

THERMODYNAMIC ANALYSIS OF Ti, Zr, V AND Cr IMPURITIES IN ALUMINUM MELT

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Abstract

Aluminum is widely used as the main material for overhead power cable because of its good electrical conductivity and light weight. Metal impurities, in particular Ti, Zr, V and Cr in the solution, affect the electrical conductivity of aluminum significantly. Industrially, boron treatment has been used to remove these impurities through the formation of borides. However, studies have shown that solution thermodynamics and the detailed reaction mechanisms of the borides formed in aluminum melts are not well understood. In the present work, thermodynamic analysis has been carried out to investigate the relative stability and to elaborate on the preferential formation of various borides in aluminum melt. It is shown that diborides (MB_2) are the most thermodynamically stable boride compounds of these impurities in the given working conditions. The ZrB_2 , TiB_2 and VB_2 phases are more stable compared to AlB_2 and CrB_2 hence do not dissolve readily. It is also shown that the relative stability of the boride phases is affected by the presence of other metal diborides.

Introduction

Aluminum can be used as an electrical conductor if the level of impurities is controlled precisely, in particular, the concentration of transitional metals Ti, Zr, V, and Cr. Their effect is minimized when they are in a combined form rather than in solution with aluminum. The detailed discussion on the effect of solute impurities to aluminum properties has been described in the literature [1-3]. The maximum solubility and the effect of transition metal impurities on electrical resistivity in and out of solution are given in Table 1. It can be seen that vanadium and chromium has the highest effect on the resistivity; and the presence of these elements in solution increases the resistivity by a factor 10 to 20.

Table 1: Transition metal impurities, their maximum solubility and effect on resistivity of aluminum [3]

Elements	Max. Solubility in Al (wt %)	Avg increase in resistivity per wt% $\mu\Omega.cm$	
		In Solution	Out of solution
Titanium	1	2.88	0.12
Zirconium	0.28	1.74	0.044
Vanadium	0.5	3.58	0.28
Chromium	0.77	4	0.18

These impurities mainly come from carbon anodes (from petroleum coke) and bauxite used in the primary production of aluminum [4]. Although there are many methods to remove transition metals (in particular V) from the petroleum coke [5-11],

their application in the petroleum industry is limited. It was also reported that there was an increasing trend in the concentration of impurities (including V) in the coke which later ends up in aluminum [12]. In anticipation of this, it is imperative that the current methods available for removing these impurities from aluminum to be optimized; or for new methods to be developed.

Commercially, boron treatment has been used to remove transition metal elements through the formation of borides. This is carried out by adding boron or aluminum-boron master alloys to the melt.[2, 12, 13] The formed borides or diborides are separated by gravity settling or by flux addition combined with mechanically mixing in the melt [14]. The reactions depend upon diffusion of the impurities in the aluminum melt and the availability of boron/aluminum borides. It has been reported that this reactions of boron with transition metals are fast enough that 70% of increase in electrical conductivity is achieved in the first couple of minutes[15]. Further increase in electrical conductivity is quite slow and takes more than two hours, i.e. after the heavy boride particles settle at the bottom of furnace [15-19]. It has been established by previous works that Ti, Zr and V can be removed from aluminum melt by boron treatment [13, 15, 20]. Laun [21] reported the removal of Cr and Mn during boron treatment along with Ti and V. Setzer[20] and Cooper [15] studied on the removal of Ti, Zr, V and Cr, Mn was not mentioned. Wang *et al.* [20] reported in their study on boron reactions with transition metals that there was no evidence of borides of Cr and Mn in the reaction products. However, there are different statements about removal of Cr and Mn through formation of borides[22].

It is obvious from previous research findings, that the detailed mechanisms of reactions between boron and transition metal impurities in liquid aluminum are not fully understood. Moreover, the exact nature of the borides type, their morphology and composition need to be evaluated and analyzed to get a full understanding of borides formation mechanism for effective boron treatment of aluminum.

In this article, a literature study on thermodynamic information and previous works on the transitional metals (i.e. Ti, Zr, V, and Cr) and their borides in Al melt will be presented. In addition, investigations on the possible stable phases; their relative stability; and their preferential formation in the presence of other transition metals borides have also been carried out using thermodynamic packages.

