Development of B_4C-hybrid-matrix C/C Composites

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Unidirectional (UD) and two-dimensional (2D) carbon/carbon (C/C) composites consisting of either a carbon matrix with B_4C or without B_4C were prepared by a new manufacturing method. Mechanical and thermal properties of the composites were investigated as a function of the heat-treatment temperature. Electron probe micro-analysis was carried out on the B_4C-hybrid-matrix C/C composites. The results showed that B_4C particles were uniformly distributed in the matrix. Adding B_4C-powder to the C/C matrix carbon increased not only oxidation resistance at temperatures below 1000 °C, but also mechanical properties as well. The tensile strength, the compressive strength and the inter-lamina shear strength of the B_4C-hybrid-matrix C/C composites in the fiber direction were about 1170, 540, and 30 MPa, respectively. The thermal conductivity of the UD C/C composite after the treatment with B_4C at a temperature of 3200 °C is about 150W/MK, which is the same as that of UD C/C composite without the treatment of B_4C at 2000 °C. It is suggested that the B_4C powder melted and boron diffused into the carbon fiber structure at a temperature over its melting point.

1. Introduction

In light of its superior mechanical properties under extreme conditions of temperature, such as high specific strength, high modulus of elasticity, and resistance to heat as well as thermal shock, carbon fiber-reinforced carbon matrix (C/C) composites are expected to play a important role in the future development of aerospace technologies. Also, in terms of functional properties, or its high thermal conductivity [1], C/C composites are promising as a key material for tiles used in the first wall for nuclear fusion reactors.

The conventional manufacturing processes require a long time [2], from a few months to upwards of a half a year. There are two main reasons. First, because the matrix precursors undergo contraction upon carbonization, a

very slow rise in temperature is necessary in order to minimize the crack formation and to assure its dispersion. Second, a cyclic densifying process is necessary in order to fill up the cracks with carbon matrix.

In order to overcome the problems described above, a new C/C composite manufacturing process has been developed in our previous study [3–4]. In this process, heat-treated pitch powder was selected as the matrix precursor so that rapid heating carbonization can be completed. The unidirectional C/C materials produced via this process did not include cracks, and was of high density (ρ = 1.9 g/cm^3) in the absence of repeated impregnation.

In this work, the addition of B_4C ceramic-powders to the matrix was successfully applied to improve the shearing, compressive, and bending strengths of the C/C composites with high densifying property in carbon materials.

2. Experimetal

Manufacturing Process of the C/C Composites

Figure 1 shows the flow chart of a new manufacturing process developed in this study to prepare the C/C composite. A mesophase pitch-based carbon fiber of 700 GPa in modulus and 350 MPa in tensile strength were used for this study. The matrix precursor consisted of high coking-yield pitch-powder of 1.0 μm in mean grain diameter, phenolic resin and solvent. Alternatively,

