# Mechanical Behaviors and Stability of Al-rich Al-Mg-B Alloys

Jae-Ik Cho<sup>1</sup> and Sungtae Kim<sup>2</sup>

<sup>1</sup>Korea Institute of Industrial Technology, 1110-9 Oryong-Dong, Buk-Gu, Gwangju, Rep. of Korea <sup>2</sup>University of Wisconsin-Madison, 1509 University Ave, Madison, WI 53706, USA

The structural evolution and mechanical behaviors of the Al-Mg-B ternary system have been investigated in order to fabricate a composite system composed of (Al,Mg)B<sub>2</sub> in a Al-Mg matrix. Several Al-Mg-B ternary alloy compositions were selected for fabrication and identification of borides and matrix formation during solidification. The in-situ (Al,Mg)B<sub>2</sub> phase was developed in an eutectic matrix of Al<sub>8</sub>Mg<sub>5</sub> and Al, and formed in the location of inter and intra the Al dendritic region, indicating that the formation of (Al,Mg)B<sub>2</sub> was developed at the initial solidification process. Dominating factors for controlling the (Al,Mg)B<sub>2</sub> phase and mechanical behaviors are discussed in terms of detailed thermodynamic stability and structural identifications.

Keywords: Al-Mg-B alloy, Phase stability, Thermodynamics, Boride

#### 1. Introduction

Developments of light metal alloy composites have been received an attention due to their recently increased demands for industrial applications. The most probable candidates for lightweight alloy composites are aluminum and/or magnesium matrix composites. It has been well known that the densities of aluminum and magnesium are  $2.7g/cm^3$  and  $1.74g/cm^3$ , respectively, and those can be potential structural materials possessing high strength with controllable microstructures. In this perspective, Al-Mg alloys can offer an improvement in strength/density ratio in replacement of low alloy steels. Furthermore, since borides has been known as one most stiff reinforcing material, the composite systems composed of (Al,Mg)B<sub>2</sub> reinforced Al-Mg alloy matrix can be one promising candidate for practical applications.

In order to evaluate Al-Mg-B ternary composite systems, it is important to scrutinize the boride phase formation. Regarding to the use of borides as reinforcement materials, the in-situ formation of AlB<sub>2</sub> in Al matrix has been received an attention due to its high stiffness and economical standpoints. The AlB<sub>2</sub> in Al matrix is usually formed from the phase transformation of AlB<sub>12</sub> phase, and the AlB<sub>12</sub> phase gives a detrimental effect on the mechanical properties of aluminum matrix composites. Elaborated efforts have been given to produce and control the AlB<sub>2</sub> phase in aluminum matrix [1], in which a controllable proportion of AlB<sub>2</sub> can be fabricated by using heat treatments with a special apparatus. At the same time, detailed study about the phase transformation has been given in order to identify the formation mechanism and phase transformation kinetics of AlB<sub>2</sub>.

Since the use of borides such as the AlB<sub>2</sub> phase usually undergoes phase transformation from the AlB12 phase, the identification of thermodynamic stability can provide a critical database for successful composite designs. However, the nature of high melting point of boron often limits the critical assessment of critical thermodynamic stability. For example in the published phase diagram of the Al-B system [2], the existence of four intermediate phases – AlB<sub>2</sub>, AlB<sub>10</sub>, AlB<sub>12</sub> (low temperature) and AlB<sub>12</sub> (high temperature) – are revealed. The L  $\rightarrow$ AlB<sub>12</sub> + B eutectic reaction is assumed to occur at about 2090°C. However, Mirkovic et al. [3] indicated that the AlB<sub>12</sub> and AlB<sub>10</sub> phases are stabilized by impurities. In this regard, the Al-B system exhibits only two intermediate phases, AlB<sub>2</sub> and AlB<sub>12</sub>, and the phase diagram should be reassessed based upon the updated

documents. Also, the binary phase diagrams of Mg-B and Al-Mg system have been recently published, leading to the construction of Al-Mg-B ternary system.