Transition Metal Borides in Aluminum

Previous investigators have indicated that there was some solubility of aluminum in transition metal diborides; *vice versa* some solubility of transition metals in aluminum diborides formed

in aluminum melts [19, 23, 24]. Setzer and Boone [20] reported in their study that transition metal borides formed in Al melt were not pure and they formed cluster of diborides (containing V, Ti, Zr, and Cr). They also investigated the morphology of the borides and observed two distinct morphologies, i.e. equiaxed hexagonal (occasionally platelet) and clustered platelet. They attributed these to the different initial boride particles used for precipitation, i.e. AlB_2 and AlB_{12} , respectively. Although the morphology of the borides were presented, it was not clear whether these borides were in some form of solid solution or clusters of separated boride phases. Wang *et al.* [22] studied the reactions of boron with transition metal and observed similar cluster of borides. Energy-dispersive x-ray spectroscopy results suggested the presence of Ti, V, and Zr. They speculated that AlB_2 formed a continuous solid solution of $(\text{Al}, \text{Ti}, \text{V}, \text{Fe})\text{B}_2$ but no further evidence was presented.

Fjellstedt [19] used optical microscopy, energy-dispersive x-ray spectroscopy and x-ray diffraction to investigate the mutual solubility in Al-Ti-B system. It was reported that the AlB_2 and TiB_2 particles were stable and found as separate phase having limited solubility with each other in the aluminum melt [19]. In some case, AlB_2 was observed to be surrounded by ring of TiB_2 phase. It was further reported that complex compounds of $(\text{Ti}, \text{Al})\text{B}_2$ were unstable and that AlB_{12} showed very low solubility of Ti [19, 23, 24]. During research of grain refinement of aluminum and its alloys using inoculants, McCartney [25] reported that TiB_2 , AlB_2 were stable but $(\text{Ti}, \text{Al})\text{B}_2$ phases were unknown in stability so far. Many other researchers have also discussed the metastability and presence of $(\text{Ti}, \text{Al})\text{B}_2$ but none have provided clear and complete explanations [25-29].

Higashi *et al.* [23] studied the solubility of aluminum in various metal borides including TiB_2 , ZrB_2 , HfB_2 , VB_2 , V_3B_4 , NbB_2 , TaB_2 and W_2B_5 by growing these crystals from aluminum melt at 1300°C to 1550°C . They reported that the solubility of aluminum in these borides was 0.1 wt% maximum. This was interpreted as AlB_2 did not form mixed crystals with the above borides. Recently, Otani *et al.* [30] investigated the solid solution ranges of ZrB_2 with refractory diborides (HfB_2 , TiB_2 , TaB_2 , NbB_2 , VB_2 and CrB_2). Mixed-boride samples were heated and melted using arc melting furnace under Ar atmosphere at 1600°C . The samples were analyzed using x-ray diffraction and inductively-coupled plasma techniques. Their study showed that ZrB_2 formed a perfect solution with NbB_2 , HfB_2 and TaB_2 . In the case of ZrB_2 - TiB_2 system, they observed two phases, i.e. ZrB_2 -rich ($\text{Zr}_{0.76}\text{Ti}_{0.24}\text{B}_2$) and TiB_2 -rich ($\text{Zr}_{0.11}\text{Ti}_{0.89}\text{B}_2$) phases. It was also reported that ZrB_2 also made a solid solution with VB_2 and CrB_2 but the solubility was very low i.e. < 3 mol% and < 1 mol %, respectively at 1600°C .

Thermodynamic Assessment of Borides Formation

In the current study, thermodynamic assessment of different compositions of transition metals and boron in aluminum have been carried out in the temperature range of 675°C to 950°C using the HSC Chemistry 7.0 and FactSage 6.1 thermodynamic packages. The light metal database (FTLite) has been used in FactSage package where modified quasichemical model has been employed for the assessment of liquid phases. This model is based on the short range ordering tendency of atoms or molecules in liquid solutions [31]. For solid boride phases (MB , and MB_2), the sub-lattice model which based on the substitutional solution

assumptions was used. In the sub-lattice model, it is considered that crystalline species are formed in two or more different lattice structures [32].