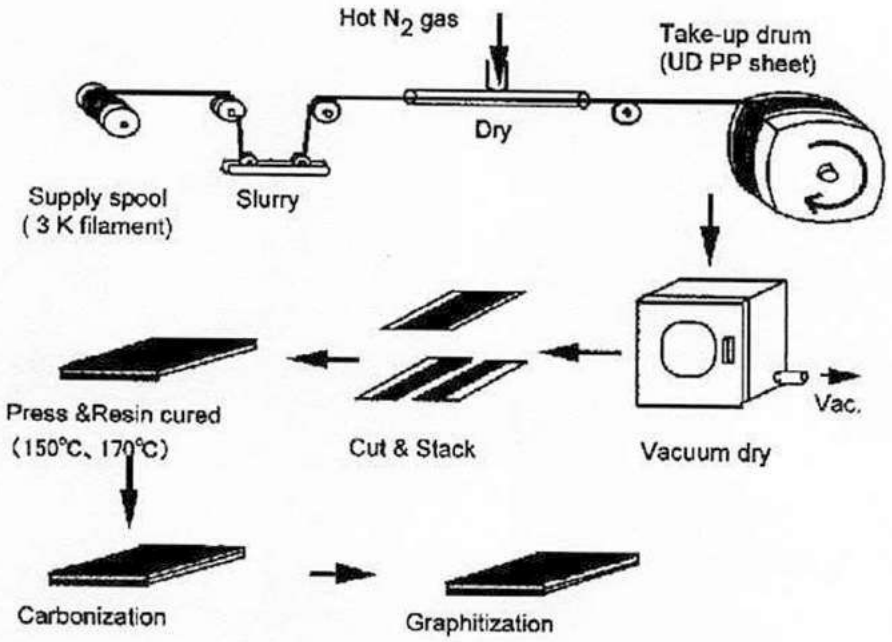

Figure 1. Steps in sheet lay up processing to prepare hybrid matrix composites

the ceramic-containing hybrid C/C material was prepared by substituting B_4C powder for the pitch-powder. In an apparatus manufacturing a pre-impregnation (abbreviated as *prepreg*) sheet, the carbon fiber was impregnated with the matrix precursor slurry and dried to yield a desired unidirectional prepreg sheet. The resulting sheets were cut in a specified size, layered, and pressed to form a molded product. The layering of the prepreg sheets was done in a unidirectional manner, when the UD C/C composite was produced. On the other hand, if the prepreg sheets are stacked so that the fibers are aligned orthogonally to each other at (0/90) s, then the 2D C/C hybrid material is manufactured. The entire procedure can be completed by a subsequent one-step carbonization/graphitization under atmospheric pressure, yielding a high-density C/C composite with a density of 1.9 g/cm^3.

In this study, two kinds of the processing systems were mainly employed. Firstly, the UD C/C hybrid material was used as test sample to evaluate the process without re-impregnation. Secondly, the 2D C/C hybrid material was re-impregnated to improve its density as well as strength. Thus, the effects of the re-impregnation were examined.

Manufacturing Procedure of the B_4C Hybrid Matrix C/C Composite

In the preliminary preparation of the B_4C-containing C/C hybrid material, B_4C powder of 0.3 μm in mean grain diameter was introduced to a slurry matrix precursor composed of heat-treated pitch powder and phenolic resin. The general manufacturing process is identical to that of the procedure outlined above. The Chemical condition was analysised by inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis for boron content and an EPMA investigation of the cross-section of the tentative sample, which revealed that a boron content was 5.8 wt%, and consequently an estimated B_4C content of 7.4 wt%. The SEM and EPMA X-ray photographs of boron and carbon clusters (Figure 2) clearly show a homogeneous dispersion of B_4C particles throughout the matrix.

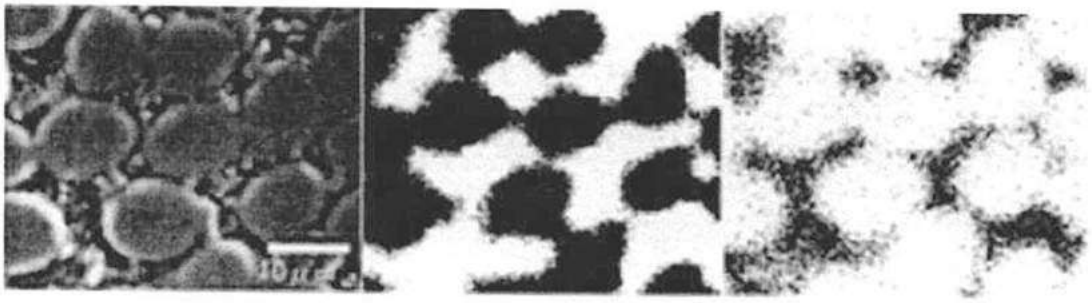

Figure 2. Micro structure of cross section of UD-C/C with B_4C hybrid matrix composites

3. Results and Discussion

Effects of Heat Treatment Temperature (HTT)

Thermal conductivity and tensile strength were found to be greater for the C/C composite material treated at higher temperature. Since the melting point of the B_4C powder used in the experiment was 2450 °C, the heat treatment at or above the melting point has to be effective on the matrix structure. An effect on the structure of the cross-section was observed for the C/C composites prepared at various heat treatment temperatures. Consequently, structural changes were also suggested from the changes in thermal conductivity and thermal expansion.

