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Thermal expansion of siliconated pyrolytic carbon

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The lattice and bulk thermal expansions perpendicular to the layer plane of siliconated pyrolytic carbon, PC(Si), produced by pyrolyzing a mixture of propane gas and silicon tetrachloride vapour at the deposition temperatures of 1440 to 2025° C, have been measured over the temperature ranges 20 to 550° C and 20 to 960° C, respectively. The expansion behaviours of PC(Si) are related to the density and the degree of preferred orientation of crystallites, as is the case for pyrolytic carbon without silicon "PC". At a deposition temperature of about 1700° C, the bulk thermal expansion coefficient of PC(Si) is about three times as large as that of PC.

1. Introduction

Recently many attempts have been made to improve high temperature properties of pyrolytic carbon "PC" by adding different atoms into the PC matrix by simultaneous pyrolytic deposition [1]. Siliconated pyrolytic carbon "PC(Si)" containing silicon in the PC matrix is one of the materials developed for this purpose [2, 3].

PC(Si) can be deposited on stationary substrates [2, 3] or movable substrates (using fluidized beds) [4] by a co-pyrolysis of gaseous mixtures of several kinds of hydrocarbons and chlorides of silicon. In the past few years a considerable amount of research has been concerned with properties of PC(Si), that is, deposition [2-4], structures [2-8], microhardness [3, 9, 10], oxidation [3], electrical resistivities [11], and mechanical properties [4, 12]. Moreover Bokros *et al.* examined properties of PC(Si) as a nuclear material [13] and a biomaterial [14]. The results of these investigations have revealed that PC(Si) has excellent and interesting properties compared to PC. However, only scant information has been given about high-temperature properties of PC(Si).

This paper presents an investigation of the lattice and bulk thermal expansions, perpendicular to the deposition plane of PC(Si), over the temperature ranges 20 to 550° C and 20 to 960° C, respectively.

2. Experimental procedures

2.1. PC(Si) samples

Details of the process used for preparing PC(Si) have already been described elsewhere [2]. PC(Si) was prepared by pyrolysis of a mixture of propane gas and silicon tetrachloride vapour by direct heating of the graphite substrate. The preparation conditions were as follows: deposition temperature (T_{dep}) = 1440 to 2025° C, total gas pressure = 50 Torr, partial pressure of silicon tetrachloride vapour = 13 Torr, gas flow rate = 410 cm^3 min^{-1}, and deposition time = 20 to 120 min. To compare the thermal expansion of PC(Si) with that of PC, the PC samples were similarly prepared, except that silicon tetrachloride was not added. In this case the partial pressure of silicon tetrachloride vapour is zero. The sample thickness was controlled to minimize heat-treatment effects [6, 15]. Consequently, at high T_{dep}, only thin samples were obtained.

PC(Si) used in the present experiments contains 0.02 to 4 wt % of silicon, depending on T_{dep} and increasing as T_{dep} is decreased [2] as shown in Fig. 1. For $T_{\mathrm{dep}} < 1730$° C, the greater part of silicon occurs as β-SiC [5]. The β-SiC is present as flake-like single crystals and the (111) plane of β-SiC is parallel to the (001) planes of graphite [5]. Silicon seems to form α-SiC in PC(Si) containing small amounts of silicon, prepared at high temperatures near

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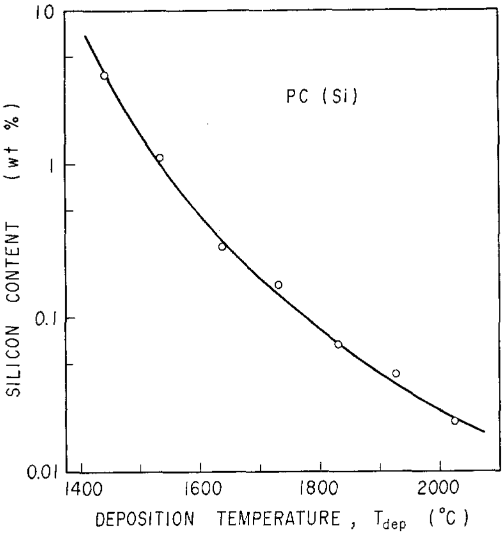

Figure 1 Silicon contents in PC(Si).

2000°C. SiC does not segregate in cone boundaries and disperses uniformly in the PC matrix [5]. In PC(Si), compared to PC, the graphite crystallites are developed, and the degree of preferred orientation of the crystallites and the boundary-fit between the crystallites are improved [6].

