Oxidation resistance of AlN/BN via mullite-type $\text{Al}_{18}\text{B}_4\text{O}_{33}$

C.S. Chari, K.T. Faber

PII: S0955-2219(22)00129-7

DOI: <https://doi.org/10.1016/j.jeurceramsoc.2022.02.037>

Reference: JECS14682

To appear in: *Journal of the European Ceramic Society*

Received date: 24 November 2021

Revised date: 13 February 2022

Accepted date: 16 February 2022

Please cite this article as: C.S. Chari and K.T. Faber, Oxidation resistance of AlN/BN via mullite-type $\text{Al}_{18}\text{B}_4\text{O}_{33}$, *Journal of the European Ceramic Society*, (2021) doi:<https://doi.org/10.1016/j.jeurceramsoc.2022.02.037>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2021 Published by Elsevier.

Oxidation resistance of AlN/BN via mullite-type $\text{Al}_{18}\text{B}_4\text{O}_{33}$

C. S. Chari and K. T. Faber*

Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 91125, USA

*Corresponding author: Katherine Faber

Email: ktfaber@caltech.edu

AlN/BN ceramic composites are materials of interest for high-temperature applications because of their low elastic modulus and high thermal shock resistance. Concerns of side products that could form, due to the oxidation of BN into reactive B_2O_3 , motivate the study of the influence of B_2O_3 on the oxidation of AlN and AlN/BN. This investigation explores such an effect by comparing the oxidation kinetics of AlN with that of B_2O_3 -coated AlN, offering insight into how liquid B_2O_3 films provide AlN with improved protection against oxidation at temperatures from 1200 to 1300 °C. These concepts are extended to AlN/BN in oxidative environments. We discuss the formation of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers from B_2O_3 and Al_2O_3 and analyze how the microstructure evolves into hollow crystals with prolonged exposure to high-temperatures. Ultimately, this study provides a novel perspective on the oxidation of AlN/BN and serves as a guide to understanding the morphological evolution of $\text{Al}_{18}\text{B}_4\text{O}_{33}$.

Keywords: Aluminum nitride composites; boria; oxidation; whiskers; hollow crystals

1. Introduction

Aluminum nitride/ boron nitride (AlN/BN) composites are popular high-temperature ceramics, desired for their improved machinability and increased thermal shock resistance over traditional aluminum nitride (AlN). The inclusion of hexagonal boron nitride (BN) in the material lowers the toughness and compliance of the composite, making it easier to machine and thus more affordable to process. The mechanical properties and the dielectric behavior of AlN/BN composites are desirable for applications in the automotive and aerospace industries.

The presence of BN in the composite, however, poses challenges due to its oxidation into boria (B_2O_3), a highly reactive material that has reportedly created unwanted side products in other BN-bearing composites, such as SiC/BN [1]. Previous studies have explored this in depth, demonstrating how the oxidation products of SiC and BN (SiO_2 and B_2O_3 , respectively) can react together in high-temperature environments over 1000 °C to form borosilicate glass, commonly found in oxidized SiC/BN/SiC ceramic-matrix composites [1,2]. With this in mind, it is an intuitive next step to study whether similar challenges could be expected in AlN/BN composites exposed to comparable conditions, where BN can oxidize into boria.

Boria exists as a liquid oxide at temperatures up to 1000 °C, after which its evaporation rate increases exponentially [3]. The viscosity of boria decreases with increasing temperature, from 100 poise at 1000 °C to 40 poise at 1200 °C [4]. It is also hygroscopic; its evaporation rate intensifies in humid environments, as it is easily converted to boric acid in the presence of water [5]. Furthermore, boria is capable of reacting with other oxides, forming products that are less volatile, e.g., borosilicate and aluminum borate [3,6,7].

Earlier studies focusing on the fabrication of composites like $\text{Al}_2\text{O}_3/\text{BN}$ [8–10], AlON/BN [11,12], $\text{AlN}/\text{B}_2\text{O}_3$ [13], AlN/HfB_2 [14], and AlN/TiB_2 [15], have noted that aluminum borate whiskers can form from the reaction between alumina and boria starting at temperatures of 1000 °C. Thus, we expect whiskers to also be detected in AlN/BN composites exposed to elevated temperatures in oxidizing environments. Interestingly, aluminum borate whiskers have also been used in other applications as reinforcements to enhance toughness in aluminum composites [16,17] and glass composites [18], given their low density (2.93 - 2.94 g/cm³), high hardness (Mohs hardness of 7) and high Young's Modulus (400 GPa) [16,18]. Nevertheless, the role of aluminum borate whiskers and boria in the oxidation of AlN/BN composites has not been the focus of any comprehensive study.

In the current study, we explore how the presence of liquid boria alters the oxidation kinetics of AlN by comparing AlN to boria-coated AlN and AlN/BN composites. We examine how boria can provide AlN with added protection against oxidation. We also investigate the chemical composition and microstructure of the aluminum borate whiskers created in these material systems. Moreover, we shed light on how the whisker morphology evolves with exposures to high-temperature environments, and how this affects the oxidation protection of AlN .

2. Materials and Methods

2.1. Materials and Processing

Commercially available sintered AlN and AlN/BN were used in this study. Sintered AlN bars (ST-200, Sienna Technologies) were cut into 6 mm x 8 mm x 8 mm sized coupons. ST-200 has a density of 3.3 g/cm³ and a purity of 95%, with the remaining 5% being from the Y-rich binder. Sintered AlN/BN (Shapal Hi-M Soft, Precision Ceramics) were cut into 3 mm x 4 mm x 6 mm sized coupons. Shapal Hi-M Soft has a density of 2.88 g/cm³, thermal expansion coefficient (from RT to 800 °C) of $5 \times 10^{-6}/^\circ\text{C}$, and a purity just under 99%, with trace amounts of O (0.9 wt.%), Ca (1300 ppm), C (300 ppm), Cr (<1 ppm), Mg (1 ppm), Ni (<2 ppm), Fe (8 ppm), Si (40 ppm) and Ti (20 ppm).

