Influence of the Mechanical Properties of B₄C/Al Composite with Graphene Nanosheet Dopping

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Abstract. Graphene nanosheet has been brought to the B₄C/Al composites to investigate the microstructure and mechanical properties of the materials which were prepared via vacuum hot press sintering at 680 °C, with sintering pressure of 30 MPa and soaking time of 90 min. XRD analysis illustrated that there was only one new phase AlB₂ detected out in the composite after sintering. The composite without GN addition was endowed better density than the GN addition one. Nevertheless, the mechanical properties of GN addition composite exhibited more superior than that of non GN addition composite, Vickers hardness, bending strength and fracture toughness were achieved respectively 54.13 ± 4.57 Hv, 238.36±10.24 MPa and 4.23±0.12 MPa·m₁/². In summary, GN has played a satisfactory character in promoting the mechanical property of B₄C/Al composites in the present experiment.

1. Introduction

Al and its alloys are endowed low density, excellent plasticity and good electrical conductivity, B₄C ceramic has numerous advantages of high strengh, high hardness and favorable corrosion resistance. Therefore, B₄C/Al composites which combines the advantage of both have become potential alternative materials in application of sport equipment, electronic device, armor protection [1-4]. In the previous research of our group, we have discussed the preparation technology and mechanical properties of 5-25vol.% B₄C/Al composites, the results showed that the comprehensive mechanical properties of the composites with lower B₄C content were weaker than that of higher B₄C content composites. For that reason, in order to improve the mechanical performance, graphene has been brought in the lower B₄C content I composites. In the present study, 5% B₄C/Al composites were selected in the exploratory experiments.

As a burgeoning two-dimensional materials, graphene has been substantially reported in enhancing the mechanics and electricity properties of metal and ceramic materials because of its specific structure and physical properties [5-7]. The reinforcing mechanism can be summarized as follows. Graphene nanosheet (GN) will dispersed at grain boundaries or implant in the matrix paticles causes the crystal grain difficult to grow up, furthermore, the actual structure of graphene is not an ideal planar network but it has tiny surface fluctuations [8-9]. Therefore, graphene can enhance the composite system by adjusting its own structure. Meanwhile, the fracture process also extend the crack propagation path, and then increase the toughness of composites with graphene addition.

Powder metallurgy which has been verified as an effective synthetic methods was used as the preparation method to fabricate graphene/B₄C/Al composites [10-11]. In the present study, the graphene/B₄C/Al composites were prepared via vacuum hot-pressing sintering and their mechanical properties has been discussed to compare that with the no graphene addition composites.
2. Experimental
Raw material: Al powder, 99.9%, average size 50 μm; B₄C powder, 99.9%, size 1-3 μm; GN, laboratory self-made. These powders were mingled into two groups as 5 vol.%B₄C/Al and 2 wt.% GN-5 vol.%B₄C/Al, respectively. It should be noted that the mass ratio of GN was contrasting to the B₄C/Al mixed powder. The mixing powders and Al₂O₃ mill balls were measured as the weight ratio of 1:5 then put in mill pots, meanwhile moderate alcohol was infused to ensure uniformity of the powders by wet mixing. After 4 hours of mixing the slurry was placed into tray and dried in a drying oven until the alcohol exhaust completely, the dry even powders remained. The two groups of powders were divided by graphite gaskets and graphite paper and inserted into a graphite die with diameter of 45 mm. Then the graphite die was put into a vacuum hot pressing furnace, setting the sintering procedure as: 10°C/min below 500°C, 5°C/min from 500°C to 680°C, heat preservation and sintering pressure of 90 min at 680°C. In addition, the sintering pressure was slowly and uniformly increased to 30 MPa in 30 min, and the initial pressure retention prevented the samples shrinkage.

The powders changed to Φ45 mm wafer shaped samples after vacuum hot pressing sintering. The samples has been cut into several specimens with the shape of 36 mm× 4 mm × 3 mm and to test the bending strength. Moreover, the flexural toughness testing specimens were cut into 36 mm× 4 mm × 2 mm with groove of 0.5mm deepness and 0.2 mm in the middle of specimens. Tensile strength has also been measured via the electronic universal testing machine. Microstructure of the samples was observed by scanning electron microscopy (SEM) and transformation of the phases was investigated by X-ray diffraction (XRD).

3. Results and Discussion

3.1. XRD Analysis
The XRD spectrogram of samples 1–2 that were respectively on behalf of 5 vol.%B₄C/Al and 2 wt.% GN-5 vol.%B₄C/Al, has been shown in Fig. 1.

![Figure 1. XRD of sample 1 and 2](image-url)
There is a new phase AlB\textsubscript{2} appearing in the composite after sintering, which was caused of the reaction between Al and B\textsubscript{4}C. The intensity of the peaks of B\textsubscript{4}C and AlB\textsubscript{2} are not obvious than that of matrix Al that was because of the content of Al and AlB\textsubscript{2} was discrepant markedly. The peaks of Al exhibited favourably that demonstrated the Al particles was endowed good crystallinity. However, the GN has not been detected because of its low content and cannot meet the minimum standards of X-ray testing. Furthermore, reaction bonding is one of the primary combination mode between metal and ceramic, as well as in the system of B\textsubscript{4}C/Al composite. The phase AlB\textsubscript{2} was generated between the reaction of Al and B\textsubscript{4}C, which would promote the impact toughness of the composite reported in the foregone references.

