

Densification of AlN using boron and carbon additives

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Abstract

The effects of boron and/or carbon on the densification of AlN were investigated. Sintering was promoted by adding the additives simultaneously. Thermo-chemical analysis indicated that a liquid phase composed of aluminum and boron were formed by the borothermal reduction of Al₂O₃ and AlN. Liquid phase sintering is believed to be the reason for the enhanced densification of AlN. The present investigation proposes a method to densify AlN using non-oxide sintering additives having high melting temperature (>2000 °C). The deterioration of AlN refractory is expected to be suppressed by preventing the formation of oxide grain boundary network which is vulnerable to corrosion caused by molten metal.

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1. Introduction

AlN has excellent thermal conductivity, good mechanical properties up to elevated temperatures, excellent creep resistance and high corrosion resistance against molten metals.¹ Accordingly, the preparation of bulk AlN has been intensively investigated during the last decades in order to use as refractories.¹ However, the covalent bonding between Al and N makes the sintering of AlN difficult without the application of sintering additives.² Consequently, additives such as Li₂O, CaO, MgO, MgO–SiO₂, SiO₂, B₂O₃, NiO, Cr₂O₃, Y₂O₃, CaF₂ and Ni have been used in order to promote the densification of AlN.² However, the melting temperature of the oxide or metal additives are often much lower than that of AlN. In addition, oxides such as Al₂O₃ are severely corroded by molten Li, while AlN is thermodynamically stable against molten Li at 500 °C.³ As a consequence, the corrosion of AlN refractory proceeded by the reduction of the oxide grain boundary network and the penetration of molten metal through the reduced pass of this network when contacting with molten metal.⁴ Because oxide

additives induced the deterioration, non-oxide ceramic additives have been highly required for the application of AlN refractory at high temperature and severe conditions.

Boron (melting point, mp: 2092 °C)⁵ and carbon have been widely used as sintering additives of SiC, and the resultant products have been reported to show excellent high temperature properties.⁶ However, the application of boron or carbon additive to AlN has been scarcely reported.^{7–8} Especially, reports using both the additives have not been available. The present research investigated on the effects of boron and carbon additives on the sintering behavior of AlN, and discussed the possible densification mechanisms.

2. Experimental

Table 1 shows the chemical composition of the systems. In the abbreviation, A, B and C represent AlN (Grade F, Tokuyama corp., Tokyo, Japan, $d_{50} = 1.23 \mu\text{m}$), boron (Amorphous boron, H.C. Starck, Goslar, Germany) and carbon which was supplied from a phenolic resin (Phenolite J-325, Dainippon Ink, Inc., Tokyo, Japan, ceramic yield: 37.4%), respectively. The raw materials were mixed intensively by a planetary mill with ethanol at 150 rpm for 4 h using SiC jar and SiC ball. The slurries were dried at 70 °C with stirring and the obtained powders were screened through a 120-mesh sieve. Then, the powder mixtures

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Table 1
Chemical composition of the systems.

Abbreviation	Weight (g)		
	AlN	B	Phenolic resin
AlN	9.78	0	0
AB	9.78	0.14	0
AC	9.78	0	0.73
ABC	9.78	0.14	0.73

were hot pressed (FVHP-1-3, Fuji Dempa Kogyo Corp., Niitaka, Japan, heating rate: 75 °C/min up to 1500 °C, 30 °C/min above 1500 °C, pressure: 20 MPa) at 1570–2100 °C for 2 h in Ar with *in situ* monitoring of the shrinkage.

After sintering, the density of the specimens was analyzed using Archimedes' method. The density value used for AlN, B and amorphous C was 3.26, 2.34 and 1.95 g/cm³, respectively.^{9–11} Phase formation during sintering was analyzed by X-ray powder diffraction (XRD, JDX-3500, JEOL, Tokyo, Japan) using Cu K α radiation. The microstructure of the specimens was analyzed by a scanning electron microscope (SEM, JSM-6700F, JEOL, Tokyo, Japan) after etching using Murakami's reagent. The chemical composition and distribution of the additives in the specimens were measured using an electron probe microanalyzer (EPMA, JXA8900RL, JEOL). Spatial resolution of the EPMA equipment was 0.5 μ m.