Measurement of Thermal Conductivity and Thermal Expansion

Thermal conductivity was calculated on the basis of the product of thermal diffusivity (obtained with of the Laser-Flash method), specific heat (measured by differential scanning calorimetry (DSC)), and bulk density. The measurement data of thermal expansion were collected according to the guidelines of JIS C2141 with a dilatometer under a nitrogen flow and in a temperature range from room temperature to 1400 °C. The experimental results of longitudinal (i.e. parallel to the fiber) thermal conductivity and transverse thermal expansion (i.e. in the cross-sectional direction to the fiber) are shown in Figures 3 and 4, respectively.

It is noted that the thermal conductivities between 1200 and 2000 °C HTT (heat treatment temperature) of the UD C/C with B_4C are close to those of UD C/C without B_4C at the corresponding temperatures. This similarity

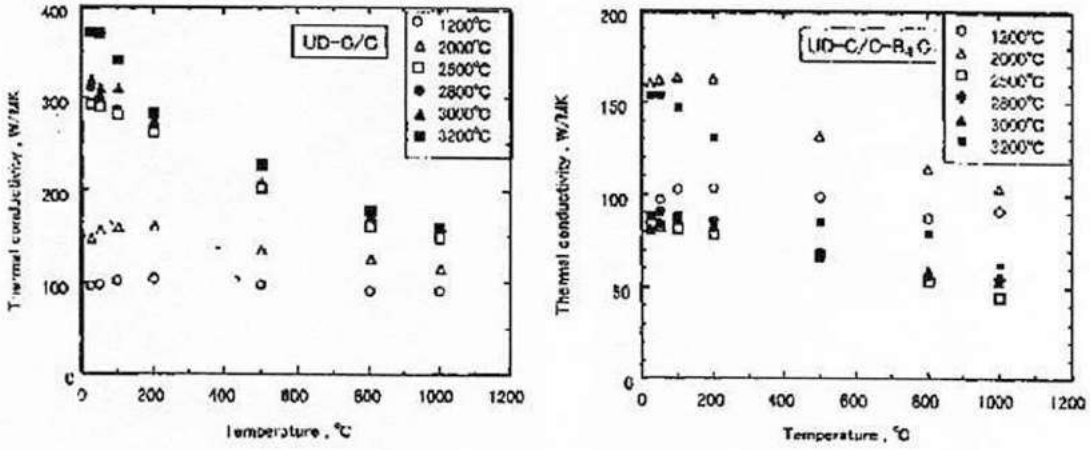

Figure 3. Effects of HTT on thermal conductivity in fiber direction.
Left: UD-C/C and right: UD-C/C with B_4C

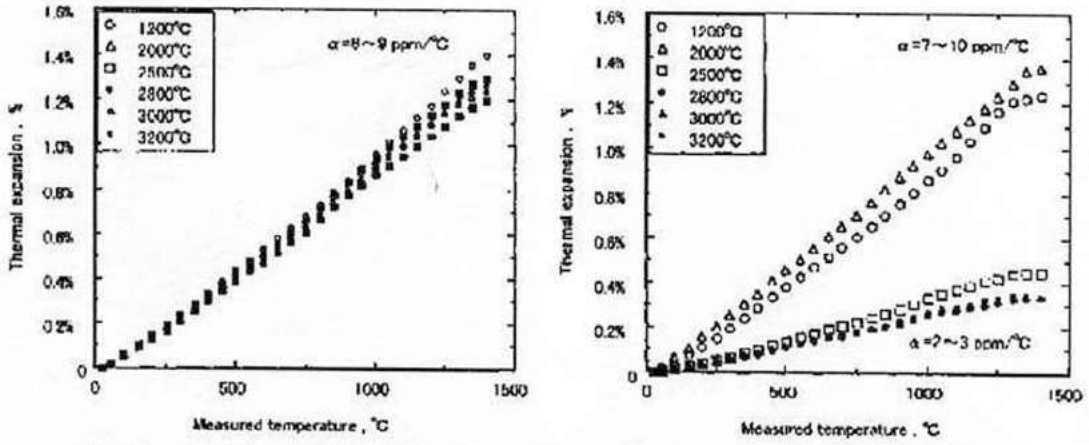

Figure 4. Effects of HTT on thermal expansion in cross sectional direction. Left: UD-C/C and right: UD-C/C with B_4C

