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Synthesis and X-ray crystallography of aluminium boron carbide, $Al_8B_4C_7$

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A new compound of aluminium boron carbide, $Al_8B_4C_7$, has been successfully synthesized. Single-crystal and powder X-ray crystallographic data on $Al_8B_4C_7$ are given, and the possible space group is identified as $P6_3cm$, $P\bar{6}c2$, or $P6_3/mcm$. Powder X-ray diffraction lines are indexed in the 2θ-range from 10° to 110°. The unit cell dimensions obtained from a least-square fit computer program are: $a = 5.906 \pm 0.002$ Å, $c = 15.901 \pm 0.001$ Å, $V = 480.43 \pm 0.03$ Å^3. In addition, the possibility of a wide range variance of boron content in this compound is denied.

1. Introduction

It has been reported [1–3] that the boric compounds such as B_4C, AlB_2 promote the dentification of SiC ceramics. Recently a new compound of aluminum boron carbide, $Al_8B_4C_7$, has been found, during compatability in the $SiC–Al_4C_3–B_4C$ system [4]. On the other hand, Matkovich *et al.* [5] have previously found a compound of $Al_4B_{1-3}C_4$ for which they reported a wide variance of boron content. However, it is reported here that this compound should correspond more closely to a stoichiometry $Al_8B_4C_7$ than to $Al_4B_{1-3}C_4$.

X-ray powder diffraction lines of $Al_8B_4C_7$ in the 2θ-range from 10° to 110° are given with their indices, calculated planar spacings, calculated and observed 2θ values, and observed relative intensity distributions. The possible space group has been identified as $P6_3$ cm, $P\bar{6}c2$ or $P6_3/mcm$ using an X-ray single-crystal diffraction technique. The unit cell dimensions obtained by a least-square fit computer program are given as $a = 5.906$ Å, $b = 5.906$ Å, $c = 15.901$ Å and $V = 480.43$ Å^3.

2. Synthesis

An attempt was made to synthesize a compound of aluminum boron carbide, $Al_8B_4C_7$. Al_4C_3 and B_4C powders (from Alfa Products Co. of size − 100 mesh) were used as starting materials. They were mixed according to the composition of $Al_8B_4C_7$ with a polyethylene ball mill. The mixture of about 3 g was packed into a graphite die (15 mm in diameter) and heated at a rate of 50° C min^{-1} up to a temperature of 1800° C in an argon atmosphere. The specimen was kept at that temperature for a few minutes and then cooled slowly (at a rate of 7° C min^{-1}) from 1800° C to room temperature. In this procedure, hot-pressing of the specimen was avoided so as to prevent the extrusion of the specimen from the die.

Also, another attempt was made to synthesize the pure aluminum boron carbide, $Al_8B_4C_7$, directly from the aluminum, boron and carbon powders rather than from the Al_4C_3 and B_4C powders which include a small amount of impurity. Pure aluminum (of 99.99% purity from the Pure Chemistry Co. Ltd, Japan), pure boron (of 99.7% purity from Herman C. Starck Co. Ltd, Berlin) and pure carbon (ash content less than 10 ppm, carbon for spectrum analysis from the Nippon Carbon Co. Ltd, Japan) were used as the starting materials for this purpose. The mixed powder of composition $Al_8B_4C_7$ was packed into a graphite die and heated up to a temperature of 1400° C at a rate of 45° C min^{-1} in an argon atmosphere. The specimen was then kept at 1400° C for 15 minutes in order that aluminum and boron may react with carbon to form pure Al_4C_3 and B_4C compounds. The specimen was further heated from 1400° C to 1830° C at a rate

0022–2461/80/123036–05$02.50/0

of 45° C min^{-1} in an argon atmosphere, and was maintained at 1830° C for 30 minutes. After this heat-treatment, the sample was cooled down by turning off the electric power of the furnace. The melting point of this compound was about 1900° C. After cooling, the recovered specimen was crushed and powdered for the X-ray powder diffraction investigation.

The single crystals of $Al_8B_4C_7$ were successfully synthesized by the following procedure. The pure powders of aluminum, boron and carbon were mixed together according to the composition of $Al_8B_4C_7$. This mixture was baked to 1400° C at a rate of 45° C min^{-1}, was kept at 1400° C for 15 minutes, was heated further from 1400° C to 2000° C at a rate of 45° C min^{-1} in an argon atmosphere, and was then cooled slowly down from 2000° C to 1820° C at a rate of 3° C min^{-1} in order to grow many single crystals from the melt. After cooling to 1820° C, the electric power of the furnace was turned off. As a result of this heat-treatment, many single crystals were found inside the specimen, which exhibited a well-developed (0 0 1) surface of hexagonal plate, appeared transparent, and were yellow in colour.

