Materials and Design 31 (2010) S30–S35

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Production of Al–Ti–C grain refiners with the addition of elemental carbon

Berke Turgay Gezer, Fatih Toptan *, Sibel Daglilar, Isil Kerti

Yildiz Technical University, Department of Metallurgical and Materials Engineering, Faculty of Chemistry and Metallurgy, Davutpasa Campus, Esenler, Istanbul, Turkey

ARTICLE INFO

Article history:
Received 14 July 2009
Accepted 2 September 2009
Available online 6 September 2009

Keywords:
Aluminium
Casting
Grain refiner
Insitu production
Titanium

ABSTRACT

Grain refining process used in aluminium alloys, has an important role for preventing columnar, coarse grains and encouraging fine, equiaxed grain formation. Al–Ti–B grain refiners are widely used as aluminium grain refiners despite the problems in application Al–Ti–C refiners have an increasing demand in recent years. In the present work, Al–Ti–C grain refiners with different Ti:C ratios were produced by insitu method with the addition of elemental carbon. Microstructures were characterised by optic microscope and scanning electron microscope equipped with energy dispersive spectroscopy. The effects of temperature, holding time and Ti:C ratio on the grain refinement process were investigated and optimum conditions were determined.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Grain refinement is widely used in aluminium industry and accepted as one of the most important process in aluminium castings [1,2]. Generally, materials with fine equiaxed grains have improved mechanical properties [3]. In addition, this process also provides improved machinability and cosmetic features, distribution of second phase and microporosity on a fine scale, better feeding to eliminate shrinkage porosity, improved ability to achieve uniform surface, better strength and fatigue life [4,5]. Grain refinement of aluminium is mostly done by Al–Ti–B grain refiners which has Al_3Ti, TiB and α-aluminium phases [6]. In last two decades, Al–Ti–B refiners have been widely used, but a lot problems have been discovered in applications such as poisoning effect of Zr/Cr and agglomeration of borides [7,8]. Therefore alternative grain refiners have been investigated and Al–Ti–C refiner became popular [9]. As a result, Anglo-Blackwells introduced commercial grain refiner based on the Al–Ti–C system which had a composition of Al–6%Ti–0.02%C. However, lower Ti:C ratio was desired for commercial applications and to meet this demand Al–3%Ti–0.15%C was introduced [8]. This refiner has Al_3Ti, TiC and α–Al phases. There are many theories that explains the grain refinement mechanism, all the mechanisms were reviewed and classified as "nucleant paradigm and solute paradigm" by Chandrashekar et al. [10]. It is thought that, the nucleation occurs directly or indirectly (with an intermediate layer between) on TiC and TiB phases [11]. Several production methods have been used for production of Al–Ti–C grain refiners, such as melting elemental blends, reaction of carbon by Al–Ti master alloy, self propagating high temperature synthesis and reaction of molten Al with K_2TiF_6 and graphite powder [12].

In the present work, Al–Ti–C grain refiners were produced by adding elemental carbon to Al–Ti melt. The aim of this study is to produce Al–Ti–C refiners economically, state the production parameters such as holding time and casting temperature and compare the refining performances with different carbon ratios to determine the most effective grain refiner composition.

2. Experimental procedure

Commercial pure aluminium (AA 1080), Al–10%Ti master alloy and Elftex 125 Cabot Carbon with average particle size of 10–20 μm was used to produce Al–Ti–C grain refiners in the induction furnace. Chemical compositions of AA1080 and Al–10%Ti master alloy are given in Table 1. Al–10%Ti alloy was diluted to Al–3%Ti composition by using commercial pure aluminium. Two experiment sets were prepared by using different carbon ratios ranges changing from 0% to 0.75% as given in Table 2. At first set Al–Ti–C refiners were produced at 900 °C and second set at 1300 °C. Firstly, commercial pure aluminium and Al–10%Ti alloy was melted in graphite crucible which was coated with boron nitride to assure that molten metal is purified from impurities. Al–3%Ti molten phase was occured. At this step, molten metal was hold at 900 °C for 15 min in order to dissolute the Al_3Ti phase, before adding elemental carbon.

After 15 min, different amounts of Elftex 125 Cabot carbon, which was dried at 200 °C for humidity elimination in aluminium foil pack, was added to molten metal in aluminium foil and stirred for 5 min with boron nitride coated graphite stick. In refiners without elemental carbon, the stirring process was skipped. When

* Corresponding author. Tel.: +90 212 3834704; fax: +90 212 3834665.
E-mail address: ftoptan@yahoo.com (F. Toptan).