ceases at temperatures above 2000 °C. Compared with the UD C/C without B_4C, thermal conductivity of the UD C/C with B_4C becomes smaller with the elevation of HTT. Consequently, the thermal conductivity has only half magnitude of the latter materials treated at 2500 °C. (Compare the left and right sides of Figure 3). Since more than 90 % of thermal conduction in UD C/C without B_4C occurs through carbon fibers [5], it is suggested that the decline of thermal conductivity in the UD C/C with B_4C is attributable to a similar decreasing behavior of thermal conductivity in carbon fibers.

Thermal expansion coefficient in the transverse direction of the C/C composites without B_4C (Figure 4, left) shows very small variation at various HTT, while that of C/C with B_4C is 2–3 ppm/°C at temperatures above 2500 °C. (Figure 4, right). However, this is still much smaller in comparison with 7–10 ppm/°C at HTTs below 2000 °C.

SEM Observations

Scanning electron Microscopic (SEM) photographs of the cross-section of the UD-C/C-B_4C sample are shown in Figure 5. The thermal conductivity of each sample at room temperature is printed in the photographs together with the HTT. At HTTs below 2200 °C, the matrix structure is mosaic-like, and though ostensible structural changes are not clear, the matrix structure of the material treated at 2350 °C appears to have melted and fused together. This matrix is characterized by a partially molten structure and its carbon fibers do not seem to have retained its original form.

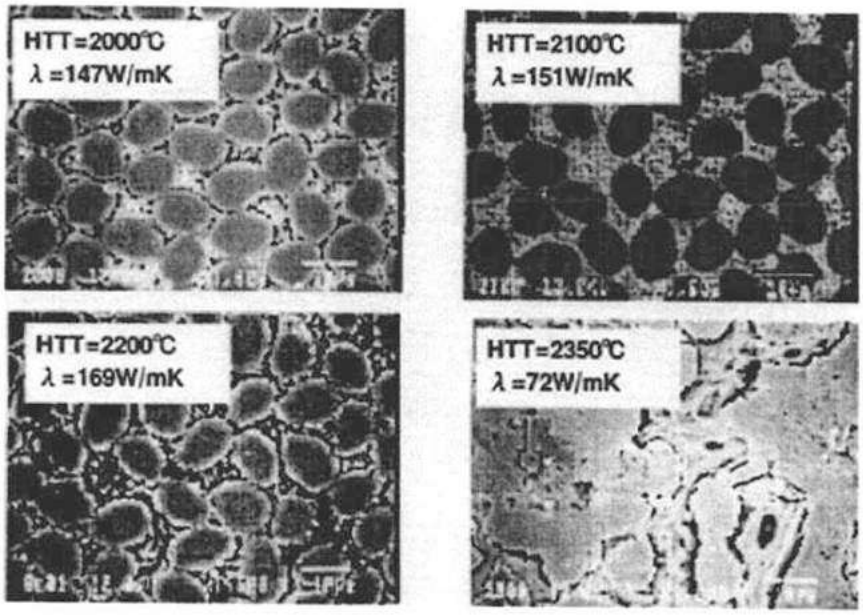

Figure 5. Effects of HTT on micro structure of C/C-B_4C hybrid matrix composites (BEI image)

It is suggested from the various effects of heat-treatment on the B_4C hybrid matrix UD C/C composites that both the melting of B_4C at temperatures above 2350 °C and subsequent diffusion of boron atoms into the carbon fiber cause the undesirable effect described above. To prevent this diffusion, the heat-treatment temperature was kept at 2000 °C in the subsequent experiments .

