

# Production of Al–Ti–B Grain Refining Master Alloys from B<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>TiF<sub>6</sub> by Microwave Irradiation

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**Abstract:** Al–Ti–B master alloys have received much attention in recent years owing to their potential as efficient grain refiners for aluminum foundry alloys. A process involving in-situ reduction of K<sub>2</sub>TiF<sub>6</sub> and B<sub>2</sub>O<sub>3</sub> with excess aluminum in the presence of cryolite flux has been developed for the preparation of Al–Ti–B master alloys using a melt reaction method by microwave irradiation. The microstructure and synthetic process of the master alloy were investigated by optical microscopy and X-ray diffraction. The results show that the

master alloy is composed of Al, Al<sub>3</sub>Ti and TiB<sub>2</sub> phases and microwave irradiation method can be used to fabricate Al–Ti–B master alloy in situ from the K<sub>2</sub>TiF<sub>6</sub>–B<sub>2</sub>O<sub>3</sub>–Na<sub>3</sub>AlF<sub>6</sub> and Al system when the aluminum melted. The synthesis mechanisms of the master alloy are as follows: Al<sub>3</sub>Ti is formed through the reaction between K<sub>2</sub>TiF<sub>6</sub> and Al melt at 850 °C.

**Key words:** Al–Ti–B; master alloys; Grain refinement; microwave synthesis

## 1. Introduction

In recent years, synthesis of Al–Ti–B master alloys has attracted much attention due to their applications in Al and its alloys [1–2]. A typical practice involves the addition of Al–Ti–B grain refiner into molten aluminium on its way to the casting station. The uniform, fine, equiaxed grain structure thus obtained not only yields superior mechanical properties but also provides alloy homogeneity. The Al–Ti–B master alloys are produced commercially by a melt reaction method that which involves adding the inorganic salts potassium fluotitanate, K<sub>2</sub>TiF<sub>6</sub>, and potassium fluotitanate, KBF<sub>4</sub>, to molten aluminium [3]. However, halide salts, KBF<sub>4</sub> in particular, are expensive compounds which add greatly to the raw material costs, and give rise to intense fluoride emissions and troublesome dross. Hence, the present work was undertaken to replace KBF<sub>4</sub> with B<sub>2</sub>O<sub>3</sub> in the production of Al–Ti–B grain refiners. B<sub>2</sub>O<sub>3</sub> is nearly four times richer in B with respect to KBF<sub>4</sub> and is less expensive [4–8]. However, it has been found experimentally that boride agglomeration is associated with wetting of the boride particles by the potassium cryolite flux. Microwave processing has received much research interest in recent times for materials synthesis. This method is a very promising preparation way for many materials because it is fast, clean, energy efficient and does not suffer from the disadvantages of the classical preparation technique [9–11]. In this paper, a novel Al–Ti–B master alloy is prepared using a melt reaction method by microwave-assisted activation synthesis, which has not been reported before. This method can be used to fabricate Al–Ti–B master alloy in situ from the K<sub>2</sub>TiF<sub>6</sub>–B<sub>2</sub>O<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. The results obtained seem to be very interesting and stimulate further research in this direction.

## 2. Experimental Procedure

Al–Ti–B alloy was prepared in the laboratory by the microwave-assisted activation synthesis method. Fig.1 shows a schematic illustration of the experimental equipment. Commercial pure K<sub>2</sub>TiF<sub>6</sub> (98% purity),

commercial pure boron oxide (99.9% purity) and commercial pure Al (99.7% purity) were used as raw materials. The required amount of these materials was well mixed and compressed to form pellet 10mm in thickness and 20mm in diameter under appropriate pressure. The samples were then placed in alumina crucible in the center of the microwave oven and the reaction was carried out under the protection of high purity Ar (99.9%). The microwave oven used in the present work consists of a 2.45GHz microwave generator with continuous adjustable power output 0–8kW. An infrared pyrometer was used (Raytek, Marathon series) for temperature measurement. Microwave heating used in the present work was carried out at the power level of 2.0kW–3.5kW and heated to a designed temperature (800–850°C) and kept at this temperature (with power level of 1.0kW–1.5kW) for 20–30min. Optical microscopy and X-ray energy-dispersive spectrum were used to analyze their microstructures and components. X-ray diffraction was used to identify the phases of the specimen. The molten K–Al–F salt was finally decanted, the dross was skimmed off and the melt was stirred thoroughly to rejuvenate the settled particles before it was cast into a permanent mold.