2.2. Density and preferred orientation measurements

In order to correlate the thermal expansion and structures of PC(Si), the density and the preferred orientation of samples prepared in this experiment were measured. The density was determined by a displacement technique using toluene, and the preferred orientation parameter, R, was measured by X-ray diffraction [16].

2.3. Thermal expansion measurements

Lattice thermal expansion, LTE, measurements, perpendicular to the deposition plane (in the c-direction), were made on flat specimens, 3 mm × 5 mm × 0.1 mm thick which had been cut from the samples. X-ray measurements were performed with the diffractometer (Rigaku Denki Ltd, SG-6) and Cu$K\alpha$ radiation. The specimens were wrapped up with an aluminium foil (0.1 mm thick) and firmly fixed in a silica sample-holder with the manganin heating element, and the temperature was measured using a thermocouple in contact with the aluminium foil. The mean interlayer distance, d, was determined from the position of the (004) reflection. The (004) peaks were recorded over the temperature range 20 to 550°C at approximately 30°C intervals. The position of the (004) reflection was corrected for the reflections of silicon powder at room temperature and of the aluminium foil at high temperatures.

The bulk thermal expansion, BTE, measurements in the c-direction were performed on specimens, usually 3 mm × 3 mm × 0.6 to 1.6 mm thick, over the temperature range 20 to 960°C. The dilatometer used in this experiment was a conventional silica tube automatic dilatometer (Shinku Riko Ltd, HPC-1500H). This was heated at a rate of 5°C min^{-1} in a vacuum furnace (1 × 10^{-3} Torr). The temperature, measured by a thermocouple in contact with the specimen, and the variation in thickness, were recorded automatically on a chart. Expansion coefficients of the specimens were corrected for the expansion of silica using the data from the International Critical Tables [17].

3. Experimental results

3.1. Density and preferred orientation

Figs. 2 and 3 represent results of the density and preferred orientation measurements, respectively, against T_{dep}. As shown in Fig. 2, PC has a minimum density at $T_{dep} \approx 1700°C$, while the density of PC(Si) does not show a minimum value and is greater than that of PC. The preferred orientation parameter, R, of PC shows a maximum value at $T_{dep} \approx 1700°C$, as shown in

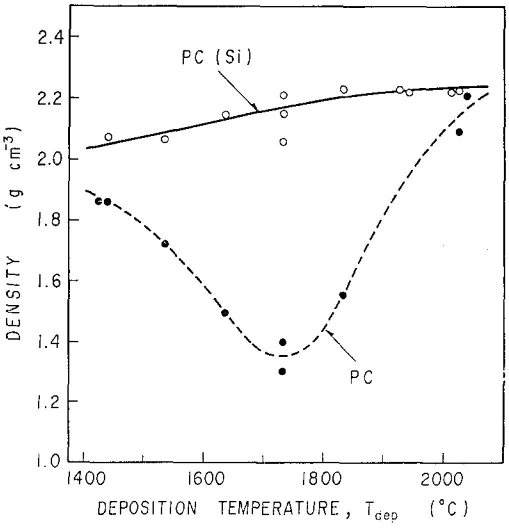

Figure 2 Densities of PC(Si) and PC.

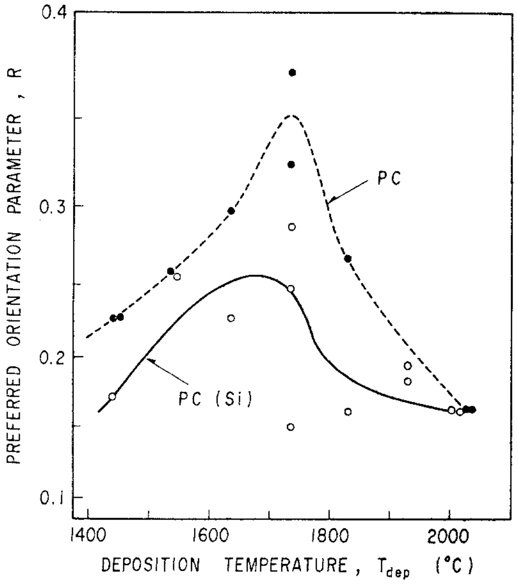

Figure 3 The preferred orientation parameters, *R*, for PC(Si) and PC.

Fig. 3, which indicates the decrease in the degree of preferred orientation and corresponds to the relation between the density and T_{dep} (Fig. 2). Similar results were obtained on PC(Si) as indicated by a solid line in Fig. 3. However, the degree of preferred orientation of PC(Si) is higher than that of PC.

