Fluidity and Microstructure Evolution of Al-12%B₄C Composites Containing Magnesium*

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The influence of 0.5% magnesium addition on the fluidity evolution and microstructure of aluminum and Al-12%B₄C composites was investigated. It was observed that the magnesium addition reduced the fluidity of aluminum and the Al-B₄C composites. Moreover, magnesium promoted the interfacial reactions between liquid aluminum and B₄C in the Al-B₄C composites. An adequate Ti addition in the composites could effectively limit the impact of magnesium on the interfacial reactions and significantly improve the fluidity by forming a dense TiB₂ protective layer on the B₄C particle surface. It was also found that a part of magnesium is consumed in the reaction product, which resulted in the reduction of magnesium available in the matrix. The effects of magnesium and titanium on the fluidity, interfacial reactions and magnesium redistribution were discussed. [doi:10.2320/matertrans.L-MZ201117]

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1. Introduction

B₄C is an attractive reinforcement for Al-based composites due to its mechanical and physical properties, especially its high capacity in neutron absorption.¹⁻³⁾ However, since boron carbide is not stable in liquid aluminum, interfacial reactions exist between liquid aluminum and B₄C particles.⁴⁻⁶⁾ The reaction products are Al₃BC and AlB₂ at 750°C.⁴⁾ Moreover, liquid aluminum has poor wettability on B₄C below 1100°C, resulting in the difficulties to produce Al-B₄C composites by liquid mixing process.^{7,8)} It was found that B₄C particle can be easily incorporated into liquid aluminum if a flux containing Ti was used.^{5,8)} Commercial Al-B₄C materials have been successfully fabricated by Rio Tinto Alcan using a liquid mixing process. In this process, titanium was added into the composites to limit the interfacial reactions and improve the composite fluidity by forming a Ti-rich (TiB₂) protective layer on the B₄C particle surface.^{3,9-11)} At present, the Al-B₄C particle-reinforced metal matrix composites have been applied for transport and storage containers of spent nuclear fuels in nuclear industries.³⁾ However, since the spent nuclear fuels generate a high heat output, the mechanical properties of the composites have to be maintained stable at elevated temperatures to meet the increasingly demand for the application.¹²⁾ To strengthen the aluminum matrix at high temperatures, one of practical avenues is solid solution strengthening.¹³⁾ Magnesium is a major element for the solid solution strengthening on aluminum alloy attributed to its high solid solubility (16.26 at%) in aluminum and large atomic size difference (5.92%) with aluminum.¹³⁾

On the other side, good fluidity is a basic requirement for the fabrication of Al-B₄C composite by liquid mixing process. It was reported that the magnesium addition reduced the fluidity of aluminum alloys.¹⁴⁾ Moreover, the interfacial reactions in Al-B₄C composites would cause a decrease of

the fluidity because of an increase of solid particles and particle agglomerates in the composite melt.^{11,15)}

In this study, the effect of magnesium addition on the fluidity evolution and the variation of the microstructure in Al-12%B₄C composites are investigated in order to understand the impact of magnesium addition in Al-B₄C composites.

2. Experimental Procedures

Prefabricated DC cast billets of Al-18%B₄C containing 0.75%Ti, fabricated by Rio Tinto Alcan, were used for the experiments. The average B₄C particle size (F400) was approximately 17 μm. In the composite preparation, commercially pure aluminum (99.7% Al) was first melted in an electrical resistance furnace. The prefabricated Al-18%B₄C cast billets, commercially pure magnesium and Al-10%Ti master alloy were then added into the molten aluminum to obtain the desired composition. As the temperature of the furnace increased, these materials were first melted, and the temperature of the composite melt continued to increase to 750°C for the fluidity tests. The melt preparation time was about 30 minutes, starting from the melting (about 660°C) to reaching the 750°C temperature. The compositions of the four experimental Al-B₄C composites are listed in Table 1.

During the fluidity tests, the composite melt was held at 750 ± 2°C for 2 hours under mechanical stirring (Fig. 1(a)). The mixer speed was 200 rpm, ensuring a uniform distribution of B₄C particles in the liquid but avoiding the formation of a vortex in the melt surface. A vacuum fluidity test set-up (Fig. 1(a)) was used for the fluidity tests. The pressure

Table 1 Compositions of experimental composites.

