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Thermal properties of chemical vapour-deposition SiC–C nanocomposites

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The relationship between the thermal properties and the microstructure of chemical vapour-deposition (CVD) SiC–C nanocomposites, covering the entire composition range from SiC to C, was investigated after measuring thermal conductivity and thermal expansion. The samples were prepared under deposition temperatures (T_{dep}) of 1673 and 1773 K and total gas pressure (P_{tot}) of 40 kPa. The thermal conductivity of CVD SiC–C nanocomposites decreased as C content increased. For the deposits containing 24.3 to 71 mol % C prepared at $T_{dep} = 1773$ K, some parts of the C phase formed a layered structure having its plane parallel to the deposition surface. This arrangement reduced the thermal conductivity in the direction perpendicular to the deposition surface to a much lower value. The CVD C and CVD C–SiC containing < 1.5 mol % SiC showed strong anisotropic thermal expansion. However, the thermal expansion of CVD SiC–C nanocomposites having a C content up to about 70 mol % was isotropic and nearly equal to that of CVD SiC. The low preferred orientation and the low modulus of elasticity of the C phase may be reasons for these results.

1. Introduction

Materials described as 'thermal stress relaxation-type functionally gradient nanocomposites', composed of SiC (with excellent oxidation resistance and high-temperature strength) and composed of C (with good thermal shock resistance), have been studied as possible materials for thermal barriers of the space plane [1–3]. SiC/C functionally gradient nanocomposites are prepared by gradually changing the compositions from SiC to C from one surface to the other, and the resulting composites are characterized by their nanometre-size dispersion phase dispersed within the matrix.

The chemical vapour-deposition (CVD) technique is an effective approach for fabricating these composites through a co-deposition process using multi-component gas reactions [4, 5]. The main advantage of the CVD technique is that it allows relatively easy control of the composition and microstructure of the deposited materials by adjustment of deposition parameters.

To design and prepare a CVD SiC/C functionally gradient nanocomposite, some essential data on the preparation conditions and the properties of CVD SiC–C nanocomposites over the entire composition range are necessary. At the present time, however, no work has been reported on this subject.

Thermal properties are important in the design of thermal barrier materials. Only a few publications [6–8] have dealt with the thermal properties of CVD SiC–C. Emyashev *et al.* [6] reported that the thermal conductivity of CVD SiC–9 mol % C was about one tenth of the CVD SiC value. Bonnke and Fitzer [7] measured thermal expansion of CVD SiC–C in the composition range of 0 to 72 mol % C and reported the average thermal expansion coefficients from room temperature to 1273 K were 3.5×10^{-6} to 5.9×10^{-6} K^{-1}. Aoki *et al.* [8] reported that the presence of a small amount of SiC (< 2 mol %) significantly affected the density, preferred orientation and thermal expansion of CVD C. However, the preparation conditions of each study were quite different and their composition ranges were rather limited. For these reasons the results cannot be considered as a sufficient database for the design of CVD SiC/C functionally gradient nanocomposites.

The present authors prepared CVD SiC–C nanocomposites over the entire composition range, using the $SiCl_4$–C_3H_8–H_2 system, and reported the preparation conditions [9] and the microstructure [10] of the dense-plate deposits. In this paper, measured results of thermal conductivity and thermal expansion of the deposits are reported, and the relationship between the properties and the microstructure are discussed.

2. Experimental procedure

CVD SiC–C nanocomposites were prepared in a cold-wall type reactor using the $SiCl_4$–C_3H_8–H_2 system as source material. The deposits were obtained on a graphite substrate (40 × 12 × 2 mm) heated by an electric current. By controlling the ratio of Si to C in the input gas. SiC–C nanocomposites from SiC to C were obtained. For further details on the depositions, see our earlier papers [9, 10].

Thermal properties were obtained from dense-plate samples prepared at $T_{dep} = 1673$ and 1773 K and $P_{tot} = 40$ kPa. Under these conditions, relatively fast growth of deposits was observed. The measurement

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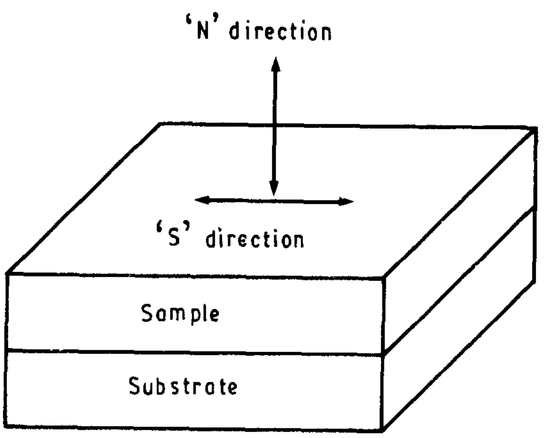

