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Room and high-temperature mechanical and thermal properties of SiC fiber-reinforced SiC composite sintered under pressure

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Abstract

Polycarbosilane-impregnated 2D woven SiC fiber-reinforced SiC composites with 52 vol% of fibers were fabricated by hot-pressing at 1650–1750°C under a pressure of 40 MPa using sintering additives of an Al_2O_3–Y_2O_3–CaO system. The composites fractured in a non-brittle manner. Maximum strength of the composites hot-pressed at 1700°C or 1750°C did not decrease up to a test temperature of 1200°C. The fracture energy increased with increasing test temperature and peaked at 1200°C. Thermal conductivity increased with increasing bulk density, and the values were 7–14 W/m K at room temperature. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Silicon carbide fiber-reinforced silicon carbide composite (SiC/SiC_f) is one of the candidate structural materials for future fusion reactors because of its low induced radioactivity, quick decay of activity, low heat evolution, low atomic number, good fracture resistance, excellent high-temperature properties and corrosion resistance [1–6]. Fundamentally, SiC shows good resistance for high-energy neutron irradiation up to very high neutron fluences [7–11]. A fusion power reactor concept based on the use of SiC/SiC_f composite has been designed by JAERI (DREAM reactor) [12] or ARIES team (ARIES-IV) [13].

There are several processes to fabricate SiC/SiC_f composites, for example, chemical vapor infiltration (CVI) method and polymer infiltration and pyrolysis (PIP) method. These processes have some advantages, such as a relatively low processing temperature and formation of pure matrix. However, these processes require a long manufacturing time that leads to high processing cost. Furthermore, the SiC/SiC_f composites fabricated by these processes usually contain 10–30 vol.% of voids, resulting in low mechanical and thermal properties [4,14–16]. In order to simplify the fabrication process and to obtain dense SiC/SiC_f composites with high mechanical and thermal properties, the authors have explored a new fabrication process using hot-pressing [17–19].

SiC/SiC_f composite was fabricated using a green sheet of SiC with Al_2O_3–Y_2O_3–CaO sintering additives and SiC slurry-impregnated two-dimensionally (2D) woven Hi-Nicalon cloth with/without BN-coating by hot-pressing at 1750°C [18,19]. Although these composites achieved nearly full density, they fractured catastrophically. It was postulated that interfacial strength between fiber and matrix was too high due to the reaction between the matrix components such as sintering additives and the BN-coating on the fiber, and the fibers were degraded severely by the exposure at a temperature as high as 1750°C. In addition, Hi-Nicalon fibers were deformed since filaments contacted each other directly due to the insufficient impregnation of the SiC slurry between each filament, resulting in low mechanical properties [18].

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In order to improve the mechanical properties, Hi-Nicalon cloths impregnated with polycarbosilane, instead of SiC slurry, were used for the reinforcement and the SiC/SiC$_f$ composite was fabricated by the same process as described above. It is expected that the SiC matrix can be formed between filaments by the use of liquid polycarbosilane. In this study, mechanical properties of the SiC/SiC$_f$ composites fabricated by this process were evaluated at room and high temperatures up to 1400°C. In addition, thermal conductivity was also measured at room temperature.

2. Experimental procedures

2.1. Fabrication of green sheet

An Al_2O_3–Y_2O_3–CaO system was chosen for the fabrication of the SiC/SiC$_f$ composite as sintering additives because of their low densification temperatures [20]. Submicron β-SiC, sintering additives (20 mass% in total) using Al_2O_3, Y_2O_3, CaO, and some organics were used. The green sheet was prepared by a laboratory-scale doctor-blade equipment and cut into pieces of 35 mm × 35 mm with a thickness of 105–125 μm. Details of the fabrication process of the green sheet were described elsewhere [18].

2.2. Fabrication of the SiC/SiC$_f$ composite

Two-dimensionally (0°/90°) plain-woven BN-coated Hi-Nicalon (Nippon Carbon, Japan) fiber cloth was used as the reinforcement. The thickness of the BN-coating was 0.4 μm. The cloth was cut into 35 mm × 35 mm squares. Polycarbosilane (PCS, density: 1.10 g/cm^3, Nippon Carbon, Japan) was dissolved in toluene at 80°C, and the cloths were impregnated with PCS-toluene solution under vacuum and dried at 130°C. The green sheets and the PCS-impregnated cloths were stacked alternately and heat-treated at 300°C for 24 h in air under a pressure of 0.02 MPa. The stacked green body was hot-pressed at 1650°C, 1700°C and 1750°C for 1 h in Ar atmosphere under a pressure of 40 MPa. Fiber volume fraction of the composites was about 52 vol.%.

