Effect of CNT addition and its orientation on thermal shock resistance of B₄C/CNT composites fabricated by hot-pressing

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ABSTRACT
This paper describes the synthesis of B₄C/carbon nanotube (CNT) composite by hot-pressing and shows the details for the effectiveness of CNT addition, additive amount and its orientation on the thermal shock resistance. CNTs tend to array perpendicular to the hot-pressing direction, which caused anisotropical mechanical and thermal properties of B₄C/CNT composite. We investigated the residual bending strength of thermally shocked B₄C/CNT composites and determined the critical temperature ΔT_C that causes precipitous strength drop. In the case of B₄C/C₁₅ vol% CNT composite, the residual bending strength almost unchanged at ~450°C; ΔT_C increased by 150°C or more than that of monolithic B₄C. Based on the thermal stress fracture-resistance parameter R of the composites, it was clarified that the excellent R is mainly due to the higher thermal conductivity and lower elastic modulus. The numerical results showed that CNT addition has a pronounced effect on the thermal shock residual bending strength and thermal stress fracture-resistance of B₄C/CNT composite.

1. Introduction
Fast reactors have been attracting attention as next-generation nuclear reactors with sustainable energy on the basis of the stable and effective use of resources. Boron carbide (B₄C) ceramics have excellent properties such as high melting point, good chemical and thermal stability, light weight and high neutron absorption cross-section [1]. Therefore, B₄C pellets have been used as neutron absorbers in control rods for fast reactors. The control rods play a major role in power control of fast reactor. However, B₄C neutron absorber pellets experience cracking due to thermal stresses caused by radial temperature gradients present in B₄C pellets [2,3]. Crack propagation and disintegration are also induced by formation of helium bubbles in irradiated B₄C pellets due to ¹⁰²B(n, α)⁴Li reaction. These problems result in extensive mechanical interaction between the B₄C pellets fragments and cladding tube and failure of a control rods in a short period of time [4–7].

Thermal stresses are classic phenomena in ceramics because they generally possess low thermal conductivity and high elastic modulus. To enhance the thermal and mechanical properties of B₄C, carbon nanotubes (CNTs) have been assumed to be effective for improvements of mechanical and thermal properties of B₄C/CNT composite [8–11]. Hirota et al. achieved homogeneous dispersion of CNTs into the B₄C matrix and good mechanical properties at wide temperature range [8,9]. Wei et al. reported the good flexural strength and fracture toughness of B₄C/CNT composite reinforced with multi-walled carbon nanotube (MWCNT) and silicon sintering aid fabricated by hot-pressing [10]. Yavas et al. fabricated B₄C/CNT composites with good fracture toughness and Vickers hardness in composite with ~3mass% CNTs by spark plasma sintering technique [11]. As for the thermal properties, Kobayashi et al. found that CNT addition effectively improves the fracture toughness and thermal conductivity of B₄C [12]. Recently, we found that the thermal shock damage resistance of B₄C/10 vol% CNT composite was clearly enhanced by CNT addition, as is evident from thermal shock test and observation for suppression of crack propagation [13]. However, the details for the effectiveness of CNT addition, additive amount and its orientation on the thermal shock resistance of B₄C/CNT composite have not yet been clarified. In the present study, we show the synthesis of B₄C/CNT composite by hot-pressing, and propose the optimum amount of CNT and its orientation effect on the thermal shock resistance of the composite. This work demonstrates the residual bending strength of thermally shocked B₄C/CNT composites and quantitatively evaluates the thermal stress fracture-resistance parameter R based on the thermal and mechanical
properties. The numerical results clarified the pronounced effect of CNT and the mechanism for improving the thermal shock resistance of B₄C/CNT composite.

2. Experimental procedures

2.1. Sample preparation

Commercial B₄C (Grade HS, average grain size: 0.8 μm, H. C. Starck, Germany), α-Al₂O₃ (TM-D, average grain size: 0.1 μm, 99.99% purity, Taimei Chemicals Co. Ltd., Japan) and CNT (VGCF-H, MWCNT, average diameter: 150 nm, average length: 5 μm, Showa Denko K.K., Japan) shown in Figure 1 were used as starting materials. The isotopic content of ¹⁰B in B₄C was the natural ratio (19.8%). CNT was added into ethanol with dispersant (SN-Sparse 2190, San Nopco Ltd., Japan), and then 95–80 vol% B₄C and 5 vol% Al₂O₃ as a sintering aid were added into CNT/ethanol suspension. The content of CNTs was 0–15 vol% versus the total solid component of B₄C, CNT and Al₂O₃. The suspension was mixed by ultrasonic treatment with a homogenizer for 10 min and ball-milling for 24 h, followed by drying with a rotary evaporator and sieving. The powder mixture was formed into a rectangular sample by uniaxial pressing of 10 MPa. The fabrication of B₄C/CNT composite was performed with hot-pressing (Hi-Multi-5000, Fuji Dempa Kogyo Co., Ltd., Japan) at 2000°C under a uniaxial pressure of 40 MPa for 1 h in Ar flow (2 L/min). The B₄C/CNT composites with 0, 2, 10 and 15 vol% CNT are denoted as C0, C2, C10 and C15, respectively. In order to evaluate the thermal and mechanical properties of B₄C/CNT composites, the fabricated samples were cut perpendicular and parallel to the axis of hot-pressing direction because CNTs in the B₄C/CNT composites were dispersed in two dimensionally random and tend to array perpendicular to the hot-pressing direction as described in the earlier paper [13].

