Steel and Composite Structures, *Vol. 19, No. 3 (2015) 777-787*
DOI: http://dx.doi.org/10.12989/scs.2015.19.3.777

Fabrication and properties of in-situ Al/AlB$_2$ composite reinforced with high aspect ratio borides

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(*Received October 01, 2014, Revised February 08, 2015, Accepted February 13, 2015*)

Abstract. Production and properties of metal matrix composites reinforced with an in-situ high aspect ratio AlB$_2$ flake have been investigated. Boron 2.2wt.% was dissolved in pure Al and Al-Cu alloy at 1300°C by adding directly boron oxide which resulted in 4 vol.% reinforcing phase. The in-situ AlB$_2$ flake concentration was increased up to 30 vol.% in order to increase the tensile strength of the composites. Hardness, compressive strength and tensile strength of the composite were measured and compared with their matrix. Results showed that 30 vol.% A1B$_2$/Al composite show a 193% increase in the compressive strength and a 322% increase in compressive yield strength. Results also showed that ductility of composites decreases with adding AlB$_2$ reinforcements.

Keywords: AlB$_2$ composite; boron oxide; aluminum boride; in-situ composite

1. Introduction

Aluminum metal-matrix composites (AMMC) is produced by aluminum alloys reinforced with hard ceramic or intermetallic particles to provide better mechanical properties (Rohatgi 2001). There are number of techniques to the production of aluminum metal matrix composites (AMMC) (Miracle 2005). In-situ techniques offer several advantages to fabricate AMMC compared to ex-situ techniques such as vortex methods (Tjong and Ma1 2000). In-situ reinforcements also provide more uniform distribution of the reinforcing particles in matrix, higher bonding strength with the matrix and higher mechanical properties (Daniel *et al*. 2007).

In-situ technique has been shown to be used to fabricate AlB$_2$/Al composites (Savaş and Kayikci 2013a). AlB$_2$ reinforcement particles in aluminum matrix are formed with exothermic reaction between aluminum and boron during solidification, so their fabrication is relatively simple and inexpensive (Savaş *et al*. 2012).

Kayikci and co-workers (Kayikci *et al*. 2007) reported that AlB$_2$ boride particles form in thin hexagonal flake shape having high aspect ratio. It is well know that high aspect ratio reinforcement phase is more advantageous compared to cubic phase for producing composites where higher stiffness and higher yield strength required (Hall 1999). Deppisch and co-workers (Deppisch *et al*.

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http://www.techno-press.org/?journal=scs&subpage=8 ISSN: 1229-9367 (Print), 1598-6233 (Online)

1997) reported that compressive and tensile strengths of aluminium alloys were significantly increased by adding up to 20% of AlB_2 flakes.

Savaş and Kayikci (2013b) reported that hardness of boride particles was measured as 3050 Hv. They also reported that, hardness of composite increased from 90 HB to 250 HB with adding 33 vol.% boride particles. Ficici and co-workers (Ficici *et al*. 2011) reported that wear resistance of composites can be increased by 30% with addition of 30 vol.% of AlB_2 boride flakes into the aluminium matrix.

In production of AlB_2/Al composites it is very important to have in-situ AlB_2 reinforcement phase formed directly within molten aluminum. As seen in the Fig. 1. Al-B binary system has a peritectic reaction at 980℃. The AlB_{12} forms directly from the melt above the peritectic reaction temperature and then transforms to AlB_2 at the peritectic temperature (Hall and Economy 2000b). Deppisch and co-workers reported (Deppisch *et al*. 1998) that Al-B alloys have to be cooled with at least 50℃/min cooling rate from the $AlB_{12(solid)}$ + $Al_{(liquid)}$ region to avoid nucleation of AlB_{12} phase which are brittle and in cuboidal shaped. Thus, direct nucleation and growth of high-aspect-ratio AlB_2 flakes can be possible. Savaş and Kayikci (2013a) reported that the most influential parameter on the formation of high-aspec-ratio AlB_2 phase were the cooling rate at the $AlB_{12(solid)}$ + $Al_{(liquid)}$ region and holding temperature in the $AlB_{2\ (solid)}$ + $Al_{(liquid)}$ region. They also indicated that the width of the flakes varies between 97-530 μm, and their thickness can be between 0.32-1.51 μm, depending on the process parameters.