Boria-coated AlN was prepared by covering the topmost face of the ST-200 coupons with 0.019 ± 0.003 g/cm² of boric acid powder (H_3BO_3 , Sigma-Aldrich) and heating the sample to 450 °C in stagnant air. H_3BO_3 powder was used instead of B_2O_3 due to the hygroscopic, volatile nature of the oxide. H_3BO_3 dehydrates into B_2O_3 at 300 °C, which then melts into a glassy film at 450 °C, below the oxidation temperature of the AlN substrate. The oxidation tests outlined in section 2.2 were carried out during the same heating cycle.

2.2. Oxidation Studies

The oxidation behavior of AlN (ST-200, Sienna Technologies) was investigated at temperatures varying from 800 °C to 1300 °C using a high-temperature box furnace (CM Rapid Temp 1700 °C Furnace) in stagnant air. The holding times at each temperature ranged from 5 h to 48 h. The heating and cooling rates were both 3 °C/min to minimize thermal shock effects. The individual experiments are further summarized in Table 1.

The oxidation experiments were then repeated with boria-coated AlN (ST-200, Sienna Technologies). The oxidation temperature range in this case was restricted from 1000 °C to 1300 °C, to ensure significant oxide growth while still limiting the amount of boria lost by evaporation. The holding times and ramp rates were identical to those used for the reference AlN samples.

The oxidation of AlN/BN composites (Shapal Hi-M Soft, Precision Ceramics) was studied using dry air (AI Z200, Airgas) to minimize the amount of water vapor influencing the oxidation of BN. Studies have shown that BN can easily oxidize into boria vapor in the presence of water [19,20]. In order to investigate the interactions between liquid boria and alumina, a dry air environment with negligible amounts of water vapor (2 ppm H₂O) was chosen. The oxidation exposures studied ranged from 1200 °C to 1300 °C over 48 h or 60 h. We chose to focus on these exposure conditions because they resulted in stoichiometric amounts of both boria and alumina that were needed for aluminum borate growth.

Table 1. Summary of oxidation conditions for each experiment.

Materials System	Oxidation Temperature (°C)	Holding Times (h)
AlN (ST-200)	800	12
	1000	5, 12, 24, 36, 48
	1100	5, 12, 24, 36, 48
	1200	5, 12, 24, 36, 48
	1300	5, 12, 24, 36, 48
Boria-coated AlN (ST-200)	1000	5, 12, 24, 36, 48
	1100	5, 12, 24, 36, 48
	1200	5, 12, 24, 36, 48
	1300	5, 12, 24, 36, 48
AlN/BN (Hi-M Shapal Soft)	1200	48
	1250	48, 60
	1300	48
	1350	48
	1450	48

2.3. Characterization

Scanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDS, ZEISS 1550VP FESEM, Carl Zeiss Microscopy GmbH, Jena, Germany) were used to detect the oxide layers of cross-sectioned samples, and to measure the whisker dimensions. The oxide thicknesses were measured after each exposure experiment using the Region of Interest Manager of the image-processing tool ImageJ (National Institutes of Health). An average of 35 thickness measurements were carried out for each sample over the length up to 800 µm, with measurements being made in evenly spaced intervals. The widths of the aluminum borate whiskers were also measured using ImageJ with an average of 100 whiskers being measured for each sample. The width was defined as the averaged thickness of the orthorhombic crystal, measured perpendicular to the direction of crystal growth. These measurements were taken near the mid-section of the whisker to avoid the narrow widths of the tips and better represent the whisker size. Note that due to the interlocking nature of the whiskers, it was not possible to determine the distribution of whisker lengths. The reported values of oxide thickness and whisker widths were determined using number averaging, with the error term representing one standard deviation.

X-ray powder diffraction (XRD, PANalytical X'Pert Pro) and transmission electron microscopy (TEM, TF-30, Tecnai) were also carried out to characterize the oxidized samples and aluminum borate crystals respectively. Mass attenuation coefficients and penetration depths were calculated using

PANalytical's HighScore Plus Software. Single crystal electron backscatter diffraction (HKL EBSD system, on the ZEISS 1550VP FESEM) was performed using a focused beam with a 70° tilted stage. The crystallographic orientation of the whiskers was determined by matching the experimental EBSD pattern with crystallographic information of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ from Ihara et al. (1980) [21].

3. Results and Discussion

3.1. Influence of Boria on the Oxidation of Aluminum Nitride

3.1.1. Oxidation of Aluminum Nitride

The oxidation kinetics of AlN were studied by tracking the growth of the Al_2O_3 layer as a function of time. This was achieved by measuring the thickness of the oxide layer of each experiment outlined in Table 1. Figure 1a illustrates the oxidation kinetics of AlN within the temperature range 1000 °C to 1300 °C.

Figure 1. a) Oxide thickness of AlN versus holding times for oxidation exposures at 1000 °C, 1100 °C, 1200 °C and 1300 °C. Scanning electron micrograph image of (b) as-received AlN surface, (c) oxidized AlN surface and (d) oxidized AlN cross-section, following exposures to 1300 °C in air for 12 h.

The results and best fits displayed in Figure 1a suggest that the oxidation of AlN behaves linearly at 1000 °C and 1100 °C. This indicates that the growth rates of the oxide layer at these temperatures are constant and completely controlled by Reaction 1.

At higher temperatures, the results and best fits shown in Figure 1a imply that the oxidation behavior of AlN is parabolic at 1200 °C and 1300 °C. This suggests that the oxide layers formed at these temperatures are sufficiently thick to act as physical barriers that restrict oxygen diffusion to AlN. In parabolic oxidation, the rate of oxidation is no longer controlled by Reaction 1, but instead is influenced by the diffusivity of oxygen into the bulk. More details of this behavior can be found in the supplementary information.

The oxidation of AlN into Al₂O₃ has been examined in the past, and is shown to depend greatly on the properties of the starting material, such as the grain size, porosity and impurity content of the reported AlN [22–27]. The surface microstructure of the as-received AlN is shown in Figure 1b. In high-temperature environments over 800 °C, AlN can oxidize into Al₂O₃ with the evolution of nitrogen gas, as seen in Reaction 1. Previous studies have demonstrated that the evolving nitrogen gas creates pores within the oxide layer [22,25,26], facilitating paths for oxygen diffusion into the substrate. There is a significant difference between the coefficients of thermal expansion (CTE) of Al₂O₃ (9×10^{-6} /°C) and AlN (5×10^{-6} /°C), which results in a large thermal mismatch between the two layers on cooling from the oxidation temperature [23]. This can cause cracks to form in the porous Al₂O₃ layer, which can extend through its thickness as seen in Figure 1c,d. The appearance of cracks, in addition to pores, assists the transport of oxygen to AlN, allowing for continued and rapid oxidation with increasing temperature and exposure time.