2.2. Characterization, mechanical and thermal properties measurement

The constitution crystalline phases on the B₄C/CNT composites were analyzed by X-ray diffraction (XRD) measurement with CuKα radiation (PW1700, Philips, the Netherlands) operated at 40 kV tube voltage and 30 mA tube current of X-ray tube. The solid solubility of carbon from CNT into B₄C was examined by measuring the lattice parameters of the pulverized B₄C/CNT composites with Si standard powder (RSRP-43275 G, α₀ = 5.430758 Å at 298.1 K, Rigaku, Japan) using a reflection-free single-crystal silicon stage. Step scan (step: 0.02° for 3 s) was done in a range of 2θ = 10–120° at room temperature, and the lattice parameters were calculated with the RIETAN-FP program [14]. The grain size distribution was measured by using image processing program (Image J [15]) based on the scanning electron microscope (SEM) images on the chemically etched surface of the composites by SEM (S-4800, Hitachi High Technologies, Japan). Their bulk density and open porosity were measured by Archimedes’ method.

The samples were cut into discs with the thickness of 1 mm and the diameter of 10 mm for thermal conductivity measurement and into 4 × 3 × 35 mm³ rectangular bars for three-point bending test. The bending strength was measured by three-point bending test with a span of 30 mm and crosshead speed of 0.5 mm/min at room temperature by using a universal testing machine (Model 1185, Instron, USA). Microstructural observation was carried out to observe the fracture surface after bending test by SEM.

The elastic modulus and Poisson’s ratio were measured by ultrasonic pulse-echo technique (5072PR, Olympus NDT). The Vickers hardness Hᵥ and fracture toughness Kᵥ were evaluated with an applying load of 0.98–98 N for duration time of 15 s and the indentation fracture (IF) method based on the equation proposed by Niihara [16,17]. In order to calculate the thermal conductivity, thermal diffusivity and specific heat were measured in a temperature range of 25–1000°C by laser flash method (LFA-457, NETZSCH Japan K.K.) and a differential scanning calorimetry (DSC404F3, NETZSCH Japan K.K.), respectively. The coefficient of thermal expansion (CTE) was evaluated in a temperature range of 40–600°C by thermomechanical analysis (DIL402CD, NETZSCH Japan K.K.). Elastic modulus, Poisson’s ratio, Vickers hardness, fracture toughness, thermal diffusivity and CTE were measured in parallel and perpendicular to the CNT-orientation dispersed in two dimensionally random in the B₄C/CNT composites.

2.3. Evaluation of thermal shock resistance

The residual bending strength after thermal shock test was measured by three-point bending test. The thermal shock test was performed with a high-
frequency induction heating furnace (SM-TKY-MU -αL, SK Medical Denshi, Japan) in Ar atmosphere. After heating the samples for 30 min, they were quenched immediately from the furnace into water at room temperature. Thermal stress fracture-resistance parameter $R'$ was calculated based on the measured thermal and mechanical properties of the B$_4$C/CNT composites using the following equation proposed by Hasselman [18]:

$$R' = \sigma_t (1 - \nu) / E a$$  

where $\sigma_t$ is the fracture strength, $\kappa$ the thermal conductivity, $\nu$ the Poisson’s ratio, $E$ the elastic modulus and $a$ the CTE. This parameter corresponds to the resistance for crack initiation under thermal stress.