Composites	Vol% B ₄ C	mass% Ti	mass% Mg
0.5Ti	12	0.5	0
0.5Ti-0.5Mg	12	0.5	0.5
1.5Ti	12	1.5	0
1.5Ti-0.5Mg	12	1.5	0.5

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Fig. 1 (a) Set-up sketch of a vacuum fluidity test; (b) sampling position; (c) quantitative analysis zones on a cross-section of a sample.

Fig. 2 Fluidity of aluminum and aluminum containing 0.5 mass% Mg.

Fig. 3 Fluidity evolution: (a) 0.5Ti and 0.5Ti-0.5Mg composites, (b) 1.5Ti and 1.5Ti-0.5Mg composites.

supplied by a vacuum system in the set-up was kept at 215 mm Hg while the composite melt filled a 6 mm inside diameter glass tube. A fluidity sample was regularly taken at every 10 to 15 minutes. The flow length of the composite in the tube was measured for the fluidity evaluation after the solidification.

For the evaluation of the influence of magnesium addition on the fluidity of liquid aluminum, commercial pure magnesium was added in liquid aluminum at 700°C, then the temperature of the melt increases to 750°C for the vacuum fluidity tests with a pressure 80 mm Hg.

Two series of fluidity tests for each experimental material were carried out to obtain reliable data.

An image analyzer (CLEMEX JS-2000, PE4.0) equipped with a 3-CCD color video camera (SONY DXC-950P) was used for quantitative microstructure characterization such as particle volume fraction measurement. Under an optical microscopy, all solid particles have different colors and grey scale. For examples, B₄C particles show a dark color while the interfacial reaction induced phases, Al₃BC and AlB₂ particles have a grey and a yellow color, respectively. In addition, enclosing B₄C particles, TiB₂ particle layer has a light grey color. The volume fraction of these solid particles was measured by the image analyzer at a 500× magnification based on the particle colors and grey scale.¹⁶⁾ A cross-section specimen near the melt entrance of the fluidity test sample was taken for the microstructural analysis (Fig. 1(b)). The area of the measured zones was about 17% of the total area of the cross-section (Fig. 1(c)).

A scanning electron microscope (JSM-6480LV), and an electron probe microanalyser (Cameca SX100) were used to examine the microstructure.

3. Results and Discussion

3.1 Influence of magnesium on fluidity of aluminum and Al-B₄C composites

3.1.1 Influence of magnesium on fluidity of aluminum

The influence of magnesium addition on the fluidity of aluminum at 750°C is illustrated in Fig. 2. The flow length of the aluminum melt containing 0.5%Mg is 46 cm, which is only 68% of the flow length (67 cm) of the melt without magnesium. This indicates that the magnesium addition significantly decreases the fluidity of liquid aluminum, which is due to the changes of solidification modes and superheat of the melt.¹⁷⁾

Figure 3(a) shows the fluidity results of the 0.5Ti composites with and without magnesium as a function of the holding time. The fluidity of the 0.5Ti composite decreases rapidly during the melt holding period at 750°C. At the initial stage, the fluidity of the magnesium containing composite is much lower than that of the composite without magnesium. However, the fluidity of the 0.5Ti-0.5%Mg composite remains almost unchanged during holding. After a 2 hour holding period, the fluidity of the composite without magnesium is worse than that of the magnesium containing composite. It is evident that the fluidity evolution of the two composites is different due to the addition of magnesium.

For the 1.5Ti composites, with and without magnesium, (Fig. 3(b)), the fluidity decreases only slightly during the melt holding period. It is clear that the fluidity of the magnesium containing composite is lower than that of the composite without magnesium. Magnesium addition has a tendency to reduce the fluidity of Al-B₄C composites. It should be noted that, for the same B₄C volume fraction, the

Fig. 4 Microstructure under optical microscope with a 2 minute holding period: (a) Al-12B₄C-0.5Ti, (b) Al-12B₄C-0.5Ti-0.5Mg, (c) a spectrum of Al-B-Mg phase.

Fig. 5 Backscattered electron images: (a) 0.5Ti-0.5Mg composite (2 minute holding period), (b) zone of (a), (c) 1.5Ti-0.5Mg composite (120 minute holding period).

fluidity of 1.5Ti composites is much better than that of the 0.5Ti composites.