2.3. Mechanical and thermal properties

The specimens were cut into rectangular bars (3.5 mm × 2.9–3.2 mm × 34 mm) and machined into disks (10 mm in diameter and 1 mm in thickness) for bending strength and thermal conductivity measurement, respectively.

Three-point bending strength was measured at room temperature (RT) in air and high temperatures up to 1400°C in vacuum (about 2.7×10^{-3} Pa) with a cross-head speed of 0.1 mm/min and a lower span of 30 mm using a universal testing machine (Instron 1185, USA). Two specimens were tested at each temperature. Fracture energy was calculated from the area of load–displacement curve in bending strength measurement divided by twice the fracture surface area.

Thermal diffusivity (α) and specific heat (C_p) were measured by the laser flash method (LF/TCM-FA8510B, Rigaku, Japan) at RT. Bulk density (ρ) was measured by Archimedes' method. Thermal conductivity (κ) was calculated from the following equation:

$$\kappa = \alpha C_p \rho.$$

3. Results and discussion

3.1. Mechanical properties

Fig. 1 shows the load–displacement curves of the SiC/SiC$_f$ composites measured at RT. These composites exhibited non-brittle fracture behavior, and the curve spread more widely with the decrease in sintering temperature. After the elastic region, the non-linear region, which would be caused by fiber-bridging and sliding after debonding, appeared. The SiC/SiC$_f$ composite hot-pressed at 1700°C showed higher maximum strength than the composites hot-pressed at 1650°C or 1750°C. Scanning electron microscope (SEM) observation showed that the SiC matrix derived from polycarbosilane formed between filaments sufficiently, and the fibers maintained round shape. In this fabrication process, polycarbosilane-impregnation into Hi-Nicalon fiber cloth was effective to form the matrix between filaments and induced non-brittle fracture.

Load–displacement curves of the SiC/SiC$_f$ composites measured at high temperatures up to 1400°C are shown in Fig. 2. The load–displacement curves at

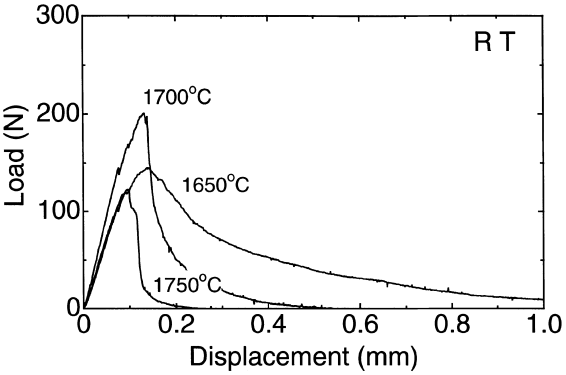

Fig. 1. Load–displacement curves of SiC/SiC$_f$ composites fabricated by hot-pressing at various sintering temperatures at room temperature.

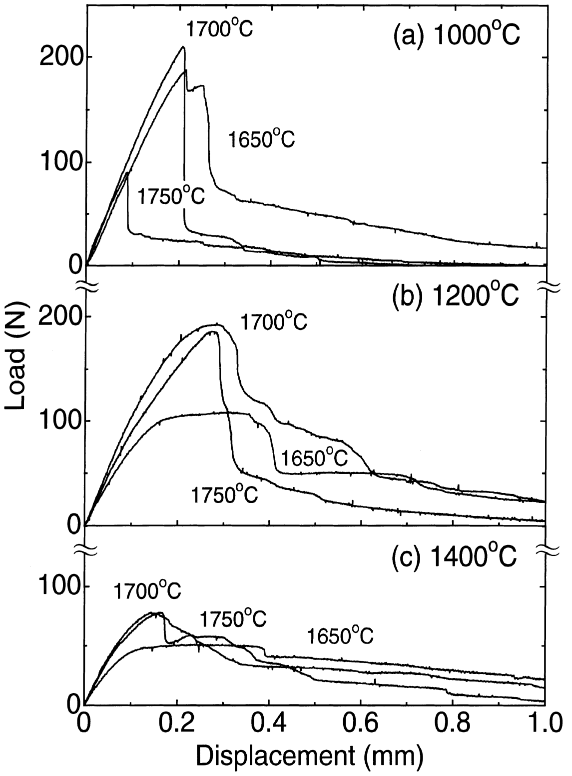

Fig. 2. Load–displacement curves of SiC/SiC$_f$ composites fabricated by hot-pressing at various sintering temperatures at: (a) 1000°C, (b) 1200°C and (c) 1400°C.

