PREPARATION AND CHARACTERIZATION OF AN ALUMINUM/ALUMINUM DIBORIDE COMPOSITE

R. Orbán[1*], I. Cora[1], I. Dódony[1]

[1]*Institute of Geography and Earth Sciences, Department of Mineralogy, Eötvös Loránd University, Pázmány Péter sétány 1/C, Budapest, Hungary, H-1117*
**orban.richard@gmail.com*

Keywords: Aluminum matrix composite (AMC), aluminum diboride (AlB_2) particles, aluminothermic reaction, borax.

Abstract

Al matrix composite reinforced with AlB_2 particles was prepared in this study by aluminothermic reduction of boron from borax ($Na_2B_4O_7*10H_2O$) at 900 °C. Polarized light microscopy, scanning electron microscopy and X-ray diffraction were used to characterize the products. Tabular habit AlB_2 particles precipitated in aluminum matrix. Aspect ratio of AlB_2 flakes is around 10. Utilization of borax instead of elemental boron as starting material makes this process more economical than previous methods, however enhancement of efficiency is still a challenge.

1 Introduction

AlB_2 particles are known to enhance wear resistance of aluminum diboride reinforced aluminum matrix composites (*e.g.* [1],[2]). Common raw materials for functionally graded Al/AlB_2 composites are elemental aluminum and boron. However the price of elemental boron is extremely high.

The pioneers of aluminothermic reduction of boron from its oxide are Wöhler and Saint-Claire Deville [3]. Hall and Economy [4] suggested producing Al/AlB_2 composite via aluminothermic reduction of boron from boron oxide and precipitating AlB_2 particles in metallic solution by controlled cooling. AlB_2 crystallizes from Al–B solution in the temperature range of 660–972 °C and melts incongruently above 972 ± 5 °C [5]. This process requires high temperature and the boron as raw material is considerably expensive. We aimed to find a cheaper receipt to produce AlB_2. The most common boron bearing mineral, that can serve as starting material, is the borax ($Na_2B_4O_7*10H_2O$). Borax proved to be ideal for AlB_2 synthesis and for Al/AlB_2 composite production. We prepared Al matrix composite reinforced with AlB_2 particles. AlB_2 particles directly crystallized from metallic solution via the aluminothermic reduction of boron from borax melt. The products of this reaction were characterized by polarized light- and scanning electron microscopy (SEM), furthermore crystal structure of synthesized AlB_2 was refined using single crystal X-ray diffraction (SXRD) technique.

2 Materials and analysis

2.1 Materials, synthesis and chemical reactions

Pure aluminum and borax were used as starting materials in the experiments. Crystallization of AlB_2 particles in Al–B solution was induced by the aluminothermic reduction of boron from borax melt.

The following steps were applied:

1. Borax (90 w%) and a piece of aluminum were melt together in a porcelain mortar.
2. The melt was heated up to the temperature of the reaction (900 ± 20 °C).
3. The melt was kept at the temperature of reaction for 3 hours.
4. The mortar was taken out from the furnace and the materials were let to cool down to room temperature.

Reactions were carried out in air atmosphere. Controlled parameters were the amounts of materials, the temperature and the duration of reaction.

The aluminum and the boron oxide of borax react above 660 °C (*Equ.* 1):

$$2Al_{(liq)} + nB_2O_{3(liq)} = 2B_{(liq)} + (B_{2n-2}O_{3n-2}, Al_2O_3)_{(liq)} \quad (1)$$

The B and Al_2O_3 components are in the Al and B_2O_3 solvents, respectively. Crystallization of the AlB_2 begins when boron becomes saturated in the high-temperature solution. As a function of temperature the following reaction (*Equ.* 2) was deduced (at 660 °C < $T \leq$ 972 °C) [5],[6]:

$$6\,Al_{(liq.)} + 3\,B_2O_{3(liq.)} = 2\,AlB_{2(sol.)} + Al_4B_2O_{9(sol.)} \quad (2)$$

AlB_2 precipitates in the aluminum melt matrix and aluminum borate crystallizes in the borax melt.

