher B_d value but a lower B_s value.

The changes in dynamic component, B_d, with structure development are clearly seen in the plots of Debye temperatures $[\theta_D]_a$ and $[\theta_D]_c$ against $\bar{d}_{002}$ in Fig. 3. With the decrease in $\bar{d}_{002}$ (in other words, with the development of graphite structure) the increase in $[\theta_D]_a$ is very remarkable, although a large scatter in experimental points for three samples is seen. By taking account of the large error in $[\theta_D]_a$, particularly at high values, a certain relation of $[\theta_D]_a$ to $\bar{d}_{002}$ is observed in common with three different samples. On the other hand, the increase in $[\theta_D]_c$ with the decrease in $\bar{d}_{002}$ is only small in comparison with $[\theta_D]_a$. Again the experimental points on three samples seem to fall on a certain curve. The needle-like coke seems to have relatively small values in comparison with the other two samples. In Fig. 4, the value of $[B_s]_c$ is plotted against $\bar{d}_{002}$. The B_s component decreases with decrease in $\bar{d}_{002}$, through different routes for the three samples.

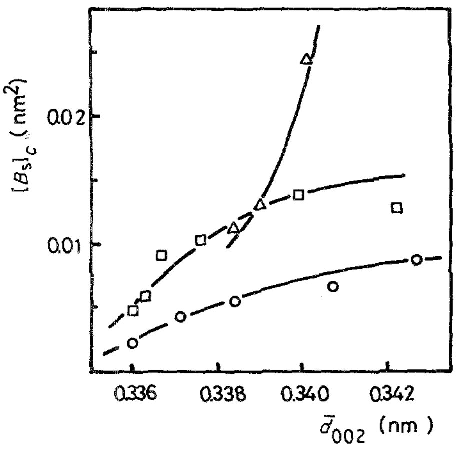

Figure 4 Changes of static component in effective Debye–Waller parameter along the *c*-axis, $[B_s]_c$, with average interlayer spacing $\bar{d}_{002}$. ○, needle-like coke; □, PVC coke; △, thermal black.

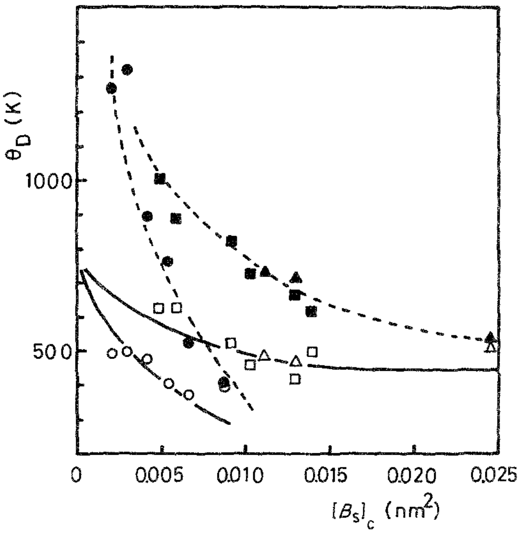

Figure 5 Relations between Debye temperatures $[\theta_D]_c$ and $[\theta_D]_a$ and static component $[B_s]_c$ on three carbon samples. $[\theta_D]_c$: ○, needle-like coke; □, PVC coke; △, thermal black. $[\theta_D]_a$: ●, needle-like coke; ■, PVC coke; ▲, thermal black.

These changes in Debye–Waller parameters can be concluded to be due to the development of graphite structure (in other words, the elimination of various defects) which has been detected mostly as a decrease in $\bar{d}_{002}$ and also the growth of crystallite; both dynamic and static components, B_d and B_s, in the Debye–Waller parameter decrease, and the decrease in B_d corresponds to the increase in Debye temperature. The increase in difference between $[\theta_D]_a$ and $[\theta_D]_c$ with decrease in $\bar{d}_{002}$ shows an increase in anisotropy of the structure and fits with the remarkable crystallite growth detected by X-ray and electron microscopy.

3.2. Relation between Debye temperature θ_D and static component $[B_s]_c$

On isotropic and monoatomic palladium metal, a relation between θ_D and B_s was observed which could be extrapolated to the θ_D value for the single crystal at $B_s = 0$. On the present carbon samples, both Debye temperatures along the *c*- and *a*-axes, $[\theta_D]_c$ and $[\theta_D]_a$, are plotted against the static component along the *c*-axis, $[B_s]_c$, in Fig. 5. In the present work, the static component along the *a*-axis, $[B_s]_a$, could not be determined, but it seems to be very small in comparison with that along the *c*-axis, $[B_s]_c$, as can be easily supposed from strong covalent bonding in the basal plane.

