Synthesis Mechanism of an Al-Ti-C Grain Refiner Master Alloy Prepared by a New Method

B.Q. ZHANG, H.S. FANG, L. LU, M.O. LAI, H.T. MA, and J.G. LI

The mechanisms of *in-situ* synthesis of an Al-Ti-C grain-refiner master alloy, prepared by adding a powder mixture of potassium titanium fluoride and carbon into an aluminum melt, have been systematically studied. It was found that vigorous reactions occurred at the initial stage of reaction and then slowed down. After about 20 minutes, the reactions, which led the formation of blocky titanium aluminides and submicron titanium carbides in the aluminum matrix, appeared to reach completion. Potassium titanium fluoride reacted with aluminum and carbon at 724 °C and 736 °C, respectively, resulting in the formation of titanium aluminides and titanium carbides in the aluminum matrix as well as in the formation of a low-melting-point slag of binary potassium aluminofluorides. The reaction between potassium titanium fluoride and carbon is believed to be the predominant mechanism in the synthesis of TiC by this method.

I. INTRODUCTION

THE effectiveness of Al-Ti-C master alloys in the grain refinement of aluminum and its alloys have been widely investigated for many years.[1] In recent years, they have been of increasing importance in aluminum casting because, unlike conventional Al-Ti-B master alloys,[2,3] they are believed to introduce a smaller volume fraction of insoluble particles into the melt.

Many attempts[4–9] have been devoted to exploring the technique of producing Al-Ti-C grain-refiner master alloys. There are, thus, two methods which may have the potential for production on an industrial scale. The first method, called "the conventional method," was reported by Banerji and Reif[10,11] in the mid-1980s, where Al-Ti-C master alloys were produced by reaction between carbon and an Al-Ti binary alloy melt. The synthesis mechanism of TiC in the alloy has been studied, and two mechanisms, namely, a solid-liquid reaction mechanism and an oversaturated precipitation mechanism, were proposed.[12] The second method, developed recently to produce Al-Ti-C master alloys, was through the reactions between a mixture of carbon, titanium-containing fluoride salt (such as potassium titanium fluoride), and an Al melt.[13,14] Large amounts of TiC could be synthesized by this method at relatively low reaction temperatures.

The present work focuses on the mechanism in the synthesis of Al-Ti-C master alloys prepared through the reaction between aluminum, graphite, and potassium titanium fluoride.

II. EXPERIMENTAL PROCEDURES

Pure aluminum was first melted at 850 °C. A given amount of powder mixture of graphite and potassium titanium fluoride was then added to the melt by light stirring. The stirring was maintained for 60 minutes. After stirring, the melt was allowed to stand at 850 °C for 5 minutes before casting. To investigate the change in phases and compositions of the slag and the aluminum melt, samples were taken *via* a quartz tube from the slag and aluminum melt at different reaction times during the preparation process. The collected metal samples were immediately quenched in cold water. Phase changes were monitored using a D/MAX/RD (12 kW, Cu-type) X-ray diffraction (XRD) machine with Cu $K_{\alpha 1}$ radiation, operated at 30 kV and 20 mA. The scanning speed used was 2 deg/min, with a scan pitch of 0.02 deg. Chemical analysis of Ti was done with an atomic-absorption spectrometer. The carbon content was determined using an automatic combustion apparatus, where the sample is combusted in a stream of oxygen and the carbon of the specimen is converted to CO_2. Microstructures and secondary phases in the master alloys were examined using a JEOL* JSM-6301 scanning electron microscope.

High-temperature differential thermal analysis (DTA) was carried out on the fluoride salt, a mixture of fluoride salt and carbon, a mixture of fluoride salt and aluminum powder, and a mixture of all the constituents. Based on the DTA results, the samples were then subjected to processing at different temperatures using platinum crucibles and were further characterized by XRD. The DTA was carried out at normal atmosphere in the temperature range of 50 °C to 950 °C, with a heating rate of 10 °C/min. Potassium titanium fluoride, carbon, and aluminum were all in powder form, of a -300 mesh size (<50 μm) and of 99.0, 98, and 99.7 pct purity, respectively. The weight ratio between the aluminum, potassium titanium fluoride, and carbon was kept at 90:30:1 in all the experiments. The ratio is close to that necessary to produce a nominal Al-6 wt pct Ti-1 wt pct C master alloy. All powders were thoroughly mixed to give a homogeneous mixture prior to the DTA test.

---

*JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

B.Q. ZHANG, Research Fellow, and L. LU and M.O. LAI, Associate Professors, are with the Department of Mechanical Engineering, National University of Singapore, Singapore 119260. Contact e-mail: mpeluli@nus.edu.sg H.S. FANG, Professor, and H.T. MA and J.G. LI, Associate Professors, are with the Department of Material Science and Engineering, Tsinghua University, Beijing, 100084, People's Republic of China.

Manuscript submitted January 10, 2002.

II. RESULTS AND DISCUSSION

A. *Examination of the Preparation Process*

To investigate the preparation process, an Al-Ti-C master alloy with a typical nominal composition of 6 wt pct Ti and 1 wt pct C was prepared at 850 °C. A powder mixture of potassium titanium fluoride and carbon was quickly melted, forming a liquid-like slag after they were added to the aluminum melt, with the help of light stirring. 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.