Figure 1 Schematic diagram of directions for the measurement of thermal properties.

directions are shown in Fig. 1. The laser-flash method (Shinku riko: TC-3000, 300 Hakusar-cho, Midori-ku, Yokhama 226, Japan) was used for the measurement of the specific heat and thermal diffusivity in the direction perpendicular to the deposition surface ('N' direction). The disc-shaped samples had a diameter of 10 mm and a thickness between 0.5 and 1.2 mm. Thermal conductivity (λ) was calculated from measured thermal diffusivity (α), specific heat (C_p) and density (ρ) using Equation 1

$$\lambda = \alpha C_p \rho \qquad (1)$$

Thermal expansion was measured by a silica-rod dilatometer (Shinku riko: TA-7000) in the temperature range of 295 to 1273 K in the 'N' direction. The thermal expansion in the direction parallel to the deposition surface ('S' direction) was measured using laser intervention equipment (Shinku riko: LIX-1) in the temperature range of 300 to 873 K. The disc-shaped samples had a diameter of 6 mm and a thickness between 0.5 and 1.2 mm. They were heated at the rate of 5 K min^{-1} in a vacuum furnace.

3. Results and discussion

3.1. Thermal conductivity

The relationship between the temperature and thermal conductivity of CVD SiC–C nanocomposites is shown in Fig. 2 for T_{dep} = 1673 K and in Fig. 3 for T_{dep} = 1773 K. At both temperatures the thermal conductivity of all the deposits from SiC to C decreased with increasing temperature. The thermal conductivity of CVD SiC at room temperature is between 56 and 58 W m^{-1} K^{-1}. These values agree well with the literature [6, 11]. CVD C and CVD C–SiC containing less than 1.5 mol % SiC showed low thermal conductivity in the range of 0.5 to 1.8 W m^{-1} K^{-1}. These low thermal conductivity values are the result of the (0 0 2) planes of C being preferentially oriented parallel to the deposition surface [10]. From Figs. 2 and 3, it can be seen that the thermal conductivity of CVD SiC–C nanocomposites decreased with increasing C content. This result may be due to the lower thermal conductivity of the C phase, as well as due to the formation of pores accompanying the C compound [10].

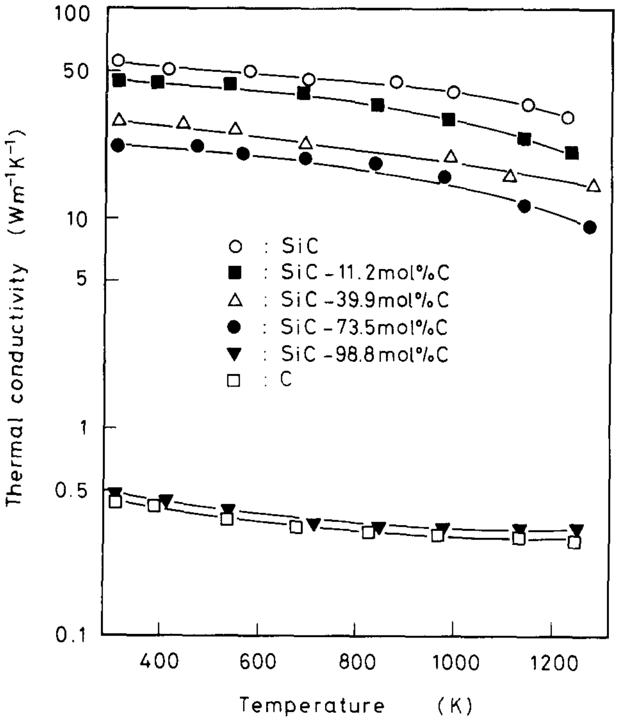

Figure 2 Thermal conductivity of CVD SiC–C nanocomposites prepared at T_{dep} = 1673 K.

