Evaluation of Al-Ti-C Master Alloys as Grain Refiner for Aluminum and Its Alloys

M.A. DOHEIM, A.M. OMRAN, A. ABDEL-GWAD, and G.A. SAYED

Al-Ti-C master alloys have a great potential as efficient grain refiners for aluminum and its alloys. In the present work, the Al-Ti-C master alloys are synthesized *via* a relatively novel technique through the reaction of a compacted mixture of K_2TiF_6 and graphite with molten aluminum. The obtained alloys are examined using scanning electron microscopy (SEM), energy-dispersive spectroscopy, and X-ray diffraction (XRD) methods. The results indicate that the produced Al-Ti-C master alloys contain TiC and $TiAl_3$ particles within the aluminum matrix. Also, these alloys were evaluated using the KBI test mold. The results indicate that the produced Al-Ti-C master alloy is an efficient grain refiner for pure aluminum and its alloys compared with the Al-Ti-B one. The factors affecting the grain refinement of aluminum and its alloys are studied. The proper conditions for evaluating the efficiency of the produced Al-Ti-C master alloy to obtain a minimum grain size are as follows: temperature, 993 K (720 °C); holding time, 2 minutes; and (Ti/Al) weight ratio, 0.01 pct.

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I. INTRODUCTION

THE aluminum industry continues to face a variety of challenges from competing materials, demands of customers for increased quality at reduced cost, and assimilation of new technology. Quality improvements are sought in terms of reduced hot cracking, better fabricability, and freedom from defects in critical products, *e.g.*, foil and aerospace alloys. Therefore, grain refinement is an important process in the aluminum industry to achieve the previous targets.[1,2] The function of grain refinement of aluminum and its alloys is to control the grain size and grain morphology during extrusion of billets and rolling slabs, so that good reproducible processing and mechanical properties can be achieved.[3,4] Several investigations were conducted for the development of different types of grain refiners.[5] Al-Ti-B master alloys for the last many years have been the preferred choice for controlling the as-cast structure (grain size and shape) of aluminum and its alloys.[6] However, they suffer from agglomeration of borides and defects during subsequent forming operations and poisoning by certain elements such as Zr and Cr.[7–9] In the last three decades, Al-Ti-C master alloy as a grain refiner for aluminum and its alloys has been widely investigated to be an acceptable replacement for Al-Ti-B master alloys.[10–15] Al-Ti-C grain refiners based on TiC are less prone to the disadvantages associated with TiB_2, which causes some quality problems in different products.[12,16] The present work aims at evaluating the Al-Ti-C master alloys, produced by the reaction of a compacted mixture of titanium-bearing salts (K_2TiF_6) and graphite with molten aluminum at different conditions, which is a special method of synthesis. The produced alloys are tested as grain refiners for aluminum and its alloys. The efficiency of Al-Ti-C alloys as grain refiners is compared with that of the commercial Al-5Ti-1B ones.

II. EXPERIMENTAL

The present work involves three steps: the preparation of Al-Ti-C master alloy, evaluation of the efficiency of the prepared Al-Ti-C master alloys as grain refiner for aluminum and some of its alloys, and finally comparison of the produced Al-Ti-C master alloy with the common Al-5Ti-1B alloy.

Al-Ti-C master alloy preparation using potassium fluotitanate (K_2TiF_6) and graphite as a source of titanium and carbon, respectively, was carried out in the laboratory according to the following procedure.

An appropriate quantity of aluminum (200 g) in a silicon carbide crucible is placed in a vertical tube furnace at a specified temperature of 973 K to 1273 K (700 °C to 1000 °C). A predetermined quantity of potassium fluotitanate (K_2TiF_6) and graphite was mixed and compacted together, and then added to the molten aluminum with different weight ratios of K_2TiF_6/Al (0.125, 0.15, 0.175, 0.2, 0.225, and 0.25) at a constant weight ratio of graphite/Al (0.01). The compaction is achieved by pressing in a mold at a fixed load. The compacted mixture is stirred manually within the molten

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Table I. Composition of Examined Master Alloys

Master Alloy	Ti Pct	C Pct
A_1	4.4	0.58
A_2	4.4	0.52
A_3	4.4	0.67

aluminum bath using a graphite rod. After a certain time (1 to 30 minutes), 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.

