Journal of Alloys and Compounds 509 (2011) 237–240

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

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

Ahmad Changizi*, Ali Kalkanli, Naci Sevinc

*Department of Metallurgical and Materials Engineering, Middle East Technical University, 06531, Ankara, Turkey*

ARTICLE INFO

*Article history:*
Received 19 January 2010
Received in revised form 17 August 2010
Accepted 24 August 2010
Available online 8 October 2010

*Keywords:*
Master alloy
$TiB_2$
Grain refinement
In situ
Slag–metal reaction

ABSTRACT

Al–$TiB_2$ 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–$TiB_2$ master alloy in situ from the $TiO_2$–$H_3BO_3$–$Na_3AlF_6$ 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 $TiO_2$, $H_3BO_3$ and $Na_3AlF_6$. Results showed that when the aluminum melted, the condensed $TiB_2$ particles that formed in situ were spherical with an average diameter of 1 μm. Furthermore, these $TiB_2$ particles were distributed uniformly through the master alloy.

## 1. Introduction

Metals like aluminum that have been combined with a high percentage of other elements such as $TiB_2$ 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 hardeners. 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–$TiB_2$, Al–TiC, and $AlB_2$. 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–$TiB_2$ 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–$TiB_2$ master alloys by the addition of inorganic salts, $K_2TiF_6$ and $KBF_4$, 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–$TiB_2$ 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, $TiO_2$ (rutile, high purity >99.8%), $H_3BO_3$ (boric acid, high purity >99.9%), and $Na_3AlF_6$ (cryolite, high purity >99.8%) powders,

---

* Corresponding author. Tel.: +1 289 887 3077; fax: +1 514 484 3432.
*E-mail address:* ah_chang@alumni.concordia.ca (A. Changizi).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.08.089

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

| Phase | AL | $TiO_2$ | $B_2O_3$ | $Al_2O_3$ | $TiB_2$ |
|---|---|---|---|---|---|
| Gibbs free energy (J) | −60017.40 | $-8.7536 \times 10^6$ | $-1.4212 \times 10^6$ | $-1.8313 \times 10^6$ | $-4.2034 \times 10^5$ |
| Enthalpy (J) | 29123.05 | $-8.7536 \times 10^5$ | $-1.1629 \times 10^6$ | $-1.56281 \times 10^6$ | $-2.5115 \times 10^5$ |
| Entropy (J/k) | 70.02613 | $1.50552 \times 10^2$ | $2.02846 \times 10^2$ | $2.10881 \times 10^2$ | $1.32887 \times 10^2$ |
| Heat capacity (J/k) | 31.8472 | $7.59551 \times 10$ | $1.29704 \times 10^2$ | $1.29619 \times 10^2$ | $8.09591 \times 10$ |

obtained from Merck and Etibank, were used in these experiments. Product information from the manufacturer indicates that the size distributions for the$TiO_2$ and $H_3BO_3$ powders are similar and are both classified as fine powders. The particle size of the $TiO_2$ and $H_3BO_3$ 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 $TiO_2$, $H_3BO_3$, and $Na_3AlF_6$ 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, $TiB_2$ 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–$TiB_2$ 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 $B_2O_3$ particles for the trough calcinations of the acid according to the reaction [12]:

$$2H_3BO_3 = 3H_2O + B_2O_3 \tag{1}$$

The overall reaction for the formation of $TiB_2$ is given by:

$$TiO_2 + B_2O_3 + \tfrac{10}{3}Al = TiB_2 + \tfrac{5}{3}Al_2O_3 \tag{2}$$

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

It can be seen that $TiB_2$ cannot be directly formed by the reaction between $B_2O_3$ and $TiO_2$ because Gibbs free energy of $TiB_2$ is much higher than that of both $TiO_2$ and $B_2O_3$. However, Gibbs free energy of $Al_2O_3$ is much lower than of both $TiO_2$ and $B_2O_3$, so the oxygen atoms may be reduced and the displacement of oxygen atoms from $TiO_2$ and $B_2O_3$ allows Ti and B atoms to be freed by the formation of $Al_2O_3$ as follows [14]:

$$3TiO_2 + B_2O_3 + 6Al = 3Al_2O_3 + 3Ti + 2B \tag{3}$$

The free Ti and B atoms can react to form $TiB_2$ as follows:

$$Ti + 2B = TiB_2 \tag{4}$$

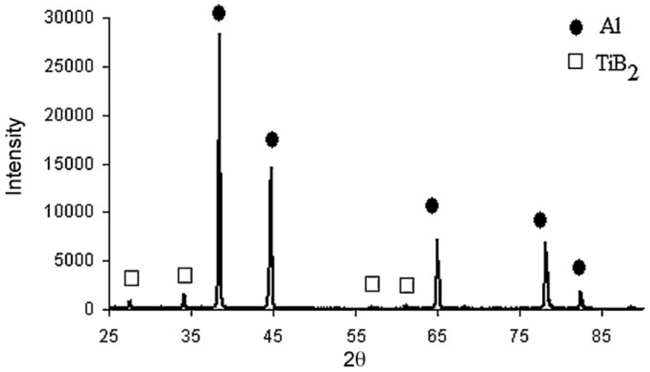

**Fig. 1.** XRD pattern of Al–$TiB_2$ master alloy.

The $TiB_2$ participles nucleated in this reaction entered the molten aluminum to form the Al–$TiB_2$ master alloy, while the $Al_2O_3$ dissolved in the cryolite in accordance with the overall reaction [15]:

$$2Al_2O_3 + 2Na_3AlF_6 = 4AlF_3 + Na_2Al_2O_4 + 2Na_2O \tag{5}$$

Charges were prepared based on stoichiometric considerations so as to have 10 volume percent $TiB_2$ in the Al–$TiB_2$ master alloy. Fig. 1 provides an X-ray diffraction (XRD) pattern of the Al–$TiB_2$ master alloy, while the diffratometric data for $TiB_2$ and Al are given in Tables 2 and 3.

The XRD pattern clearly indicates that $TiB_2$ is present within the aluminum specimen, indicating that Al–$TiB_2$ 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], $Al_2O_3$ 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 $Al_2O_3$ generated in the reaction (Eq. (5)) entered the liquid cryolite phase.

**Table 2**
X-ray data of $TiB_2$.

| 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 |

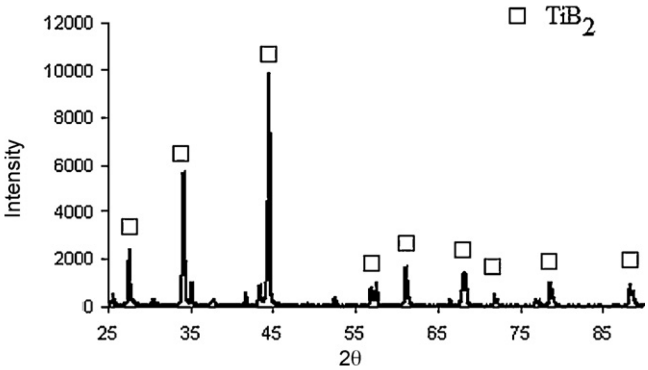

**Fig. 2.** XRD pattern of TiB$_2$ particles extracted from master alloy.

### 3.2. Determination of the amount of TiB$_2$

During the experiments, charges were prepared on the basis of stoichiometric considerations based on reaction (3). X-ray patterns indicated the presence of TiB$_2$ in the samples, but do not provide information as to the amount of TiB$_2$ in the samples. In order to determine the amount of TiB$_2$ in the matrix, the alloy was leached with a suitable agent, which dissolves Al but does not affect TiB$_2$. Hydrochloric acid (HCl) was chosen for this purpose. After dissolving the alloy in HCl, undissolved residue was separated from the solution by filtration. The residue was washed, dried and then weighed. The residue was then subjected to XRD analysis and SEM examination. The XRD pattern of the residue, presented in Fig. 2, and the SEM and EDX analysis of the extracted TiB$_2$shown in Fig. 3(a) and (b), indicated that the residue did not contain any compound other than TiB$_2$ in any appreciable quantity.

