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Sintering and mechanical properties of titanium diboride with aluminum nitride as a sintering aid

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Abstract

Titanium diboride (TiB_2) was hot-pressed at 1800 °C with aluminum nitride (AlN) as a sintering aid. The presence AlN had a strong influence on the sinterability and mechanical properties of the TiB_2. When a small amount ($\leqslant$5 wt.%) of AlN was added to the TiB_2 the titania (TiO_2) present on the surface of the TiB_2 powder was eliminated by a reaction with AlN to form TiN and Al_2O_3. The elimination of TiO_2 markedly improved the sinterability and consequently the mechanical properties of TiB_2. However, when too much AlN was added ($\geqslant$10 wt.%), the sinterability and the mechanical properties decreased, apparently due to the remaining unreacted AlN.

Keywords: AlN; Hot pressing; Mechanical properties; Sintering; TiB_2

1. Introduction

Titanium diboride has attracted much attention for various applications as cutting tools, armor material and wear-resistant materials due to its excellent mechanical properties, such as high hardness, elastic modulus, and abrasion resistance.[1,2] Additionally, in contrast to most other ceramics, this material can be machined using the electrical-discharge-machining (EDM) method as it has high electrical conductivity.[3] This high electrical conductivity, coupled with its excellent corrosion resistance to molten metals, allows this ceramic to be used as a cathode material in aluminum refining furnaces.[4]

The applications of TiB_2 are presently limited mainly due to its low sinterability and poor mechanical properties, such as flexural strength and fracture toughness. The diffusion coefficient of TiB_2 is very low and accordingly the mass transport for densification is quite restricted. Therefore, an extremely high temperature ($\geqslant$2000 °C) is required for densification of TiB_2. However, high sintering temperature induces excessive grain growth, and resultant microcracks, that are detrimental to the mechanical properties.[5–8] To improve TiB_2 sinterability, transition metals such as iron, nickel, and cobalt have been used as sintering aids.[6–9] However, the presence of metallic phases at the grain boundaries after sintering are not desirable for hard and stiff ceramics. Many attempts have been made to improve the mechanical properties and sinterability of TiB_2 by adding non-metallic secondary phases. When a small amount of carbon (C) was added, the sinterability significantly improved by elimination of the oxide layer that originally existed on the powder's surface.[10] Silicon nitride (Si_3N_4) and silicon carbide (SiC) were more effective in improving the sinterability of TiB_2 as they not only eliminated the oxide layer but also formed an amorphous SiO_2 phase during sintering.[11,12]

It is of interest to observe the densification behavior of TiB_2 when other non-oxide ceramics were used as a sintering aid. In the present study, we investigated the effect of aluminum nitride (AlN) as a sintering aid on the microstructural evolution and mechanical properties of TiB_2. Specimens were prepared by adding up to 20 wt.% of AlN to TiB_2 powder and hot-pressing this mixture at 1800 °C for 1 h. The microstructural and compositional changes were measured with reference to the varying amount of AlN. Mechanical properties such as flexural strength, fracture toughness, Vickers hardness, and elastic modulus were measured and correlated to the specimens' microstructure and composition.

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2. Experimental procedure

Commercially available TiB_2 powder (Grade F, H.C. Starck GmbH and Co., Goslar, Germany) was used as the starting material. The powder had an average particle size ($D_{v,0.5}$) of 2.14 μm after sedimentation in acetone. As a sintering aid, AlN powder (Grade C, H.C. Starck Co., Berlin, Germany) was added in various amounts up to 20 wt.%. The powders were mixed by wet ball-milling for 5 h in a polyethylene bottle using Si_3N_4 balls and acetone as the grinding media. After mixing the slurry was dried in a rotary evaporator and passed through a 60-mesh screen. The powder mixtures were hot-pressed at a temperature of 1800 °C for 1 h under an applied pressure of 30 MPa in a flowing argon atmosphere.

The hot-pressed specimen's microstructure was observed using a scanning electron microscope (SEM; JSM-6330F, Jeol, Tokyo, Japan) after its polished surface was chemically etched with a dilute solution of hydrochloric and hydronitric acids ($HCl–HNO_3$). The specimen's relative density was determined using an image analysis method. This was done to avoid the difficulty of estimating the theoretical density of bodies that contained significant amounts of secondary phases. The grain-boundary phases were identified using an X-ray diffractometer (XRD; M18XHF-SRA, Mac Science Co., Yokohama, Japan) and a transmission electron microscope (TEM; CM 20, Philips Research Laboratories, Eindhoven, The Netherlands).

