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ORIGINAL ARTICLE

Effect of magnesium aluminum silicate glass on the thermal shock resistance of BN matrix composite ceramics

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Abstract

The effects of magnesium aluminum silicate (MAS) glass on the thermal shock resistance and the oxidation behavior of *h*-BN matrix composites were systematically investigated at temperature differences from 600°C up to 1400°C. The retained strength rate of the composites rose with the increasing content of MAS showing a maximum value at the 60 wt% MAS. Compared with the original strength, the retained strength of the specimen after thermal shock increased to 77% ($\Delta T=1000^\circ\text{C}$). The strengthening effect of MAS and the surface microstructural evolution of composites are responsible for the improved thermal shock resistance. Surface oxidation of the composites during the thermal shock process plays a positive role in enhancing the retained strength by self-healing cracks and the appearance of the compressive stress. The oxide layer also acted as a thermal barrier to decelerate the actual thermal stress. Furthermore, this dense layer also improved the oxidation resistance of *h*-BN matrix composites by prevent diffusion of oxygen. These results indicated that short-term surface oxidation during thermal shock process is favorable to the enhancement of the thermal shock resistance of BN-MAS composite ceramics.

KEYWORDS

boron nitride, ceramic matrix composites, microstructure, oxidation, thermal shock resistance

1 | INTRODUCTION

The continuous rapid changes in the aerospace industry provide an impetus to the increasing demand for advanced materials and properties. When operated in extreme environments, structural parts and components must meet more severe design constraints. An essential property needed to operate materials at high temperatures is correlated with their melting points.¹ Naturally, not only high melting points are necessary, but also need to take into consideration the tolerance to thermal and mechanical stress to avoid catastrophic failure during operation.^{1,2} In addition, materials with suitable and optimized oxidation resistance are urgently required. Among the various structural materials, hexagonal boron nitride-based ceramics, offer unique

combinations of low dielectric coefficient and low loss tangent (5.16 and $10\text{--}11 \times 10^{-4}$ at room temperature), high melting points, good ablation resistance, and great thermal shock resistance. Thus, they represent premiere pioneer materials for potential applications including thermal protective structures for radome and antenna windows on aerospace vehicles, metallurgy, and energy.^{3,4} However, the use of single-phase *h*-BN materials for high-temperature structural applications is rather limited because of poor sinterability and weak oxidation resistance as well as relatively poor lower mechanical properties.^{5,6} Therefore, the densification and mechanical properties of *h*-BN combined with second phase have been studied in the past decades.^{7,8}

Although enhanced mechanical performance of *h*-BN-based ceramics is a crucial step forward, to make it an

attractive choice under extreme environmental conditions, several properties are still need to be improved.^{1,9,10} As a thermal protection component of high-speed vehicles, they served in an oxidizing environment of high velocity dissociated air, which are susceptible to catastrophic failure under severe thermal stress.^{11,12} In this regard, BN ceramics and their composites associated with the aforementioned properties have a favorable ability of forming a protective B_2O_3 surface oxide in oxidizing environments at $\sim 450^\circ\text{C}$.¹³ Nevertheless, the volatilization of gaseous B_2O_3 in higher temperatures will lead to formation of pores in the oxide surface, resulting in reduction of the oxidation resistance. In addition, the remaining defects on the surface caused by vaporization of B_2O_3 also weaken thermal shock resistance, resulting in catastrophic failure.^{9,14}

The B_2O_3 can co-melt with MAS glass to produce a stable and viscous $MgO-Al_2O_3-SiO_2-B_2O_3$ glass.^{15,16} So, the BN-MAS composites could form a high viscosity MAS-borosilicate glass on the surface acting as an oxidative protective layer, which will prevent the gas volatilization, heal surface defects, and decrease the thermal stress of composites. Hence, the introduction of MAS glass to BN matrix composites offers a promising approach to improve its thermal shock resistance and oxidation resistance.

