Aluminothermal reaction to prepare Al-Ti-C master alloy[①]

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Abstract: An investigation was carried out on the reaction process and mechanism between K_2TiF_6, graphite powder and aluminum melt with the common Ti concentration of 5% ~ 7% in the grain-refiner Al-Ti-C master alloys and the reaction temperature of 750~ 950 ℃, aiming at understanding their reaction mechanism and putting forward the aluminothermal reduction reaction method to practical use. During experimental investigation, K_2TiF_6 and graphite wrapped in aluminum foils were introduced into the aluminum melt at 850 ℃. Samples of alloy and slag were investigated by chemical analysis, XRD examination, SEM observation, and EDS analysis as well. It was found that the reaction was very vigorous at the beginning of the process and then reached a dynamic equilibrium. There were 3 particular reactions during the aluminothermal reaction process. At the beginning stage of the reaction, there emerged the phases of TiC and one type of metastable intermetallic phase $TiAl_9$ as well as $TiAl_3$ in aluminum melt. At the late stage of the reaction, the metastable phase $TiAl_9$ disappeared and another phase of Al_4C_3 emerged.

Key words: Al-Ti-C master alloys; aluminothermal reaction; reaction mechanism; K_2TiF_6　　　　**Document code: A**

1 INTRODUCTION

Since aluminothermal reaction was put forward to prepare Al-Ti master alloy in 1958[1], it has been widely used to produce Al-Ti master alloy through the reaction between Ti-containing fluoride salts such as potassium titanium fluoride, K_2TiF_6, and aluminum melt, and was later adapted successfully to produce Al-Ti-B master alloy[2~ 7]. However, hitherto little work has been done in the production of Al-Ti-C master alloy through this kind of reaction, not to say its practical use[8, 9]. It is well known that second phase particles such as $TiAl_3$ formed in the reaction between K_2TiF_6 and aluminum melt have a strong influence on the refining efficiency of the Al-Ti based master alloys[3~ 7, 10, 11]. Reaction temperature and reaction time directly influence the microstructure of the master alloys, especially the morphology of the $TiAl_3$ phase[4, 6, 11]. The exact reaction mechanism between molten aluminum and Ti-containing fluoride salts is not reported in literature. The exact process of master alloy preparation by this salt route is only available in the patents[12~ 15]. Lately, Prasad *et al*[16] pointed out that K_2TiF_6 only reacts with aluminum above the melting point of aluminum, but no further investigation was made on the exact mechanism.

Aluminothermal reaction is usually carried out at a suitable temperature from 660 ℃ to 1 800 ℃, depending on the Ti concentration in the master alloys. In the present work, an investigation was made on the reaction process and mechanism between K_2TiF_6, graphite powder and aluminum with the common Ti concentration of 5% ~ 7% in the grain-refiner Al-Ti-C master alloys and the reaction temperature of 750~ 950 ℃ for aluminothermal reaction in practical use.

2 EXPERIMENTAL

200 g high pure aluminum (> 99. 99%) was melted at 850 ℃ using Al_2O_3 crucible. 60 g K_2TiF_6 and 0. 6 g graphite wrapped in aluminum foils were introduced into the aluminum melt. Samples of slag and alloy were obtained at different processing times. The compositions of the samples were determined using normal chemical analysis method. XRD and SEM equipped with EDS were performed to examine the phases and microstructures in the samples and to determine the compositions of second phases in the alloy samples.

3 RESULTS

Vigorous reactions were found after K_2TiF_6 and graphite powders were introduced into aluminum melt. The added reactants turned to be black melt (it is termed as slag) very quickly, then changed white as the reaction proceeded. The process was exothermal, which caused about 20 ℃ rise in the melt. Similar phenomenon was reported in Ref. [13].