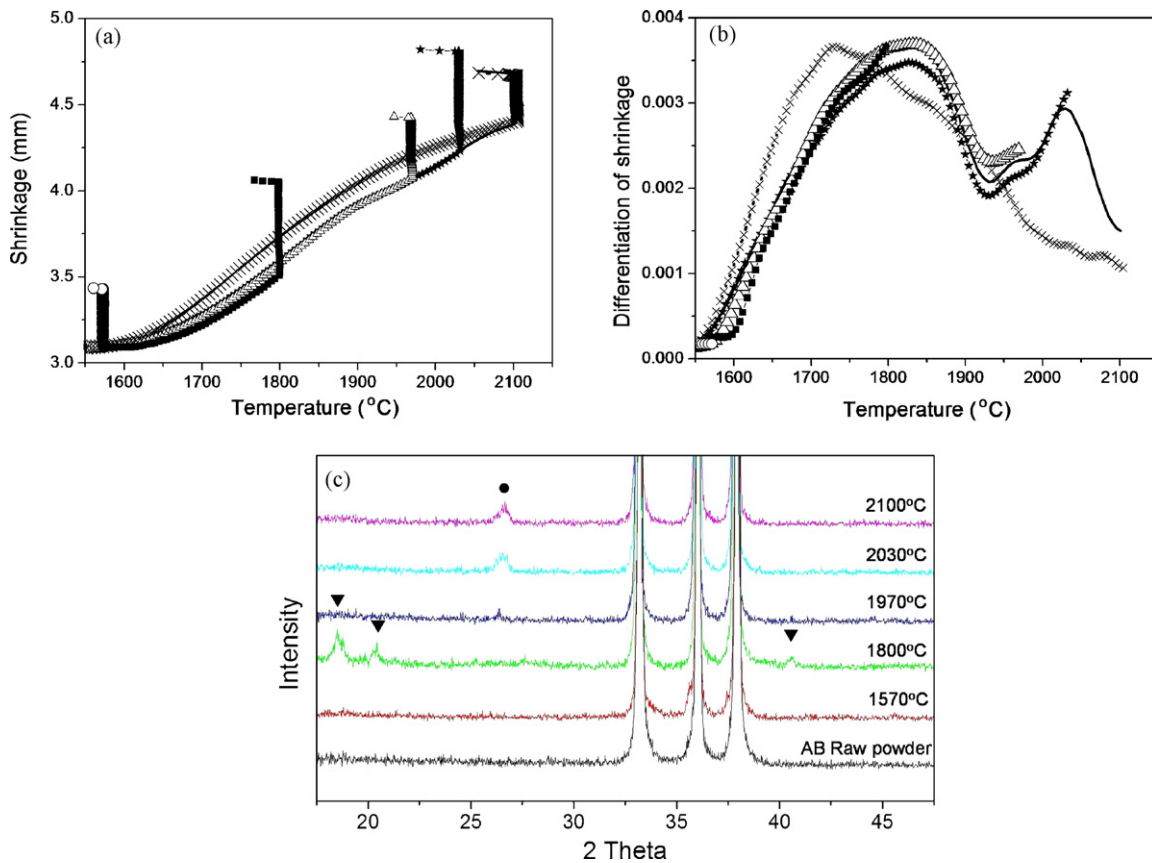


Fig. 2. (a) sintering shrinkage curve during hot pressing for 2 h under 20 MPa pressure in Ar, (b) differentiation curve of the data shown in (a) ((\times) AlN, others: the AB system at (\circ) 1570 °C, (\blacksquare) 1800 °C, (Δ) 1970 °C, (\star) 2030 °C, ($-$) 2100 °C) and (c) XRD data of the AB system ((\bullet) BN, (\blacktriangledown) unidentified peaks and others: AlN). The samples were heat treated at 1500 °C for 30 min in vacuum without pressure before hot pressing (heating rate: 30 °C/min).

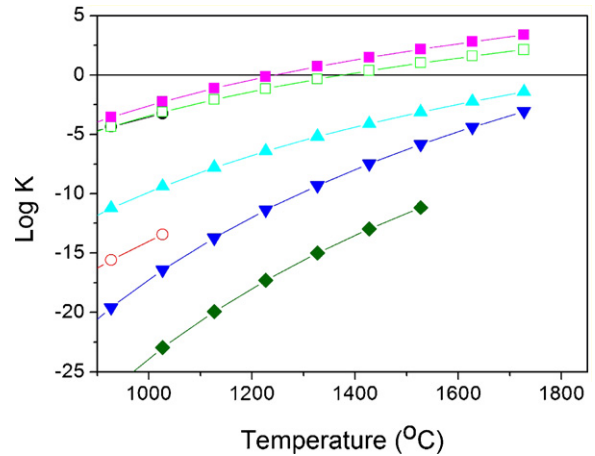


Fig. 1. Logarithm of the equilibrium constant vs. temperature (\bullet) reaction (1), (\circ) reaction (2), (\blacklozenge) reaction (3), (\square) reaction (4), (\blacktriangledown) reaction (5), (\blacktriangle) reaction (6) and (\blacksquare) reaction (7).

