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Effect of in situ synthesized TiB_2 on the reaction between B_4C and Al in a vacuum infiltrated B_4C–TiB_2–Al composite

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Abstract The in situ reaction equation of B_4C and TiO_2 was identified using thermodynamic calculations and XRD analysis. The optimum presintering process was determined according to investigating the effect of presintering temperature on the flexural strength and porosity of the porous B_4C–TiB_2 preform. The effect of in situ synthesized TiB_2 on the reaction products and initial reaction temperature of B_4C and Al was discussed based on DSC and XRD analysis. The results showed that the in situ synthesized TiB_2 could effectively improve the mechanical properties of the B_4C–TiB_2–Al composite, elevate the initial reaction temperature of B_4C and Al, change the reaction products, and moderate the reaction of B_4C and Al. The mechanism of reaction between B_4C and Al was discussed.

Introduction

Boron carbide (B_4C) ceramics is a promising material with unique properties such as high melting point and hardness, low density, good wear resistance, excellent resistance to chemical attack as well as high capability for neutron absorption [1–7]. Due to the outstanding properties, B_4C ceramics has shown the potential for use in various industrial fields, such as military, engineering, and nuclear energy [8–10]. However, the widespread application of B_4C ceramics has been restricted by its low strength (<300 MPa) and low fracture toughness ($K_{IC} < 2.2$ MPa $m^{1/2}$) [11–14]. In order to improve the mechanical properties, many reports about the B_4C ceramics with dispersed TiB_2 particles have been available [15, 16]. Furthermore, many researchers focused their attention on improving the mechanical property of the B_4C–Al composite due to the low density and good ductility of Al [17, 18]. There have been some different opinions about the reaction products of B_4C and Al and the initial formation temperature of each product so far [19, 20]. Viala et al. [21] reported that at temperatures equal to 1141 ± 4 K, the reaction products were Al_3BC and AlB_2, and at temperatures higher than 1141 K, Al_3BC was still formed while $Al_3B_{48}C_2$ (β-AlB_{12}) replaced AlB_2. However, there is no report about the effect of in situ synthesized TiB_2 on the reaction between B_4C and Al. In this work the B_4C–TiB_2–Al composite was fabricated by infiltrating aluminum into the porous B_4C–TiB_2 preform in vacuum. The optimum presintering process was determined. The effect of in situ synthesized TiB_2 on the reaction between B_4C and Al was investigated using DSC and XRD analysis. The mechanism of reaction between B_4C and Al was discussed.

Experimental procedures

In this article, B_4C powder ($B_4C > 98$ mass %, Dalian Juxing Superhard Material Ltd, China), TiO_2 powder ($TiO_2 > 99$ mass %, rutile, Shenyang Guangda Lighting Ltd, China) and Al alloy (Trademark 5083, Everest Metals (Suzhou) Co., Ltd, China) were used as the starting materials. Two types of B_4C powders were used with different mean sizes (d_{50}), 20 and 1 μm, respectively. The mass ratio of B_4C ($d_{50} = 20$ μm) to B_4C ($d_{50} = 1$ μm) was 4:1. The mean sizes of TiO_2 and Al alloy powder were 1 and 10 μm, respectively. The TiB_2 was in situ synthesized by the reaction of B_4C, TiO_2, and C, where C was supplied from

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carbonization of the phenolic resin. The B_4C and TiO_2 powders and phenolic resin were weighed considering 40 mass % TiB_2 in situ synthesized in the B_4C–TiB_2 preform. The B_4C and TiO_2 powders were mixed with phenolic resin–acetone solution using a planetary ball mill with a nylon jar and Al_2O_3 balls in absolute alcohol for 86.4 ks. The slurry was dried in a rotary vacuum evaporator for 3.6 ks, followed by oven drying at 373 K for 43.2 ks. The resulting powders were granulated using a 60 mesh sieve for further use.