To date, the microstructures, mechanical properties, densification behavior, and strengthening mechanism of MAS reinforced *h*-BN ceramics have been thoroughly assessed, whereas little is known about the effects of MAS on thermal shock resistance and oxidation resistance. Aiming at this target, BN-MAS composites with different MAS contents were designed and fabricated. Phase transformation behavior, microstructural evolution, and retained flexural strength of the as-sintered specimens are studied systematically. Meanwhile, the effects of introducing of MAS phase on the thermal expansion, thermal shock resistance, and oxidation behavior of *h*-BN matrix composites also are evaluated.

2 | EXPERIMENTAL PROCEDURES

2.1 | Manufacturing process

A series of BN-MAS ceramic samples with varying MAS contents were fabricated by hot-press sintering. The starting materials used were *h*-BN powders (APS of $2.29\ \mu\text{m}$, purity $>99\%$, Advanced Technology & Materials Co. Ltd., Beijing, China), MgO (APS of $5.83\ \mu\text{m}$, purity $>98\%$, Tianjin Guanfu Fine Chemical Research Institute, Tianjin, China), Al_2O_3 (APS of $0.73\ \mu\text{m}$, purity $>98\%$, Showa Denko, Yokohama, Japan), and fused quartz (APS of $3.39\ \mu\text{m}$, purity $>98\%$, Guangyu Quartz Co. Ltd., Lianyungang, China). α -Cordierite (MAS) with stoichiometric

TABLE 1 Composition design of the BN-MAS composites

Composites	S1	S2	S3	S4	S5	S6
<i>h</i> -BN (wt%)	80.00	70.00	60.00	50.00	40.00	30.00
MgO (wt%)	2.76	4.14	5.52	6.90	8.28	9.66
Al_2O_3 (wt%)	6.98	10.47	13.96	17.45	20.94	24.43
SiO_2 (wt%)	10.26	15.39	20.52	25.65	30.78	35.91

composition is determined by the amounts of MgO , Al_2O_3 , and SiO_2 . Table 1 displays the detailed compositions of the specimens.

The raw powders were mixed in a wet mode inside a 1.5-L plastic bottle filled with Al_2O_3 balls (size of 10 mm) and appropriate hydrous ethanol predissolved as mixing media for 24 hours with a rotation speed of 60 rpm, then dried at 80°C in a rotary evaporator, and screened through a 120 mesh sieve. The mass ratio of Al_2O_3 balls to powders was 6:1. Finally, the composites in shape of $\Phi 60$ mm disk were prepared via a hot press sintered in a graphite die with a *h*-BN releasing agent at 1450°C for 60 minutes under a uniaxial pressure of 10 MPa in 1 atm N_2 atmosphere, and the ramping rate is $20^\circ\text{C}/\text{min}$.

2.2 | Thermal shock experiments

Thermal shock experiments with only one cycle were carried out in a Muffle furnace at temperatures between 625°C and 1425°C ($\Delta T = 600^\circ\text{C}$ – 1400°C) in air atmosphere via the water-quenching method. Before water-quenching tests, all specimens were machined into standard bar samples ($3\ \text{mm} \times 4\ \text{mm} \times 36\ \text{mm}$), ground, and polished with emery paper down to a $1\ \mu\text{m}$ finish. The edges of all the specimens were chamfered at an angle of 45° to minimize the effect of stress concentration due to machining flaws. Water with a constant room temperature of 25°C was used as a quench medium. After heating the furnace to the desired temperatures, the specimens were put into it and held for 10 minutes. Then, the specimens were taken out immersed into water immediately with a volume of about 30 L for 30 seconds to ensure temperature uniformity. Six specimens were used and tested in one group, and the average values were calculated.

2.3 | Characterization

The phase composition was identified by X-ray diffractometry (XRD; D/max- γ B, Ricoh, Japan) using CuK_α radiation with scanning speed of $4^\circ/\text{min}$ from 10° to 90° . Morphologies were characterized by SEM (Philips XL-30 FEG ESEM, Amsterdam, The Netherlands) operating at 5 kV acceleration voltage. Energy dispersive spectroscopy (EDS, Hitachi, Tokyo, Japan) was used to analyze the elemental

composition. Confocal microscopy (Nanofocus μ Surf, Oberhausen, Germany) was used to measure the surface profile of the thermal shocked specimens.

