



# Production of in situ aluminum–titanium diboride master alloy formed by slag–metal reaction

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## ABSTRACT

Al–TiB<sub>2</sub> master alloys have received much attention in recent years owing to their potential as efficient grain refiners for aluminum foundry alloys. In this study, the process of production of master alloys was investigated to develop a low cost method, namely, slag–metal reaction. This method can be used to fabricate Al–TiB<sub>2</sub> master alloy in situ from the TiO<sub>2</sub>–H<sub>3</sub>BO<sub>3</sub>–Na<sub>3</sub>AlF<sub>6</sub> and Al system. Since the price of the raw materials is low and the technology is simple, the processing technique appears to reduce the cost of the master alloy. Because of exothermic reactions, not much energy is needed to melt materials. In this process, Titanium diboride particles were formed in situ through the reactions of TiO<sub>2</sub>, H<sub>3</sub>BO<sub>3</sub> and Na<sub>3</sub>AlF<sub>6</sub>. Results showed that when the aluminum melted, the condensed TiB<sub>2</sub> particles that formed in situ were spherical with an average diameter of 1 μm. Furthermore, these TiB<sub>2</sub> particles were distributed uniformly through the master alloy.

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## 1. Introduction

Metals like aluminum that have been combined with a high percentage of other elements such as TiB<sub>2</sub> are called a master alloy [1]. Master alloys can be designed for a specific application by adjusting the composition of the liquid metal. By adding elements to pure metals during solidification, we gain structural control and optimize the mechanical behavior of metals [2,3]. It is possible to control properties such as electrical conductivity, tensile strength, ductility, castability and surface appearance [4]. A master alloy is sometimes also referred to as a hardener, grain refiner or modifier depending on its application [4,5]. Furthermore, master alloys are also used to eliminate well-known disadvantages of foundry alloys, such as the unfavorable effects on the as-cast structure and the substandard properties in the cast parts. One of the advantages of using a master alloy instead of a pure metal can be economical, technical or both; moreover, some of the elements show high losses when added in pure form, while others are not dissolved in furnace temperatures. Master alloys often dissolve much faster at lower temperatures, saving valuable energy and production time [6,7]. In the aluminum wrought and foundry alloys world, aluminum based master alloys are usually distinguished into different groups. There uses additive for composition adjustment to catch the particular chemical specification. Aluminum industries are added to strengthen the alloys and are therefore often referred to as harden-

ers. Examples are AlMn, AlFe, AlCr, AlCu, AlV, either in the form of waffle ingot or as a compact powder. Another significant group is called “grain refiners”, which are added for structure control. Grain refiners have some great effects on the aluminum alloys during the solidification process. Mainly, master alloys prevent cracking, combat shrinkage and porosity and increase the casting speed. Examples are Al–TiB<sub>2</sub>, Al–TiC, and AlB<sub>2</sub>. These kinds of master alloys which use a grain refiner are widely used in the form of a coiled rod for continuous inoculation during casting. However, the most standard and predominant application of Al–TiB<sub>2</sub> master alloys is in grain refining, which has well documented technical and economic benefits [8,9].

Much research has been done on the effects and applications of master alloys, but little attention has been given to the production of the master alloys themselves. Lee et al. [10,11] reported production of Al–TiB<sub>2</sub> master alloys by the addition of inorganic salts, K<sub>2</sub>TiF<sub>6</sub> and KBF<sub>4</sub>, to molten aluminum. Generally, master alloy producers need specialized equipments, such as high temperature induction furnaces, to produce an alloy composition suitable for use by the regular metal industry [7]. In this study, we investigate the in situ production process of the Al–TiB<sub>2</sub> master alloy, using low cost raw materials and simple technology. Furthermore, the presented method is environmentally friendly and reduces used energy. Moreover, microstructural aspects are investigated.

## 2. Experimental procedure

### 2.1. Raw materials

Commercial purity Al (>99.7% Al) ingot, TiO<sub>2</sub> (rutile, high purity >99.8%), H<sub>3</sub>BO<sub>3</sub> (boric acid, high purity >99.9%), and Na<sub>3</sub>AlF<sub>6</sub> (cryolite, high purity >99.8%) powders,

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**Table 1**  
Thermodynamic data of different phases at 1273 K.

Phase	Al	TiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	TiB <sub>2</sub>
Gibbs free energy (J)	−60017.40	−8.7536 × 10 <sup>6</sup>	−1.4212 × 10 <sup>6</sup>	−1.8313 × 10 <sup>6</sup>	−4.2034 × 10 <sup>5</sup>
Enthalpy (J)	29123.05	−8.7536 × 10 <sup>5</sup>	−1.1629 × 10 <sup>6</sup>	−1.56281 × 10 <sup>6</sup>	−2.5115 × 10 <sup>5</sup>
Entropy (J/k)	70.02613	1.50552 × 10 <sup>2</sup>	2.02846 × 10 <sup>2</sup>	2.10881 × 10 <sup>2</sup>	1.32887 × 10 <sup>2</sup>
Heat capacity (J/k)	31.8472	7.59551 × 10	1.29704 × 10 <sup>2</sup>	1.29619 × 10 <sup>2</sup>	8.09591 × 10

obtained from Merck and Etibank, were used in these experiments. Product information from the manufacturer indicates that the size distributions for the TiO<sub>2</sub> and H<sub>3</sub>BO<sub>3</sub> powders are similar and are both classified as fine powders. The particle size of the TiO<sub>2</sub> and H<sub>3</sub>BO<sub>3</sub> powders are below 1 μm.