Physical Properties of the B_4C Hybrid Matrix C/C Composite

The evaluation of physical properties of the UD C/C B_4C was made in order to elucidate the effects of the B_4C. The test sample was prepared from two stacks of eight UD prepreg sheets (one UD C/C with B_4C, the other without). Both of the stacks were treated at 2000 °C. Its basic properties are listed in Table 1. In case of the UD C/C without B_4C, a crack-free sample was obtained after graphitization and hence re-impregnation was not required.

Table 1. Principal properties of 2D-C/C-B_4C hybrid matrix composites used

Sample	Density	Vf	B4C content	ILSS	Hardness
	g/cm^3	vol%	wt%	MPa	Hv
UD-C/C-B4C	1.91	70	7.4	31	200
C/C	1.57	53	–	20	20

The conditioning and testing methods of the sample followed the guidelines outlined in the RIMCOF standard [6]. Bending and shearing tests were made based on the three-point bending test of different span lengths, and compression tests were conducted according to the SACMA standard [7]. Also, a weight of 500 g was employed for the Vickers hardness test and the sample hardness in the transverse direction was recorded.

The test results are shown in Figure 6. For comparison, the data obtained on the C/C composites without B_4C is also provided. The results reveals a drastic improvement in the physical properties of the UD C/C composites with the B_4C supplement. Because of the dissimilarity in bulk density and Vf between the two C/C composites, direct comparison cannot adequately be made. However, the large discrepancy between 20 Hv in Vickers hardness of the UC C/C without B_4C (essentially identical to other graphite materials) and 200 Hv of the UD C/C with B_4C is certainly remarkable. It turns out conceivable from this result that the addition of B_4C is responsible for the remarkable improvement of hardness, as well as the overall amelioration of other mechanical properties such as interaminate shear-strength (ILSS).

Physical Properties of the 2D B_4C Hybrid Matrix C/C Composite

A test material of 2D C/C B_4C was prepared from two stacks of eight prepreg sheets, using the same prepreg sheets as those employed for the tests of the UD hybrid matrix C/C composites.

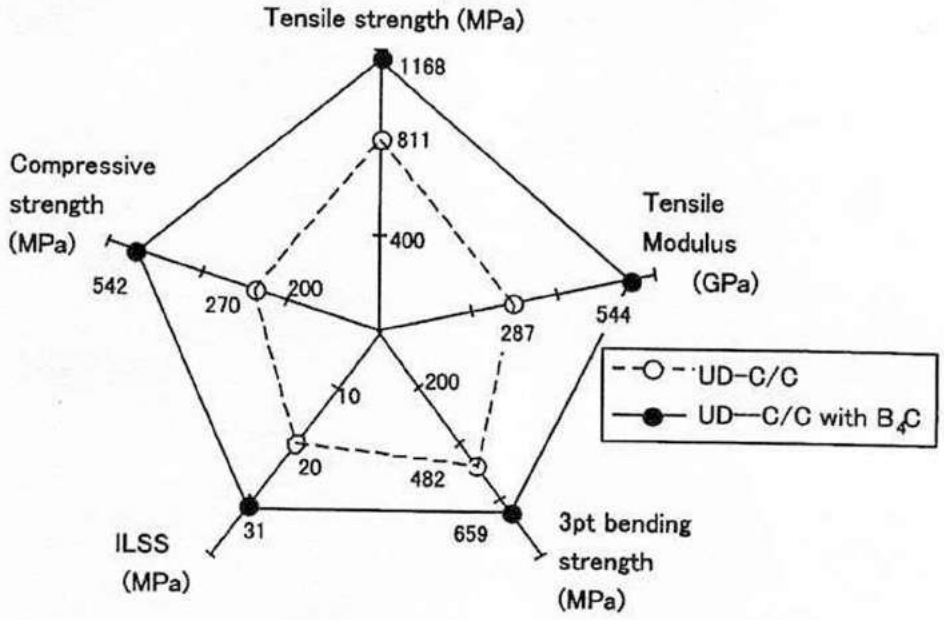

Figure 6. Balance sheet of mechanical properties of UD-C/C-B4C at room temperature