XRD analysis of the slag (Fig. 1) showed that phase ingredients changed a lot within a very short period of time (1 min) after the reaction began, including:

1) Very strong characteristic diffraction peaks of $KAlF_4$ and K_3AlF_6 as well as some peaks of KF and
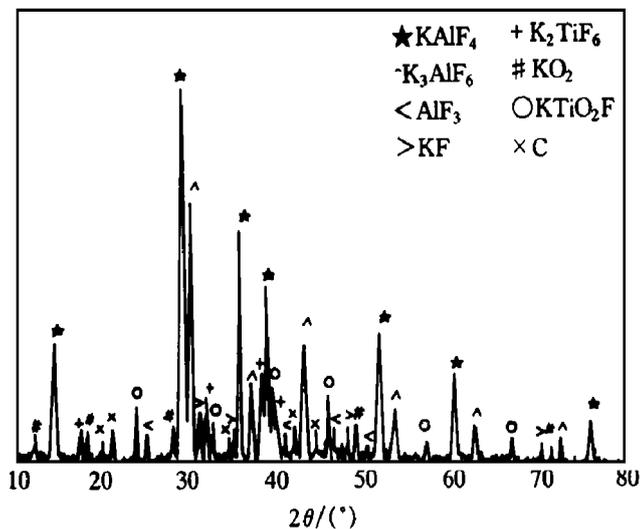
Fig. 1 X-ray diffraction pattern of slag

AlF_3 were measured, while peaks of K_2TiF_6 were rather weak;

2) Oxides of $KTiO_2F$ and K_2O were found;

3) Graphite carbon was found in slag.

The composition analyses (Fig. 2) show that compositions in slag and alloy melts changed remarkably soon after the reaction began. Within 1 min, Ti
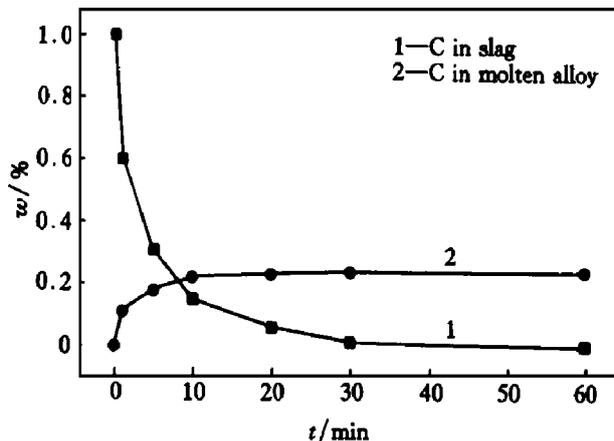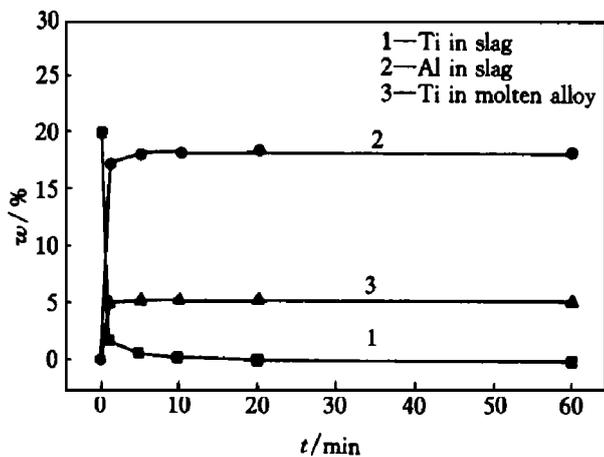
content decreased from 19.95% in K_2TiF_6 to 1.98% in slag, while Al content rose to 17.01%. At the same time, Ti content in alloy melt rose to 4.92%. Carbon content in slag decreased substantially at the beginning stage of the reaction. When the process went on, compositions in the slag and alloy melts changed more and more slowly. Contents of Ti and Al in slag kept constant at 0.15% and 18.38% respectively after 20 min and carbon was consumed up after 30 min. Contents of Ti and C in alloy melt changed correspondingly with final constant values of 5.48% and 0.24%.