1000°C were similar to that at RT (Fig. 2(a)). The load dropped suddenly after reaching a maximum.

At temperatures above 1200°C, the load–displacement curves were different from that at RT and 1000°C. At 1200°C (Fig. 2(b)), the load tended to reduce slowly after the maximum load, and then, the load–displacement curves spread more widely compared with that at test temperatures below 1200°C. In the case of the composite hot-pressed at 1650°C, the maximum strength decreased and the flat region which would be caused by sliding between matrix and fiber cloth layer, i.e., shear fracture, could be observed. At 1400°C (Fig. 2(c)), the maximum strength decreased significantly, and the reduction in load was small after the maximum load and load–displacement curves were almost flat. In particular, the composites hot-pressed at 1650°C showed a flat curve. These curves indicate that the composites fractured in shear fracture mode rather than in tensile fracture mode.

Maximum strength of the SiC/SiC$_f$ composites at RT and high temperatures is shown in Fig. 3. Each data point shows the average of two tests. In the case of the composite hot-pressed at 1750°C, the maximum strength had the highest value of 260 MPa at 1200°C, which was about 100 MPa higher than the RT-strength. The composite hot-pressed at 1700°C kept RT-strength up to 1200°C. Maximum strength of the composites hot-pressed at 1650°C was kept up to 1000°C and decreased significantly at temperatures higher than 1000°C.

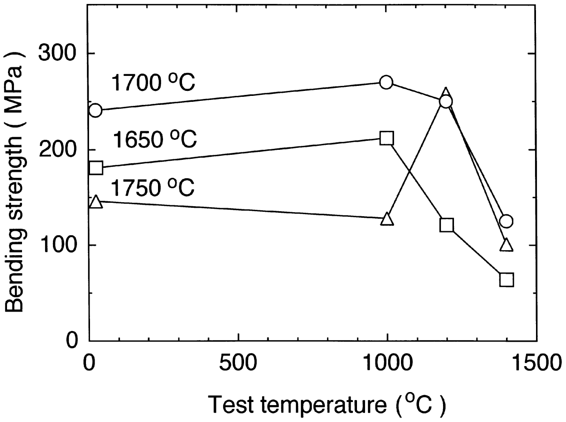

Fig. 3. Maximum strength of hot-pressed SiC/SiC$_f$ composites as a function of test temperature.

Fracture energy of the composites increased with increasing test temperature and showed a maximum value at 1200°C. In the case of the composite hot-pressed at 1700°C, fracture energy at 1200°C was about 4.3 kJ/m^2 and this value was about four times higher than that at RT.

These results can be attributed to an increase in crack propagation resistance and promotion of fiber pull-out by the softening of the grain boundary phase in the matrix at high temperature. Densification of SiC with Al_2O_3–Y_2O_3–CaO additives proceeds via liquid-phase sintering mechanism, and glassy phase exists in grain boundaries derived from SiO_2 on the surface of SiC and oxide sintering additives. In our preliminary work, bending strength of monolithic SiC with Al_2O_3–Y_2O_3–CaO additives hot-pressed at 1750°C was measured at RT and high temperatures, and inelastic deformation behavior could be observed at high temperatures above 1200°C due to the softening of grain boundary phases. In the composite, it was expected that crack propagation was arrested, and fiber pull-out occurred easily by softening of grain boundary phase at high temperature.

Furthermore, residual stress caused by the difference in thermal expansion coefficient between matrix and fiber probably affected the fracture behavior of the SiC/SiC$_f$ composite. In the case of the composite obtained in this study, the thermal expansion coefficient of the matrix was considered to be higher than that of the fiber, because the SiC matrix contained components with higher thermal expansion coefficient, such as Al_2O_3 (8.8×10^{-6} K^{-1}) and yttrium–aluminum garnet (YAG: $Y_3Al_5O_{12}$) (5.1×10^{-6} K^{-1}), compared with Hi-Nicalon fiber (3.5×10^{-6} K^{-1}). Then, the tensile residual stress on the matrix and the compressive residual stress on fibers would have taken place and the tight interface between fiber and matrix was formed. As a result, the composite would show a reduction in strength for matrix cracking and have difficulty in fiber pull-out at RT. At high temperature, the residual stress was released, and the composite showed high fracture energy due to large fiber pull-out with initial strength.

3.2. Thermal properties

Fig. 4 shows thermal conductivity of the SiC/SiC$_f$ composites measured at RT. The bulk density of the SiC/SiC$_f$ composites obtained in this study was 2.72–2.86 g/cm^3 (90–95% of relative density). The thermal conductivity increased with an increase in bulk density and the value was 7–14 W/m K.