0261-3069/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.matdes.2009.09.002

Table 1
Chemical compositions of AA1080 and Al–10%Ti master alloy.

Alloy	Al (%)	Fe (%)	Si (%)	Cu (%)	Ti (%)	Zn (%)	Bal (%)
AA 1080	99.80	0.15	0.10	0.03	0.02	0.03	0.10
	Ti (%)		Fe (%)		Si (%)		Al (%)
Al–10%Ti	9.947		0.179		0.126		Rest

Table 2
The grain refiner compositions and experiment parameters.

Grain refiner composition	Carbon addition temperature (°C)		Casting temperature (°C)		Holding time after carbon addition (min)	
	Experiment 1	Experiment 2	Experiment 1	Experiment 2	Experiment 1	Experiment 2
Al–3%Ti	–	–	900	1300	10–20	10–20
Al–3%Ti–0.15%C	900	1300	900	1300	10–20	10–20
Al–3%Ti–0.30%C	900	1300	900	1300	10–20	10–20
Al–3%Ti–0.45%C	900	1300	900	1300	10–20	10–20
Al–3%Ti–0.60%C	900	1300	900	1300	10–20	10–20
Al–3%Ti–0.75%C	900	1300	900	1300	10–20	10–20
Al–3%Ti–0.90%C	900	1300	900	1300	10–20	10–20

stirring was completed, samples were taken from the crucible at 900 °C in every 10 min and 20 min and casting was made to steel mold preheated at 200 °C. The aim of this holding process was to detect the effect of time in the formation of TiC phases. This processes were also made in the 1300 °C experiment set. After production step completed, the samples taken from the refiners were polished and examined under JEOL JSM 5400 LV SEM and JEOL JSM 7000F FEG-SEM both equipped with EDS analysis.

In the grain refiner performance test, all composition samples including 10 min and 20 min of holding time after carbon addition, were chosen for comparison. For experiments, 250 g of commercial pure aluminium and 2.5 g of grain refiner samples were prepared. After melting step of commercial pure aluminium in boron nitride coated crucible, the melt temperature was raised to 750 °C and hold stable at this temperature, 2.5 g of refiner addition was made and the melt stirred about 2 min with boron nitride coated graphite stick. After stirring, melt was hold about 3 min and casted at 750 °C into cylindrical metal mold which was preheated at 200 °C. Cylindrical samples with a dimension of 150 mm length and 20 mm diameter was taken from this mold and grain refiner performance samples were taken from 50 mm above from the bottom part. With a thickness of 20 mm. This samples were polished and etched by Keller's reagent and macro images were taken.

3. Results and discussion

In the grain refiner samples produced at 900 °C, Al_3Ti was detected with blocky morphology which is related with low production and casting temperatures. This morphology changes to needle-like at high production temperatures as stated in [13]. The change of the morphology is related with dissolving behaviour of the Al_3Ti particles with increasing temperatures. SEM images of the grain refiners produced at 900 °C and 1300 °C are shown in Fig. 1. Al and Ti elements are detected with EDS analyse shown in Fig. 2. The morphology and amount of Al_3Ti phase changed dramatically at high production temperatures as can be seen on microstructures.

In these samples, occurence TiC phase is seldom. The refiners produced at 1300 °C were also investigated and Al_3Ti phase with needle morphology together with TiC particles are detected. TiC phases are accepted as an effective heterogeneous nucleants [8]. The possible reactions of Ti and C formation are summarized in [14].

$$T_i + C_{(s)} \rightarrow TiC_{(s)} \quad (1)$$

$$T_i + C \rightarrow TiC_{(s)} \quad (2)$$

$$T_i + Al_4C_3 \rightarrow TiC_{(s)} + Al_{(1)} \quad (3)$$

For the formation of TiC via reaction (1) high temperatures above 1100 °C are needed as stated in experiments made by [15,16]. Therefore, second group grain refiners were produced at 1300 °C in order to generate TiC phase formation. The SEM images of Al–3%Ti–0.60%C and 0.75C including TiC particles are shown in Fig. 3.

Ti and C content of these phases are confirmed by elemental map analyses and results are shown in Fig. 4. It is clear that with increasing temperatures Ti reacts with residual C in aluminium forming TiC.