The retained strengths of the specimens were measured by three-point bending strength test, which was conducted on a computerized Instron-5969 testing system, with a span of 30 mm at a crosshead speed of 0.5 mm/min.

The linear thermal expansion behavior of composites from 200°C to 1400°C was determined with a high-temperature dilatometer (Netzsch DIL 402C, GmbH, Selb, Germany) at 5°C/min in an Ar gas atmosphere, and the data were corrected using the known thermal expansion of a certified standard carbon. The final dimension of the sample was approximately 3 mm $\times$ 4 mm $\times$ 20 mm, and was carefully polished before thermal expansion measurement.

TG and DTA (Netzsch STA 449C) of specimens were carried out in an atmosphere of flowing air in alumina crucibles over a temperature range from 25°C to 1400°C at 5°C/min.

3 | RESULTS AND ANALYSIS

3.1 | Thermal shock resistance

Retained strength after thermal shock can be used to estimate the thermal shock resistance of composites. Figure 1 shows the retained strength for BN-MAS composites as a function of thermal shock temperature differences (ΔT). The retained strength achieve maximum at $\Delta T=1000^\circ\text{C}$ (S5, 288 ± 19 MPa), and then decrease gradually with further increase in thermal shock temperature differences. The results prove that the BN-MAS composites exhibit an abnormal high thermal shock resistance, and their retained

strengths are even higher than that of the original strength. Especially for S5, the retained strength maintains 178 ± 27 MPa, about 10% higher than that of unquenched samples even though the temperature difference occurred at 1400°C . The results indicate that the thermal shock resistance of BN-MAS composites is significantly enhanced with the increasing content of MAS glass. The decline of retained strength values of the composites at $\Delta T=800^\circ\text{C}$ be attribute to the microstructural evolution of the composites, which discussed in the following section.

In contrast to the unquenched specimens, defects (cracks and pores) appear in the fractured surfaces of all quenched specimens, see Figure 2. These defects were caused by thermal stress damage during the water quenching, which indicates that enhanced retained strength of the BN-MAS composites strongly depends on the surface microstructural evolution.

3.2 | Surface phase composition

XRDs obtained from the surface of S5 samples before and after water quenching are presented in Figure 3. *h*-BN (JCPDS No. 85-1722), mullite (JCPDS No. 79-1455), and amorphous phase are identified as the original products. During thermal shock experiment, oxidation, evaporation, and other physical and chemical process take place on specimen's surface. *h*-BN is oxidized to B_2O_3 with a completely fluid liquid state above 450°C .^{9,13} The presence of liquid B_2O_3 will influence the phase transition by dissolving with MAS glass to form $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ glass. At an elevated temperature, α -cordierite (JCPDS No. 85-1722) emerges, whereas, it is very hard to acquire the XRD data due to the heavy oxidation behavior, which leads to the formation of rough oxide surface layers at $\Delta T=1400^\circ\text{C}$.

Figures 4 and 5 provide XPS full-spectra and fine spectra by deconvolution after thermal shock at a temperature difference of 1200°C , offering information about the chemical bonding of the specimen's surface. The B 1s observed at 191.9 eV is attributed to B-N bonds coupled with B-O bonds, respectively, revealing that *h*-BN is oxidized to B_2O_3 . The existence of B-O bond on the specimen surface confirms that MAS glass prevents its evaporation and dissolves the liquid B_2O_3 within the MAS glass under certain conditions. The main N 1s peak at 398.4 eV belongs to N-B bonds, and lower peaks at 397.1 and 397.6 eV are attributed to N-Al and N-Si, respectively, indicating a certain amount of O is substituted by N in the surface layer. From Figure 4C, peaks at 529.8 and 531.1 eV are in accordance with O-Mg and O-Al bonds, respectively; however, the peak at 532.5 eV can be assigned to O-X (X=Si or B) bonds as both have the same peak positions. The Si 2p XPS spectra can be fitted by two components located at

FIGURE 1 Retained strength of the specimens as a function of quenching temperature differences [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 2 SEM micrographs of fracture surfaces of S5 specimen after thermal shock at several temperature differences: (A) original specimen; (B) 600°C; (C) 800°C; (D) 1000°C; (E) 1200°C; and (F) 1400°C [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 3 XRD of S5 specimen surface after thermal shock at several temperature differences: (A) original specimen; (B) 600°C; (C) 800°C; (D) 1000°C; (E) 1200°C; and (F) 1400°C [Color figure can be viewed at wileyonlinelibrary.com]

≈102.0 and 102.6 eV. The first one reflects the presence of Si–N bonds, and the Si–O bonds are the largest contribution to the second one.