In production of AlB_2/Al type composites other important point is to increase the volume fraction of AlB_2 boride particles. Basically, the volume fraction of AlB_2 flakes can be increased with increasing the amount of dissolved boron in molten aluminum. As seen in Fig. 1 boron dissolution in aluminum is very small and it increases with increasing temperature. Savaş and kayikci (2013a) reported that maximum 2.14wt.% boron has been dissolved in the aluminium at 1400℃. Deppisch and co-workers (Deppisch *et al*. 2007) reported that the boride volume fraction in the composite has been increased from 4% to 20% using a filtration device at 800°C. Savaş and Kayikci (2013b) also studied the production of an in-situ AlB_2/Al-Cu composite. They

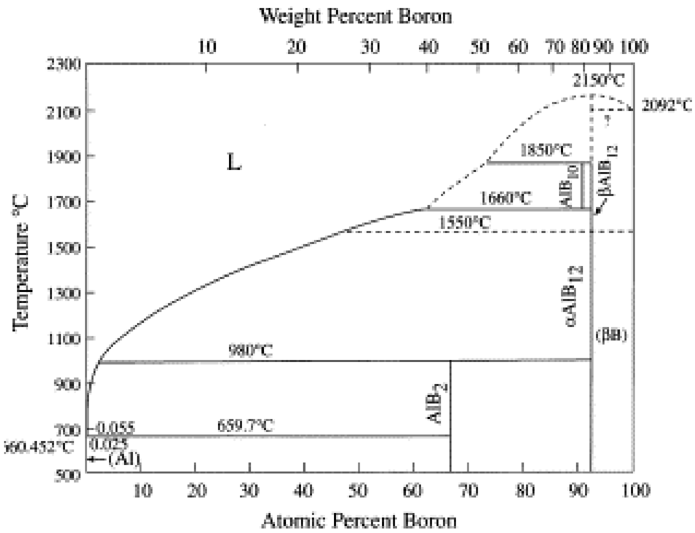


Fig. 1 Al-B phase diagram (Carlson 1990)

reported that the boride particle concentration in Al-Cu matrix can be increased up to 33 vol.% using similar filtration device in the AlB$_{2(solid)}$ + Al$_{(liquid)}$ region (at appx. 1000℃).

Although, AlB$_2$/Al composites are generally produced by using Al–B master alloys which is also fabricated by using KBF$_4$ or using inexpensive boron oxides (Hall and Economy 2000a). Past studies on AlB$_2$/Al composites show no accessible research works available for these composites produced by using boron oxides.

Therefore, in the present study, production of AlB$_2$/Al composites has been studied by direct synthesizing the boron from boron oxide (B$_2$O$_3$). A two stage fabrication method has been applied. At the first stage, the reinforcing high aspect ratio boride phase has been formed by exothermic reaction between molten aluminum and boron. At the second stage, the AlB$_2$ boride volume fraction in the composite has been increased using a novel filtration device. Then, properties of AlB$_2$/Al composites have been investigated.

2. Experimental procedure

2.1 Materials

In this study, a commercially pure Al and Al-Cu alloys have been used as the matrix materials. Their composition is given in Table 1. Boron oxide (B$_2$O$_3$) powder was used as the boron source which facilitates to form in-situ AlB$_2$ reinforcements within Al matrix. The boron oxide powders were heated to 500℃ for 15 minutes to remove any physical water molecules before being added to melting crucible.

2.2 Processing

A two-step process was used in manufacturing the composite materials. In the first step, a master composite having high aspect ratio AlB$_2$ reinforcement particles were in-situ produced within molten aluminum. In the second step, the boride volume fraction in the master composite has been increased using a novel filtration device.