2.2 Sample preparation and analysis

The residue of borax is solvable in distilled water. Polished section was prepared from one part of the water-insoluble products, whereas the other part was analyzed by X-ray powder diffraction (XRPD). Texture of polished sections was studied by reflected polarized light microscopy and scanning electron microscopy (SEM).

AlB_2 crystals were extracted by hydrochloric acid (aluminum is soluble in it). A slab AlB_2 crystal was measured using single crystal X-ray diffraction (SXRD) for structure refinement.

3 Results

3.1 XRPD measurement

Figure 1 shows the XRPD pattern of reaction products, such as aluminum (Al), aluminum diboride (AlB_2), dialuminum monoborate ($Al_4B_2O_9$), aluminum oxide (α-Al_2O_3) and sodium borate ($NaBO_2$). The AlB_2, $Al_4B_2O_9$ and the α-Al_2O_3 are reaction products. The only detected crystalline phase with sodium content is the $NaBO_2$.

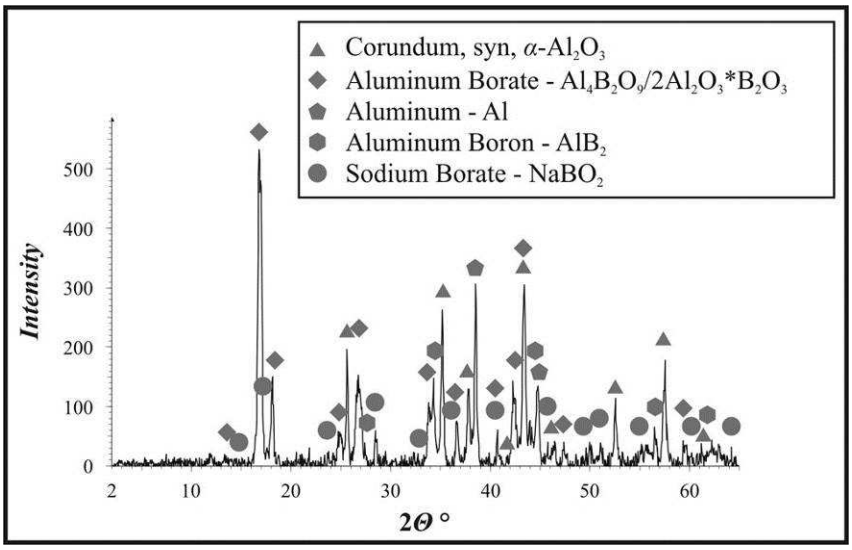

Figure 1. XRPD pattern of reaction products.

3.2 Reflected polarized light microscopy and SEM backscattered electron images

Texture of the solidified reaction zone between aluminium and borax is shown in **Figure 2.a** and **Figure 2.b**. Components of the reaction zone are (1) aluminum borate, (2) aluminum oxide and (3) aluminum diboride in aluminum matrix, respectively. Aluminum borate precipitates in borax–aluminum oxide solution, whereas aluminum diboride precipitates in aluminum–boron solution having an aluminum metal matrix. Aluminum oxide can be derived from an Al_2O_3-containing slag that is built up at borax/aluminum interface [4]. The presence of the stable slag slows down the reaction.