XRD analyses of alloy samples (Fig. 3) show that there are TiC, $TiAl_3$, Al and several uncertain diffraction peaks at the beginning stage of the reaction. At the late stage, the uncertain diffraction peaks disappear and some weak peaks of Al_4C_3 emerge coexisting with peaks of TiC, $TiAl_3$ and Al.

Through SEM observation, two types of block-like particles were found in alloys at the beginning stage of the reaction. A small amount of the particles have a size of more than dozens of microns. Most of the particles are small with a size below 10 μm (Fig. 4(a)). There also exist some particulate agglomerates composed of fine particulates less than

Fig. 2 Curves of compositions in slag and alloy melts against reaction time

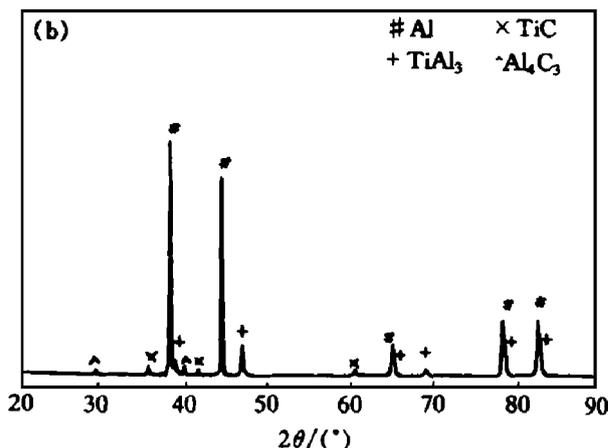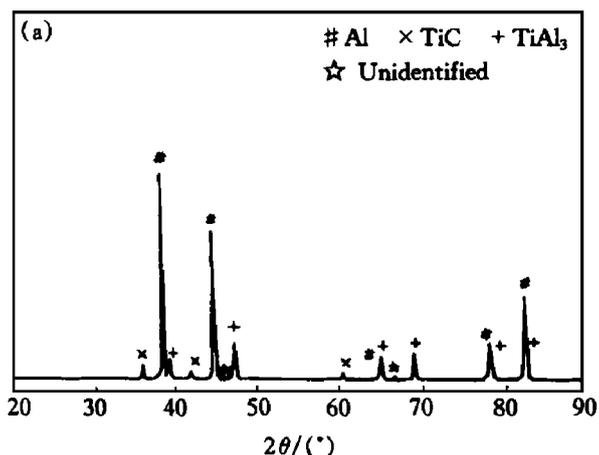**Fig. 3** X-ray diffraction patterns of alloys
(a) —At beginning stage of reaction; (b) —At late stage of reaction

1 μm (Fig. 4(b)). At the late stage, the large size block-like particles disappear and the number of fine particulates increases (Fig. 4(c)). In addition, EDS combined with the above XRD analyses (Fig. 5) show that at the beginning stage of the reaction, the small size and large size block-like particles are $TiAl_3$ and $TiAl_9$ respectively, while the fine particulates are TiC. At the late stage, a small amount of Al_4C_3 particles are detected in the alloy samples.

4 DISCUSSION

4.1 Aluminothermal reducing reaction

It was reported[16] that K_2TiF_6 didn't dissociate when it was heated up to 800 ℃ under the atmosphere of Ar. Adamkovicova[17] also didn't observe the dissociation of K_2TiF_6 even at its melting point of 899 ℃ when determining the fusion heat of K_2TiF_6. It is reasonably supposed that under the present experimental conditions, K_2TiF_6 would react with aluminum melt in its solid state without any dissociation and fusion when it was added into aluminum melt together with graphite powder.

