

LOW TEMPERATURE SYNTHESIS OF Al-B-C MULTI-PHASE COMPOSITES VIA REACTIVE SINTERING OF B₄C AND Al

M.C. Kim, Y.M. Eun, J. H. Han., K.H. Han*

School of Materials Science and Engineering, Yeungnam University, Gyeongsan, Gyeongbuk Korea

*Corresponding author(khhan@ynu.ac.kr)

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1 Introduction

Light weight boron carbide-aluminum composites have attracted interests owing to their excellent mechanical properties, such as high strength and stiffness for structural and armor applications, wear resistance for automotive applications, and excellent neutron shielding property for structural neutron absorber application.[1-5]

Essentially, boron carbide-aluminum powder mixtures are known to possess poor sinterability due to the high wetting angle between the constituents at lower temperatures.[6-8] Hence, to enhance their sinterability by improving the wetting, the compact must be heated to higher temperature, *i.e.*, above 1100°C.[9] For high ceramic compositions, the method to utilize the infiltration of the molten aluminum into B₄C preform has been reported to be successful.[3]

Boron carbide, however, has high reactivity with aluminum at elevated temperatures, especially above the melting point of Al. The reaction between B₄C and Al results in the formation of various phases, depending on the reaction temperature, such as borocarbides, boride and carbide. Yet, in view of B₄C-Al composites, the retention of B₄C compounds is also important after the processing via either sintering or melt infiltration and such reactions could be considered undesirable. However, those products can enhance wettability of reinforcements with aluminum, or they can be used to produce Al-B-C multi-phase composites as an alternative having improved densification. These composites also possess attractive properties.[4-6]

In this study, we performed low-temperature synthesis of Al-B-C multi-phase composites, using the powder mixtures of Al and B₄C via pressureless reactive sintering. To enhance the densification, we

utilized mechanically milled B₄C-Al composite powders.

2 Experimental Procedure

2.1 Starting Materials and Mechanical Milling

Four compositions, as given in Table 1, consisting of 99.8% Al powders of an average size of 5 μ m, 99.7% B₄C powders of an average size of 3.4 μ m, Mg powders of an average size of 10 μ m and Al-12%Si brazing powders were used as starting materials.

Table 1 Composition of composite materials

Specimen designation	Composition, wt.%			
	B ₄ C	Al	Mg	Al-12%Si
A	60	39	1	-
B	60	29	1	10
C	40	59	1	-
D	40	49	1	10

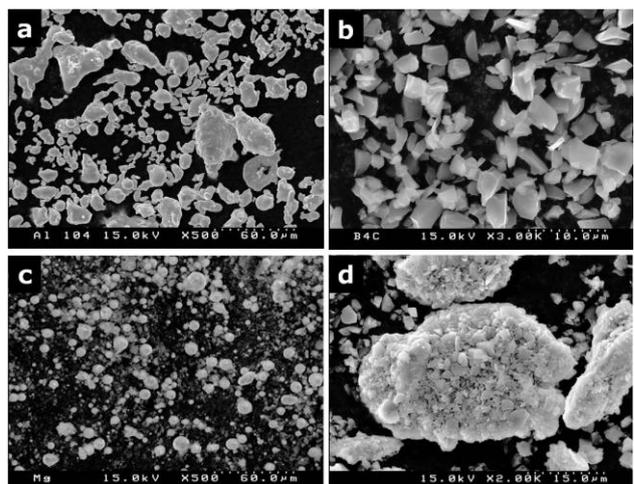


Fig. 1. SEM images of powders used in this study; (a) Al, (b) B₄C, (c) Mg and (d) B₄C-Al-Mg powders after milling for 8 hrs, respectively.

The mechanical milling was carried out, using a planetary mill equipped with 250cc jars lined with thick cemented carbide inner layer and cemented carbide balls. The ball size was 10 mm in diameter and the ball-to powder ratio was 10 to 1. Also, 1% of polyethylene wax was used as the process controlling agent (PCA) to prevent any possible excessive cold welding of aluminum powders during milling. The milling was done under Ar atmosphere at 200rpm for 8hrs. As shown in Fig. 1(d), the milled Al powders contained many B₄C particles partly embedded in them. Since we used fine aluminum powders whose average size is smaller than that of hard B₄C powders and a large amount of B₄C powders were to be incorporated, mechanical milling resulted in larger particles of B₄C-Al clusters as well as some isolated milled B₄C particles. This inhomogeneous milled powder mixture produced rather complex microstructure as shall be presented. For comparison, another experiment using simply blended powders without mechanical milling were also performed.

