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Fabrication of C/SiC composites by an electrodeposition/sintering method and the control of the properties

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Carbon fibre reinforced SiC matrix composites (C/SiC composites) were fabricated using an electrodeposition/sintering method and the control of properties such as flexural strength, Young's modulus and thermal expansion coefficient was investigated in order to fabricate C/SiC-based functionally gradient materials. By means of choosing the condition of electrodeposition and sintering, C/SiC composites with volume fraction of fibre (V_f) ranging from 45 to 78% were fabricated. Maximum flexural strength and Young's modulus were 185 MPa and 47.5 GPa with V_f of 75%, but both properties decreased with the decrease in V_f. Conversely, the thermal expansion coefficient increased with the decrease in V_f; the value varied from 0.2 to $2.75 \times 10^{-6}\,K^{-1}$.

1. Introduction

Carbon fibre reinforced carbon composites (C/C composites) are expected to be the material of choice for aerospace use [1] such as nose cone, and combustor of the spaceplane because of a variety of excellent properties at high temperature, such as high specific strength [2], and high fracture toughness. Many kinds of coating techniques, for example SiC coating by chemical vapour deposition [3], have been studied in order to compensate for the lack of oxidation-resistance and erosion-resistance of C/C composites. However, satisfactory results have not been obtained. The low thermal expansion coefficient of C/C composites [4] exacerbate the problem. Thermal cracks occur in the coating layers because of the thermal stress which generates between C/C composites and the coated layers during cooling after coating [5]. Oxidation proceeds through the thermal cracks [6].

On the other hand, many studies related to carbon fibre reinforced SiC matrix composites (C/SiC composites) have been performed using chemical vapour infiltration [7–9] or liquid impregnation methods in order to improve oxidation-resistance and erosion-resistance of C/C composites themselves. It has been reported that the substitution of SiC for the carbon matrix led to an increase in the thermal expansion coefficient, Young's modulus and mechanical strength of the composites [9], in addition to the improvement of oxidation-resistance. The increase of the thermal expansion coefficient decreases the degree of mismatch between the C/SiC composites and the SiC coated layer.

However, there are some problems in the above conventional processes. First, much time is needed to densely infiltrate the matrix in carbon fabrics [10], which leads to the high cost of the composites. Second, the differences in density of matrix infiltration occur between the surfaces and the inner parts in the composites [11].

We have a new technology which is called electrodeposition/sintering method. This has been developed for the fabrication of C/C composites [12]. This process has some advantages compared to conventional processes. One of them is that carbon fibre reinforced ceramic matrix composites, as well as C/C, can be fabricated in a short time. Another is that functionally gradient materials (FGMs) [13] based on carbon fibre reinforced composites can be fabricated by using this process.

The properties of C/SiC composites significantly depend on the volume fraction of carbon fibre (V_f). Lower V_f should increase the specific gravity, Young's modulus and thermal expansion coefficient of the composites, and conversely, fracture behaviour should transfer from non-brittle mode to brittle.

We have been investigating the fabrication of a C/SiC-based FGM as shown in Fig. 1. The concept is as follows. In the composite, the outer layer, which is exposed to an oxidative and erosive atmosphere at high temperature, consists of a C/SiC composite with low V_f. The inner layer, which requires fracture toughness and specific strength, consists of a high V_f composite. If a two-layer composite consisting of the outer and the inner layer is fabricated by a sintering process, the composite will be destroyed by thermal stress because the thermal expansion coefficient of the C/SiC composite with low V_f is larger than that of the composite with high V_f. In order to reduce the thermal stress, some layers of C/SiC are introduced as intermediate layers so that the thermal expansion coefficient

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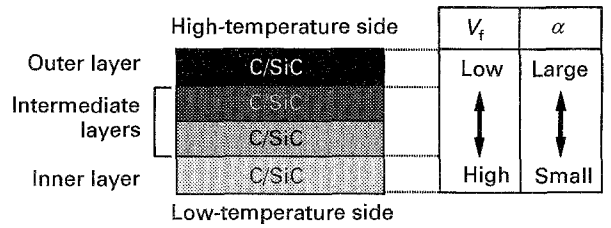

Figure 1 The conceptual structure of a C/SiC-based FGM. V_f: volume fraction of fibre; α: thermal expansion coefficient.

changes in a series of steps from the outer to the inner layer.