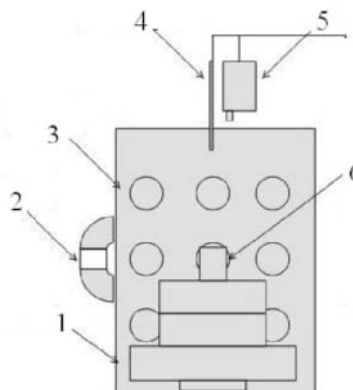


Figure.1. Schematic view of microwave system setup  
1—rotating table; 2—peep hole; 3—magnetron tube; 4—infrared thermometer; 5—thermocouple; 6—crucible;

### 3. Results and discussion

#### 3.1 Examination of the Preparation Process

To investigate the preparation process, a powder mixture of potassium titanium fluoride, boron oxide and pure Al was quickly melted, forming a liquid-like slag under microwave field. It was observed that the color of the solidified slag changed with holding time, changing from black at the initial stage to gray and, finally, to white.

The XRD analysis in Figure 2 shows the structural change in the slag. After 20 minutes of reaction, peaks from potassium aluminofluorides ( $KAlF_4$  and  $K_3AlF_6$ ), and potassium titanium oxyfluorides ( $K_3TiOF_5$  and  $K_2TiO_2F_4$ ) were detected (Figure 2(a)). After 30 minutes of reaction, the diffraction from  $K_3TiOF_5$  and  $K_2TiO_2F_4$  showed no noticeable change, but that of the  $KAlF_4$  and  $K_3AlF_6$  peaks increased (Figure 2(b)).

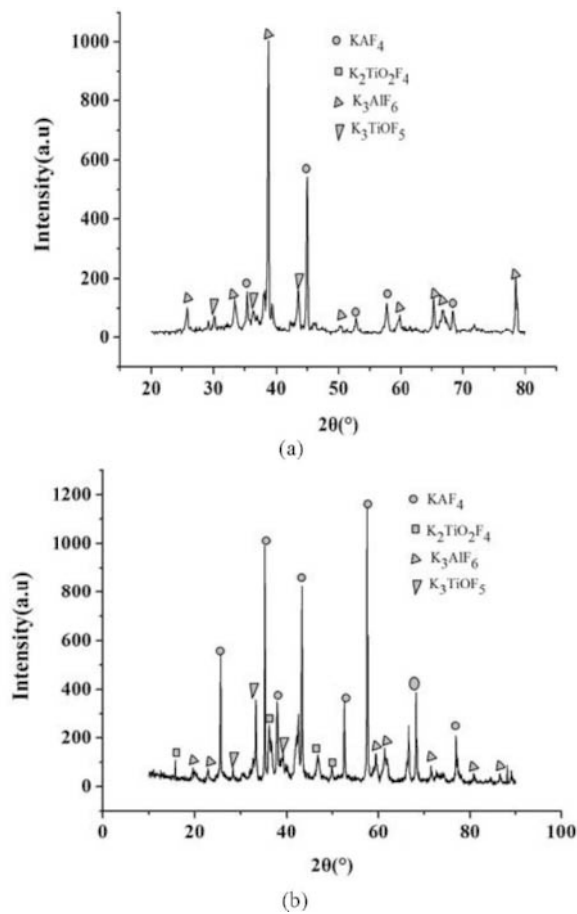


Figure 2. XRD diffraction patterns of slag at different reaction times: (a) 20 min and (b) 30 min

#### 3.2 Reaction between Potassium Titanium Fluoride and Aluminum

Figure 3 shows the DTA results of a mixture of potassium titanium fluoride and aluminum powders. Apart from the endothermic peaks at 390 °C and 580 °C associated, respectively, with the demosturizing and oxidization of potassium titanium fluoride, an endothermic peak at 660°C (the melting point of pure aluminum) and an

exothermic one at 720°C were detected. The exothermic peak at 720°C was caused by the formation of  $Al_3Ti$ , an aluminothermal reaction which produces aluminofluorides and titanium aluminide.