The Gibbs free energy change (ΔG^0) of the in situ reaction equation of B_4C and TiO_2 in vacuum was calculated. B_4C–TiO_2 mixed powders were pressed into compacts under 150 MPa and then held for 3.6 ks under a vacuum of 1×10^{-2} Pa at selected temperatures (1273, 1373, and 1473 K) based on the thermodynamic calculations. Then the specimens were tested using X-ray diffraction (XRD, X'Pert Pro MRD, Panalytical B.V., Holand). The pressed specimens were also used to investigate the effect of presintering temperature (Temperature range of 1473–2373 K, 1.8 ks holding time, 0.1 MPa Ar pressure) on the flexural strength and porosity of the TiB_2–B_4C preform. The flexural strength was measured by three-point bending tests (specimen size = 40 mm × 4 mm × 3 mm, bend span = 30 mm, and load speed = 0.05 mm/min) using hydraulic universal testing machine (WE-10A, Mts Systems (China) Co., Ltd, China). The porosity of the preform was investigated using the mercury injection apparatus (AutoPore IV 9500, Micromeritics Instrument Corporation, USA). The B_4C and the B_4C–TiB_2 preform powders (Both presintered at 2323 K for 1.8 ks) were mixed with Al alloy powder, respectively. The reactions of B_4C–Al and B_4C–TiB_2–Al systems were analyzed using differential scanning calorimetry (DSC, STA 409CD, Netzsch Instrument Corporation, Germany) from 300 to 1373 K with a 10 K/min heat rate under a vacuum of 1×10^{-2} Pa same with the aluminum infiltration process for fabricating B_4C–TiB_2–Al composite. The B_4C–Al and the B_4C–TiB_2–Al mixed powders were also held for 3.6 ks at peak temperatures (906, 1009, 1169 K and 906, 1174 K, respectively) based on the DSC results. Then the phase identification was performed by XRD.

Results and discussion

In B_4C–TiB_2–Al composite, the TiB_2 addition was achieved by the in situ synthesis of B_4C and TiO_2. TiB_2 could be likely in situ synthesized as either of the followings.

$$B_4C + 2TiO_2 + 3C = 2TiB_2 + 4CO \uparrow \tag{1}$$

$$B_4C + 2TiO_2 + C = 2TiB_2 + 2CO_2 \uparrow \tag{2}$$

where C was supplied from carbonization of the phenolic resin. The temperature (T) dependence of Gibbs free energy change (ΔG^0) in reaction Eqs. 1 and 2 can be derived from the thermodynamic data [22] of the following reactions:

$$\begin{aligned} &\mathrm{C\,(solid) + O_2\,(gas) = CO_2\,(gas)} \\ &\Delta G^0 = -395350 - 0.54T \end{aligned} \tag{3}$$

$$\begin{aligned} &\mathrm{C\,(solid) + 0.5O_2\,(gas) = CO\,(gas)} \\ &\Delta G^0 = -114400 - 85.77T \end{aligned} \tag{4}$$

$$\begin{aligned} &\mathrm{Ti\,(solid) + O_2\,(gas) = TiO_2\,(solid,\ rutile)} \\ &\Delta G^0 = -941000 + 177.57T \end{aligned} \tag{5}$$

$$\begin{aligned} &\mathrm{4B\,(solid) + C\,(solid) = B_4C\,(solid)} \\ &\Delta G^0 = 41500 + 5.56T \end{aligned} \tag{6}$$

$$\begin{aligned} &\mathrm{Ti\,(solid) + 2B\,(solid) = TiB_2\,(solid)} \\ &\Delta G^0 = -333340 + 24.0T \end{aligned} \tag{7}$$

For reaction (1), Gibbs free energy change could be calculated as $\Delta G^0(1) = 896900 - 662.78T$ and for reaction (2), $\Delta G^0(2) = 563800 - 320.78T$. Figure 1 shows the temperature dependence of Gibbs free energy change $\Delta G^0(1)$ and $\Delta G^0(2)$. As shown in Fig. 1, $\Delta G^0(1) < 0$ at temperatures higher than 1353.2 K while $\Delta G^0(2) < 0$ at temperatures higher than 1757.6 K. Based on the second law of thermodynamic the theoretical initial formation temperature of TiB_2 phase was 1353.2 K for reaction (1) and 1757.6 K for reaction (2). On the other hand, Fig. 2 shows the XRD patterns of B_4C–TiO_2 compacts at different temperatures of 1273, 1373, and 1473 K for 3.6 ks in vacuum. The temperature selection was based on the thermodynamics calculation results mentioned above. As shown in Fig. 2a, there were only B_4C and TiO_2 phases appeared in the XRD pattern at 1273 K showing no evidence of the reaction. As shown in Fig. 2b although