In this study, C/SiC composites with various V_f were fabricated using the electrodeposition/sintering method, and the control of Young's modulus, strength and thermal expansion coefficient of the composites, which are the most important properties for designing an FGM, by means of V_f control were considered.

2. Principle of electrodeposition

Fig. 2 shows the experimental procedure. First, ceramic powder is mixed with a carrier substance which can undergo electrophoresis. Second, the mixture is dispersed in water, and the carbon fabrics and electrode are dipped in it. When the electric current is applied between the fabrics and the electrode, electrodeposition is performed through four phenomena as shown in Fig. 3.

(a) Electrophoresis. The particles dispersed in water are negatively charged. When the electric current is applied, the particles move toward the anode (carbon fabrics).

(b) Electrodeposition. When the particles reach the anode, they lose their charges and stick to the surfaces of the anode.

(c) Electro-osmosis. After the particles deposit on the surfaces of the anode and lose their charges, they form an absorbed insoluble film.

(d) Electrolysis. Electrolysis of water occurs at the anode and cathode according to the following equations:

$$\text{anode: } 2H_2O \rightarrow 4H^+ + O_2 + 4e^-$$

$$4OH^+ \rightarrow O_2 + 2H_2O + 4e^-$$

$$\text{cathode: } 4H_2O + 4e^- \rightarrow 4OH^+ + 2H_2$$

$$4H^+ + 4e^- \rightarrow 2H_2$$

If ceramic powder is dispersed with the carrier substance in the water, ceramic powder to which the charged carrier is attached, begins to move toward the fabrics and starts to deposit on the surfaces. As the deposition proceeds, the deposited parts become electrically insulated, so the succeeding particles deposit on new surfaces of carbon fabrics. Thus the deposited layers have a uniform thickness. As shown in Fig. 4 the electric current decreases with deposition time. The amount of matrix deposited is determined by the total electric charge as transfer and exchange of electric charge carries out the electrodeposition.

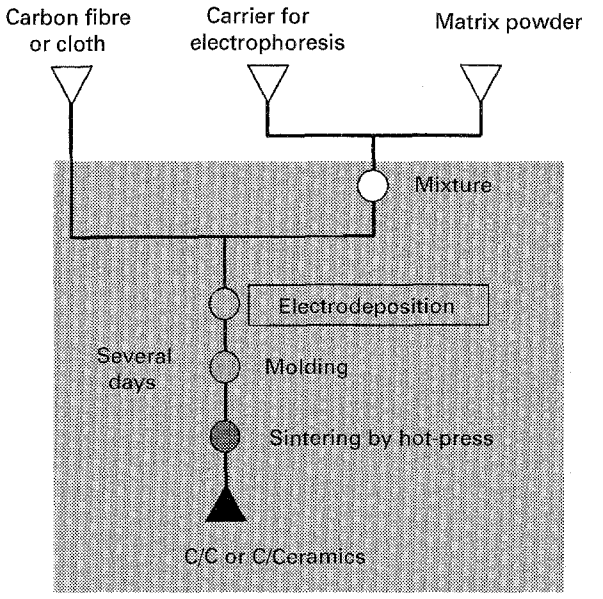

Figure 2 Fabrication process of carbon fibre reinforced carbon or ceramics matrix composites using electrodeposition/sintering method.

