

## ANALYSIS OF BORON TREATMENT FOR V REMOVAL USING $AlB_2$ AND $AlB_{12}$ BASED MASTER ALLOYS

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Keywords:  $AlB_{12}$ ,  $AlB_2$ ,  $VB_2$ , boron treatment, settling of boride, vanadium removal

### Abstract

Boron treatment is a widely used practice in industry for removing transition metals such as Ti, V, and Zr. Mostly, Al-B master alloys containing  $AlB_2$  and  $AlB_{12}$  are used for the treatment. This paper describes the analysis and comparison of the boron treatment using these two types of Al-B master alloys. Kinetic experiments of V removal using the two alloys were carried out for alloy Al-1wt %V at 750°C in a resistance furnace. Samples were taken at regular interval and characterized using scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). The change of V concentration, analyzed using ICP (inductively coupled plasma) analysis, was also tracked with reaction time. It has been shown that the kinetics of boron treatment using  $AlB_2$  based alloy was faster compared to those using  $AlB_{12}$ , which was related to the particle size and available interfacial area for reaction. Boride particles settling was also analyzed in the present study using multi-locations sampling technique that revealed faster settling for  $AlB_{12}$  based master alloys compared to  $AlB_2$ .

### Introduction

Aluminum has been used to replace copper for electrical conductor applications due to low-cost supply and better mechanical properties. However, the presence of transition metal impurities such as Ti, Zr, V and Cr languish the electrical conductivity of smelter grade aluminum. Gauthier [1] investigated the effect of small addition of elements on the conductivity of super pure aluminum. It was reported that Au, Ga, Ni, Si, Fe and Zn had little effect compared to Cu, Ag and Mg. The elements Ti, V, Mn and Cr in the third group were more deleterious to the conductivity of the aluminum. The addition of 0.005% to 0.025% vanadium to the high purity aluminum reduced its conductivity from 64.25% to 60.00% of copper, which is not acceptable for electrical grade applications [1]. The impact of transition metal impurities on the electrical conductivity is more pronounced when they are present in solution with aluminum. The adverse effect on conductivity is minimized when impurities are present out of solution such as borides [2].

In casthouse, transition metal impurities are removed by the addition of Al-B master alloys and the process is called boron treatment [3-13]. Dube [3] investigated the removal of Ti and V from smelter grade aluminum, using Al-B ( $AlB_2/AlB_{12}$ ) and borax in the presence of chlorides and fluorides fluxes and melt agitation. Industrially, Stiller and Ingenlath [4] evaluated the removal of Ti, V, Zr, Cr and Mn, the electrical conductivity and grain refinement of smelter grade aluminum. It was reported that the excess boron addition is required for the removal of transition metal impurities, to meet the electrical conductor specifications.

Industrially, Al-B master alloys containing  $AlB_2$  and  $AlB_{12}$  phases are employed during boron treatment of molten aluminum. Al-B master alloys are available in the form of waffles, ingots, rods and wires that can be employed, based on the needs of a casthouse. Various researchers investigated the action mechanism of  $AlB_2/AlB_{12}$  and transition metal impurities in molten aluminum. Setzer and Boone [13] studied the relative effect of  $AlB_{12}$  and  $AlB_2$  phases on the electrical conductivity and the settling of borides in molten aluminum. During study, Al-4%B ( $AlB_{12}$ ) and Al-5%B ( $AlB_2$ ) master alloys were added in excess to the stoichiometric requirement of diborides formation. The increase in electrical conductivity of aluminum was high after the addition of Al-B master alloys, as shown in Figure 1. The conductivity escalated from 60.0% IACS to 62.0% IACS (international annealed copper standard) within first minutes of reaction and remained constant with further holding of the melt. Figure 1 also shows that the increase in electrical conductivity using  $AlB_2$  phase of Al-B binary system was faster compared to  $AlB_{12}$ .

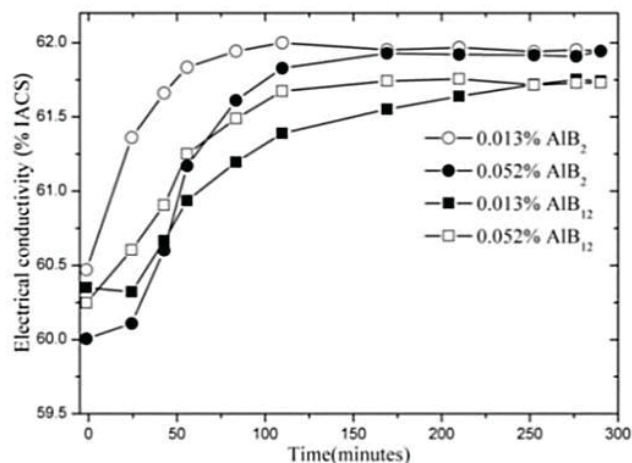


Figure 1 - Increase in the electrical conductivity of smelter grade aluminum by the addition of different Al-B master alloys [13]

They also investigated the settling of transition metal borides formed during boron treatment. The percentage of Ti, Zr, V borides settled with reaction time (minutes) is shown in Figure 2. It can be seen that the settling of borides was faster, using  $AlB_{12}$  compared to  $AlB_2$ .