3.2 Microstructure of the experimental composites

3.2.1 Influence of magnesium on interfacial reactions and its distribution

In Al-B₄C composites, the interfacial reaction between liquid aluminum and B₄C particles (1) generates two reaction-induced phases, Al₃BC and AlB₂:^{4,10,18)}

When Ti is added into the composite melt, AlB₂ is gradually replaced by TiB₂ because TiB₂ is more stable than AlB₂ based on their Gibbs energy of formation (TiB₂: -331.0, AlB₂: -108.8 KJ/mol).¹¹⁾ When an adequate Ti amount is present in the melt, TiB₂ completely replaces AlB₂ in the composites, i.e. the interfacial reaction become:

The phases Al₃BC, AlB₂ and TiB₂ can be seen under optical microscopy in the microstructure of the 0.5Ti composite (Fig. 4(a)). Here, the coexistence of AlB₂ and TiB₂ is because the amount of Ti in the composite is not enough. Moreover, it was often observed that, in the 0.5Ti-0.5Mg composite, the surfaces of some B₄C particles were heavily attacked, caused by interfacial reactions, whereas some B₄C particles still kept a good shape due to a Ti-rich (TiB₂) protective layer enclosing the particles (Fig. 5(a) and (b)). The titanium mapping, measured by an electron probe microanalyser, indicates that at a low Ti level, not all the B₄C particles can be protected by the TiB₂ layer on the B₄C particle surface (Fig. 6(a) and (c)).

Magnesium was detected in the yellow phases in the 0.5Ti-0.5Mg composite (Fig. 4(b) and (c)). Thus, the interfacial reaction-induced phase AlB₂ in the composite without Mg was substituted by Al-B-Mg phase in the magnesium containing composite. According to,¹⁹⁾ the crystal structure of the Al-B-Mg phase is the same as the AlB₂ phase. It is believed that some Al atoms can be replaced by Mg atoms in the AlB₂ lattice structure and result in a variation of the chemical composition and lattice parameter of the phase, which commonly is referred to as (Al, Mg)B₂,¹⁹⁾ i.e.

The magnesium mapping in the 0.5Mg-0.5Ti composite (Fig. 6(a) and (b)) shows that some of the magnesium concentrates in the (Al, Mg)B₂, whereas some of the magnesium remains in the aluminum matrix. This phenomenon results in a significant reduction of the magnesium amount in the aluminum matrix, which decreases the capability of solid solution strengthening and age hardening response of the material.

Similar to the low Ti composites, the interfacial reaction-induced phases, Al₃BC and AlB₂ or Al₃BC and (Al, Mg)B₂ were observed in the 1.5%Ti composites with and without magnesium, respectively (Fig. 7). However, the amount of AlB₂ or (Al, Mg)₂B was much less than that in 0.5Ti, or 0.5Ti-0.5Mg composites. It is interesting to note that, after a 120 minute holding period, the shape and surface of most of the B₄C particles were clear and kept well in these two composites. Backscattered electron images indicate that a dense Ti-rich (TiB₂) layer encloses B₄C particles, which plays an important role in protecting the B₄C particles (Fig. 5(c)). It is expected that when an adequate Ti is

Fig. 6 Element mapping of Al-12B₄C-0.5Ti-0.5Mg composite (100 minute holding time) using an electron probe microanalyser: (a) backscattered electron image, (b) Mg mapping, (c) Ti mapping.

Fig. 7 Microstructure under optical microscope with 120 minute holding period: (a) 1.5Ti composite, (b) 15Ti-0.5Mg composite.

presented in the composite, most Mg can retain in the matrix instead of consuming in the reaction product.

3.2.2 Particle volume fraction evolution

The evolution of the volume fraction of interfacial reaction-induced compounds AlB₂, (Al, Mg)B₂, and the total reaction products in the four experimental composites is shown in Fig. 8. The total reaction products are Al₃BC, AlB₂/(Al, Mg)B₂, and TiB₂ in the composites. Since TiB₂

was formed in the melt preparation period and its amount was almost constant, the increase of the total reaction products is actually caused by the increase of the other two compounds, Al₃BC and AlB₂/(Al, Mg)B₂.