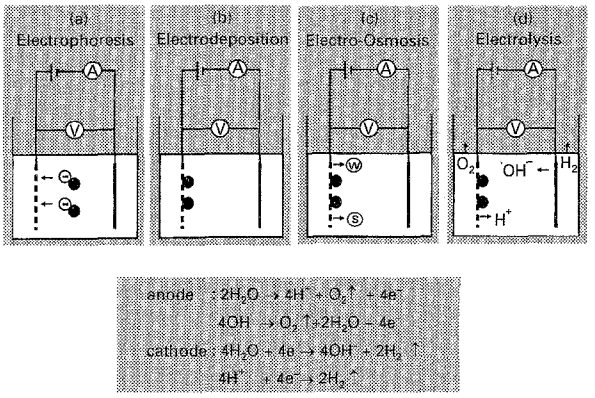

Figure 3 Four phenomena in electrodeposition.

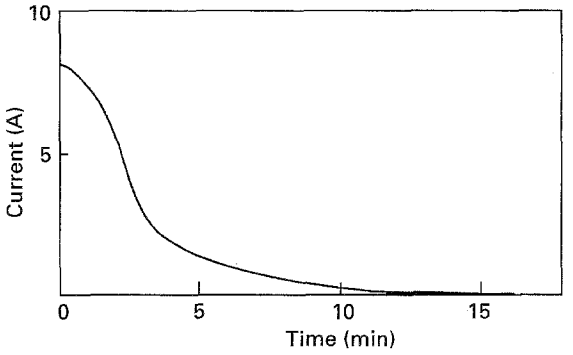

Figure 4 The relationship between current and time during electrodeposition.

3. Experimental procedure

3.1. Fabrication of C/SiC composites

Two-dimensionally woven PAN-base carbon fabrics (Toreka T-300, plain fabrics of 1000 or 3000 fibres, produced by Tore, Ltd., Tokyo Japan) were used as a substrate for electrodeposition. α-SiC and Al_2O_3 powder of 1 wt % as sintering additives were mixed by

ball-milling. The powder mixture was mixed with a carrier substance, and then was dispersed in water. The mixing ratio of the former to the latter was 2 to 1. After carbon fabrics and an electrode were dipped in the water, electric current was applied between the fabrics and the electrode. Finally, the prepreg sheets obtained were laid up and sintered by hot-pressing at a pre-determined pressure, and 2000 °C. In this way, we obtained C/SiC composites.

Structures as shown in Fig. 5 were designed for control of V_f in composites. According to the concept, experimental conditions were adjusted as shown in Table I. In the case of fabrication of composites with high V_f, which should show non-brittle behaviour in fracture, fabrics woven with 3000 pieces of fibres were used. Furthermore, a small amount of matrix was deposited in electrodeposition as thick matrix layers were not formed on the surface of the fabrics. Oppositely, in the case of fabrication of composites with low V_f, fabrics woven with 1000 pieces of fibres were used, and a large amount of matrix was deposited as thick matrix layers were formed on the surfaces as well as depositing into the fabrics.

Additionally, two types of hot-pressing patterns were used for control of the thickness of matrix layers. One pressing was started from room temperature, which was mainly the condition for high V_f, since matrix layers were not formed between the fabrics. Another was started at 1773 K in order to inhibit flowing-out of the matrix, which led to the formation of matrix layers between fabrics. This was mainly the condition for low V_f.

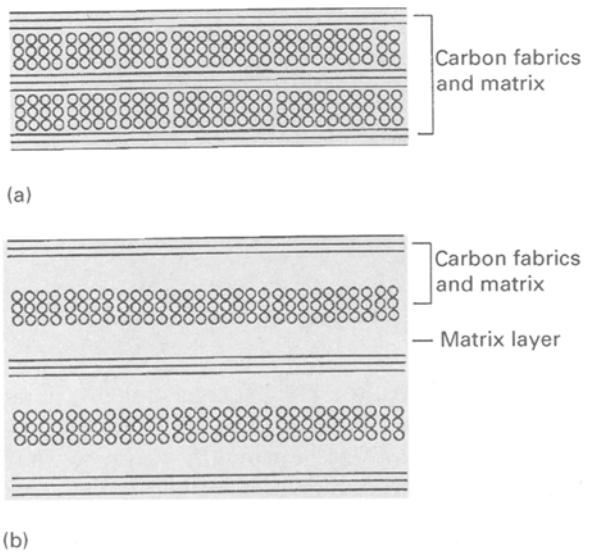

Figure 5 The aming structures of the C/SiC composites: (a) high V_f, (b) low V_f.