Cooper and co-workers [5, 6] investigated the removal of transition metals impurities from molten aluminum and reported the adoption of either  $AlB_2$  or  $AlB_{12}$  was insignificant. Indeed, the particle size of Al-B binary phases was more important during

boron treatment. Karabay and Uzman [8, 9] performed industrial trials on the removal of transition metal impurities from smelter grade aluminum, using various Al-B master alloys. It was reported that the required level of electrical conductivity (min 61.5% IACS) was achieved using Al-3% B ( $\text{AlB}_2$ ) in the launder during continuous casting line (CCL). The Al-3%B master alloy was used in the form of wires.

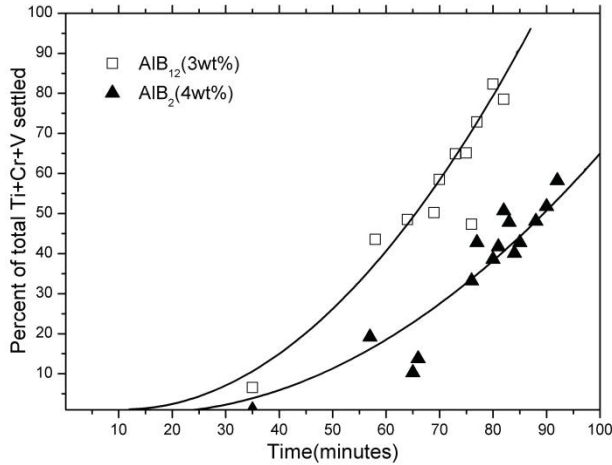


Figure 2 - Settling rate of borides generated by  $\text{AlB}_2$  and  $\text{AlB}_{12}$  phase, re-produced after [13]

Previously, boron treatment was investigated in relation to the increase in electrical conductivity of the smelter grade aluminum. Khaliq *et al.* [10-12, 14-17] investigated the thermodynamics and kinetics of the Al-X-B (X = V, Zr, Ti and Cr) alloys. The diborides formation and their stability were predicted from thermodynamic analysis. It was predicted that excess addition of boron will favour the complete removal of transition metal impurities. The formation of  $\text{VB}_2$  rings, encapsulating the initially added  $\text{AlB}_{12}$  were revealed during experimental investigation of Al-V-B alloys. Moreover, the formation  $\text{VB}_2$  rings in the early stage revealed the reaction was rapid that lead to the increase in electrical conductivity of molten aluminum as reported by previous investigators. It was further reported that the reaction between  $\text{AlB}_{12}$  and V was incomplete due the formation of  $\text{VB}_2$  ring [11]. The kinetic analysis and the mechanism of  $\text{VB}_2$  formation in molten aluminum was elucidated using different rates of melt stirring and boron addition. It was established that the reaction between  $\text{AlB}_{12}$  and V was controlled by two mechanisms. In the early stage, reaction was controlled by the mass transfer of V in bulk melt. Diffusion of B through  $\text{VB}_2$  layer was the rate controlling step in the second stage of reaction [12].

A kinetic plot of Al-1wt%V-0.412wt%B alloy, showing the removal of V with reaction time and the mechanism of  $\text{VB}_2$  formation, is shown in Figure 3. The rate of V removal is fast in the early stage (up to 10 minutes) but slowed down with further reaction time. The SEM images of samples taken during both stages are also shown in Figure 3. The rings of  $\text{VB}_2$  and partially dissolved  $\text{AlB}_{12}$  were observed during first stage of reaction. In the second stage, rings of  $\text{VB}_2$  are thickened and only in some cases,  $\text{AlB}_{12}$  completely dissolved as shown in Figure 3.

#### Al-B master alloys

The analysis of Al-B binary system is important for boron treatment process. Boron has limited solubility in solid aluminum,

and the reported values are less than 100 ppm at room temperature. The liquid solubility of boron is not well documented. However, molten aluminum dissolves about eight times more boron compared to solid [18]. Boron in excess to the solubility of limits reacts with aluminum to form Al-B compounds such as  $\text{AlB}_2$  and  $\text{AlB}_{12}$  as shown in Figure 4.