For evaluating the efficiency of the Al-Ti-C master alloy; appropriate quantities of aluminum were charged in a silicon carbide crucible and placed in the furnace. The aluminum was melted at the required temperature, 973 K, 993 K, 1023 K, 1073 K, or 1123 K (700 °C, 720 °C, 750 °C, 800 °C, or 850 °C), and held at this temperature for a predetermined time to ensure the homogeneity of temperature throughout the charge. The crucible was then taken out of the furnace and any oxides on the surface were skimmed off. A predetermined quantity of the prepared Al-Ti-C master alloy at a designated ratio, which is related to the titanium percentage, was added to the molten aluminum and stirred in the melt using a graphite rod for 10 seconds. The crucible was then put back into the furnace to keep the temperature of the melt, being held for the required holding time, and then taken out of the furnace and poured in the KBI ring mold placed on the top of a silica foam block. As soon as the solidification is completed, the solidified sample is quenched in water and dried. The sample was etched for macrostructure examination and then examined microscopically to determine the grain size using the linear intercept method, which is based on the number of grains that intercept with four crossing rays, which were counted using an optical microscope with eye lenses designed to overlay the field with these rays. This method was repeated many times for the same sample surface with the average grain size for the entire sample taken at each location. The samples for microscopic examination were prepared using electrolytic polishing and etching with 0.5 pct HF aqueous solution.

A series of experiments were carried out to investigate the efficiency of the produced Al-Ti-C master alloys.[15] Three produced Al-Ti-C master alloys, A_1, A_2, and A_3 (chemical composition shown in Table I), were examined using a KBI ring mold test for the grain refining of commercial pure aluminum and some of its alloys such as 6063 and 5052.

III. RESULTS AND DISCUSSION

A. *Preparation of the Al-Ti-C Master Alloy*

Figure 1 shows a scanning electron microscopy (SEM) photomicrograph of a representative sample of the produced Al-Ti-C master alloys, which indicates that the alloys contain TiC and $TiAl_3$ particles within the aluminum matrix.[15] The technique is used to prepare the present master alloy through the one-step process, while the traditional technique uses the two-step process. The binary Al-Ti master alloy is first prepared and then the graphite is added to the alloy in a second step to produce the Al-Ti-C master alloy.[17,18] Fluorine salt plays a key role in TiC formation. At the beginning of the reaction, Al_3Ti was formed very quickly, and with time, the Al_3Ti turns to TiC.[19] Also, Figure 2 shows point analysis using energy-dispersive spectroscopy for the same sample at point 1; this figure proved that the phase in point 1 is Al_3Ti, and the results were confirmed with the X-ray diffraction (XRD) pattern, as shown in Figure 3.

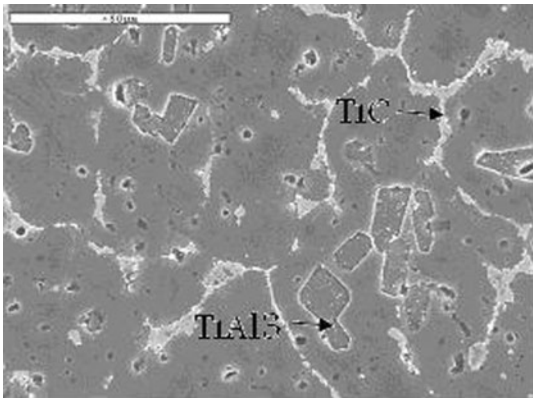

Fig. 1—SEM photomicrograph of Al-4.5Ti-0.6C master alloy.

With regard to the purity of the master alloy and the presence of K and F, it was assumed they are in the slag. However, the master alloy was analyzed using the ES ARL 351 and found to be as follows: Fe = 0.12 pct; Si = 0.2 pct; Ti = 4.1 pct; and K, Ca, Na, and V less than 0.001 pct.

B. *Evaluation of the Al-Ti-C Master Alloy*

Three groups of experiments were carried out to investigate the influencing parameters on the efficiency of the produced Al-Ti-C master alloys as grain refiner.