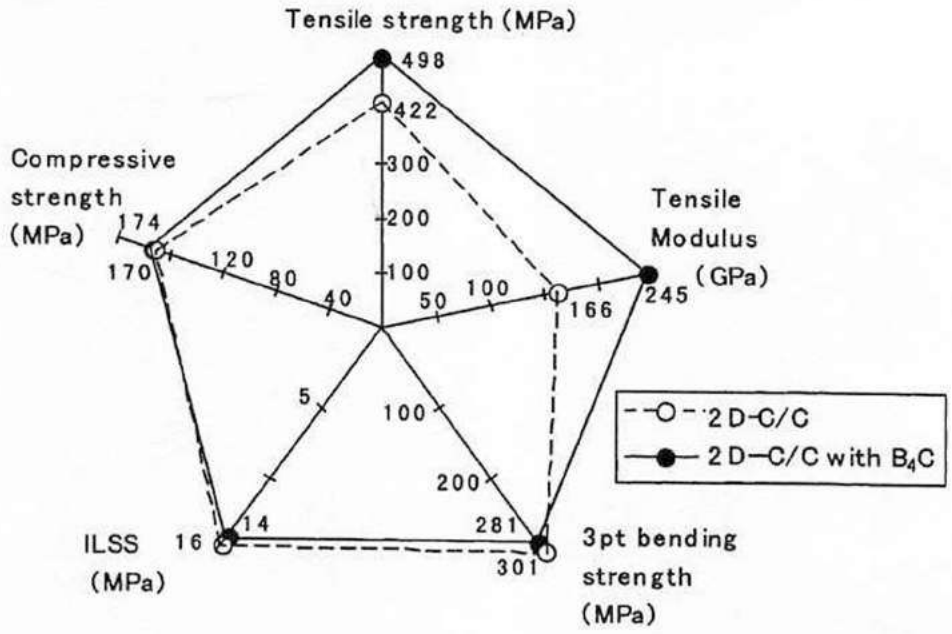

Figure 7. Balance sheet of mechanical properties of 2D-C/C-B_4C at room temperature

The principal properties of the both C/C composites are listed in Table 2. The conditions and the methods to test the samples were the same as those used in the previous tests. The physical properties are shown in Figure 7. It turns out that the tensile strength and the tensile modulus are improved. The modulus of elasticity of the matrix is considered to be a key to the overall improvement.

Tensile Properties of the B_4C Hybrid Matrix C/C Composite at high Temperatures

Evaluations of tensile properties of UD-C/C-B_4C and 2D-C/C-B_4C composites were carried out at 2000 °C. The results are shown in Figures 8 and 9. The fracture patterns of the test samples are also demonstrated in Figure 10 for a visual understanding. Analogously to the C/C composites without B_4C, an increase in hardness and a depreciation of elasticity at 2000 °C compared to room temperature is recognized from the general patterns for both UD and 2D hybrid matrix C/C composites. As shown in Figure 10, the UD-C/C-B_4C test sample did not undergo tensile fracture at 2000 °C, but a vertical crack is produced and followed by the tab peeling. The tensile stress at the peel crack encountered was extraordinarily large, or greater than 1250 MPa.

