Thermal expansion of interlayer spacing and thermal vibrational displacement of carbon atoms in petroleum coke

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On petroleum coke heat-treated at various temperatures in the range from $\sim$ 1600 to $\sim$ 3000°C, thermal expansion of the interlayer spacing and the mean-square displacement along the c-axis due to thermal vibration of carbon atoms were measured from room temperature to $\sim$ 1050°C by means of X-ray diffractometry. The static mean-square displacement due to imperfect crystallization was also estimated for each sample.

The c-axis spacing increases linearly with temperature and the slopes had almost the same values (1.85×10^{-4} to 1.89×10^{-4} Å/°C) for all samples. The mean-square thermal vibrational displacements of carbon atoms increased almost linearly from 0.012 Å^2 at room temperature to ~ 0.047 Å^2 at 1000°C for all samples, except for the sample heat-treated at 1640°C.

A mean "free space" between the layer planes, that is the interlayer spacing minus twice the total root-mean-square displacement of carbon atoms along the c-axis direction, was obtained in consideration of the mean-square thermal vibrational displacement and the mean-square static displacement. The mean "free space" increases abruptly with decrease of c-spacing from 6.86 to 6.85 Å (heat-treatment temperatures of 1640 and 2100°C respectively), then decreases slowly and eventually again begins to increase with further decrease of c-axis spacing to 6.73 Å.

1. Introduction
It is known that the hexagonal network layer is the fundamental structure of carbon in graphitization and that the stacking order increases as the degree of graphitization develops. It has been reported [1], however, from the viewpoint of the ordering of carbon atoms in the layer, that the displacement of carbon atoms perpendicular to the layer plane from the mean position of the layer decreases with the progressive development of graphite structure. This decrease of the displacement of carbon atoms may be clarified at least partially by a study of the relative position, measured along the c-axis direction, between the carbon atoms in a mean layer plane and those in the next nearest mean layer plane.

Kellett *et al* [2] introduced the idea of a mean "free space" between the layer planes, that is the interlayer spacing minus twice the root-mean-square displacement as shown by the following equation; free space $= c_0/2 - 2\sqrt{(\overline{u_c^2})}$ and

measured the mean "free space" for the samples of spectroscopic carbon and pyrolytic carbon. But they considered only the amplitude of thermal vibration, without considering also the *static* displacement of carbon atoms along the c-axis out of the mean layer plane.

The mean-square displacement of carbon atoms $\overline{u_c^2}$ along the c-axis from the position of the mean layer plane consists of two components. One is a mean-square static displacement $\overline{u_s^2}$, and the other is a mean-square thermal vibrational displacement $\overline{u_v^2}$. Both of them can be evaluated from the integrated intensity of the 00*l* X-ray reflection, based on the assumption that the value of $\overline{u_s^2}$ is constant over a range of temperatures so long as the temperature is lower than the previous heat-treatment temperature [3]. The value of $\overline{u_c^2}$ is evaluated from the comparison of relative integration intensities of 002, 004 and 006 reflections and the value of $\overline{u_v^2}$ from the temperature-dependence of the inte-

grated intensity of 004 reflection, using the following equation [4]:

$$\overline{u_{\mathrm{v}}^2} = \beta T + \gamma/T \qquad (1)$$

where

$$\beta \equiv \frac{3}{mk}\left(\frac{h}{2\pi}\right)^2\frac{1}{\theta_{\mathrm{M}}^2}, \quad \gamma \equiv \frac{1}{12mk}\left(\frac{h}{2\pi}\right)^2$$

and θ_{M} is the characteristic Debye temperature for the sample and the value of γ can be calculated from known constants.

If the value of $\overline{u_{\mathrm{s}}^2}$ is constant, the mean "free space" varies in accordance with the temperature-dependence of the c-axis spacing c_0 and the mean-square thermal vibrational displacement $\overline{u_{\mathrm{v}}^2}$, according to the following equation:

$$\text{free space} = c_0/2 - 2\sqrt{(\overline{u_{\mathrm{s}}^2} + \overline{u_{\mathrm{v}}^2})} \qquad (2)$$

The temperature-dependence of the mean-square thermal vibrational displacement and of the mean "free space" from room temperature to $\sim 1050°$C for petroleum coke are presented in this paper.

2. Experimental

2.1. Materials

Petroleum coke heat-treated in a stream of argon gas in the range from ~ 1600 to $\sim 3000°$C and held for 15 min at the desired top temperature was used in this experiment.

2.2. Apparatus and procedure

The X-ray diffraction pattern of the powdered sample was obtained by using a diffractometer with Ni-filtered Cu K_α radiation. For the measurement of X-ray diffraction intensity above room temperature, a high-temperature furnace was attached to the diffractometer provided with an automatic temperature controller. The temperature was measured with a 0.2 mmϕ Pt-PtRh$_{13}$ thermocouple. The temperature was raised at a rate of 6°C/min in a high vacuum. The intensity of the 004 reflection was measured at temperature intervals of $\sim 150°$C from room temperature to $\sim 1050°$C; 2 to 3 wt % of tungsten was mixed in the sample as an internal standard.

