

EFFECT OF h-BN AS AN ADDITIVE ON PHYSICAL AND MECHANICAL PROPERTIES OF Al_2TiO_5 COMPOSITE

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Abstract

Aluminum titanate (Al_2TiO_5) is a promising material for high-temperature applications due to its low thermal expansion, high melting point, and excellent corrosion resistance. In this study, the effect of h-BN addition on the properties of Al_2TiO_5 composites was investigated. The composites were prepared by sintering a mixture of Al_2O_3 and TiO_2 at a 1:1 molar ratio, with varying amounts of h-BN (5-20 mol%) added to the mixture. The samples were sintered at 1,500°C for 4 h in N_2 atmosphere, and the bulk density, porosity, phase transition, microstructure, flexural strength, and hardness of the composites were investigated. XRD analysis confirmed the presence of Al_2TiO_5 , Al_2O_3 , and $\text{Al}_{18}\text{B}_4\text{O}_{33}$ phases in the composites. The addition of h-BN in increasing amounts from 5 to 20 mol% resulted in a gradual improvement in the bulk density, flexural strength, and hardness of the Al_2TiO_5 composites. The composite with the highest h-BN content (20 mol%) exhibited a bulk density of 3.12 g/cm³, as well as the highest flexural strength and hardness values of 123.6±8.9 MPa and 11.2±4.1 GPa, respectively.

Keywords: Aluminum titanate; reaction sintering; XRD; mechanical properties; composite

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Introduction

Aluminum titanate (Al_2TiO_5) is a ceramic material that has attracted considerable interest due to its remarkable thermal properties, including a high melting point of $1,860^\circ\text{C}$, a low coefficient of thermal expansion of $\sim 1.5 \times 10^{-6} \text{ K}^{-1}$, and high corrosion resistance (Skala *et al.*, 2009; Bueno and Baudín, 2021). These characteristics make Al_2TiO_5 a highly promising material for employment in high-temperature applications such as diesel particulate filters (DPF), furnace linings, and crucibles (Hongzhi *et al.*, 2012; Wang *et al.*, 2018). Although Al_2TiO_5 has excellent thermal and chemical properties, its usage in certain applications is limited due to some drawbacks. One of the main concerns is its pseudo-brookite crystal structure that causes anisotropic expansion and leads to severe microcracking, resulting in poor mechanical properties (Skala *et al.*, 2009). Another issue is that Al_2TiO_5 undergoes eutectoid decomposition to become Al_2O_3 and TiO_2 at temperatures between 750 and $1,300^\circ\text{C}$, leading to the instability of the material (Kim and Gauckler, 2012). Therefore, further improvements are required to enhance the strength and stability of Al_2TiO_5 to make it applicable in a wide range of applications.

To overcome these issues, several studies have been conducted, including the addition of various dopants, combinations of various compounds, and using different processing methods. Previous studies have reported that adding oxides such as MgO , Fe_2O_3 , SiO_2 , and ZrO_2 (Jiang *et al.*, 2011; Perera *et al.*, 2011; Chen *et al.*, 2021) as well as compounds such as spodumene (LiAlSiO_4), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), and feldspar (Zhao *et al.*, 2013; Li, *et al.*, 2018), to Al_2TiO_5 has resulted in improved mechanical strength and thermal stability. Perera *et al.* (2011)

and Jiang *et al.* (2011) have reported that the incorporation of additives such as MgO , Fe_2O_3 , SiO_2 , and their combinations with Al_2TiO_5 ceramics have been found to increase the density and decrease the porosity which therefore enhanced the mechanical properties of Al_2TiO_5 ceramics.

According to the literature review, most research has focused on the effects of oxide additives on the properties of Al_2TiO_5 , however, there is limited investigation on the potential benefits of incorporating nitride compounds like hexagonal boron nitride (h-BN). Nitride compounds are known to possess exceptional strength and thermal conductivity, making them attractive as additives to improve the mechanical properties of Al_2TiO_5 ceramics. One potential benefit of incorporating h-BN into Al_2TiO_5 ceramics is the improvement of their mechanical strength, which is a major concern for the commercialization of Al_2TiO_5 ceramics in various applications. So, the objective of this study is to produce Al_2TiO_5 ceramic composites through reaction sintering at $1,500^\circ\text{C}$ for 4 h, using Al_2O_3 and TiO_2 as the primary precursors in a 1:1 molar ratio. The effects of h-BN addition content on the phase composition, physical properties, microstructure, and mechanical properties were investigated.