The comparison of these refiners was made in commercial pure aluminium. The grain size comparison of commercial pure aluminium without refiner and including Al–3%Ti–0.60C grain refiners is shown in Fig. 5. The columnar grains changed to fine equiaxed grains after grain refiner additions. In Figs. 6–11 produced refiner performances are compared. Results showed that production temperatures directly affect the grain refiner performance. Because of the lower amounts of Al_3Ti phase and by the absence of TiC particles, the refiners produced at 900 °C had a poor refining performance.

The effect of holding time, after carbon addition and stirring step in the grain refiner production was also investigated. However, results are not clear. As seen in Fig. 9 among the refiners produced 1300 °C, the sample with 20 min of holding time, clearly had better refining efficiency but this situation is not valid for Al–3%Ti–0.30C refiners which is shown in Fig. 8.

In continued studies, reduction of grain size is detected when the Ti:C ratio of the grain refiner is increased above the TiC stoichiometry and Al–3%Ti–0.15%C is accepted as the most effective grain refiner which includes TiC and excess Ti in the solution. Also importance of excess Ti into the melt along with the carbide particles is stated [1]. Hypernucleation theory hypothesized by Jones, claims that segregation of the Ti atoms to the TiB_2/melt interface provides a stable layer of Ti and Al atoms on the TiB_2 crystalsurface, that supports the growth of primary α-Al from the bulk with virtually no undercooling [9]. The Al–3%Ti–0.75%C is declared as a poor

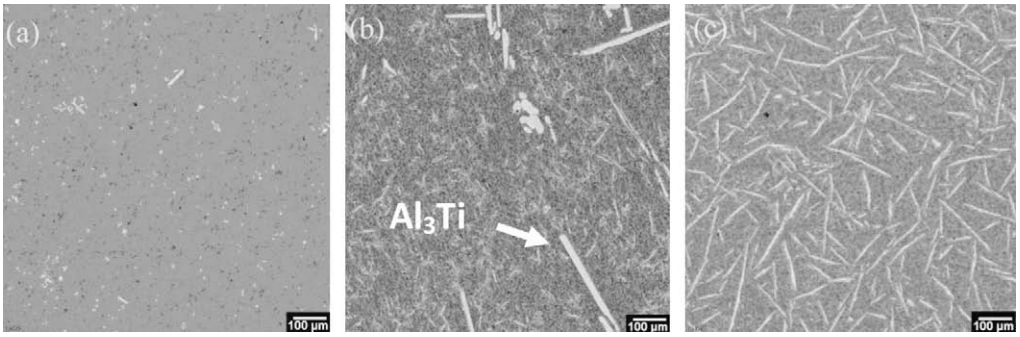


Fig. 1. SEM microstructures of: (a) Al–3%Ti (900 °C 10 min), (b) Al–3%Ti–0.15%C (900 °C 20 min) and (c) Al–3%Ti–0.60%C (1300 °C 10 min) samples.

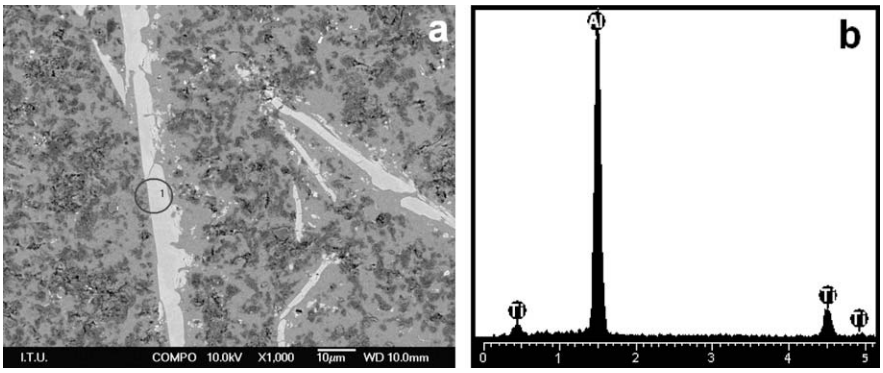


Fig. 2. (a) SEM image and (b) EDS analysis of Al–3%Ti–0.30%C (10 min) sample.