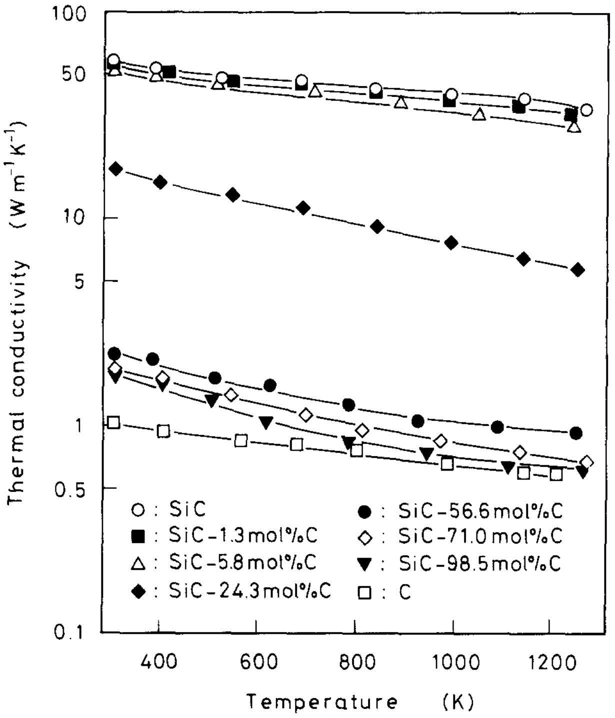

Figure 3 Thermal conductivity of CVD SiC–C nanocomposites prepared at T_{dep} = 1773 K.

Fig. 4 shows the relationship between the composition and thermal conductivity of CVD SiC–C nanocomposites at room temperature. Deposits prepared at T_{dep} = 1673 K have a thermal conductivity higher than 20 W m^{-1} K^{-1} even for deposits containing 73.5 mol % C, while that of the deposits prepared at T_{dep} = 1773 K shows a rapid decrease with increasing C contents. The thermal conductivity decreased to 2 W m^{-1} K^{-1} in the composition range beyond 56.6 mol % C. This value is close to that of CVD C.

Thermal conductivity of ceramic composites are affected by the porosity and the state of the dispersion

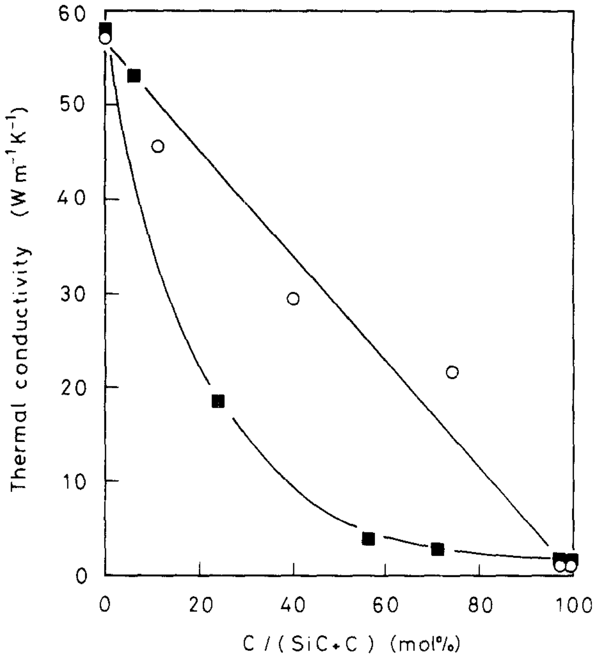

Figure 4 Effect of composition on thermal conductivity of CVD SiC–C nanocomposites measured at 295 K. T_{dep} = ○, 1673; ■, 1773 K.

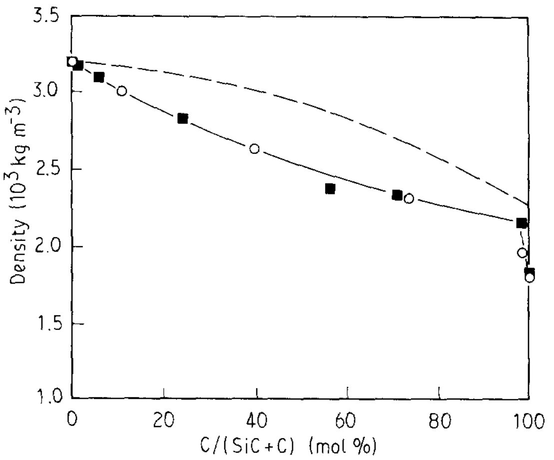

Figure 5 Relationship between composition and density of CVD SiC–C nanocomposites [10]. P_{tot} = 40 kPa. T_{dep} = ○, 1673; ■, 1773 K. (- - -), Calculated.

