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DEVELOPMENT OF Al-Ti-C GRAIN REFINING MASTER ALLOY USING Ti-BEARING SALTS

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Al-Ti-C grain refining master alloys have been successfully prepared by the reaction of K_2TiF_6 and graphite with molten aluminium under different conditions. The produced Al-Ti-C master alloys contain TiC and $TiAl_3$ particles in the aluminium matrix. The wettability of graphite particles in the molten aluminium have been improved in this technique and the incorporated carbon reacts with the dissolved of Ti to produce TiC particle. Also, $TiAl_3$ dissolved with time and temperature and reacted with carbon to form TiC particles. The Ti content in the produced Al-Ti-C master alloys varied with the different conditions of the production process. The most proper conditions of the process to obtain a good percentage of Ti in the produced Al-Ti-C master alloy are: (710-750^oC), (5 min.)and (0.25) for temperature, time and K_2TiF_6 / Al weight ratio respectively.

KEYWORDS: *Grain refinement of aluminium, Al-Ti-C master alloy, TiC particles and K_2TiF_6.*

INTRODUCTION

Grain refinement of aluminium and its alloys is now a common industrial practice [1]. The need to develop efficient grain refiners is growing. The Al-Ti-B master alloys as grain refiners are very popular due to their high grain refining efficiency, but they suffer from agglomeration of borides, defects during subsequent forming operations and poisoning by certain elements like Zr and Cr [2-4]. This offers a strong incentive for developing Al-Ti-C master alloy as grain refiner [5-8].

Al-Ti-C master alloys have been prepared by several methods, one of which is the reaction of molten aluminium with K_2TiF_6 and graphite powder [9-11]. The other methods include the reaction between carbon and Al-Ti binary alloy melt [6,8] and the reaction between high purity titanium powder, carbon powder and aluminium powder compacted together and roasted by an ignition furnace [12]. Investigations of all methods involving aluminium melt revealed the formation of $TiAl_3$ along with TiC particles. The Al-Ti-C master alloy containing only TiC particles was found to be the most efficient grain refiner [13].

This work is concerned with the development of Al-Ti-C master alloys as grain refiners by reaction of K_2TiF_6 salt and graphite powder with molten aluminium. The different factors affecting the preparation of the Al-Ti-C master alloy and the content of Ti in the master alloys are investigated.

EXPERIMENTAL

The production of Al-Ti-C master alloys using K_2TiF_6 and graphite powder about 20μm, as a source of titanium and carbon respectively, with molten aluminium were carried out in the laboratory. Appropriate quantity of aluminum (99.7% purity) were placed into a silicon carbide crucible, and then melted in a muffle furnace at the required temperature. Predetermined quantities of potassium fluotitanate (K_2TiF_6) and graphite were mixed, compacted together and added to the molten aluminium at designated ratios. The added compacted mixture was stirred manually within the molten aluminium using a graphite rod. After a certain time, the crucible containing the molten alloy and slag was taken out of the furnace to separate the slag from the melt, and then the molten alloy was poured into a steel mold (30mm diameter and 25mm depth). The produced alloys were analyzed chemically using Induction Coupled Plasma instrument (ICP) to determine the content of titanium. The carbon content was determined using an automatic combustion apparatus, where the sample is combusted in a stream of oxygen, and then the carbon of specimen is converted to CO_2. The produced Al-Ti-C master alloys were characterized by X-Ray Diffraction (XRD) analysis using X-ray diffractometer (model D5000) with Ni-filtered Cu-K_β radiation (λ=1.5408A), Optical Microscopy (BHM 313B) up to 1000X magnifications and Scanning Electron Microscopy (SEM) (JSM-S410 model Jeol, Japan) to identify the phases and microstructure**.**

Three sets of experiments were carried out under different conditions of addition rate, temperature, and reaction time that affect the composition and microstructure of Al-Ti-C master alloys.