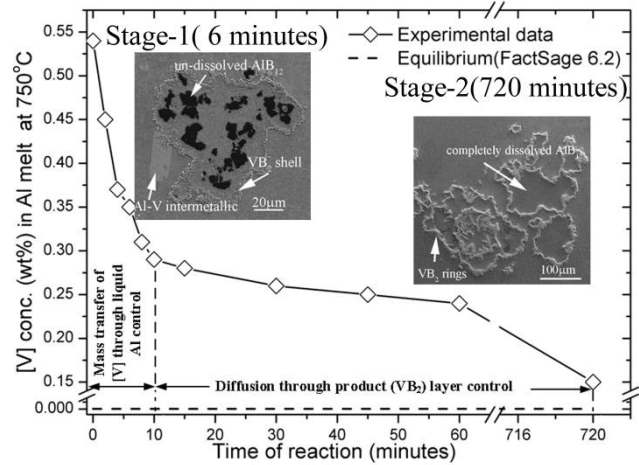


Figure 3 - Kinetic plot of V removal from Al-1wt% V-0.412wt% B alloy at 750°C, showing the mechanism of  $\text{VB}_2$  formation [12].

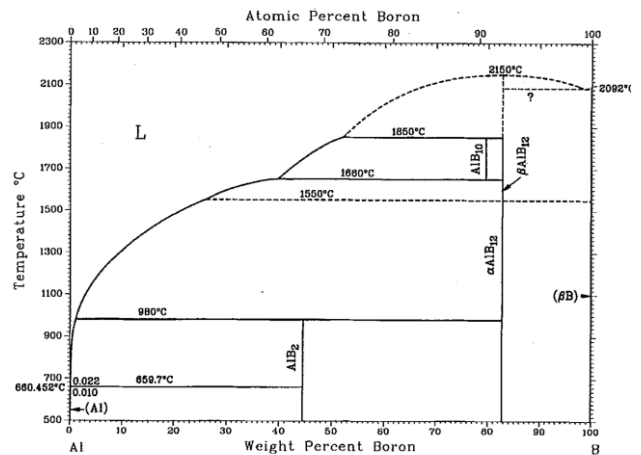
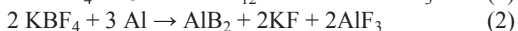
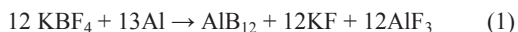


Figure 4 - Phase diagram of Al-B binary system [19]

In the Al-B binary system,  $\alpha$ - $\text{AlB}_{12}$  phase exist at low temperature. At higher temperatures,  $\beta$ - $\text{AlB}_{12}$  and  $\gamma$ - $\text{AlB}_{12}$  were reported but no experimental evidence was provided [19-21]. The melting temperature of  $\beta$ - $\text{AlB}_{12}$  is  $2150 \pm 50^\circ\text{C}$ . Carlson [19] accepted  $\alpha$ - $\text{AlB}_{12}$  and  $\beta$ - $\text{AlB}_{12}$  as stable phases for construction of an Al-B phase diagram. The  $\text{AlB}_2$  phase of the Al-B binary system, forms peritectically at  $980^\circ\text{C}$  and has a melting temperature of  $1655 \pm 50^\circ\text{C}$ . The stability of  $\text{AlB}_2$  was confirmed by Serebryanskii *et al.* [21], during quenching experiments. The  $\text{AlB}_4$  stoichiometric phase was also reported during X-ray diffraction analysis, but later was omitted by Serebryanskii *et al.*

Al-B master alloys Al-10wt% B ( $\text{AlB}_{12}$ ), Al-6wt% B ( $\text{AlB}_{12}$ ), Al-5wt%B ( $\text{AlB}_2$ ) and Al-wt4%B ( $\text{AlB}_{12}$ ) are commonly used for the boron treatment of aluminum melt in casthouse [5, 13, 14]. Al-B master alloys are produced by the reduction of  $\text{KBF}_4$  salts directly

in the molten aluminum at a specified temperature [22-24]. The following reactions have been written for the production of either  $\text{AlB}_{12}$  or  $\text{AlB}_2$  phase Al-B master alloys using  $\text{KBF}_4$  salts and aluminum.  $\text{AlB}_{12}$  and  $\text{AlB}_2$  produced are dispersed in the molten aluminum.