3.2. Characterizations

The cross-sectional surfaces of the C/SiC composites were observed by optical microscope. Porosities and specific gravities were measured by Archimedes' method. From these values and the weight of fabrics used, V_f values were determined. Young's modulus and flexural strengths were measured by a three-point bending test. Thermal expansion coefficients in the direction parallel to the fibre were measured in the temperature range from room temperature to 600 °C using a thermal expansion measurement apparatus which employs the differential transformer method.

4. Results and discussion

4.1. The control of properties of C/SiC composites

Fig. 6 shows typical microstructures of the C/SiC composites. In the specimens sintered using press-pattern 2, matrix layers between fabrics were observed in all the specimens, and the thickness increased with the decrease in V_f. In the case of fabrication using press-pattern 1, the matrix layers were observed in all the specimens except for that with V_f above 75%; the thickness increased with the decrease in V_f. Comparing specimens with the same V_f values, however, the thicknesses in specimens obtained from pattern 1 were smaller than those of specimens from press-pattern 2. It is considered that the matrix was easily impregnated into the carbon fabrics using press-pattern 1 because pressing was started before the carrier substance was hardened and carbonized at high temperature. On the other hand, the amount of matrix flowing-out in sintering was small using press-pattern 2, which led to matrix layers between the carbon fabrics, because pressing was started after the hardening and carbonization of the carrier substance at high temperature. There were many thermal cracks perpendicular to carbon fabrics in the matrix layers, some of which passed through the fabrics. This phenomenon was more pronounced with specimens having low V_f. The thermal cracks were caused by thermal stress generated between the SiC matrix and the carbon fibres during the cooling process after sintering due to a difference in the thermal expansion coefficients of the materials. Naslain *et al.* [14] have reported that the thermal cracks were not found in C/SiC composites fabricated using chemical vapour infiltration (CVI) process. Generally, the operating temperatures used for fabrication of C/SiC composites by CVI were in the range from 800 to 1100 °C [11]. It appears that sintering temperature, higher than that in CVI, made the thermal stress larger and promoted crack generation.

TABLE I The prepreg sheets and the press-starting temperatures used for fabrication of the C/SiC composites

V_f	Prepreg sheet		Press-starting temperature (K)	
	Carbon fabrics	Matrix amount	Condition 1	Condition 2
High	3000 pieces	Small	300	1773
Middle	1000 pieces	Middle	300	1773
Low	1000 pieces	Large	300	1773