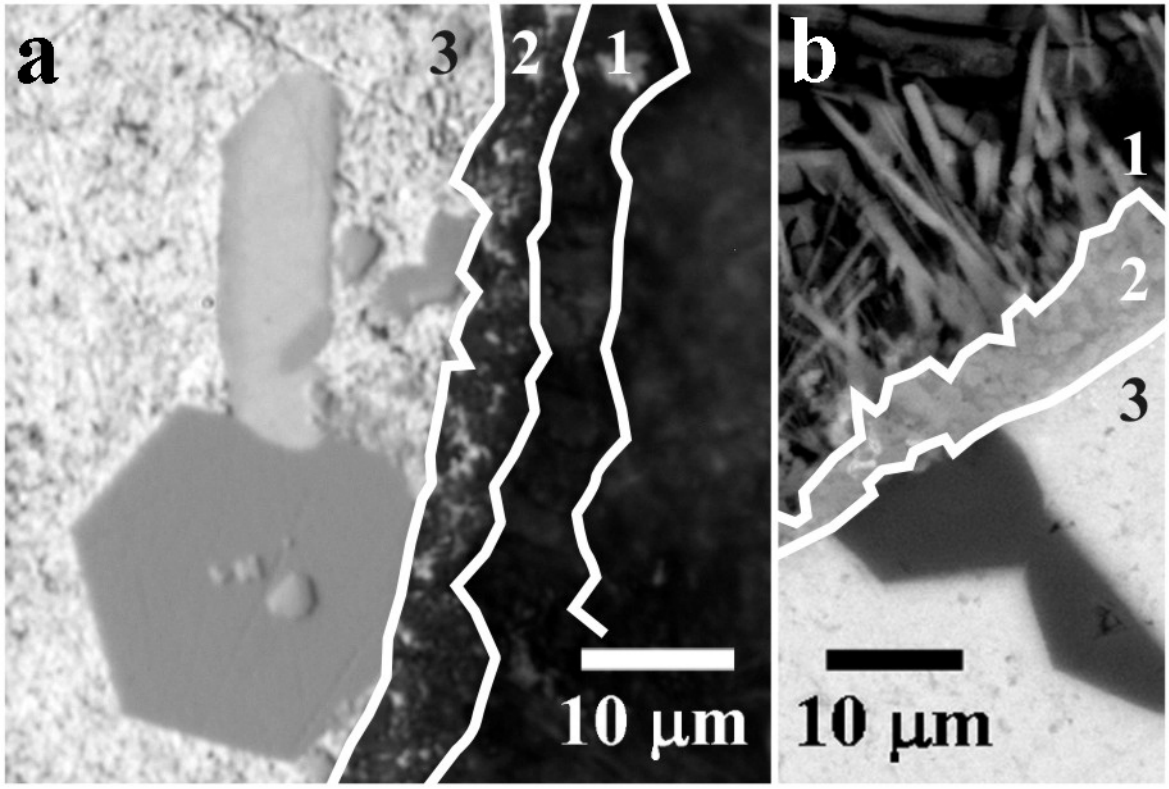

Figure 2. Texture of the reaction zone. **a.** Reflected polarized light microscopic image. **b.** Scanning electron microscopic backscattered electron image. Notations: (1) aluminum borate, (2) aluminum oxide and (3) aluminum diboride in aluminum matrix.

AlB_2 is opaque and appears in lath shaped or hexagonal sections (**Figure 2.a**). The AlB_2 in the hexagonal section shows light brown colour, the lathes exhibit yellow to light brown reflection pleochroism in plane polarized light. If the elongation is parallel to the oscillation plane of the applied light the reflection colour will be yellow and when perpendicular then it will be light brown. Between crossed polarizers hexagonal sections are isotropic, the lathes are anisotropic.
A representative texture of synthesized Al/AlB_2 composite is shown in **Figure 3**. AlB_2 dominantly appears with randomly oriented, elongated sections in aluminum matrix.