3. Results and discussion

AlN may react with boron and/or carbon, *e.g.*, as follows:

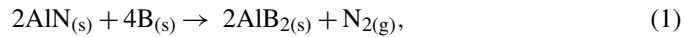


Table 2
Relative density of hot-pressed samples for 2 h under 20 MPa pressure in Ar.

Sintering condition	Relative density
AlN, 2100 °C	97.7
AB, 1800 °C	76.5
AB, 1970 °C	88
AB, 2030 °C	94.4
AB, 2100 °C	95.7
AC, 1750 °C	65.0
AC, 1950 °C	90.5
AC, 2100 °C	98.1
ABC, 1810 °C	77.0
ABC, 1950 °C	97.7
ABC, 2040 °C	98.8
ABC, 2100 °C	98.1

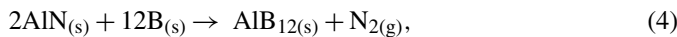
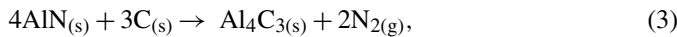
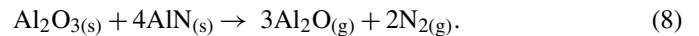


Fig. 1 shows the change of the equilibrium constant of reaction (1)–(7) with temperature. The thermo-chemical data of the components were obtained from a reference.¹² The values of reaction (1) and (2) could be calculated up to 1027 °C because of the decomposition of AlB_2 into a liquid and AlB_{12} .⁵ Among the reactions described above, the sign of reaction (4) and (7)

became positive above 1377 and 1244 °C, respectively. The results indicated that the reaction temperature to form aluminum borides decreases when using both the additives by borothermic reduction process.

Fig. 2 shows the sintering shrinkage of AlN and AlN containing boron additive (termed AB) during hot pressing. The differentiation of shrinkage curve indicated that the sintering shrinkage of AlN began to occur below 1600 °C and the rate increased with temperature up to 1730 °C (Fig. 2(b)). Al_2O_3 and oxynitrides, which were formed on the surface of AlN powder, were reported to enhance the densification of AlN above 1500–1650 °C.¹¹ The shrinkage rate decreased above 1730 °C, which was presumably caused by the decomposition of Al_2O_3 above this temperature¹³:



AlN was reported to decompose above 1950 °C in Ar¹⁴:



However, the decomposition did not have strong effect on the sintering shrinkage of AlN (Fig. 2(b)). A small peak was observed at 2030 °C (Fig. 2(b)) most probably by the melt of residual Al_2O_3 (mp: 2053 °C).^{10,15} The densification of AlN continued during sintering at 2100 °C for 2 h (Fig. 2(a)) and the relative density of the specimen was 97.7%.

Three peaks were detected at 1800, 1960 and 2030 °C in the differentiated shrinkage curve of the AB system (Fig. 2(b)). Boron suppressed the densification of AlN below 1800 °C (Fig. 2(a) and (b)). The sign of the equilibrium constant of the