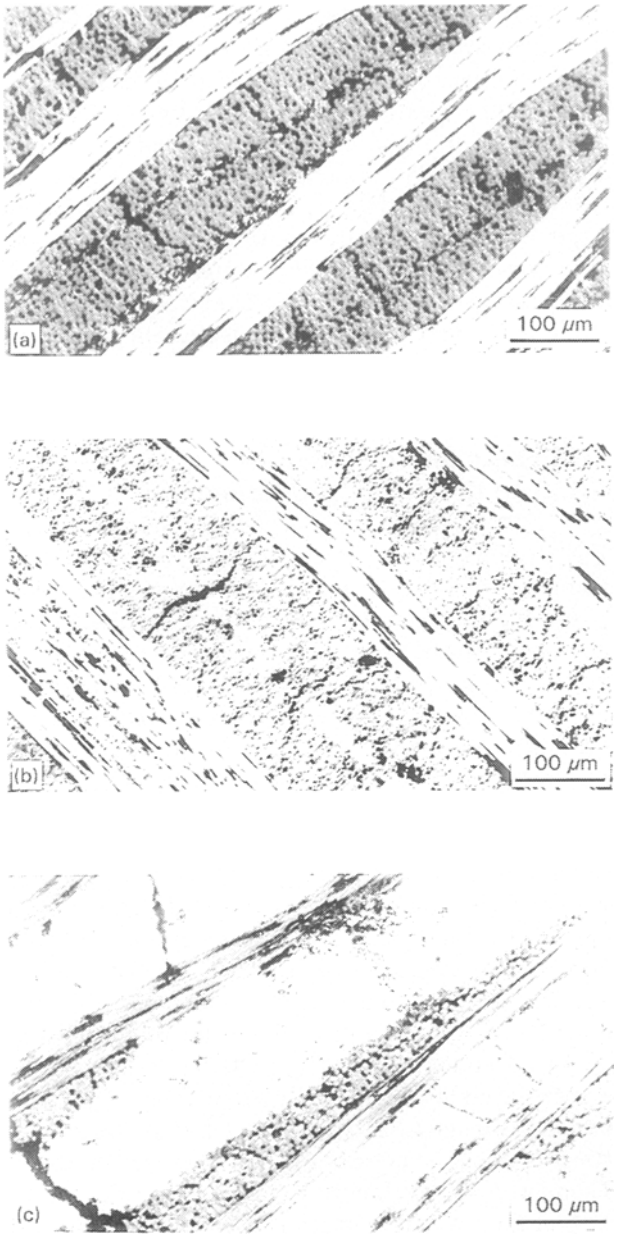

Figure 6 The cross-sectional surfaces of the C/SiC composites. (a) 75% V_f (press-pattern 1), (b) 75% V_f (press-pattern 2), and (c) 45% V_f (press-pattern 2).

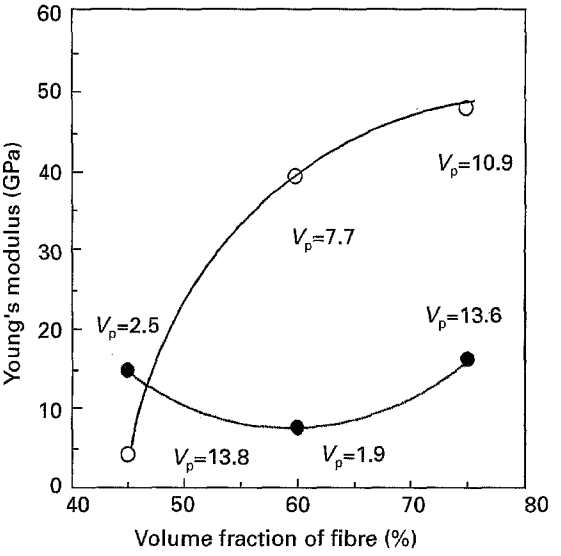

Figure 7 The relationship between V_f and Young's modulus of the C/SiC composites. ○ press-pattern 1; ● press-pattern 2.

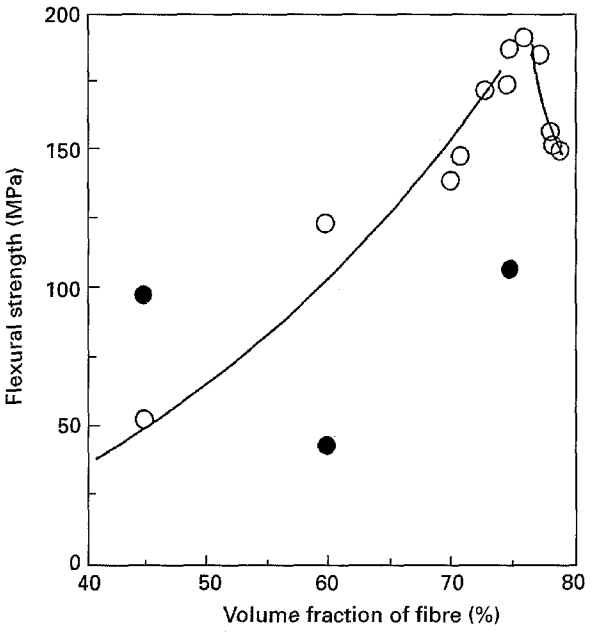

Figure 8 The relationship between V_f and flexural strength of the C/SiC composites. ○ press-pattern 1; ● press-pattern 2.