3. X-ray crystallographic data

3.1. Single-crystal diffraction data

A crystal of good size, 0.2 mm x 0.2 mm x 0.02 mm, was selected under an optical microscope for X-ray single-crystal diffraction analysis. The unit cell dimensions and space group were revealed by the single-crystal method using a Weissenberg camera with CuKα-radiation and using a precession camera with MoKα-radiation. As a result, the approximate unit cell dimensions were found to be $a = 5.90$ Å, $b = 5.90$ Å and $c = 15.9$ Å in a hexagonal lattice. The conditions limiting possible reflections are as follows:

$hkil$: No condition

$hh\bar{2}hl$: No condition

$h\bar{h}0l$: $l = 2n$

On the basis of the systematic extinctions [6], the possible space group of this crystal were shown to be either $P6_3cm$, $P\bar{6}c2$ or $P6_3/mcm$. The precession photographs of $(h0l)$ and $(h1l)$ planes taken by MoKα radiation at 40 kV x 30 mA, $\mu = 25°$ are shown in Figs 1 and 2, respectively. As is evident from Figs. 1 and 2, the diffraction patterns of the $00l$, $\pm 30l$, $\pm 60l$, $11l$, $41l$, $\bar{2}1l$ and $\bar{5}1l$ rows are far stronger than the others. If a small hexagonal sub-cell of $a = 3.41$ Å, $b = 3.41$ Å and $c = 15.9$ Å is considered, one can regard these strong diffraction patterns as those from this small sub-cell. A relation between a sub-cell of $a = 3.41$ Å and super lattice of $a = 5.90$ Å is schematically shown by two dimensional lattice

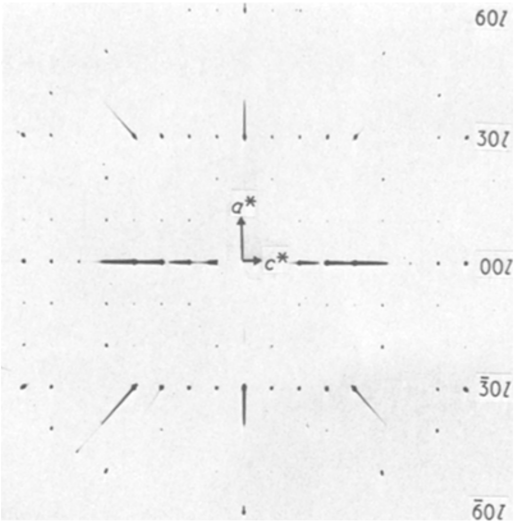

Figure 1 A precession photograph on the $(h\,0\,l)$ plane of an $Al_8B_4C_7$ single-crystal. The reflections of the $0\,0\,l$, $\pm\,3\,0\,l$ and $\pm\,6\,0\,l$ rows are far stronger than the others.

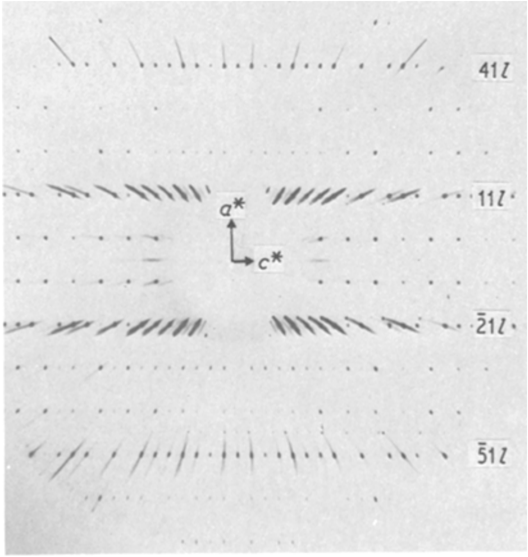

Figure 2 A precession photograph on the $(h\,1\,l)$ plane of $Al_8B_4C_7$ taken by MoKα radiation. The reflections of the $1\,1\,l$, $4\,1\,l$, $\bar{2}\,1\,l$ and $\bar{5}\,1\,l$ rows are far stronger than the others.