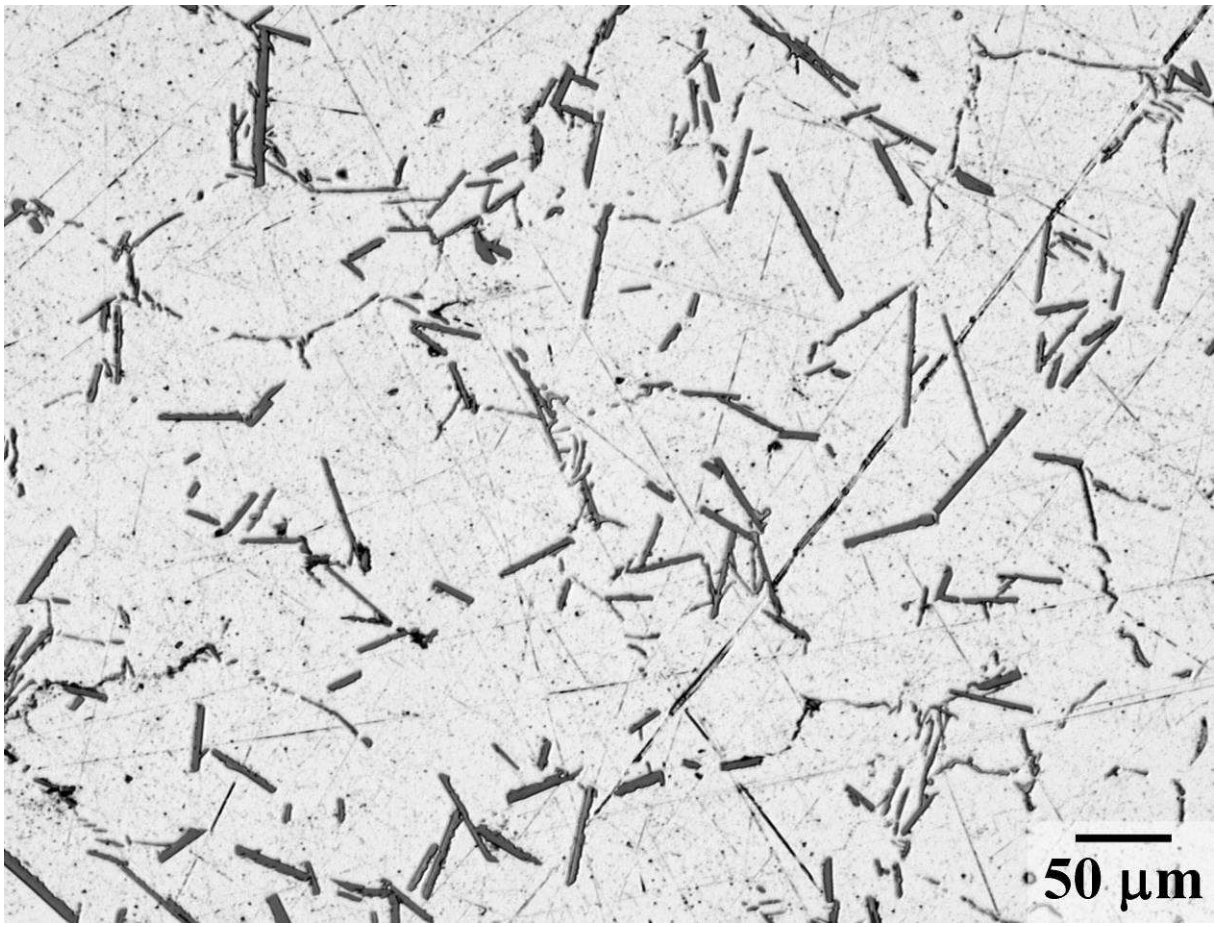

Figure 3. Texture of Al/AlB_2 composite, a reflected polarized light microscopic image.

3.3 SEM secondary electron images
Separated AlB_2 particles have hexagonal tabular habit (**Figure 4.**). Dominant crystal shape is hexagonal pynacoid but hexagonal dipyramid subordinately appears, also. Observed crystal shapes are conform to the known dihexagonal dipyramidal (6/*mmm*) point group symmetry of AlB_2 (*e.g.* [7]). Aspect ratio of the altitude and diagonal of AlB_2 flakes is around 10.

