Enhanced thermal shock and oxidation resistance of $\text{Si}_2\text{BC}_3\text{N}$ ceramics through MWCNTs incorporation

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Abstract: Multi-walled carbon nanotubes (MWCNTs) reinforced $\text{Si}_2\text{BC}_3\text{N}$ ceramics were prepared through mechanical alloying (MA) and following spark plasma sintering (SPS). The thermal shock resistance of $\text{Si}_2\text{BC}_3\text{N}$ ceramics was evaluated comparatively through ice water quenching test and theoretical prediction. Furthermore, the oxidation resistance of MWCNTs incorporated $\text{Si}_2\text{BC}_3\text{N}$ ceramics was evaluated under high temperature. The results show that the calculated parameters such as the critical thermal shock temperature (R) and the thermal stresses resistance (R_{st}), as well as the toughness (R''') are improved with addition of 1 vol% MWCNTs. In addition, the crack propagation resistance of 1 vol% MWCNTs incorporated $\text{Si}_2\text{BC}_3\text{N}$ ceramics is obviously improved through generating more tortuous crack propagation paths attributing to the “crack bridging”, “pull-out”, and “crack deflection” mechanisms of MWCNTs. Therefore, the residual strengths of 1 vol% MWCNTs containing specimens remained the highest after the thermal shock tests. Besides, the present work also reveals that the oxidation resistance is more sensitive to relative density than MWCNTs addition.

Keywords: $\text{Si}_2\text{BC}_3\text{N}$ ceramics; MWCNTs; thermal shock resistance; oxidation resistance

1 Introduction

High temperature ceramics (HTCs) are important ceramics and promising candidates for high temperature applications such as leading edges and nose-cones for

a next generation of sharp re-entry space vehicles [1]. Up to date, the intensively investigated HTCs are mainly composed of binary (e.g., SiC, Si_3N_4 , and ZrB_2), ternary (SiCN), and quaternary (including SiBCN and SiCNTi) composites [2–4]. In the last decade, we have successfully prepared bulk SiBCN ceramics through MA and subsequently HP/SPS sintering. With preparing bulk SiBCN ceramics, the measurements of properties such as flexural strength, fracture toughness, and thermal shock resistance became feasible [5–9]. Among

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these parameters, the thermal shock resistance is a critical parameter in HTC's service since catastrophic failures may occur under severe thermal shocks, attributing to their inherent brittleness. Therefore, it is indispensable to improve the fracture toughness and crack propagation resistance in order to satisfy the practical demands.

In fact, many efforts have been made to improve the fracture toughness of SiBCN ceramics, which thereby enhanced the thermal shock resistance. Our previous works have demonstrated that the additives such as LaB_6 [10], C_f [11], SiC_f [12], Al_4SiC_4 [13], and graphene [14], etc., are potential candidates for improving the fracture toughness. Besides these additives, MWCNTs have been confirmed as one of the most promising reinforcements in oxides [15,16], carbides [17,18], nitrides [19,20], and borides [21,22]. The well-known strengthening and toughening mechanisms are “crack bridging”, “pull-out”, and “crack deflection”. Lately, we have found that the MWCNTs could also enhance the bulk SiBCN ceramics remarkably [23]. Although the MWCNTs have shown positive influences on the strengths and toughness, their specific influence on thermal shock behavior has not been revealed yet. Additionally, the traditional method for evaluating the thermal shock resistance was mainly through quenching test, which is energy and time consuming. Therefore, an effective theoretical prediction should be employed as a substitution or supplementary method. In addition to the thermal stress damage, the oxidation is another technique barrier for the application of MWCNTs containing ceramics under high temperature, attributing to the fact that no enhancement can be obtained after MWCNTs oxidation. Consequently, it is of great importance to evaluate the oxidation resistance of MWCNTs containing SiBCN ceramics.