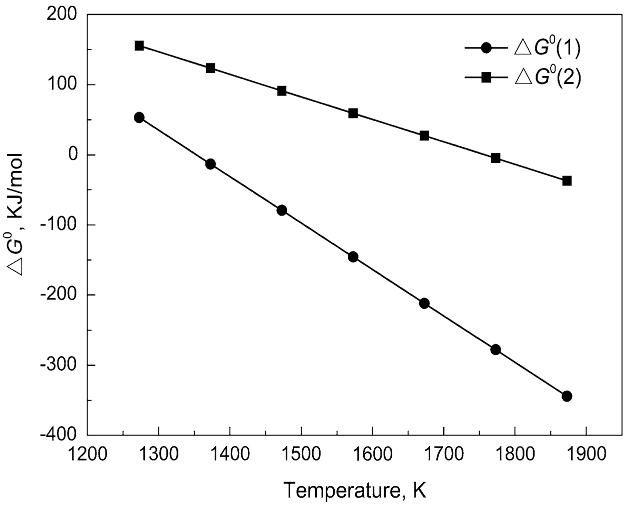

Fig. 1 The temperature dependence of Gibbs free energy change (ΔG^0)

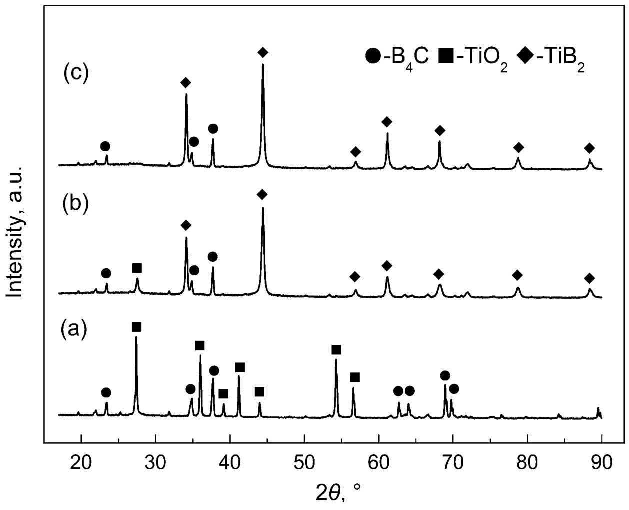

Fig. 2 XRD patterns of B_4C–TiO_2 compacts at different temperatures for 3.6 ks in vacuum: **a** 1273 K, **b** 1373 K, and **c** 1473 K

there was a few of TiO_2 remained, B_4C and TiB_2 could be identified at 1373 K implying that the actual initial formation temperature of TiB_2 in situ synthesized was no more than 1373 K, which was much lower than the theoretical initial formation temperature of TiB_2 phase (1757.6 K) deduced from reaction (2). So the in situ reaction of B_4C and TiO_2 was determined followed by the reaction (1). Figure 2c showed TiB_2 and B_4C phases while no TiO_2 phase was identified at 1473 K. We assumed that at higher temperature it was possible to make TiO_2 convert to TiB_2 completely in a relative short time and avoid abnormal growth of TiB_2 grain resulted from excessive holding time.

In this work, the B_4C–TiB_2 preform with high strength should be achieved by sintering at higher temperature due to the poor sinterability of B_4C. Besides the good strength, the B_4C–TiB_2 preform was also expected to have a favorable porosity and form a three-dimensional network of interconnected capillaries, which could facilitate the aluminum infiltration to fabricate the B_4C–TiB_2–Al composite with excellent mechanical properties. So a relative low preparation temperature was also required for making the porous B_4C–TiB_2 preform. It was very important to choose the proper presintering temperature considering these two factors. Table 1 shows the effect of presintering temperature on the flexural strength and porosity of the B_4C–TiB_2 preform. With increasing the presintering temperature, the flexural strength increased while the porosity decreased gradually. The preform showed good flexural strength and porosity presintered at 2323 K in Table 1. When the temperature was up to 2373 K, the flexural strength increased slightly while the porosity decreased sharply which was not beneficial to the aluminum infiltration to fabricate B_4C–TiB_2–Al composite. Therefore, the optimum presintering process for the porous B_4C–TiB_2 preform was first heated at 1473 K for 3.6 ks in vacuum and then at 2323 K for 1.8 ks in an Ar atmosphere.