Al-B master alloys, containing  $\text{AlB}_{12}/\text{AlB}_2$  phases have been used successfully for boron treatment of molten aluminum. However, the behavior of  $\text{AlB}_{12}$  and  $\text{AlB}_2$  is not well understood. There have been some disagreements on the detailed mechanisms of reactions between  $\text{AlB}_{12}$  and  $\text{AlB}_2$  with the transition metal impurities reported in the literature.

In this study, the removal of V from molten aluminum was investigated using  $\text{AlB}_{12}$  and  $\text{AlB}_2$  based master alloys. A comparative analysis was carried out to establish whether, the form of Al-B binary phases ( $\text{AlB}_{12}/\text{AlB}_2$ ) or their particle sizes, determine the kinetic of V removal from molten aluminum. Moreover, the settling of borides was investigated by taking samples from multiple locations at the melt inside the crucible. The main objective of the second experiments was to evaluate the concentration gradient inside crucible and the settling rates of borides with reaction time.

## Experimental

### Materials

In this study, pure Al (99.90%), Al-10%V, Al-10%B ( $\text{AlB}_{12}$ ) and Al-5%B ( $\text{AlB}_2$ ) master alloys were used. Pure Al was supplied by CSIRO Clayton, Melbourne. Al-V and Al-B master alloys were supplied by KB alloys, AMG Aluminum, USA.

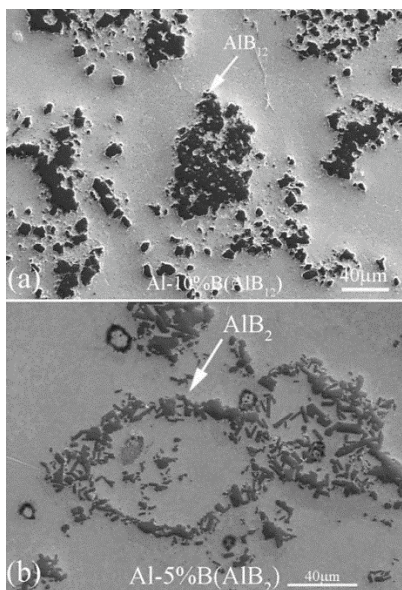


Figure 5 - SEM-SE image of original borides in Al-B master alloy: (a) Al-10%B ( $\text{AlB}_{12}$ ) and (b) Al-5%B ( $\text{AlB}_2$ ) master alloy

SEM-SE image of Al-10%B master alloy is shown in Figure 5(a). Clusters of  $\text{AlB}_{12}$  are present in the Al matrix having particles in the range of  $1\mu\text{m}$  to  $60\mu\text{m}$ .  $\text{AlB}_{12}$  particles possess irregular morphology, while  $\text{AlB}_2$  are smaller in size and more elongated,

as shown in Figure 5(b).  $\text{AlB}_2$  particles also form clusters and dispersed in the matrix with higher aspect ratio (length/diameter).

### Experimental Plan

The experimental study involved the reactions between Al-1%V, and Al-10%B ( $\text{AlB}_{12}$ ) and Al-5% ( $\text{AlB}_2$ ) master alloys in a BN coated graphite crucible. The procedure for the preparation of Al alloys has been explained elsewhere [15]. Two batches of experiments were performed in this study.

Batch 1 composed of 1 kg of Al-1wt%V-0.72wt%B alloys. Boron was added in the form of Al-10wt%B ( $\text{AlB}_{12}$ ) and Al-5wt% B ( $\text{AlB}_2$ ) master alloys. Samples were taken at regular intervals (0, 2, 4, 6, 8, 10, 15, 30, 45 and 60 minutes), after the addition of Al-B master alloys into molten Al-1wt%V at  $750^\circ\text{C}$ . Batch 2 consisted of 5 kg of Al-1wt%V-0.72wt%B alloys. The alloys were held at  $750^\circ\text{C}$  and samples were taken from multiple locations from the melt inside the crucible at same time. The assembly used for sampling is shown in Figure 6. During sampling, both shafts were introduced in the molten alloy while covering the scoops. One shaft was removed to allow melt to fill empty scoops and then covered again to prevent possible metal spill. The whole assembly was raised up from molten alloy and samples from different locations of crucible were allowed to solidify in air. Top, middle and bottom samples were taken from scoop 3, 2 and 1, respectively.