Therefore, the present work was devoted to preparing the MWCNTs incorporated SiBCN ceramics and evaluating their thermal shock and oxidation resistance. To better verify the feasibility of theoretical prediction, the thermal shock behaviors under different temperatures were evaluated systematically. As a result, 1 vol% MWCNTs could enhance the thermal shock resistance attributing to the increased energy consumption mechanisms. Simultaneously, the theoretical calculations revealed a high level of consistency with practical thermal shock tests. Besides, 1 vol% MWCNTs incorporated SiBCN ceramics exhibited good oxidation resistance under high temperature due to the higher relative density.

2 Experimental

2.1 Preparation of MWCNTs– $\text{Si}_2\text{BC}_3\text{N}$ nanocomposites

The starting raw materials were well crystalline cubic silicon powder (95% in purity, $45.0\text{ }\mu\text{m}$, Beijing Mountain Technical Development Center, China), hexagonal boron nitride power (98.0% in purity, $\text{B}_2\text{O}_3 < 0.4\text{ wt\%}$, $0.6\text{ }\mu\text{m}$, Advanced Technology & Materials Co., Ltd., Beijing, China), and graphite flake (99.5% in purity, $8.7\text{ }\mu\text{m}$, Qingdao Huatai Lubricant Sealing S&T Co., Ltd., China). According to our previous works, the molar ratio of Si:BN:C was set as 2:1:3 and the ball to powder mass ratio was 20:1 [23]. Then the mixed powder was loaded into the silicon nitride vials along with identical component balls under argon atmosphere and milled by a planetary ball mill (P4, Fritsch GmbH, Germany). The rotation speed of the main disk was set as 350 rpm, and the vials were 600 rpm in reverse. The machine was paused for 10 min every 40 min, and the effective milling time was 20 h. The machine was paused for 10 min to avoid over-heat of the vials during the high-speed milling. MWCNTs (95 wt% fixed carbon, Chengdu Organic Chemicals Co., Ltd., China, with outer diameters around 10–30nm) were achieved commercially.

In the present work, 1 vol% and 3 vol% MWCNTs were added and milled with the amorphous $\text{Si}_2\text{BC}_3\text{N}$ powder given the relatively poor dispersion of MWCNTs. Correspondingly the powder was named as $\text{Si}_2\text{BC}_3\text{N}$ -1 and $\text{Si}_2\text{BC}_3\text{N}$ -3 respectively. For a uniform distribution of MWCNTs in $\text{Si}_2\text{BC}_3\text{N}$ powder, planetary mill with zirconia vessel and balls were adopted. The ball to powder mass ratio was set as 20:1 here and taken ethanol as milling medium. The MWCNTs and $\text{Si}_2\text{BC}_3\text{N}$ powder was ball milled for 6 h at a speed of 250 rpm. After that, the slurries were dried at $80\text{ }^\circ\text{C}$ for 24 h for evaporating the ethanol. The corresponding SEM microstructures of as-prepared SiBCN powder, MWNCTs, and MWCNTs– $\text{Si}_2\text{BC}_3\text{N}$ composites were referred to Ref. [23].

2.2 Spark plasma sintering and characterization

The MWCNTs– $\text{Si}_2\text{BC}_3\text{N}$ powder was loaded into a cylindrical graphite die of 40 mm in diameter. A sheet of graphite paper was placed between the punch and the powder for removing the sample easily out of the die after cooling. The SPS (FCT-HP25) sintering process

was conducted under protection of high purity N₂ and a uniaxial pressure of 40 MPa was applied throughout the sintering. The sintering temperature was set at 1900 °C at a rate of 100 °C/min accompanied with a holding time of 5 min. The temperature was measured using a single-color optical pyrometer that was focused to the powder sample within the die. The sintering temperature profile and variation of shrinkage were kept recording during the sintering process. The sintered samples were labeled as T0, T1, and T3 according to their MWCNTs contents, respectively.

The sintered samples were ground and polished with 0.4 μm SiC abrasive paper. The property measurement was carried out on omnipotence mechanics tester (Instron 5569, Instron Corp., USA). The flexural strength and the Young's modulus were obtained using three-point bending test on 3 mm × 4 mm × 20 mm bars with a span of 16 mm and a crosshead speed of 0.5 mm/min. The flexural strength was evaluated according to GB/T 4741-1999. The phases and fracture surface of ceramics were analyzed using X-ray diffraction spectrum (XRD, 40 kV/100 mA, D/max-γB Cu Kα, Rigaku Corp., Japan) and scanning electron microscopy (SEM, 30 kV, Quanta 200 FEG, FEI Co., USA), respectively. STEM (Talos F200x, 200 kV, FEI Company, USA) was also used to analyze the microstructure details of various Si₂BC₃N ceramics.