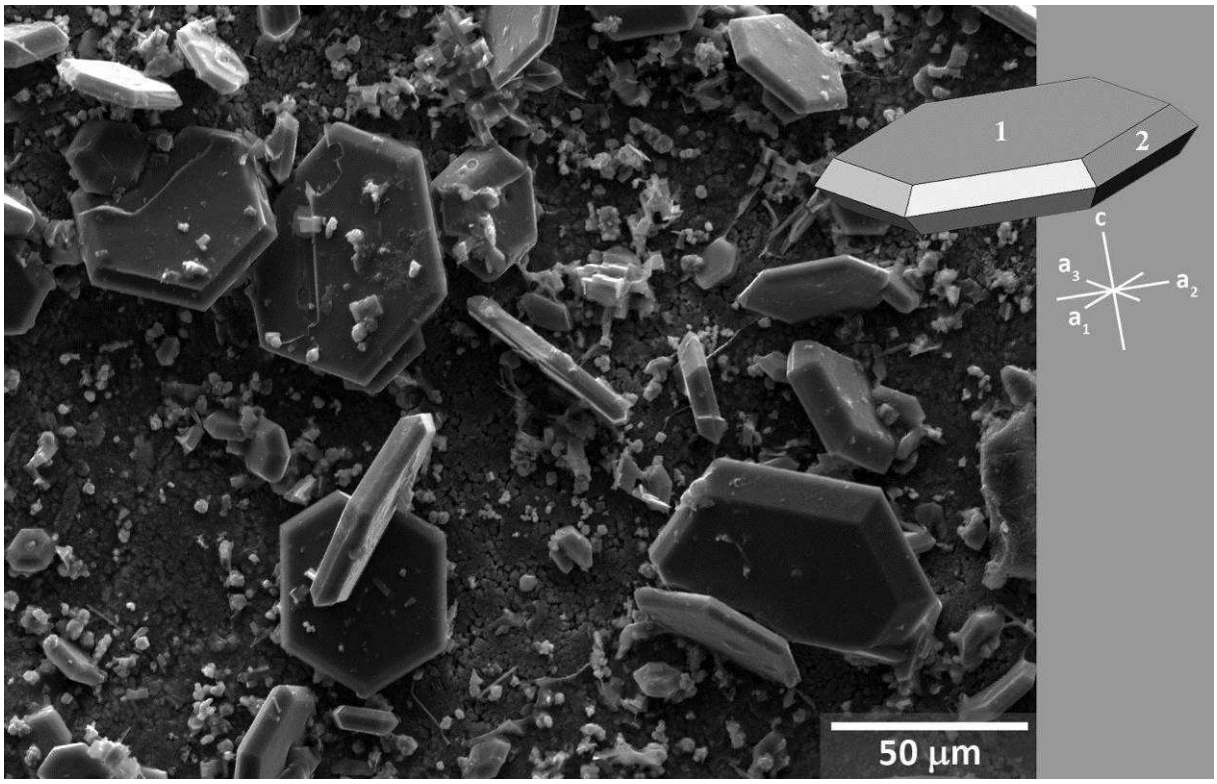

Figure 4. Crystal shape of AlB_2 in scanning electron microscopic secondary electron image. Notations: 1 hexagonal pynacoid, 2 hexagonal dipyramid.

3.4 SXRD measurement

Structure of AlB_2 was determined and refined (**Figure 5.**) using SHELX97 [8] with *R*=0.024 and *wR*2 =0.031 (res.=0.80 Å, 346 meas. refl., 20 uq. refl.) in space group *P*6/*mmm* with cell dimensions a = 3.007(2) Å and c = 3.254(2) Å. Both Al and B are in special position (Al: (0,0,0); B: (1/3,2/3,1/2)) (**Table 1.**). The refined structure is conform with the earlier published results [7].