3.1.2. Oxidation of Boria-coated Aluminum Nitride

In Figure 2a-d, we compare the oxidation of AlN with that of boria-coated AlN. At 1000 °C, seen in Figure 2a, the measured oxide thickness of boria-coated AlN is greater than the thicknesses measured for AlN at the same temperature due to the inclusion of boria as a coating in the former. The added liquid oxide increases the overall thickness of the oxide layer, which remains constant at 6 ± 2 μm for all holding times. The constant thickness reflects the low evaporation rate of boria at 1000 °C [3]. At 1100 °C, seen in Figure 2b, the oxide thicknesses for boria-coated AlN remains constant at 10 ± 2 μm for all the holding times, indicating that the low evaporation rate of boria is maintained at this temperature [3].

Figure 2. Oxide thickness of AlN (empty markers) and boria-coated AlN (filled markers) versus holding times for oxidation exposures at a) 1000 °C, b) 1100 °C, c) 1200 °C and d) 1300 °C. e) SEM-EDS maps of oxidized coupons exposed to different oxidative conditions: AlN (left), boria-coated AlN (right).

At 1200 °C, seen in Figure 2c, the oxide thicknesses for the boria-coated AlN samples are superseded by the oxide layer thickness of corresponding AlN samples. Oxide thickness is reduced by as much as 86% with the inclusion of boria, demonstrating a protection against oxidation and against Al₂O₃

formation due the inclusion of the boria coating. This protection diminishes with increased holding time because of the significant evaporation rate of boria at 1200 °C [3]. Likewise at 1300 °C, seen in Figure 2d, the added boria continues to protect AlN against oxidation, as evidenced by the lower oxidation rate compared to uncoated AlN. However, this protection is not as effective as what was observed at 1200 °C because of the higher volatility of boria at 1300 °C compared to 1200 °C [3].

Figure 3. a) XRD spectra of boria-coated AlN at oxidation temperatures ranging from 800°C to 1300°C in contrast to as-received AlN, b) XRD spectra of boria-coated AlN compared to AlN at an oxidation temperature of 1200 °C for 12 h, 24 h and 36 h. Spectra show presence of AlN (○), $\text{Al}_{18}\text{B}_4\text{O}_{33}$ (●), boria (◇), YAG/YAP (□), Al_2O_3 (■).

To further elucidate the observed oxidation behavior, X-ray diffraction spectra of boria-coated AlN coupons were collected after exposure. It was revealed that the oxide layers formed in every oxidation experiment contained varying mixtures of unreacted B_2O_3 , Al_2O_3 , and aluminum borate, as seen in Figure 3a. There are two stable phases of aluminum borate, $\text{Al}_4\text{B}_2\text{O}_9$ and $\text{Al}_{18}\text{B}_4\text{O}_{33}$ [28]. Both arise from the reaction between B_2O_3 and Al_2O_3 .

The $\text{Al}_{18}\text{B}_4\text{O}_{33}$ phase forms when there is a low concentration of boria and high concentration of alumina, while the $\text{Al}_4\text{B}_2\text{O}_9$ phase forms with higher concentrations of boria. Due to the volatile nature of boria, $\text{Al}_4\text{B}_2\text{O}_9$ transforms into $\text{Al}_{18}\text{B}_4\text{O}_{33}$ with increasing temperatures, commencing near 1040 °C [18,28]. Similarly, $\text{Al}_{18}\text{B}_4\text{O}_{33}$ converts to Al_2O_3 when boria completely volatilizes out of the crystal [28].

Figure 3a shows that the $\text{Al}_{18}\text{B}_4\text{O}_{33}$ phase was present within the oxide layer of boria-coated AlN coupons after treatments at 1000 °C, 1100 °C and 1200 °C, indicating a low initial concentration of boria relative to alumina. The diffraction peaks that correspond to $\text{Al}_{18}\text{B}_4\text{O}_{33}$ decrease in intensity as the temperature increases. Simultaneously, Al_2O_3 peaks grow in intensity with increasing temperature,

beginning at 1100 °C. This suggests that the $\text{Al}_{18}\text{B}_4\text{O}_{33}$ crystals start to convert to Al_2O_3 with the high-temperature evaporation of boria. This conversion appears to be complete by 1300 °C. Figure 3 also indicates the presence of YAG (yttrium aluminum garnet) and YAP (yttrium aluminum perovskite), which originate from the commercially available sintered AlN. Y-rich additives are commonly added to high-temperature ceramics like AlN to improve their sinterability [29,30]. However, these Y-rich phases are not considered any further for this analysis.

A notable observation from the X-ray diffraction data is that the underlying AlN substrate is protected against oxidation by the addition of the boria coating. This protection is particularly obvious during 12 h holds at 1200 °C, seen in Figure 3b, where the AlN peaks are strong in boria-coated AlN coupons, but greatly diminished in uncoated AlN coupons. To verify this observation, we refer to the expected X-ray penetration depths for each system, assuming that 95% of the information collected pertains to the volume of the material from the surface to the penetration depth, and not the material below this layer [31]. In samples of boria-coated AlN that had been exposed to air for 12 h at 1200 °C, we see that the X-rays can penetrate the $23 \pm 4 \mu\text{m}$ thick $\text{Al}_{18}\text{B}_4\text{O}_{33}$ -rich oxide layer and probe the underlying AlN substrate as seen in Figure 3b. In contrast, for samples of uncoated AlN exposed to the same conditions, the X-ray penetration is limited within the $164 \pm 13 \mu\text{m}$ thick Al_2O_3 layer, never reaching the underlying AlN substrate, seen in Figure 3b. This suggests that the addition of boria creates a superficial liquid barrier to oxygen diffusion that ultimately results in thinner oxide layers, and thus, a greater protection against oxidation. Figure 3b shows that the $\text{Al}_{18}\text{B}_4\text{O}_{33}$ -rich oxide layer in boria-coated AlN only starts to oxidize into Al_2O_3 past 24 h exposures, when the trapped boria within $\text{Al}_{18}\text{B}_4\text{O}_{33}$ starts to evaporate.