2.3 Thermal shock test, theoretical prediction, and oxidation resistance

The thermal shock behavior of MWCNTs–SiBCN composites was explored using a conventional water-quenching technique. In the present work, ice water bath (0–5 °C) was adopted for the test. Namely, 20 mm × 4 mm × 3 mm test bars were quickly placed into furnace at air atmosphere and maintained for 10 min at the target temperature to eliminate the temperature gradient. Then the test bars were quickly dropped into the cooling water bath paralleled to their length direction to minimize the artificial thermal gradient. Five specimens were tested for each condition. The thermal shock resistance was assessed by measuring the residual bending strength at room temperature using the aforementioned Instron 5569 testing machine with a crosshead speed of 0.5 mm/min. The water quenching temperature differences (Δ*T*) were chosen as 400, 600, and 1000 °C.

To better analyze the thermal shock behavior of SiBCN ceramics, the thermal shock resistance (TSR)

theory should be introduced. In general, the TSR theories for the ceramics fall into two broad categories: the thermal-shock fracture (TSF) theory and the thermal-shock damage (TSD) theory [24–26]. The first determines the minimum thermal shock required to initiate a crack and the resistance to initiation of fracture by thermal stress. The second expresses the possibility for further damage caused by the thermal stress. The TSF theory is based on the thermo-elasticity theory [25,26], which regards the equilibrium of thermal stresses σ_H and the strength of the material σ_f as the criterion of TSR. The thermal shock fracture resistance parameters R , R' , and R'' were calculated using the equations:

$$R = \frac{\sigma_f \cdot (1 - \mu)}{E \cdot \alpha} \quad (1)$$

$$R' = \frac{\sigma_f \cdot (1 - \mu) \cdot \lambda}{E \cdot \alpha} \quad (2)$$

$$R'' = \frac{\sigma_f \cdot (1 - \mu) \cdot \varnothing}{E \cdot \alpha} \quad (3)$$

where σ_f is the bending strength, E is Young's modulus, α means thermal expansion coefficient, μ is Poisson's ratio, λ is the thermal conductivity, and $\varnothing$ is a stress reduction term. The parameter R is applicable for the case of an instantaneous change in surface temperature for conditions of rapid heat transfer. Meanwhile, R' and R'' are critical thermal shock coefficients under slow heating (or cooling) condition and constant heating (or cooling) condition, respectively. Judging from the equations, high resistance to fracture initiation can be achieved with high strength and thermal conductivity, and with low values of thermal expansion and Young's modulus. However, we should keep it in mind that increasing the strength blindly could lead to catastrophic crack propagation once the cracks initiate. Moreover, it should be noted that the above equations take no account of the variations of the material parameters with temperature. Normally, the thermal expansion coefficient increases with increasing temperature, while the thermal conductivity decreases [26].

In comparison, the TSD theory [27–29] is established from the theory of fracture mechanics, which regards the equilibrium of the thermo-elastic strain energy W and the fracture surface energy U as the criterion of TSR. According to this theory, when the thermo-elastic strain energy W caused by the thermal stress is enough to provide the new surface energy γ_{WOF} caused by the crack extension, i.e., W is greater than U , cracks will

yield, extend, and result in the damage of the material. Here, γ_{WOF} represents the work of fracture over a large area, rather than to initiate fracture. Therefore, Hasselman [27] derived following thermal shock parameters R''' and R'''' , expressing the ability of material to resist crack propagation:

$$R''' = \frac{E}{\sigma_f^2 \cdot (1 - \mu)} \quad (4)$$

$$R'''' = \frac{E \cdot \gamma_{\text{WOF}}}{\sigma_f^2 \cdot (1 - \mu)} \quad (5)$$