Methods

Figure 1 illustrates the schematic diagram of process used to prepare the Al_2TiO_5 composites. To synthesize the Al_2TiO_5 composites, a molar ratio of 1:1 of Al_2O_3 (99% purity, particle size of $1 \mu\text{m}$, Nippon Light Metal Co., Ltd., Japan) and TiO_2 (95.5% purity, particle size of $1\text{--}2 \mu\text{m}$, Alfa-Aesar

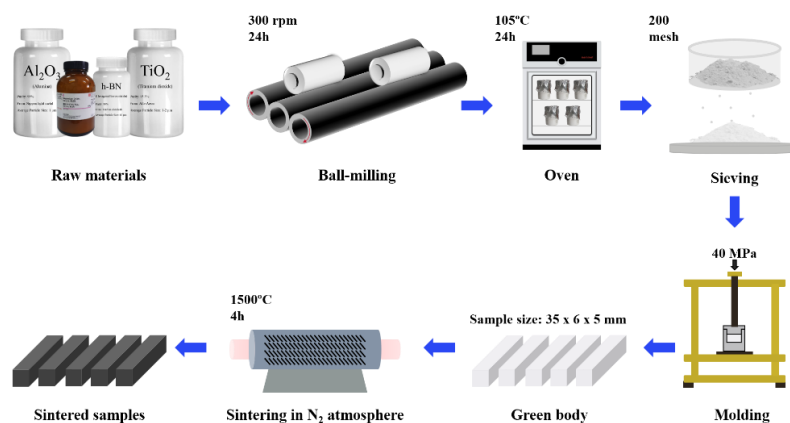


Figure 1. Schematic diagram of process used to prepare the Al_2TiO_5 composites

Co., Ltd., USA) powders were used. Additionally, 1 mol% of MgO (99.9% purity, 0.2 μm , Fujifilm Wako Chemical Co., Ltd., Japan) was employed as a sintering additive. To prepare AT/h-BN composites, h-BN (99% purity, 10 μm , TanYun Chemicals Co., Ltd., China) was mixed into the starting materials at varying content of 5, 10, 15, and 20 mol%. The mixed powder was ball-milled for 24 h in a polypropylene bottle using ZrO_2 balls and ethanol as the grinding medium. After mixing, the powders were dried in an oven at 105°C for 24 h and then sieved through a 200-mesh sieve. The mixed powders were uniaxially pressed at 40 MPa into rectangular green bodies with dimensions of 35 mm $\times$ 6 mm $\times$ 5 mm. Finally, the green bodies were embedded in h-BN powder and sintered in a N_2 atmosphere at 1,500°C for 4 h with a heating and cooling rate of 5°C/min. In this study, the two types of samples are distinguished as pure Al_2TiO_5 and h-BN-added Al_2TiO_5 , denoted as AT and ATBN, respectively. The numerical values following the ATBN designation indicate the percentage of h-BN content in mol%. For example, the ATBN sample with 5 mol% h-BN is identified as ATBN5. The photograph of samples after sintering is shown in Figure 2. The average weights of each sample are 2.42 g, 2.42 g, 2.40 g, 2.36 g, and 2.32 g for AT, ATBN5, ATBN10, ATBN15, and ATBN20, respectively.

The physical properties of the sintered samples, including bulk density, and porosity were determined using the Archimedes method. The phase composition was analyzed using an X-ray diffractometer (XRD; Miniflex 600, Rigaku, Japan) with $\text{CuK}\alpha$ radiation at 40 kV and 15 mA in the scanning range of 10-90 degrees and a scanning rate of 0.02°/min. The microstructure of the polished surface of the sample was observed using a scanning electron microscope (SEM; EVO®MA10, Zeiss, Germany). The flexural strength of the samples was

measured using the three-point bending method with the universal testing machine (Instron 8872, US) with a support span length (L) of 20 mm and a constant loading rate of 1.0 mm/min. The flexural strength (σ) was calculated using Equation (1):