Hence, we see that boria serves as a barrier to oxygen diffusion, protecting the underlying AlN substrate from being oxidized, while actively reacting with any created alumina to form aluminum borate on the surface of the samples, as seen in Reactions 2 and 3. Thus, we can deduce that it is a combination of Reactions 1-3 that results in an overall diminished thickness of the oxide layers seen in Figure 2a-e.

Figure 4. Scanning electron micrographs of boron-coated AlN after 12 h hold at described oxidation temperatures (a-g), including insets of transmission electron microscopy micrographs (b,e). Green arrows indicate features of interest, such as whiskers, dimple craters and hollow crystals. h) Histograms show whisker width distributions from images displayed in 4b,c,e,g.

The resulting surface microstructures of the boron-coated AlN coupons, observed using SEM, can be seen in Figure 4a-g. In contrast to the as-received AlN surface (Figure 1b), we can identify acicular crystals on these surfaces, indicating that $\text{Al}_{18}\text{B}_4\text{O}_{33}$ is present in whisker form. At 800 °C, boron melts into a thin amorphous film that covers the surface of the AlN coupon. The cracks that are seen in Figure 4a are a result of the thermal expansion mismatch that occurs during cooling of the glassy film to room temperature, as noted earlier. No whiskers are observed, indicating that boron has not yet reacted with any alumina that may be present from AlN oxidation. At 1000 °C, this is no longer the case, and we observe highly acicular crystals (Figure 4b) growing from many nucleation sites. The $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers can be seen again at 1100 °C (Figure 4c), appearing coarser and with a shape that is consistent with the orthorhombic morphology of $\text{Al}_{18}\text{B}_4\text{O}_{33}$. Exposing boron-coated AlN coupons to 1100 °C for an additional 12 h (Figure 4d), we observe that $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers start to develop dimple craters on their tips (noted by green arrows), a feature that we will refer to later in this discussion.

At 1200 °C or higher (Figure 4e-g), the whiskers appear deformed due to the evaporation of boron. Porous Al_2O_3 whiskers, confirmed by XRD in Figure 3, result with the loss of boron, some of which have shrunk in size (Figure 4g), as noted by the shift in the whisker width distribution to smaller sizes in Figure 4h. Curiously, under prolonged exposure to high-temperature environments, tube-like hollow

crystals can be seen in Figure 4f,g. The whiskers can be seen on both the micro and the nanoscale. Displayed in the insets in Figure 4b,e are bright field TEM images that show whiskers grown at 1000 °C and 1200 °C for 12 h. The morphology of the nanocrystals closely resembles their micro-sized counterparts.

3.2. Oxidation of AlN/BN Composites

X-ray diffraction patterns indicate that $\text{Al}_{18}\text{B}_4\text{O}_{33}$ crystals formed during the dry air exposures of AlN/BN composites, seen in Figure 5a. Unlike the previously discussed boria-coated AlN system, the formation of aluminum borate in the composite depends on the oxidation of AlN into alumina as well as the oxidation of BN into boria. During these experiments, the stoichiometric quantities of alumina and boria needed to produce $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers were developed between 1200 °C to 1300 °C, after exposures of 48 h or longer.

Figure 5. a) XRD spectra of oxidized AlN/BN composites in dry air from 1200°C to 1450°C, showing AlN (○), BN (○), $\text{Al}_{18}\text{B}_4\text{O}_{33}$ (●), Al_2O_3 (■), in contrast to as-received AlN/BN. SEM images of b) as-received AlN/BN composite,

(c-h) oxidized AlN/BN composites in dry air, including oxidation temperature and exposure time. i) Histograms show whisker width distributions from images displayed in 5d-g.

Figure 5 b-h shows SEM images of the as-received composite and the composite surface after being exposed to dry air from 1200 °C to 1450 °C, for holding times ranging from 48 h to 60 h, further described in Table 1. The images reflect the various stages of whisker growth produced from the reaction between boria and alumina. Early stages of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ growth can be seen in Figure 5c on the surface of the oxidized AlN grains after 48 h long exposures to 1200 °C. The pores and crevices present between the AlN grains are due to the oxidation of the BN flakes into liquid boria. The growth of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ acicular crystals can be seen in Figure 5d with an increase in temperature to 1250 °C for 48 h. As the temperature is increased further to 1300 °C (Figure 5e) or the exposure time is increased to 60 h (Figure 5f), we see a change in whisker morphological characteristics from solid to hollow crystals of $\text{Al}_{18}\text{B}_4\text{O}_{33}$, both longer and wider than the acicular crystals seen at 1250°C for 48 h (Figure 5d). Although the morphology of the crystals is significantly different in Figures 5d-g, the corresponding XRD data confirms that the aluminum borate phase present in every case is $\text{Al}_{18}\text{B}_4\text{O}_{33}$.

X-ray diffraction patterns (Figure 5a) show that $\text{Al}_{18}\text{B}_4\text{O}_{33}$ starts to convert to Al_2O_3 at 1350 °C. One possible explanation for the inter-whisker voids, seen in Figure 5g, is the collapse of hollow crystals. By 1450 °C seen in Figure 5h, the conversion is complete and isotropic grains of Al_2O_3 cover the surface with no signs of $\text{Al}_{18}\text{B}_4\text{O}_{33}$. The whisker width distributions are summarized in Figure 5i. The distribution of whiskers exposed to 1200 °C for 48h is narrow, centered near 0.5 μm . In contrast, at higher holding times or temperatures, the distribution widens, predominantly from widths < 1 μm to > 5 μm . The broad distributions, seen in both Figures 5i and 4h, may be attributed to the scatter in nucleation times, coarsening, and whisker deterioration, the latter being due to the high-temperature transition of the whiskers into porous Al_2O_3 .