Figure 1 shows the change in the amount of Ti and C in the slag and metal melt as a function of reaction time. It was found that the contents of Ti and C in the metal melt sharply increased during the first 10 minutes of reaction. The increase then slowed down until constant values of about 5.53 wt pct Ti and 0.48 wt pct C were reached after 20 minutes of reaction. The Ti and C contents in the slag changed inversely with those in the metal melt and almost disappeared after 20 minutes of reaction, indicating that Ti and C had been displaced from the slag to the melt.

The XRD analysis shown in Figure 2 shows the structural changes in the slag after the powder mixture of potassium titanium fluoride and carbon had been added to the metal melt. After 2 minutes of reaction, in addition to peaks of potassium titanium fluoride and carbon, peaks from titanium carbide, 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)). When the reaction time was increased to 10 minutes, the intensity of the potassium titanium fluoride and carbon peaks was lowered, but that of the TiC, $KAlF_4$, and K_3AlF_6 peaks increased. The diffraction from K_3TiOF_5 and $K_2TiO_2F_4$ showed no noticeable

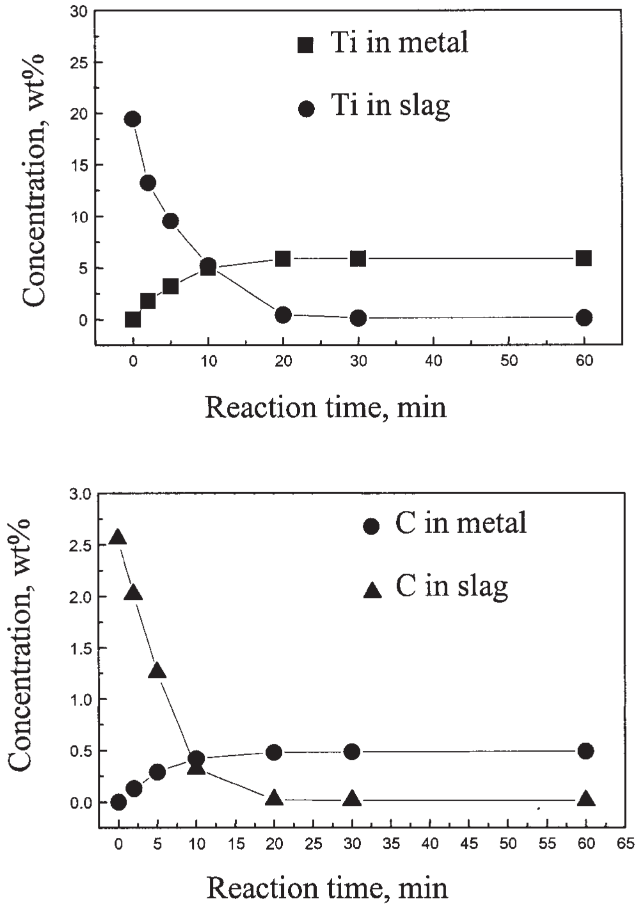


Fig. 1—Contents of Ti and C in metal melt and slag as a function of reaction time.