The melting and casting processes used to synthesize high-aspect-ratio AlB$_2$ flakes involved a chemical reaction between aluminum and boron oxide at high temperature. In this work, the matrix alloy and B$_2$O$_3$ powder were initially melted together in an alumina crucible at 800 ℃. The boron synthesizing reaction occurs according to the following reaction (Nafisi and Ghomashchi 2007)

$$2Al + B_2O_3 \rightarrow \alpha_{(L)} + Al_2O_{3(S)} + 2[B]_{(L)} \quad (1)$$

$$\Delta G^0_{298^\circ} = -416.9\ kJ/mol$$

Table 1 Chemical composition of the matrix alloys (wt.%)

Alloys	Element, %							
	Si	Fe	Cu	Mn	Mg	Cr	B	Al
Pure Al	0.132	0.290	0.001	0.000	0.001	0.001	0.000	99.421
Al-Cu	0.450	0.321	3.442	0.120	0.551	0.051	0.000	95.119

$$\Delta H^0_{298^\circ} = -402.7\ kJ/mol$$

Then the temperature was raised up to 1300℃, the molten mixture was held at this temperature for 60 minutes to increase amount of boron dissolved in liquid aluminum. Finally, the oxide layer on top of molten Al-B alloy was skimmed off before being poured into a cooling plate in order to have a fast cooling to form high aspect ratio AlB_2 flakes. According to the Al-B binary system (see Fig. 1), the expected exothermic reaction between aluminium and boron and their Gibbs free energies are given as follows

$$2[B] + Al \rightarrow AlB_2$$
$$\Delta G^0_{AlB_2} = -65\ 557 - 5.5T\ J/mol \quad (2)$$

In order to increase the in-situ AlB_2 boride particles concentration, a filtration system was constructed as shown in Fig. 2, which was similar to squeeze casting as used by Savaş and Kayikci (2013b). The system has small discharge holes having 0.5 mm of diameters, in order to filter out some of liquid matrix from the "$Al_{(liquid)}$ + $AlB_{2(solid)}$" mixture. Pressure was applied on the molten mixture as shown in Fig. 2 through the plunger and exces molten metal was removed at 700℃. The concentration of the aluminum boride phase was controlled by the remaining aluminum to the remaining composite.

After filtration and cooling to room temperature, composite samples were prepared for examinations. Olympus optical microscope and a JEOL JSM 6060LV SEM (Scanning electron microscope) were used for microstructural examinations. An XRD (x-ray diffraction pattern) was also taken using a D/MAX 2200/PC type device. The measurement of the total weight percent of boron within the composite materials were carried out by a chemical method, as detailed by Savaş *et al*. (2012) in a previous work.

Compressive and tensile strengths were measured using a 50 kN computerized universal testing machine as per the ASTM–E8M standards. The hardness of the composites was measured after polishing to a 1 μm finish. Brinell Hardness (BHN) values of the samples were obtained using a 2.5 mm diameter ball at load of 31.25 kgf for 15 sec.

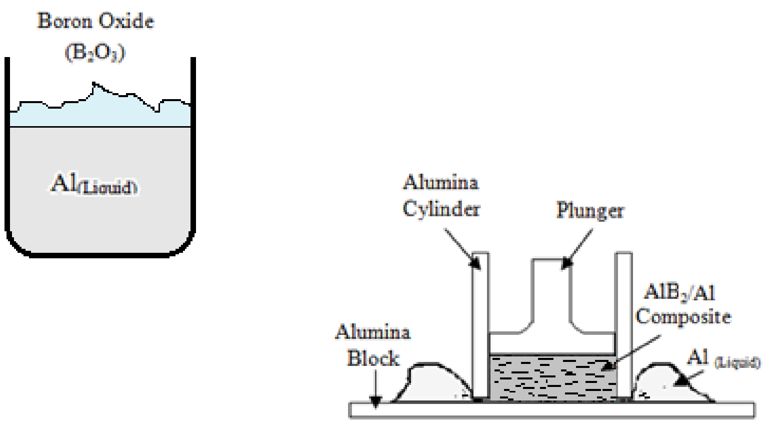


Fig. 2 The production scheme of the composite materials: (a) reaction melted aluminum with B_2O_3 at 1300℃, structures; and (c) increase the AlB_2 boride concentration by the filtration system at 700℃

