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Ablation behavior and mechanism of boron nitride - magnesium aluminum silicate ceramic composites in an oxyacetylene combustion flame

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ABSTRACT

In the present study, ablation behavior and properties of BN-MAS (magnesium aluminum silicate) composites impinged with an oxyacetylene flame at temperatures up to 3100 °C were investigated. As ablation time ranged from 5 to 30 s, the mass and linear ablation rates increased from 0.0027 g/s and 0.001 mm/s to 0.0254 g/s and 0.087 mm/s, respectively. A SiO₂-rich protective oxide layer formed during the ablation process, which contributed to the oxidation resistance of the composites. Ablation products mainly consisted of magnesium-aluminum borosilicate glass, mullite, spinel and indialite. The thermal oxidation of *h*-BN during flame ablation and scouring of MAS by high-speed gas flow were the main ablation mechanisms.

1. Introduction

Extreme environmental erosion and high aerodynamic loads on wave-transparent thermal protection systems, e.g. antenna windows, are extremely important to control aerospace vehicles. As these parts, they must be able to withstand the high temperatures, high thermal fluxes and aerodynamic pressures associated with vibrations at high velocity launch and re-entry in Earth's atmosphere [1,2]. The harsh service environment always requires that these materials possess critical properties including good mechanical and dielectric properties, high chemical stability, superior thermal conductivity, good oxidation resistance, excellent thermal shock resistance, high ablation resistance and dimensional stability as well [3]. Conventional thermal protection materials like fused silica [4], Al₂O₃ [5], Si₃N₄ [6], SiO₂/SiO₂ [7] and glass ceramics [8,9] do not offer properties sufficient for more harsh and special environment.

Amongst the various structural and functional materials, *h*-BN and its composites are considered to be a promising material for high temperature applications. Similar to graphite, *h*-BN also consists of stacked layers of boron and nitrogen atoms bound by strong sp² covalent bonds, with the adjacent layers interacting via weak van der Waals forces [10,11,12]. These structural characteristics make *h*-BN an important protective material offering extremely high sublimation

temperature up to 3000 °C (non-oxidizing atmosphere), excellent thermal shock resistance, good machinability, a low dielectric coefficient and loss tangent at room temperature [11,13,14,15]. Nevertheless, *h*-BN's inherent poor mechanical properties and low oxidation resistance at temperatures above 900 °C [16,17] (monolithic *h*-BN) have greatly limited its wide application as a thermal protective material. To overcome this problems, composites with fused silica, Al₂O₃, ZrO₂ and MAS (magnesium aluminum silicate) glass have been used to enhance mechanical properties [3,18,19,20,21].

BN-based ceramics are typically oxidized to B₂O₃ firstly at about 450 °C. Due to its relatively low melting temperature, liquid B₂O₃ then forms a continuous layer on the sample surfaces which can prevent inward transport of oxygen below 900 °C. However, above this temperature, B₂O₃ evaporates rapidly due to its high vapor pressure [22,23]. The addition of metal oxides or silicides is an effective approach to enhance oxidation resistance in bulk ceramics borides [24,25]. At high temperatures, metal cations incorporate into the borosilicate glass, inducing liquid immiscibility and forming phase separated glasses of high viscosity [26,27]. For instance, MAS glass co-melts with B₂O₃ to produce a stable and viscous MgO-Al₂O₃-SiO₂-B₂O₃ glass [28,29] that acts as an effective oxygen barrier. Therefore, *h*-BN oxidation resistance on addition of MAS should offer superior ablation behavior.

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Monolithic *h*-BN ceramics used in high-speed vehicles also suffer from signal attenuation during re-entry. *h*-BN exhibits a relatively low dielectric loss from room temperature to 1000 °C at 10 GHz. However, dielectric loss increases rapidly from 1000 °C to 1800 °C. The dielectric loss at 1800 °C is 40 times more than that at room temperature. This rapid increase in dielectric loss is mainly caused by boron vacancy (V_B) defects and electron hopping phenomena at high temperature [30]. Thus, signal attenuation results from the high ablation surface temperature of the material [31]. Hence, efforts to reduce the surface temperatures of *h*-BN represents an important research objective and represents another motivation to use relatively low melting point MAS glass to improve the ablation property of *h*-BN.