RESULTS AND DISCUSSION

● Characterization of the produced Al-Ti-C master alloy

Al-Ti-C master alloys were prepared with different contents of titanium and carbon by adding the compacted mixture of K_2TiF_6 and graphite into the molten aluminium at different conditions. The microstructure characterizations of the produced Al-Ti-C master alloys using optical microscopy and scanning electron microscopy are shown in Figures 1 and 2 respectively. The photomicrographs of the produced Al-Ti-C master alloys exhibit a blocky-like particles of $TiAl_3$ with size about 20-40μm at the grain centers of α-Al grains and aggregates of submicron particles of TiC are present at the grain boundaries.

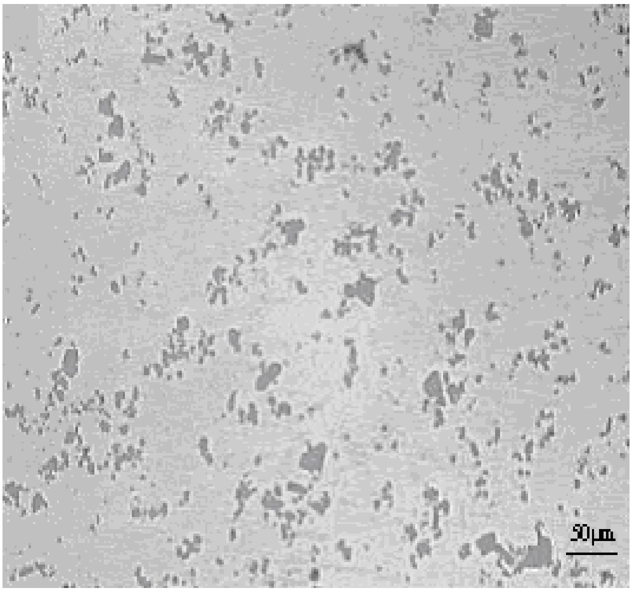


Fig. 1. Optical photomicrograph of the produced Al-4.3Ti-0.55C master alloy at 800^{o}C

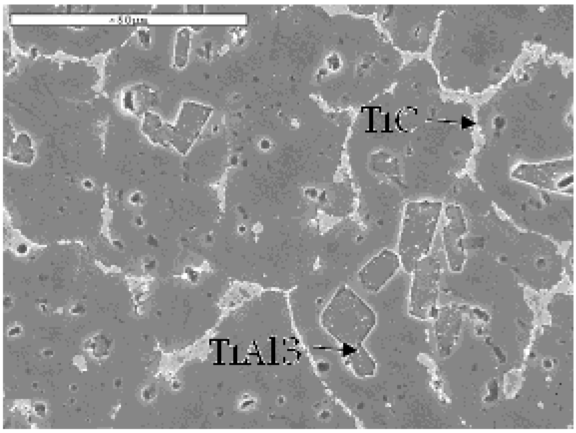
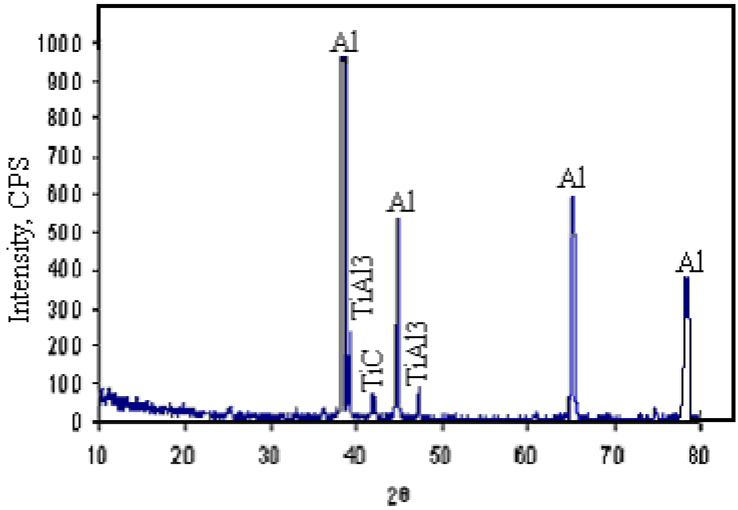
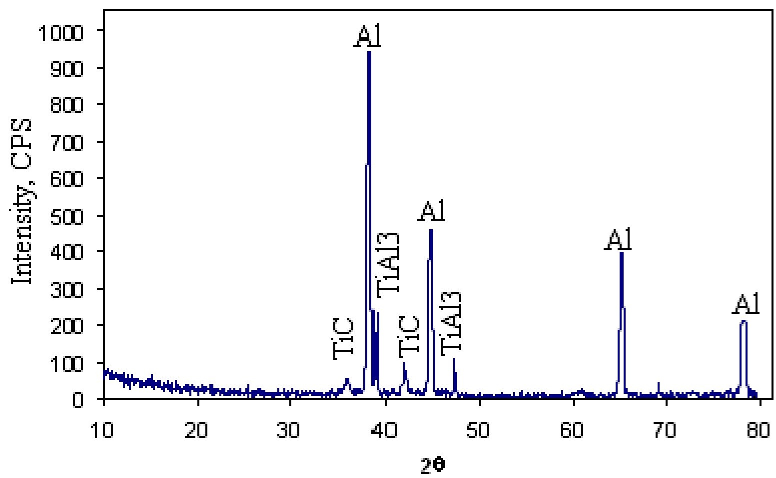