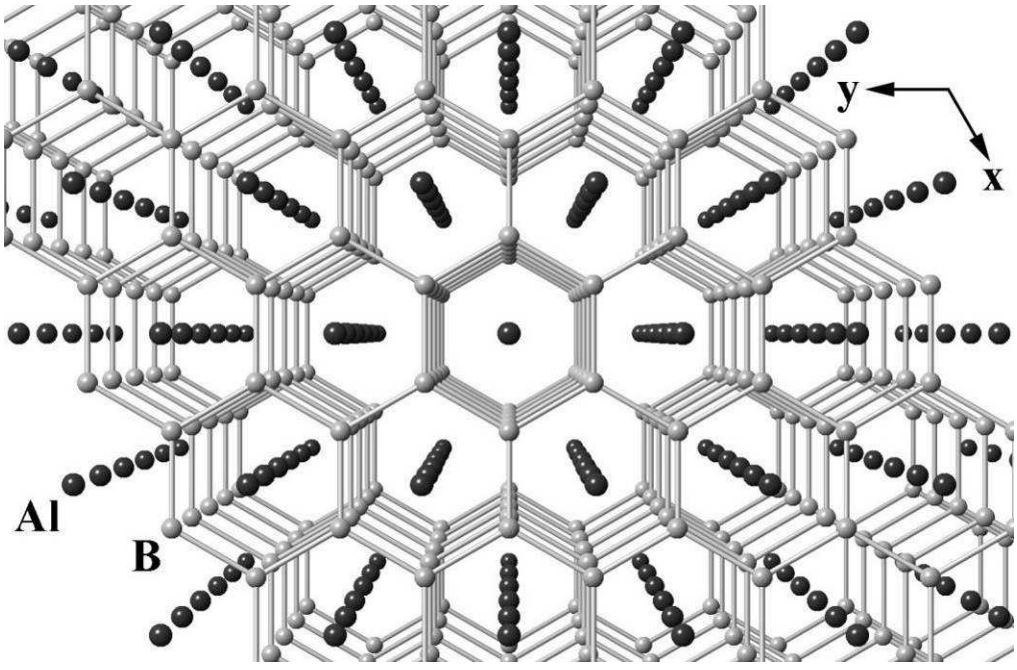

Figure 5. Crystal structure of AlB_2 view along **c** (perspective).

aluminum diboride	**AlB_2**
a_0	3.007(2) Å
c_0	3.254(2) Å
α, β	90.00°
γ	120.00°
Space group:	*P*6/*mmm*
Z	1
λ	0.71075 Å
Measured reflections:	346
	-3 =< h =< 3
	-3 =< k =< 3
	-4 =< l =< 4
Independent reflections:	20
Parameters:	3
Structure determination and refinement:	SHELXL97
$R(F^2 > 2\sigma(F^2))$	0.024
$wR(F^2)$	0.031
GooF	1.074
Resolution:	0.8 Å

Atom	**x**	**y**	**z**	**U_{iso}**
Al	0	0	0	0.0085(14)
B	1/3	2/3	1/2	0.0000(11)

Table 1. Result of structure determination and refinement of AlB_2.

4 Conclusion

AlB_2 is efficiently synthesized by application of aluminum-flux high-temperature solution growth.

Precipitated AlB_2 has hexagonal tabular habit with aspect ratio around 10.

Precipitation of AlB_2 in aluminum matrix gives us an applicable process to prepare Al/AlB_2 composite, however enhancement of efficiency is still a challenge.

The AlB_2 particles proved to be single crystals by SXRD measurements. The refinement quickly converged to the following results: a = 3.007(2) Å, c = 3.254(2) Å; *P*6/*mmm*; Z = 1 (Al: (0,0,0); B: (1/3,2/3,1/2)).

Acknowledgement

The authors express their sincere thanks to Mátyás Czugler and HAS CRC for the single crystal X-ray data collection.

References

[1] Melgarejo Z.H., Suárez O.M., Sridharan K. Wear resistance of a functionally-graded aluminium matrix composite. *Scripta Materialia*, **55**, pp. 95-98 (2006).

[2] Melgarejo Z.H., Resto P.J., Stone D.S., Suárez O.M. Study of particle-matrix interaction in Al/AlB_2 composite via nanoindentation. *Materials Characterization*, **61**, pp. 135-140 (2010)

[3] Wöhler F., St.-Claire Deville H. Analysen und physikalische Eigenschaften des Bors. *Journal für Praktische Chemie*, **71**, pp. 38-45 (1857)

[4] Hall A., Economy J. The $Al_{(L)}$ + AlB_{12} ↔ AlB_2 peritectic transformation and its role in the formation of high aspect ratio AlB_2 flakes. *Basic and Applied Research*, **21**, pp. 63-69 (2000)

[5] Mirković D., Gröbner J., Schmid-Fetzer R., Fabrichnaya O., Lukas H.L. Experimental study and thermodynamic re-assessment of the Al-B system. *Journal of Alloys and Compounds*, **384**, pp. 168-174 (2004)

[6] Gielisse P.J.M., Foster W.R. The system Al_2O_3 – B_2O_3. *Nature*, **195**, pp. 69-70 (1962)

[7] Hofmann W., Jäniche W. Der Strukturtyp von Aluminiumborid. *Naturwissenschaften*, **23**, pp. 851-851 (1935)

[8] Sheldrick G.M. A short history of SHELX. *Acta Crystallographica*, **A64**, pp. 112-122 (2008)