1. *Effect of addition rate*

The effect of the addition rate of the Al-Ti-C master alloy on the grain refining efficiency of commercially pure aluminum (99.7 pct Al) was studied at different weight ratios of titanium contained in the Al-Ti-C master alloy to the weight of the refined aluminum (R). A series of experiments were conducted using the weight ratio of (0.005, 0.0075, 0.01, 0.0125, and 0.02) pct Ti at constant temperature 993 K (720 °C) and holding time 2 minutes. Figure 4 shows the photomacrographs and the variation of the grain sizes of the commercial pure aluminum (99.7 pct Al) refined with different addition ratios of Al-Ti-C master alloys A_1 and A_2. The difference can be observed between the grain sizes in the refined aluminum compared with the as-cast aluminum without a refiner addition. Figure 5 illustrates the relationship between the addition ratio of the produced Al-Ti-C master alloys A_1 and A_2 *vs* the grain size of the

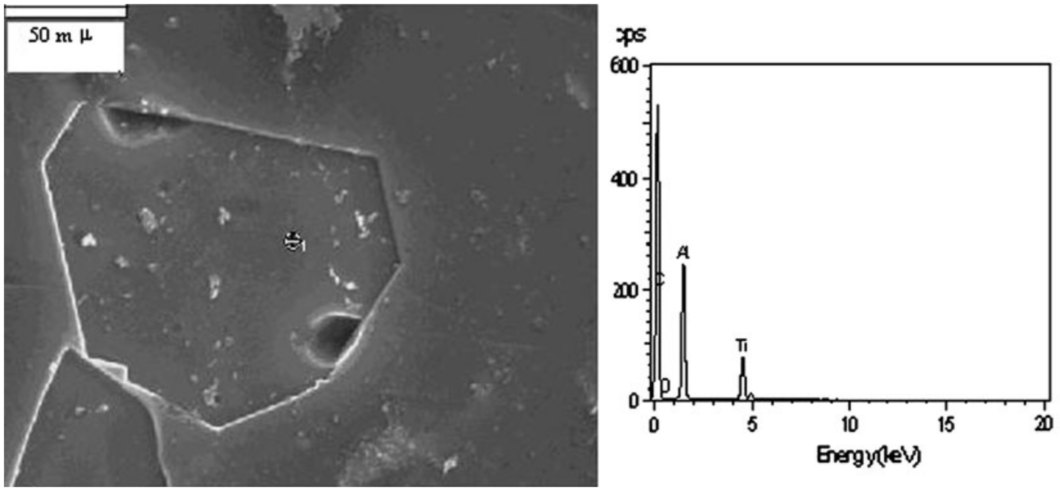

Fig. 2—Point analysis at point 1 for Al-4.5Ti-0.6C master alloy.

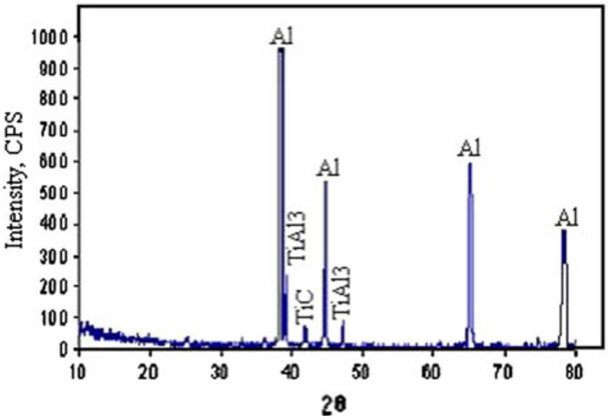

Fig. 3—XRD pattern of Al-4.5Ti-0.6C master alloy.

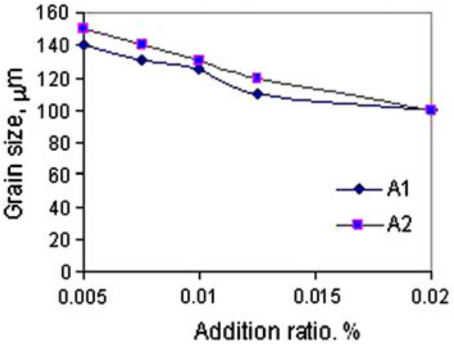

Fig. 5—Relationship between the grain size of the commercially pure aluminum refined with A_1 and A_2 master alloys at different Ti weight ratios.