$$\sigma = \frac{3FL}{2bh^2} \quad (1)$$

where F is the breaking load, L is the distance between two support pins, b is the width of the sample, and h is the thickness of the sample. The hardness of the samples was determined using the Vickers indentation tester (HVM-2T, Shimadzu, Japan) with a 1 kg load applied for 10 s on the polished sample, and the Vickers hardness (HV) was calculated using Equation (2):

$$\text{HV} = 1.854 \left(\frac{P}{d^2} \right) \quad (2)$$

where P is the applied load and d is the average diagonal length.

Results and Discussion

The X-ray diffraction (XRD) patterns of sintered AT and ATBN composites with different amounts of h-BN are shown in Figure 3. The XRD analysis of all samples revealed the presence of aluminum borate ($\text{Al}_{18}\text{B}_4\text{O}_{33}$; PDF 00-032-0003; space group *Amam*(63), orthorhombic structure), Al_2TiO_5 (PDF 01-070-1435; space group *Bbmm*(63), orthorhombic structure), and Al_2O_3 (PDF 01-076-7774; space group *R-3c*(167), trigonal structure). However, no significant peaks corresponding to h-BN were detected at 26° (Matović *et al.*, 2016). Moreover, with an increase in the amount of h-BN, the peak intensity of both $\text{Al}_{18}\text{B}_4\text{O}_{33}$ and Al_2O_3 phases was found to increase, while the peak intensity of

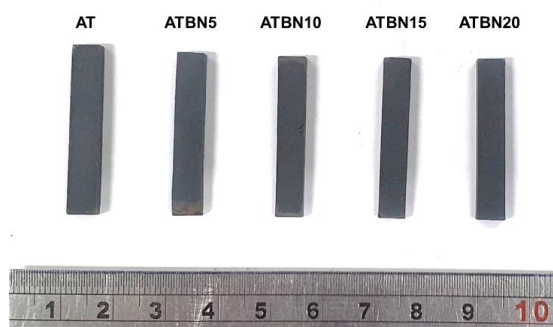


Figure 2. Photograph of AT and ATBN specimens after sintering

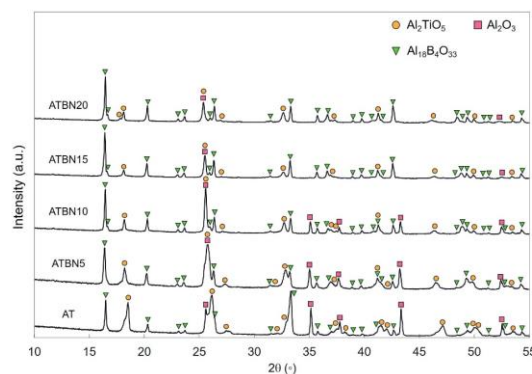


Figure 3. The XRD patterns of sintered AT and ATBN composites

Al_2TiO_5 decreased. The formation of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ typically involves the reaction of Al_2O_3 and B_2O_3 at high temperatures in a solid-state reaction. It is possible that during the initial reaction, the reduction of TiO_2 resulted in the release of oxygen (Sperisen and Mocellin, 1992), which could have reacted with h-BN and oxidized it to form B_2O_3 (Kostoglou *et al.*, 2015). Due to the consumption of TiO_2 during the initial step, the reaction between TiO_2 and Al_2O_3 was retarded, leading to a reduction in the formation of Al_2TiO_5 . As a result, there was an increase in the formation of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ and a corresponding decrease in the formation of Al_2TiO_5 , which was observed in the final composite. It is noticed that $\text{Al}_{18}\text{B}_4\text{O}_{33}$ was also formed in the AT specimen, despite the initial powder did not contain h-BN. This phenomenon could be explained by the possibility that the starting powder reacted with h-BN, which was used as the embedded powder. $\text{Al}_{18}\text{B}_4\text{O}_{33}$ is a compound with complex crystal structure and unique properties, such as high hardness, high melting point, and excellent thermal stability. These properties therefore significantly affect the properties of Al_2TiO_5 composites. The XRD analysis also revealed a shift of the peak position of Al_2TiO_5 towards the lower angle, which could indicate a possible solid solution in the lattice structure. The formation of a solid solution in the composite could potentially lead to improved mechanical properties due to the altered crystal structure and resulting microstructure. However, additional analyses are needed to verify the presence of a solid solution and its potential impact on the properties of the composite.