Fig. 7 shows the relationships between V_f and Young's modulus and porosity. Fig. 8 shows the relationship between V_f and flexural strength. Porosities of specimens obtained from press-pattern 1 were greater than those obtained from press-pattern 2 except for specimens with a V_f of 75%. It is considered that the flowing-out of carrier substance produced pores in the matrix layers between the carbon fabrics. Significant differences in porosity were not found in specimens with V_f of 75%. This is probably because the thickness of the matrix layer in the specimen obtained from press-pattern 1 is thin. In the V_f range from 75 to 60%, Young's modulus and flexural strength of specimens obtained from press-pattern 1 were higher than those from press-pattern 2. The low values in the latter are caused by the existence of matrix layers between the carbon fabrics, which include thermal cracks, and a low degree of impregnation of matrix into the carbon fabrics. The low degree of impregnation led to weak bonding strength between carbon fibres, for which a high strength characteristic with carbon fibre was not fully observed. The decrease in flexural strength in the V_f range above 75% indicates that the amount of matrix was small against the carbon fabrics. We predicted that Young's modulus and flexural strength would increase with the decrease in V_f. However, these values decreased with the decrease in V_f. As described above, this result is also contributed to thermal cracks in the matrix layers between the carbon fabrics, that is, the cracks became fracture origins in the bending test and led to deformation under low stress. Increase in crack size accompanied by increase in thickness of matrix layers lowers both properties.

However, the decrease in V_f down to 45% reversely increased Young's modulus and flexural strength with respect to specimens obtained from press-pattern 2. For this result, we considered that the increase in

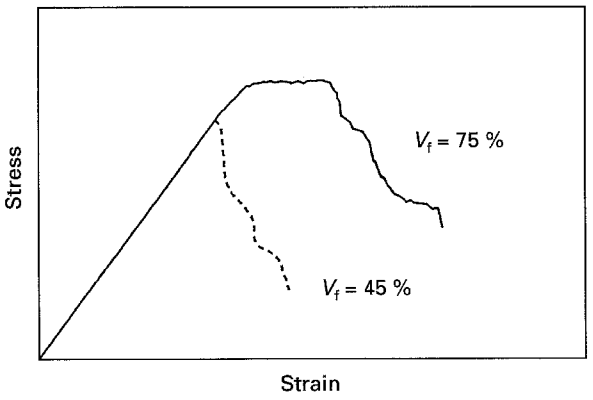

Figure 9 The stress–strain curves of the C/SiC composites.

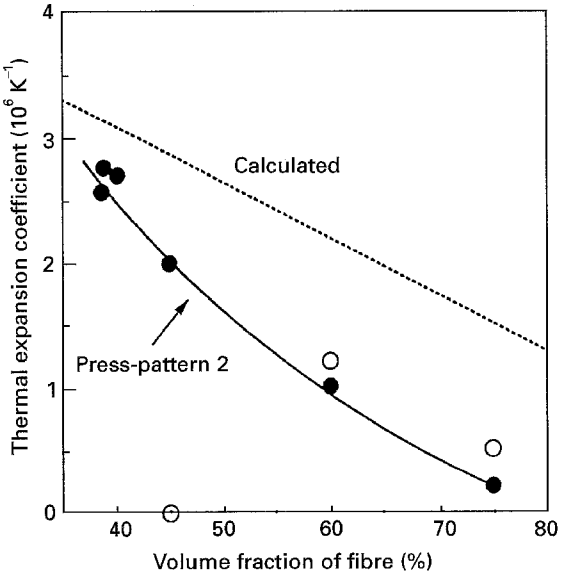

Figure 10 The relationship between V_f and thermal expansion coefficient of the C/SiC composites.

thickness of the matrix layers made the composites similar to monolithic ceramics. That is, the appearance of strength depends on carbon fibres in the case of high V_f, and depends on ceramic matrix in the case of low V_f. The stress–strain curves of the C/SiC composites, as shown in Fig. 9, suggest this presumption. On the other hand, low strength of specimens with V_f of 45% obtained from press-pattern 1 was probably caused by high porosity in the composite.