The X-ray intensity was measured with a scintillation counter and pulse-height analyser. The integrated intensity of the 00l reflection was estimated from the area between the background level and the diffraction curve. The background level was drawn between the two points on the diffraction curve at a fixed interval of 2θ on either side of the peak centre.
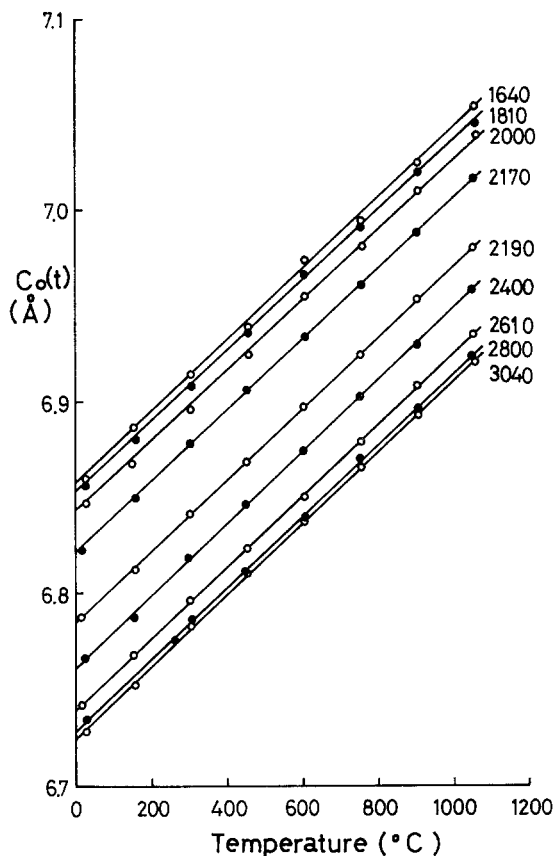
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Figure 1 Thermal expansion of c-axis spacing $c_0(t)$ of petroleum coke samples.

3. Results and discussion

As shown in Fig. 1, the c-spacing $c_0(t)$ of petroleum coke samples increases almost linearly with increase of measurement temperature t. For example, the value of $c_0(t)$ for petroleum coke heat-treated at 1810°C increases from 6.856Å at room temperature to 7.038Å at 1000°C, and the sample heat-treated at 3040°C increases from 6.729Å at room temperature to 6.913Å at 1000°C. Table I shows the value of c-axis spacing at 0°C, c_0, and the slopes of the lines in Fig. 1, calculated by least-squares method. The slope of $c_0(t)$ was obtained within a range of 1.85×10^{-4} to 1.89×10^{-4}Å/°C for all the samples.

The temperature-dependence of the mean-square displacement of carbon atoms along the c-axis due to thermal vibration $\overline{u_{\mathrm{v}}^2}$ was obtained from Equation 1 and the values of the coefficient β are shown in Table I. Fig. 2 shows the change

TABLE I

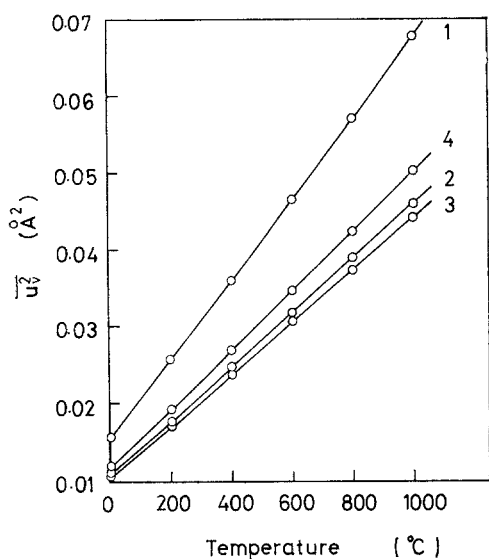| HTT (°C)	1640	1810	2000	2100	2170	2190	2400	2610	2800	3040
z_0 (Å)	6.86	6.85	6.84	6.84	6.82	6.78	6.76	6.74	6.73	6.72
Slope (Å/°C)	1.87	1.85	1.88	1.86	1.87	1.87	1.89	1.87	1.88	1.88
$\beta \times 10^5$ (Å²/K)	5.30	3.90	3.64	3.55	3.92	3.61	3.65	3.45	3.66	3.93
$\overline{u_s^2} \times 10^2$ (Å²)	5.44	3.09	2.32	1.93	2.43	2.85	2.24	1.59	0.909	0.749
Mean "free space" at room-temperature (Å)	2.90	3.01	3.05	3.07	3.03	2.99	3.01	3.04	3.08	3.08

Figure 2 Variation of mean-square thermal vibrational displacement $\overline{u_v^2}$ with temperature. 1;HTT–1640°C, 2;HTT–2190°C, 3;HTT–2610°C, 4;HTT–3040°C.

of the thermal vibrational displacement $\overline{u_v^2}$ along the c-axis with measurement temperature for petroleum cokes heat treated at 1640, 2190, 2610 and 3040°C. The value of $\overline{u_v^2}$ increases almost linearly with increase of measurement temperature.