Table 1 The effect of presintering temperature on the flexural strength and porosity of the B_4C–TiB_2 preform

Presintering temperature (K)	Flexural strength (MPa)	Porosity (%)
1473	31.3 ± 7.5	46.5
1773	37.6 ± 5.3	45.6
1973	80.6 ± 5.5	41.3
2073	85.8 ± 6.2	39.7
2173	113.6 ± 4.8	38.6
2323	155.3 ± 5.6	36.5
2373	160.2 ± 6.5	28.7

Figure 3a shows the DSC curve of the reaction between B_4C perform and Al in the temperature range of 300–1373 K. The DSC curve showed three peaks: one was an endothermic peak and the other two were exothermic peaks at temperatures of 906, 1009, and 1169 K, respectively. Figure 3b shows the XRD patterns of B_4C–Al mixed powders held for 3.6 ks at the peak temperatures of the DSC curve. As shown in Fig. 3b, there were only B_4C and Al phase existing in the mixed powders at 906 K. It was identified that the endothermic peak at 906 K shown in Fig. 3a was resulted from the heat absorption caused by aluminum melting in the temperature range of 887–915 K. At 1009 K, Al_3BC as a reaction product of B_4C and Al was present in XRD pattern with a great exothermic reaction. This drastic exothermic reaction in the temperature range of 933–1073 K was the result of the great heat release due to the Al_3BC phase formation. When the temperature was up to 1169 K, another phase AlB_2 was found by XRD besides B_4C, Al and Al_3BC accompanied with a little heat release. It was assumed that the small exothermic peak might be caused by the AlB_2 formation in the temperature range of 1157–1187 K.

Figure 4a shows the DSC curve of the reaction between B_4C–TiB_2 preform and Al in the temperature range of 300–1373 K. As shown in Fig. 4a, the DSC curve showed two peaks: one was an endothermic peak and the other was an exothermic peak in the temperature range of 873–915 K and 1152–1190 K, respectively. Compared with Fig. 3a the exothermic peak in 933–1073 K shown in Fig. 3a was not present in Fig. 4a. It was assumed that the TiB_2 addition significantly elevated the initial reaction temperature of B_4C and Al for about 219 K. Figure 4b shows the XRD patterns of B_4C–TiB_2–Al mixed powders held for 3.6 ks at the peak temperatures of DSC curve. As shown in Fig. 4b, there were B_4C, TiB_2, and Al phases at 906 K. Same as Fig. 3a, the endothermic peak was also caused by the heat absorption due to aluminum melting. At 1174 K, Al_3BC as the only reaction product was identified by XRD besides

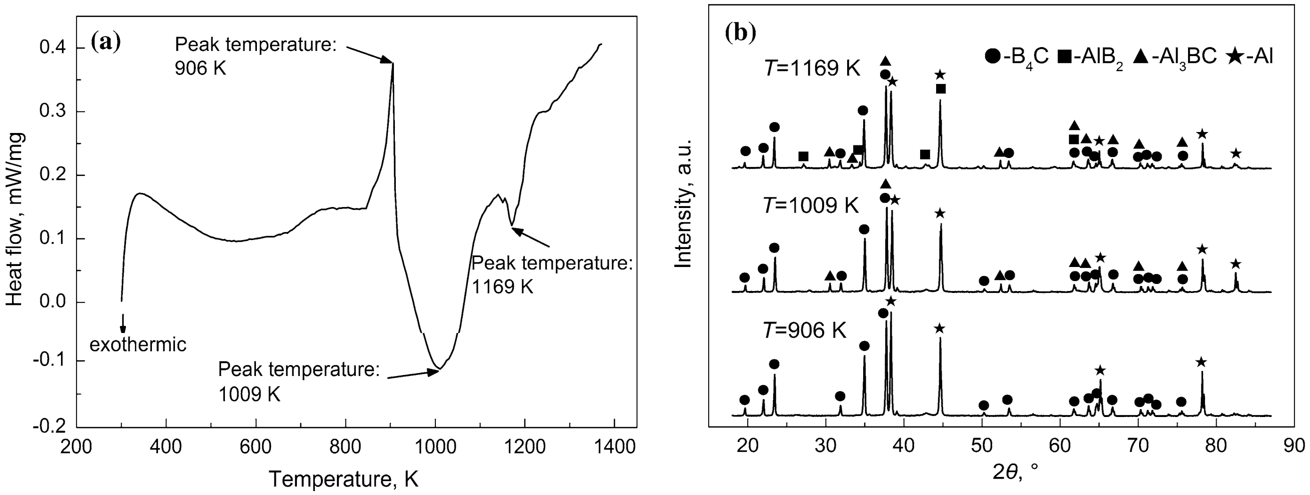

Fig. 3 DSC of the reaction of B_4C preform and Al (**a**) and XRD patterns of B_4C–Al mixed powders at selected temperatures (**b**)