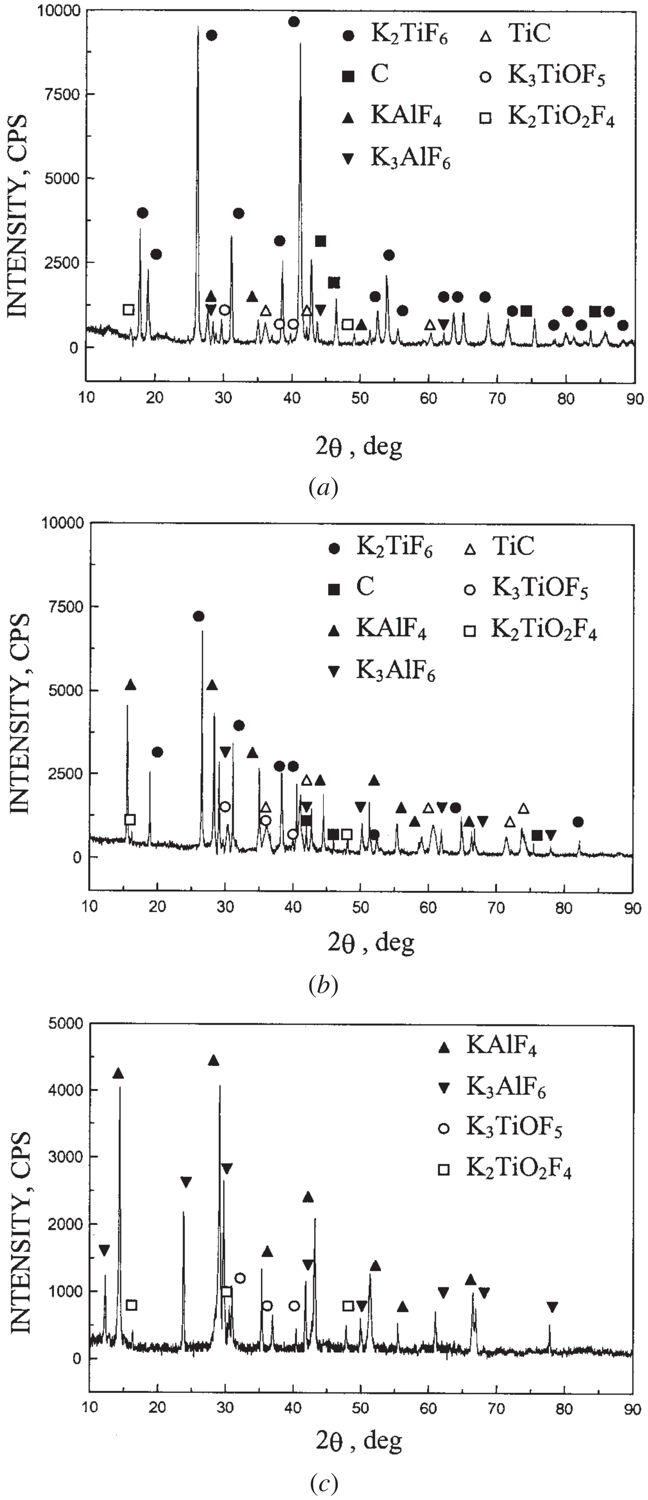


Fig. 2—XRD diffraction patterns of slag at different reaction times: (*a*) 2 min, (*b*) 10 min, and (*c*) 60 min.

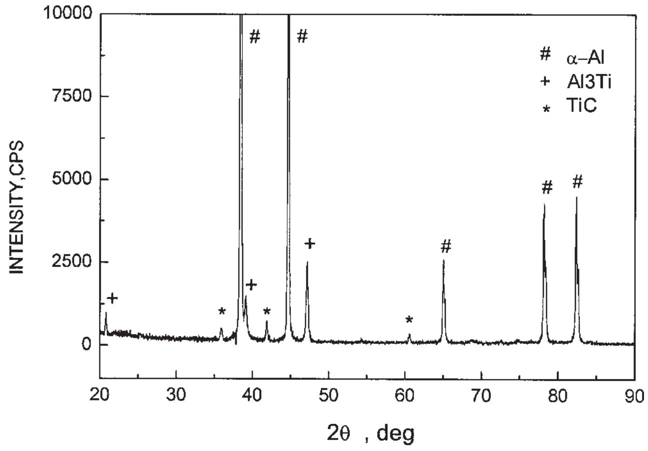


Fig. 3—XRD diffraction pattern of Al-Ti-C master alloy.

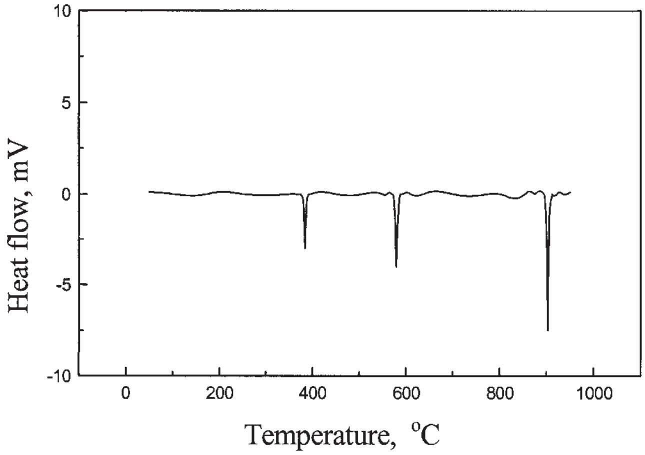


Fig. 5—DTA result of potassium titanium fluoride.

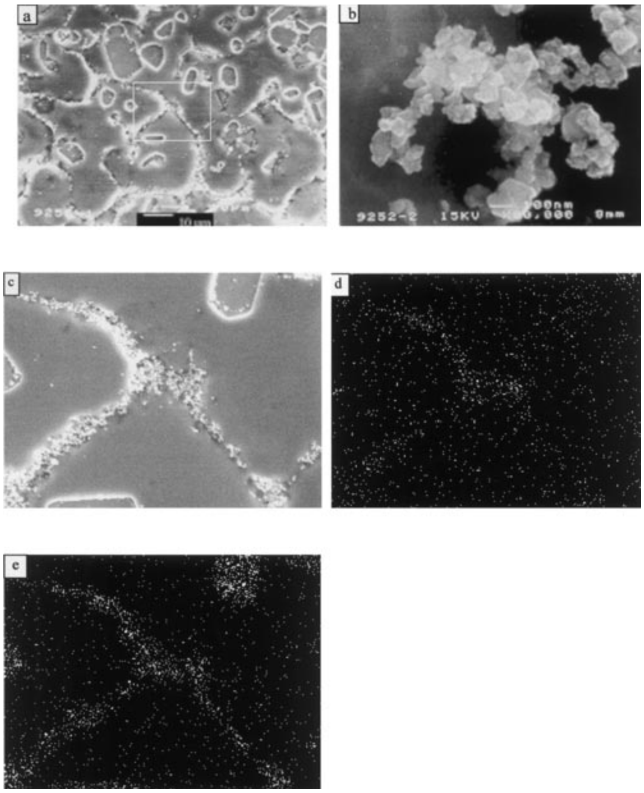


Fig. 4—SEM examination of the master alloy: (*a*) typical microstructure, (*b*) SEI of segregated particles, and (*c*) through (*e*) selected region and its X-ray mapping of Ti and C.

change (Figure 2(b)). After 60 minutes of reaction followed by 5 minutes holding time, only $KAlF_4$, K_3AlF_6, K_3TiOF_5, and $K_2TiO_2F_4$ were left in the slag (Figure 2(c)). For the aluminum matrix, shown in Figure 3, however, only two secondary phases were detected, namely, Al_3Ti and TiC.