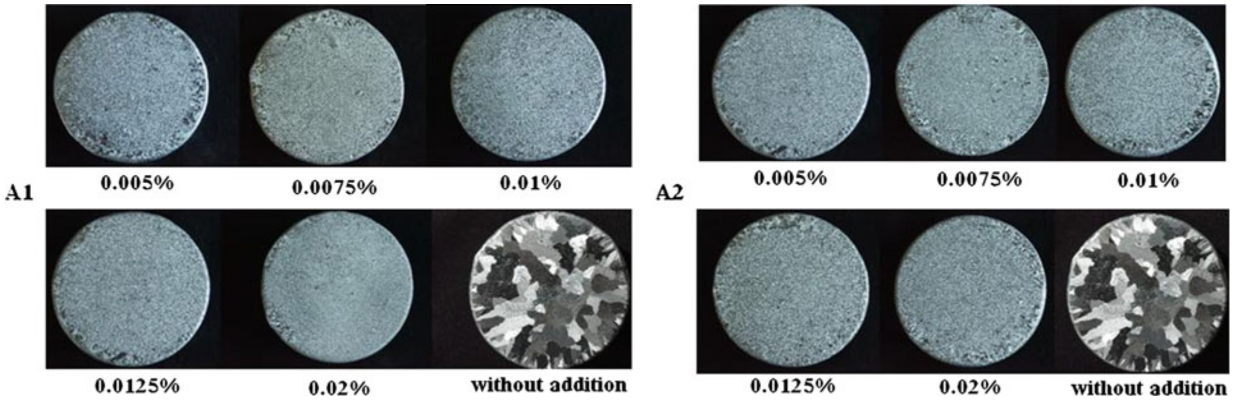

Fig. 4—Photomacrographs for the refined commercially pure Al using A_1 and A_2 master alloys with different addition ratios.

refined aluminum. It indicates that the grain size decreases with the increasing Ti weight ratio. It may be due to the increase of the nucleating ratio with the increase of the Ti content according to the carbide and pretectic theories.[10,20]

2. *Effect of holding time*

The effect of holding time on the grain refining efficiency of commercially pure aluminum (99.7 pct Al) was studied in a range of 30 seconds to 30 minutes. The experiments were carried out at constant temperature of

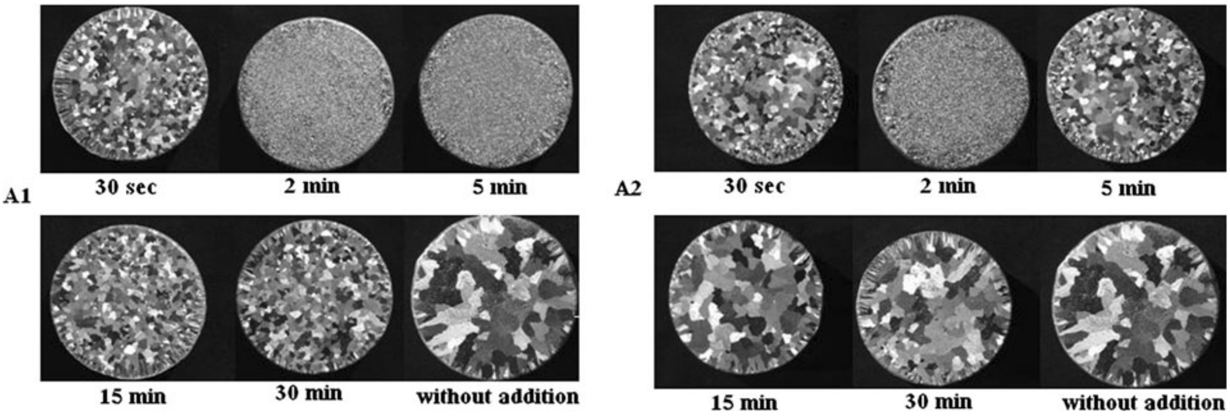

Fig. 6—Photomacrographs for the refined commercially pure aluminum using A1 and A2 master alloys with various holding times.

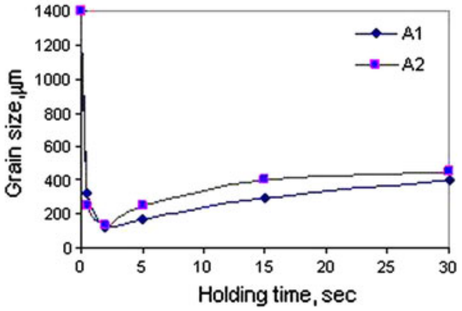

Fig. 7—Relationship between the grain size of 99.7 pct Al refined with A_1 and A_2 master alloys and holding time.

