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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 $SiO_2$-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], $Al_2O_3$ [5], $Si_3N_4$ [6], $SiO_{2f}/SiO_2$ [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 sp [2] 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, $A1_2O_3$, $ZrO_2$ 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 $B_2O_3$ firstly at about 450 °C. Due to its relatively low melting temperature, liquid $B_2O_3$ then forms a continuous layer on the sample surfaces which can prevent inward transport of oxygen below 900 °C. However, above this temperature, $B_2O_3$ 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 $B_2O_3$ to produce a stable and viscous $MgO\text{-}Al_2O_3\text{-}SiO_2\text{-}B_2O_3$ 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 Ø 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 Ø 36 × 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-Kα 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 μSurf) 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/m$^2$, and 3100 °C, respectively. [34] The ablation specimens of BN-MAS ceramic composites were Ø 36 × 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

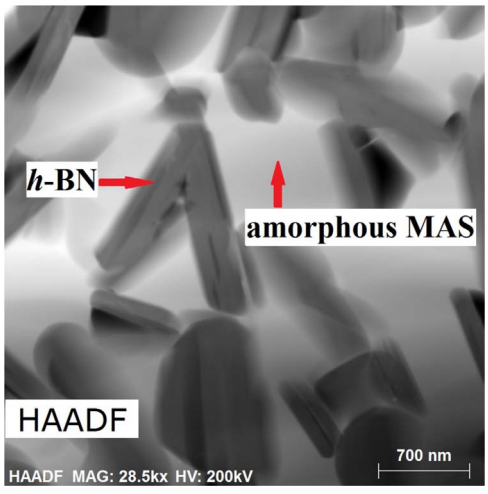


**Fig. 1.** STEM micrographs of the BN-MAS specimen.