A typical microstructure of the master alloy revealed blocky-type particles located in the grains and particulates that were segregated normally along the grain boundaries (Figure 4(a)). The latter consisted of fine particles usually in the submicron size (Figure 4(b)). Figures 4(c) through (e) are the secondary electron images of a selected region from the typical microstructure (Figure 4(a)) and its X-ray mappings of Ti and C, respectively. Enrichment of Ti in the blocky particles and enrichment of both Ti and C in the segregated particulates, together with the results from XRD shown in Figure 3, confirmed that the blocky particles were Al_3T_i and the submicron-sized particulates were TiC.

B. *Thermal Analysis of Potassium Titanium Fluoride*

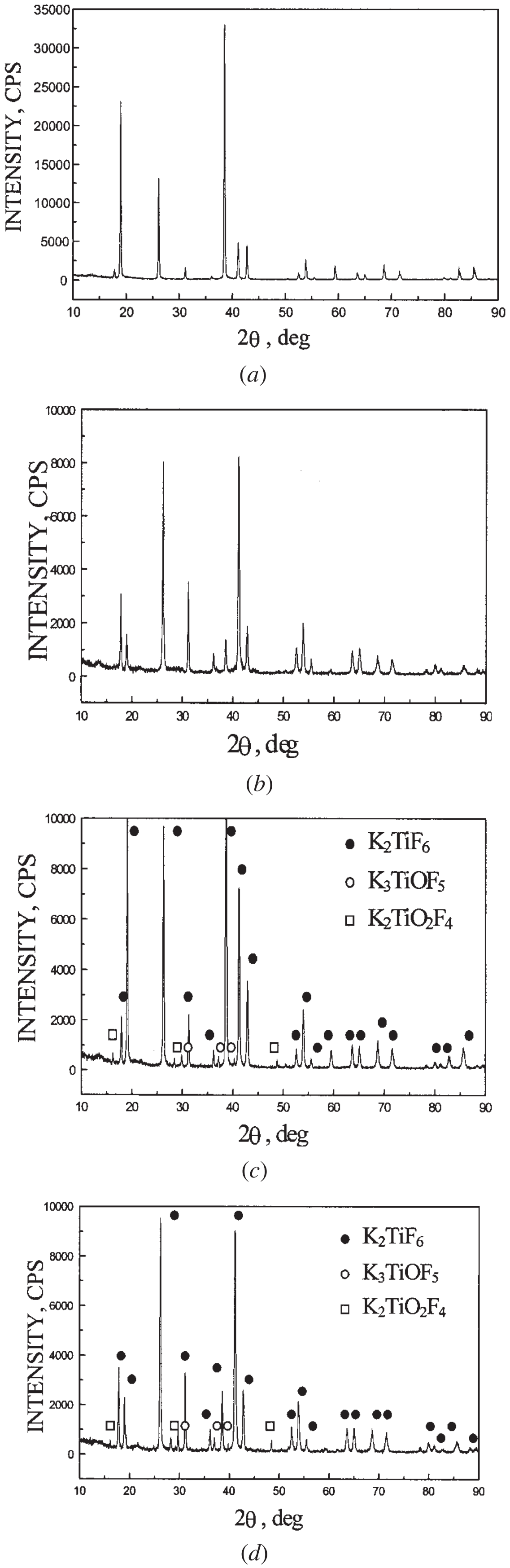
The DTA study of potassium titanium fluoride in Figure 5 shows three endothermic peaks located at 384 °C, 580 °C, and 903 °C. To understand the changes occurring in the salt at these endothermic peaks, the salt was heat treated in the normal atmosphere at three different temperatures of 400 °C, 600 °C, and 920 °C for 30 minutes.

Compared with the pattern of the original salt (Figure 6(a)), the XRD showed no change in the salt when it was heat treated at 400 °C (Figure 6(b)). Heat treatment at the higher temperature of 600 °C led to the formation of the oxyfluorides of K_3TiOF_5 and $K_2TiO_2F_4$, as shown in Figure 6(c). This suggests that the endothermic peak at 580 °C is associated with the oxidation of potassium titanium fluoride. When heat treated at 920 °C, the powder salt melted, but no new phase was formed (Figure 6(d)). This confirms that the endothermic peak at 903 °C is due to the melting of potassium titanium fluoride.