The thermodynamic analyses carried out include:

- Evaluation of Gibbs free energy formation of aluminum and transitional metal borides.
- Evaluation of binary and ternary phase diagrams (Al-B, Al-Ti-B, Al-Zr-B and Al-Cr-B).
- Equilibrium calculations of different compositional systems (Al-Ti-B, Al-Ti-Zr-B, Al-Ti-Zr-V-B, and Al-Ti-Zr-V-Cr-B) with stoichiometric and excess boron concentration for transition elements (assuming the formation of diborides).

Borides Gibbs Free Energy Evaluation

The Gibbs free energy formation of various metal borides phases has been evaluated using HSC Chemistry 7.0 package in the temperature range of 650°C to 900°C . The results obtained are presented in Figure 1. During the evaluation, it was found that diborides phases (AlB_2 , TiB_2 , ZrB_2 , VB_2 , and CrB_2) of transitional metals were the most stable in the given conditions as compared with their other possible phases (AlB_{12} , TiB , VB , V_3B_4 , V_5B_6 , CrB , Cr_3B_4 , Cr_5B_3). Figure 1 suggest the order of stability of pure diborides in aluminum melt from ZrB_2 , TiB_2 , VB_2 , AlB_2 , CrB_2 to AlB_{12} in the given temperature range (650°C to 950°C). This order of stability also suggests that the elements Zr, Ti, V can be removed by the addition of Al-B master alloys through the formation of borides (as has been demonstrated experimentally by previous investigators). Chromium diborides (CrB_2), however, shows a lower stability compared to AlB_2 , thus boron treatment may not be the appropriate method for removing chromium. This agrees with the findings of Wang *et al.* [20] who reported that there was no evidence of borides of Cr and Mn in the reaction products during reactions between boron and transition metals.

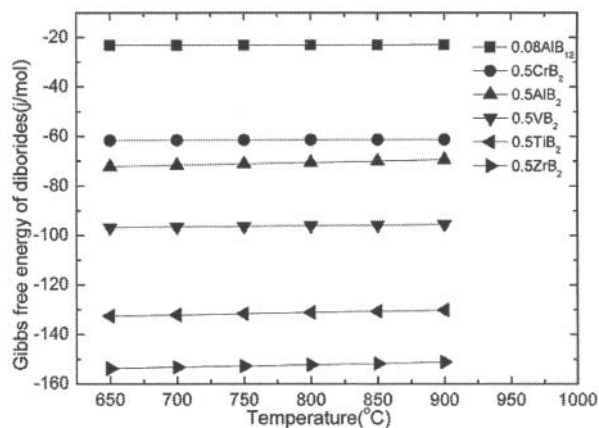


Figure 1: Gibbs free energy evaluation of pure metal borides

Phase Diagrams and Equilibrium Calculations

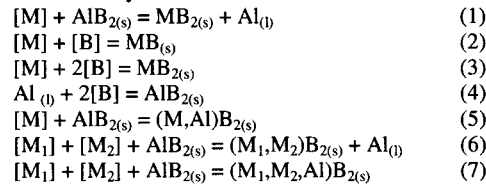
Equilibrium calculations of different Al-M-B (M = Ti, Zr, V, Cr) systems in Al melt were carried out using FactSage 6.1 thermodynamic package in the temperature range of 675°C to 900°C . The "Equilib" module of FactSage was used for the calculations which incorporate the Gibbs free energy minimization technique to predict the thermodynamically stable

phases in different conditions. Due to lack of solution thermodynamic information, in these calculations it was assumed for the boride systems that:

- ZrB₂ formed an ideal solution with TiB₂, i.e. (Zr,Ti)B₂
- There was only a very small solubility of Al in (Zr,Ti)B₂ and *vice versa*
- AlB₁₂, VB₂, CrB₂ (and other borides) were pure

The total concentration of the transition metals varied from 1.1 – 1.5 wt% in the Al alloy-boride systems under discussion. Stoichiometric and 75wt% excess amounts of boron (assuming diborides formation) were added to the systems to investigate the boride formation preferences. It has been suggested by previous investigators [13, 15] that excess boron may be required for efficient formation of the metal transition borides.