In terms of this theory, the superior TSR depends on the high Young's modulus and fracture work, and the low flexural strength of the materials. Additionally, R_{st} was also proposed as a thermal shock resistance parameter by Hasselman [29] according to Eq. (6). In summary, the TSR theory has been applied successfully in the past few decades for various ceramics, including ZrC [30], SiC [31], ZrB₂-SiC [32–34], and ZrB₂-graphite [35] composites. Certainly, some modifications can also be made to better explain the thermal shock behaviors in specific system [36,37].

$$R_{\text{st}} = \sqrt{\frac{\gamma_{\text{WOF}}}{\alpha^2 E}} \quad (6)$$

Besides, oxidation resistance of prepared ceramics was also evaluated and the target oxidation temperatures were set as 1000, 1200, 1400, and 1600 °C with a holding time of 3 h. After oxidation test, the phase compositions, oxidation layer morphologies, and thicknesses were evaluated with the help of aforementioned XRD and SEM. Thermogravimetry-differential scanning calorimetry (TG-DSC, STA449, NETZSCH, Germany) was employed to analyze the mass change of ceramics during the heating process up to 1400 °C in air.

3 Results and discussion

3.1 Microstructure observations

Figure 1 shows the SEM micrographs of specimens sintered with SPS at 1900 °C for 5 min. As can be seen in Fig. 1(a), micro scaled BN(C) plates and much smaller SiC particles are observed in the pristine Si₂BC₃N ceramics. In comparison, some MWCNTs are found in the specimens T1 and T3 as shown in Fig. 1(b) and Fig. 1(c), respectively. Besides, it can still be seen that the particle sizes of BN(C) plates are decreased gradually with the increasing of MWCNTs contents. This result reveals that the introduction of MWCNTs could hinder the growths of BN(C) and SiC particles due to the restrained solid phase diffusion of nano BN(C) and SiC crystals [23].

Furthermore, TEM has been also applied to better observe the detailed microstructures. Figure 2(a) shows the characteristic structure with SiC embedded BN(C) plates. It is apparent that the SiC particle size is around 100–150 nm. In comparison, the TEM micrographs of MWCNTs containing specimens present smaller SiC particles (see Fig. 2(b) and Fig. 2(d)). These observations are in good agreement with the SEM observations. Besides, MWCNTs are inserted in the SiC particles or connected with the BN(C) matrix, which would be beneficial to enhance the ceramics (Figs. 2(c) and 2(e)).

To investigate the specific influences of various microstructures on the fracture behavior of ceramics, the micro-crack propagation after an indentation test have been observed. Figure 3 shows the micro-cracks' propagation of various Si₂BC₃N ceramics. The triangle areas in Figs. 3(a), 3(b), and 3(c) represent the initiation

Fig. 1 SEM microstructures of Si₂BC₃N ceramics: (a) T0, (b) T1, and (c) T3.

Fig. 2 TEM microstructures of $\text{Si}_2\text{BC}_3\text{N}$ ceramics: (a) T0, (b, c) T1, and (d, e) T3.

Fig. 3 Micro-crack propagation in $\text{Si}_2\text{BC}_3\text{N}$ ceramics after an indentation test: (a) T0, (b) T1, and (c) T3.

of micro-cracks closed to the indentation. In contrast to the pristine $\text{Si}_2\text{BC}_3\text{N}$ ceramics, specimens T1 and T3 have much narrower crack initiation, which suggests that the introduction of MWCNTs could suppress the propagation of micro-cracks. Furthermore, the magnified pictures also demonstrate that the main toughening mechanisms for pure $\text{Si}_2\text{BC}_3\text{N}$ ceramics are “pull-out” and “crack deflection” of BN(C). In comparison, the adoption of MWCNTs could further toughen the composites through “crack bridging”, “pull-out”, and “crack deflection” mechanisms [23].