To clarify the origin of the endothermic peak at 384 °C, infrared (IR) spectroscopy was carried out on the salt. The IR spectrum from Figure 7(a) shows the presence of moisture in the original potassium titanium fluoride. It can, therefore, be deduced that the original potassium titanium fluoride may be formulated as $K_2TiF_6 \cdot xH_2O$. After the heat treatment at 400 °C for 30 minutes, the peaks of the IR spectrum corresponding to H_2O disappeared (Figure 7(b)), indicating that the endothermic peak at 384 °C seen from the DTA was attributed to the loss of moisture from the salt, namely,

$$K_2TiF_6 \cdot x\ H2O \rightarrow K_2TiF_6 + x\ H_2O \uparrow \qquad [1]$$

After demoisturization, the K_2TiF_6 was further oxidized to form oxyfluorides when heat treated above 580 °C. The exact oxidation mechanism—whether K_2TiF_6 was oxidized by oxygen in the air or by water vapor from the surroundings—needs to be further confirmed.



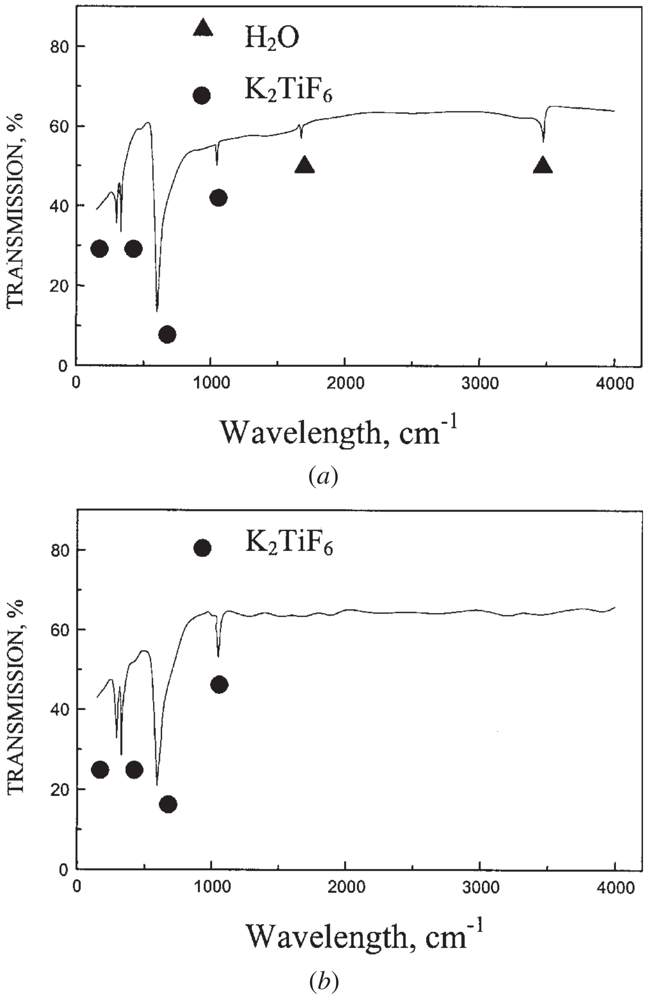
(*a*)

(*b*)

(*c*)

(*d*)

Fig. 6—XRD diffraction patterns of potassium titanium fluoride: (*a*) original and heated for 30 min at (*b*) 400 °C, (*c*) 600 °C, and (*d*) 920 °C.



(*a*)

(*b*)

Fig. 7—IR spectra of potassium titanium fluoride: (*a*) original and (*b*) heat treated at 400 °C for 30 min.

C. *Reaction between Potassium Titanium Fluoride and Aluminum*

Figure 8 shows the DTA results of a mixture of potassium titanium fluoride and aluminum powders. Apart from the endothermic peaks at 384 °C and 580 °C associated, respectively, with the demoisturizing and oxidization of potassium titanium fluoride, an endothermic peak at 660 °C (the melting point of pure aluminum) and an exothermic one at 724 °C were detected. It is noted that the endothermic peak associated with the melting of potassium titanium fluoride at 903 °C has disappeared. To investigate the origin of the exothermic peak at 724 °C, the mixture was heat treated at 800 °C for 30 minutes. It was found that the heat-treated mixture formed two layers. The lower layer was Al and Al_3Ti, as shown in Figure 9(a). The upper layer was a slag consisting mainly of aluminofluorides ($KAlF_4$ and K_3AlF_6), as well as small amount of oxyfluorides (K_3TiOF_5 and $K_2TiO_2F_4$) (Figure 9(b)). The result suggests that the exothermic peak at 724 °C was caused by the formation of Al_3Ti, an alumi-nothermal reaction which produces aluminofluorides and titanium aluminide. This reaction may be written as