The B–O bond exists as $[\text{BO}_3]$ or $[\text{BO}_4]$ units in the glass system, which is a glass network former.^{17,18} The substitution of cations in the MAS glass (Mg, Al, and Si) by B atom would increase the glass-network connectivity, promoting a phase transition for MAS glass. Meanwhile, the substitution of O atom by N atom would also changes the structure of MAS glass, because each N can bond to three Si, while each O could bond to only two Si. Consequently, the number of Si–(O, N) bonds in the network increase, leading to the surface phase transition.

3.3 | Surface microstructure

The surface topography of S5 bears different thermal shock temperatures are given in Figure 6. Unlike the original specimen, at $\Delta T=600^\circ\text{C}$, some needle-shaped constructs appear on the surface. The EDS result indicates the main component is likely $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$. Due to the short hold time in this temperature, only a slight oxide layer forms on the surface with a few cracks or pores. Although B_2O_3 can co-melt with MAS to produce a stable and viscous

FIGURE 4 XPS full-spectrum of the surface of S5 specimen after thermal shock at temperature differences of 1200°C [Color figure can be viewed at wileyonlinelibrary.com]

MgO–Al₂O₃–SiO₂–B₂O₃ glass, the liquids temperature of the multiphase glass is close to 1000°C.^{15,16,19} Hence, reactions between B₂O₃ and MAS glass are incomplete. Further heating leads to extensive oxidation, slight evaporation of B₂O₃ and restructures the porous surface structure ($\Delta T=800^{\circ}\text{C}$). When specimens are loaded, defect tips will produce stress concentrations and the composites can be destroyed at low stress.

The dense oxide layer consist of magnesium aluminum borosilicate glass ceramics, forms on surface (α -cordierite, mullite, and an amorphous phase) when $\Delta T>1000^{\circ}\text{C}$. Furthermore, the burst bubbles and craterlets resulting from escape of gaseous products through the glass layer are readily observed on the surface of the specimen at 1400°C. More extensive loss of N₂ and B₂O₃ from the oxide surface causes the oxide layer to become quite fluidic at this temperature. Nevertheless, no obvious microcracks can be found in the oxidation layer.

FIGURE 5 XPS fine spectra of (A) B 1s; (B) N 1s; (C) O 1s; (D) Si 2p for the surface of S5 specimen after thermal shock at temperature differences of 1200°C [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 6 SEM micrographs showing the surface of S5 after thermal shock at several temperature differences: (A) original specimen; (B) 600°C; (C) 800°C; (D) 1000°C; (E) 1200°C; and (F) 1400°C [Color figure can be viewed at wileyonlinelibrary.com]

3.4 | Thermal expansion properties and surface oxidation behavior

The results of dilatometric measurements for BN-MAS composite ceramics are displayed in Figure 7. The average CTEs rise from $4.03 \times 10^{-6} \text{ K}^{-1}$ (S1) to $6.89 \times 10^{-6} \text{ K}^{-1}$ (S5) with increasing MAS loading, likely a result of enhanced formation of mullite and the degree of crystallization of *h*-BN.⁸ As seen in Figure 7A, CTEs of composites increase with the rise of temperature, which can be attributed to the increasing atomic spacing at elevated temperatures.