2.3 Compaction and Sintering

The milled powders were compacted at room temperature to form disk-shaped specimens having a dimension of 15mm in diameter and 5mm in thickness. The compaction pressure was 600MPa. The sintering of the green compacts was done in a tube furnace in either vacuum, argon or nitrogen gas atmosphere. The sintering temperature was varied up to 800°C.

2.4 Microstructure Observation and Phase Analysis

Microstructural characterizations were made by an optical microscope and a field-ion scanning electron microscope (Hitachi s-4800 model) equipped with an EDX analyzer. Specimens for metallography were prepared according to the standard method with diamond grinding discs and diamond polishing powders. The phase analysis of heat-treated samples was carried out by the x-ray diffraction, using a diffractometer (Rigaku Denki Dmax-2000 model) and Cu-K_α radiation.

2.5 Hardness and Biaxial Flexural Strength Measurements

The hardness measurements were made using a microvickers hardness tester under a load of 500g.

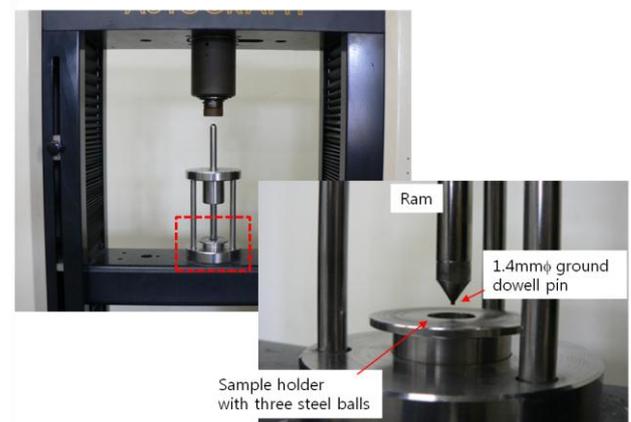


Fig. 2. Jig fixture used for the biaxial flexural strength measurements

For the measurements of biaxial flexural strength, thin disk samples of 15mm in diameter and 1.4 mm in thickness were cut from the sinters and polished using diamond grinding powders. A standard fixture jig having a design consisting of a ram with a dowell pin at one end and three balls according to ISO 6872, was utilized. A 1-ton capacity tensile tester was used and the measurements were made with a cross-head speed of 0.1mm/min. (Fig. 2)

3 Results and Discussion

3.1 Effects of Milling and Sintering Atmosphere

Preliminary sintering experiments were performed with two composite A powders of B₄C and Al, prepared by mere blending and mechanical milling. On sintering at 700°C, the compacts of blended powders revealed exudation of molten aluminum, irrespective of sintering atmospheres such as vacuum, Ar and N₂, indicating an insufficient wetting between the molten aluminum and boron

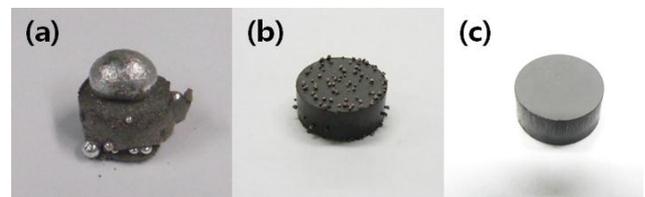


Fig. 3. The appearance of sinters of 60%B₄C-40%Al after sintering at 700°C; (a) non-milled powders sintered in vacuum, (b) non-milled powders sintered in N₂ and (c) milled powders sintered in N₂, respectively

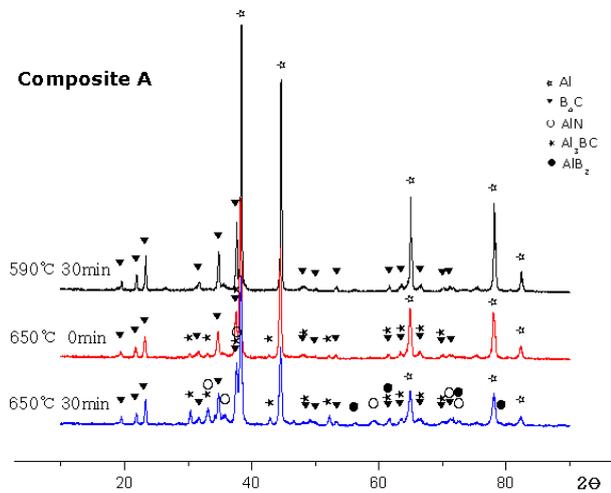


Fig. 4. X-ray diffraction patterns taken from the composite A compacts in different stages of heating for sintering in N_2 gas.