With decreasing $[B_s]_c$, i.e. neglecting defects in the structure, $[\theta_D]_a$ increases remarkably and $[\theta_D]_c$ only slightly. This again shows a rapid increase in anisotropy of the Debye temperature. Experimental values of both $[\theta_D]_a$ and $[\theta_D]_c$ on the needle-like coke are smaller than those on the other two samples for a constant $[B_s]_c$ value. The scattering of experimental points in this plot is much smaller than that in the relations

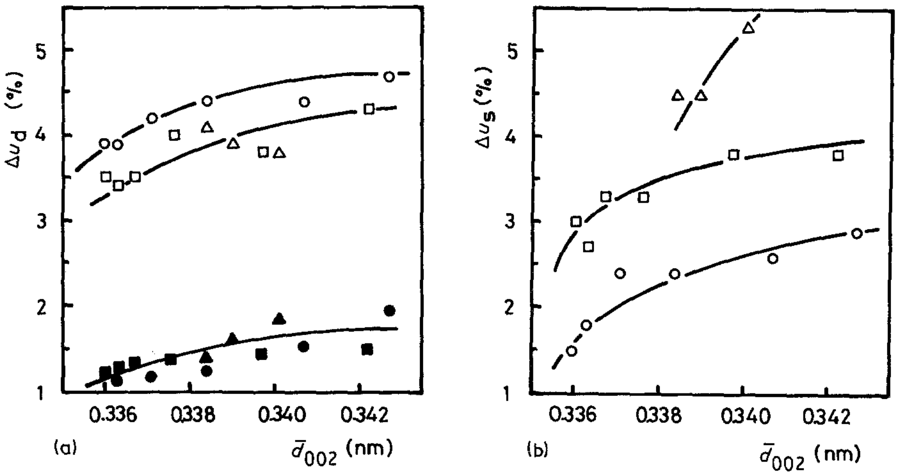

Figure 6 Changes of relative values of root mean square displacements with average interlayer spacing $\bar{d}_{002}$. (a) $[\Delta u_d]_c$, $[\Delta u_d]_a$ against $\bar{d}_{002}$. (b) $[\Delta u_s]_c$ against $\bar{d}_{002}$. ○, needle-like coke; □, PVC coke; △, thermal black.

between θ_D and $\bar{d}_{002}$. So two cokes may follow different routes of structure improvement.

The relation between $[\theta_D]_c$ and $[B_s]_c$ may be extrapolated to the values reported for the graphite single crystal, 760 K along the *c*-axis [15], although the experimental points are rather far from $[B_s]_c = 0$ and also have a large scatter. The relation between $[\theta_D]_a$ and $[B_s]_c$ suggests a value for the single crystal ($[B_s]_c = 0$) as large as 2280 K, as pointed out by Magnus [15].

3.3. Atomic displacement in carbon materials

By applying Equation 3 to the dynamic component B_d, we tried to calculate the root mean square amplitude $\langle u_d^2 \rangle^{1/2}$ of thermal vibration of carbon atoms at room temperature in the present samples. The ratio of root mean square amplitude along the *c*-axis to the average interlayer spacing $\bar{d}_{002}$, $[\Delta u_d]_c$, and that of root mean square amplitude along the *a*-axis to the *c–c* distance in the basal plane (0.1421 nm), $[\Delta u_d]_a$, were calculated, and plotted against $\bar{d}_{002}$ in Fig. 6a. The values of $[\Delta u_d]_c$ fall in the rather narrow range of 3 to 5%. The values of $[\Delta u_d]_a$ are small, about 1 to 2%, because of a strong covalent bond between carbon atoms in the basal plane. Both values decrease in $\bar{d}_{002}$.

The value of $[B_s]_c$ was converted to the root mean square displacement $\langle u_s^2 \rangle^{1/2}$ by assuming the same relation as Equation 4. The ratio of $\langle u_s^2 \rangle^{1/2}$ to average interlayer spacing, $\bar{d}_{002}$, $[\Delta u_s]_c$, is plotted against $\bar{d}_{002}$ in Fig. 6b. The ratio decreases with decrease in $\bar{d}_{002}$, but it differs from sample to sample, as discussed in relation with Fig. 2e. The thermal black has high values of about 5% and the needle-like coke has low values.

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