Figure 8 shows the TG-DTA curves of S5 specimen in air. TG curve of S5 can be divided into two stages. Almost no obvious weight loss happened before 1200°C, because only slight oxidation of *h*-BN occurred in this stage. Subsequently, the TG curves climbs up above 1220°C, which means extensive oxidation of the composites. One exothermic and two endothermic peaks are observed in DTA curve, which can be used to determine the oxidation and crystallization of the composites. Combined with XRD, XPS, and EDS results, the exothermic peak observed at 550°C is

related to the oxidation of *h*-BN to B_2O_3 . The first endothermic peak at 1255°C is mostly associated with the formation of α -cordierite while the second one above 1400°C belongs to the melting point of MAS-borosilicate glass.

To further examine the oxidation behavior of the composites, the cross-sectional morphologies of S5 were characterized. As shown in Figure 9A, the oxide layer is very dense, less than 1 μm . According to the EDS mapping, the compact layer mainly contained MAS glass and B_2O_3 . After thermal shock at $\Delta T = 1400^\circ\text{C}$, the thickness of oxide layer reaches to 30–50 μm and numerous bubbles are observed on the surface, revealing a striking contrast with the former. The formation of defects (pores and bubbles) can be attributed to the rapid loss of B_2O_3 through the low viscosity glass layer.

At the initial stage of oxidation in the thermal shock process ($\Delta T \leq 800^\circ\text{C}$), *h*-BN would be oxidized to form B_2O_3 on the surface and evaporated tardily. The defects in the surface provide a route for oxygen to infiltrate into the composites.²⁰ Further increasing the temperature, B_2O_3 would dissolve with MAS to form a more viscous magnesium aluminum borosilicate glass before the end of B_2O_3

FIGURE 7 Thermal expansion curves of BN-MAS composite ceramics as a function of temperature: (A) technical thermal expansion coefficients of composites (200°C–1400°C); (B) average thermal expansion coefficients of composites (200°C–1400°C) [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 8 TG and DTA curve of S5 in the air environment [Color figure can be viewed at wileyonlinelibrary.com]

volatilization. This viscous layer would prevent the further oxidation of *h*-BN by acting as a barrier for diffusion of oxygen. However, when $\Delta T \geq 1400^{\circ}C$, the volatilization of gas product would be enhanced strongly and meanwhile the viscosity of glass phase decreases, forming a porous structure on the oxide layer.

4 | DISCUSSION

Generally, material performance indices are summarized for both strength- and toughness-controlled failure.²¹ The maximum thermal shock temperature difference (ΔT) of materials with a small Biot number ($Bi < 1$) was calculated based on Equation 1:

$$\Delta T = A_1 \frac{\sigma_f}{E\alpha} \frac{1}{Bi} \quad (1)$$

where Bi is the Biot modulus, $Bi = hH/k$, H is the specimen dimension, h is the heat transfer coefficient, k is the

thermal conductivity, E is the Young's modulus, and α is the coefficient of thermal expansion (CTE); $A_1 \approx 3.2$ for cold shock, and $A_1 \approx 6.5$ for hot shock. It is clear from Equation 1 that for poor surface heat transfer the highest temperature difference are achieved for composites with a large value of $k\sigma_f/E\alpha$.

A similar strategy can be employed to rank materials on the basis of failure from a dominant crack by thermal shock. The maximum thermal shock temperature difference (ΔT) of materials with a small Biot number ($Bi < 1$) was calculated according to Equation 2:

$$\Delta T = A_2 \frac{K_{IC}}{E\alpha\sqrt{\pi H Bi}} \quad (2)$$

where K_{IC} is the fracture toughness, $A_2 \approx 9.5$ for cold shock, and $A_2 \approx 12$ for hot shock. From Equation 2, it can be deduced that for toughness-controlled thermal shock the best candidate materials have a high value of $kK_{IC}/E\alpha$. A transition plate thickness value H_t exists for which ΔT is equal for toughness-controlled failure and for strength-controlled failure. By considering the limit of poor heat transfer ($Bi < 1$), equating ΔT according to Equations 1 and 2 gives²¹:

$$H_t \approx \left(\frac{K_{IC}}{\sigma_f} \right)^2 Bi \quad (3)$$

Composites with a large value of H_t can be considered to have high damage tolerance, compared with materials of low H_t value, therefore, the H_t value can be thought of as a useful measure of thermal shock damage tolerance. The calculated H_t are presented in Table 2, and shows a similar tendency with the retained strength rate. Thus, it can be concluded that thermal shock resistance of composites were improved due to the higher K_{IC}/σ caused by adding MAS.