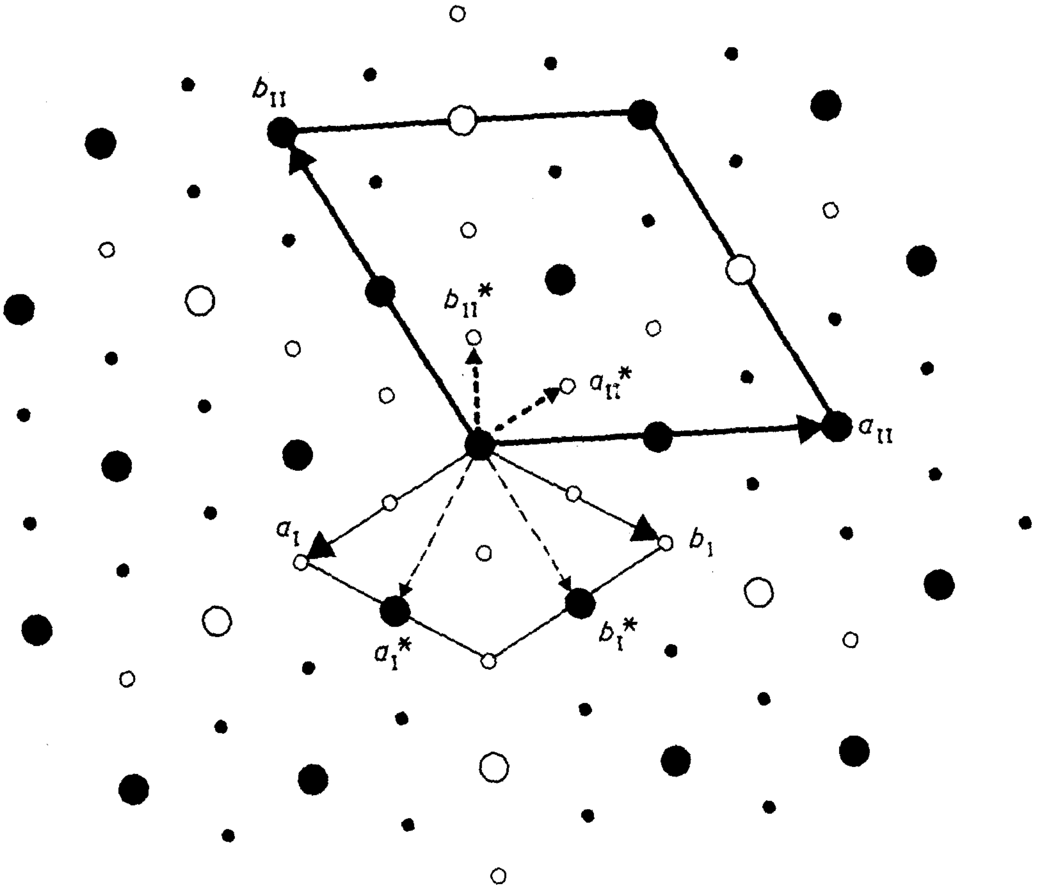

Figure 3 A schematic relation between sub-cell ($a = 3.41$ Å) and super-cell ($a = 5.90$ Å) of $Al_8B_4C_7$ projected on the (0 0 1) plane. Suffixes I and II indicate the sub-cell and super-cell, respectively. The corresponding reciprocal lattices are shown by an asterisk. The rows of strong reflection spots corresponding to sub-cell are represented by large open circles and large dots. The open circles mean the reciprocal lattice rows which bear a condition limiting possible reflections of $l = 2n$.

projected on (0 0 1) shown in Fig. 3. A super lattice is three times as large as a sub-cell. The strong diffraction patterns from the sub-cell suggest that the crystal structure of $Al_8B_4C_7$ comprises three sub-cells which are of similar structural unit.

3.2. X-ray powder diffraction data

The X-ray powder diffraction data was taken using a Rigaku Geigerflex with CuKα radiation together with an Ni-filter and a scintillation counter detector scanning 2θ–1° per 4 minutes. The X-ray diffraction peaks were collected in the range of 2θ from 10° to 110°, and were then indexed by taking account of the primary unit cell dimensions.

The unit cell dimensions were calculated by a least-square fit computer program of Appleman and Evans [7]. Twenty-eight reflections, which gave clear intensity peaks and which were not superimposed on other reflections, were selected for the least-square calculation. The refined unit cell dimensions are as follows:

$$a = 5.906 \pm 0.002 \text{ Å}$$

$$c = 15.901 \pm 0.001 \text{ Å}$$

$$V = 480.43 \pm 0.03 \text{ Å}^3.$$

The X-ray powder diffraction data of the index, the calculated planar spacing d_c, calculated $2\theta_c$, observed $2\theta_0$, and observed intensity I_0 are given in Table I.