Specimens for mechanical testing were cut from the hot-pressed disks and machined into rectangular bar shapes of 3×4×40 mm. Each specimen was ground with a diamond wheel and polished with diamond slurries to a 1 μm finish. The specimens' edges were chamfered to minimize stress concentration effects from machining flaws. Strength was measured in a four-point bending configuration using a crosshead speed of 0.5 mm/min, an inner span of 10 mm and an outer span of 30 mm. The fracture toughness was measured via the direct indentation method by using a Vickers indenter, with an applied load of 98 N for 15 s. Fracture toughness was calculated using the equation of Anstis et al.[13] Vickers hardness was measured using a load of 2.94 N for 15 s and the elastic modulus was measured by the ultrasonic pulse-echo method with a two-channel digital real-time oscilloscope (Model TDS 220, Tektronix Beaverton, OR, USA). A minimum of five specimens were tested for each experimental condition.

3. Results and discussion

Addition of AlN markedly improved the sinterability of TiB_2. The specimen's SEM micrographs for different

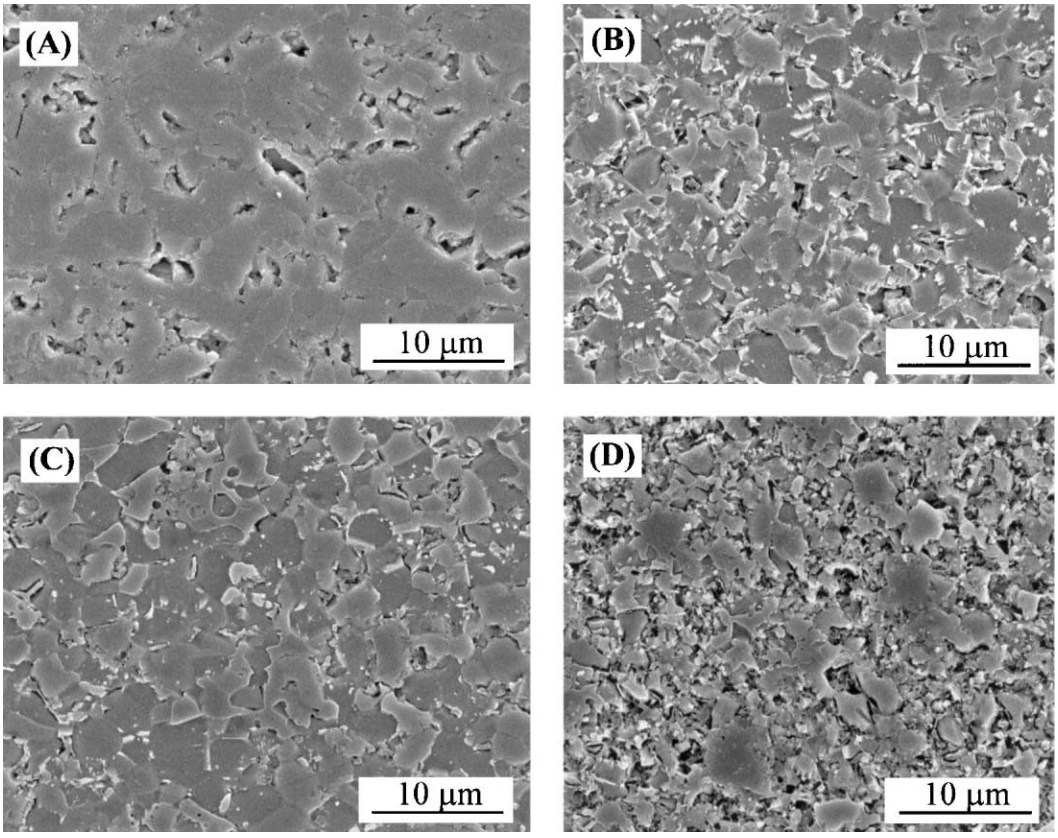


Fig. 1. Scanning electron micrographs of TiB_2 specimens hot-pressed at 1800 °C for 1 h containing (A) 0 wt.% (B) 2.5 wt.% (C) 5 wt.% and (D) 10 wt.%.

amounts of AlN are shown in Fig. 1. When pure TiB_2 was hot-pressed at 1800 °C for 1 h the densification was severely limited, as shown in Fig. 1(A). The addition of 2.5 wt.% AlN enhanced the specimen's densification behavior as shown in Fig. 1(B). The densification was further improved when the amount of AlN was increased to 5 wt.%, Fig. 1(C). However, too much AlN ($\geqslant$10 wt.%) did not help the material's densification, as illustrated in Fig. 1(D).