The reaction phenomenon and the composition analysis of slag and alloys show that K_2TiF_6 reacts with aluminum vigorously, by which most of the Ti in K_2TiF_6 (about 90%) is reduced by Al. The strong characteristic diffraction peaks of $KAlF_4$ and
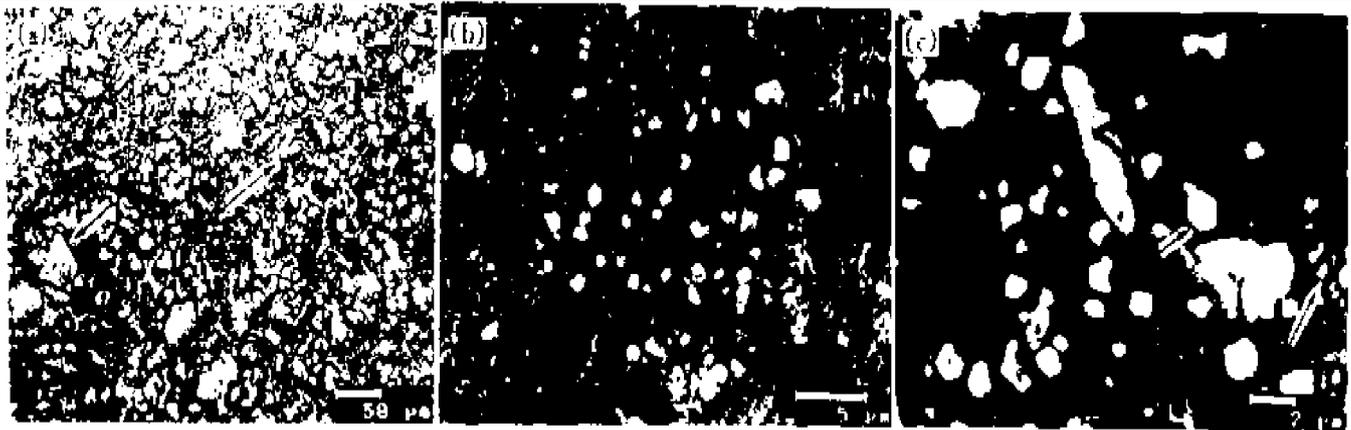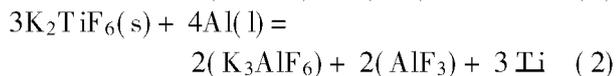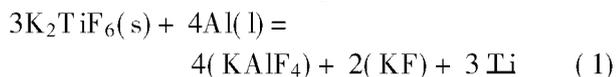

Fig. 4   M icrostructures of alloy (SEM)
(a) —At beginning stage of reaction;   (b) —Particle agglomerates of TiC;   (c) —At late stage of reaction
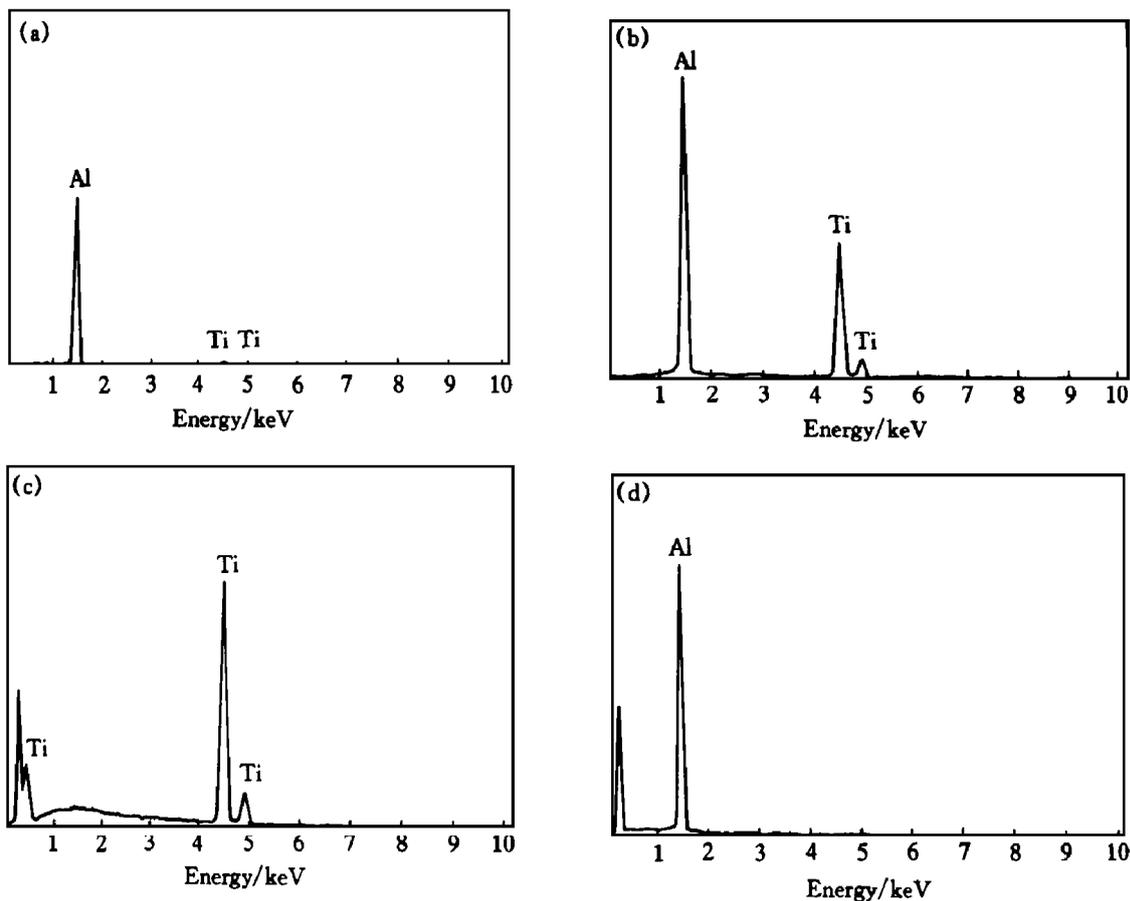
Fig. 5   EDS analyses of second phases in alloys
(a) —Particle 1 in Fig. 4(a);   (b) —Particle 2 in Fig. 4(a);   (c) —Particle 1 in Fig. 4(c);   (d) —Particle 2 in Fig. 4(c)