3.2 Thermal shock parameters

Several necessary parameters, including the flexural strength (σ_f), Young’s modulus (E), thermal expansion coefficient (α), and work of fracture (γ_{WOF}) were obtained to calculate the thermal shock parameters. As shown in Table 1, σ_f , E , and γ_{WOF} of specimen T1 are higher than those of specimens T0 and T3. The improvement of mechanical properties should be attributed to the strengthening mechanisms of MWCNTs and the accompanied higher relative density

as well. However, the 3 vol% MWCNTs could no longer improve the mechanical properties due to the lower relative density and potential MWCNTs agglomerations [23]. Additionally, the thermal expansion coefficients of specimens increase slightly with the increasing of MWCNTs content.

Based on the above parameters, the thermal shock related parameters can be calculated based on the above-mentioned equations and the results are listed in Table 1. The R parameter increases obviously with the introduction of MWCNTs. Specifically, R is 470 °C for specimen T0 and it arises to 615 °C for 1 vol% MWCNTs containing specimen. This demonstrates again that the introduction of MWCNTs could improve the resistance to fracture initiation attributing to their “crack bridging”, “pull-out”, and “crack deflection” mechanisms [23]. Meanwhile, it also reveals that the higher content of MWCNTs leads to lower R parameter due to lower mechanical properties.

Besides the fracture initiation, the R''' and R_{st} parameters must be also considered given the crack propagation caused by thermal stress. Basically, the R''' and R''' parameters exhibit similar patterns, while R''' can predict the damages of materials with various γ_{WOF} . As can be seen from Table 1, R''' increases with 1 vol% MWCNTs addition, which implies that the introduction of 1 vol% MWCNTs could improve the thermal shock damage resistance. In comparison, the higher amount of MWCNTs has no further advantage

owing to the lower E and lower relative density, as well as slight agglomeration of MWCNTs. Additionally the R_{st} parameters also reveal that specimen T1 has the highest crack growth resistance. Therefore, it is reasonable to deduce that MWCNTs could improve the resistance to crack initiation, propagation, and growth during the thermal shock.

3.3 Thermal shock evaluation and discussion

To validate the above theoretical calculations, the following experiments were conducted. Generally, R parameter represents the maximum temperature that the ceramic can sustain without catastrophic failure. According to the above calculations, two temperature differences were selected in present work, namely 400 and 600 °C. As shown in Fig. 4(a), it is apparent that specimen T0 shows obvious strength loss, whilst the specimens T1 and T3 have no obvious strength loss at $\Delta T = 400$ °C. This variation suggests that the cracks in specimen T0 propagate stably at the temperature differences below 400 °C, otherwise the crack extends unstably when temperature differences are equal to or greater than 400 °C. In comparison, the cracks propagate stably in MWCNTs containing specimens when temperature difference is lower than 600 °C. In addition, the E of all the specimens varies differently comparing with the residual strengths (Fig. 4(b)) and this should be ascribed to the variations of relative

Table 1 Mechanical properties and thermal shock related parameters

Index	σ_f (MPa)	E (GPa)	γ_{WOF} (J/m ²)	α (10 ⁻⁶ K ⁻¹)	R (°C)	R''' (mm)	R_{st} (K·m ^{1/2})
T0	320.1±25.8	106.4±0.6	1349.3±205.0	4.51	470	1.8	23.5
T1	426.1±35.2	116.0±0.6	2676.5±450.3	4.85	615	1.9	31.3
T3	322.1±6.4	93.2±0.9	1449.6±264.2	4.89	530	1.7	25.5

Fig. 4 Flexural strength and Young's modulus as a function of quenching temperature difference.

density, porosity, and the enhancing effects of MWCNTs. In summary, it can be found that these practical experiments are in good agreement with the calculations though there is small deviation.

Furthermore, the thermal shock tests were also performed with a temperature difference at 1000 °C to better highlight the resistance of various composites against intensive thermal shock damage. It is apparent that the strengths of all the specimens decrease significantly while the E decreases slightly. Nevertheless, specimen T1 achieves the highest residual strength and Young's modulus. The enhanced thermal shock resistance of specimen T1 should be attributed to that the introduction of MWCNTs arouses more energy dissipation mechanisms, which consume more energy used for crack generation and propagation. As a result, the Young's modulus of specimen T1 decreases much slower than that of specimen T0.