In this study, in order to provide thermodynamic stability of the potential lightweight Al-Mg-B ternary system, the binary Al-B system has been re-estimated by Pandat program® by Computherm, LLC, and isothermal ternary phase diagrams have been assessed, for the first time, with thermodynamic data of Al-B, Mg-B and Al-Mg binary systems at elevated temperatures and room temperature. At the same time, the microstructural evolutions and corresponding mechanical properties of the in-situ (Al,Mg)B<sub>2</sub> in Al-Mg matrix composites have been investigated.

# 2. Experimental

Since the target phase should be selected with a reliable database, thermodynamic analyses have been carried out by using Pandat program® with previously published data. Based upon the reassessed phase stability information (binary and ternary phase diagrams), alloy compositions were selected. A special attention has been given to the microstructures and the corresponding mechanical behaviors at room temperature upon variation of Mg and/or B contents in Al matrix, so that various compositions of, as aforementioned, the in-situ  $(A1,Mg)B_2$  reinforced Al-Mg matrix composites were fabricated. In order to fabricate Al-Mg-B ternary alloys, a master alloy with a composition of Al-5at%B has been purchased from KB Alloys, and additional elements have been added into the melt of the mother alloy. However, in order to identify the strengthening mechanism in a simplified system, the addition of 4th or 5th elements was not considered at the present study. All of the alloys were targeted towards the formation of (Al,Mg)B<sub>2</sub> phase in a Al-Mg matrix and melted in an electric furnace under a purging of an Ar gas and cast in a mold with a dimension of 200 mm × 50 mm × 70 mm (length, width and height). For observations of microstructures, the alloy pieces were cut and polished with an Al<sub>2</sub>O<sub>3</sub> powders in a cloth. The microstructures were investigated by SEM (Secondary electron microscopy, Jeol 6100), and the phase analyses were undertaken by XRD (X-ray diffraction, Rekaku 3100). For the measurements of mechanical behavior, tensile tests were performed with an universal mechanical tester (INSTRON). It is specially noted that since the compositions of the fabricated alloys contain the boron element, EPMA (electron probe micro analysis, CAMECA SX-50) was carried out for analyzing boron contents.

## 3. Results and discussion

## 3.1 Thermodynamic estimation and stability

Since the stability of intermediate phases in Al-Mg-B ternary system is one critical factor for designing successful composite systems, thermodynamic stability of the associated phases has been estimated. For the Al-B binary system [2], the existence of four intermediate phases – AlB<sub>2</sub>, AlB<sub>10</sub>,  $\alpha$ AlB<sub>12</sub> (low temperature) and  $\beta$ AlB<sub>12</sub> (high temperature) – has been reported. However, as mentioned earlier, the two AlB<sub>2</sub> and AlB<sub>12</sub> intermediate phases were identified and indicated as line compounds with a stoichiometric composition.

The entropy of an aluminum boride phase,  $AIB_x$  can be described as:

$$S_{AIB_x} = S_{AI} + xS_B \tag{1}$$

where  $S(AlB_x)$ ,  $S_{Al}$  and  $S_B$  are the entropies of  $AlB_x$ , Al and B, respectively. Also, the temperature dependence of the entropy may be written as follows:

$$\left(\frac{dS}{dT}\right) = \frac{C_P}{T} \quad \text{and} \qquad S_T = S_{298.15K} + \int \frac{C_P}{T} dT \tag{2}$$

where T is temperature and  $C_P$  is the heat capacity.  $S_{298.15K}$  is the entropy at 298.15K.