993 K (720 °C) and Ti weight ratio in Al-Ti-C master alloy of 0.01 pct with different times of 30 seconds, and 2, 5, 15, and 30 minutes. Figure 6 shows the photomacrographs of the refined commercially pure aluminum (99.7 pct Al) using A_1 and A_2. We can see the difference in grain size of the refined aluminum at different holding times. Figure 7 illustrates the relationship between the grain size of the refined commercially pure aluminum using A_1 and A_2 *vs* holding time. It can be observed that the trend of the two curves is similar. At the start of reaction, the grain size decreases sharply with the holding time and then increases slowly. This means that the Al-Ti-C grain refiner fades with the increase of holding time. It can be concluded that the holding time plays an important role in the case of both dissolution and settling of TiC particles, whether they are dissolving in the melt or being precipitated or agglomerated. The results make the Al-Ti-C master alloys very suitable to be used in casting practices with very small holding times such as in case of DC casting.

3. *Effect of pouring temperature*

The effect of pouring temperature on the grain refining efficiency of commercially pure aluminum was investigated from 973 K to 1123 K (700 °C to 850 °C). A series of experiments were carried out at different pouring temperatures of 973 K, 993 K, 1023 K, 1073 K, and 1123 K (700 °C, 720 °C, 750 °C, 800 °C, and 850 °C) at constant holding time of 2 minutes and Ti weight ratio of 0.01 pct. Figure 8 shows the photomacrographs for the refined commercially pure aluminum using A_2 and A_3 master alloys. The difference in grain size can be seen in the refined aluminum at different pouring temperatures. Figure 9 illustrates the relationship between the grain size of the refined commercially pure aluminum (99.7 pct Al) using A_2 and A_3 *vs* the pouring temperature. It can be observed that the trend of the two curves is almost similar; *i.e.*, the grain size

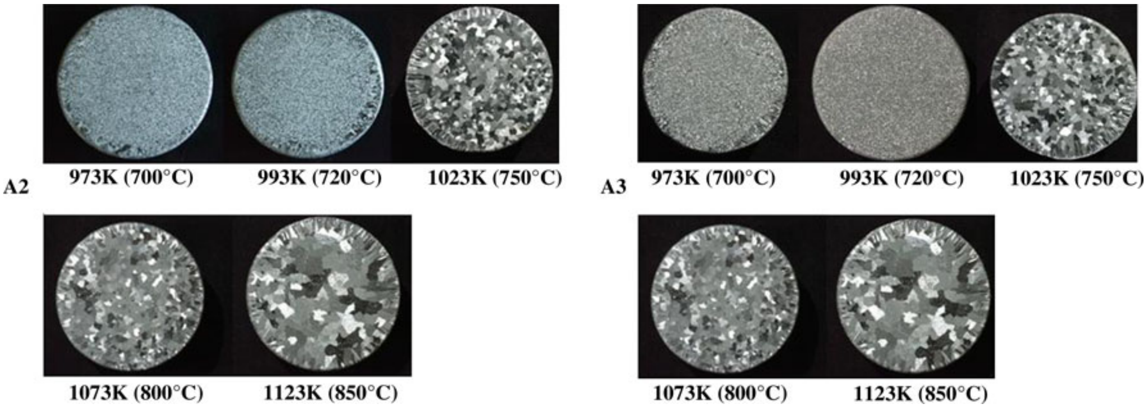

Fig. 8—Photomacrographs for the refined commercially pure aluminum using A_2 and A_3 master alloys with various pouring temperatures.

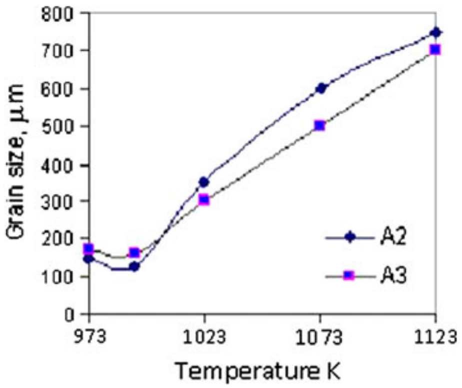

Fig. 9—Relationship between the grain size of the refined commercially pure aluminum using A_2 and A_3 with the pouring temperatures.

decreases slightly with the increase of pouring temperature until reaching a minimum value of grain size at 993 K (720 °C). Then, the grain size increases noticeably with a pouring temperature up to 1123 K (850 °C). The decrease in the grain refining action in the case of increasing the temperature up to 993 K (720 °C) may be due to the fact that the TiC nuclei tend to dissolve in the aluminum melt at high temperature. These results indicate that the suitable range of pouring temperature is within 983 K to 1003 K (710 °C to 730 °C). The increase of grain size above 993 K (720 °C) may be due to the slight increase of solidification time, which leads to slight grain growth.