Ablation resistance is the most critical issue for high temperature ceramics used in the aerospace industries. In ablation environments, mechanical loads are inflicted on the materials in addition to the oxidation and showed great variation compared with the sole oxidation process [32,33]. Thus, evaluation of microstructural evolution and its influence on ablation properties represents an important yet complicated task in materials subjected to ablation. The current study is dedicated to evaluating the ablation performance of BN-MAS composites using an oxyacetylene torch for potential applications in extreme service environments. Ablation behavior was systemically investigated based on changes in surface temperature, phase composition, surface morphology and distributions of ablation depth during the ablation process. The effect of different ablation times on the BN-MAS composite reflecting different stages were studied corresponding to different ablation environments as well.

2. Experimental

BN-MAS composite ceramics were prepared by hot-press sintering, and the weight ratio of BN:MAS was controlled as 70:30. The MAS ($Mg_2Al_4Si_5O_{18}$) with stoichiometric composition determined the amounts of MgO, Al_2O_3 and SiO_2 . The starting materials were *h*-BN powders (APS (average particle size) of 2.29 μm , purity > 99%, Advanced Technology & Materials Co. Ltd., Beijing, China), MgO (APS of 5.83 μm , purity > 98%, TianjinGuanfu Fine Chemical Research Institute, Tianjin, China), Al_2O_3 (APS of 0.73 μm , purity > 98%, Showa Denko, Yokohama, Japan), and fused quartz (APS of 3.39 μm , purity > 98%, Guangyu Quartz Co. Ltd., Lianyungang, China).

The raw powders were mixed in a wet mode inside a 1.5 L plastic bottle filled with Al_2O_3 balls (10 mm dia.) and appropriate ethanol predissolved as mixing media for 24 h with a rotation speed of 60 rpm, afterward 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, composite disks $\varnothing$ 36 mm were hot-press sintered in a graphite die with a BN release agent at 1800 °C for 60 min under a pressure of 10 MPa in 1 atm N_2 atmosphere, and at a ramp rate of 20 °C/min. Before the test, all specimens were machined into standard samples of $\varnothing$ 36 $\times$ 10 mm, ground and polished with emery paper down to a 1 μm finish.

The phase composition was identified by X-ray diffractometry (XRD; D/max- γ B, Ricoh, Japan) using Cu-K α radiation with scan speed of 4°/min from 10° to 90°. The morphology and crystallographic structure were characterized by transmission electron microscopy techniques (TEM; Tecnai G2 F30, FEI, USA) along with energy dispersive X-ray spectroscopy (EDS; Hitachi, Tokyo, Japan) for chemical composition analysis using the Cu-grid as the sample holder. The TEM specimens were prepared by cutting and grinding the sintered specimens into a plate with a thickness of 50 μm , then dimpling and ion beam milling. Morphologies of specimens were characterized by scanning electron microscopy (SEM; Quanta 200FEG, 15 kV, FEI Co., USA; LYRA, 5 kV, TESCAN Co., Czech). Energy dispersive spectroscopy (EDS) was used to analyze the elemental composition. For SEM observations, a thin Au layer was applied on the surface of the composites to avoid charging. Confocal microscopy (Nanofocus μ Surf) was used to measure the

surface profile of the thermal shocked specimens.

The ablation test was carried out under an oxyacetylene flame in air following GJB323A-96 (test methods for ablation of ablators, China). The pressures of oxygen and acetylene were controlled as 0.4 and 0.095 MPa, while the gas fluxes were 1512 and 1116 L/h, respectively. There corresponding heat flux and flame temperature were approximately 4.2 MW/m², and 3100 °C, respectively. [34] The ablation specimens of BN-MAS ceramic composites were $\varnothing$ 36 $\times$ 10 mm and fixed into graphite fixture, all specimens were polished with a 3000-grit SiC sandpaper before the ablation tests. The distance between the nozzle tip and the surface of the specimen was 10 mm, and the flame was perpendicular to the specimen surface. The inner diameter of the nozzle top was 2.0 mm. The surface temperature of the sample was monitored with an optical pyrometer with the range of 1000–2500 °C. The ablation gun was ignited and adjusted first using a graphite pellet with the same dimensions as the testing samples. Once the flame was steady the fixture disk was turned automatically to let the torch exactly moved to the central area of the testing sample surface for ablation, then moved to the next one, and the ablation time were controlled as 5 s, 10 s, 15 s and 30 s, respectively.