The above equations of (1) and (2) were utilized to determine the free energy for  $AlB_{12}$ , together with the formation enthalpy of  $AlB_{12}$  at 298.15K [4]. Mirkovic *et al.* [3] experimentally identified

that the peritectic reaction,  $L + AlB_{12} \rightarrow AlB_2$ , occurs at 972±5 °C. Serebryansky et al. [5] analyzed the liquidus temperature between liquid and  $AlB_{12}$ . These experimentally studied phase boundary data [3,5] and the published Al-B phase diagram [2], were used to optimize thermodynamic model parameters for AlB<sub>2</sub> and liquid. Using the free energy data of the AlB<sub>2</sub> and AlB<sub>12</sub> phases (Fig. 1(a)), we have attempted to assess the phase diagram of the Al-B system that is shown in Fig.1 (b). Further detailed information about estimation of the Al-B system will be reported elsewhere.



Fig. 1 Constructed Al-B binary system : (a) accessed binary phase diagram with reference points, (b) re-accessed binary phase diagram

The recently published Mg-B and Al-Mg binary systems are shown in Fig. 2. Since the published data has presented with sufficient database, the published Mg-B, Al-Mg and the estimated Al-B binary database has been used for evaluating the Al-Mg-B ternary system. Based on the binary phase diagrams, we initiated calculating a ternary isotherm at temperature below 900°C, where the incomplete Al-Mg-B ternary isotherm [6] is known. This ternary isotherm demonstrates that a continuous solid solution between AlB2 and MgB2 forms (Al,Mg)B2, which exhibits broad compositional homogeneity. As indicated the above, in the MgB<sub>2</sub> crystal structure all Mg atoms occupy the Mg sublattice (named  $\alpha$  sublattice) sites and all B atoms occupy the B sublattice (named  $\beta$ sublattice) sites. AlB<sub>2</sub> has the same crystal structure as MgB<sub>2</sub>, so in the AlB<sub>2</sub> crystal structure all Al atoms occupy the  $\alpha$  sublattice sites and all B atoms occupy the  $\beta$  sublattice sites. Likewise in  $(Al,Mg)B_2$  crystal structure all Al and Mg atoms are supposed to occupy the  $\alpha$  sublattice sites and all B atoms to occupy the  $\beta$  sublattice sites. However, the existence of broad homogeneity in (Al,Mg)B<sub>2</sub> indicates that there may exist anti-site defects (Al or Mg on the  $\beta$  sublattice site, or B on the  $\alpha$ sublattice site) and constitutional vacancies (vacancy on the  $\alpha$  or  $\beta$  sublattice site). As an initial step, we considered that (Al,Mg)B<sub>2</sub> exhibits a linear connectivity between AlB<sub>2</sub> and MgB<sub>2</sub>, meaning that no defect structure is considered for the (Al,Mg)B<sub>2</sub> crystal structure. From thermodynamic assessments of binary Al-B and Mg-B phase diagrams, the free energies for both AlB2 and MgB2 were determined. The interaction parameter that is related to bonding energy between Al and Mg atoms on the  $\alpha$  sublattice sites and B atoms on the  $\beta$  sublattice sites was optimized on basis of the linear connectivity between AlB<sub>2</sub> and MgB<sub>2</sub>. The thermodynamically estimated Al-Mg-B ternary isotherms are shown in Fig. 3, in which  $(Al,Mg)B_2$  is in equilibrium with intermediate phases in the Al-Mg system – Al solid solution, Al<sub>8</sub>Mg<sub>5</sub>, and Mg solid solution. The phase diagram allows to predict and design the in-situ composite based on the Al-Mg matrix and the (Al,Mg)B<sub>2</sub> reinforcement compound phase. As a result of the above estimations, the nominal compositions of the composite that would be composed of the reinforcing (Al,Mg)B<sub>2</sub> phase in the Al-Mg matrix have been selected; constant boron of 1, 1.5 and 2.0wt% with increasing Mg contents of 0 to 10wt%.