When considering these diborides systems, the following reactions may occur:



In the above reactions M refers to transition metals (Zr, Ti, V and Cr), subscript *l* and *s* represent liquid and solid respectively, and the [] symbol refers to the associated elements in solution.

Binary & Ternary Phase Diagrams of Al-B, Al-M-B Systems

Binary phase diagrams of the elements B, Ti, Zr, V and Cr with aluminum revealed their limited solubility at low temperature which increases with temperature [33, 34]. Figure 2 & 3 shows the solubility of selected elements in liquid and solid aluminum from literature. It is clear from curves of solute elements in liquid and solid aluminum that their solubility increase with temperature in particular for Cr, Mn and Fe.

The general features of aluminum interaction with transition metals include the formation of supersaturated solid solution, quasi-crystalline and amorphous compounds at some particular composition and cooling rate during solidification[33]. The current equilibrium calculations showed that at 1.1 - 1.5 wt%, boron, aluminum and transition metals (Ti, Zr, V and Cr) may possibly form AlB₂, TiB₂, (Ti,Zr)B₂, VB₂(s), CrB₂(s) in the temperature range of 675°C to 900°C. The possible phases in aluminum binary and ternary alloys with boron and some transition metals are summarized in Table 2.

Table2: Thermodynamically possible stable phases in Al binary and ternary systems in temperature range of 675°C to 900°C.

Alloy Systems	Possible Stable Solid Phases	
	Stoichiometric B	75 wt% Excess B
Al-B	AlB ₂	AlB ₂
Al-Ti-B	TiB ₂ *	TiB ₂ *, AlB ₂
Al-Zr-B	ZrB ₂ *	ZrB ₂ *, AlB ₂
Al-V-B	VB ₂ (s), Al ₇ V(s)	VB ₂ (s), AlB ₂
Al-Cr-B	CrB ₂ (s)	CrB ₂ (s), AlB ₂

*very small solubility of Al

In case of Al-Ti-Zr-B system, mixed borides are composed of almost equal proportion of TiB₂ and ZrB₂. In the alloy systems containing V and Cr with B and Al, VB₂(s) and CrB₂(s) phases have been predicted along with AlB₂ borides. It is assumed that there is some solubility of TiB₂ and ZrB₂ in AlB₂ and vice versa. According to the given analysis there is no solubility of Ti, Zr or Al in CrB₂ and VB₂ as they have been predicted as separate solid phases. The stability of each and every phase depends upon the temperature and composition of solute in the aluminum melt.

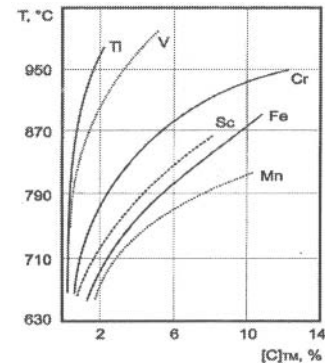


Figure 2: Solubility of some transition metals in liquid Al [33].

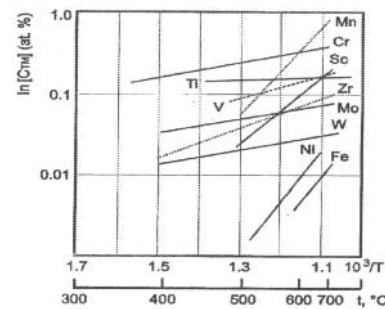


Figure 3: Solubility of some transition metals in solid Al [33].

Under equilibrium solidification Al₃Ti, AlB₂ and TiB₂ were predicted in the Al-Ti-B ternary systems as proposed by Abdelhamid *et al.*[35]. The Al₃Ti phase possesses a tetragonal crystal structure but AlB₂ and TiB₂ phases are composed of hexagonal crystal structures with only a minor difference in their lattice parameters. Hence, there are possibilities for the stability of a continuous range of (Al, Ti) B₂ solid solution [33]. In the thermodynamic analysis complete solid solutions of ZrB₂ and TiB₂ was predicted. On the other hand solid solution of AlB₂ with TiB₂ and ZrB₂ does exist having limited solubility.