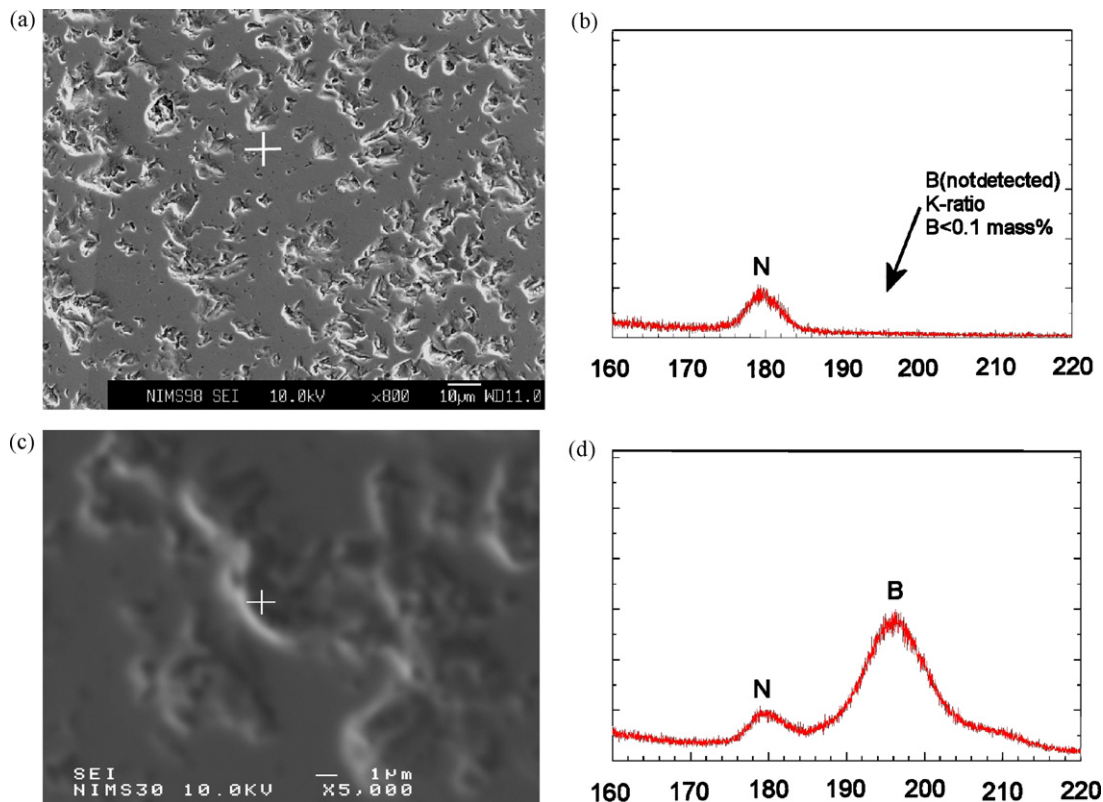
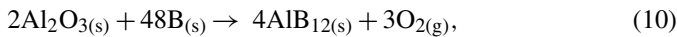


Fig. 3. Morphology and chemical composition of the AB system: (a and b) AlN grain and (c and d) grain containing boron and nitrogen.

following reaction:



was negative up to 2027 °C, indicating that the loss of Al_2O_3 by reaction (10) did not occur below 1800 °C. Al_2O_3 was reported to react with B_2O_3 to form $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$.¹⁶ The reaction is believed to induce the depletion of Al_2O_3 in the AB system, which presumably caused the shift of the first peak in Fig. 2(b) from 1730 to 1800 °C. The shrinkage at about 1960 °C is believed to be promoted by the formation of a liquid phase composed of $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$ (mp: 1965 °C).¹⁷

AlB_{12} , which was possibly formed by reaction (4), might melt and contributed to the third shrinkage above 2000 °C (Fig. 2(b)). The melting temperature of AlB_{12} (2050 °C)⁵ might be affected by impurities such as excess boron or Al_2O_3 . The thermal decomposition of AlN may also promote the third shrinkage of the AB system. Aluminum and nitrogen vapor, which was formed above 1950 °C by reaction (9), possibly reacted with boron to form AlB_2 , AlB_{12} and BN ¹⁸:



AlB_2 decomposes into a liquid and AlB_{12} at this condition, and AlB_{12} also melt above 2050 °C.⁵ Fig. 2(c) shows the XRD data of the AB system. The presence of amorphous boron was not detected in the raw powder mixture. Aluminum borides in the sintered specimens were also not clearly identified presumably due to the formation of liquid phases. A peak which indicated the formation of BN by reaction (13) was observed at and above 1970 °C. However, the peak may be originated from graphite which was incorporated from the graphite furnace. The X-ray reflections of BN and graphite resemble each other due to the similarity of their lattice parameter (C–C distance: 1.42 Å, B–N distance: 1.45 Å) and crystalline structure (hexagonal).¹⁰ Accordingly, EPMA analysis was performed to confirm the formation of BN (Fig. 3). Boron was not distinctly incorporated into the AlN grains of the AB system after densification (Fig. 3(a) and (b)). The localization of boron and nitrogen was clearly detected in small and dark grains which were presumably located at the pocket area in between large AlN grains (Fig. 3(c) and (d)).