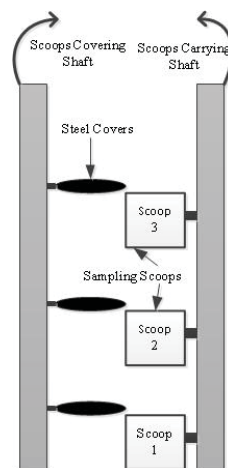


Figure 6 - Multiple locations sampling assembly

### Samples Characterization

Samples were analyzed for V removal, concentration gradient inside crucible, boride formation, and their settling with reaction time. Samples preparation for SEM and ICP-AES analyses have been explained elsewhere [15]. For spark emission spectrometer, samples were polished, and analyzed for chemical composition.

## Results and Discussion

### Observation of $\text{VB}_2$ Formation

The formation of  $\text{VB}_2$  was observed by SEM analysis of boride sludge. At the end of experiment, molten alloy was casted in a cast iron mold, and boride residue was collected from the bottom of the crucible. The settled residue was called boride sludge that was heavy and dense. An SEM-SE image of boride sludge collected from Al-1wt%V-0.72wt%B, using Al-10wt%B ( $\text{AlB}_{12}$ ) master alloy is shown in Figure 7(a). A reaction between V and  $\text{AlB}_{12}/\text{B}$  had taken place and reaction product was formed. It was believed that early reaction was taken place in the vicinity of

$\text{AlB}_{12}$ , which was added as a source of boron. It was proposed that the dissolution of  $\text{AlB}_{12}$  provided free boron for reaction with V to form  $\text{VB}_2$  in the molten alloy. Simultaneously, the mass transfer of V to the interface of  $\text{AlB}_{12}$  took place and, therefore the formation of  $\text{VB}_2$  by chemical reaction. In the early stage of reaction, mass transfer of V superseded the dissolution of  $\text{AlB}_{12}$  which lead to the formation of  $\text{VB}_2$  ring within minutes of reaction, as shown in Figure 7(a). Partially dissolved black phase ( $\text{AlB}_{12}$ ) were another feature of boride sludge.

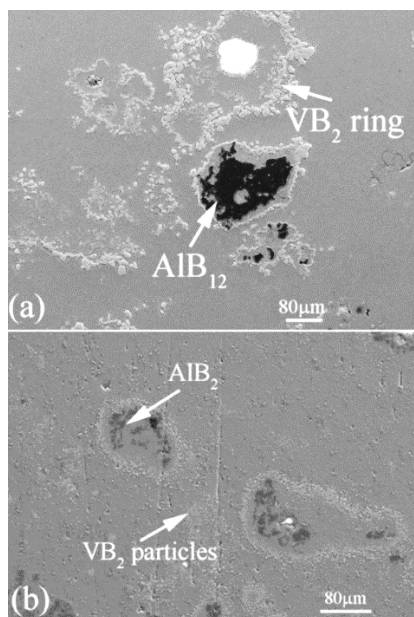


Figure 7 - SEM images of Al-1 wt%V-0.72wt%B boride sludge collected from the bottom of crucible, using (a) Al-10%B ( $\text{AlB}_{12}$ ) and (b) Al-5%B ( $\text{AlB}_2$ ) master alloys

It was believed that smaller  $\text{AlB}_{12}$  particles completely dissolved and provided boron for the formation of  $\text{VB}_2$ . However, larger  $\text{AlB}_{12}$  particles partially dissolved that were due to the formation of  $\text{VB}_2$  ring. A detail analysis of  $\text{VB}_2$  formation in molten aluminum, using  $\text{AlB}_{12}$  phase has been given in our previous work [11]. It was reported that reaction between V and  $\text{AlB}_{12}/\text{B}$  was rapid that form  $\text{VB}_2$  ring similar to discussed earlier in this paper. Further reaction was hampered due to the formation of  $\text{VB}_2$  ring that adversely affected the dissolution of  $\text{AlB}_{12}$ . It was further suggested that the later stage of reaction was controlled by the diffusion of boron through  $\text{VB}_2$  ring.

An SEM-SE image of Al-1wt%V-0.72wt%B boride sludge, using Al-5wt%B ( $\text{AlB}_2$ ) is shown in Figure 7(b). The formation of  $\text{VB}_2$  ring was also observed. However the  $\text{VB}_2$  formed had smaller particle size and the boride ring possessed less thickness, as shown in Figure 7(b). It appeared that the borides ( $\text{VB}_2$ ) formed during reaction were more dispersed in the aluminum matrix. Partially dissolved  $\text{AlB}_2$  particles as clusters were also observed, as shown in Figure 7(b). Common features of both borides sludge were the formation of  $\text{VB}_2$  ring and partially dissolved  $\text{AlB}_{12}$  and  $\text{AlB}_2$  particles. This further supports that the reaction was incomplete and therefore, the system was far from equilibrium, as also described elsewhere [11]. However, it can be seen from the Figure 7 that the extent of dissolution and reaction were higher in the case of  $\text{AlB}_2$ .