For the low Ti composites, the volume fraction of (Al, Mg)B₂ in the 0.5Ti-0.5Mg composite is much higher than that of AlB₂ in the 0.5Ti composite (Fig. 8(a)) at the beginning of the holding period. However, the increase rate

Fig. 8 The evolution of volume fraction of reaction particles as a function of holding time: (a) AIB₂ and (Al, Mg)B₂ phases, (b) total reaction particles.

Table 2 Reaction products in the 0.5%Ti containing composites.

Reaction products	Volume fraction of reaction products		
	Prefabricated billets	0.5Ti composite with (2 min holding)	0.5Ti-0.5Mg composite with (2 min holding)
AIB ₂ or/and (Al, Mg)B ₂ (%)	0.6	0.6	2.0
Total reaction products (%)	6.1	6.9	9.0

of the former is slower than that of the latter. At the end of the holding period, the volume fraction of AIB₂ in the 0.5Ti composite is higher than that of (Al, Mg)B₂ in the 0.5Ti-0.5Mg composite. The same phenomena on the total reaction products appear for the low Ti composites (Fig. 8(b)). This indicates that the magnesium addition significantly affects the evolution of the reaction compounds during the melt holding period. Table 2 lists the data of the reaction products in the prefabricated billets and the fluidity samples taken at the beginning of the holding in the 0.5%Ti and 0.5Ti-0.5Mg composites. Results show that the amount of reaction products increases rapidly in the magnesium containing composites during the melt preparation, about 30 min from the melting point (about 660°C), to the temperature reaching 750°C. However, during this period, the increase of the reaction products is not obvious in the composites without magnesium. This indicates that magnesium addition promotes the interfacial reactions between the liquid aluminum and the B₄C particles.

It is interesting to note that the increase rate of the reaction compounds in the 0.5Ti-0.5Mg composite is much slower than that of the 0.5Ti composite during the melt holding period. This is probably due to a layer formed by the reaction compounds during the melt preparation which attached and enclosed the B₄C particles (Fig. 5(a) and (b)). This layer would limit the decomposition of B₄C particles to some degree.

For the high Ti composites, the amount of interfacial reaction-induced compounds increases slightly while the melt is held at 750°C (Fig. 8). In general, the amount of the reaction compounds in the magnesium containing composite is a little more than that in the composite without magnesium. This further confirms that magnesium addition elevates the interfacial reactions in Al-B₄C composites, although the

impact of magnesium addition is not serious in the high Ti composites. Moreover, the volume fraction of the Mg-contained reaction compound in the high Ti composites is much lower than those in the low Ti composites (Fig. 8(a)). It significantly reduces the magnesium amount that consumed in the reaction compound. It is evident that a high Ti addition is better than a low Ti addition to limit the interfacial reactions. A dense TiB₂ layer enclosing the B₄C particles limits the decomposition of these B₄C particles by a solid diffusion process (Fig. 5(c)).

It is established that the increase of particle volume in composite melt caused by interfacial reactions decreases the fluidity of composites.²⁰ Moreover, the agglomeration formed by reaction particles also has a contribution to the decrease of composite fluidity.^{11,15,17} The amount of reaction compounds increases when prolonging the holding period in Al-12%B₄C composites. Therefore, the more reaction particles are enclosed in the composite, the lower is the fluidity of the composite. The evolution of the volume fraction of reaction-induced particles (Fig. 8) agrees well with the fluidity variation of the composites during the melt holding period (Fig. 3). In addition, magnesium remaining in aluminum matrix also contributes to the fluidity decrease of the magnesium containing composites since magnesium addition significantly decreases aluminum fluidity (Fig. 2).

4. Conclusions

- (1) Magnesium addition reduces the fluidity of the Al-B₄C composites to some degree. However, an adequate Ti addition can significantly improve the fluidity of the magnesium containing composites.
- (2) Magnesium addition promotes the interfacial reactions in Al-B₄C composites, especially for the composites with a low titanium level. However, a sufficient high Ti concentration can effectively limit the affection of Mg on the interfacial reactions due to forming a dense TiB₂ layer on the B₄C particle surface.
- (3) Due to the interfacial reaction, a part of magnesium is consumed in the (Al, Mg)B₂ reaction product, which declines the magnesium strengthening effect on the aluminum matrix. A high Ti reduces the consumption of magnesium in the reaction product and helps most magnesium retaining in the matrix.

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