FIGURE 9 Cross-sectional morphologies of S5 after thermal shock at (A) 1200°C and (B) 1400°C. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Properties of BN-MAS composite⁸

Composites	Bending strength (MPa)	Fracture toughness (MPa m ^{1/2})	Young's modulus (GPa)	CTE (10 ⁻⁶ K ⁻¹)	<i>k</i> (W/m·K, 1200°C)	<i>H_t</i> (10 ⁻⁶)
S1	30.3±1.5	0.35±0.12	10.0±0.4	4.03	2.74	133Bi
S2	40.6±8.2	0.57±0.15	13.9±0.4	4.13	1.26	197Bi
S3	121.1±11.0	1.63±0.12	39.3±0.6	4.51	1.79	181Bi
S4	213.2±24.9	2.49±0.33	73.5±3.0	5.42	2.38	136Bi
S5	162.6±24.2	2.51±0.13	83.4±2.9	6.70	2.45	238Bi
S6	150.2±15.2	2.59±0.21	91.1±5.0	6.56	3.29	297Bi

The enhanced retained strength of BN-MAS composites contradicts conventional damage mechanics. This is mainly results from surface microstructure evolution and consumption of the thermal stresses during thermal shock tests in air atmosphere.

Especially, the improving retained strength of composites mainly results from the healing of the surface defects. On the original specimens' surface, the defects inevitably appear during machining because of its brittle nature. When specimens are loaded, defect-tips will produce stress concentrations. However, *h*-BN is oxidized to liquid B₂O₃ and form a glass layer with MAS on the surface when the specimens heated in air. This glassy phase would heal surface flaws and decreases thermal stress concentrated at defect-tips. So, the retained strength is enhanced after the introduction of MAS.^{22–24} The decrease in retained strength of the composites at Δ*T*=800°C is mainly attributed to the high volatility of B₂O₃ (have not react with MAS to form glassy layer effectively) at this temperature which leads to the cracks and pores on the surface.

Under water-quenching conditions (*T_i*>*T_∞*), the surface layers experience a tensile stress transient while a compressive zone is developed at the center of the plate. For all values of *Bi*, the maximum tensile stress is attained at the surface and the compressive stress is largest at the center of the plate. The overall magnitude of the stresses increases with increasing *Bi*.²¹ The appearance of the compressive stress zone beneath the surface oxide layers is favorable to

inhibit the crack initiation and propagation to damage matrix of the BN-MAS composites, which is beneficial to resistance to thermal shock because the thermal stress is consumed partially due to the appearance of the compressive stress. The residual compressive stresses (σ_c) of the oxidation layers can be estimated according to the classical lamination theory²⁵:

$$\sigma_c = \frac{nE_1E_2d_2(\alpha_2 - \alpha_1)\Delta T}{n(1 - \nu_1)E_2d_2 + (n + 1)(1 - \nu_2)E_1d_1} \quad (3)$$

When the thermal expansion of the odd layers is smaller than the even ones ($\alpha_1 < \alpha_2$), the composite is tailored to develop compressive residual stresses in the outer layers. The specimens after thermal shock test can be regarded as a three layer composite (*n*=1), the change in compressive stresses with the thickness ratio ($x=d_2/d_1$) of the layers, taking $\nu_1=\nu_2=\nu$, is given by Equation 4²⁵:

$$\sigma_c = \frac{E_1E_2(\alpha_2 - \alpha_1)\Delta T}{(1 - \nu)} \frac{x}{2E_1 + E_2x} \quad (4)$$

In order to simplify the equation derivation process, assuming that the $x=d_2/d_1 \approx 4000$, Δ*T*=1000°C, *E₁*≈160 GPa (mullite and cordierite), $2.5 \leq \alpha_1 \leq 5.3 \times 10^{-6} \text{ K}^{-1}$ (mullite: $5.3 \times 10^{-6}/\text{K}$, cordierite: $2.5 \times 10^{-6}/\text{K}$), the calculated residual stresses $\sigma_c \approx 223(1 - \nu) - 670(1 - \nu)$ MPa. The compressive stress increases when the *d₂/d₁* ratio increase, and α_1 decrease.