During the reaction, the Ti was reduced from  $K_3AlF_6$  further reacted with the molten aluminum, resulting in the formation of titanium aluminide as a second phase existing in the aluminum matrix. According to the structural theory of slag [12], both  $KAlF_4$  and  $K_3AlF_6$  in their molten state may be regarded as molten mixtures of KF and  $AlF_3$ . This reaction was accompanied by the formation of aluminofluorides floating on top of the melt as slag.

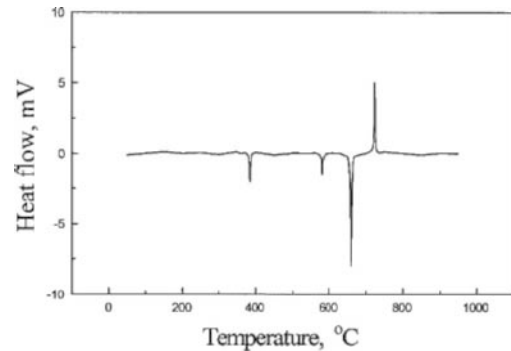
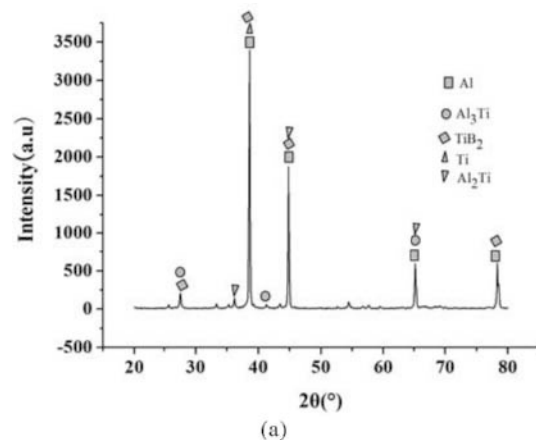
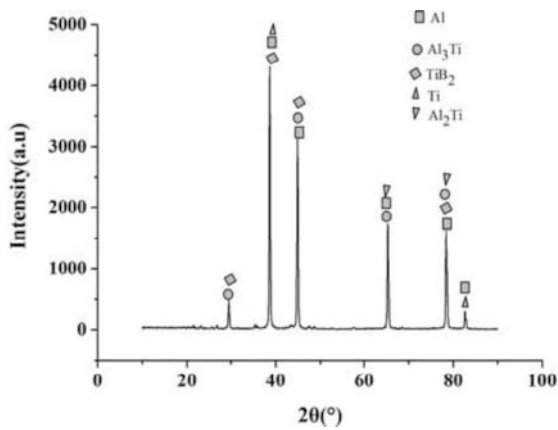


Figure 3. DTA result of mixture of potassium titanium fluoride and aluminum.

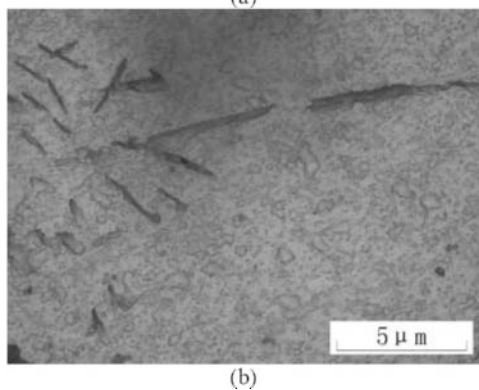
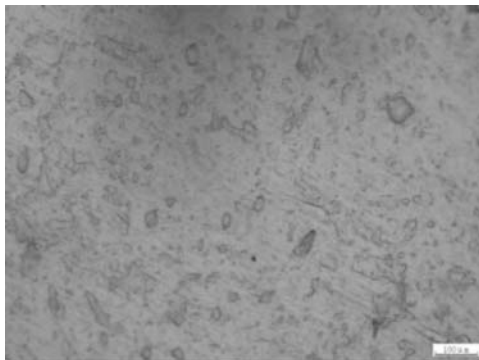
#### 3.3 Microstructure of Al-Ti-B alloy