carbide. Poor sinters were produced for blended powder compact, as can be seen in Fig. 1(a) and 1(b). On the other hand, the compacts made of milled powders of composite A, showed fewer tendencies for liquid exudation. In particular, sintering in N_2 could completely prevent the exudation of molten

aluminum and sinter with clean surface was produced. (Fig. 3) For the reason, we proceeded our investigation mainly on the consolidation of B_4C -Al milled powders via sintering in N_2 at various temperatures up to $800^\circ C$.

3.2 Phase Formation

In their earlier researches, Halverson et al [1,2], Pyzik and Beaman [3], Viala et al [7], and Arsian et al [8] have performed detailed phase analysis for various B_4C -Al composites produced by different processes, such as hot consolidation and melt infiltration. From those efforts, it has been known that various phases including Al_3BC , AlB_2 , AlB_{12} , Al_4C_3 , etc. can be produced in via the reactions between B_4C and aluminum in solid state and molten state.

In order to get more insight into the phase formation during our sintering schedule, interrupted heating experiments were performed. Fig. 4 shows the changes of X-ray diffraction patterns of composite A during heating schedule. As seen in Fig. 4, on reaching the sintering temperature, the evolution of diffraction lines of Al_3BC was recognized first in the diffraction pattern. This is consistent with previous

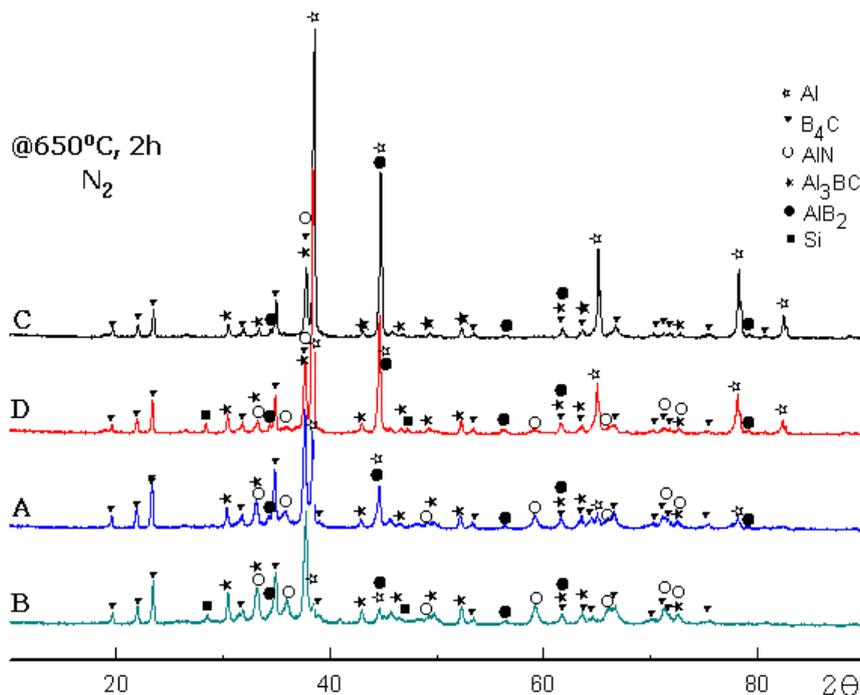


Fig. 5. X-ray diffraction patterns taken from the composites A, B, C and D after sintering at $650^\circ C$ for 2hrs in N_2 .



However, for some kinetic reason, AlB_2 phase does not form simultaneously at the same rate, even when Al is in molten state.[9] It appear as chunky precipitate in the matrix [7], as can be seen in Fig. 5. The compound Al_3BC phase started to form in the periphery of B_4C being in contact with Al.[7]

Fig. 5 shows the X-ray diffraction patterns taken from the sinters made of the four composite powders as listed in Table 1. With increasing Al content, more densification was achieved. In addition, during sintering in nitrogen atmosphere, AlN was formed via direct contact between aluminum. The formation of AlN was promoted by the addition of Al-12%Si brazing powders which melt at $577^\circ C$ on heating. The brazing powder promoted densification of compacts, perhaps via transient liquid phase formation. The pore content for the composite D (Fig. 7) was determined to be about 9% by the image analysis through the areal fraction measurements.