Kellett *et al* [2] reported that the root-mean-square amplitude of vibration varied linearly with temperature above 1200°C. However, in the range from room temperature to 1050°C in the present experiments, the root-mean-square value $\sqrt{(\overline{u_v^2})}$ did not show a linearity with temperature, whereas the mean-square value $\overline{u_v^2}$ showed almost linear increase with temperature, as was expected from Equation 1 where the term βT is much larger than the second term γ/T. The value of root-mean-square displacement $\sqrt{(\overline{u_v^2})}$ due to thermal vibration for the sample heat-treated at 1640°C varies from 0.13Å at room temperature to 0.26Å at 1000°C, and that heat-

treated at 3040°C varies from 0.11Å at room temperature to 0.22Å at 1000°C.

As shown in Fig. 2, the mean-square thermal vibrational displacement of carbon atoms $\overline{u_s^2}$ seems to be almost independent of heat-treatment temperature for the samples at the same ambient temperature in the range from room temperature to 1050°C, except for the sample heat-treated at 1640°C. The difference of this sample from the others is attributed at least in part to the imperfect atomic ordering, as deduced from the absence of the 1 1 2 reflection from this sample and larger value of mean-square static displacement in the sample heat-treated at 1640°C (see Table I).
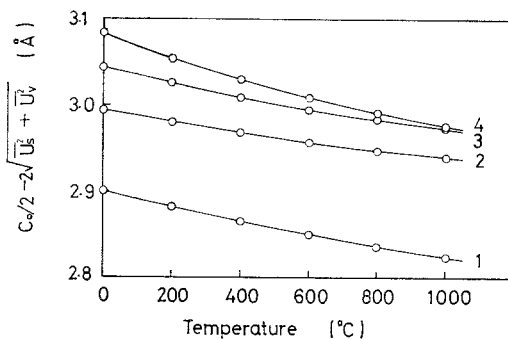

Figure 3 Variation of "free space" with temperature. 1;HTT–1640°C, 2;HTT–2190°C, 3;HTT–2610°C, 4;HTT–3040°C.

The values at room-temperature of the mean free space between the layer planes as calculated by Equation 2 are shown in Table I together with the values of $\overline{u_s^2}$, and in Fig. 3 as a function of ambient temperature for the samples heat-treated at 1640, 2190, 2610 and 3040°C. The value of the mean free space decreases with increase of the measurement temperature, although the rate of variation depends on the sample. The results indicate that the change of the interlayer spacing due to change of measure-

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ment temperature is smaller than twice the value of the root-mean-square thermal vibrational displacement. This implies that the notional thermal expansion of the thickness of each layer plane as estimated from the static displacement and the thermal vibrational displacement of carbon atoms in the layer planes, is larger than the actual thermal expansion between neighbouring two layer planes.
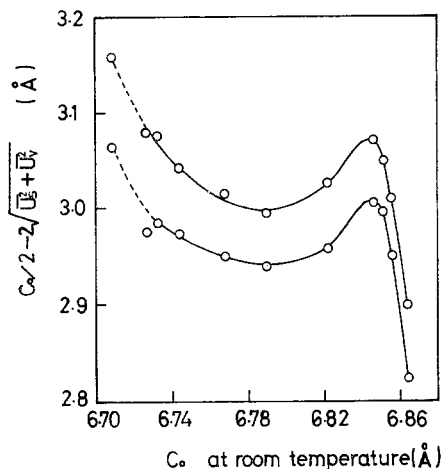

Figure 4 Relationship between "free space" and c-axis spacing c_0. Upper: "free space" at room-temperature, Lower: "free space" at 1000°C.

Fig. 4 shows the variation of the mean free spaces at room-temperature and at 1000°C with the c-axis spacing c_0 at room-temperature. The mean free space at room temperature at first increases abruptly with decrease of c_0 to show a maximum at c_0 of about 6.85Å, then decreases and begins to increase again for c_0 smaller than about 6.76Å. The dashed extrapolation of this curve is to the point corresponding to the value of the free space of ideal graphite, based on the assumption that the coefficient β can be evaluated from the mean-square displacement due to thermal vibration, 0.0098Å² at 300 K [5], and that the mean-square static displacement $\overline{u_s}^2$ is zero. The curve of the mean free space at 1000°C shows same behaviour as that at room temperature. It is seen from Fig. 4 that the difference between the mean free space at room temperature and that at 1000°C begins to increase with decrease of c_0 below 6.74Å.

The mean free space at room temperature varies from 2.90 to 3.08Å for petroleum coke samples heat-treated at various temperatures as shown in Table I. This variation may be compared with that of the mean-square static displacement of carbon atoms, $\overline{u_s}^2$. It is interesting that the mean free space increases with the development of the degree of graphitization of the samples, in spite of the fact that the mean free space between neighbouring layer planes is considerably larger than the diameter of carbon atoms and the fact that the c-axis spacing decreases with the development of the degree of graphitization.

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