Semi-quantitative chemical composition of gray particles was carried out using EDS technique. The EDS analysis revealed that the borides formed during reaction were composed of V, B and Al, with possible chemical formula of  $\text{Al}_{8.4}\text{V}_{87.3}\text{B}_{4.3}$ . These borides were more enriched with V compared to that given in the previous work [11]. The presence of Al in the boride proposed the formation of mixed borides rather than pure  $\text{VB}_2$  compound, predicted during thermodynamic modeling of Al-V-B system. The full quantification of boron was not possible due to the detection limit of the EDS detector. However, boron was estimated from relative intensity of counts from EDS spectra.

From the SEM and EDS analysis, the formation of  $\text{VB}_2$  rings and partially dissolved  $\text{AlB}_{12}/\text{AlB}_2$  were in agreement with previous investigations. V-borides formed using  $\text{AlB}_2$  were enriched with V and possessed smaller particle size range. Moreover, the thickness of  $\text{VB}_2$  ring was less compared to the alloy using  $\text{AlB}_{12}$  for the removal of V from molten aluminum. It could be suggested from the SEM/EDS analysis that:

- (1) The reaction between V and  $\text{AlB}_{12}/\text{AlB}_2$  is rapid to produce  $\text{VB}_2$  rings. The adjoining of further reaction is due to the formation of  $\text{VB}_2$  ring that adversely affected the dissolution of  $\text{AlB}_{12}/\text{AlB}_2$ .
- (2) The presence of partially dissolved  $\text{AlB}_{12}/\text{AlB}_2$  in the alloys, suggests that the reaction was incomplete. Therefore, the system was far from equilibrium. However it appeared that the extent of reaction was higher in the case of  $\text{AlB}_2$ .
- (3) Large proportion of smaller  $\text{VB}_2$  particles were formed when  $\text{AlB}_2$  based alloys were used.
- (4) Borides formed using  $\text{AlB}_2$  were enriched with V compared to  $\text{AlB}_{12}$ .

#### Kinetic of V removal using $\text{AlB}_{12}$ and $\text{AlB}_2$

Experiments were conducted using Al-10wt% B ( $\text{AlB}_{12}$ ) and Al-5wt% B ( $\text{AlB}_2$ ) to investigate their relative effect on the removal of V from Al-1wt% V-0.72wt% B alloy at 750°C. The plots of V removal and integrated rate with reaction time for both master alloys are shown in Figure 8. The concentration of V in solution with molten aluminum was decreasing with reaction time as shown in Figure 8(a). The V removal was rapid at the start and slowed down with reaction time for both  $\text{AlB}_{12}$  and  $\text{AlB}_2$  alloys.

The initial rate of reaction was similar in both  $\text{AlB}_2$  and  $\text{AlB}_{12}$ , case, as shown in Figure 8(b). This is indicated by the similar mass transfer capacity coefficient ( $K_1 = kS/V \sim 0.1 \text{ m}^{-1}$ ) in the early stage advocated the comparable rate of V removal. This is reasonable as previous work indicated that the formation of  $\text{VB}_2$  in the early stage of reaction is controlled by the mass transfer of V in bulk melt [12]. Aluminum shell formation and melting, release and dissolution of  $\text{AlB}_{12}/\text{AlB}_2$  particles, mass transfer of V and chemical reaction were the main steps in early minutes [12]. In the case of  $\text{AlB}_{12}$ , the rate was slowed down after 6 minutes (indicated by small  $K_2 = 0.02 \text{ m}^{-1}$ ), due to the formation of  $\text{VB}_2$  rings, as shown in Figure 8(b). The characteristic of the  $\text{AlB}_{12}$  particles of a dense shape provided limited active interfacial area for further reaction to form of  $\text{VB}_2$ . In the case of  $\text{AlB}_2$ , the mass transfer capacity coefficient K remained 0.10 until 30 minutes of reaction. This suggested that the reaction could proceed further and that interruption due the formation of dense  $\text{VB}_2$  ring was insignificant compared to the case of  $\text{AlB}_{12}$ . It was suggested that the smaller and elongated  $\text{AlB}_2$  particles provided higher available surface area for further reaction. It also appeared that the  $\text{VB}_2$  ring that was formed in the case of  $\text{AlB}_2$  was less dense compared to

the case of  $\text{AlB}_{12}$  as shown in Figure 7.