In fact, the thermal fatigue of the ceramics is another failure mode during the periodic thermal shock. Therefore, the present work still investigated the cyclic thermal shock behaviors of various $\text{Si}_2\text{BC}_3\text{N}$ ceramics. The residual strengths and Young's modulus of the

specimens were evaluated and the stress–strain curves were also recorded. Figure 5(a) shows the stress–strain curves before thermal shock test, which show that specimen T1 has the highest strength. In comparison, the curves of specimens T0 and T3 are slightly bended after the first thermal shock (Fig. 5(b)). The bending curves should be caused by the generation of micro-cracks when encountering intense temperature variation. As for specimen T0, the cracks would generate and propagate at the interfaces of SiC and BN(C) mainly. Similarly, the pores and weak bonding MWCNTs aggregations act as flaws in specimen T3, which may be in favor of the crack initiation and growth. After the second thermal shock (Fig. 5(c)), specimens T0 and T1 reveal straight stress–strain curves again, which may be ascribed to the slight surface oxidation and this will be discussed later. However, specimen T3 has more bended curve owing to much more micro-cracks generated. Furthermore, all the specimens present bended curves after the third cycles (Fig. 5(d)), suggesting the generation of large number of micro-cracks despite the enhancing mechanisms of MWCNTs.

Fig. 5 Stress–strain curves of $\text{Si}_2\text{BC}_3\text{N}$ ceramics with various number of thermal shock cycles at $\Delta T = 1000$ °C: (a) before thermal shock, (b) one cycle, (c) two cycles, and (d) three cycles.

Figure 6 depicts the residual strengths and Young's modulus of specimens before and after different cycles of thermal shock test. Generally, when the specimens are heated instantaneously, the maximum stress is the compressive stress on the surface and the interior is subjected to the tension stress, which could initiate the cracks at the inner part [25]. On the contrary, the tension stress emerges at the surface during quick cooling. Furthermore, the tension stress increases with the increasing of temperature gradient, leading to the cracks propagation [31]. Therefore, the strengths decrease sharply after the first water quenching for all the specimens. Interestingly, different variations are detected for various composites. For pristine $\text{Si}_2\text{BC}_3\text{N}$ ceramics, the residual strength almost remains constant regardless of the cycle numbers. In comparison, specimen T1 shows slight increase instead of decrease. However, the values for specimen T3 decrease gradually with increasing of cycle times. In the present work, at the first quenching cycle, cracks would initiate at the weak bonding sites that cannot withstand the thermal stresses. Subsequently, some cracks may traverse along the interfaces between SiC particles and BN(C) plates or even through the BN(C) plates. However, a higher thermal stress is required for propagating the cracks quickly, which can be hardly achieved under the same quenching conditions [31]. Therefore, the following quenching cycles cannot induce the generation of substantial cracks and the original cracks act as stress concentrators and propagated until they are arrested by the strong bonding. As for specimens T0 and T1, relatively strong bonding could hinder the propagation of cracks during the cycling. In contrast, specimen T3 shows gradually deteriorated performances due to the existence of much more pores and some agglomerations of MWCNTs, which act as weaker points for the crack

generation and propagation. Besides, it is worth noting that specimen T1 has the highest residual strengths and modulus under all conditions, attributing to more energy dissipations of MWCNTs during the crack initiation and propagation. Judging from the residual strengths of specimens T0 and T1, it can be concluded that the thermal shock resistance is not so sensitive to cycle times than the temperature gradient.

The above results reveal that the residual strengths of the ceramics vary differently with the increasing of cycle times. To illustrate the specific reasons, the microstructures of the specimens after thermal shock test are observed. As shown in Fig. 7, oxidation happens for all the specimens after the first thermal shock. Apparently, specimen T1 has the thinnest oxidation layer while T3 possesses the thickest one. This indicates that higher relative density could improve the oxidation resistance, which will be discussed in detail later. It is worth noting that specimen T1 presents even higher strengths after thermal shock, which should be attributed to the formation of thin layer of oxidation layer. Besides, the phase compositions of the specimen surfaces before and after one cycle thermal shock test have been analyzed (as depicted in Fig. 8). Figure 8 suggests that only the diffraction peaks of BN(C) phase decrease slightly and no obvious oxide peaks are detected within such a short oxidation time.