Fig. 10 shows the relationship between V_f and thermal expansion coefficient of the C/SiC composites. The broken line shows values calculated from Equation 1 proposed by Turner, as the rule of mixture for the thermal expansion coefficient.

$$\alpha = \sum \alpha_i V_i E_i / \sum V_i E_i \quad (1)$$

where, α_i, E_i, and V_i are, respectively, the thermal expansion coefficient, Young's modulus and volume fraction of the i-component, 0.1×10^{-6} K^{-1}, 230 GPa and 4.5×10^{-6} K^{-1}, 320 GPa were, respectively, used for carbon fibre and SiC matrix in this study. In the case of specimens obtained from press-pattern 2, the thermal expansion coefficient increased with the decrease in V_f. However the values were smaller than those calculated. It is thought that there are two

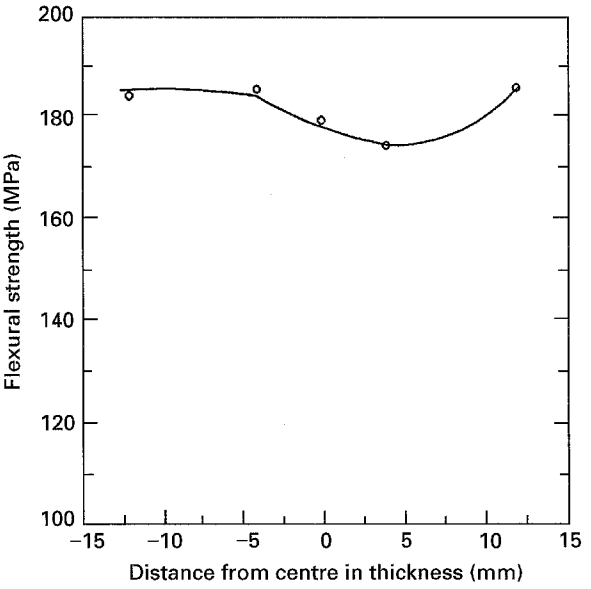

Figure 11 Strength distribution in a C/SiC composite fabricated using electrodeposition/sintering method.

reasons for this result. First, actual Young's modulus of the matrix must be lower than that of monolithic SiC because the residue of carrier substance was included in the matrix. Next, pores and thermal cracks in the matrix layers should restrict thermal expansion behaviour of the composites. The difference in thermal expansion coefficient between experimental and calculated values became small as V_f decreased. This seems to be due to the decrease of pores. The low thermal expansion coefficient of the specimen with 45% V_f obtained from press-pattern 1, which is comparable to the value for carbon fibre, is explained as follows. Thermal expansion behaviour was limited by carbon fibres in the case of high porosity and the small amount of matrix.

4.2. Uniformity of C/SiC composites fabricated using electrodeposition method

The uniformity of individual composites is a significant factor in the fabrication of FGM based on C/SiC composites because significant differences in properties between the outer part of the composite and the inner part should restrict the effect of thermal stress reduction induced by means of gradation of the composition. As an example of the uniformity, flexural strength as a function of distance from the centre in a direction parallel to the thickness of composites are shown in Fig. 11. Significant differences depending on the position, were not found. This result indicates that this process has high potential for fabrication of FGM.

5. Conclusions

For the purpose of collection of basic data to fabricate functionally gradient materials based on two-dimensional C/SiC composites, C/SiC composites having a variety of fibre volume fraction (V_f) were fabricated

using electrodeposition. Maximum Young's modulus and flexural strength of C/SiC composites were 47.5 GPa and 185 MPa, respectively, and were obtained at 75% V_f. The strength decreased with V_f. However, thermal expansion coefficient increased with the decrease in V_f, and the values were varied from 0.2 to 2.75×10^{-6} K^{-1}. These results suggest the possibility of FGM based on C/SiC composites.

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