The improving retained strength of composites also has a close relationship with the crystal structure of *h*-BN. The crystal form of *h*-BN is hexagonal, and the thermal expansion coefficients of *h*-BN has great different between *c*-axis and *a*-axis. The thermal expansion coefficients of *h*-BN has been found by XRD analysis to be highly anisotropic, the α for the *c*-axis is $40.5 \times 10^{-6} \text{ K}^{-1}$ and zero along *a*-axis at 770°C .²⁶ At the temperatures used for fabricating the BN-MAS composites, the *h*-BN grains would be greatly expanded along *c* and upon cooling undergo considerable contraction in this direction relative to the basal plane, which results in the delamination of *h*-BN plates as observed in the transmission electron micrographs, in Figure 10. When the composites are rapidly heated, the *h*-BN grains will respond by expanding anisotropically. The expansion of the plates along *c*, however, can be accommodated by closure of the gaps between them and little change in the thermal expansion of the bulk specimen is expected. The flexible and delaminated nature of *h*-BN grains would provide favorable sites for the dissipation of energy associated with crack growth. Besides, the platelet *h*-BN particle can produce crack bridging and crack deflection, therefore improve the thermal shock resistance of composites. In addition, the appropriate residual pores of BN-MAS composites also have great influence on the thermal shock resistance of composites by inhibiting crack propagation.²⁷ The smaller pores in composites can be more densely distributed to act as crack stoppers by crack tip blunting.

In addition, the low thermal conductivity of BN-MAS composites ($3.1\text{--}11.1 \text{ W/m}\cdot\text{K}$, 25°C ; $1.3\text{--}3.3 \text{ W/m}\cdot\text{K}$, 1200°C) and the formation of a thin film of steam on the

specimen surface during water quenching would dramatically diminish the heat transfer rate and hence decrease the thermal stress. Therefore, the actually tensile stress occurring during quenching on the composites is relative small.

In the further work, the high-temperature strength, creep resistance, and crack healing phenomena of the BN-MAS composites at high temperature should be investigated. The properties of the oxidation layer and measurement data of compressive stress also would be covered in our future papers, including the bonding between the layer and the substrate and distribution of the compressive stress in the quenched specimens.

5 | CONCLUSIONS

In this work, the thermal shock resistance of BN-MAS composite ceramics was investigated by measuring the residual strength after water quenching for the temperature differences ranging from 600°C up to 1400°C in air atmosphere and calculating thermal shock resistance parameters.

According to the results, the calculated thermal shock resistance to fracture initiation of BN-MAS composite ceramics deteriorated with increasing MAS content. However, the residual strength rate after water quenching versus thermal shock temperature difference showed good relationships with the calculated thermal stress damage resistance parameter, R'' . The crack propagation of the composites occurred primarily in a quasi-static manner as a result of pulling-out and bridging toughening effects of *h*-BN platelets and the relatively low Young's modulus of the composites.

Improved thermal shock resistance of *h*-BN matrix composites was achieved by adding MAS glass: (i) the healing of the surface defects which leads to the increase in the flexural strength; (ii) the decrease in the thermal stress; (iii) the appearance of the compressive stress zone beneath the surface oxide layers; (iv) consumption of the thermal stress; and (v) the increase in K_{IC}/σ rate. The dense layer also prevents the extensive oxidation of *h*-BN by acting as a barrier for the diffusion of oxygen. Thus, the BN-MAS composites demonstrate enhanced oxidation resistance. The results here point to a promising method of improving thermal shock resistance of *h*-BN matrix composites, which can be applied to aid materials engineering design for the development of quality assurance and characterization assessment of durability.

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FIGURE 10 TEM micrographs of S5 composites shows the delamination of *h*-BN grains caused by anisotropic contraction [Color figure can be viewed at wileyonlinelibrary.com]

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