Fig. 4 shows the sintering shrinkage of AlN containing carbon additive (termed AC). Compared to AlN , the onset temperature of shrinkage increased to 1625 °C and densification was suppressed when adding carbon additive (2.7 wt% after pyrolysis). Carbon suppressed the densification of AlN below 1850 °C by reducing the amount of oxide grain boundary phase, e.g., as

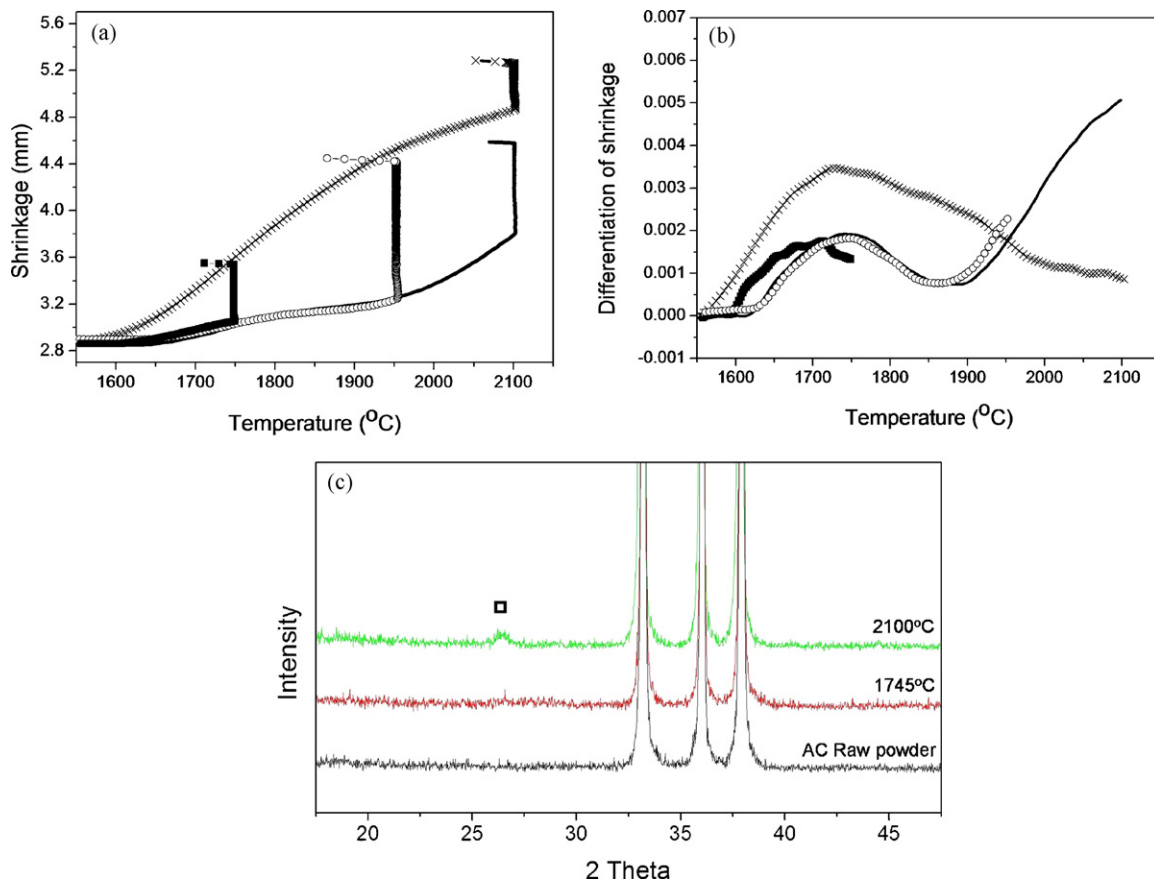
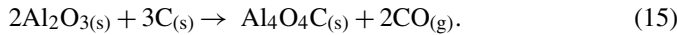
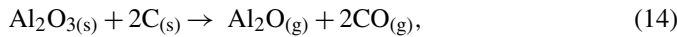


Fig. 4. (a) sintering shrinkage curve during hot pressing for 2 h under 20 MPa pressure in Ar, (b) differentiation curve of the data shown in (a) ((\times) AlN , others: the AC system at (\blacksquare) 1745 °C, (\circ) 1950 °C, (—) 2100 °C) and (c) XRD data of the AC system (\square) carbon and others: AlN). The samples were heat treated at 1500 °C for 30 min in vacuum without pressure before hot pressing (heating rate: 30 °C/min).

follows^{19–20}:



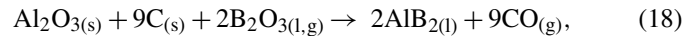
The formation of $\text{Al}_4\text{O}_4\text{C}$ was reported to become intensive at and above 1500°C .²¹