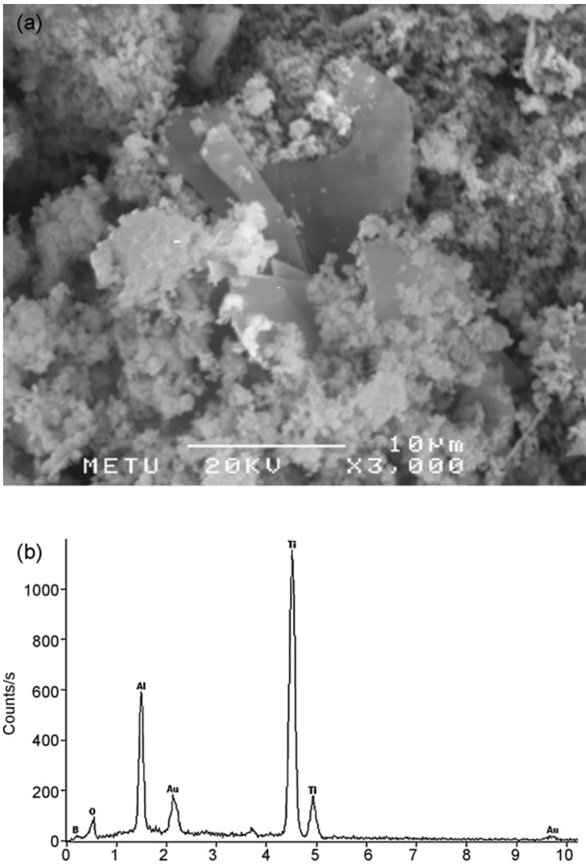

**Fig. 3.** (a) The morphology of TiB$_2$ particles extracted from master alloy with leaching, (b) EDX analysis.

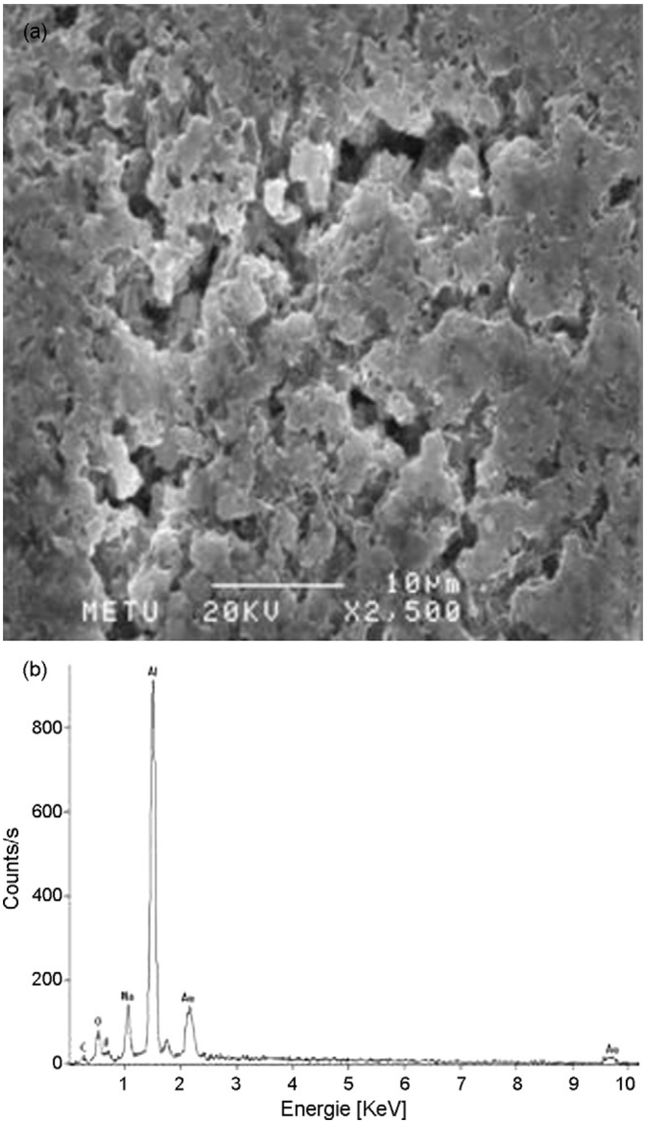

**Fig. 4.** (a) SEM micrograph of slag, (b) general EDX analysis of slag.

The residue was thus considered to be pure TiB$_2$ and its weight was found to be as expected based on the stoichiometric considerations. These results were taken as indication that almost all of the TiO$_2$ and B$_2$O$_3$, charged into the system in stoichiometric amounts, reacted and almost none remained in the slag at the end of the process. Fig. 4(a) shows the SEM micrograph of the slag phase from the experiment aimed. . The EDX analysis in Fig. 4(b) shows that the slag does not contain any Ti or B.