Fig. 2 Binary phase diagrams of published (a) Mg-B binary system (b) Al-Mg binary system



Fig. 3 Isotherm of the Al-Mg-B ternary system : (a) at 1300°C, (b) 900°C and (c) 50°C

#### 3.2 Phase stability and mechanical properties

The microstructures of the as-received Al-5at% B master alloy is shown in Fig. 1(a), indicating that the alloys are mainly composed of  $AlB_{12}$  precipitates in an aluminum matrix. When the master alloy was hold at 1600°C for 30 minutes in an electric furnace under purging of an Ar gas and cast in a mold, the  $AlB_{12}$  phase has transformed into  $AlB_2$  phase. It appears that the morphology of the  $AlB_2$  phase is similar to the previously reported one [1], i.e. a plate-like shape (Fig. 4(b)).

The microstructures of the magnesium added aluminum boride phases are shown in Fig. 5. EPMA shows that the AlB<sub>2</sub> borides were transformed into (Al,Mg)B<sub>2</sub> for the alloys with magnesium additions. The location of (Al,Mg)B<sub>2</sub> is placed inter and intra aluminum dendrites, indicating that the borides are formed from liquid state. The resultant microstructures were composed of aluminum dendrites, fine eutectic matrix composed of Al-Al<sub>8</sub>Mg<sub>5</sub>, and (Al,Mg)B<sub>2</sub> precipitates were observed for Al-Mg-B ternary systems. It was specially noted that the high boron content AlB<sub>12</sub> phase with a size of ~ 1 µm was observed inside the (Al,Mg)B<sub>2</sub> precipitates (Fig.5(b)). While the detailed structural evolution needs further investigation, it is probable that the phase transformation of (Al,Mg)B<sub>2</sub> is originated from AlB<sub>12</sub>, implying that the formation of (Al,Mg)B<sub>2</sub> may be in the order of liquid  $\rightarrow$  AlB<sub>12</sub>  $\rightarrow$  AlB<sub>12</sub> + Mg  $\rightarrow$  (Al,Mg)B<sub>2</sub>. It appears that the AlB<sub>12</sub> phase inside the (Al,Mg)B<sub>2</sub> precipitates depicted in Fig. 5(b) is originated from untransformed phase, and further heat treatment would accelerate the transformation kinetics. However, at the present stage, further heat treatments have not been undertaken, since the small AlB<sub>12</sub> phase would not critically affect the mechanical

properties of the composites. Upon addition of magnesium or boron, no significant microstructural phase changes have been observed for different Al-Mg-B compositions (not shown), since the target nominal compositions were designed to locate in the Al-Al<sub>8</sub>Mg<sub>5</sub>-(Al,Mg)B<sub>2</sub> equilibrium region, so that a certain level of ductility can be obtained and controlled for the composite. Especially, it is considered that the proportion of aluminum matrix may contribute to ductility of the composites, and both of the fine eutectics (Al and Al<sub>8</sub>Mg<sub>5</sub>) and borides would work for the strength of the composites.



Fig. 4 (a) SEM BSE image of Al-5wt%B master alloy indicating the presence of  $AlB_{12}$  and  $AlB_2$ , where the majority of precipitates is composed of  $AlB_{12}$ , (b) remelted at 1600°C with an air cooling indicating that only the needle shape  $AlB_2$  phase is observed.



Fig. 5 SEM BSE image of the Al-Mg-B ternary alloys

The tensile strength, yield strength and elongation are enlisted in Table 1. It is specially noted that the addition of magnesium increases the strength by increasing proportions of  $Al_8Mg_5$  in the  $Al_8Mg_5$  and Al eutectic phase. A small amount addition such as 1 at% of magnesium increases the strength of the composites and reduces the elongation drastically. Compared with alloy No. 1 and alloy No. 5, it is manifested that the tensile strength of alloy No. 5 was increased by about 2.3 times with only 7 at% of increase of magnesium. However, the amount of borides did not significantly increase the strength of the composite, compared with alloy No. 5 and No. 16. It appears that the addition of magnesium in the Al-B system is the critical key factor for achieving high strength. The above results show that the strength and elongation can be tailored for structural parts such as piston. Also, it clearly shows that the density of the composites can be reduced without sacrifice of strength and elongation, and the increased strength by addition of Mg and/or boron in aluminum alloys gives a new insight for materials selection of light weight applications.