3.4 Oxidation resistance

The former [23] and above evaluation demonstrated that the introduction of 1 vol% MWCNTs could enhance the mechanical properties and thermal shock resistance. Apart from the thermal stress damage, the SiBCN composites still suffer from the thermochemical erosion. Therefore, the present work also investigated

Fig. 6 (a) Residual strength and (b) Young's modulus as a function of the number of thermal shock cycles at $\Delta T = 1000\text{ }^{\circ}\text{C}$.

Fig. 7 Fracture surfaces of $\text{Si}_2\text{BC}_3\text{N}$ ceramics after the 1st thermal shock: (a) T0, (b) T1, and (c) T3.

Fig. 8 XRD patterns of $\text{Si}_2\text{BC}_3\text{N}$ ceramics surfaces: (a) before and (b) after the 1st thermal shock.

the oxidation resistance of $\text{Si}_2\text{BC}_3\text{N}$ ceramics. Firstly, the TG test has been conducted and the result is shown in Fig. 9. It is clear to see that specimen T0 has no obvious mass change with the temperature up to 1400 °C in air. However, the MWCNTs containing specimens show slight mass loss up to 1000 °C. Especially, with higher amount of MWCNTs introduction, the slightly higher mass loss is detected. This result only indicates that the oxidation of MWCNTs on the surface is ahead of the SiC and BN(C). Meanwhile, this result also indicates that relative density may affect the TG test.

Fig. 9 TG curves of $\text{Si}_2\text{BC}_3\text{N}$ ceramics.

Nevertheless, the TG test cannot provide more information on the oxidation resistance of bulk ceramics during prolonged oxidation process.

To better evaluate the oxidation resistance of $\text{Si}_2\text{BC}_3\text{N}$ ceramics, the oxidation tests were conducted under high temperature with a dwell time of 3 h. Figure 10 shows the phase compositions of $\text{Si}_2\text{BC}_3\text{N}$ ceramics after oxidation test. In addition to the BN(C) and SiC phases, cristobalite is detected at 1000 and 1200 °C and no obvious difference is found for the specimens tested below 1400 °C. At 1400 °C, specimens T0 and T3 present much higher diffraction peaks of cristobalite than specimen T1. In comparison, as for the specimens treated at 1600 °C, the cristobalite phase is the main phase and some residual SiC peaks are still detected. The residual SiC peaks in specimen T1 are much higher than those obtained in specimens T0 and T3. The XRD patterns indicate that 1 vol% MWCNTs addition could hinder the formation of oxides during oxidation process, demonstrating better oxidation resistance of specimen T1.

Furthermore, the surface morphologies of $\text{Si}_2\text{BC}_3\text{N}$ ceramics after oxidation test were observed and are exhibited in Fig. 11. At 1200 °C, there is no distinctive

Fig. 10 XRD patterns of $\text{Si}_2\text{BC}_3\text{N}$ ceramics after oxidation: (a) T0, (b) T1, and (c) T3.

Fig. 11 SEM microstructures of $\text{Si}_2\text{BC}_3\text{N}$ ceramics after oxidation test.

variation among these specimens and all the specimens' surfaces are covered by a dense layer of oxides, which should be mainly borosilicate. In contrast, the specimens present quite different microstructures at 1400 °C. Specifically, oxide clusters are found adhere to the surface of the pristine $\text{Si}_2\text{BC}_3\text{N}$ ceramics and the oxides should be mainly SiO_2 . For specimen T1, much

denser oxidation layer is observed and only some small cracks are located around the oxides particles. However, some extruded oxides are found in specimen T3 and the oxide particles are larger than those found in the pristine $\text{Si}_2\text{BC}_3\text{N}$ ceramics. When specimen T0 is treated at 1600 °C, more holes and larger oxide particles are observed. While, specimen T1 still has much denser

oxidation layer. Furthermore, specimen T3 shows isolated oxides and large pores, which should be left by the evaporation of larger amount of B_2O_3 .