After 30 minutes, in the case of  $\text{AlB}_2$ , and the level of V was rising again in the molten alloy, as shown in Figure 8(a). It was suggested that this was due to the re-dissolution of Al-V ( $\text{Al}_3\text{V}/\text{Al}_{10}\text{V}$ ) intermetallics in the molten alloy. At the start of reaction, the total V in the alloy was 1wt%. Of this, 0.53wt% of V was present in solution (maximum solubility at  $750^\circ\text{C}$ ), and the rest was in the form of intermetallics  $\text{Al}_3\text{V}$  and  $\text{Al}_{10}\text{V}$ . Therefore, the level of V concentration decreased with reaction time, however, at some point was compensated by the dissolution of Al-V intermetallics. At this stage, the dissolution of Al-V intermetallics superseded the removal of V through the formation of  $\text{VB}_2$ . By this time, most of the  $\text{AlB}_2$  particles were consumed and remaining clusters were encapsulated by  $\text{VB}_2$  rings. Therefore, it was suggested that the last two data points at 45 and 60 minutes in the case of  $\text{AlB}_2$  did not represent the true V concentration due to boron treatment rather it was a combined effect with re-dissolution of Al-V intermetallics. In the absence of Al-V intermetallics dissolution, the V level should not increase in the melt because  $\text{VB}_2$  is stable at  $750^\circ\text{C}$ . It should be mentioned that from selected repeat experiments, the relative error of the data in the Figure 8 was estimated to be 5%.

It is reasonable to believe that the large surface area associated with  $\text{AlB}_2$  particles enhances the reaction kinetic. This will allow larger proportion of boron in contact with V to form  $\text{VB}_2$ . It was suggested from the comparison of  $\text{AlB}_{12}$  and  $\text{AlB}_2$  that the kinetics of process is faster for  $\text{AlB}_2$  based Al-B master alloys.

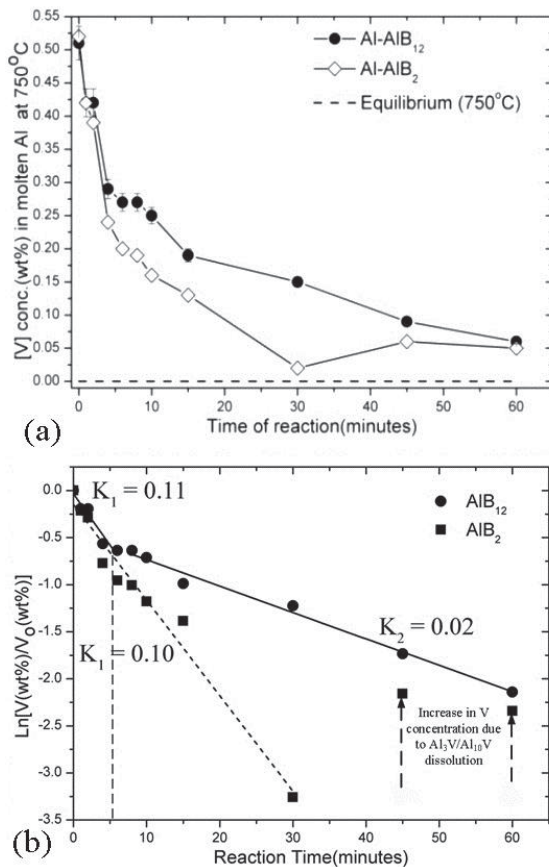


Figure 8 - Plots of V removal and integrated rates with reaction time for  $\text{AlB}_{12}$  and  $\text{AlB}_2$  based alloys, added to Al-1wt% V alloy at  $750^\circ\text{C}$

## Settling of Borides in Molten Al Alloys

Settling of  $\text{VB}_2$  in molten Al alloys was investigated using multiple locations sampling technique. The purpose was to quantify the concentration gradient of vanadium in the crucible that also represents the settling of  $\text{VB}_2$  with reaction time. The  $\text{VB}_2$  borides settling in a vertical crucible versus reaction time is shown in Figure 9. The concentration of V represents the total amount in the analyzed samples, which include V,  $\text{VB}_2$  and Al-V ( $\text{Al}_3\text{V}/\text{Al}_{10}\text{V}$ ) intermetallics.