### 3. Results and discussion

#### 3.1. Characterization

Figure 2 shows XRD patterns of hot-pressed B$_4$C/CNT composites on the plane in parallel and perpendicular to the CNT-orientation. XRD revealed that the hot-pressed B$_4$C/CNT composites consisted of B$_4$C and secondary phases such as Al$_2$O$_3$ and Al$_5$BO$_9$. Al$_5$BO$_9$ was formed by the reaction of Al$_2$O$_3$ and B$_2$O$_3$ in the starting B$_4$C powder [19,20]. Diffraction peak intensities of CNT at $2\theta = 26.5^\circ$, which correspond to the interplanar distance of $d_{002}$ of MWCNT, on the plane in perpendicular direction to the long axis of CNTs were much higher than that on the plane in parallel direction, which indicated the CNT orientation in the sintered body as described in the previous study [13]. As B$_4$C has a wide solid solution range between 9 and 24.3 at.% C [21,22], the lattice parameters of B$_4$C, especially $c$-axis, strongly depend on the carbon content [23,24]. Therefore, the carbon contents of the B$_4$C in the obtained composites were examined by measuring the lattice parameters. Figure 3 shows the lattice parameters of the B$_4$C in the composites as a function of CNT contents. Aselage et al. reported that the $c$-axis length decreased linearly in a solid solution range of 13.3–20.5 at.% C and varied averagely about 0.014 Å every 1 at.% C [23]. In this study, the lattice parameters of $a$ and $c$ almost unchanged with increasing the CNT content. The $c$-axis varied only 0.003 Å from 0 vol% to 15 vol% CNT addition, which indicated that the solid solubility of carbon from CNT could be ignored: It can be seen that there is no significant change in densification of B$_4$C due to mass transport of carbon, and no effect on the physical properties. On the other hand, the formation of Al$_5$BO$_9$ secondary phase could allow to fill gaps, voids and pores between grains, which results in higher density and lower porosity of B$_4$C [20].

Figure 4 shows SEM micrographs of chemically etched surface of B$_4$C/CNT composites and average grain size as a function of CNT content. The brighter contrast area in the SEM image corresponded to Al-rich phase, possibly Al$_2$O$_3$ and Al$_5$BO$_9$. On the other hand,
the dark-contrasted grains were found to be B₄C. The average grain size of B₄C scarcely varied from 1.4 ± 0.9 µm to 1.2 ± 0.7 µm with increasing the CNT content. In our previous work, it was clearly found that the CNTs in the hot-pressed B₄C/CNT composites are dispersed during B₄C grains and tend to array perpendicular to the hot-pressing direction [13]. Bulk density of hot-pressed B₄C/CNT composites are shown in Figure 5. The relative density was almost the same in the range of 0–10 vol% CNT contents, and the values were around 97–98%. However, 15 vol% CNT addition induced the lower relative density of 95.8% and higher open porosity due to the suppression of sintering and densification by CNTs dispersed between B₄C grains.

### 3.2. Mechanical and thermal properties

Three-point bending strength was measured in parallel to the CNT-orientation dispersed in two dimensionally random in the composites. Figure 6 shows the bending strength of hot-pressed B₄C/CNT composites as a function of CNT contents. The bending strength of C₀, C₂, C₁₀ and C₁₅ composite were 736, 621, 645 and 520 MPa, respectively. The bending strength decreased by CNT addition especially on C₁₅ composite (15 vol% CNT) due to the decrease in the relative density and lack of good dispersion of Al₂O₃ and CNTs. The existence of large Al₂O₃ grains (~50 µm) and CNT-agglomerates were observed on the fracture surface by SEM (Figure 7). In C₂ composite, it is considered that the large Al₂O₃ grain was the cause of crack initiation because a formation of mirror region was clearly confirmed around the Al₂O₃ grain (Figure 7(a-c)) although the inherent defect size calculated from the bending strength and fracture toughness (described below) was about ~17 µm. The calculation was conducted based on Ref [25]. On the other hand, the CNT-agglomerates (~5 µm) existing in the center of the mirror region could not be observed. The calculated defect size was about ~20 µm, so it is considered that CNT-agglomerate was not the cause of crack initiation.

![Figure 3. Lattice parameters a and c of the B₄C in the B₄C/CNT composites as a function of CNT contents.](image)

![Figure 4. SEM micrographs of chemically etched surface of B₄C/CNT composites: (a) C₀, (b) C₂ and (c) C₁₅ composite. (d) Average grain size as a function of CNT content.](image)
Figure 8 shows the elastic modulus ($E$), Vickers hardness ($H_v$) and fracture toughness ($K_{IC}$) of B$_4$C/CNT composites as a function of CNT contents. These mechanical properties were measured in different directions, parallel ($//$) and perpendicular ($\perp$) to the CNTs-orientation. With increasing the CNT content, $E$ and $H_v$ decreased; $E$ from ~476 to 264 ($\perp$) and 230 ($//$) GPa, and $H_v$ from ~30 to 19 ($\perp$) and 15 ($//$) GPa, respectively. On the other hand, $K_{IC}$ slightly increased from 2.7 to 3.3 ($\perp$) and 3.4 ($//$) MPa·m$^{1/2}$. The reduction in $E$ and $H_v$ could be explained in terms of the addition of the soft CNTs [9]. Concerning about the accession in $K_{IC}$, it is well-known that CNTs improve the fracture toughness of the composite through a range of toughening mechanisms such as CNT pull-out, bridging effect and crack deflection [26,27]. Figure 9 shows the fracture surfaces of the C0 and C10 composites and crack propagations, which were induced by Vickers indentation. The bridging and pull-out of CNTs were clearly observed, and the induced cracks slightly deflected comparing to monolithic B$_4$C. Hence, the enhancement of $K_{IC}$ was due to the CNT bridging and pull-out, crack deflection, CNT-agglomerations and decrease in relative density.