Figure 4 shows XRD analysis of the structural change in Al-Ti-B alloy in microwave oven. The phase analysis of the XRD patterns reveals that  $\alpha(Al)$ ,  $Al_3Ti$  and  $TiB_2$  is the major phase in the sample. After 20 minutes of reaction, peaks from  $Al_3Ti$ ,  $Al_2Ti$ ,  $TiB_2$  and unknown phases were detected (Figure 4(a)). After 30 minutes of reaction, the diffraction from  $Al_3Ti$  and  $TiB_2$  showed no noticeable change, but that of the unknown phases peaks decreased (Figure 4(b)). Hence it shows that complete reaction has been carried out when the heating time is only 30 minutes.



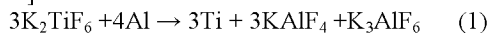


(b)  
Figure 4. XRD diffraction pattern of Al-Ti-B master alloy  
(a) 20 min and (b) 30 min



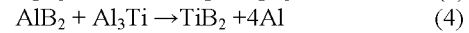
(a)  
(b)  
Figure 5. Optical micrographs of Al-Ti-B alloy

The results show that Ti presents in the aluminum in the form of  $\text{Al}_3\text{Ti}$  and  $\text{TiB}_2$  when Al-Ti-B master alloys were prepared in the alumina crucible by microwave irradiation. Formation of  $\text{Al}_3\text{Ti}$  particles may involve the reduction of  $\text{K}_2\text{TiF}_6$  by aluminium in the “halide salt” route [13-14]:

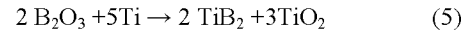


$\text{K}_2\text{TiF}_6$  is reduced by molten aluminium, releasing Ti which dissolves in the melt before precipitating out as  $\text{Al}_3\text{Ti}$  particles as soon as its solubility limit is exceeded. A considerable amount of Ti and  $\text{Al}_3\text{Ti}$  seems to suggest

that reaction (1) is also taking place in the optical micrographs (Figure 5). Formation of  $\text{TiB}_2$  particles, on the other hand, may involve the reduction of  $\text{B}_2\text{O}_3$  by molten aluminium and the subsequent reaction of  $\text{AlB}_2$  with the  $\text{Al}_3\text{Ti}$  phase:



or may occur through direct reduction of  $\text{B}_2\text{O}_3$  by solute Ti:

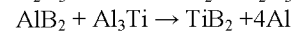
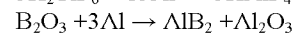


Reaction (4) of the former route was shown to be extremely sluggish even when both  $\text{AlB}_2$  and  $\text{Al}_3\text{Ti}$  particles were abundant in the melt [8]. Reaction (5), on the other hand, enjoys a much larger driving force [15] and provides, implying oxidation of Ti, a plausible account of Ti recovery in alloy. Evidence, in the XRD spectrum and optical micrographs, of a considerable amount of  $\text{AlB}_2$  seems to suggest that reaction (3) is also taking place.

## 4 Conclusions

(1) A process involving in-situ reduction of potassium titanium fluoride, boron oxide with excess aluminium in the presence of cryolite flux has been developed for the preparation of Al-Ti-B master alloys. It has been found possible to produce Al-Ti-B alloys on holding the charge for 30min by microwave-assisted synthesis techniques.

(2) The synthesis mechanisms of the master alloy are as follows:  $\text{TiB}_2$  and  $\text{Al}_3\text{Ti}$  are formed by the reactions:



## 5 Acknowledgements

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