3.2. Lattice thermal expansion, LTE

For PC(Si), the relation between the mean interlayer distance, *d*, and ambient temperature is shown in Fig. 4; the symbols on the figure denote the measuring points. As shown in Fig. 4, *d* increases linearly with ambient temperature. From the cooling cycle of the measurements, the same slope of the lines was obtained. The slope of the lines is independent of T_{dep} and silicon content. The mean lattice thermal expansion coefficient, α_{CL} ($\approx$ 27 × 10^{-6} °C^{-1}), is nearly equal to that of natural graphite [18].

3.3. Bulk thermal expansion, BTE

Fig. 5 shows typical results of BTE (fractional change in thickness, $\Delta L/L$) of PC(Si) prepared at T_{dep} = 1440 and 1925°C. Similar results were obtained for all samples, PC(Si) and PC, measured in the present experiments.

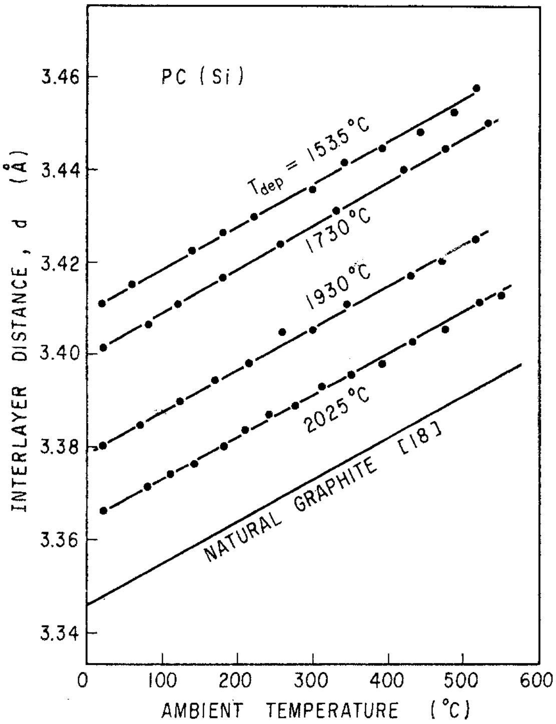

Figure 4 Temperature dependence of the interlayer distance, *d*, of PC (Si).

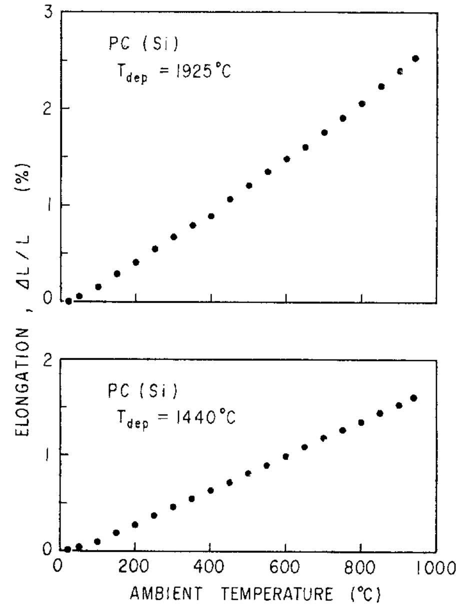

Figure 5 Temperature dependence of the elongation in the *c*-direction of PC(Si).

The mean bulk thermal expansion coefficients, α_{CB} (20 to 960°C), of samples were calculated from these results and plotted in Fig. 6 against T_{dep}. Each data point shown in Fig. 6 is a mean of the measured values for two or three specimens. The bars indicate the range of variation of

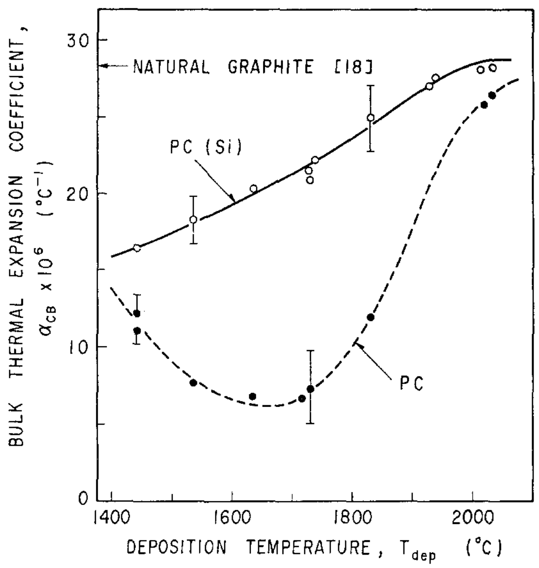

Figure 6 The bulk thermal expansion coefficient of PC(Si) and PC.

the data for different specimens. For PC(Si), α_{CB} increases with T_{dep} and reaches a value of the heat-treated PC [19] whose thermal expansion behaviour is very similar to that obtained for a single crystal of graphite [18]. On the other hand, α_{CB} for PC has a minimum value at $T_{dep} \approx 1700°C$. The variation of the expansion coefficient with T_{dep} for PC corresponds approximately to that of the density (Fig. 2).