Fig. 2. SEM photomicrograph of the produced Al-4.5Ti-0.6C master alloy at 1000^{o}C

The microstructure results were confirmed by XRD analyses, which revealed $TiAl_3$ and TiC reflections in addition to those of the aluminium matrix, as shown in Figure 3 (a) and (b).



(a) Al-4.5Ti-0.6C, at 1000°C



(b) Al-4.5Ti-0.7C, at 1000°C

Fig. 3. XRD analysis of the produced Al-Ti-C master alloys

• TiC Formation

A vigorous exothermic reaction occurred with heat release as soon as the addition of the compacted mixture of K_2TiF_6 and graphite to the molten aluminium takes place, then disappeared after a little time. During the reaction, the Ti was reduced from K_2TiF_6 and reacted with the molten aluminium and graphite to give $TiAl_3$ and TiC in the aluminum matrix. In addition, the slag was formed through this reaction and composed essentially of $KAlF_4$ and K_3AlF_6 according to the following reactions.

$$3K_2TiF_6 + 13Al \rightarrow 3KAlF_4 + K_3AlF_6 + 3TiAl_3 \quad (1)$$

$$K_2TiF_6 + 5C \rightarrow TiC + 2KF + 4CF\uparrow \quad (2)$$

Figure 4 illustrates an analysis of slag sample by XRD analysis. This analysis is agreed with that mentioned in literature [10].

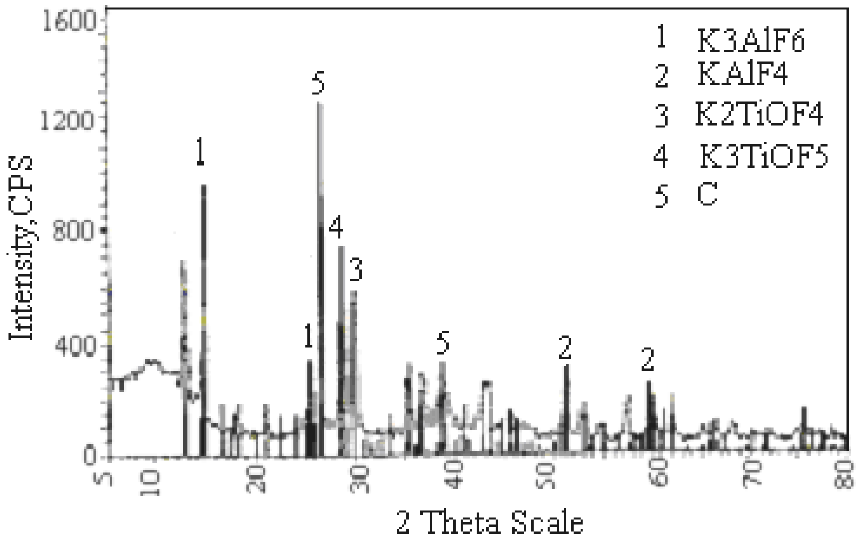


Fig. 4. XRD analysis of slag sample, at 1000°C and 20min

The optical photomicrographs shown in Figure 5 of the produced Al-Ti-C master alloys at various temperatures (800, 850, 900 and 1000 ºC) indicate that TiC particles increase with increasing of temperature, since TiC is more stable with respect to $TiAl_3$ in the higher temperature ranges. Also, the SEM photomicrographs shown in Figure 6 indicate that there are some changes that appear in the colour on the boundaries and on the surface of $TiAl_3$ particles. This change in the colour prone to the colour of TiC particles and $TiAl_3$ phase decrease with increasing of time. It can be said that, TiC may form also by the reaction between $TiAl_3$ and graphite particles according to the following reaction.