Figure 12 depicts the oxidation layer thickness of Si_2BC_3N ceramics tested at different temperatures. Generally, specimen T1 presents the thinnest oxidation layer and specimen T3 possesses the thickest one regardless of the testing temperatures. To be specific, the oxidation layer thicknesses are around 2–5 μm for all the specimens tested below 1400 $^{\circ}C$. At 1400 $^{\circ}C$, the oxidation layer thickness increases obviously, especially for specimens T0 (around 10 μm) and T3 (around 20 μm). In comparison, thicker oxidation layer is observed with increasing the treating temperature further. All these oxidation layer thicknesses explain the variation of above XRD and SEM microstructures. Again, the cross-section observations demonstrated that the 1 vol% MWCNTs containing SiBCN ceramics have best oxidation resistance under present condition. Furthermore, the 1 vol% MWCNTs containing composites also have better oxidation resistance than the reported graphene enhanced SiBCN ceramics [38].

Based on the former studies, the formation of SiO_2 clusters should be attributed to the evaporation of B_2O_3 . According to the TG test, the oxidation resistance of MWCNTs should be lower than the pristine SiBCN ceramics. However, the present work demonstrates that the 1 vol% MWCNTs have much better oxidation resistance. Namely, the introduction of 1 vol% MWCNTs could hinder the evaporation of B_2O_3 and the oxidation of SiC significantly. The main reason accounting for this is that the introduction of 1 vol% MWCNTs improves the relative density and lowers the porosity, and therefore the exchange of oxygen is significantly suppressed.

Fig. 12 Oxidation layer thicknesses of Si_2BC_3N ceramics.

In summary, the thermal shock resistance of ceramics is mainly associated with the dimensions, strength, toughness, Young's modulus, thermal expansion coefficient, thermal conductivity, Poisson's ratio, and emissivity of the specimens [31]. These parameters need to be considered dialectically when applying the TSR theories. As for the thermal shock fracture theory, low strength cannot effectively prevent the production and propagation of cracks, which will result in the ceramics fracturing finally. Therefore, high strength seems to be necessary for resisting the initiation of cracks. Nevertheless, the concept of thermal shock damage theory is mainly to resist the formation of cracks, and then to resist the extension. The stored elastic energy must be transformed into the effective surface energy with the generation of cracks. To maintain the slow and stable crack propagation, the reduction of the elastic energy stored at cracks is believed to be essential. Therefore, increasing the surface energy and fracture toughness of ceramics could be useful for improving the thermal shock resistance [26,36]. Based on these considerations, the present work improved strengths and toughness of Si_2BC_3N ceramics simultaneously with the introduction of MWCNTs. On one hand, higher strengths improve the critical thermal shock temperature; on the other hand, the "crack bridging", "pull-out", and "crack deflection" mechanisms of MWCNTs enhance the toughness through generating more tortuous crack propagation paths. Besides, the hindered oxidation resistance of Si_2BC_3N ceramics with introduction 1 vol% MWCNTs guarantees the specimen T1 with higher thermal shock resistance under high temperature. The work on improving the oxidation resistance of MWCNTs will be conducted.

4 Conclusions

Based on the above results and discussions, the following conclusions can be drawn:

(1) With the presence of MWCNTs, more energy dissipation mechanisms are introduced, which stimulate the generation of more tortuous crack propagation paths in Si_2BC_3N ceramics. Therefore, the addition of 1 vol% MWCNTs could improve the critical thermal shock temperature from 400 to 600 $^{\circ}C$. Furthermore, the MWCNTs incorporated Si_2BC_3N ceramics show lower brittleness (high R'''') and higher thermal shock

resistance (high R_{st}).

(2) The thermal fatigue damages are more sensitive to the flaws in the $\text{Si}_2\text{BC}_3\text{N}$ ceramics. 1 vol% MWCNTs containing composites have higher density and fewer defects, which lead to higher resistance to thermal fatigue. As a result, the residual strengths of specimen T1 remained the highest after thermal shock test at different temperatures. Meanwhile, thin layer of oxides generated during thermal shock may protect the ceramics from further damage to some extent through micro-cracks healing. The 1 vol% MWCNTs containing SiBCN ceramics have improved oxidation resistance due to its higher relative density.

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