Rigorously, some TiO$_2$ and B$_2$O$_3$ should have remained in the cryolite solution. This arises because there are two liquid phases, liquid Al and liquid cryolite, in the system and thermodynamics necessitates the equality of the chemical potentials of every species in each of the two phases. The experiment results indicate that the quantities of TiO$_2$ and B$_2$O$_3$ in the cryolite are negligibly small. These results indicate that Al–TiB$_2$ composites having a certainTiB$_2$ content can be produced by using a charge composed of cryolite and stoichiometric amounts of TiO$_2$ and B$_2$O$_3$.

### 3.3. Microstructure analysis

In this study, all of the sample surfaces were ground using SiC grinding paper of 220, 400, 800 and 1200 grids. Samples were then polished with alumina suspension and the surfaces were cleaned

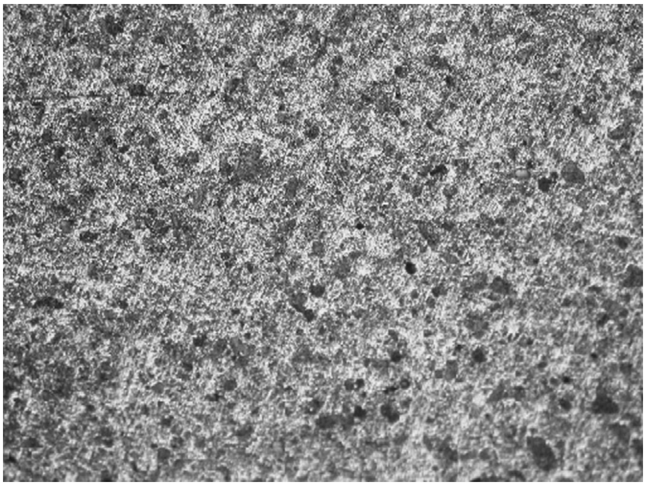

**Fig. 5.** Optical micrograph of Al–$TiB_2$ master alloy X200.

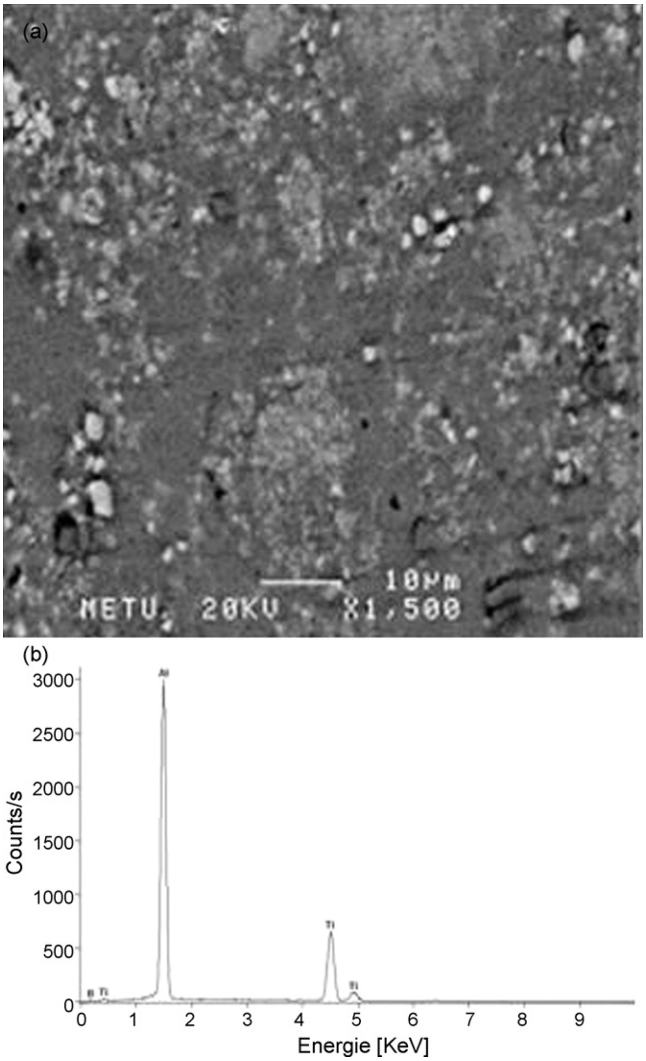

**Fig. 6.** (a) SEM micrograph of the master alloy, (b) general EDX analysis.

in alcohol in an ultrasonic cleaner and etched with Keller solution (15%HF, 45%HCL, 15%$HNO_3$, and 25%$H_2O$) [4].