4. Discussion

A comparison of these X-ray powder data of $Al_8B_4C_7$ with those of Matkovich *et al.* [5] for

TABLE I X-ray powder diffraction data of $Al_8B_4C_7$. d_c, $2\theta_c$, $2\theta_0$ and I_0 represent the calculated planar spacings, calculated 2θ-values, observed 2θ-values, and observed diffraction intensities, respectively.

h k l	d_c	$2\theta_0$	$2\theta_c$	I_0
0 0 2	7.951	11.12	11.119	53
0 0 4	3.975	22.35	22.345	24
1 1 0	2.953	30.24	30.236	36
1 1 1	2.904	30.77	30.766	100
0 0 6	2.650	33.80	33.793	43
1 1 3	2.580	34.75	34.743	32
1 1 4	2.371	37.93	37.920	65
1 1 5	2.164	41.70	41.700	14
0 0 8	1.988	45.61	45.601	40
1 1 6	1.972	45.97	45.972	18
1 1 7	1.801	50.66	50.654	28
3 0 0	1.705	53.70	53.710	76
3 0 2	1.667	55.03	55.034	3
3 0 4	1.567	58.87	58.883	6
1 1 9	1.516	61.05	61.064	11
2 2 1	1.470	63.19	63.184	10
3 0 6	1.434	64.98	64.981	12
2 2 3	1.422	65.57	65.570	4
3 1 0	1.419	65.76	65.765	1
2 2 4	1.384	67.62	67.621	11
2 2 5	1.339	70.23	70.214	3
1 1 11	1.298	72.78	72.776	8
3 0 8	1.294	73.07	73.051	27
2 2 6	1.290	73.32	73.329	17
2 2 7	1.238	76.94	76.946	5
1 1 12	1.209	79.14	79.154	8
5 $\bar{1}$ 1	1.114	87.53	87.534	7
4 1 3	1.092	89.67	89.686	2
4 1 4	1.075	91.57	91.569	8
4 1 7	1.002	100.50	100.50	3
1 1 15	0.998	101.07	101.07	3
2 2 12	0.986	102.70	102.71	5
3 3 0	0.984	102.96	102.97	10
4 1 9	0.944	109.41	109.42	3
2 2 13	0.942	109.70	109.71	3

$Al_4B_{1-3}C_4$, shows apparent differences in the X-ray diffraction intensity distributions even though account is taken of the preferred orientation effect of Matkovich's sample on the (0 0 *l*) reflections. So far it is not definitely known why there are differences between $Al_8B_4C_7$ and $Al_4B_{1-3}C_4$.

On the other hand, Matkovich *et al.* have reported the existence of a wide variance in the boron content, ranging from 1 to 3. An attempt was made in this work to determine whether such a wide variance of boron content exists around the compound of $Al_8B_4C_7$. As the starting materials, the pure aluminum, boron and carbon powders were mixed according to the composition of $Al_4B_1C_4$, $Al_4B_2C_4$ and $Al_4B_3C_4$, respectively, and these specimens were each heated to 1830° C in the same process as that mentioned in the latter half of Section 2. The resulting reaction products of each specimen were identified using the X-ray powder diffraction method. When the chemical composition of starting materials shifted a little from the stoichiometry $Al_8B_4C_7$ to the direction of graphite and/or Al_4C_3 and/or B_4C, the minor phase of graphite, Al_4C_3, B_4C appeared according to the direction and amount of deviation. The specimen of $Al_4B_1C_4$ composition was mainly composed of $Al_8B_4C_7$ with the minor phase of graphite and aluminum carbide Al_4C_3. The $Al_4B_2C_4$ specimen produced $Al_8B_4C_7$ with a trace of graphite. The $Al_4B_3C_4$ was composed of $Al_8B_4C_7$ and a trace of graphite and B_4C. These results are given in Table II. In addition, each of $Al_8B_4C_7$ specimens, which were synthesized from

TABLE II The chemical reactions of $Al_4B_1C_4$, $Al_4B_2C_4$ and $Al_4B_3C_4$ mixtures at 1830° C.

Chemical composition of starting materials	Products detected by X-ray diffraction methods	Chemical reactions at 1830° C
$Al_4B_1C_4$	$Al_8B_4C_7$ graphite Al_4C_3	$4(Al_4B_1C_4) \rightarrow Al_8B_4C_7 + 3C + 2Al_4C_3$
$Al_4B_2C_4$	$Al_8B_4C_7$ graphite	$2(Al_4B_2C_4) \rightarrow Al_8B_4C_7 + C$
$Al_4B_3C_4$	$Al_8B_4C_7$ graphite B_4C	$4(Al_4B_3C_4) \rightarrow 2(Al_8B_4C_7)$ + graphite + B_4C
$Al_8B_4C_7$	$Al_8B_4C_7$	

the starting materials of $Al_4B_1C_4$, $Al_4B_2C_4$ and $Al_4B_3C_4$, gave the same X-ray diffraction intensity distribution and did not cause any positional shift of the powder diffraction peaks, i.e. there was no shift of the 2θ-diffraction angle. From these experimental results, it is concluded that there is no wide variance of boron content in the $Al_8B_4C_7$ compound as long as the same synthetic procedure mentioned earlier is adopted.

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