The differentiated shrinkage curve of the AC system (Fig. 4(b)) exhibited two peaks. Similar to the case of AlN, the first peak occurred at 1740°C , but with a lower intensity due to the loss of Al_2O_3 and aluminum oxynitride by carbothermal reduction. The second peak at $1870\text{--}1900^\circ\text{C}$ was presumably induced by the formation of a liquid phase. The eutectic temperature between Al_2O_3 and $\text{Al}_4\text{O}_4\text{C}$ formed by reaction (15) was reported to be 1850°C .²² The density of the AC system was 90.5% after hot pressing at 1950°C for 2 h, which increased to 98.1% at 2100°C . Densification continued at 2100°C (Fig. 4(a)).

Fig. 4(c) shows the XRD peaks of the AC system. The formation of $\text{Al}_4\text{O}_4\text{C}$ was not detected after sintering at 1745°C presumably due to the insufficient amount. After sintering at 2100°C , a broad peak was formed at 26.5° , indicating the beginning of crystallization of graphite. The graphitization of carbon obtained by the pyrolysis of phenolic resins was reported to become distinct above 2100°C .²³

In contrast to AlN, the AB and AC systems, the densification of AlN containing boron and carbon additives (termed ABC) was nearly completed at 2080°C during the increase of temperature (Fig. 5(a)), and dense specimens were obtained after hot pressing at 1950°C for 2 h (Table 2). Boron and carbon additives promoted the densification of AlN when applied simultaneously. The differentiation of the shrinkage curve showed a three-step sintering behavior of the ABC system (Fig. 5(b)). EPMA analysis showed that boron was not distinctly incorporated into the AlN grains in the ABC system (Fig. 6), indicating that presumably boron did not promote solid state sintering of AlN.

The onset temperature of shrinkage of the ABC system was higher than that of monolithic AlN (1700°C vs. 1600°C , Fig. 5(b)) presumably due to the loss of Al_2O_3 by borothermal reduction processes, *e.g.*, as follows^{24–25}:



The equilibrium constant of reaction (19) was calculated to become positive above 1085°C , indicating that the reduction