Figure 6. a) Oxidation plot from Figure 1 including data points from AIN (empty markers), boria-coated AIN (filled markers), and AIN/BN (★) at 1200 °C (black) and 1300 °C (blue). SEM-EDS maps of oxidized AIN/BN cross-sections b) held at 1200 °C for 48 h, c) 1250 °C for 48 h, d) 1300 °C for 48 h, e) 1200 °C for 60 h, f) 1350 °C for 48 h, and g) 1450 °C for 48 h.

Cross-sections of oxidized AIN/BN composites were analyzed using SEM-EDS to measure the thickness of the $\text{Al}_{18}\text{B}_4\text{O}_{33}$ oxide layer. In Figure 6a, the oxide thickness of AIN/BN after 48 h at 1200 °C (Figure 6b) and 1300 °C (Figure 6d) were included in the oxidation plot from Figure 2. From this comparison, it is clear that the oxidation protection previously discussed in boria-coated AIN coupons can also be seen in AIN/BN composites. The inclusion of liquid boria within the system, both through an applied coating or from BN, can impede the oxidation of AIN.

The whisker morphology can also significantly influence the oxide layer's ability to protect the underlying composite. We see that the $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers (Figures 5d) result in an oxide layer that is $184 \pm 6 \mu\text{m}$ thick (Figure 6c). In contrast, the hollow crystals (Figures 5f) lead to an oxide layer that is $262 \pm 10 \mu\text{m}$ thick (Figure 6e). The increase in oxide thickness observed by exposing the composite to 1250 °C for an additional 12 h can be explained by the tubular morphology of the hollow crystals, observed in Figure 5f. Such crystals provide additional pathways for oxygen diffusion into the AIN/BN substrate via tunnels through the crystal. Similar observations can also be made of boria-coated AIN samples. Referring to Figure 2, the oxide layers of coupons with hollow crystals (Figure 4f,g) appear to be thicker than those of coupons with capped whiskers and dimples (4b-e). The thickness of the oxide layer is obviously also a function of temperature and time, yet it is worth noting that the whisker morphology could also influence the transport of oxygen into the AIN-rich material. With this in mind, the oxidation protection witnessed via the growth of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ greatly depends on the whisker morphology.

Figure 6f suggests that the oxide layer developed after 48 h at 1350 °C is comparable to the same time at 1300 °C. The hollow crystals seen at 1300 °C create pathways that are still present at 1350 °C in the form of voids between coarsened $\text{Al}_{18}\text{B}_4\text{O}_{33}$ crystals. In contrast, Figure 6g demonstrates the full conversion of AlN/BN into porous Al_2O_3 , and no protection against oxidation is observed in the absence of $\text{Al}_{18}\text{B}_4\text{O}_{33}$.

3.3. Aluminum Borate Crystal Microstructures

When boria-coated AlN coupons and AlN/BN composites are exposed to high-temperature oxidative environments, liquid boria can form and react with oxidized AlN to produce $\text{Al}_{18}\text{B}_4\text{O}_{33}$ (Reaction 2). Referring to the Al_2O_3 - B_2O_3 phase diagram by Gielisee [28], the liquid oxide layer can contain dissolved aluminum borate and unreacted boria within the temperature range of 470 °C to 1035 °C. Once supersaturation is reached, $\text{Al}_{18}\text{B}_4\text{O}_{33}$ starts to crystallize out of the liquid oxide [32]. Based on SEM observations, nucleation and growth results in highly anisotropic whisker-like crystals.

Figure 7. a) Back-scattered electron image of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers, where green cross shows point analyzed in EBSD, white dotted line shows outline of analyzed whisker, white arrow shows direction of crystal growth. b) Proposed orientation of crystallographic axes of outlined whisker with corresponding pole figures from this analysis. Note that crystallographic information from Ihara et al. (1980) was used for indexing [21].

Electron backscatter diffraction was used to determine the direction of crystal growth. Figure 7a shows a back-scattered electron image of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers, taken from the sample seen in Figure 4c. The indexed EBSD patterns (provided in supplementary information) and corresponding pole figures (Figure 7b) were used to determine that the direction of growth of the analyzed crystal was perpendicular to the (001) plane. Previous studies on $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers have shown similar results, supporting that the direction of the anisotropic crystal growth of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ is $\langle 001 \rangle$ [32,33].

Figure 8. a) Super cell (3x3x6) of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ with black arrows showing direction of crystal growth along $\langle 001 \rangle$, b) view of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ along the (001) plane, showing channels through crystal, and c) close-up of exposed BO_3 units along the channels. Lattice parameters are defined as $a = 0.7692 \text{ nm}$, $b = 1.4973 \text{ nm}$, $c = 0.5682 \text{ nm}$ [21,34].

It is possible to link the acicular morphology of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ to the fundamental structure of the single crystal. Referring to Figure 8a, uninterrupted chains of strong bonds run parallel to the c-axis of $\text{Al}_{18}\text{B}_4\text{O}_{33}$, including structural chains of AlO_6 octahedra, chains of AlO_4 tetrahedra, and chains of alternating AlO_4 tetrahedra and planar BO_3 groups. According to Hartman et al.'s periodic bond chain (PBC) theory, crystal growth in the direction of such continuous chains is preferred [35,36]. The theory states that crystal faces that are parallel to two or more strong chains dominate the crystal habit, and can grow from the vapor through spiral growth from a dislocation, or through layer-by-layer growth [36,37].

There is a separate yet critical observation that can be made when looking at the crystal structure of $\text{Al}_{18}\text{B}_4\text{O}_{33}$. Across the (001) plane shown in Figure 8b, we see empty channels running along $\langle 001 \rangle$. Such channels directly expose planar BO_3 groups along the length of the crystal, seen in Figure 8b,c. This structure provides a pathway for high-temperature volatilization of trapped boria within the crystal structure, which can result in the breaking of PBC chains. The release of boria is considerable at temperatures over 1200°C , when the evaporation rate [3] of boria is sufficient to initiate the transformation of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ to porous Al_2O_3 , as seen in Figures 3 and 4. The structural change observed with the loss of boria is significant, affecting the crystal's composition and microstructure.