4. Discussion

4.1. Lattice thermal expansion, LTE

Kellett and Richards [20] examined LTE in the *c*-direction of a number of carbons and graphites, having different *p*-values (the proportion of disoriented layers; $p = 0$ for natural graphite, $p = 1.0$ for hemicellulose), and showed essentially similar curves translated parallel to the *d*-axis as reported by other authors [21-24]. Values of α_{CL} seem to be in the range of 25 to 29 × $10^{-6}°C^{-1}$ [25]. Kellett and Richards [20] concluded that the increase in *d* for a given temperature rise was not significantly dependent on stacking disorder. At the present time, it is believed that the thermal expansion of any carbon material, whether it is fully graphitic or turbostratic, depends primarily on the degree of preferred orientation of the crystallites in the material and internal accommodations.

With regard to PC there are very few data on LTE. The measurements reported by Lowell [24] and Kellett *et al.* [26] were limited to highly oriented PC which had been heat-treated at high temperatures of about 2500 to 3100°C. Their results on the heat-treated PC were in good agreement with those for carbons and graphites. More recently, Pellegrini [27] measured LTE in the *c*-direction of various as-deposited PC prepared in a fluidized bed, and reported that LTE of the PC was structure sensitive and depended on the stacking height. In his experiments α_{CL} (10 to 1200°C) increased from 18 × $10^{-6}°C^{-1}$ for PC (T_{dep} = 1650°C) with small crystallites and low density (1.55 g cm^{-3}) to 24 × $10^{-6}°C^{-1}$ for PC (T_{dep} = 2100°C) with large crystallites and high density (2.03 g cm^{-3}). He also examined the relations between α_{CL} and various structures, and found that α_{CL} was linearly related to the apparent crystallite size in the *c*-direction L_c, α_{CL} increasing with L_c. On the other hand, in the relation of *d* versus ambient temperature, the lower slope than that of natural graphite was observed in a natural graphite-glassy carbon system, in which LTE of the natural graphite flakes embedded in the glassy carbon matrix is suppressed with respect to the natural graphite powder [28]. This behaviour was interpreted to have been caused by the constraint of the large *c*-axis expansion of the natural graphite flake by the isotropic small expansion of the glassy carbon matrix.

The low temperature PC, especially prepared in a fluidized bed, seems to contain nongraphitic parts, such as amorphous carbons and single hexagonal network-layers [27, 29, 30]. These nongraphitic parts may suppress LTE of the low temperature PC. Amounts of the nongraphitic parts can be estimated from the density measurements [30].

As shown in Fig. 4, the temperature dependence of LTE of PC(Si) is similar to that of carbon materials [20-24]. As reported in a previous paper [6], structures of PC(Si) prepared at low T_{dep} correspond to those of PC prepared at high T_{dep}. Therefore, it seems likely that PC(Si) used here does not contain large amounts of nongraphitic parts.

4.2. Bulk thermal expansion, BTE

Many researchers [19, 31-36] measured BTE of as-deposited and heat-treated PC, and discussed the relation between α_{CB} and the preferred orientation. The thermal expansion coefficient, α, of a sample of polycrystalline graphite can be given by the expression of Bacon [37]:

$$\alpha = R\alpha_a + (1 - R)\alpha_c\,, \qquad (1)$$

where α_a and α_c are the single-crystal expansion coefficients in the a- and c-directions, respectively, and R is a preferred orientation parameter. In the case of the thermal expansion in the c-direction, R can be expressed as [38]

$$R = \frac{\int_0^{\pi/2} I(\omega) \, . \, \sin^3\omega \, . \, d\omega}{\int_0^{\pi/2} I(\omega) \, . \, \sin\omega \, . \, d\omega} \, . \quad (2)$$