$$TiAl_3 + C \rightarrow TiC + 3Al \quad (3)$$

These results are in good agreement with other findings [10,11], that the halide salt plays a key role in the TiC formation. The soluble Ti reacts with the carbon to produce TiC particles owing to the improvement of the wettability of graphite particles and aluminium. The improved incorporation of the graphite particles linked with $KAlF_4$ and K_3AlF_6 compounds, which are generated through the slag formation, is due to the cleaning of the particles surface and removal of the oxide layer from the surface of the melt by such compounds [11].

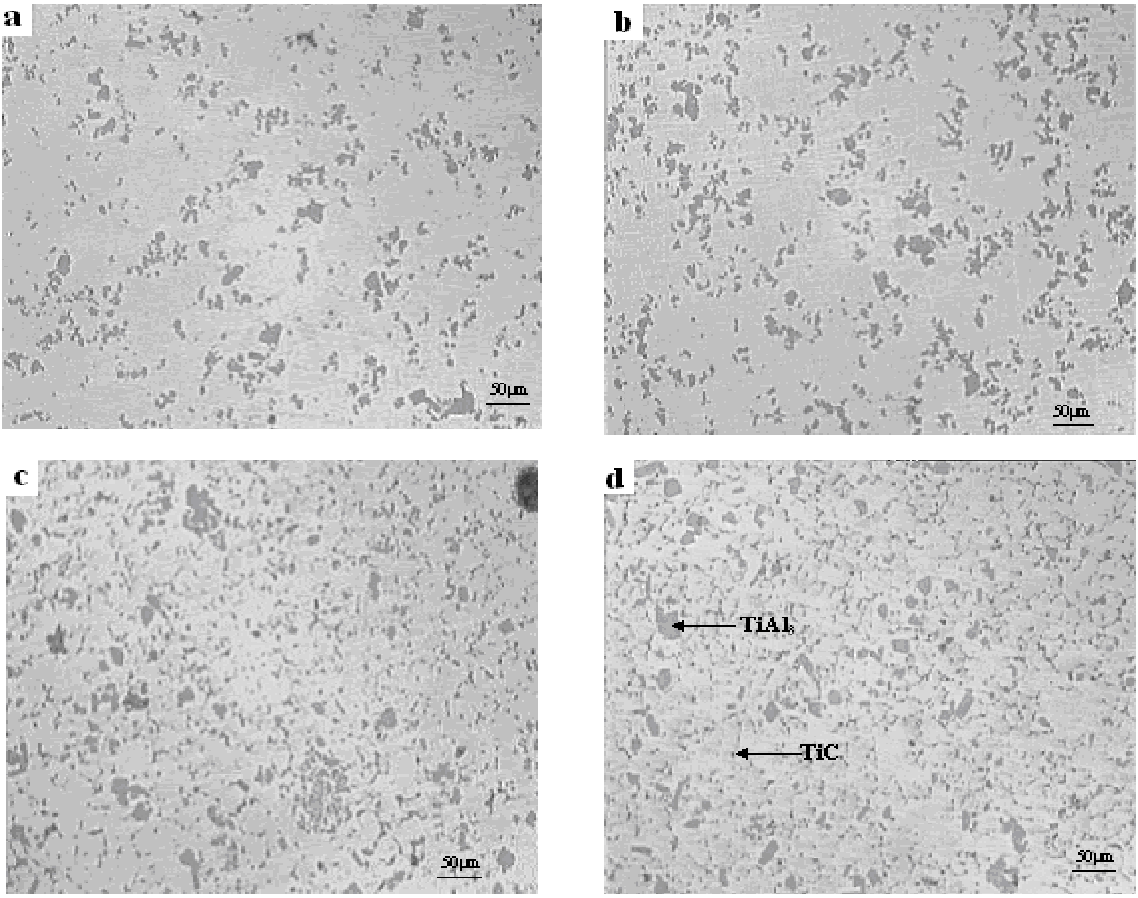


Fig. 5. Optical photomicrographs of the produced Al-Ti-C master alloys at 20 min and various temperatures.
a) Al-4.3Ti-0.55C, at 800 ºC b) Al-4Ti-0.58C, at 850 ºC
c) Al-4Ti-0.53C, at 900 ºC d) Al-4Ti-0.5C, at 1000 ºC

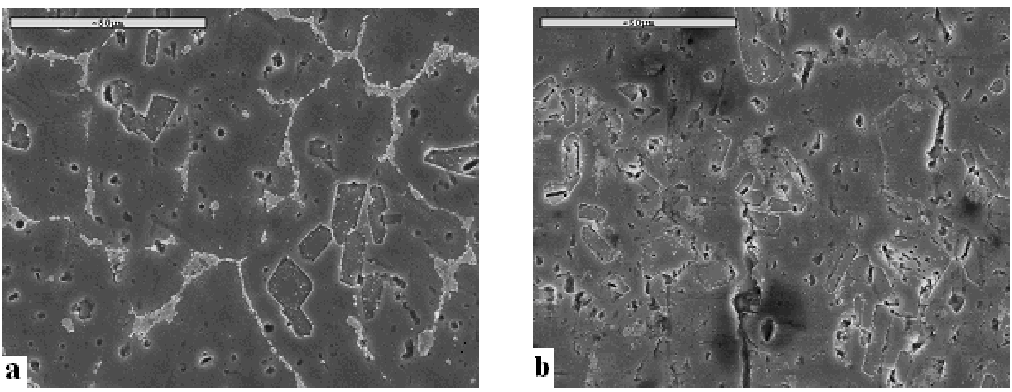


Fig. 6. SEM photomicrographs of the produced Al-Ti-C master alloys at 1000 ºC and different reaction times.
a) 10 min b) 20 min

• Effect of K_2TiF_6/Al weight ratio (R)

The first group of experiments was carried out to investigate the effect of K_2TiF_6/Al weight ratio on the recovery of titanium in the produced Al-Ti-C master alloys. These experiments were carried out at various weight ratios of 0.125, 0.15, 0.175, 0.2, 0.225 and 0.25 at constant reaction temperature of 1000 ºC, reaction time 20 minutes and graphite/Al weight ratio (R_1) 0.01. Figure 7 indicates the relationship between the content of titanium in the produced Al-Ti-C master alloys versus K_2TiF_6/Al weight ratio. It can be seen that the content of Ti in the produced Al-Ti-C master alloys increases linearly with increasing of K_2TiF_6/Al weight ratio. This may be attributed to the increase of the amount of K_2TiF_6 in relation to the amount of molten aluminium, which increases the chance for a large amount of titanium to dissolve in the molten alloy.