The specimens' relative densities were estimated by image analysis of their SEM micrographs shown in Fig. 1. The density increased with increasing AlN content and reached 98% when the amount of AlN added was 5 wt.%, as shown in Fig. 2. However, as clearly illustrated by the SEM micrographs, more than 10 wt.% AlN was detrimental to the densification of the TiB_2 material.

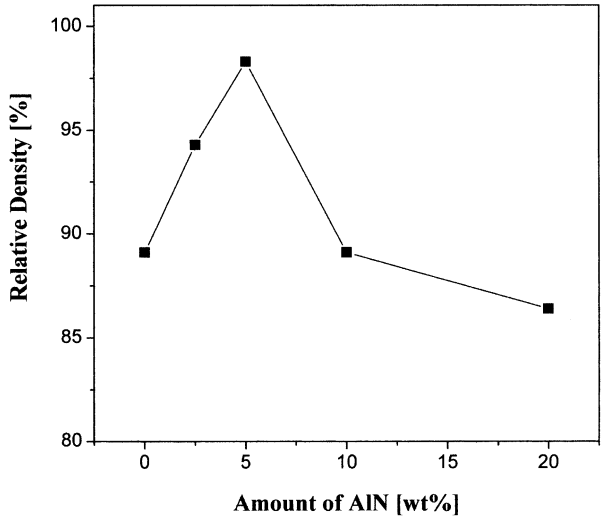


Fig. 2. Relative density of TiB_2 specimens with different amounts of AlN.

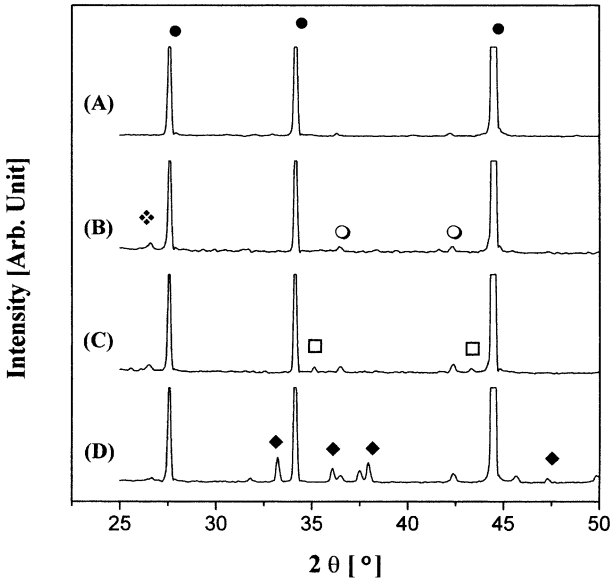


Fig. 3. XRD patterns of TiB_2 specimens containing different amounts of AlN: (A) 0 wt.% (B) 2.5 wt.% (C) 5 wt.% and (D) 10 wt.% AlN. (●) TiB_2, (❖) BN, (○) TiN, (□) Al_2O_3, and (◆) AlN.

The specimen's composition was analyzed using XRD patterns as shown in Fig. 3. As expected, without the addition of AlN only TiB_2 peaks were detected as is shown Fig. 3(A). When a small amount of AlN (2.5 wt.%) was added the TiN and BN peaks were detected as shown in Fig. 3(B). The TiN was apparently formed by a reaction between AlN and the TiO_2 that existed on the TiB_2 powder's surface, as follows:

$$3\,TiO_2(s) + 4\,AlN(s) \rightarrow 3\,TiN\,(s) + 2Al_2O_3(s) + \frac{1}{2}N_2(g) \quad (1)$$

The standard Gibbs free energy of reaction (1) at 2100 K is strongly negative ($\Delta G^\circ = -1240$ kJ/mol).[14] In addition, the reaction was expected to have been expedited because the specimen was hot pressed in Ar atmosphere. The N_2 gas generated by reaction (1) is believed to have subsequently reacted with TiB_2 to form BN, as follows:

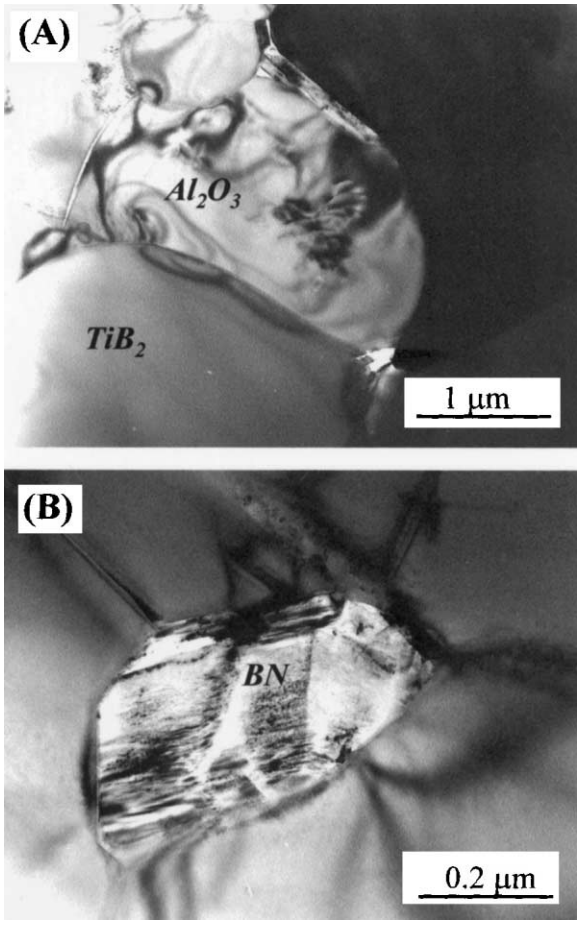


Fig. 4. TEM images of TiB_2 specimen with 5 wt.% AlN, showing (A) Al_2O_3 and (B) BN as reaction products.

$$TiB_2(s) + \frac{3}{2}N_2(g) \rightarrow TiN(s) + 2BN(s) \quad (2)$$

The equilibrium partial pressure of nitrogen gas (P_{N_2}) for reaction (2), at 2100 K, is 0.26 atm ($\sim 2.6\times10^{-2}$ MPa). The equilibrium P_{N2} for reaction (1), at the same temperature, is about 10^{19} atm ($\sim 10^{18}$ MPa). This means that reaction (2) is thermodynamically favorable. By these reactions the formation of BN and TiN is explained. According to reaction (1), formation of Al_2O_3 is also expected. Actually, when 5 wt.% AlN was added, peaks of Al_2O_3 as well as peaks of BN and TiN were detected, as shown in Fig. 3(C). When more than 10 wt.% AlN was added the AlN remained unreacted, Fig. 3(D). The remaining AlN is clearly not beneficial to TiB_2 densification.

Reaction products' formation was confirmed by TEM micrographs in Fig. 4. TEM images of Al_2O_3 and BN formed during the densification process are shown in Fig. 4(A) and (B), respectively. These are images of the specimen with 5 wt.% AlN, however, similar morphology was observed from other specimens containing different amounts of AlN. Interestingly, even with our all efforts TiN was not detected. However, the presence of TiN in the specimen was determined by using XRD patterns and thermodynamic analyses.

These variations in the densification behavior had a strong influence on TiB_2's mechanical properties. AlN effects on TiB_2's flexural strength and fracture toughness is shown in Fig. 5. Strength and fracture toughness of pure TiB_2 hot-pressed at 1800 °C were 360 MPa and 4.5 MPa $m^{1/2}$, respectively. With the addition of 5 wt.% of AlN, the strength increased to 650 MPa and the fracture toughness to 6.8 MPa $m^{1/2}$. Increases in strength and fracture toughness were mainly attributed to the body's density improvement. With further additions of AlN the mechanical properties decreased rapidly, reflecting the material's densification behavior.

Similar trends were observed in the specimens' Vickers hardness and elastic modulus, as shown in Fig. 6.