From our observations, the morphology of the $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers evolves with increased exposure to high-temperature environments. For example, whiskers grown on AlN/BN composites at 1250 °C after 48 h appeared to be capped by pyramid tips. In contrast, in AlN/BN composites oxidized at 1250 °C for 60 h, dimples craters and hollow cores begin to emerge in the crystals, as shown in Figure 5f.

The occurrence of dimples and hollow cores in $\text{Al}_{18}\text{B}_4\text{O}_{33}$ is not fully understood. One possible reason for these morphological features can be ascribed to Frank's theory of capillary equilibria [38], a theory that assumes spiral crystal growth. Frank argued that hollow cores can form in single crystals to minimize the strain energy from screw dislocations. With increased exposure to high temperatures, a balance is sought between the surface tension and the line tension of the dislocation, which can lead to the creation of a free surface along the dislocation line that produces a hollow core in the crystal [37]. The diameter of the hollow core can be directly related to the strain energy of the dislocation, being a function of the square of the Burgers vector [39]. In Figure 5f, we see that the core diameters can range from $\sim 0.5\ \mu\text{m}$ to $6\ \mu\text{m}$. Based on Frank's theory, this would imply that there is a wide discrepancy in dislocation strain energies from whisker to whisker. Thus, there may be other factors contributing to the development of such large cores.

A second possible cause could be the partial dissolution of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers, potentially from excess boria in the environment. Studies on zeolites [40] and quartz [41] have described how voids and etch pits can form from the dissolution of these crystals in strong bases and silica melts respectively. Interestingly, these studies suggest that dissolution is most likely to occur in areas along boundaries, and where defect sites are abundant. The hollow cavities in $\text{Al}_{18}\text{B}_4\text{O}_{33}$ might therefore arise from the dissolution of dislocations within its core (e.g., screw dislocations) or of energetically unstable phases located in the core, through excess boria, a liquid oxide known to dissolve alumina [28,32]. In order to establish this, future studies might explore how easily $\text{Al}_{18}\text{B}_4\text{O}_{33}$ crystals dissolve in liquid boria, and if screw dislocations are truly responsible for the acicular growth of $\text{Al}_{18}\text{B}_4\text{O}_{33}$.

A third potential reason for these features relates back to PBC theory. At high temperatures, the breaking of PBCs from the loss of boria could induce a roughening transition that transforms steps (along the edges and corners of the crystal) into kinks [35]. The rough edges from the kinks could act as preferred sites for layered growth along $\langle 001 \rangle$ [42], causing the crystal to protrude out on its edges and corners, as seen in Figure 5f. Consequently, this preferred growth along the edges and corners could account for the formation of hollow cores within $\text{Al}_{18}\text{B}_4\text{O}_{33}$ which, as previously outlined and shown in Figure 6d-f, provide additional, yet undesirable, pathways for oxygen diffusion [37]. Though beyond the scope of the current work, these three hypotheses point to future experiments.

4. Summary and Implications

The oxidation kinetics of AlN were compared to that of boria-coated AlN, where it was shown that the inclusion of liquid boria resulted in the growth of thinner oxide layers containing $\text{Al}_{18}\text{B}_4\text{O}_{33}$. Based upon SEM-EDS and XRD results, the boria film protected the AlN substrate from oxidation by 1) acting as a barrier to oxygen diffusion and 2) reacting with freshly oxidized AlN to form $\text{Al}_{18}\text{B}_4\text{O}_{33}$ crystals, actively trapping boria into the oxide layer as it is incorporated within the $\text{Al}_{18}\text{B}_4\text{O}_{33}$ crystal structure. The porous oxide layer of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ has a CTE similar to that of AlN and AlN/BN [7,23]. This offers a more compatible oxide layer for AlN ceramics than Al_2O_3 , where thermal mismatch cracks are widely observed in the latter [23]. The $\text{Al}_{18}\text{B}_4\text{O}_{33}$ layer eventually transforms to Al_2O_3 with prolonged exposure to high-temperature environments, behaving as a transitional oxide layer that slows down the rate at

which AlN oxidizes to Al_2O_3 . Similar observations were revealed in AlN/BN composite structures, indicating that the inclusion of BN in the composite results in a similar oxidation retardance in high-temperature, dry air environments.

$\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers display a variety of morphological features, with some crystals exhibiting dimples or hollow cores after prolonged exposure to high-temperature environments. This change in morphology is still not fully understood. Nevertheless, potential reasons were offered, including dislocation strain energy, dissolution, and promoted growth along the edges and corners. It was further shown that the crystal morphological features could greatly affect the oxidation protection of the composite, with hollow cores providing pathways for oxygen diffusion that could be damaging to the non-oxide. This, coupled with the transformation of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ to Al_2O_3 , indicates that the oxidation protection witnessed from the $\text{Al}_{18}\text{B}_4\text{O}_{33}$ layer is temporary, and depends on the duration and temperature of the exposure.

Overall, the role of boria on the oxidation kinetics of AlN was revealed in detail, with helpful new insights into $\text{Al}_{18}\text{B}_4\text{O}_{33}$ growth and how the crystal morphological features can affect the oxidation protection of AlN/BN composites.

5. Acknowledgments

The authors would like to acknowledge the support from NASA's Jet Propulsion Laboratory through a Research and Technology Development Grant, and for C. S. Chari, the Amelia Earhart Fellowship from Zonta International. SEM work was performed in the Division of Geology and Planetary Science Analytical Facility at Caltech. The authors would like to thank Prof. George R. Rossman and Mark Garcia for their help in accessing and photographing minerals from the Mineral Room Collection of the Division of Geology and Planetary Science Analytical Facility at Caltech, and Dr. Bryan W. McEnerney (Materials Engineering, Test & Evaluation, NASA JPL) for his encouragement and enthusiasm about the project.