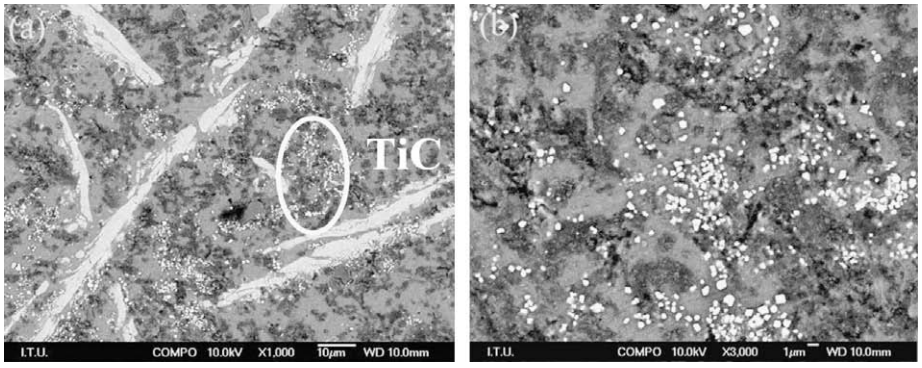


Fig. 3. Microstructures of: (a) Al–3%Ti–0.60%C (10 min) and (b) Al–3%Ti–0.75C (10 min) samples.

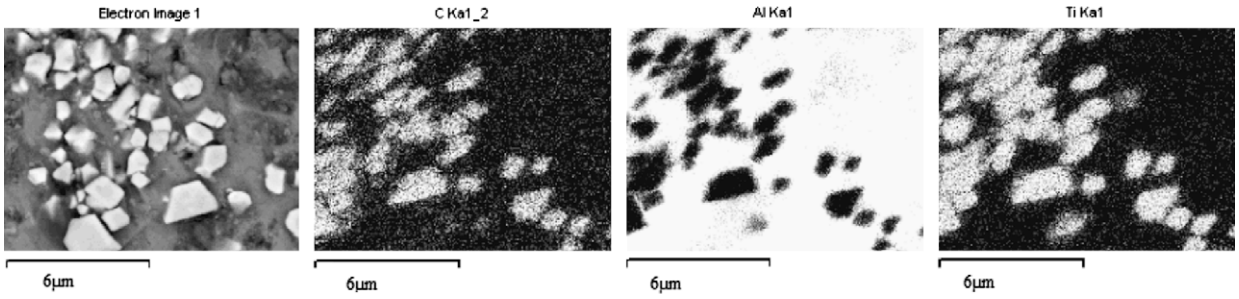


Fig. 4. Elemental maps of sample Al–3%Ti–0.45%C (10 min).

refiner due to agglomeration of TiC particles both production and in grain refining steps [1].

When the refiners produced in 1300 °C is compared, the grain refiner becomes more efficient when the carbon amount increases

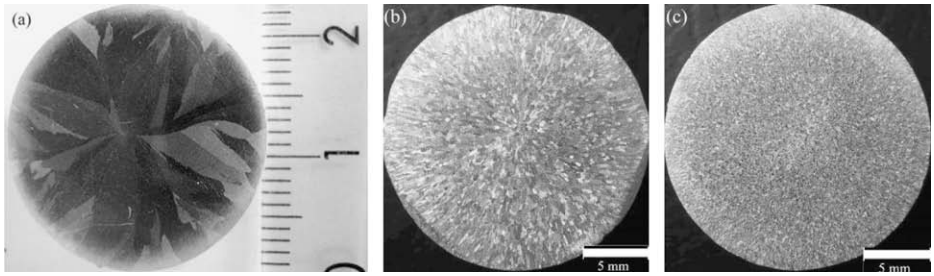


Fig. 5. Comparison of: (a) AA1080 commercial pure aluminium, (b) Al–3%Ti–0.60%C 900 °C 20 min and (c) 1300 °C 20 min.

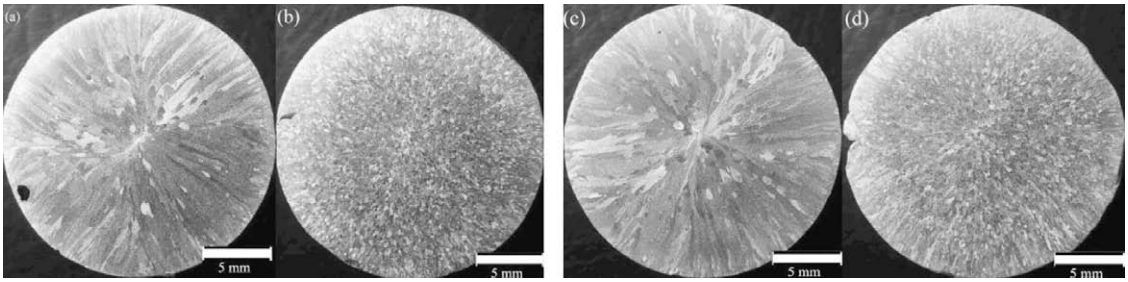


Fig. 6. Commercial pure Al including Al–3%Ti refiner produced at: (a) 900 °C 10 min, (b) 1300 °C 10 min, (c) 900 °C 20 min and (d) 1300 °C 20 min.