3. Results and discussion

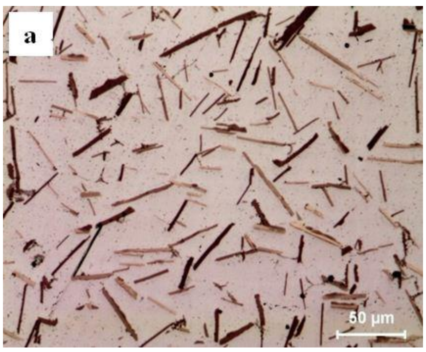
In this study, direct formation of in-situ high-aspect-ratio AlB_2 flakes, boron oxide powder was added into molten Al-B and Al-Cu-B base alloys and then the alloys were heated at 1300℃. Casting process was aimed to obtain a fast cooling rate, which should be above 50°C/ min using a cooling plate type metallic mold. The reason of this was to nucleate and growth of AlB_2 phase and to avoid nucleation of undesired AlB_{12} crystals which are the primary solid phase during cooling in Al-B system (Deppisch *et al*. 1998, Savaş and Kayikci 2013a, Hall and Economy 2000a). The superheated Al-B melt was poured into the mold through the cooling plate in order to obtain a fast cooling below the peritectic reaction temperature.

Microstructure of typical as-cast (master) Al-B alloy is shown in Fig. 3(a). It is known that almost no boron can be solved by aluminum at room temperature in Al-B system as seen Fig 1 all the boron atoms within the Al-B alloys can be considered in compounds as reported in previous studies (Karantzalis *et al*. 2011, Wang 2005, Ficici *et al*. 2011).

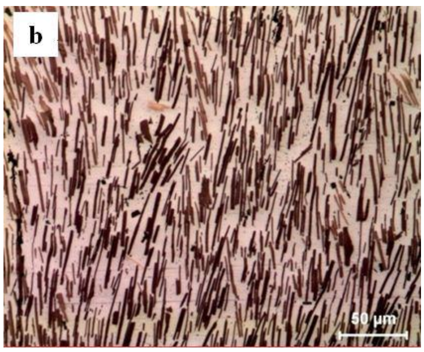
The XRD pattern of the as-cast Al-B alloys is given in Fig. 4. The XRD pattern shows that phases in the sample include only Al and AlB_2, This is consistent with the phase diagram shown in Fig 1. Figs. 3(a)-(b) shows the resulting microstructure with only flake structure embedded in the aluminum alloy. As there are no cuboidal boride structures apparent in the microstructures in Fig. 3, it can be suggested that initial nucleation and growth of higher boride structures such as AlB_{12} have been successfully avoided. These results are also in good agreement with similar previous studies by (Deppisch *et al*. 1997, Savaş and Kayikci 2013a, Savaş *et al*. 2012, Ficici *et al*. 2011, Deppisch *et al*. 1998).

The volume fraction of the AlB_2 boride structure within the as-cast Al-B and Al–Cu–B master alloys were measured as 4 vol.%, which is inadequate to produce a composite material. After the filtration process the volume fraction of the composites were measured as 30%, which show almost 8 times increase in the volume compared to their master versions. This results shows the efficiency of the filtration system used to enhance the composites in terms of the reinforcement phase. This is also obvious in the final microstructure of the AlB_2/Al composite material which is given in Fig. 3(b).

Figs. 5(a)-(b) shows typical SEM images of deep etched AlB_2/Al composites before and after the filtration process respectively. It can be seen that boride particles are virtually in high aspect ratio flake shaped and having random distribution in aluminum matrix. It is also evident from Fig.