$$3K_2TiF_6 + 13Al \rightarrow 3KAlF_4 + K_3AlF_6 + 3Al_3Ti \qquad [2]$$

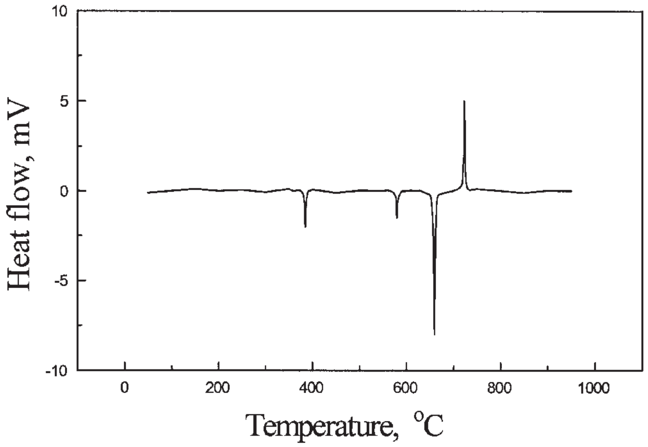
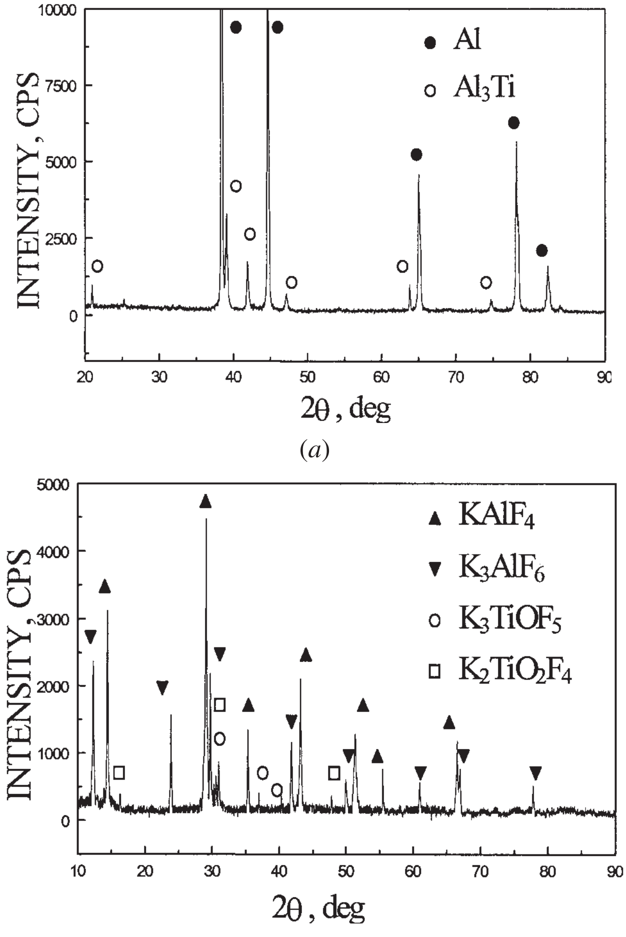


Fig. 8—DTA result of mixture of potassium titanium fluoride and aluminum.



(*a*)

(*b*)

Fig. 9—XRD analysis of heat-treated samples of mixture of potassium titanium fluoride and aluminum at 800 °C for 30 min: (*a*) upper layer and (*b*) lower layer.

During the reaction, the Ti that was reduced from K_2TiF_6 further reacted with the molten aluminum, resulting in the formation of titanium aluminide as a second phase existing in the aluminum matrix. This reaction was accompanied by the formation of aluminofluorides floating on top of the melt as slag.

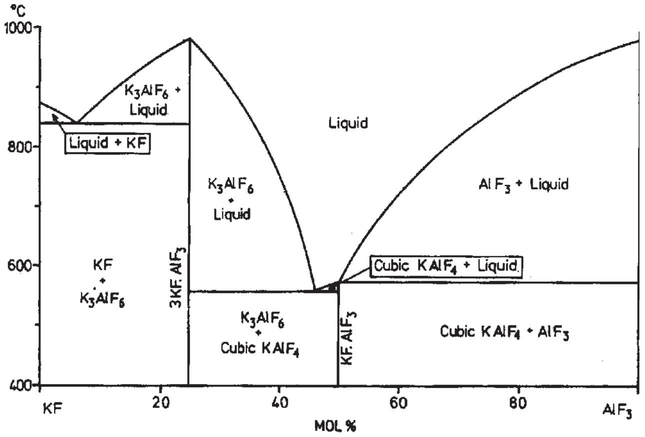


Fig. 10—Phase diagram of KF-AlF_3 binary system.[16]

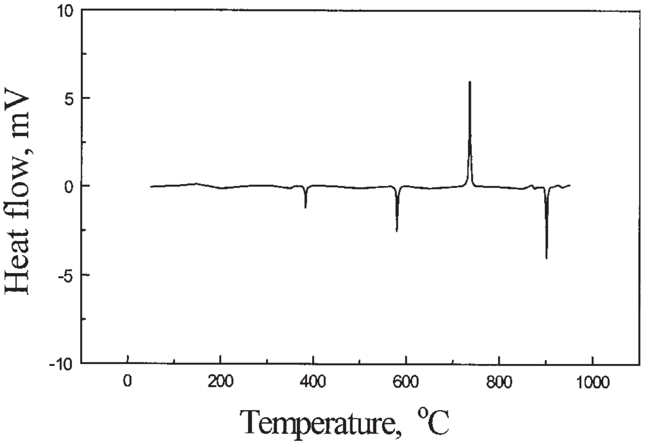


Fig. 11—DTA result of mixture of potassium titanium fluoride and carbon.