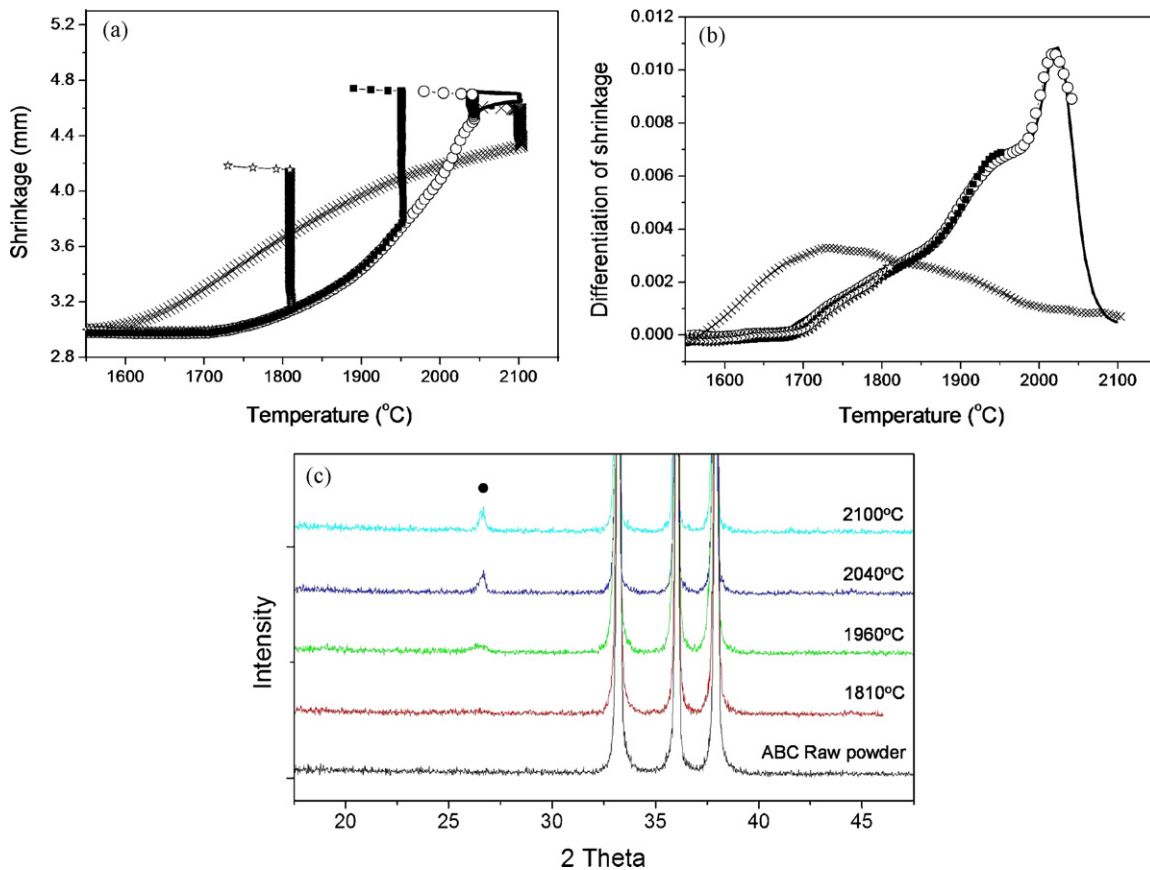


Fig. 5. (a) sintering shrinkage curve during hot pressing for 2 h under 20 MPa pressure in Ar, (b) differentiation curve of the data shown in (a) ((\times) AlN, others: the ABC system at (\star) 1810°C , (\blacksquare) 1960°C , (\circ) 2040°C , ($-$) 2100°C) and (c) XRD data of the ABC system ((\bullet) BN, others: AlN). The samples were heat treated at 1500°C for 30 min in vacuum without pressure before hot pressing (heating rate: $30^\circ\text{C}/\text{min}$).

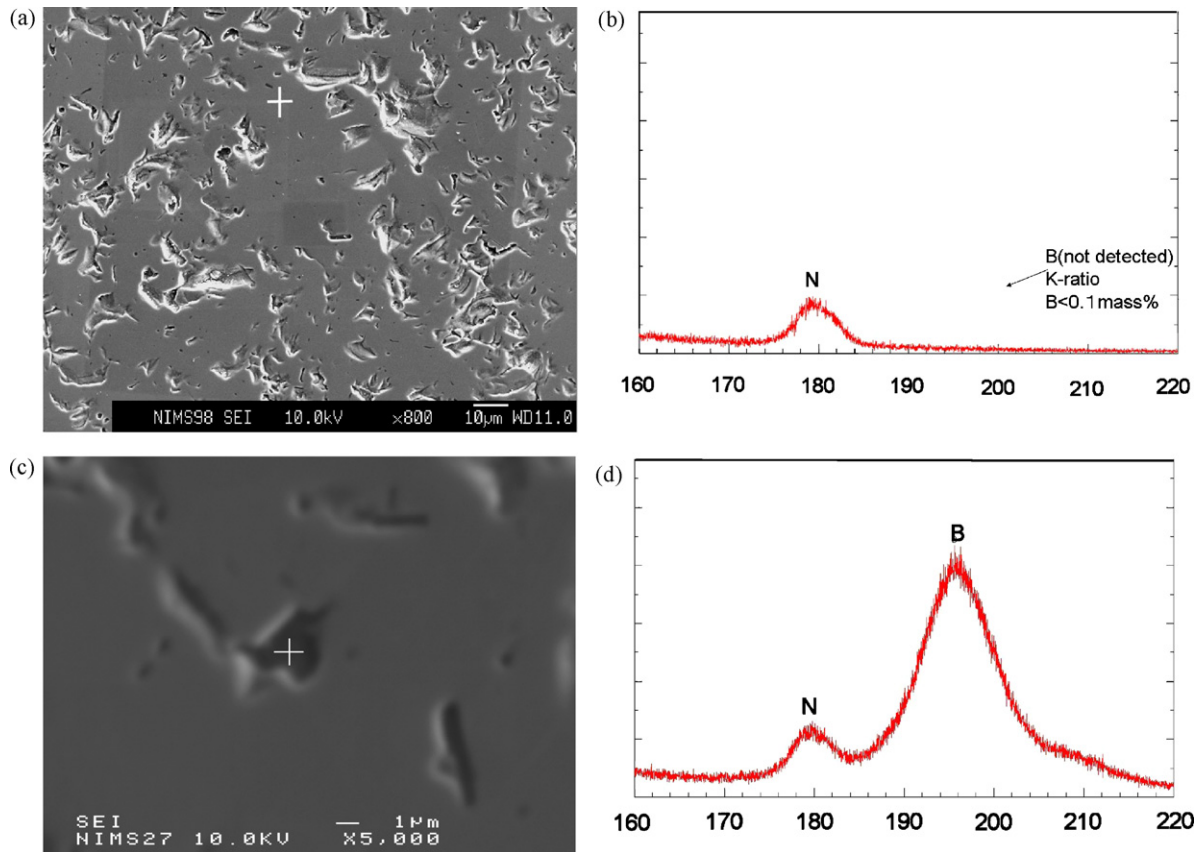


Fig. 6. Morphology and chemical composition of the ABC system: (a and b) AlN grain and (c and d) grain containing boron and nitrogen.

temperature of Al_2O_3 decreased by the addition of boron and carbon simultaneously.