(a)



(b)

Fig. 3 Microstructure of (a) the as-cat master Al-B alloy; and (b) AlB_2/Al composite material after filtration

5(a) that the shape of the boride flakes is mostly hexagonal in shape. This result is good agreement with literature where it has also being referred as in hexagonal shape (Deppisch *et al*. 1998, Savaş and Kayikci 2013a). It is also seen in Fig. 5(b) that All AlB_2 flakes have lined up in the same orientation. This can be advantageous to improve the uniaxial tensile properties of the composite through the direction of alignment.

The average widths and thicknesses of AlB_2 flakes were measured from both as-cast master Al–B alloys and the final AlB_2/Al composite after filtration and their average aspect ratios

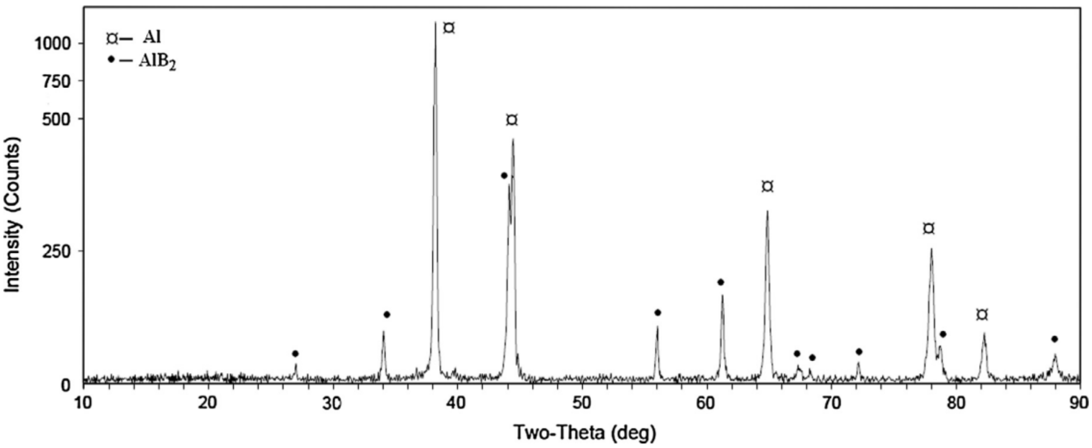
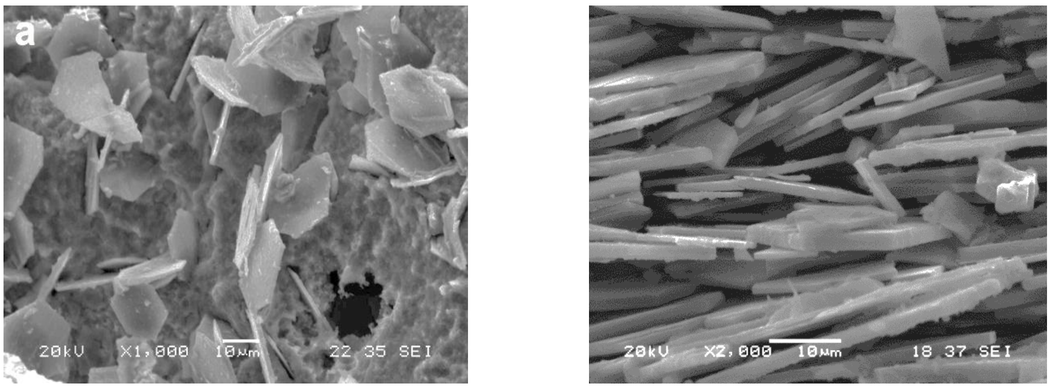


Fig. 4 The XRD spectra of the Al-B alloy



(a) (b)

Fig. 5 SEM image of the deep etched: (a) as cast Al–B alloy before filtration; and (b) AlB_2/Al composite after filtration

Table 2 Measured average AlB_2 flake width, thickness and calculated aspect ratios (widths/thickness)

Materials	Width, μm	Thickness, μm	Aspect ratios
Al-B alloy	32.10 ± 25	0.60 ± 0.1	59.88
AlB_2/Al composite	29.41 ± 15	0.61 ± 0.1	55.32

(widths/thickness) were calculated. These values are given in Table 2. As seen in the table, after the filtration process at 700℃, the average values of the aspect ratio of AlB_2 flakes decreased. The reason for this can be that some of the larger AlB_2 flakes may have been damaged by the applied pressures during the filtration process as also reported by Deppsch *et al*. (1997).