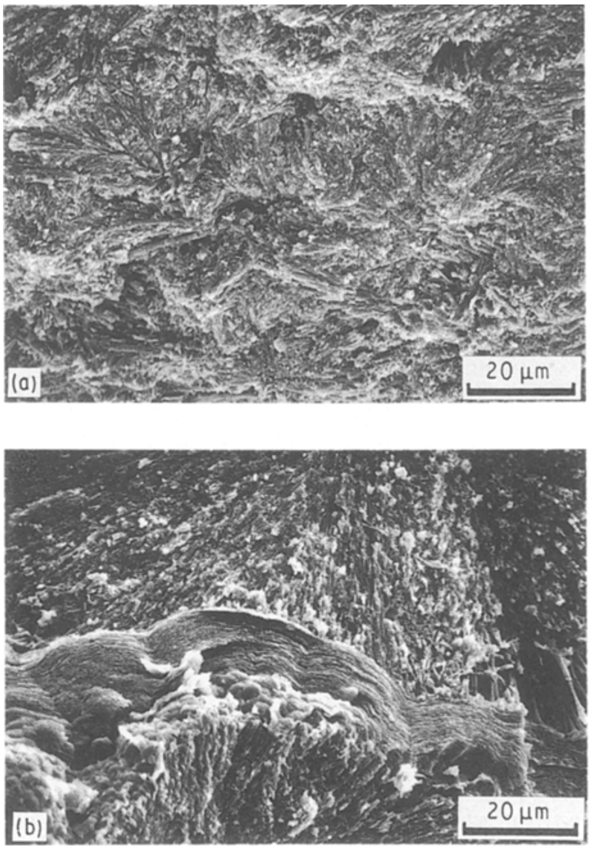

Figure 6 Scanning electron micrographs of cross-sectional surface of (a) CVD SiC–73.5 mol % C prepared at T_{dep} = 1673 K and (b) CVD SiC–71 mol % C prepared at T_{dep} = 1773 K.

phase. In this work, deposits prepared at T_{dep} = 1673 and 1773 K showed the same relationship between density and composition as shown in Fig. 5. However, the microstructure of the deposits prepared at T_{dep} = 1673 K are more uniform than those prepared at T_{dep} = 1773 K [10]. Fig. 6 shows the cross-section surface micrographs of CVD SiC–C nanocomposites containing about 70 mol % C prepared at T_{dep} = 1673 and 1773 K. For the deposit prepared at T_{dep} = 1773 K, a layered structure of C phase similar to that appeared in CVD C was observed. A portion of that C phase exists parallel to the deposition surface.

Emyashev *et al.* [6] reported that thermal conductivity of CVD SiC–C containing only 9 mol % C showed a value as small as one tenth of that of CVD SiC. They stated that the lower thermal conductivity values are due to the mutually connected C particles forming a film perpendicular to the measurement direction. In this work, the thermal conductivity for the deposits prepared at T_{dep} = 1773 K may be affected by the observed layer-structured C phase.

The thermal conductivity of ceramic composites consisting of the matrix and dispersion phases can be calculated by Equation 2 [12]

$$\lambda = \lambda_1 \frac{1 + 2v(1 - \lambda_1/\lambda_2)/(1 + 2\lambda_1/\lambda_2)}{1 - v(1 - \lambda_1/\lambda_2)/(1 + 2\lambda_1/\lambda_2)} \tag{2}$$

where λ is the thermal conductivity of the composite; λ_1 and λ_2 are the thermal conductivity of the matrix and the dispersion phase, respectively; and v is the volume fraction of the dispersion phase. When the dispersion phase is in the form of pores, and $\lambda_1 \gg \lambda_2$, the thermal conductivity is given by $\lambda = \lambda_1(1 - v)/(1 + 0.5v)$. On the other hand, for the composite consisting of a series of slabs of two phases, the thermal conductivity in the direction perpendicular to the slabs is given by Equation 3

$$1/\lambda = v_1/\lambda_1 + v_2/\lambda_2 \tag{3}$$

where λ_1, λ_2 are the thermal conductivity and v_1, v_2 are the volume fractions of the two phases.

Applying Equations 2 and 3 to this work, if C is randomly oriented, the thermal conductivity of CVD SiC–C nanocomposites is given by Equation 4

$$\lambda = \lambda_C \frac{1 + 2v_{SiC}(1 - \lambda_C/\lambda_{SiC})/(1 + 2\lambda_C/\lambda_{SiC})}{1 - v_{SiC}(1 - \lambda_C/\lambda_{SiC})/(1 + 2\lambda_C/\lambda_{SiC})} \times \frac{(1 - v_p)}{(1 + 0.5v_p)} \tag{4}$$

where λ_{SiC} is the thermal conductivity of CVD SiC measured in this work, and λ_C is the thermal conductivity of isotropic C heat-treated at 1773 K [13]. The pore volume fraction, v_p, contained in the deposits was introduced into the equation to calculate the effects of pores. In Equation 4, the matrix was assumed to be C because the C phase tends to form a continuous network at the boundaries of SiC [10].