According to the structural theory of slag,[15] both $KAlF_4$ and K_3AlF_6 in their molten state may be regarded as molten mixtures of KF and AlF_3. Therefore, Reaction [2] can be rewritten as

$$3K_2TiF_6 + 13Al \rightarrow 6KF + 4AlF_3 + 3Al_3Ti \qquad [3]$$

From the KF-AlF_3 phase diagram shown in Figure 10,[16] it can be seen that the binary salt system of KF-AlF_3 at a ratio of 3:2 is located in the range where $KAlF_4$ and K_3AlF_6 are the phases present at room temperature. It can also be seen that this mixture of salt products has a melting point of about 750 °C, which may seem to explain the formation of the upper layer of melt slag when the powder mixture of K_2TiF_6 and aluminum was held at 800 °C.

D. *Reaction between Potassium Titanium Fluoride and Carbon*

The DTA analysis on the powder mixture of potassium titanium fluoride and carbon showed that, in addition to the endothermic peaks at 384 °C, 580 °C, and 903 °C, an exothermic peak at 736 °C emerged (Figure 11). The powder mixture remained in powder form after heating at 800 °C for

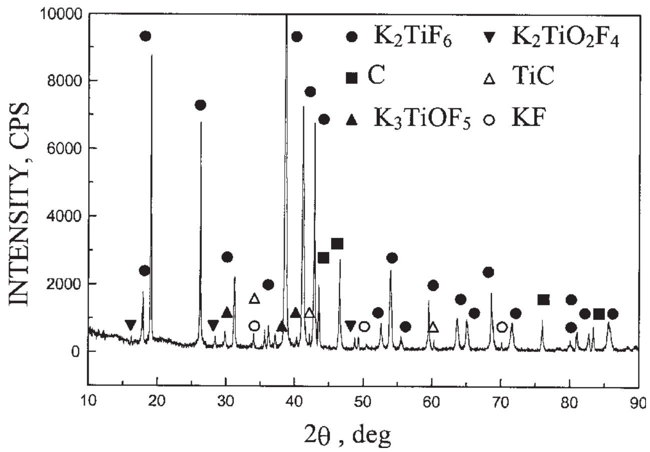


Fig. 12—XRD analysis of heat-treated samples of mixture of potassium titanium fluoride and carbon at 800 °C for 30 min.

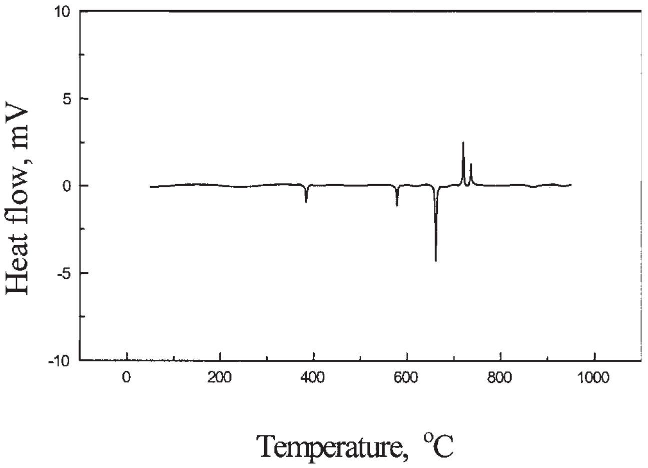


Fig. 13—DTA result of mixture of potassium titanium fluoride, aluminum, and carbon.

30 minutes. The XRD study shown in Figure 12 indicates that new phases of TiC and KF were detected following the heat treatment, in addition to the oxyfluorides K_3TiOF_5 and $K_2TiO_2F_4$, the unreacted potassium titanium fluoride, and carbon. It can be concluded from the previous analysis, together with the principle of conservation of mass in chemical reactions, that an exothermic reaction between potassium titanium fluoride and carbon occurs at 736 °C, as follows:

$$K_2TiF_6 + 2C \rightarrow TiC + 2KF + CF_4\uparrow \qquad [4]$$

Since TiC has a very high melting temperature and KF is stable, with a melting temperature of 858 °C,[17] both of them remain after the heat treatment. However, CF_4 is a vapor at room temperature,[18] so it cannot be detected since it leaves the system. Equation [4], therefore, explains the loss of carbon in the processing of the Al-Ti-C master alloy *via* this new synthesis method.[19]

E. *Reaction between Potassium Titanium Fluoride, Aluminum, and Carbon*

The DTA result of the mixture of potassium titanium fluoride, aluminum, and carbon is shown in Figure 13. No new peak could be observed other than the two exothermic peaks at 724 °C and 736 °C, representing respectively, the reactions between potassium titanium fluoride and aluminum and carbon. There are also three endothermic peaks detected at 384 °C, 580 °C, and 660 °C. This observation suggests that the potassium titanium fluoride reacted with both aluminum and carbon simultaneously, resulting in the formation of titanium aluminide and titanium carbide, which exist as secondary phases in the aluminum matrix.

The TiC in Al-Ti-C master alloys prepared at elevated reaction temperatures by the conventional method is believed to be synthesized through two mechanisms, as follows:[12]

$$\underline{Ti} + C\ (s) = TiC\ (s) \qquad [5]$$

$$\underline{Ti} + \underline{C} = TiC(s) \qquad [6]$$

where $\underline{Ti}$ and $\underline{C}$ stand for solute Ti and C, respectively, in the aluminum melt. Solute C is obtained through the dissolving of graphite particles into the aluminum melt:

$$C\ (s) = \underline{C} \qquad [7]$$

Reaction [5] is known as a solid-liquid synthesis mechanism, in which TiC particles are formed through the reaction between carbon particles and solute Ti in the aluminum melt. The synthesis mechanism expressed by Reaction [6] is actually a precipitation process of TiC when the solubility product of solute Ti and solute C in the aluminum melt surpasses the saturated solubility product of TiC.