Brinell hardness (HB) traces on both types of the composites before and after filtration are seen in Figs. 6(a)-(d). Average 1120, 645, 874 and 570 μm sized tracks have formed under 31.5 kgf loads for a period of 15 s on the pure Al, filtered AlB_2/Al composite, Al-Cu matrix and filtered AlB_2/Al-Cu composite respectively. According to these track sizes, the average hardness value of each material was calculated as 30.3, 94.5, 50.7 and 121.8 HB, respectively. These results show that the hardness of pure Al and Al–Cu matrix were increased almost three times with increasing the volume fraction of AlB_2 boride flakes from 4% to 30% by the filtration process. This result is in good agreement with previous experimental works reported for AlB_2 boride reinforced composites (Adelakin and Suarez 2011, Savaş and Kayikci 2013a or b).

Table 3 lists the results obtained from compression and tensile test measurements from both the matrix (pure Al and Al-Cu) and their composites (AlB_2/Al and AlB_2/Al-Cu) after filtration. The results show that the compressive and tensile yield strength of the composites have been increased by increasing the $A1B_2$ flake volume fraction. Compared with commercially pure Al and Al-Cu matrix alloys, the 30 vol.% $A1B_2$ composites show 193% and 76% increase in the compressive UTS strength, 322% and 449% increase in compressive yield strength, respectively. It is also seen in Table 3 that 69% and 17% increase in tensile UTS strengths of 30 vol.% AlB_2/Al and AlB_2/Al-Cu composites have been achieved respectively. However, the elongation properties of

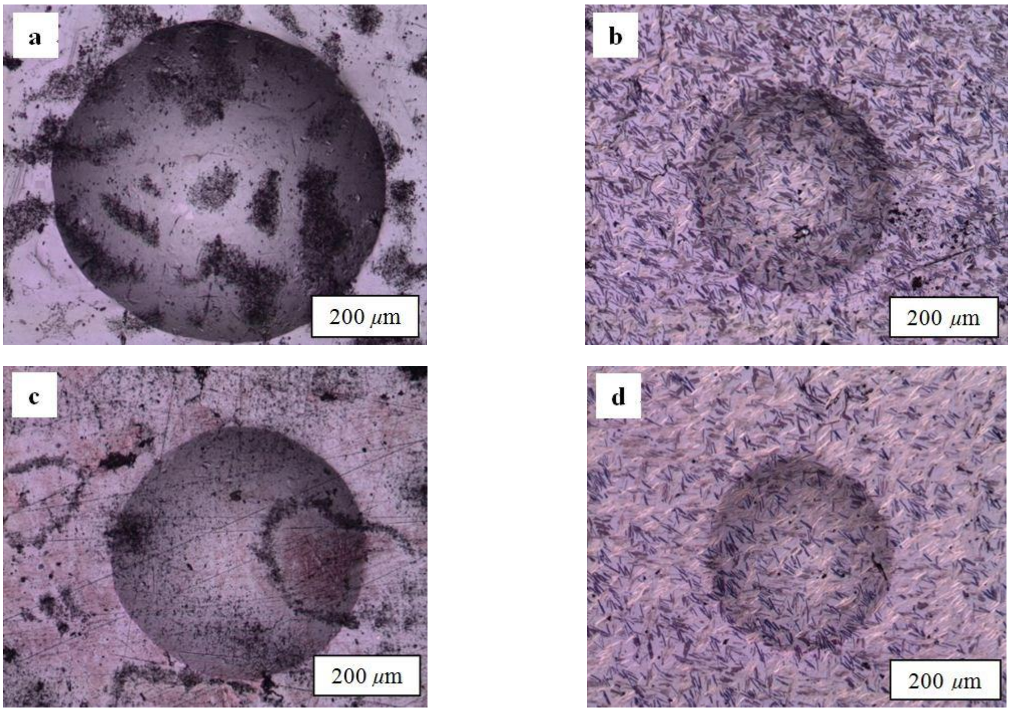


Fig. 6 Response graph for the tensile shear strength g. 6 Brinell hardness traces on (a) the pure Al matrix; (b) AlB_2/Al composite; (c) Al-Cu matrix; and (d) the AlB_2/Al-Cu composite