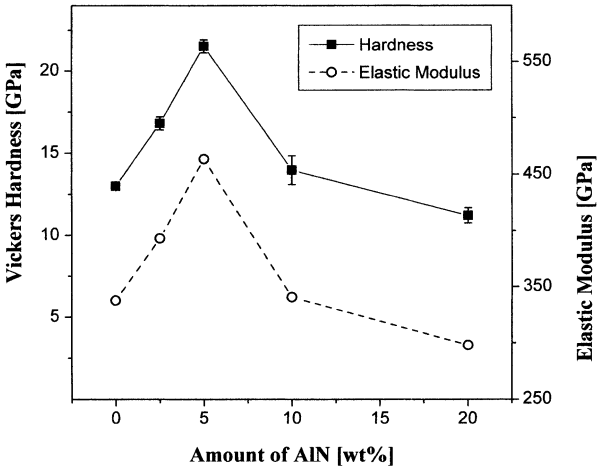
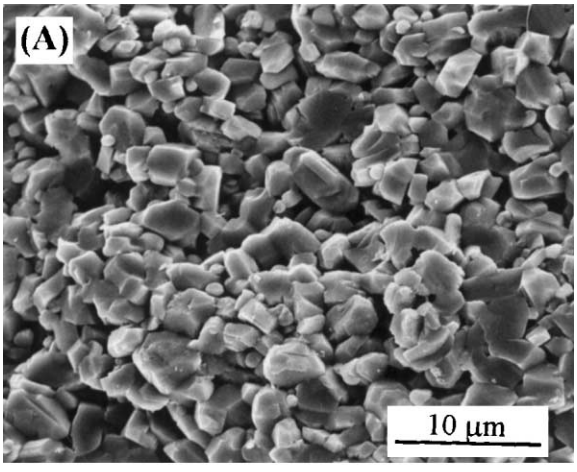


Fig. 6. Vickers hardness and elastic modulus of TiB_2 specimen as a function of AlN content.



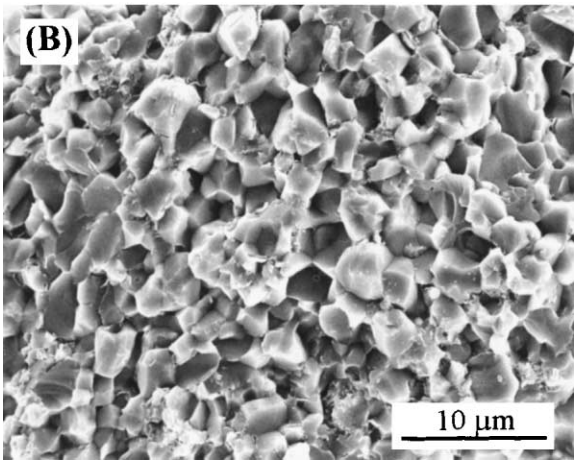


Fig. 7. Scanning electron micrographs of fracture surface of TiB_2 specimen: (A) pure and (B) with 5 wt.% AlN.

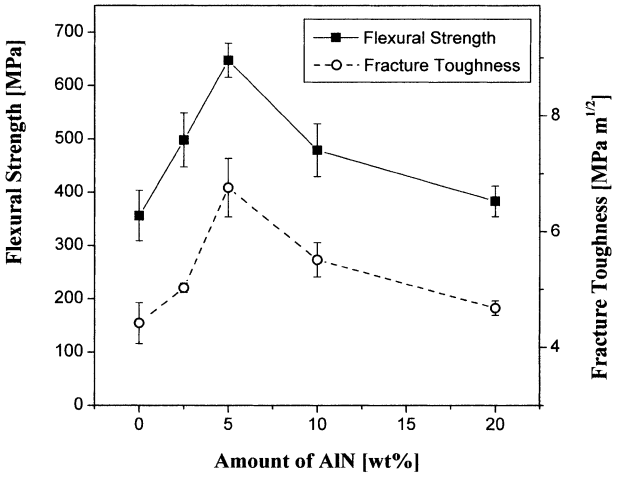


Fig. 5. Flexural strength and fracture toughness surface of TiB_2 specimen as a function of AlN content.

The specimens' mechanical properties were highest when 5 wt.% AlN was added, and decreased with further additions.

Fracture surfaces of TiB_2 specimens are shown in Fig. 7. The fracture of the pure TiB_2 occurred mainly by an intergranular pattern, Fig. 7(A), apparently due to the high porosity of the body. When 5 wt.% AlN was added the specimen exhibited transgranular fracture as shown in Fig. 7(B). Reduction of pores and formation of reaction products are also clearly observed in this micrograph.

4. Conclusions

The effect of AlN addition on the densification behavior and the mechanical properties of TiB_2 was investigated. When a small amount ($\leqslant 5$ wt.%) of AlN was added to TiB_2 and hot pressed at 1800 °C for 1 h the sinterability of TiB_2 was markedly improved. This improvement was attributed to elimination of the TiO_2 present on the surface of the starting powder by a reaction with AlN. The mechanical properties (flexural strength, fracture toughness, Vickers hardness, and elastic modulus) were also improved as a result of this improvement in the sinterability. However, when too much AlN was added ($\geqslant 10$ wt.%), sinterability and mechanical properties decreased and this was apparently due to the remaining AlN unreacted.

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