6. References

- [1] B.W. Sheldon, E.Y. Sun, S.R. Nutt, J.J. Brennan, Oxidation of BN-Coated SiC Fibers in Ceramic Matrix Composites, *Journal of the American Ceramic Society*. 79 (1996) 539–543. <https://doi.org/10.1111/j.1151-2916.1996.tb08163.x>.
- [2] E.J. Opila, R.C. Robinson, M.J. Verrilli, Borosilicate Glass-Induced Fiber Degradation of SiC/BN/SiC Composites Exposed in Combustion Environments, *Int. J. Appl. Ceram. Technol.* 13 (2016) 434–442. <https://doi.org/10.1111/ijac.12499>.
- [3] H. Hatta, T. Sohtome, Y. Sawada, A. Shida, High temperature crack sealant based on SiO₂-B₂O₃ for SiC coating on carbon–carbon composites, *Advanced Composite Materials*. 12 (2003) 93–106. <https://doi.org/10.1163/156855103772658498>.
- [4] A. Napolitano, P.B. Macedo, E.G. Hawkins, Viscosity and Density of Boron Trioxide, *J American Ceramic Society*. 48 (1965) 613–616. <https://doi.org/10.1111/j.1151-2916.1965.tb14690.x>.
- [5] E. Pérez-Enciso, M.A. Ramos, S. Vieira, Low-temperature specific heat of different B₂O₃ glasses, *Phys. Rev. B*. 56 (1997) 32–35. <https://doi.org/10.1103/PhysRevB.56.32>.
- [6] J. Schlichting, Oxygen transport through glass layers formed by a gel process, *Journal of Non-Crystalline Solids*. 63 (1984) 173–181. [https://doi.org/10.1016/0022-3093\(84\)90396-X](https://doi.org/10.1016/0022-3093(84)90396-X).
- [7] S.P. Ray, Preparation and Characterization of Aluminum Borate, *J American Ceramic Society*. 75 (1992) 2605–2609. <https://doi.org/10.1111/j.1151-2916.1992.tb05622.x>.
- [8] D. Goeuriot-Launay, G. Brayet, F. Thevenot, Boron nitride effect on the thermal shock resistance of an alumina-based ceramic composite, *J Mater Sci Lett*. 5 (1986) 940–942. <https://doi.org/10.1007/BF01729282>.
- [9] Y. Li, G. Qiao, Z. Jin, Machinable Al₂O₃/BN composite ceramics with strong mechanical properties, *Materials Research Bulletin*. 37 (2002) 1401–1409. [https://doi.org/10.1016/S0025-5408\(02\)00786-9](https://doi.org/10.1016/S0025-5408(02)00786-9).
- [10] A. Abreal, D. Goeuriot, F. Thevenot, M. Lagace, B. Gueroult, M. Rigaud, Effect of Y₂O₃ addition on alumina-hex boron nitride composites, *Journal of the European Ceramic Society*. 15 (1995) 841–849. [https://doi.org/10.1016/0955-2219\(95\)00056-Z](https://doi.org/10.1016/0955-2219(95)00056-Z).
- [11] Shimpo A., Ueki M., Naka M., Mechanical Properties of AlON-Based Composite Ceramics at High Temperature. (Part 1). Effect of Oxidation on Mechanical Properties of AlON-BN Composite Ceramics., *Nippon Seramikkusu Kyokai gakujutsu ronbunshi*. 109 (2001) 127–131. https://doi.org/10.2109/jcersj.109.1266_127.
- [12] H. Yamashita, A. Yamaguchi, Oxidation of Aluminum Oxynitride-Boron Nitride (AlON-BN) Composite Prepared by Reaction Sintering., *Journal of the Ceramic Society of Japan*. 109 (2001) 94–99. https://doi.org/10.2109/jcersj.109.1266_94.
- [13] S. Kurita, Z.-Q. Zeng, H. Takebe, K. Morinaga, Reaction and Phase Relations in the AlN-B₂O₃ System, *Materials Transactions, JIM*. 35 (1994) 258–261. <https://doi.org/10.2320/matertrans1989.35.258>.
- [14] D. Mattia, M. Desmaison-Brut, S. Dimovski, Y. Gogotsi, J. Desmaison, Oxidation behaviour of an aluminium nitride–hafnium diboride ceramic composite, *Journal of the European Ceramic Society*. 25 (2005) 1789–1796. <https://doi.org/10.1016/j.jeurceramsoc.2004.12.011>.
- [15] S.V. Schneider, M. Desmaison-Brut, Yu.G. Gogotsi, J. Desmaison, Oxidation Behaviour of a Hot Isostatically Pressed TiB₂-AlN Composite, *KEM*. 113 (1995) 49–58. <https://doi.org/10.4028/www.scientific.net/KEM.113.49>.
- [16] K. Suganuma, T. Fujita, N. Suzuki, K. Niihara, Aluminium composites reinforced with a new aluminium borate whisker, *J Mater Sci Lett*. 9 (1990) 633–635. <https://doi.org/10.1007/BF00721787>.
- [17] K. Suganuma, T. Fujita, G. Sasaki, N. Suzuki, Evaluation of strength and heat-resistance for aluminum-borate whisker reinforced AC8A aluminum alloy composite., (1991) 270–275. <https://doi.org/10.2464/JILM.41.270>.