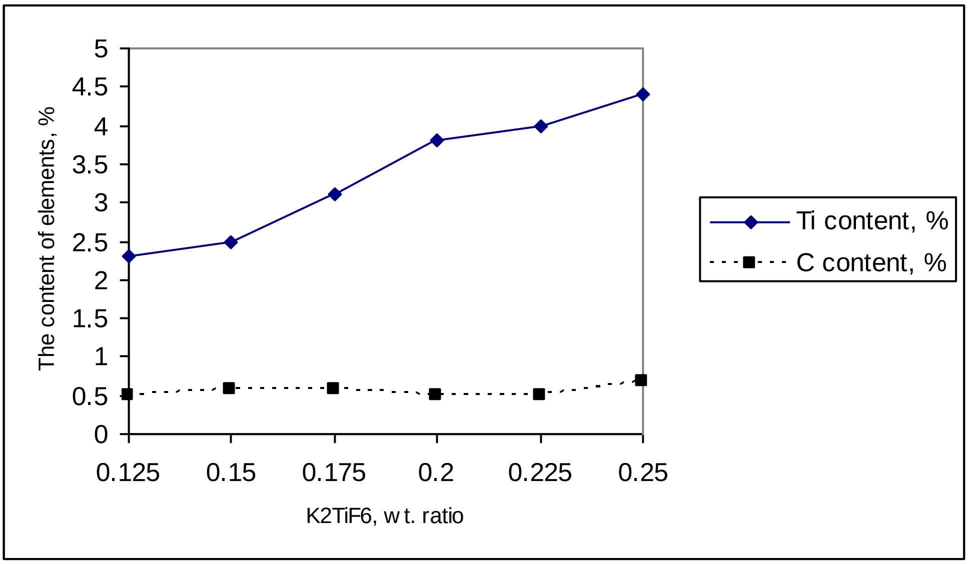


Fig. 7. The relationship between the K_2TiF_6/Al weight ratio and the content of Ti and C in Al-Ti-C master alloys at constant temp. = 1000 ºC, time = 20 min and R_1= 0.01.

• Effect of Reaction Time

The second group of experiments was carried out to investigate the effect of reaction time on the content of titanium in the produced Al-Ti-C master alloys. These experiments were carried out at various reaction times, ranging from 1 to 30 min, at constant reaction temperature of 1000 ºC, K_2TiF_6/Al weight ratio of 0.25 and graphite/Al weight ratio of 0.01. Figure 8 shows the relationship between the content of titanium in the produced Al-Ti-C master alloy versus reaction time. It was found that the content of titanium in the master alloys sharply increased in the first minute of the reaction, and then increasing rate slowed down and then becomes essentially constant. Thermal release was observed at the start of the process, and then disappeared after a little time. It indicates that, as soon as the compacted mixture of

K_2TiF_6 and graphite is immersed in the molten aluminium, with the help of mild stirring, the dissolution of titanium into the molten aluminium started with a vigorous exothermic reaction between K_2TiF_6 and the molten aluminium to reach a maximum value, and then stopped with the time according to the reaction (1).

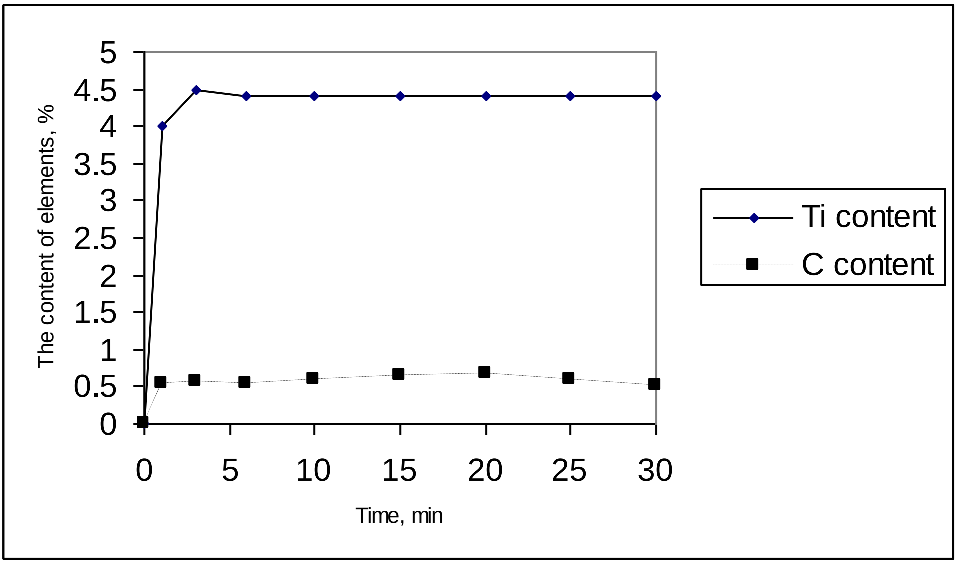


Fig. 8. The relationship between the reaction time and the content of Ti and C in Al-Ti-C master alloys at constant temp. = 1000 ºC, R= 0.25 and R_1= 0.01.