3.2. Relative Density and Microstructure
Relative density was calculated by weigh the dry weight, wet weight, buoyant weight based on the Archimedes principle. The computational formula of relative density was [12]:

\[ P = \frac{D}{W-S} \times 100\% \quad (1) \]

Where \( W \) is wet weight, \( D \) is dry weight, \( S \) is buoyant weight, respectively.

After calculating, the relative density of sample 1 and 2 both exceed 98\%, respectively reach 99.23\% and 98.82\%. The composite without GN addition exhibited the higher density than the addition composite. The reason was that the wettability of GN and Al was inferior and no reaction happened at the sintering temperature. Therefore the juncture of Al and GN was relatively loose.

The microstructure of fracture surface of sample 1 and 2 after stretching has been characterized by scanning electron microscope listed in Fig. 2. Thereinto, Fig. 2(a)-(b) and (c)-(d) respectively were the SEM images of sample 1 and 2. It can be found obviously that the dimples distribute homogeneously in the fracture surface showed in Fig. (a). The metal Al has appeared liquid phase during the sintering process which can be seen in Fig. (b). Compared to sample 1, the composite with GN addition, sample 2 has displayed relatively loose structure in Fig. (c). The wettability of GN and Al was poor at the present sintering temperature, therefore GN gathered in the interface of Al and B\textsubscript{4}C. Besides, the typical transgranular fracture phenomenon has been found in the composite in Fig. (c), which can improve the mechanical property significantly. Fig. (d) showed that B\textsubscript{4}C particles grow homogeneously from the size of 1~3 \( \mu \)m to 5~8 \( \mu \)m during the sintering period. Few pores can be seen in the fracture surface of sample 2 from Fig. (d). GN was also seen in the interface of Al and B\textsubscript{4}C.
3.3. Mechanical Property
Bending strength and the fracture toughness of sample 1 and 2 have been calculated after testing by a universal testing machine. The computational formula of bending strength and fracture toughness are[12]:

\[
\sigma_f = \frac{3PL}{2bh^2}\quad (2)
\]

\[
K_{IC} = Y \times \frac{3PL}{2bh^2} \times \sqrt{a}\quad (3)
\]

Where P is breaking load, L is span, b is breadth of sample, h is height of sample, Y is the constant associated with the sample. When the ratio of L:b:h is 8:2:1, Y can be calculate as follow[12]:

\[
Y = 1.96 - 2.75 \left(\frac{a}{W}\right) + 13.66 \left(\frac{a}{W}\right)^2 - 23.98 \left(\frac{a}{W}\right)^3 + 25.22 \left(\frac{a}{W}\right)^4 \quad (4)
\]

According to formula (2)-(4), the bending strength and the fracture toughness of sample 1 and 2 have been worked out as 238.36±10.24 MPa, 219.31 ± 14.21 MPa and 4.23±0.12 MPa·m$^{1/2}$, 3.98±0.18 MPa·m$^{1/2}$, respectively. Nevertheless, these samples can not be broken because of the favourable plasticity of matrix Al, therefore the rolling reduction of pressure head was controled as 1.2 mm. Compared with the bending strength and the fracture toughness of sample 1 and 2, it was obviously that the composite with GN addition was equipped with the better mechanical property. That was because of the specific lamellate structure of GN will adhere at the interface of Al and B$_4$C, reinforced the combining capacity of the particles, thereby causing the composites different to destroy. The main enhancement principle was caused of the pinning effect and fiber pull-out of GN. What was more, GN
as a kind of two-dimension nano materials, also possessed excellent mechanical property, which can promote the mechanical performance of the B$_4$C/Al composites in the current research.

Vickers hardness of sample 1 and 2 has been tested by a Vickers hardness tester. The computational formula was [12]:

$$H_V = \frac{P}{F} = 1.8544 \frac{P}{d^2}$$ (5)

Where P is the loading, F is the indentation area, d is the average of two diagonal lengths. After calculating, the hardness of sample 1 and 2 respectively were 48.69 ± 5.42 Hv and 54.13 ± 4.57 Hv. Similarly, GN also played a satisfactory role in promoting the hardness of the composite.

4. Conclusion
The 5 vol.%B$_4$C/Al and 2 wt.% GN-5 vol.%B$_4$C/Al composite have been successfully fabricated via vacuum hot-pressing sintering with the sintering temperature 680°C, sintering pressure 30 MPa, soaking time 90 min. The phase composition and microstructure were characterized by XRD and SEM test, respectively. The result of XRD detection illustrated that there is only one new phase AlB$_2$ has been found in the composite. Due to the low graphene content, it was not detected by X-ray diffraction. Compared the section microstructuremic of sample 1 and 2, the non GN addition sample 1 exhibited more compact structure than that of GN addition sample 2. The reason was because of the sintering temperature can not reach the reaction condition of Al and GN, which caused them difficult to wetting, thereby resulting in the GN addition sample the poor density. However, the sample 2 showed the better properties in Vickers hardness, bending strength and fracture toughness than that of sample 1, which was ascribed to the pinning effect and preferable mechanical properties of GN. While the Vickers hardness, bending strength and fracture toughness of 2 wt.% GN-5 vol.%B$_4$C/Al composite were 54.13 ± 4.57 Hv, 238.36±10.24 MPa and 4.23±0.12 MPa·m$^{1/2}$, respectively.

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6. References
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