Furthermore, when a part of C exists as a layer structure perpendicular to the measurement direction as shown in Fig. 6b, the thermal conductivity, λ_m, can be calculated by Equation 5

$$\frac{1}{\lambda_m} = \frac{1-fv_C}{\lambda} + \frac{fv_C}{\lambda_{C1}} \tag{5}$$

where λ_{C1} is the thermal conductivity of CVD C in the 'N' direction measured in this work; λ is thermal conductivity of CVD SiC–C void of the layer structural C; and f is the fraction of layer structural C in the total C phase. The value of λ was calculated by Equation 4.

The calculated results for CVD SiC–C nanocomposites at room temperature are shown in Fig. 7 compared with the experimental results. From the calculated result, it can be seen that the thermal conductivity of CVD SiC–C nanocomposites is much smaller when a part of the C phase exists as a layer structure perpendicular to the measurement direction. At $T_{dep} = 1673$ K, the thermal conductivity of the deposits in the composition range up to 73.5 mol % C is close to that of the calculated result, assuming that C is randomly oriented. While at $T_{dep} = 1773$ K, the thermal conductivity of the deposits in the composition range of 24.3 to 71 mol % C agreed with the calculated results, assuming that a part of C phase existed as a layer structure. These results correspond well with the microstructure shown in Fig. 6. Therefore we can conclude that the decrease of thermal conductivity for the deposits prepared at $T_{dep} =$ 1773 K is caused by the presence of layer-structured C.

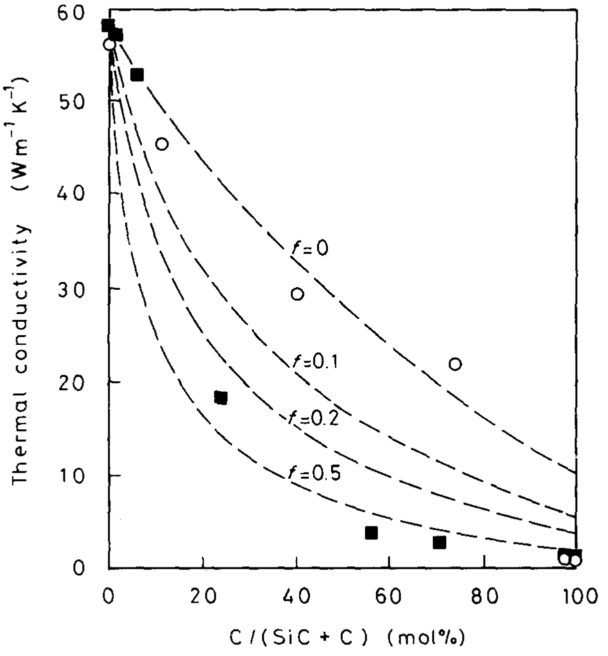

Figure 7 Calculated thermal conductivity of CVD SiC–C nanocomposites for various fraction of layered C in all the C phase 'f' compared with the experimental results. ○, $T_{dep} = 1673$; ■, $T_{dep} = 1773$ K.

3.2. Thermal expansion

Figs 8 and 9 show the thermal expansion of CVD SiC–C nanocomposites in the 'N' direction measured in the temperature range of 295 to 1273 K. The average thermal expansion coefficient of CVD SiC is 5×10^{-6} K^{-1} and is almost equal to results reported elsewhere (4.9×10^{-6} K^{-1}) [7, 11].

Generally, CVD C shows anisotropic properties because of its structural anisotropy. It is known that the thermal expansion in the direction perpendicular to the (002) plane is greater than that in other directions, and the thermal expansion is significantly influenced by the microstructure (preferred orientation, etc.) [8, 14, 15]. In this work, the measured thermal expansion coefficient of CVD C in the temperature range of 295 to 1273 K was a relatively low value between 12×10^{-6} and 13×10^{-6} K^{-1} due to its low preferred orientation. These values are much lower than those of highly oriented graphite (about 28×10^{-6} K^{-1}). However, the deposits containing less than 1.5 mol % SiC showed a high expansion coefficient of 25×10^{-6} K^{-1}. This higher thermal expansion coefficient may be caused by the improvement in the preferred orientation of $(002)_C$ by the addition of a small amount of SiC [10]. These results are in good agreement with the work of Aoki *et al.* [8].

From Figs 8 and 9 it can be seen that although the C phase in CVD SiC–C nanocomposites increased to about 70 mol %, the thermal expansions only changed in a small range. This is nearly in agreement with results reported by Bonnke and Fitzer [7].