It has been reported[10] that when Al-Ti-C alloys were prepared by the conventional method, an elevated reaction temperature of up to 1300 °C was needed to practically obtain a meaningful amount of TiC particulates in the alloys. The rate of synthesis of TiC has been largely decelerated by the lower reaction temperature. This was confirmed by the results in Reference 19, where little TiC was formed in the alloys when prepared at 850 °C by the conventional method. It is, therefore, reasonable to propose that the reaction between potassium titanium fluoride and carbon is the predominant mechanism in the synthesis of TiC using the new method.

IV. CONCLUSIONS

1. During the processing of an Al-Ti-C master alloy *via* a new method by adding a powder mixture of potassium titanium fluoride and carbon to an aluminum melt at around 850 °C, a vigorous reaction between them was observed at the initial stage. The reaction slowed down and appeared to reach completion after about 20 minutes.
2. Potassium titanium fluoride reacted with aluminum and carbon at 724 °C and 736 °C, respectively, resulting in the formation of titanium aluminides and titanium carbides in the aluminum matrix. A low melting point slag of binary potassium aluminofluorides was also formed by the reactions

$$3K_2TiF_6 + 13Al \rightarrow 3KAlF_4 + K_3AlF_6 + 3Al_3Ti$$

$$K_2TiF_6 + 2C \rightarrow TiC + 2KF + CF_4\uparrow$$

3. Microstructural characterization revealed the in-situ-formed blocky titanium aluminide and particulate titanium carbide. The size of the titanium aluminide was in the micron-size range, and the titanium carbide was in the submicron-size range.
4. The reaction between potassium titanium fluoride and carbon was believed to be the predominant mechanism to synthesize TiC in the new method.

REFERENCES

1. A. Cibula: *J. Inst. Met.*, 1951–1952, vol. 76, pp. 321-60.
2. W. Schneider: *Z. Metallkd./Mater. Res. Adv. Technol.*, 2000, vol. 91, pp. 800-06.
3. A.J. Whitehead, P.S. Cooper, and R.W. McCarthy: *Light Metals: Proc. Sessions*, TMS Annual Meeting, TMS, Warrendale, PA, 1999, pp. 763-72.
4. A. Cibula: *J. Inst. Met.*, 1951–1952, vol. 80 (2), pp. 1-16.
5. W. Thury: *Z. Metallkd.*, 1955, vol. 65, pp. 488-90.
6. F.A. Crossley and L.F. Mondolfo: *Trans. AIME*, 1951, vol. 191, pp. 1143-48.
7. J.A. Marcantonio and L.F. Mondolfo: *Metall. Trans.*, 1971, vol. 2, pp. 465-71.
8. F. Lihl and J. Sagoschen: *Metallurgy*, 1957, vol. 11, pp. 179-89.
9. Y. Nakao: *J. Jpn. Inst. Light Met.*, 1967, vol. 17, pp. 65-75.
10. A. Banerji and W. Reif: U.K. Patent Specification No. 2171723A, 1986, vol. 3, p. 9.
11. A. Banerji and W. Reif: *Metall. Trans. A*, 1986, vol. 17A, pp. 2127-36.
12. A.M. Kanury: *Metall. Trans. A*, 1992, vol. 23A, pp. 2349-56.
13. H.S. Fang, H.T. Ma, B.Q. Zhang, and J.G. Li: China Patent No. 98119377.3, 1998, vol. 9, p. 25.
14. B.Q. Zhang, J.G. Li, H.T. Ma, and H.S. Fang: *Trans. Nonferrous Met. Soc. China*, 2000, vol. 10 (3), pp. 298-303.
15. E.V. Prikhodko: *Steel USSR*, 1990, vol. 20 (10), pp. 471-77.
16. R. Chen, G.H. Wu, and Q.Y. Zhang: *J. Am. Ceram. Soc.*, 2000, vol. 83 (12), pp. 3196-98.
17. O. Knacke, O. Kubaschewski, and K. Hesselmanu: *Thermochemical Properties of Inorganic Substances*, 2nd ed. Springer-Verlag, Berlin, 1991, vol. 1, p. 960.
18. O. Knacke, O. Kubaschewski, and K. Hesselmanu: *Thermochemical Properties of Inorganic Substances*, 2nd ed., Springer-Verlag, Berlin 1991, vol. 2., p. 2065.
19. B.Q. Zhang, H.S. Fang, L. Lu, and M.O. Lai: *Proc. 2002 TMS Annual Meeting and Exhibition*, Seattle, WA, Feb. 17–21, 2002, F.H. (Sam) Froes, E. Chen, R.R. Boyer, E.M. Taleff, L. Lu, D.L. Zhang, C.M. Ward-Close, and D. Eliezer, eds., TMS, Warrendale, PA, 2002, pp. 193-201.