Figure 4 depicts the relationship between the bulk density and porosity of composites with h-BN addition. As the h-BN addition amount increased

from 0 to 20 mol%, the bulk density gradually increased. The composites without h-BN (AT sample) exhibited the lowest bulk density of 2.70 g/cm^3 , whereas the composites with 20 mol% h-BN (ATBN20) demonstrated the highest bulk density of 3.12 g/cm^3 . Conversely, the porosity of the composite exhibited an inverse trend with bulk density. The AT sample exhibited the highest porosity of 25.98%, while increasing the h-BN amount led to a decrease in porosity of the ATBN composite. The lowest porosity value of 2.75% was observed for the ATBN20 composite. In this study, the addition of h-BN and the subsequent reaction sintering likely played a significant role in promoting the densification of the composites. As the h-BN content increased, it reacted with the other starting materials, which promoted the formation of solid phases $\text{Al}_{18}\text{B}_4\text{O}_{33}$ and Al_2TiO_5 and released heat (Hernández *et al.*, 2017; Bueno and Baudín, 2021). The heat generated by the exothermic

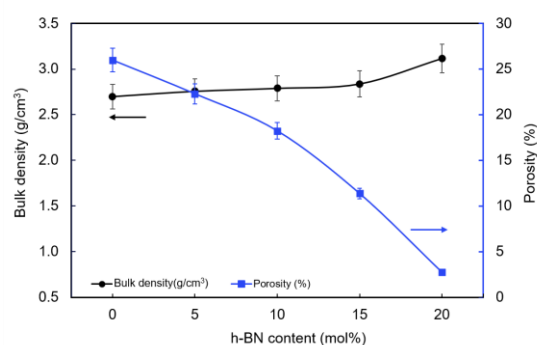


Figure 4. The relationship between the bulk density and porosity of composites with h-BN addition

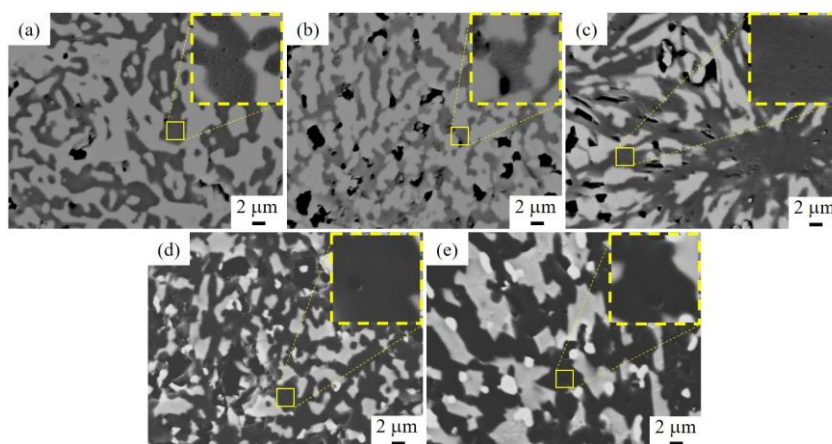


Figure 5. BSE-SEM images of polished surface of (a) AT, (b) ATBN5, (c) ATBN10, (d) ATBN15, and (e) ATBN20. The inset image in each figure represents a high magnification of a rectangular area

reactions then caused the particles to consolidate and densify, thus contributing to the densification of the composites. In addition, the densification of the composites can also be attributed to the elimination of pores and defects during reaction sintering. This mechanism of densification through reaction sintering could further improve the strength and hardness of the composites.

The polished surface of AT and ATBN composites was observed using backscattered electron scanning electron microscopy (BSE-SEM) as presented in Figure 5. The SEM images showed the presence of both dark and bright phases that were homogeneously distributed throughout composites. However, further investigation is required to accurately identify and verify the composition of each phase. It can be observed that the addition of h-BN to the composite led to a reduction in the number of large pores which is consistent with the porosity results discussed earlier. Furthermore, when observed a high magnification image at the dark area (inset image), the number of small pores also decreased significantly. This suggests that the addition of h-BN to the composite not only reduced number of large pores but also resulted in the elimination of small pores within the microstructure. The elimination of pores and defects during reaction sintering can further contribute to the improved mechanical properties of the composite.