The ABC system showed a more rapid sintering shrinkage than AlN above 1850°C (Fig. 5(b)). Boron and carbon reacted to form B_4C , but most probably the reaction did not have strong effect on the densification of AlN because the melting temperature of B_4C is very high (2350°C).¹⁰ Instead, a liquid phase originated from the decomposition of AlB_2 which was formed, e.g., by reactions (2) and (16)–(18) is believed to promote the densification of AlN.¹⁶

The XRD data of the ABC system indicated the formation of BN by reaction (13) at and above 1960°C (Fig. 5(c)). EPMA data also showed the formation of small and dark grains composed of boron and nitrogen which presumably located at the pocket area in between large AlN grains (Fig. 6(c) and (d)). The decomposition of AlN above 1950°C is believed to induce the formation of BN and aluminum borides simultaneously by reactions (11)–(13). The rapid shrinkage of the ABC system above 2000°C was most probably induced by the melting of aluminum borides similar to the case of the AB system. Different from the

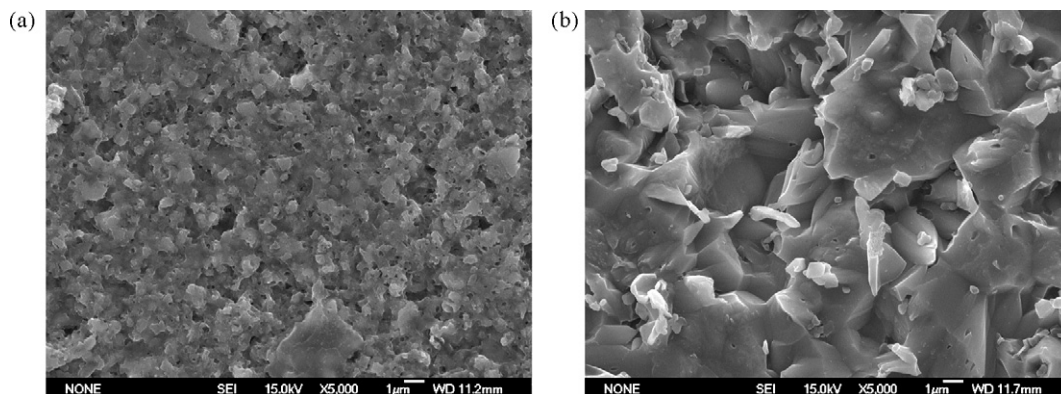


Fig. 7. Morphology of the ABC system after etching with Murakami's reagent. Sintered for 2 h under 20 MPa pressure in Ar at (a) 1810°C and (b) 2100°C .

AB system, the formation of the aluminum borides was promoted in the ABC system by borothermal reduction such as reactions (7), (16), (17), (18) and (19).

The grain growth of the ABC system did not strongly occur at 1810 °C (Fig. 7(a)) when considering the average particle size of the raw powder ($d_{50} = 1.23 \mu\text{m}$). On the other hand, the grain growth became distinct after densification at 2100 °C (Fig. 7(b)). The liquid phase is believed to promote growth of AlN grains together with densification.

The corrosion of oxide grain boundary by molten metal has been one of the key problems for the application of AlN refractory in metal industry. Because of the borothermic reduction of alumina during densification, AlN sintered with boron and carbon additives are expected to have non-oxide grain boundary network. Accordingly the penetration of molten metal through the reduced pass of oxide grain boundary network is expected to be suppressed.

4. Summary

The densification of AlN was enhanced when adding boron and carbon additives simultaneously. Dense specimens were obtained by hot pressing at 1950 °C. Thermo-chemical analysis indicated that the reduction of Al₂O₃ and AlN to aluminum borides (AlB₂ and AlB₁₂) was promoted by borothermal reaction when adding both the additives. The beneficial effects of the additives are attributed to the formation of a liquid phase originated from the melting of the aluminum borides.

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