The CTE of B$_4$C/CNT composites as a function of CNT content is shown in Figure 10. The CTE of the composites measured in perpendicular to the CNT-orientation ($\perp$) were almost unchanged with increasing CNT content. On the other hand, CTE of the composites in parallel direction ($//$) decreased from $5.1 \times 10^{-6}$ to $4.9 \times 10^{-6}$ K$^{-1}$ due to the negative CTE in the axial directions of CNTs [28]. The temperature dependence of the thermal

Figure 5. Bulk density of hot-pressed B$_4$C/CNT composites as a function of CNT contents.

Figure 6. Bending strength of hot-pressed B$_4$C/CNT composites as a function of CNT contents.

Figure 7. (a) SEM micrograph of the fracture surface of C2 composite and (b) the expanded region around Al$_2$O$_3$ grain. (c) Schematic image for the fracture surface and (d) CNT-agglomerates observed on the fracture surface of C10 composite.
conductivity of B₄C/CNT composites is shown in Figure 11. In perpendicular to the CNT-orientation (⊥), the thermal conductivity decreased with increasing CNT content at room temperature but almost same at high temperature range of 700–1000°C. In parallel to the CNT orientation (∥), the thermal conductivity enhanced with increasing CNT content even at high temperature range owing to the excellent thermal conductivity along the long axis of CNTs [29]. The highest thermal conductivity was found to be 36 W/m·K on C2 composite at room temperature, but in a temperature range of 300–1000°C, C15 composite had the highest value.

### 3.3. Thermal shock resistance

The residual bending strength after thermal shock test is shown in Figure 12. The strength remains unchanged when the thermal shock ΔT is less than a critical temperature ΔTc at which the crack initiation occurs. C2, C10 and C15 composites demonstrated the higher ΔTc than that of C0 composite on which ΔTc was less than 300°C. The residual bending strength of C2 and C10 composites did not decrease at ~350°C and ~400°C, respectively. In the case of C15 composite, the residual bending strength almost unchanged at ~450°C; ΔTc increased by 150°C or more. The numerical result clarified that the CNT addition effectively enhances the thermal shock resistance of B₄C/CNT composite. To evaluate the thermal stress fracture-resistance of the B₄C/CNT composites, R’ was calculated based on the mechanical and thermal properties. Herein, the bending strength was used to calculate R’. Mechanical and thermal properties of the B₄C/CNT composites and calculated R’ are summarized in Table 1. R’ of B₄C/CNT composite significantly increased by CNT addition; the
of $C_0$, $C_2$, $C_10$ and $C_15$ composite were $6.3 \pm 0.6$, $7.1 \pm 0.9$, $10.6 \pm 0.5$ and $9.7 \pm 0.6$, respectively. The excellent $R'$ is mainly due to the higher thermal conductivity and lower elastic modulus of the composite. This pronounced effect of CNT addition on the resistance for crack initiation under thermal stress is in agreement with the bending strength of thermally shocked $B_4C$/CNT composites.

4. Conclusions
We fabricated $B_4C$/CNT composite by hot-pressing and investigated the effect of CNT addition and its orientation on the thermal shock resistance of the composite. It was found that CNTs in the composites were dispersed in two dimensionally random, which tend to array perpendicular to the hot-pressing direction, which caused anisotropic mechanical and thermal properties. Thermal conductivity and CTE were especially different in two directions, parallel and perpendicular to the CNT orientation in $B_4C$/CNT composite. In parallel to the CNT-orientation, CTE decreased due to the negative CTE in the axial directions of CNTs, and the thermal conductivity enhanced owing to the excellent thermal conductivity of CNTs. With increasing the CNT content in the composite, $E$ and $H_v$ decreased, but $K_{IC}$ slightly increased due to the CNT bridging and pull-out. As a result, the thermal shock residual bending strength clarified the pronounced effect.
of CNT on the thermal shock resistance of B₄C/CNT composite in parallel to the CNT-orientation. In the case of C15 composite, \( \Delta T_C \) increased by 150°C or more than that of monolithic B₄C. This excellent thermal shock resistance is mainly due to the higher thermal conductivity and lower elastic modulus of the composite.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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