Figs 10 and 11 show the thermal expansion of CVD SiC–C nanocomposites in the 'S' direction measured in the temperature range of 300 to 873 K. In the

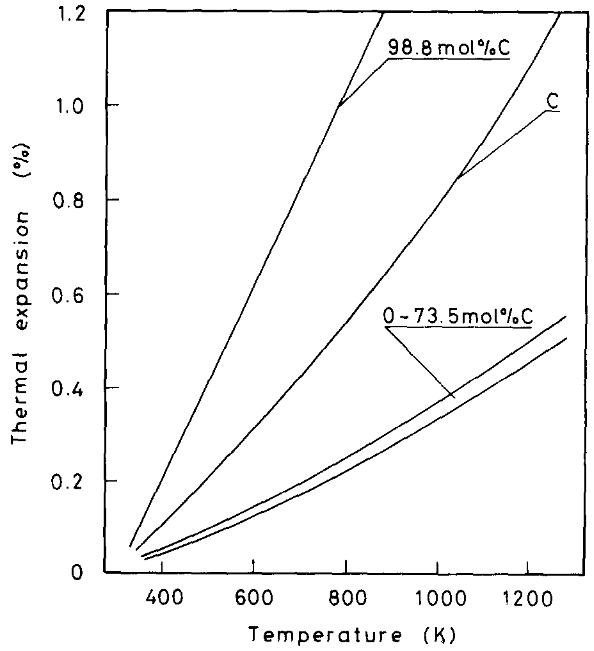

Figure 8 Thermal expansion of CVD SiC–C nanocomposites in a direction perpendicular to the deposition surface $T_{dep} = 1673$ K.

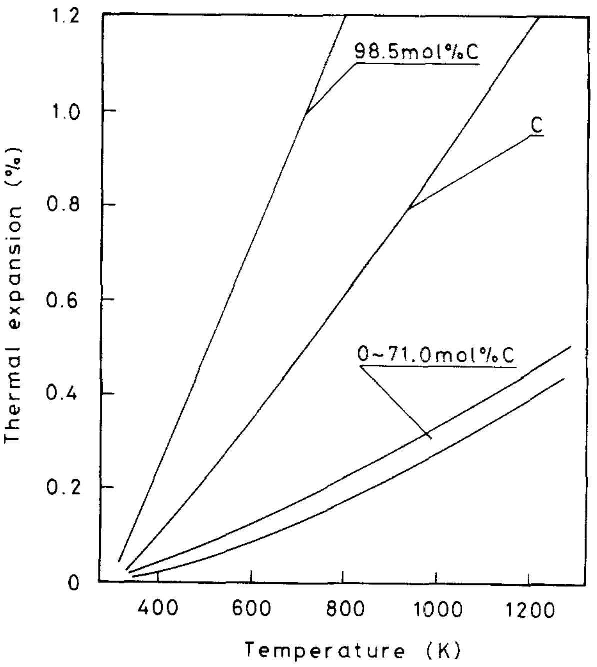

Figure 9 Thermal expansion of CVD SiC–C nanocomposites in a direction perpendicular to the deposition surface $T_{dep} = 1773$ K.

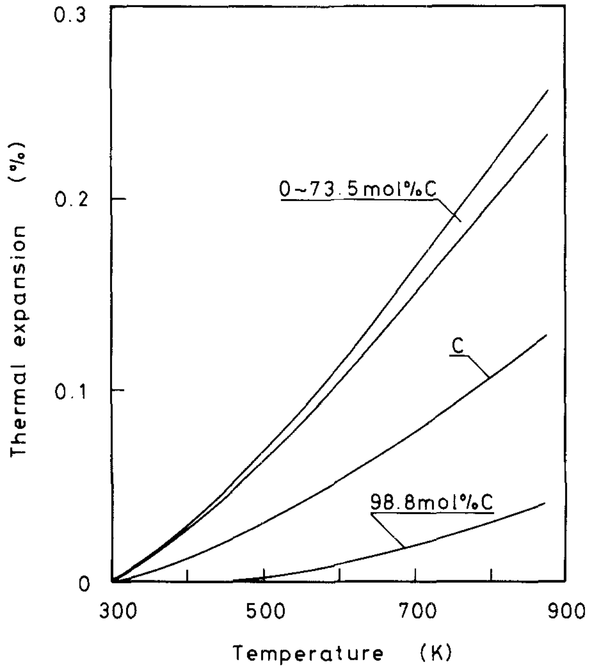

Figure 10 Thermal expansion of CVD SiC–C nanocomposites in a direction parallel to the deposition surface $T_{dep} = 1673$ K.