• Effect of Reaction Temperature

The third group of experiments was carried out to investigate the effect of reaction temperature on the content of Ti in the produced Al-Ti-C master alloys. These experiments were carried out at various reaction temperatures of 710, 730, 750, 780, 800, 850, 900 and 1000 ºC at constant K_2TiF_6/Al weight ratio of 0.225, reaction time 20 min and graphite/Al weight ratio 0.01. Figure 9 shows the content of Ti in the produced Al-Ti-C master alloys as a function of reaction temperature. The data indicate a decrease in the content of Ti in the produced Al-Ti-C master alloys with increasing of bath temperature from 710 ºC to 850 ºC and then approximates to a constant value. The increase of temperature favours the formation of K_3TiOF_5 and K_2TiOF_4 compounds that were revealed in the XRD analysis of slag as shown in Figure 4 and these compounds are difficult to reduce and go to the upper layer of slag [10].

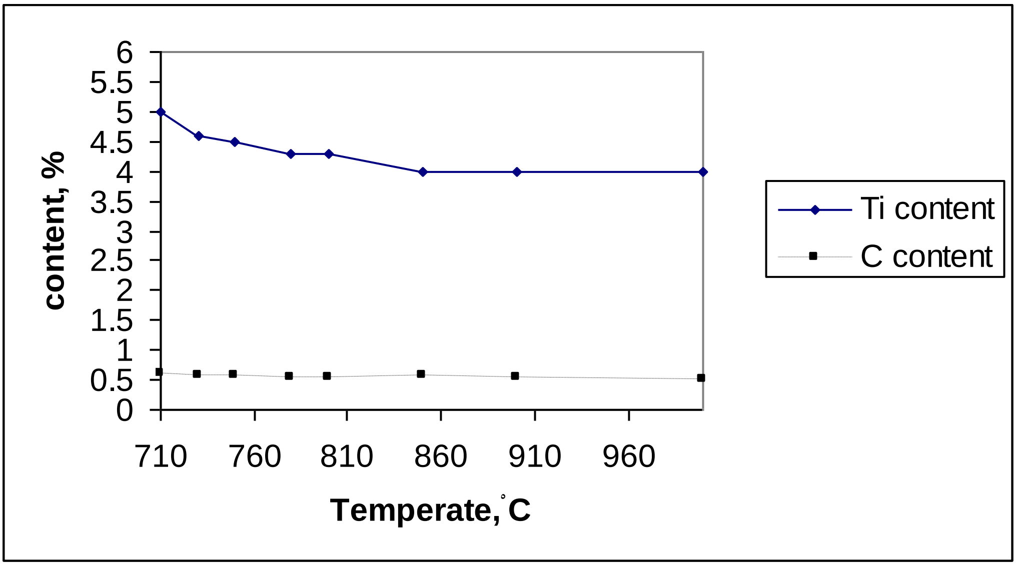


Fig. 9. The relationship between the reaction temperature and the content of Ti and C in the Al-Ti-C master alloys at constant time = 20min, R= 0.225 and R_1= 0.01.

CONCLUSIONS

- The Ti-bearing salt is used successfully in obtaining Al-Ti-C master alloys for grain refining of aluminium and its alloys.
- TiC particles form through the reaction between $TiAl_3$ and carbon and the rate of this reaction increases with increasing of time and temperature of the process.
- The most proper conditions of the process to obtain a good percentage of Ti in the produced Al - Ti -C master alloy are: (710-750 ºC), (5 min) and (0.25) for temperature, time and K_2TiF_6/Al weight ratio respectively.

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إنتاج السبيكة الأساسية الألومينوم ـ تيتانيوم ـ كربون المدققة للحبيبات باستخدام أملاح التيتانيوم

تعد عملية تدقيق الحبيبات من أهم العمليات في صناعة الألومينوم . وتعتبر الوظيفة الأساسية لعملية تدقيق حبيبات الألومينوم هي التحكم في حجم وشكل الحبيبات أثناء عمليات التشكيل المختلفة مثل عملية البصق والدرفلة. وبهذا يتم الحصول على خواص تشغيلية وميكانيكية أفضل للألمونيوم وسبائكه المختلفة. ونظراً لحاجة صناعة الألومينوم الماسة لعملية تدقيق الحبيبات أجريت أبحاث متعددة للحصول على أنواع مختلفة من المدققات ، بداية من استخدام عنصر التيتانيوم أو سبائك اللألومينوم الأساسية التي تحتوي على التيتانيوم أو التيتانيوم والبورون أو التيتانيوم والكربون للحصول على نويات تعمل على تجمد حبيبات اللألومينوم.