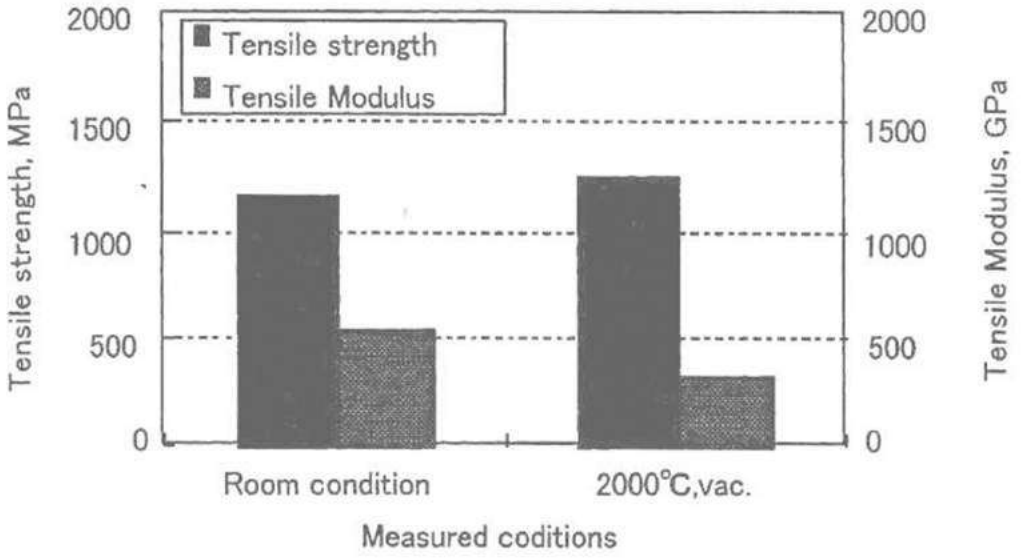

Figure 8. Tensile test results of UD-C/C-B_4C hybrid matrix composite

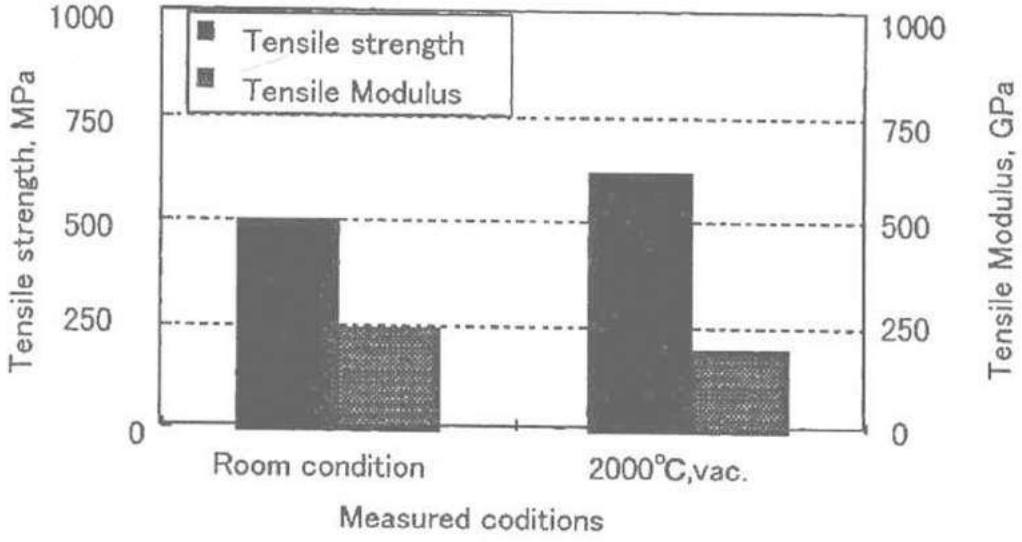

Figure 9. Tensile test results of 2D-C/C-B_4C hybrid matrix composite

Table 2. Principal properties of 2D-C/C-B_4C hybrid matrix composites used

Sample	Density	Vf	B4C content	Impregnation	HTT
	g/cm^3	vol%	wt%	times	°C
2D-C/C-B4C	1.95	60	6.3	3	2000
2D-C/C	1.88	52	–	5	2000