K_3AlF_6 and the existence of KF and AlF_3 in slag suggests the reactions between K_2TiF_6 and Al as follows:

$$3K_2TiF_6(s) + 4Al(l) =$$
$$4(KAlF_4) + 2(KF) + 3\underline{Ti} \qquad (1)$$
$$3K_2TiF_6(s) + 4Al(l) =$$
$$2(K_3AlF_6) + 2(AlF_3) + 3\underline{Ti} \qquad (2)$$

The existence of K_2O in slag shows the existence of the following reaction:

$$(K_2TiF_6) + 2Al(l) = 2(AlF_3) + 2K + \underline{Ti} \qquad (3)$$

The reduced K in reaction (3) is then oxidized to K_2O.

It was reported in Ref. [1] that the reaction between K_2TiF_6 and Al proceeded by the former two particular reactions. However, Thury[9] reported the probability of reaction (3). In the present work, the above three particular reactions are found to coexist, among which the former two are predominant.

The oxides in slag may be introduced by two means, oxidized by oxygen in atmosphere or by the moisture in the salts and graphite powder[16].

4. 2　Titanium aluminides

$TiAl_3$ is the only intermetallic phase in Al-Ti master alloy grain refiners produced through the aluminothermal reaction between K_2TiF_6 and Al[1, 9, 16, 18]. In the present work, another intermetallic phase of $TiAl_9$ was detected in the alloy melt at the beginning stage of aluminothermal reaction. It was stated in some thermodynamic literatures[19,20] that there are totally five stable intermetallic phases in Al-Ti binary system, namely, Ti_3Al, $TiAl$, $TiAl_2$, Ti_2Al_5 and $TiAl_3$. So $TiAl_9$ should be a metastable phase, which dissolves and disappears because of the homogenization of the alloy melt at the late stage of the process.