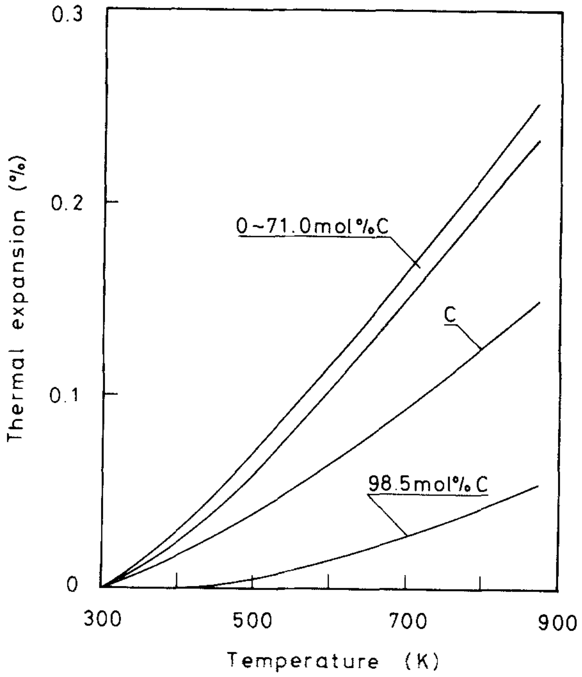

Figure 11 Thermal expansion of CVD SiC–C nanocomposites in a direction parallel to the deposition surface $T_{dep} = 1773$ K.

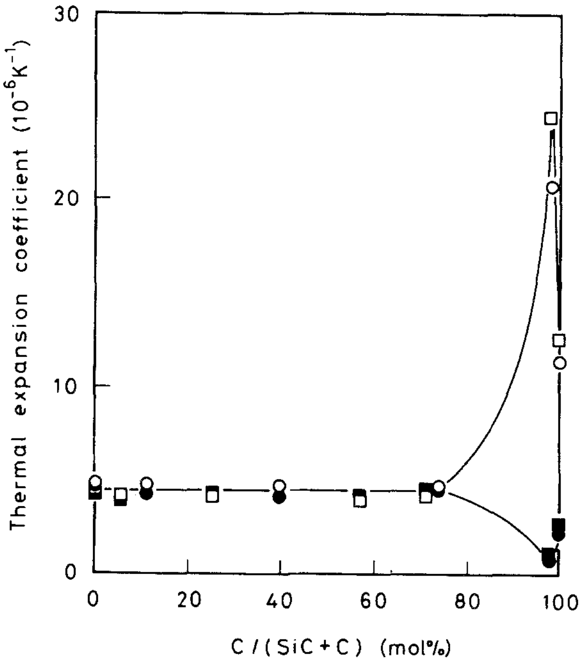

Figure 12 Thermal expansion coefficient of CVD SiC–C nanocomposites between the temperature range of 300 to 873 K. (open symbols) Perpendicular to the deposition surface; (closed symbols) parallel to the deposition surface. T_{dep}, circles, 1673 K; squares, 1773 K.

composition range up to about 70 mol % C, the thermal expansions were nearly equal to those in the 'N' direction. However, CVD C and CVD C–SiC containing < 1.5 mol % SiC showed about 1/6 and 1/25 lower values, respectively, than those in the 'N' direction. This anisotropic behaviour in thermal expansion is caused by anisotropy in the C structure, especially in preferential crystalline orientation.

Fig. 12 shows the average thermal expansion coefficient of CVD SiC–C nanocomposites in the temperature range of 300 to 873 K. From Fig. 12, it can be seen that the thermal expansion coefficient of the deposits are independent of T_{dep}. Furthermore, though the CVD C showed a strong anisotropy in thermal expansion, for the deposits containing up to about 70 mol % C, the thermal expansion coefficients (4.5×10^{-6} to 5.2×10^{-6} K^{-1}) are isotropic and show only a little difference from that of CVD SiC.

Turner [16] proposed an equation (Equation 6) for the thermal expansion coefficient of composite materials

$$\alpha = \frac{\Sigma \alpha_i v_i E_i}{\Sigma v_i E_i} \qquad (6)$$

where α_i, v_i and E_i are thermal expansion, volume fraction and modulus of elasticity of ith component, respectively. Kingery [17] applied the equation to MgO–W and SiO_2–Al systems, and reported that the calculated results are in good agreement with the experimental values.

The thermal expansion coefficient of CVD SiC–C nanocomposites in the 'N' direction were calculated by Equation 6. The data used in the calculation are shown in Table I and the calculated results are shown in Fig. 13. To study the effect of the preferred orientation of the C phase on the thermal expansion of CVD SiC–C nanocomposites, in the calculation, the C phase was assumed to be all higher oriented or lower oriented or isotropic.