The previous research by Higashi[23], Jones[24] and Fjellstedt[19] found that there was some solubility of Ti in AlB₂ and some Al in TiB₂ but there was no evidence of any solubility among these borides particles. Moreover, Fjellstedt[19] explained that (Ti,Al)B₂ type compounds are unstable and cannot exist at room temperature. From the FactSage assessment and previous studies, it may be assumed that TiB₂, ZrB₂ and AlB₂ are mixed with each other and making a metal boride solid solution (MB₂) phases.

Equilibrium Composition Analysis

In the first case, equilibrium calculations of liquid aluminum with 1wt % V and stoichiometric (and 75 wt% excess) amounts of boron were conducted. During the thermodynamic assessment of Al-V-B system, separate solid $VB_{2(s)}$ particles and AlB_2 were predicted (See Table 2).

In the Al-1wt%V-B system, vanadium diboride (VB_2) was predicted to be little stable in the given temperature range but dissolve slowly at higher temperatures(900°C).The changes in the vanadium, VB_2 and AlB_2 equilibrium concentration in Al melt with temperature are given in figure 4. It can be seen from figure 4 that in the case of stoichiometric addition of boron, the concentration of V in the metal at 675°C was 8 to 10 ppm. The concentration of V increased with increasing temperature which suggested that the VB_2 was dissolving back into melt with increasing temperature. With excess boron, both VB_2 and AlB_2 were predicted. It appeared that the excess boron combined with Al to form AlB_2 . By adding excess boron, the VB_2 also appeared to be more stable in the temperature range studied. No dissolution of VB_2 was predicted in the temperature range of 675°C to 900°C, as shown in figure 4, i.e. no V was predicted in the Al melt as a solute.

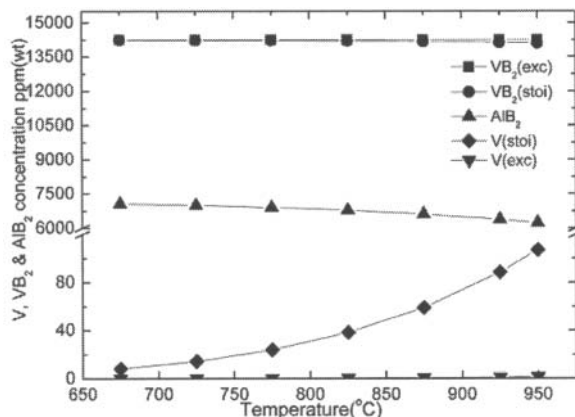


Figure 4: V, VB_2 and AlB_2 equilibrium concentrations in Al melt with stoichiometric and excess B addition having 1.2 to 1.4 wt% of Al.

The second case studied was the equilibrium between Al-1wt%M (where M = Zr, Ti, V, Cr) with stoichiometric and 75% excess boron additions. In the case of stoichiometric addition of boron, the following diborides were predicted: $(Zr,Ti)B_2$ with very little solubility of AlB_2 (i.e. 0.001 wt% at 750°C), VB_2 and CrB_2 . Figure 5 shows the equilibrium concentrations of metal diborides predicted in the system Al-1wt%M (M = Zr, Ti, V, Cr each 0.25wt%)-0.357wt%B. The figure shows $(Zr,Ti)B_2$ was stable and the concentration remained unchanged in the temperature range studied. On the other hand, the diborides of Cr and V were relatively unstable and predicted to be dissolving back into the melt with increasing temperature. VB_2 was predicted to be stable only up to 825°C, where above this it started to dissolve. The equilibrium concentration of CrB_2 was predicted to be 12.5wt% at 675°C and decreased with increasing temperature; at 750°C CrB_2 was completely dissolved in Al melt over the temperature range studied.

Figure 6 shows the associated equilibrium solute concentration changes in the Al melt. In the temperature range studied, no solute Zr and Ti were predicted in the Al melt as they were present in the stable $(Zr,Ti)B_2$ phase. V was predicted above 825°C when VB_2 started to dissolve. The equilibrium concentrations of Cr and B were 0.16wt% and 0.04wt% at 675°C, respectively. CrB_2 was the least stable phase compared to other diboride phases. It was assumed that CrB_2 will start dissolving first in the melt which may result in the early increase of Cr and B concentrations with increase in temperature. At above 750°C no further increase in Cr and B concentrations were predicted, as all CrB_2 had already dissolved. A slight increase in B solute concentration was predicted above 825°C, likely associated with dissolution of VB_2 to the melt.