The mass ablation rate and linear ablation rate are calculated by the following formulas:

$$R_m = (m_0 - m_t)/t \quad (1)$$

$$R_l = (l_0 - l_t)/t \quad (2)$$

Here, R_m , R_l mean the mass ablation rate and linear ablation rate. m_0 and l_0 mean sample mass and thickness before ablation. m_t and l_t mean sample mass and thickness at the ablation center after ablation, respectively. t means ablation test time. TG and DTA (Netzsch STA 449C, Germany) of specimens were carried out in an atmosphere of flowing air in alumina crucibles over a temperature range from 25 to 1400 °C at 5 °C/min.

3. Results and discussion

3.1. Oxidation properties

In the BN-MAS composites, the amorphous phase continuously distributes in the composite, with discontinuous plate-like *h*-BN crystals (Fig. 1). There are no obvious cracks or voids at the interface between amorphous phase and *h*-BN suggesting good bonding. The oxidation of *h*-BN in the composites depends on the diffusion of oxygen in the pores and cracks of the matrix. Thus, it is possible that the effective combination of MAS and *h*-BN offers potential for good oxidation resistance.

The TG-DTA for BN-MAS composites in air is shown in Fig. 2. The

Fig. 1. STEM micrographs of the BN-MAS specimen.

Fig. 2. TG and DTA curve of BN-MAS composites in the air environment.

mass change can be divided into two stages: i) RT ~ 1252 °C and ii) 1252–1400 °C, respectively. There is almost no mass change in stage i, with only a small amount of *h*-BN oxidation. The TG curve climbs in stage ii, likely as a consequence of extensive oxidation. DTA shows three exotherms. Compared with XRD results and the literatures, the first exotherm at 490 °C arises from oxidation of *h*-BN to B₂O₃ while the second endotherm at 1090 °C likely results from crystallization of mullite. The last exotherm above 1400 °C can be associated with α -cordierite crystallization.

In the initial oxidation stage, *h*-BN on the specimen surface oxidizes to B₂O₃ and releases nitrogen. The liquid B₂O₃ layer formed at 450 °C covers the sample surface uniformly and starts to volatilize at $\leq$ 1252 °C. With further increase in temperature, B₂O₃ would evaporate [22,35]. However, liquid B₂O₃ co-melts with MAS to form a more viscous magnesium-aluminum borosilicate glass before B₂O₃ fully volatilizes, preventing severe *h*-BN oxidation by acting as a barrier to oxygen diffusion. In stage ii, volatilization is enhanced as the viscosity of the glass phase decreases, leading to the further oxidation. Thus, BN-MAS composites shows superior oxidation resistance compared to simple *h*-BN bulk ceramics.

3.2. Ablation properties

Fig. 3 shows the surface temperature evolution of BN-MAS composites as ablation time increases to 30 s. The ablation surface temperature of composites increases sharply within 4 s and then remains stable to ~ 2080 °C (*T_s*). In contrast to the BN-SiO₂ composites (2450–2850 °C) [3], a dramatic decrease in ablation surface temperature is achieved due to the addition of MAS. Such temperature reductions are beneficial for wave-transparent applications as they would

Fig. 3. Ablation surface temperature pattern of BN-MAS composites.

Fig. 4. Ablation property of BN-MAS specimens.

reduce signal attenuation.

Fig. 4 presents the ablation properties of the specimens. The results indicate that the mass ablation rates and linear ablation rates of *h*-BN matrix composites are related with the ablation time. When the ablation time is 5 s, the mass ablation rate and linear ablation rate of composites are 0.0027 g/s and 0.001 mm/s, respectively. At 30 s, they are 0.0254 g/s and 0.087 mm/s, both of which increase with ablation time. Compared with the sole oxidation process, the actual oxidation course is quite complicated during ablation. The BN-MAS composites were subjected to large aerodynamic loads in addition to the aerothermal. With increase of the ablation time, the surface dense oxidation layer will be scoured away by high speed gas and the matrix would suffer severe oxidation. Therefore, mass loss and linear loss of the composites showed great variation with increase of the ablation time. Compared with other ablation resistant materials (Table 1), the BN-MAS composites exhibit more favorable ablation properties.