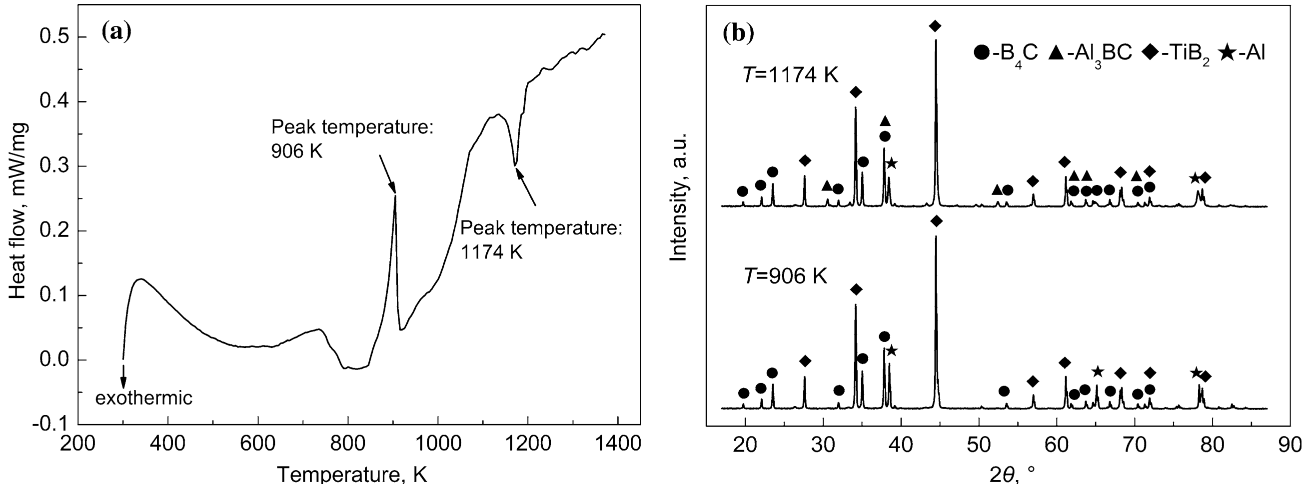

Fig. 4 DSC of the reaction of B_4C–TiB_2 preform and Al (**a**) and XRD patterns of B_4C–TiB_2–Al mixed powders at selected temperatures (**b**)

B_4C, TiB_2, and Al. Compared to B_4C–Al system, no AlB_2 phase was formed during aluminum infiltration of B_4C–TiB_2–Al at 1373 K for 3.6 ks in vacuum. The in situ synthesized TiB_2 not only changed the reaction products of B_4C and Al but also moderated the reaction that could make the more B_4C and Al phases remained. In addition, the existence of TiB_2 and the more B_4C and Al phases might improve the mechanical properties of B_4C–TiB_2–Al composite.

The reaction of B_4C and Al could be considered as a process of atom diffusion. Al atoms diffused toward B_4C, on the contrary B and C atoms in B_4C diffused into Al simultaneously during aluminum infiltration. The diffusion rates of B, C and Al atoms were $Al > C > B$ in turn. During aluminum infiltration inside B_4C next to the interface of B_4C and Al (marked region 1), the C/B atomic ratio increased significantly due to the diffusion rate of C atoms higher than that of B atoms. Meanwhile carbon-depleted area (marked region 2) with plentiful B atoms remained could be formed in the interior of B_4C away from the interface of B_4C and Al. Considering diffusion rate of Al atom was much higher than that of B and C atoms, we assumed that the diffusion of B and C atoms could only happen in region 1 and region 2, and few B and C atoms diffused into Al area. We could also assume that the reaction of B_4C and Al was basically the process of Al atoms diffusing into B_4C. Figure 5 shows the schematic figures on the mechanism of reaction between B_4C and Al. The B_4C–Al system in lower temperature was represented in Fig. 5a With increasing the temperature, Al atoms first diffused into region 1 (Fig. 5b). Consequently hexagonal Al_3BC was formed as a barrier that might block the Al atoms diffusing into region 2. With the increasing diffusion rate of Al atoms in higher temperatures, Al atoms could overcome the diffusion barrier and move into region 2 to form AlB_2 bonding with B atoms (Fig. 5c). For B_4C–TiB_2–Al system, in situ synthesized TiB_2 around the B_4C