The reaction of K_2TiF_6 with molten Al releases Ti which dissolves into the Al melt. When the solubility limit of Ti in liquid aluminum at the reaction temperature is exceeded, $TiAl_3$ precipitates as follows[16]:

$$\underline{Ti} + 3Al(l) = TiAl_3(s) \qquad (4)$$

4. 3　Reaction of graphite and its products

For its good wettability with slag[18] but bad wettability with aluminum melt, graphite powders will disperse in slag melt. At the beginning stage of the aluminothermal reaction, the content of graphite in slag decreased remarkably, then decreased more and more slowly until it was consumed up after about 30 min. Graphite powders may be consumed by the following two ways:

$$C(s) + Ti = TiC(s) \qquad (5)$$
$$C(s) + \underline{Ti} = TiC(s) \qquad (6)$$

where　Ti means the just reduced atomic titanium through reactions of (1), (2) and (3). $\underline{Ti}$ means so-

lute titanium in alloy melt. At the beginning stage of the aluminothermal reaction, some just reduced atomic titanium dissolves in aluminum melt to be solute titanium or reacts with Al to form intermetallic phases, the other atomic titanium reacts directly with graphite particles to form TiC particles as reaction (5) describes. Reaction (5) may be vigorous because of the high reactivity of the newly reduced atomic titanium, and it may also be of short duration for the short duration of reaction between K_2TiF_6 and aluminum. During a short period of time (1 min), graphite in slag were consumed remarkably to form TiC particulate in alloy melts. At the late stage, reaction (6) played a more and more important role in the formation of TiC particulate. Because the reactivity of solute titanium is much weaker than those newly reduced from salts, reaction (6) is relatively slow, which explains the slow consumption rate of graphite at the late stage of the aluminothermal reaction.

At the beginning stage of the aluminothermal reaction, TiC particulate formed, then a small amount of Al_4C_3 particles emerged at the late stage. It was stated that the latter is more stable than the former in Al-Ti-C ternary system[21~23]. But some researchers found that TiC forms when graphite reacts with Al-Ti melt at the temperatures below 1 273 K. Banerji[24] found that TiC particulate forms first when graphite is added into Al-Ti melt, then Al_4C_3 and/or Ti_3AlC may form. In the present work, no Ti_3AlC was found but a small amount of Al_4C_3 particles was detected at the late stage of the reaction.
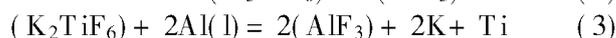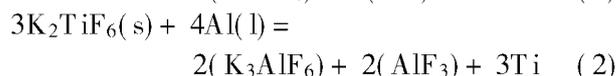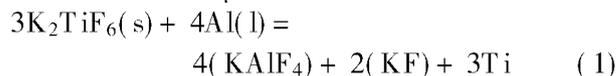
4. 4　Reaction equilibrium

The aluminothermal reaction was vigorous at the beginning stage, then slowed down quickly. The reaction reached dynamic equilibrium with the content of Ti and Al in slag keeping constant after about 20 min. K_2TiF_6 was detected in molten slag of KF-AlF_3 when the slag coexisted with Al-Ti melt[18], which supports the existence of equilibrium state for the aluminothermal reaction. Under the present conditions, the equilibrium contents of Ti and Al in slag are 0. 15% and 18. 38% respectively.

5　CONCLUSIONS

1) The reaction is very vigorous at the beginning stage of the process, then reached a dynamic equilibrium.

2) There are 3 particular reactions in the aluminothermal reaction process as follows:

$$3K_2TiF_6(s) + 4Al(l) =$$
$$4(KAlF_4) + 2(KF) + 3Ti \qquad (1)$$
$$3K_2TiF_6(s) + 4Al(l) =$$
$$2(K_3AlF_6) + 2(AlF_3) + 3Ti \qquad (2)$$
$$(K_2TiF_6) + 2Al(l) = 2(AlF_3) + 2K + Ti \qquad (3)$$

Among them, reactions (1) and (2) are predominant.

3) At the beginning stage of the reaction, TiC and one type of metastable intermetallic phase $TiAl_9$ as well as $TiAl_3$ form in the aluminum melts. At the late stage of the reaction, the metastable phase $TiAl_9$ disappears and another phase Al_4C_3 form.

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