Then sample was examined with optical and scanning electron microscopy. The optical micrograph is given in Fig. 5.

$TiB_2$ particles are so fine that they could not be observed through the optical microscope, although they were observed in SEM micrographs. The SEM micrographs and EDX analysis of the master alloy can be seen in Fig. 6.

These micrographs correspond to particles of $TiB_2$. Based on the results, it can be said that these particles are most probably titanium diboride particles. Moreover, the sizes of the $TiB_2$ particles, determined from this micrograph, are in the order of 1 µm and are spherical in shape.

## 4. Conclusions

In this study, the production of Al–$TiB_2$ master alloys was investigated. A master alloy was produced with slag–metal reactions using Al, boric acid, $TiO_2$ and cryolite, which are not expensive materials. Because of the exothermic reaction in this method of production, energy savings were considerable. Using raw materials and reducing used energy make this method environmentally friendly. To summarize:

1. $TiB_2$ particles were formed in situ within the aluminum matrix through the reaction of $TiO_2$ and $H_3BO_3$ in the $Na_3AlF_6$ by molten Al.
2. $TiB_2$ particles formed by the slag–metal reaction were spherical in shape and approximately 1 µm in size.
3. $TiB_2$ particles could be successfully precipitated in the aluminum, creating a more homogenous distribution compared with other processing techniques such as solid state reactive sintering.

## References

[1] P.S. Cooper, M.A. Kearns, Removal of transition metal impurities in aluminum melts by boron additives, Mater. Sci. Forum 217–222 (1996) 141–146.
[2] D. Apelian, G.K. Sigworth, K.R. Whaler, Foundry Alloys by Thermal Analysis, American Foundrymen's Society Inc., 1984, pp. 297–307.
[3] X. Wang, The formation of $AlB_2$ in an A–B master alloy, J. Alloys Compd. 403 (1,2) (2005) 283–287.
[4] C. Wang, M. Wang, B. Yu, D Chena, P. Qin, M. Feng, Q. Dai, The grain refinement behavior of $TiB_2$ particles prepared with in situ technology, Mater. Sci. Eng. A 459 (2007) 238–243.
[5] Y. Birol, Production of Al–B alloy by heating Al/KBF4 powder blends, J. Alloys Compd. 481 (1,2) (2009) 195–198.
[6] Y. Birol, Production of Al–Ti–B grain refining master alloys from $Na_2B_4O_7$ and $K_2TiF_6$, J. Alloys Compd. 458 (1,2) (2008) 271–276.
[7] S.A. Kori, B.S. Murty, M. Chakraborty, Development of an efficient grain refiner for Al–7Si alloy, Mater. Sci. Eng. 280A (2000) 58–61.
[8] T Sagstad, N Dahle, Proceedings of the Fifth International AFS Conference on Molten Aluminum Processing, American Foundrymen's Society, Orlando, 1998, p. 100.
[9] J. Pearson, G.P. Jones, Factors affecting the grain-refinement of aluminum using titanium and boron additives, Metal. Trans. 2B (1976) 223–234.
[10] M.S. Lee, B.S. Terry, P Grieveson, Interfacial phenomena in the reactions of Al and Al–Ti melts with KF–$AIF_3$ and NaF–$AIF_3$ melts, Metall. Trans. 24B (1993) 955–961.
[11] M.S. Lee, P. Grieveson, The production of Al–Ti–B grain refining master alloys, Scand. J. Metall. 32 (2003) 256–262.
[12] H. Zhu, H. Wang, Liangi, S. Chen, S. Wu, Formation of composites fabricated by exothermic dispersion reaction inAl–$TiO_2$–$B_2O_3$ system, Trans. Nonferrous Met. Soc. China 17 (2007) 590–594.
[13] O. Kubaschewski, E.L.L. Evans, C.B. Alcock, Metallurgical Thermochemistry, Pergamon Press, New York, 1967.
[14] N.L. Yue, L. Lu, M.O. Lai, Application of thermodynamics calculation in the in-situ process of Al/$TiB_2$, Compos. Struct. 47 (1999) 691–694.
[15] L. Lu, M.O. Lai, Y. Su, H.L. Teo, C.F. Feng, In situ $TiB_2$ reinforced Al alloy composites, Scripta Mater. 45 (9) (2001) 1017–1023.
[16] A. kuroğlu, Aluminum oxide titanium diboride reinforced metal matrix composite and its mechanical properties, M.Sc thesis, METU (2004).