Figure 6 displays the effect of h-BN content on the flexural strength of AT and ATBN composites. The results indicate that the flexural strength of the composite significantly increased as the amount of h-BN was increased. The flexural strength of AT composites was 13.7 ± 4.0 MPa, while the highest flexural strength of 123.6 ± 8.9 MPa was achieved by ATBN20. Similarly, Figure 7 illustrates the effect of h-BN content on the Vickers hardness of the composites. The results demonstrate an increase in

Vickers hardness from 5.6 ± 1.9 GPa to 11.2 ± 4.1 GPa as the h-BN content was increased from 0% to 20%. These results are consistent with physical properties examination, which showed increased bulk density and decreased porosity as the amount of h-BN was increased. This improvement in mechanical properties can be attributed to the densification of the composites as a result of the reaction sintering process, which reduced the amount of porosity. The present study demonstrated that the incorporation of h-BN in the AT composites led to the formation of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ and an enhanced reaction sintering process, resulting in significant improvements in the mechanical properties of the composites. The increased density, decreased porosity, and homogeneous microstructure also played a significant role in achieving the high strength Al_2TiO_5 composites. These properties make it useful in a variety of applications, such as in the production of refractory materials and structural ceramics component. It has been noted in previous studies that an excessive content of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ has the potential to restrict the flexural strength (Hernández *et al.*, 2017). Therefore, further research is required to better understand the appropriate amount of h-BN addition for enhancing the performance of ATBN composite.

Conclusions

In this study, Al_2TiO_5 composites were synthesized by sintering a mixture of Al_2O_3 , TiO_2 , and h-BN at $1,500^\circ\text{C}$ for 4 h in a nitrogen atmosphere. The effects of different amounts (5-20 mol%) of h-BN on the phase formation, physical properties, microstructure, and mechanical properties of Al_2TiO_5 composites were investigated. The results indicated that the formation of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ and the subsequent reaction sintering process were

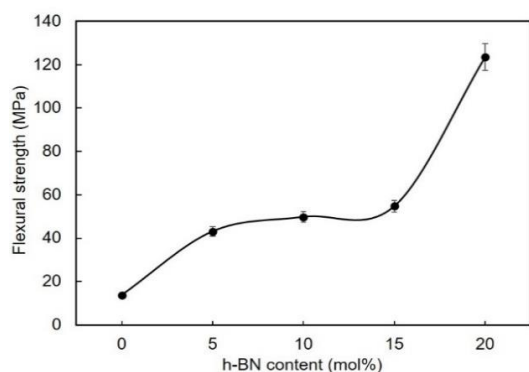


Figure 6. The effect of h-BN content on the flexural strength of Al_2TiO_5 composites

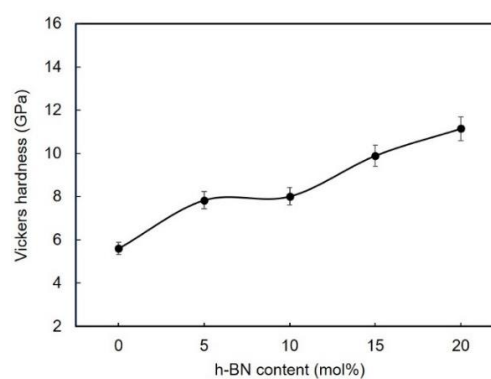


Figure 7. The effect of h-BN content on the Vickers hardness of Al_2TiO_5 composites

responsible for the increased density, reduced porosity, and improved microstructure of the composites. The increase in h-BN amount led to an increase in bulk density, flexural strength, and Vickers hardness. The composite with the 20 mol% h-BN addition (ATBN20) exhibited the best results in terms of density, flexural strength, and Vickers hardness, with values of 3.12 g/cm³, 123.6±8.9 MPa, and 11.2±4.1 GPa, respectively.

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