4. Conclusion

Using the mesophase pitch-based carbon fibers, mechanically strong C/C composites could prepared by heat treatment at a high temperature of 2800 °C. The developed C/C composites possess Vf increased by 60%. In additions, fracture deformation was decreased, leading to the drastic increase in tensile strength up to 1000 MPa. In this study, carbon/B_4C hybrid matrix C/C composites could be successfully developed using a matrix precursor consisting of pitch and B_4C powders. The homogeneous dispersion of the B_4C powder in the carbon matrix of this hybrid composite was also confirmed experimentally. The oxidation-resistance tests conducted at temperatures below 1000 °C revealed that the oxidation resistance of the C/C composites containing B_4C was remarkably improved. The C/C composites without B_4C gave a reduction of 25% in weight after the treatment for 20 minutes at 700 °C, while the change in weight was negligibly small for those with B_4C even after 30 min. The mechanical properties of the UD-C/C composites with B_4C, such as strength, three-point bending strength, ILSS and compression strength, increased compared to those of the C/C composites without B_4C. The tensile strength of the

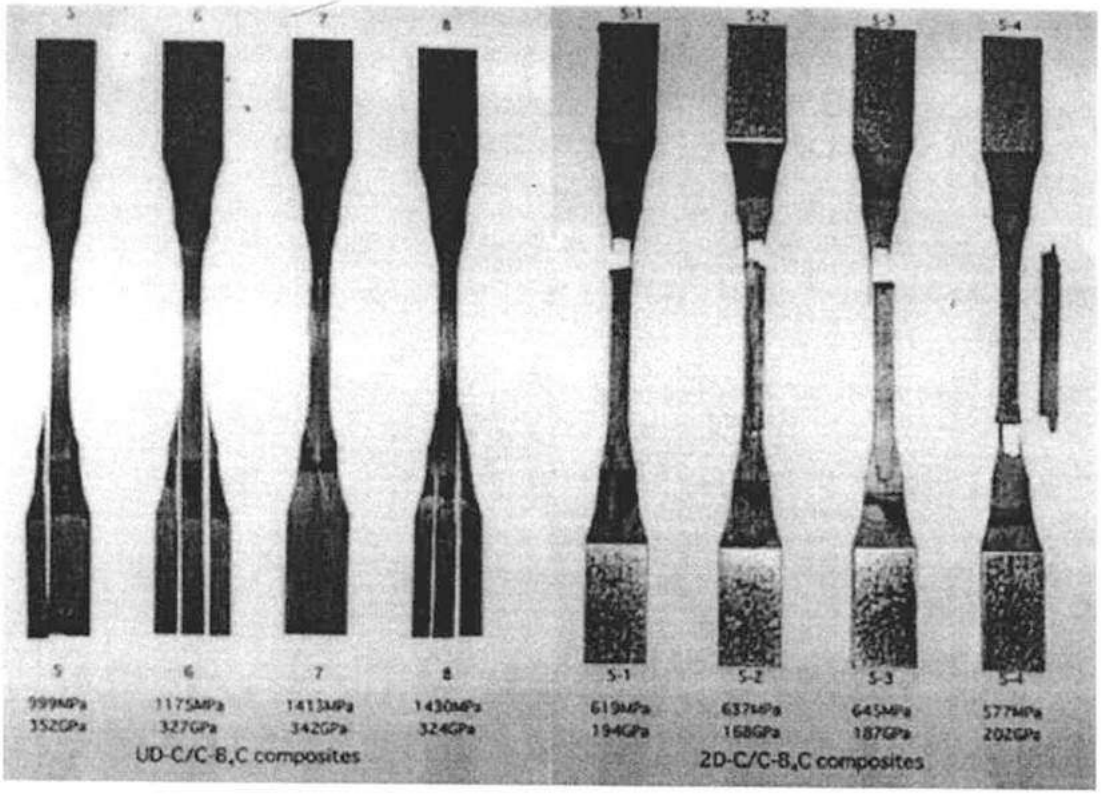

Figure 10. Fracture specimens of tensile test at 2000 °C

2D-C/C composites with B_4C was greater than that of the 2D C/C composites without B_4C. However no appreciable improvement were obtained in three-point bending strength, ILSS, and compression. It turns out from the ILSS test indicated that the initial fracture occurred at the 0/90 layer interface.

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