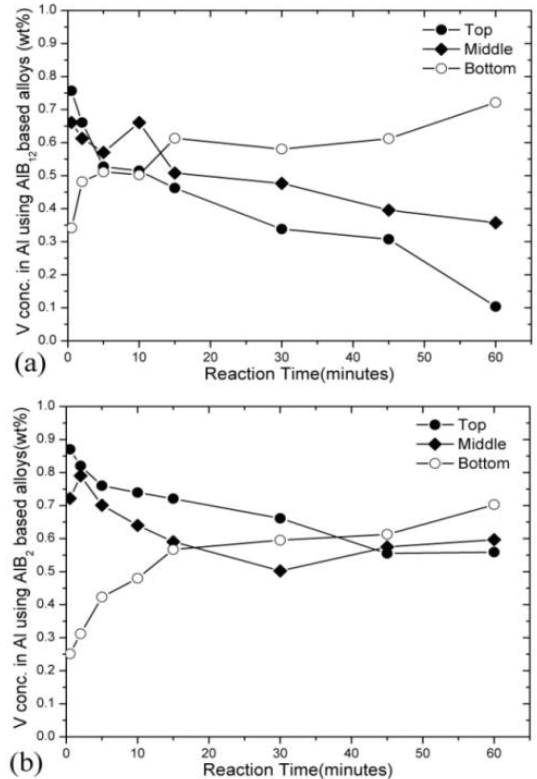


Figure 9 - Change in the concentration of V at top, middle and bottom of crucible with reaction time, for (a)  $\text{AlB}_{12}$  and (b)  $\text{AlB}_2$  based alloys

The settling of  $\text{VB}_2$  and the change in concentration of V in the case of  $\text{AlB}_{12}$  based Al-B alloys are shown in Figure 9(a). In the start of experiment, the concentration of V at top of the melt was 0.76wt% that decreased gradually to 0.1wt% with reaction time. The gradual decrease in concentration was due to the formation of heavy  $\text{VB}_2$  clusters that were settling at the bottom of crucible. In the middle, the drop in the concentration of V was less than that discussed earlier for the top location. With reaction time, the concentration of V in the bottom location increased, as shown in Figure 9(a). It was believed that the escalation of V in bottom location was due to the settling of heavy borides with reaction time. Over the period, the concentration of V in the bottom location increased from 0.34wt% to 0.73wt%.

The settling of  $\text{VB}_2$  using  $\text{AlB}_2$  based Al-B master alloys is shown in Figure 9(b). The concentration of V dropped from 0.87wt% to 0.56wt% for top location that showed comparatively limited settling of borides. In the middle, the change in the concentration was not significant. However, increase in the V concentration was observed in the bottom that was attributed due to the settling of

larger particles and clusters of  $VB_2$  formed during reaction. Overall, the trends of V concentration for top, middle and bottom locations were similar to that shown in Figure 9(a).

Considering the above, the following conclusions can be made:

- (1) Gravity settling of borides was faster in the case of  $AlB_{12}$  phase because of their larger and denser particles. Large proportion of  $VB_2$  encapsulating  $AlB_{12}$  settled in the early minutes of reaction.
- (2) The rate of reaction was faster in the case of  $AlB_2$  based alloys. However, settling was slower due to smaller  $VB_2$  particles formed during boron treatment.

Therefore,  $AlB_{12}$  based alloys were recommended for holding furnaces where melt treatment time is in hours.  $AlB_2$  based should be used in the processes where holding time is limited (launders) and inclusions ( $VB_2$ ) pose no threat to the further processing.

### Conclusions

Analysis of vanadium removal from molten aluminum was carried out by employing  $AlB_{12}$  and  $AlB_2$  based master alloys. SEM-SE analysis of boride sludge revealed the formation of  $VB_2$  and partially dissolved  $AlB_{12}/AlB_2$  in the alloys. The mechanism of  $VB_2$  formation was similar to that explained in literature. Comparatively, smaller  $VB_2$  particles were formed and were also enriched with V, in the case of  $AlB_2$  - based alloys. The rate of reaction and the removal of V were faster for  $AlB_2$  based alloys. Those were attributed due to higher interfacial area for reaction because of smaller  $AlB_2$  particles in the starting Al-B alloy. Investigation on the boride settling in molten alloy revealed faster rates of settling in the case of  $AlB_{12}$  compared to  $AlB_2$ .

Based on the kinetic of V removal and settling of  $VB_2$  borides, it was recommended to use  $AlB_{12}$  based alloys for longer treatment processes (e.g. in holding furnaces).  $AlB_2$  based master alloys should be used for the processes where limited reaction time is available and the presence of inclusions ( $VB_2$ ) have no impact on further processing of alloys. Therefore, understanding of the chemistry and morphology of  $AlB_{12}/AlB_2$  phases in the Al-B master alloys play an important role for optimizing boron treatment of molten aluminum.

### Acknowledgement

Authors thanks Swinburne University of Technology and CAST CRC for the funding of this project.

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