In Fig. 5, it is also noted that, for composites with lower aluminum content and with the addition of Al-12%Si brazing powders showed an increase in the amounts of Al_3BC and AlN, indicating the enhanced decomposition of B_4C and nitriding of aluminum. In the composite B that contained 60% B_4C and 10% of Al-12%Si, the diffraction peaks from the remaining aluminum is hardly seen. The increase of the sintering temperature above the melting point of Al facilitate the reaction between B_4C and Al, leading to further reduction of the B_4C content. After

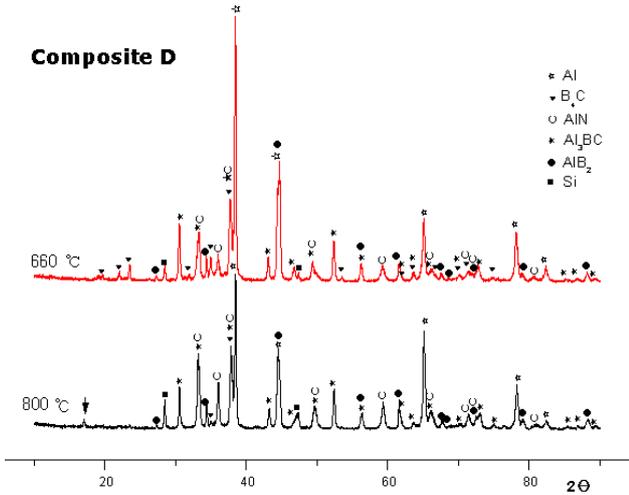


Fig. 6. X-ray diffraction pattern of the composite D after sintering for 2hrs at $660^\circ C$ and $800^\circ C$, respectively; ↓ stands for an unidentified peak.

observation by Pyzik and Beaman [6] and suggests that that the reaction between B_4C and aluminum, would initiate with the formation of Al_3BC . The reaction can be described as



Considering extremely low solubility of B in Al [10], it is assumed that the excessive boron atoms in aluminum would form aluminum boride phase such as Al_2B . Granting this scheme, the entire reaction would then be described as

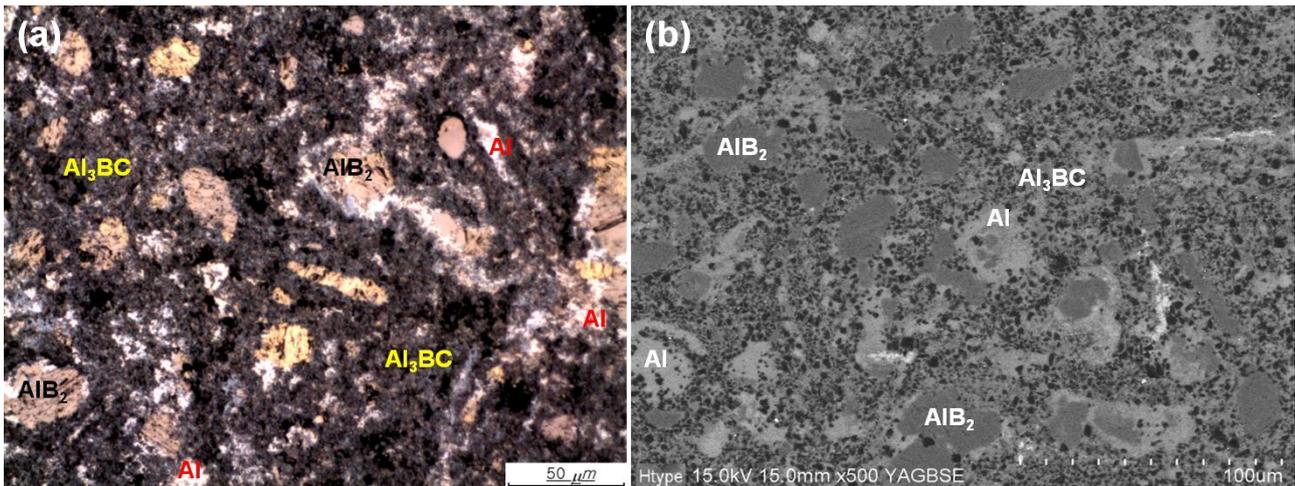


Fig. 7. Optical (a) and back-scattered scanning electron image of composite D after sintering $650^\circ C$ for 2hrs in N_2 : Al_3BC and AlB_2 phases appear as bluish gray and yellowish pink in (a) and light gray dark gray in (b), respectively; Both AlN and Si phases are not indicated.