Table 3 Mechanical properties of the composites and their matrix alloys

Materials	Tensile test results			Compressive test results		Hardness, HB
	UTS, Mpa	Yield strength, Mpa	Elongation, %	UTS, MPa	Yield strength, Mpa	
Pure Al	105	60	24	121	68	30,3
30 vol.% AlB_2/Al composite	177 (69%)	137 (128%)	2.9	354 (193%)	287 (322%)	94 (210%)
Al–Cu matrix	193	100	20	298	145	50,7
30 vol.% AlB_2/Al–Cu composite	226 (17%)	160 (60%)	2.15	523 (76%)	449 (210%)	121 (139%)

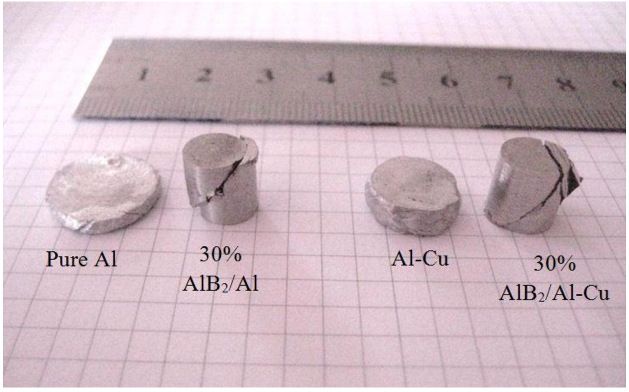
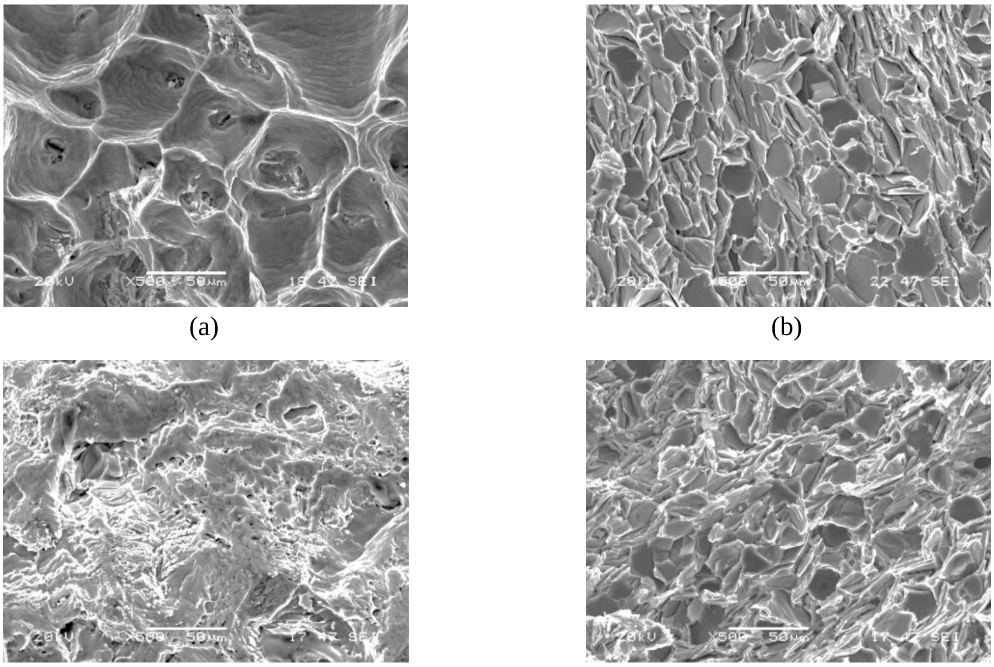


Fig. 7 Compressive strength test samples of the composites and their matrix materials

both types of the composites became significantly lower compared to the base matrix alloys. This can be attributed to enhanced stiffness of the base alloys due to excellent bonding between the matrix ally and the 30 vol.% of *in-situ* reinforcement after the filtration processes.