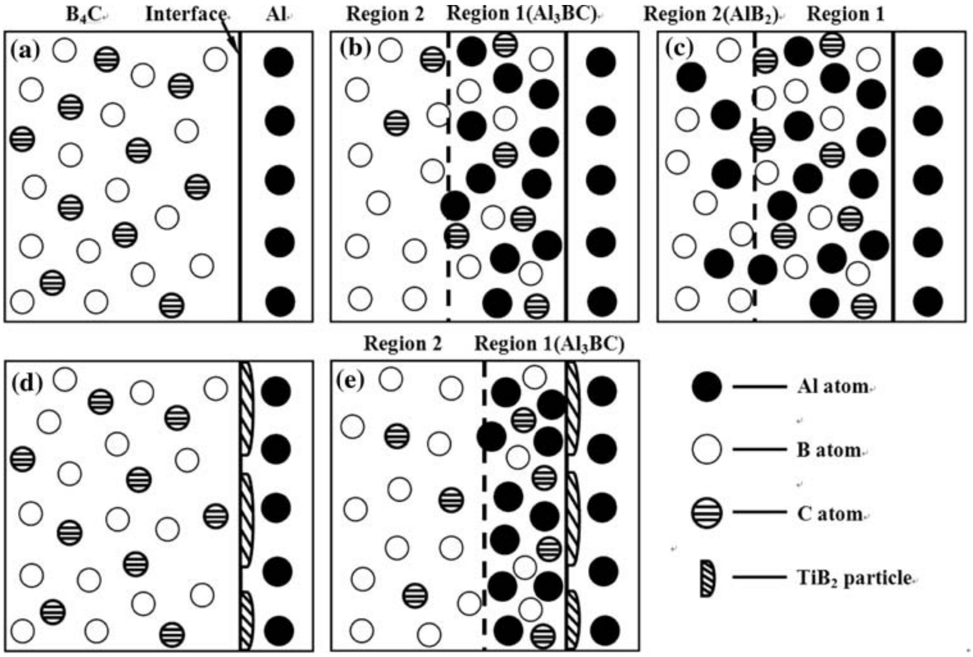

Fig. 5 Schematic figures on the mechanism of reaction between B_4C and Al for B_4C–Al system before reaction (**a**), Al_3BC formation (**b**), AlB_2 formation (**c**) and for B_4C–TiB_2–Al system before reaction (**d**), and Al_3BC formation (**e**)

obstructed Al contacting B_4C and prevented Al atoms diffusion (Fig. 5d). Namely TiB_2 addition increased indirectly the diffusion activation energy of Al atoms diffusing into B_4C. Compared with B_4C–Al system, the Al_3BC formation required higher temperature so that Al atoms could break through the diffusion barrier and move into region 1 (Fig. 5e). It could be presumed that Al atoms could obtain enough energy to diffuse into region 2 forming AlB_2 phase when the temperature is more or much higher than 1373 K.

Conclusions

In summary, the reaction equation of B_4C and TiO_2 was identified as $B_4C + 2TiO_2 + 3C = 2TiB_2 + 4CO\uparrow$ using thermodynamic calculations and XRD analysis, and the optimum presintering process for the porous B_4C–TiB_2 preform was first heated at 1473 K for 3.6 ks in vacuum and then at 2323 K for 1.8 ks in an Ar atmosphere. The in situ synthesized TiB_2 could prevent Al atoms diffusion and increase indirectly the diffusion activation energy of Al atoms. The TiB_2 addition could effectively improve the mechanical properties of the B_4C–TiB_2–Al composite, elevate the initial reaction temperature of B_4C and Al, change the reaction products and moderate the reaction between B_4C and Al.

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