Nakano and Yamada [21] reported that 2D SiC/SiC$_f$ composites fabricated by CVI method had a thermal conductivity of 2–14 W/m K at RT, and it was influenced by the porosity. Porosity of the SiC/SiC$_f$ composite fabricated by hot-pressing in this study was lower than that of the SiC/SiC$_f$ composite fabricated by CVI method; however, thermal conductivity of the hot-pressed SiC/SiC$_f$ composites was nearly the same or slightly higher compared with that of the CVI-SiC/SiC$_f$ composites. This can be mainly attributed to the fibers with low thermal conductivity. Hi-Nicalon fiber has a thermal conductivity of 7.8 W/m K at 25°C and 10.1 W/m K at 500°C [22]. The SiC/SiC$_f$ composites fabricated in this study contained large amount of fibers, about 52 vol.%, resulting in low thermal conductivity.

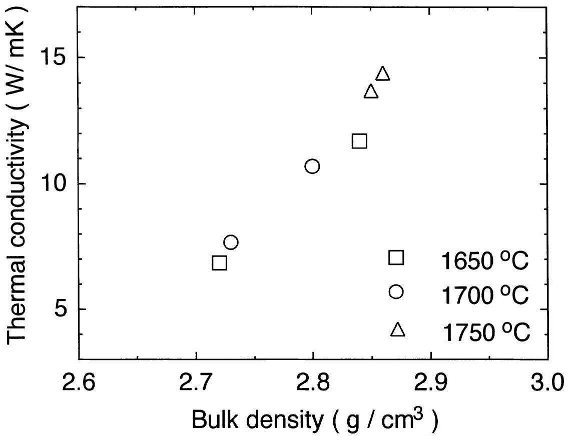

Fig. 4. Thermal conductivity of hot-pressed SiC/SiC$_f$ composites measured at room temperature as a function of bulk density. Symbols indicate different sintering temperature as shown in the figure.

In addition to large amount of fibers with low thermal conductivity, the SiC matrix would also affect the thermal conductivity of the composites. In our preliminary work, the thermal conductivity of monolithic SiC with Al_2O_3–Y_2O_3–CaO additives hot-pressed at 1750°C was measured to be 32 W/m K at RT. Intrinsic thermal conductivity of SiC has been estimated to be 490 W/m K [23]. In general, SiC ceramics have a thermal conductivity of 50–200 W/m K, which is much lower than the intrinsic value. The thermal conductivity of the SiC matrix hot-pressed with Al_2O_3–Y_2O_3–CaO additives was much lower, which may be attributed to the microstructure and the constituent phases of this matrix. It has been experimentally demonstrated that thermal conductivity of polycrystalline ceramics, κ, increases with an average grain size, L ($\kappa \propto L^{1/2}$ [24]). From SEM observation, the SiC matrix had a relatively uniform microstructure composed of fine grains with a size of smaller than 1 μm, and the grain growth during sintering was very small. Moreover, glassy phase exists in grain boundaries in the matrix, having a lower thermal conductivity of less than 1 W/m K [25]. Furthermore, oxides and their compounds, such as YAG derived from sintering additives, also have low thermal conductivity.

From these results, to obtain a high thermal conductivity SiC/SiC$_f$ composite, it is necessary to increase the thermal conductivity of the SiC matrix. Microstructural improvements, such as crystallization of grain boundary phases and desirable grain growth, are effective ways for high thermal conductivity as well as good mechanical properties. In addition, the amount of sintering additives should be reduced for high thermal and mechanical properties.

4. Conclusions

Green sheets of SiC with Al_2O_3–Y_2O_3–CaO additives prepared by doctor-blade method and polycarbosilane-impregnated 2D woven Hi-Nicalon fiber cloths with BN-coating were used for the fabrication of SiC/SiC$_f$ composite by hot-pressing at 1650–1750°C.

The obtained composites fractured in a non-brittle manner. Maximum strength of the composites hot-pressed at 1700°C or 1750°C did not decrease up to a test temperature of 1200°C. The fracture energy increased with increasing test temperature up to 1200°C. This result may be attributed to increasing crack propagation resistance and promoting fiber pull-out by softening the grain boundary phase at high temperature. Furthermore, residual stress probably affected the fracture behavior of the composite.

Thermal conductivity increased with increasing bulk density. The values were 7–14 W/m K at room temperature. This result would be due to the SiC matrix consisting of fine grains with a size smaller than 1 μm and due to the presence of the low-thermal conductivity phases in grain boundaries such as the glassy phase, in addition to low thermal conductivity of the SiC fiber itself.

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