Compressive strength test samples, after testing of the composites and matrix alloys were given in Fig. 7. It is obvious that both matrix materials underwent substantial deformation without breaking. The composites, whereas, show no obvious plastic deformation other than abrupt fall apart under the compressive stress as seen in Fig. 7. Tensile fracture surfaces of both matrix (pure Al and Al-Cu) and the composites (AlB_2/Al and AlB_2/Al-Cu) are shown in Fig. 8. In Fig. 8(a) and 8(c), fracture surface for pure Al and Al-Cu matrix alloys revealed a ductile fracture as is in most aluminum alloys. The fracture surfaces of both AlB_2/Al and AlB_2/Al-Cu composites are very similar. Both reveal predominantly brittle failure surface property. It can be seen that rarely observed ductile fracture regions on the fracture surface of composites are due to ductile aluminum matrix. It can also be observed that no AlB_2 flake decohesion occurred and this shows that good bonding between boride reinforcement and the matrix has been achieved which is one of the advantageous of the in-situ method. Composites became more brittle compared to their aluminum matrix is not specific to the present study. Previous work on similar composites have been concluded that boride reinforcement increase the hardness and stiffness of the matrix alloy but reduce their ductility (Calderon and Suarez 2008, Koksal *et al*. 2013, Deppisch *et al*. 1997).



(a) (b) (c) (d)

Fig. 8 SEM micrographs of the tensile fracture surfaces of; (a) commercially pure Al matrix; (b) AlB_2/Al composite after filtration; (c) Al-4wt.% Cu matrix alloy; and (d) AlB_2/ Al-Cu composite after filtration

4. Conclusions

The production and properties of an in-situ Al/AlB_2 type composites reinforced with high aspect ratio borides have been studied. The composites were prepared by liquid reaction of aluminum matrix with boron oxide (B_2O_3) at 1300℃. The reinforcement volume fraction concentration increased by using a filtration device. The conclusions from this work can be drawn as follows:

- After production of Al-B and Al–Cu–B alloy by liquid reaction of aluminum with boron oxide (B_2O_3) at 1300℃ for 1 h, the average in-situ AlB_2 flake content was determined as 4.0 vol.%. This have been increased up to 30 vol.% using a novel filtration device at 700℃.
- The average width of AlB_2 flakes within the composites was about 30 μm while the average thickness was only 0.6 μm. This has resulted in a high aspect ratio (width/thickness) of the reinforcement particles within the matrix.
- The bulk Brinell hardness of the composites increased three times after adding 30 vol.% AlB_2 flake reinforcement.
- The $A1B_2$/Al composite and AlB_2/Al-Cu composite showed 128% and 60% increase in yield strength compared to their matrix alloys. Similarly, compared to their matrix alloys, the 30 vol.% boride reinforced $A1B_2$/Al and AlB_2/Al-Cu composites showed 193% and 76% increase in the compressive UTS strength respectively.

The ductility of the aluminum matrix decreased dramatically with addition of 30 vol.% AlB_2 flake reinforcement. Tensile fracture surfaces of the composites reveal an excellent bonding between AlB_2 flakes and the matrix interface as there is no AlB_2 flake decohesion. Brittle failure occurs in both 30 vol.% boride reinforced AlB_2/Al and AlB_2/Al-Cu composites in opposition to their matrix alloys.

Acknowledgments

This work has been carried out at Sakarya University with financial support from Scientific and Technological Research Council of Turkey (TÜBİTAK) under the project number 107M023. Thus, the authors gratefully acknowledge TÜBİTAK and Sakarya University.

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