Since $I(\omega) \approx \cos^n\omega$, we obtain

$$R = 2/(n + 3) \, . \quad (3)$$

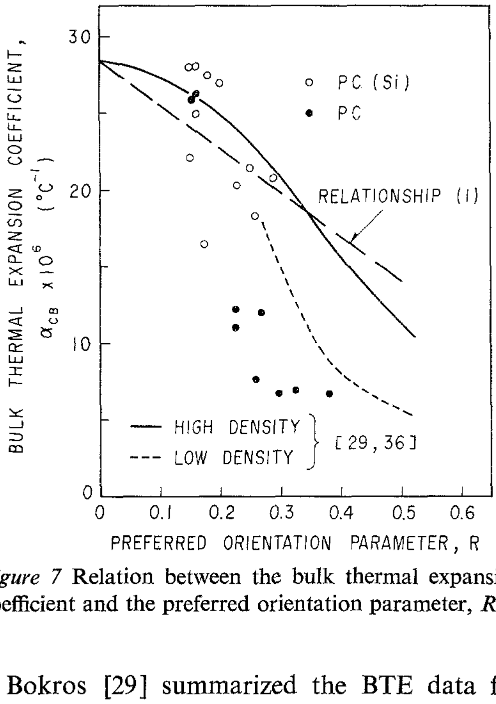

Figure 7 Relation between the bulk thermal expansion coefficient and the preferred orientation parameter, *R*.

Bokros [29] summarized the BTE data for PC, and showed the experimental relations (Fig. 7) for high (1.8 to 2.2 g cm^{-3}) and low (1.2 to 1.7 g cm^{-3}) densities of PC, with solid and dotted lines, respectively. Fig. 7 includes the present experimental data for PC(Si) and PC, and also Equation 1 with a broken line. The data for $R < 0.2$ show a positive deviation, while for $R > 0.2$ there is a negative deviation from the relationship. Such deviations may be interpreted in terms of the behaviours of pores and soot particles and by the elastic restraint [38], no detailed interpretation of which is given here.

Little has been known about the relation between α_{CB} and T_{dep}. As shown in Fig. 6, the relation between α_{CB} and T_{dep} is quite similar to that between density and T_{dep} (Fig. 2). Consequently, one can obtain Fig. 8, in which α_{CB} of PC(Si) and PC is plotted against the density. In Fig. 8, the data after Price *et al.* [36] are also included. This relation implies that the thermal expansion behaviours of both PC(Si) and PC are nearly identical, but vary markedly above and below the densities of 1.7 to 1.9 g cm^{-3}. This range of density seems to correspond to the occurrence of the variation between the solid and dotted lines shown in Fig. 7. Figs. 7 and 8 indicate that α_{CB} depends primarily on the density and secondarily on the degree of preferred orientation.

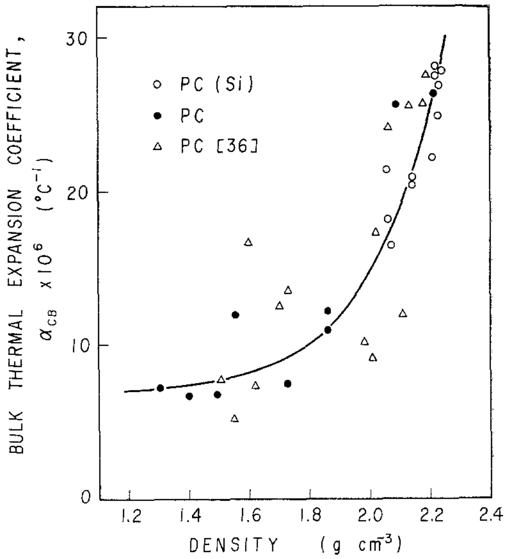

Figure 8 Relation between the bulk thermal expansion coefficient and density.

The effect of SiC on the thermal expansion of PC(Si) is negligibly small, because of its small expansion coefficient (3 to 5 × 10^{-6}°C^{-1}) [39, 40]. This was checked by using the Turner equation [41], considering PC(Si) as the composite material composed of PC and SiC.

5. Conclusions

1. The mean lattice thermal expansion coefficient of PC(Si) is about 27 × 10^{-6}°C^{-1} in the temperature range of 20 to 550°C and is nearly equal to that of natural graphite.

2. The mean bulk thermal expansion coefficient, α_{CB}, (20 to 960°C) of PC(Si) increases almost linearly with T_{dep} from 16.4 × 10^{-6}°C^{-1} at 1440°C to 28.2 × 10^{-6}°C^{-1} at 2025°C. For $T_{dep} \approx$ 1700°C, α_{CB} of PC(Si) is about three times as large as that of PC.

3. The thermal expansion of PC(Si) seems to depend strongly on the density, as is the case for PC.

4. The expansion behaviour of PC(Si) prepared at relatively low T_{dep} corresponds to that of PC prepared at high T_{dep}.

5. The expansion behaviour varies markedly above and below the densities of 1.7 to 1.9 g cm^{-3}.

6. The effect of β-SiC among the crystallites on the expansion behaviour of PC(Si) can be neglected in the estimation of the thermal expansion coefficient.

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