تعتبر السبائك الأساسية (اللألومينوم ـ تيتانيوم ـ بورون) كمدقق لحبيبات اللألومينوم هي الأكثر استخداما في السنوات السابقة والتي تحتوي على ثان ببوريد التيتانيوم ، إلا أن حبيبات ثاني بوريد التيتانيوم تميل إلى تكوين تجمعات تعمل على فقد الكفاءة في عملية تدقيق حبيبات اللألومينوم ، بالإضافة إلى إحداث خدوش في ماكينات التشغيل حيث أن صلادة هذه التجمعات عالية ، وأثبتت الأبحاث مؤخراً عدم كفاءة السبائك الأساسية (اللألومينوم ـ تيتانيوم ـ بورون) في تدقيق حبيبات سبائك اللألومينوم التي تحتوي على العناصر مثل الزركونيوم والكروم .

أجريت بعض الأبحاث في العقود الثلاثة الأخيرة لإستخدام السبائك الأساسية (اللألومينوم ـ تيتانيوم ـ كربون) التي تحتوي على حبيبات كربيد التيتانيوم كبديل للسبائك الأساسية (الألومينوم ـ تيتانيوم ـ بورون)حيث أن كربيد التيتانيوم يعمل نفس عمل ثاني بوريد التيتانيوم كنويات لتجمد حبيبات اللألومينوم ، إلا أن حبيبات كربيد التيتانيوم ليس له ميول لتكوين تجمعات تفقد عملية التدقيق كفاءتها مثل ما تؤول إليه حبيبات ثان بوريد التيتانيوم ، ويتضح كذلك أن السبائك الأساسية (اللألومينوم ـ تيتانيوم ـ كربون) تعمل بكفاءة مع سبائك اللألومينوم التي تحتوي على عناصر الزركونيوم والكروم . وتنتج السبائك الأساسية (اللألومينوم ـ تيتانيوم ـ كربون) بعدة طرق ، الطريقة الأولى وهي التقليدية من خلال تفاعل الجرافيت مع مصهور السبيكة الأساسية (اللألومينوم ـ تيتانيوم)، الطريقة الثانية عن طريق كبس وصهر مسحوق

التيتانيوم عالي النقاوة ومسحوق الجرافيت مع مسحوق اللألومنيوم ، والطريقة الثالثة عن طريق إضافة خليط من أملاح التيتانيوم والجرافيت إلى مصهور اللألومينوم عند درجة حرارة معينة .

وقد تم في هذا البحث دراسة طريقة إنتاج السبكة الأساسية (اللألومينوم ـ تيتانيوم ـ كربون) عن طريق إضافة خليط من فلوريد التيتانيوم والبوتاسيوم مع الجرافيت إلى مصهور اللألومينوم عند الظروف المختلفه من درجات حرارة وزمن التفاعل ونسب الإضافة . وكذلك تم دراسة سلوك التيتانيوم في السبائك الأساسية المنتجة (اللألومينوم ـ تيتانيوم ـ كربون) مع تغيير ظروف عملية الإنتاج . وقد تم التوصل في هذا البحث إلى إنتاج السبائك الأساسية (اللألومينوم ـ تيتانيوم ـ كربون) محتوية على كربيد التيتانيوم . حيث تلعب المكونات الأساسية للخبث المتكون أثناء عملية الإضافة وهي KAlF4 , K3AlF6 دوراً كبيراً في تحسين إبتلال حبيبات الكربون داخل المصهور ، حيث تعمل على تنظيف الحبيبات وإزالة الأكاسيد من على سطح حبيبات اللألومينوم . مما يتيح الفرصة لتفاعل التيتانيوم المذاب مع الكربون المندمج في مصهور اللألومينوم لتكوين حبيبات كربيد التيتانيوم داخل اللألومينوم .