C. *Comparison between the Behavior of AlTiC and AlTiB Grain Refiners*

The comparison between the produced Al-Ti-C master alloys represented by A_1, A_2, and A_3 and the common type Al-5Ti-1B master alloys as grain refiners was examined for commercially pure aluminum (99.7 pct Al) and aluminum alloys 6063 and 5052. The comparison between the two master alloys is carried out at the prevailing conditions in industry for the Al-Ti-B alloy, *i.e.*, a well-established grain refining practice in industry. Such conditions, pouring temperature of 993 K to 1023 K (720 °C to 750 °C) and rate of addition of 0.003 to 0.015, are a result of many published works and recommendations of companies producing the Al-Ti-B alloy. The Al-Ti-B alloy is a commercial one, and consequently, it was not necessary to repeat the experiments at other temperatures and rates of additions. A number of experiments were carried out under similar conditions at a Ti weight addition ratio of 0.01 pct, holding time of 2 minutes, and pouring temperature of 993 K (720 °C). The choice of these conditions is in accordance with previous results, which could be the most suitable conditions for the grain refining processes. The results of these experiments are represented in Figure 10 for comparison. It can be seen that the grain size of all cases ranged from 80 to 100 μm, and the grain refining efficiency of the Al-Ti-C master alloys is comparable with that of the common type Al-5Ti-1B. The TiC particles within Al-Ti-C master alloys play the same role as the TiB_2 particles in Al-Ti-B master alloys, to act as nucleating sites in the aluminum matrix. Also, TiC is a good nucleate for α-Al, and this could be due to the fact that TiC has an fcc structure.[21] Al-Ti-C grain refiners based on TiC are less prone to the disadvantages associated with TiB_2 present in Al-Ti-B grain refiner such as damages to the surface of the rolls during rolling and scratches on the surfaces of extruded sections caused by agglomerates of TiB_2 particles. Thus, Al-Ti-C grain refiner could be preferred in some applications and practices over Al-Ti-B grain refiner.

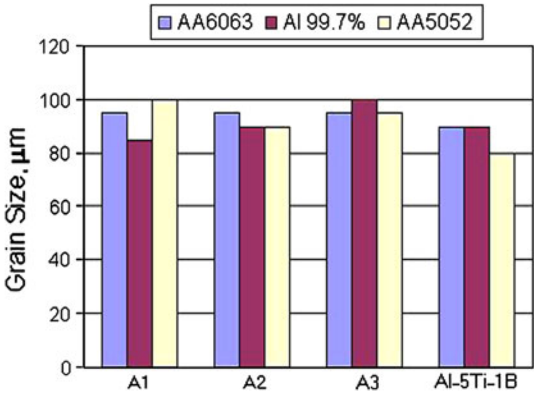

Fig. 10—Comparison between the produced Al-Ti-C master alloys and the common Al-5Ti-1B master alloy as grain refiners for aluminum and some of its alloys, at R = 0.01 pct, pouring temperature = 993 K (720 °C), and holding time = 2 min.

Considering Al, TiC, and TiB_2, some of the crystal parameters and properties are as follows. Al: fcc, lattice parameter = 0.405 nm, and density 2.70 g/cm^3; TiC: fcc, lattice parameter = 0.43 nm, and density 4.91 g/cm^3; and TiB_2: hcp, lattice parameters = 0.303 nm, 0.323 nm, and density 4.5 g/cm^3. Kennedy[22] indicated that the particles should have close lattice matching with the solid (more efficient grain refiner). Also, Kennedy *et al.*[23] indicated that TiC increased the tendency for nucleation of solid on the particle surfaces compared to TiB_2. Thus, TiC has favorable wettability (contact angle) and ability to initiate freezing at minimal undercooling. Discussion of other aspects can be found elsewhere.[24]

IV. CONCLUSIONS

1. The Al-Ti-C master alloys produced in the one-step process using Ti-bearing salts and graphite, which is a relatively novel technique, are an efficient grain refiner for pure aluminum and aluminum alloys compared with the common type Al-5Ti-1B master alloy.
2. The proper conditions for the evaluation of the efficiency of Al-Ti-C master alloys to obtain a minimum grain size are 993 K (720 °C), 2 minutes, and 0.01 pct for temperature, holding time, and (Ti/Al) weight ratio, respectively.

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