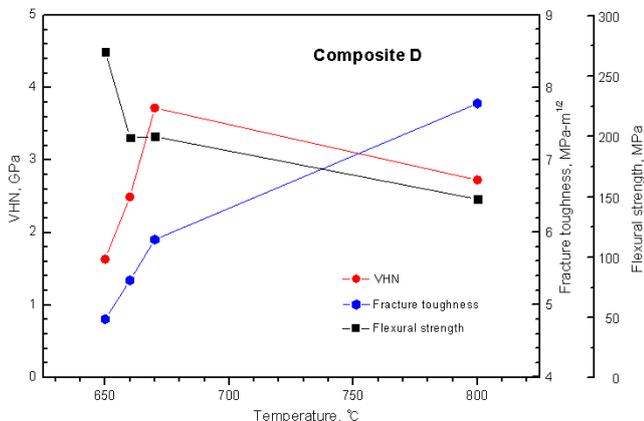


Fig. 8. Microhardness, fracture toughness and biaxial flexural strength of composite D with the sintering temperature; sintering time, 2hrs.

sintering at 800°C for 2hrs, the presence of B_4C peaks in the x-ray diffraction pattern cannot be appreciated. (Fig. 6)

3.3. Mechanical Properties

The composites B (60% B_4C) and D (40% B_4C) prepared with the addition of 10% of Al-12%Si brazing powders showed improved mechanical properties, compared with the composites A and B of the same B_4C contents. The microhardness of the composite A was 7.9GPa but for the composite B, it was 11.1GPa. For the composite D containing less amount of B_4C , the hardness was much smaller than these two, and it was 1.6GPa. The fracture toughness K_{IC} for the composites B and D was 8.81MPa·m^{1/2} and 5.27MPa·m^{1/2}, respectively. However, the biaxial flexural strength was higher for the composite D than the composite B of higher B_4C content; it was 270MPa for the composite D and 200MPa for the composite B, respectively.

Further, the sintering temperature dependence of mechanical properties was investigated for the composite D, which showed the highest flexural strength after sintering at 650°C. Fig. 8 shows the changes in microhardness, fracture toughness and biaxial flexural strength for composite D as a function of sintering temperature up to 800°C. Both hardness and fracture toughness increased with increasing sintering temperature above the melting point of aluminum, while the flexural strength showed a rapid drop. On further increase of the sintering temperature above 670°C the flexural

strength decreased slightly and the hardness decreased, too. The fracture toughness, however, increased to 7.8MPa·m^{1/2}. Initial rapid increase in hardness seems related to the melting of Al to enhance densification, and also in part to the increased amounts of AlN. But with increasing sintering temperature far above the melting point of Al the conversion of hard B_4C particulates into aluminum borocarbide and aluminum boride phases would be accelerated, thereby the hardness has decreased. But, the formation of AlN is enhanced at higher temperature at the same time, the decrease of hardness and flexural strength was not drastic.

The increase of fracture toughness at higher temperature, *i.e.*, at 800°C, would be related mainly to the improved densification. The estimation of pore fraction in the sinter by the areal measurements on optical micrographs for the composite D sintered at 650°C and 800°C indicated a change from 9% to 5%. For the composite D sintered at 800°C, only negligible amounts of B_4C has retained in the matrix.

4. Conclusions

In this study, we attempted synthesis of Al-B-C multi-phase composites at lower temperatures using Al and B_4C as starting materials. The following conclusions have been drawn:

- The mechanical milling of B_4C and Al powder mixtures enhances their sinterability at lower temperatures by promoting the reaction between them. Sintering the milled powder compact at temperature above the melting point of Al did not produce exudation of molten Al when sintered in N_2 . On the other hand, sintering of milled powders in vacuum and Ar, as well as sintering of non-blended powder compact in N_2 , did show insufficient wetting.
- Sintering in nitrogen atmosphere produces fairly dense parts but accompanied the formation of AlN. The addition of liquid phase forming composition, say, Al-12%Si brazing powder, enhances densification and promotes the conversion of B_4C into Al_3BC and AlB_2 phases. It also promote the formation of AlN on sintering in N_2
- Finally, it was demonstrated that Al-B-C multi-phase composites can be synthesized at lower temperature below 800°C in N_2 atmosphere. The

phases that constitute Al-B-C composites can be varied with the composition of starting materials and the sintering temperature.

Acknowledgements

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