Fig. 5 provides the optical micrograph of the BN-MAS composites surface at different ablation times. No catastrophic damage was observed under such violent thermal shock conditions. At 5 s, no ablation pits are observed (Fig. 5(a)). At longer ablation times, pitting could be observed corresponding to the ablation flame impingement. There also exists a peak in the ablation pit, which can be divided into several parts. The translucent spherical ablation product forms at the bottom and the periphery of the ablation pit. When the ablation time exceeds 30 s, the spherical product becomes bigger in an irregular shape. The composites surface also peeled off after ablation because of thermal stresses and scouring, as indicated in Fig. 5(b)–(d). Based on the different morphologies after ablation, the surface of ablated specimens can be divided into three parts, namely ablation center region (marked as A), transition region (marked as B) and heat-affected region (marked as C) as shown in Fig. 5(d).

The 3D confocal microscopy of BN-MAS composites (Fig. 6) provides the surface profile of ablation center region. The surface layer of center region consists of a series of small burst bubbles and potholes (Fig. 6(a)) when the ablation time is 5 s. With increase of the ablation time, the bubbles become bigger and the matrix becomes more rugged, indicative of extensive erosion. In addition, no visible micro-cracks are observed on the central region of all ablated specimens' surface.

Table 1
Ablation property of several ablation resistant materials [2,34–36].

Ablation time	Mass ablation rate, g/s	Linear ablation rate, mm/s
SiNO ₂ /BN	0.057 (5 s)	0.132 (5 s)
SiC _f /SiBCN	0.0134 (10 s)	0.0237 (10 s)
C _f /SiBCN	0.0215 (10 s)	0.0455 (10 s)
3 D C/ZrC-SiC	0.0089 (90 s)	0.0136 (90 s)
GO/SiBCN	0.012 (10 s)	0.007 (10 s)

Fig. 5. Digital camera images of BN-MAS specimens under different ablation time: (a) 5 s; (b) 10 s; (c) 15 s; (d) 30 s.

Fig. 6. Confocal microscopy images showing the surface profile of BN-MAS specimens under different ablation time: (a) 5 s; (b) 10 s; (c) 15 s; (d) 30 s.

3.3. Phase composition and ablation morphologies

In order to investigate the phase composition and morphologies of BN-MAS composites after ablation, the XRD, SEM and EDS were characterized. XRDs obtained from the ablation center of specimens are presented in Fig. 7. Before the ablation, the specimens (BN-30 wt% MAS) only consist of *h*-BN and amorphous MAS [36]. After ablation testing, indialite (JCPDS No. 85-1722), spinel (JCPDS No. 73-1959) and mullite phase (JCPDS No. 79-1455) appear on the specimen's surfaces. However, no B_2O_3 peaks are detected likely because of its low melting point and high evaporation rate.

During the experiment, the pressures of oxygen and acetylene were 0.4 MPa and 0.095 MPa, respectively. The atmosphere applied in the specimens was oxidizing atmosphere [37]. The flame temperature is

Fig. 7. XRD of specimens surface after ablation at difference time: (a) 5 s; (b) 10 s; (c) 15 s; (d) 30 s.

about 3100 °C and surface temperatures rise significantly to about 2080 °C detected by optical pyrometer. Therefore, oxidation, evaporation and other physical and chemical changes normally take place on composite surfaces. The reactions that might occur in the ablation experiment are listed as follows:

The boiling points of $B_2O_3(l)$, $SiO_2(l)$, $Al_2O_3(l)$ and $MgO(l)$ are 1500 °C [16,22], 2230 °C [38], 2980 °C and 3600 °C, respectively. Most of these boiling temperatures are much lower than the ablation flame temperature (~3100 °C). Therefore, under such ablation condition, the reactions above may generate gas emitting and would cause the mass loss of the composites. Meanwhile, the evaporation of $B_2O_3(g)$, $SiO_2(g)$ and $Al_2O_3(g)$ beneficially lowers ablation surface temperatures, which in turn can improve the ablation properties, thermal protective and wave-transmission performance of BN-MAS composites.