Series No.	Alloy No.	Compositions	UTS (MPa)	YS (MPa)	E (%)
Ι	1	Al-1%Mg-1%B	100.271	56.9618	28.466
	2	Al-2%Mg-1%B	142.087	67.9173	24.311
	3	Al-3%Mg-1%B	174.024	76.2514	25.764
	4	Al-5%Mg-1%B	240.114	114.008	16.213
	5	Al-8%Mg-1%B	225.369	159.324	3.104
II	6	Al-0%Mg-1.5%B	68.0445	50.33	30.874
	7	Al-1%Mg-1.5%B	106.309	80.23	22.739
	8	Al-2%Mg-1.5%B	135.005	120.001	14.201
	9	Al-3%Mg-1.5%B	164.760	120.003	8.670
	10	Al-5%Mg-1.5%B	238.788	134.018	8.550
	11	Al-10%Mg-1.5%B	194.860	163.839	1.644
III	12	Al-1%Mg-2%B	94.9239	61.6245	21.547
	13	Al-2%Mg-2%B	133.951	68.6871	14.669
	14	Al-3%Mg-2%B	168.783	78.2600	16.868
	15	Al-5%Mg-2%B	220.653	113.7490	11.243
	16	Al-8%Mg-2%B	249.975	156.0290	5.143

Table 1 Tensile strength, yield strength and elongation of the fabricated Al-Mg-B alloys

## 4. Summary

The structural evolution and mechanical behaviors of the Al-Mg-B ternary system have been investigated in order to fabricate a composite system composed of  $(Al,Mg)B_2$  in a Al and  $Al_8Mg_5$  matrix. The stability of the Al-Mg-B ternary system has been successfully evaluated via updated binary phase diagrams and corresponding isothermal ternary systems were identified. It appears that the structural evolution of the boride is undertaken by the following kinetics: Liquid  $\rightarrow AlB_{12} \rightarrow AlB_{12} + Mg \rightarrow (Al,Mg)B_2$ . Several Al-Mg-B ternary alloy compositions were selected for fabrication and identification of borides and matrix formation during solidification. The in-situ  $(Al,Mg)B_2$  phase was developed in an eutectic matrix of  $Al_8Mg_5$  and Al, and, and the tensile strength was increased by two distinct manners, the increased amount of the reinforcing  $(Al,Mg)B_2$  phase in the matrix and the addition of magnesium, resulting to the matrix reinforcement by increasing the eutectic structure of Al and  $Al_8Mg_5$ . It appears that increased strength by addition of Mg and/or boron in Al gives a new insight for materials selection of light weight applications.

## References

[1] C. Deppisch, G. Liu, J. K. Shang and J. Economy: Mater. Sci. Eng. A225 (1997) 153-161.

[2] T. B. Massalski, H. Okamoto, P.R. Subramanian and L. Kacprzak: *Binary Alloy Phase Diagrams,* 2<sup>nd</sup> edition, (ASM International, Materials Park, OH, 1990)

[3] D. Mirković, J. Gröbner, R. Schmid-Fetzer, O. Fabrichnaya and H. L. Lukas: J. Alloys Comp. 384 1-2 (2004) 168-174.

[4] S. V. Meschel and O. J. Kleppa: J. Alloys Comp. 227 1 (1995) 93-96.

[5] V. T. Serebryansky, V. Z. Epelbaum and G. S. Zhdanov: Russ. J. Inorg. Chem., 12 (1967) 543.

[6] P. Villars, A. Prince and H. Okamoto: *Handbook of Ternary Alloy Phase Diagrams*, (ASM International, Materials Park, OH, 1995)