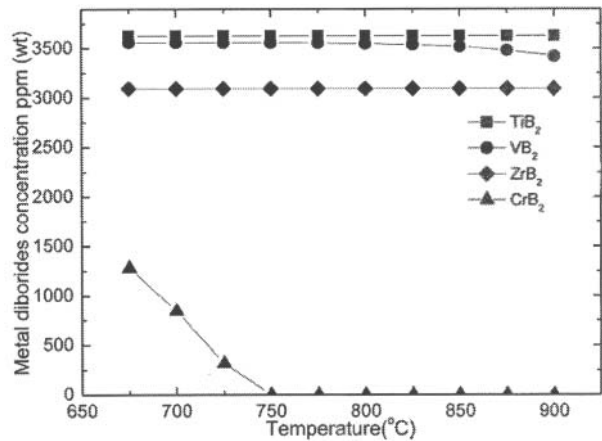


Figure 5: Equilibrium concentration of metal diborides in Al-M-B system with stoichiometric B addition having 1.2 wt% elements in Al melt. The ZrB_2 and TiB_2 are in the form of $(Zr,Ti)B_2$.

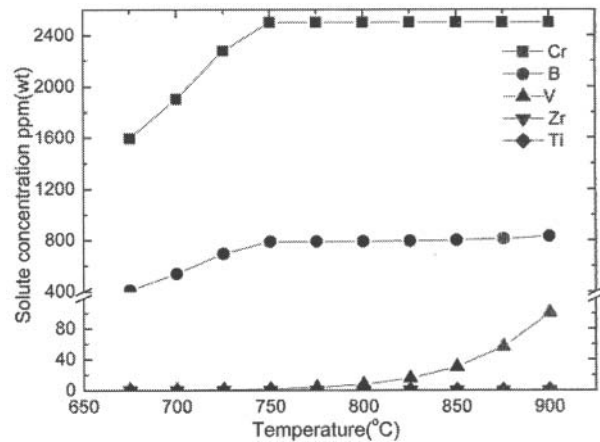


Figure 6: Equilibrium solute concentrations in aluminium melt with stoichiometric B addition with total 1.2 wt% elements.

Figure 7 shows the change of diborides concentration with temperature in the case of 75% excess boron with Al-1.4wt%M. In this case, AlB_2 was predicted in addition to $(Zr,Ti)B_2$, VB_2 and CrB_2 phases. Similar to first case (Al-1wt%Ti with excess B), it was assumed that the excess boron combined with aluminium to form AlB_2 . The model predicted there was a little solubility of Ti

and Zr in the AlB_2 phase; and Al in $(\text{Zr,Ti})\text{B}_2$, i.e. 0.001 wt% at 750°C .

It can be seen from Figure 7 that $(\text{Zr,Ti})\text{B}_2$ and VB_2 are more stable compared to AlB_2 and CrB_2 under the given conditions. The equilibrium concentration of CrB_2 was predicted to be 9.2 wt% of total metal borides at 675°C . As the temperature was increased, CrB_2 dissolved first, hence the decrease in CrB_2 concentration up to 750°C where all CrB_2 was completely dissolved. Afterward AlB_2 started to dissolve. The concentration of $(\text{Zr,Ti})\text{B}_2$ and VB_2 remained unchanged in the melt in temperature range 675°C to 900°C .

Also of note is the relative stability of phases depends upon the presence of other diboride phases. For example, in the first case (stoichiometric addition of boron), where no AlB_2 was present, the VB_2 phase remained thermodynamically stable only up to 875°C (as shown in Figure 5). In the presence of AlB_2 (excess boron added), VB_2 was predicted to be stable up to 900°C , as shown in Figure 7.