Fig. 8 shows the SEM morphology of the different regions of specimen after 10 s ablation. The composite morphology consists of two zones: porous zone and dense zone. In the ablation center region and transition region, the matrix is porous and numerous platelet particles are clearly visible. The composition analysis reveals that the main elemental components in the transition region surface are Al, Si, Mg, O, B, and N. The surface of the heat-affected region is covered with a dense glassy layer with a few pores. The composition analysis suggests that Si content increases from the central to heat-affected region apart from the obviously different morphologies. Compared with the stoichiometric composition of MAS ($Mg_2Al_4Si_5O_{18}$), the central region and transition region are rich in Mg and Al, while the heat-affected region is rich in Si.

Compared with the center region, the ablation flowing gas-stream in the transition region is parallel to the specimen surface from the nozzle

Fig. 8. (a)–(c) shows the SEM morphology of ablation specimen (10 s): (a) center region (composition of region 1: 19 wt% B, 16 wt% N, 9 wt% O, 7 wt% Mg, 24 wt% Al, 25 wt% Si); (b) transition region (composition of region 2: 3 wt% B, 4 wt% N, 13 wt% O, 12 wt% Mg, 37 wt% Al, 31 wt% Si); (c) heat-affected region (composition of region 3: 6 wt% B, 5 wt% N, 12 wt% O, 5 wt% Mg, 14 wt% Al, 58 wt% Si).

tip to the specimen in the center region. SiO_2 can not only flow to the adjacent regions from the ablation pits but evaporate in the center region. Therefore, the transition region is constituted by a thin and relatively dense glassy layer. EDS reveals that the main surface components are Si, Al, Mg and O. With temperature decreasing from the ablation center to the edge of specimens, SiO_2 viscosity increases. Based on the thermodynamic calculation, the reactions should emit SiO (g), SiO_2 (g), B_2O_3 (g) and N_2 (g) during ablation. Despite of the increases of viscosity, SiO_2 can still flow on the surface to seal pores. Therefore, the ablation surface is covered by a dense SiO_2 -rich phase, as Fig. 8(c) shows.

As mentioned in Section 3.2, some white spherical particles appear in the ablation center. EDS indicates that these particles are likely magnesium-aluminum borosilicate glass (Fig. 9(a)). Borosilicate glass phase forms in the ablation surface which is dominated by the oxidation reactions (discussed in Section 3.1). During ablation, the liquid glass can be expected to form spherical particles as they offer the lowest Gibbs free energy surface. In the transition region and heat-affected region, larger translucent spherical particles are also observed (Fig. 9(b)–(c)). Many irregular microcrystalline grains form from the spherical particles matrix rich in Al and Mg. Given that the boiling points of MgO and Al_2O_3 are much higher than that of SiO_2 and B_2O_3 , it can be expected to precipitate first from the magnesium-aluminum borosilicate glass during cooling process to form mullite or spinel microcrystalline grains.

The cross-sectional morphologies of ablation center region are illustrated in Fig. 10. The boundary of oxidation product and composite matrix is indistinct, which is different from the heat-affect region. Since the oxyacetylene torch test is a very aggressive method, the ablation corrosion is more severe than other regions. No obvious transition layers can be observed in the center region, indicating good ablation resistance of the composites.

The Fig. 11 SEM shows cross-sections of ablation samples. In the inner heat-affected region, the BN-MAS composites matrix maintains its own morphology. There are no transition layers between spherical particles and the matrix, which means that oxygen does not penetrate into the BN-MAS composites. The numerous bubbles in the particles are caused by evolution of SiO_2 (g), B_2O_3 (g) and N_2 (g) (Fig. 11(a)). Most bubbles are not broken because the glass viscosity increases gradually during cooling. Meanwhile, several micro-cracks are observed in the spherical particle, ascribed to thermal stress resulting from mismatch of the thermal expansion coefficients between the magnesium-aluminum borosilicate glass and BN-MAS composites matrix. There is also a dense magnesium-aluminum borosilicate glass layer of about 5 μm (Fig. 11(b)) in the heat-affected zone. No obvious interfaces are observed indicating strong adhesion. This glass layer acts as a protective barrier against further erosion as it limits inward diffusion of oxygen.