From the calculated results as shown in Fig. 13, we can see that as the randomly oriented C has a thermal expansion coefficient equal to that of CVD SiC, the thermal expansion coefficient of the composites showed no change by compounding isotropic C to SiC. On the other hand, even the C phase in CVD SiC–C nanocomposites is highly oriented, the compounding of C has only a small effect on the thermal expansion coefficient of the composites in the composition range up to about 70 mol % C due to its low modulus of elasticity.

In the present work, the fact that the thermal expansion of the deposits in the composition range of up to about 70 mol % C is in good agreement with that of CVD SiC may be the consequence of randomly oriented C. At $T_{dep} = 1773$ K, the presence of the layer structural C did not affect the value of thermal expansion of the composites even though the thermal conductivity had decreased greatly, as shown earlier. The reason for this might be the low modulus of elasticity of C.

TABLE I Data used in the calculation on thermal expansion coefficient

	α (10^{-6} K^{-1})	E (GPa)
CVD SiC	5.0	400 [19]
Higher oriented CVD C	25	34 [20]
Lower oriented CVD C	14	31 [21]
Isotropic CVD C	5.0 [18]	27 [22]

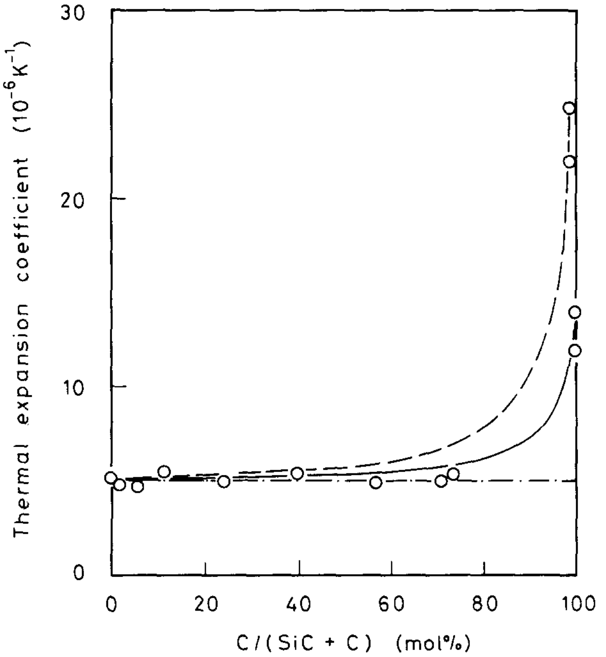

Figure 13 Calculated thermal expansion coefficient of CVD SiC–C nanocomposites compared with the experimental results (○). Calculated by (– – –) higher oriented C; (——) lower oriented C; (— · —) isotropic C.

4. Conclusions

Thermal conductivity and thermal expansion were measured for CVD SiC–C nanocomposites over the entire composition range of SiC to C prepared under the conditions $T_{dep} = 1673$ and 1773 K, $P_{tot} = 40$ kPa. The following results were obtained.

1. The thermal conductivity of CVD SiC–C nanocomposites decreased with an increase of temperature: thermal conductivity of SiC at room temperature it was 56 to 58 $W m^{-1} K^{-1}$. The thermal conductivity decreased with an increase in C content. Thermal conductivity of CVD C at room temperature was 0.5 to 1.1 $W m^{-1} K^{-1}$.
2. At $T_{dep} = 1773$ K, a part of the C phase formed a layered structure with its plane parallel to the deposition surface. This made the thermal conductivity of the deposits containing 24.3 to 71 mol % C much lower than those prepared at $T_{dep} = 1673$ K.
3. The average thermal expansion coefficient of CVD SiC (from 295 to 1273 K) was $5 \times 10^{-6} K^{-1}$. CVD C and CVD C–SiC containing < 1.5 mol % SiC showed strong anisotropy in thermal expansion. The values obtained were 12×10^{-6} to $25 \times 10^{-6} K^{-1}$ (from 293 to 1273 K) in the direction perpendicular to the deposition surface, and 0.7×10^{-6} to $2.6 \times 10^{-6} K^{-1}$ (from 300 to 873 K) in the direction parallel to the deposition surface.
4. In the composition range up to about 70 mol % C, the thermal expansion coefficients of CVD SiC–C nanocomposites were isotropic and their values were in the range of 4.5×10^{-6} to $5.2 \times 10^{-6} K^{-1}$ (from 295 to 1273 K). These values correspond to that of CVD SiC. The result is considered to be the effect of low preferred orientation and low modulus of elasticity of the C phase.

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