## 2.2. Production processes

The raw powders were fully blended and then dried at 300 °C for one hour in order to completely remove humidity. Boric oxide and water vapor were produced during this process. Then, the TiO<sub>2</sub>, H<sub>3</sub>BO<sub>3</sub>, and Na<sub>3</sub>AlF<sub>6</sub> powder mixture was added to a graphite crucible containing the aluminum ingot. Since powders are not electrically conductive, the graphite crucible was used to melt them in the induction furnace. The graphite crucible is conductive and during the melting process, the crucible itself is heated, which results in the heating and melting of the powders. When the system was heated to 1000 °C in the induction furnace, aluminum melted first, and then the powders turned “mushy”. Then, these semisolid powders melted and formed a slag, which lay on top of the molten aluminum. Next, aluminum entered into an exothermic reaction with the slag and tiny sparks were seen. During this reaction, the furnace was turned off to prevent excessive heating of the system. Continuous stirring provided better contact between the reactants. This procedure was continued until no sparks were observed, as this indicated that the reaction was complete. Through this reaction between the slag and the metal, TiB<sub>2</sub> was formed, and it precipitated in the liquid aluminum. Aluminum oxide, formed by the reaction, dissolved in the cryolite, so that the system at the end of the reaction consisted of a slag of cryolite and aluminum oxide and a slurry of aluminum and titanium diboride under the slag. When the reactions were completed, the slag was removed from the crucible and the produced Al–TiB<sub>2</sub> alloy was poured into molds.

In this experiment, the mixture of powders was being added slowly above the molten aluminum to produce the alloy. In other addition methods, molten aluminum is added above the powders. In another experiment, the mixture of powders was melted separately in a different graphite crucible and was added into the molten aluminum. The same experiment was repeated by adding molten aluminum to the molten powders mixture. Using all of the above mixing methods yielded the same results.

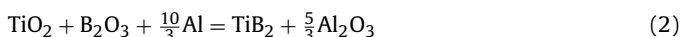
## 3. Results and discussion

### 3.1. Formation of particles

Boric acid was used to provide a source of B<sub>2</sub>O<sub>3</sub> particles for the trough calcinations of the acid according to the reaction [12]:

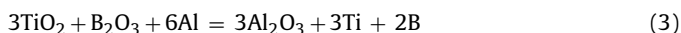


The overall reaction for the formation of TiB<sub>2</sub> is given by:



The thermodynamics data of these reactions are presented in Table 1 [13].

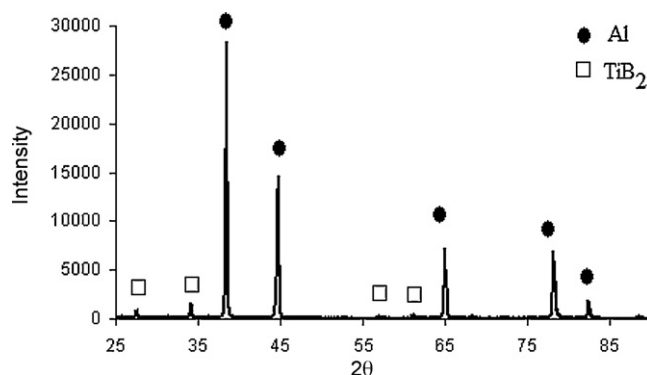
It can be seen that TiB<sub>2</sub> cannot be directly formed by the reaction between B<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> because Gibbs free energy of TiB<sub>2</sub> is much higher than that of both TiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>. However, Gibbs free energy of Al<sub>2</sub>O<sub>3</sub> is much lower than of both TiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>, so the oxygen atoms may be reduced and the displacement of oxygen atoms from TiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> allows Ti and B atoms to be freed by the formation of Al<sub>2</sub>O<sub>3</sub> as follows [14]:



The free Ti and B atoms can react to form TiB<sub>2</sub> as follows:

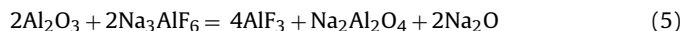


The TiB<sub>2</sub> particles nucleated in this reaction entered the molten aluminum to form the Al–TiB<sub>2</sub> master alloy, while the Al<sub>2</sub>O<sub>3</sub>



**Fig. 1.** XRD pattern of Al–TiB<sub>2</sub> master alloy.

dissolved in the cryolite in accordance with the overall reaction [15]:



Charges were prepared based on stoichiometric considerations so as to have 10 volume percent TiB<sub>2</sub> in the Al–TiB<sub>2</sub> master alloy. Fig. 1 provides an X-ray diffraction (XRD) pattern of the Al–TiB<sub>2</sub> master alloy, while the diffractometric data for TiB<sub>2</sub> and Al are given in Tables 2 and 3.

The XRD pattern clearly indicates that TiB<sub>2</sub> is present within the aluminum specimen, indicating that Al–TiB<sub>2</sub> master alloy has been successfully produced. Intermetallic Ti–Al components, which may form in the system and have been observed to form in some studies [16], Al<sub>2</sub>O<sub>3</sub> or any other compound could not be detected in these samples. It appears that no, or negligible amounts of, intermetallic compounds of titanium and aluminum were formed and that all Al<sub>2</sub>O<sub>3</sub> generated in the reaction (Eq. (5)) entered the liquid cryolite phase.

**Table 2**  
X-ray data of TiB<sub>2</sub>.

2θ	Int	h	k	l
27.607	233	0	0	1
34.150	626	1	0	0
44.462	999	1	0	1
57.004	84	0	0	2
61.137	192	1	1	0
68.152	117	1	0	2
68.355	138	1	1	1
71.924	46	2	0	0
78.672	120	2	0	1
88.436	105	1	1	2

**Table 3**  
X-ray data of Al.

2θ	Int	h	k	l
38.471	999	1	1	1
44.719	455	2	0	0
65.095	230	2	2	0
78.226	228	3	1	1
82.433	62	2	2	2

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