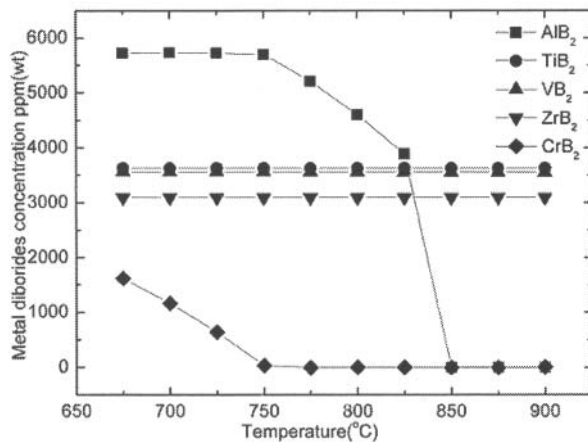


Figure 7: Equilibrium concentration of metal diborides in Al-M-B system with 75% excess B addition having total 1.4 wt% of Al. The ZrB_2 and TiB_2 are in the form of $(\text{Zr,Ti})\text{B}_2$.

Figure 8 shows the solute concentrations in Al melt in the case of excess boron addition. The solute concentrations in the case of stoichiometric boron addition are also shown for comparison. It can be seen from the figure 8 that the addition of stoichiometric or excess boron may be carried out to remove Zr, Ti and V from the melt. However, the model predicts that Cr would remain in the melt; as the excess boron appeared to be reacting with Al to form AlB_2 rather than forming CrB_2 .

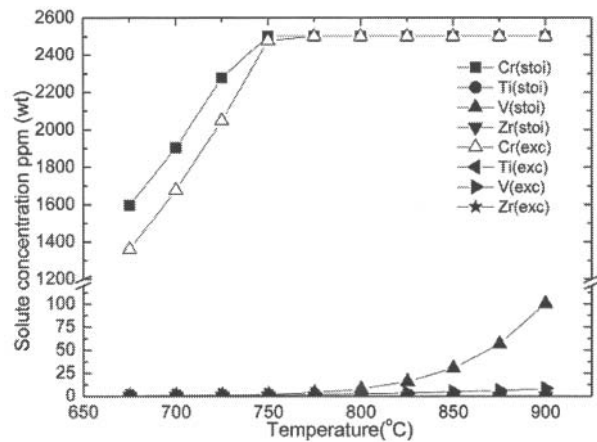


Figure 8: Transition metals solute concentration with stoichiometric and excess Boron addition in system Al-M-B having 1.2 to 1.4 w% of solute elements.

Concluding Remarks

A thermodynamic assessment of various aluminum systems with Ti, Zr, V, Cr and B have been carried out at temperature range between 675°C to 900°C . Two main cases were analyzed one stoichiometric composition and the other with 75 wt% excess of boron addition to aluminum melt composed of 1.4 wt% of total transition metal (Ti, Zr, V and Cr). According to the results, the Gibbs free energy for formation of the pure diboride compounds, ZrB_2 was found to be most stable under the given conditions as compared with other transition metal diborides. The order of stability (from most stable to least stable) of these boride phases was ZrB_2 , TiB_2 , VB_2 , AlB_2 , CrB_2 within the given temperature range.

The equilibrium calculations predict that Cr could not be effectively removed from aluminum above 750°C through boron treatment as aluminum diboride was more stable compared to chromium diboride. When boron was added to the aluminum melt containing Zr, Ti, V and Cr, the results suggested that boron would be tied up by Zr and Ti, then V, Al, and Cr, forming $(\text{Zr,Ti})\text{B}_2$, VB_2 , AlB_2 and CrB_2 , respectively. In the case of excess boron, with increasing temperature the least stable CrB_2 dissociated first, followed by AlB_2 at 750°C leaving behind the Al melt with stable borides $(\text{Zr,Ti})\text{B}_2$ and VB_2 . It may be suggested (from thermodynamic perspective only) that boron treatment would be most effective for removing Zr and Ti.

It should again be emphasized that the current study took into account thermodynamic factors only which have provided the theoretical limits. The equilibrium calculations were also carried out with various assumptions. These limitations aside, the results provided an insight on the relative stability and preference of transition metal borides which may form in aluminum melt. Further research including experimental work is required for a complete understanding of boride formation in liquid aluminum.

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