- [18] H.K. Lee, S. Zerbetto, P. Colombo, C.G. Pantano, Glass–ceramics and composites containing aluminum borate whiskers, *Ceramics International*. 36 (2010) 1589–1596. <https://doi.org/10.1016/j.ceramint.2010.02.039>.
- [19] G.N. Morscher, D.R. Bryant, R.E. Tressler, Environmental Durability of BN-Based Interphases (for $\text{SiC}_f/\text{SiC}_m$ Composites) in H_2O Containing Atmospheres at Intermediate Temperatures, in: *Proceedings of the 21st Annual Conference on Composites, Advanced Ceramics, Materials, and Structures—A: Ceramic Engineering and Science Proceedings*, John Wiley & Sons, Ltd, 1997: pp. 525–534. <https://doi.org/10.1002/9780470294437.ch58>.
- [20] N. Jacobson, S. Farmer, A. Moore, H. Sayir, High-Temperature Oxidation of Boron Nitride: I, Monolithic Boron Nitride, *Journal of the American Ceramic Society*. 82 (2004) 393–398. <https://doi.org/10.1111/j.1551-2916.1999.tb20075.x>.
- [21] M. Ihara, K. Imai, K. Fukunaga, N. Yoshida, Crystal structure of boroaluminate, $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$, *Journal of the Ceramic Association, Japan*. 88 (1980) 77–84.
- [22] A. Bellosi, E. Landi, A. Tampieri, Oxidation behavior of aluminum nitride, *J. Mater. Res.* 8 (1993) 565–572. <https://doi.org/10.1557/JMR.1993.0565>.
- [23] H.-E. Kim, A. J. Moorhead, Oxidation Behavior and Flexural Strength of Aluminum Nitride Exposed to Air at Elevated Temperatures, *J American Ceramic Society*. 77 (1994) 1037–1041. <https://doi.org/10.1111/j.1151-2916.1994.tb07264.x>.
- [24] J.W. Lee, I. Radu, M. Alexe, Oxidation behavior of AlN substrate at low temperature, *Journal of Materials Science: Materials in Electronics*. 13 (2002) 131–137. <https://doi.org/10.1023/A:1014377132233>.
- [25] A. Maghsoudipour, F. Moztarzadeh, M. Saremi, J.G. Heinrich, Oxidation behavior of AlN– Al_2O_3 composites, *Ceramics International*. 30 (2004) 773–783. <https://doi.org/10.1016/j.ceramint.2003.10.004>.
- [26] C.-T. Yeh, W.-H. Tuan, Oxidation mechanism of aluminum nitride revisited, *J Adv Ceram.* 6 (2017) 27–32. <https://doi.org/10.1007/s40145-016-0213-1>.
- [27] D. Suryanarayana, Oxidation Kinetics of Aluminum Nitride, *J American Ceramic Society*. 73 (1990) 1108–1110. <https://doi.org/10.1111/j.1151-2916.1990.tb05167.x>.
- [28] P.J.M. Gielisse, W.R. Foster, The System $\text{Al}_2\text{O}_3\text{--B}_2\text{O}_3$, *Nature*. 195 (1962) 69–70. <https://doi.org/10.1038/195069a0>.
- [29] M. Coëffe-Desvaux, T. Tabarès-Medina, N. Pradeilles, P. Marchet, M. Joinet, A. Maitre, New Insight on the Effect of Yttria-Based Secondary Phases on Sintering and Electrical Behavior of Aluminum Nitride Ceramics, *J. of Materi Eng and Perform.* (2022). <https://doi.org/10.1007/s11665-022-06588-9>.
- [30] D. Huang, Z. Tian, W. Cui, L. Gao, Z. Liu, X. Diao, G. Liu, Effects of Y_2O_3 and yttrium aluminates as sintering additives on the thermal conductivity of AlN ceramic substrates, *Ceramics International*. 44 (2018) 20556–20559. <https://doi.org/10.1016/j.ceramint.2018.07.178>.
- [31] B.D. Cullity, *Elements of X-ray Diffraction*, Addison-Wesley Publishing Company, 1956.
- [32] Y. Li, R.P.H. Chang, Synthesis and characterization of aluminum borate ($\text{Al}_{18}\text{B}_4\text{O}_{33}$, $\text{Al}_4\text{B}_2\text{O}_9$) nanowires and nanotubes, *Materials Chemistry and Physics*. 97 (2006) 23–30. <https://doi.org/10.1016/j.matchemphys.2005.06.023>.
- [33] C. Cheng, C. Tang, X.X. Ding, X.T. Huang, Z.X. Huang, S.R. Qi, L. Hu, Y.X. Li, Catalytic synthesis of aluminum borate nanowires, *Chemical Physics Letters*. 373 (2003) 626–629. [https://doi.org/10.1016/S0009-2614\(03\)00672-9](https://doi.org/10.1016/S0009-2614(03)00672-9).
- [34] K. Momma, F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Crystallogr.* 44 (2011) 1272–1276. <https://doi.org/10.1107/S0021889811038970>.
- [35] P. Hartman, W.G. Perdok, On the relations between structure and morphology of crystals. I, *Acta Cryst.* 8 (1955) 49–52. <https://doi.org/10.1107/S0365110X55000121>.
- [36] P. Hartman, W.G. Perdok, On the relations between structure and morphology of crystals. II, *Acta Cryst.* 8 (1955) 521–524. <https://doi.org/10.1107/S0365110X55001679>.

- [37] I. Sunagawa, Crystals: Growth, Morphology, & Perfection, Cambridge University Press, 2007.
<https://doi.org/10.1017/CBO9780511610349>.
- [38] F.C. Frank, Capillary equilibria of dislocated crystals, *Acta Cryst.* 4 (1951) 497–501.
<https://doi.org/10.1107/S0365110X51001690>.
- [39] K. Maiwa, M. Plomp, AFM observation of barium nitrate (111), and (100), faces: spiral growth and two-dimensional nucleation growth, *Journal of Crystal Growth.* (1998) 214–223.
[https://doi.org/10.1016/S0022-0248\(97\)00446-6](https://doi.org/10.1016/S0022-0248(97)00446-6).
- [40] Y. Wang, M. Lin, A. Tuel, Hollow TS-1 crystals formed via a dissolution–recrystallization process, *Microporous and Mesoporous Materials.* 102 (2007) 80–85.
<https://doi.org/10.1016/j.micromeso.2006.12.019>.
- [41] S.L. Brantley, S.R. Crane, D.A. Crerar, R. Hellmann, R. Stallard, Dissolution at dislocation etch pits in quartz, *Geochimica et Cosmochimica Acta.* 50 (1986) 2349–2361. [https://doi.org/10.1016/0016-7037\(86\)90087-6](https://doi.org/10.1016/0016-7037(86)90087-6).
- [42] W.F. Berg, Crystal growth from solutions, *Proc. Roy. Soc. (London).* A164 (1938) 79–95.
<https://doi.org/10.1098/rspa.1938.0006>.

Declaration of Competing Interest

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests

Highlights

- Oxidation kinetics of AlN were compared to B₂O₃-coated AlN and AlN/BN composites.
- Presence of B₂O₃ in AlN led to Al₁₈B₄O₃₃ surface layers that retarded Al₂O₃ growth.
- Protective layers of Al₁₈B₄O₃₃ compared to Al₂O₃ are thermally compatible with AlN.
- Evolution of hollow cores in Al₁₈B₄O₃₃ limit its use for AlN oxidation protection.