3.4. Ablation mechanism

During ablation, BN-MAS composite ceramics are eroded by aerodynamic loads in addition to the aerodynamic heating. A series of complicated physical and chemical processes take place between the ultra-high temperature oxidative gases and BN-MAS composites [39,40]. A probable mechanism can be suggested based on the different surface morphologies and microstructures that form at different ablation times in chronological order, as shown in Fig. 12. In the initial stage, the specimen is under relatively low temperature. In this stage, h -BN oxidation is the main ablation process. The ablation product B_2O_3 forms at this stage. N_2 (g) and B_2O_3 gas emit from the surface, leading to a mass loss and substantial numbers of small pits. After extent ablation times, the surface temperature increases and B_2O_3 evaporates [22]. The MAS glass melts, but its high viscosity makes it difficult to fill the pores and cracks. However, B_2O_3 dissolves with MAS to form a less viscous magnesium-aluminum borosilicate glass before the B_2O_3 volatilization ends [41]. This viscous phase slows down B_2O_3 evaporation and prevents rapid oxidation of h -BN by acting as a barrier for diffusion of oxygen. However, only when the generation rate of oxide is higher than the erosion rate, can the oxide layer play a positive role during ablation.

The final ablation step involves chemical and physical erosion. The aerodynamic loads play an important part during ablation in this stage. The liquid magnesium-aluminum borosilicate glass flows by the high speed gas scouring under such severe ablation. Thereafter, the effective protection is lost due to scouring and rapid volatilization of B_2O_3 and N_2 . Moreover, the ablation flame temperature (up to 3100 °C) is higher than SiO_2 and Al_2O_3 's vaporization temperature (2230 °C and 2980 °C). Thus, part of SiO_2 and Al_2O_3 can evaporate from the ablation surface in the center region. In the final stage, the chemical and physical erosion are severe and massive ablation pits form.

4. Conclusions

The ablation behavior of the BN-MAS composites were investigated by exposure to an oxyacetylene torch flame with different times. As expected, introducing MAS glass to the h -BN-matrix composites can significantly decrease the ablation surface temperature to ~ 2080 °C. The ablation properties of composites depend on the ablation time. With the increment of ablation time, the mass ablation rate increases from 0.0027 g/s to 0.0254 g/s and the linear ablation rate increases from 0.001 mm/s to 0.087 mm/s.

In addition, the ablation mechanism of the composites has been carefully studied based on the morphologies and phases under different ablation time. The ablation mechanism of BN-matrix composites ceramic includes chemical erosion and physical denudation under the oxyacetylene torch ablation environment. During the ablation process, five ablation actions contribute to the various ablation regions: (1) oxidation of the matrix, mainly of h -BN; (2) evaporation of B_2O_3 (g), N_2

Fig. 9. 9 (a)–(c) shows SEMs of the spherical particles after 10 s ablation: (a) center region (composition of region1: 5 wt% B, 3 wt% N, 20 wt% O, 12 wt% Mg, 31 wt% Al, 29 wt% Si); (b) transition region (composition of region 2: 0 wt% B, 3 wt% N, 11 wt% O, 10 wt% Mg, 69 wt% Al, 7 wt% Si; composition of region 3: 3 wt% B, 4 wt% N, 13 wt% O, 13 wt% Mg, 39 wt% Al, 28 wt% Si); (c) heat-affected region (composition of region 4: 2 wt% B, 3 wt% N, 19 wt% O, 15 wt% Mg, 54 wt% Al, 7 wt% Si; composition of region 5: 4 wt% B, 3 wt% N, 20 wt% O, 11 wt% Mg, 28 wt% Al, 34 wt% Si).

Fig. 10. Cross-section of ablation center region of specimen after 10 s ablation.

(g) and softening of MAS (l); (3) scouring away of magnesium-aluminum borosilicate glass; (4) high-viscosity SiO_2 -rich liquid flowing with ablation atmosphere stream; (5) evaporation of SiO_2 (l) and Al_2O_3 (l).

The results here point to the oxidation property, ablation behavior and mechanism of BN-MAS composites, which can be applied to aid materials engineering design for the development of quality assurance and characterization assessment of durability. The BN-MAS composite ceramics should be paid further attention for applications involving elevated temperature dielectric materials.

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Fig. 11. Cross-section of the inner heat-affect region of specimen after 10 s ablation.

Fig. 12. Schematic of BN-MAS composites ablative mechanism.

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