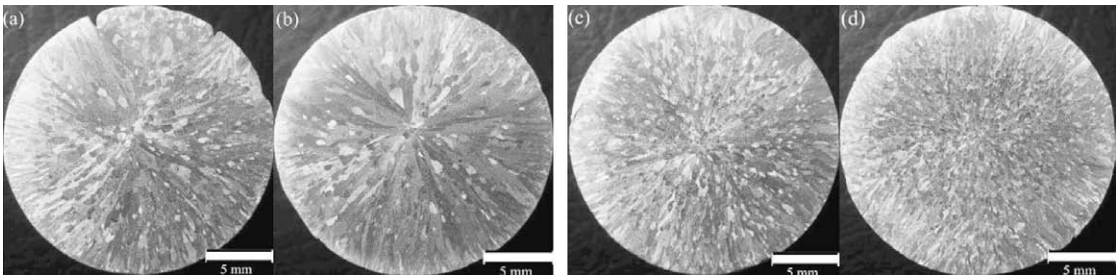


Fig. 7. Commercial pure Al including Al–3%Ti–0.15C refiner produced at: (a) 900 °C 10 min, (b) 1300 °C 10 min, (c) 900 °C 20 min and (d) 1300 °C 20 min.

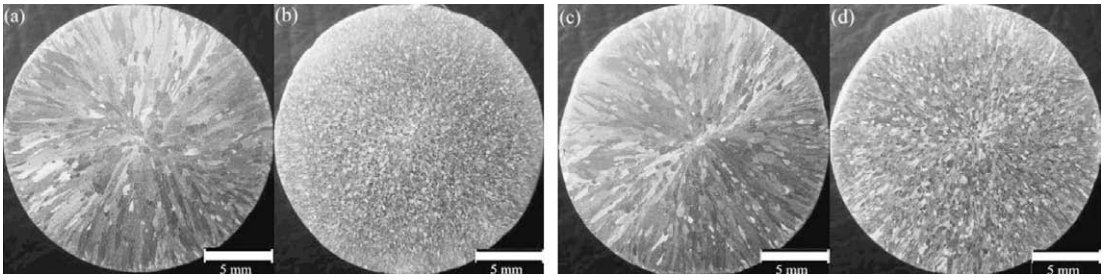


Fig. 8. Commercial pure Al including Al–3%Ti–0.30C refiner produced at: (a) 900 °C 10 min, (b) 1300 °C 10 min, (c) 900 °C 20 min and (d) 1300 °C 20 min.

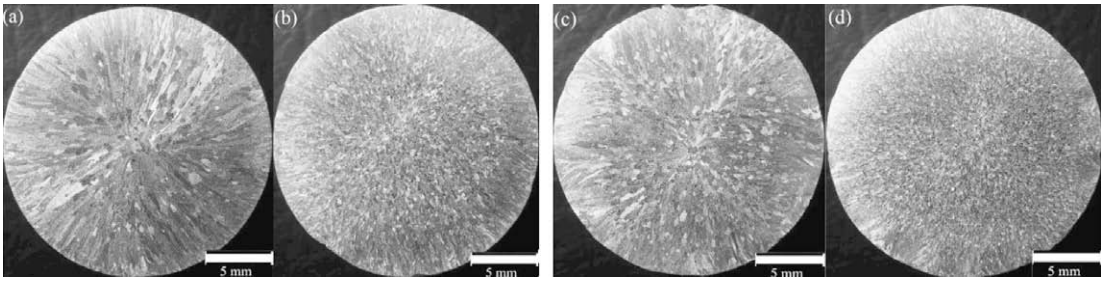


Fig. 9. Commercial pure Al including Al–3%Ti–0.45C refiner produced at: (a) 900 °C 10 min, (b) 1300 °C 10 min, (c) 900 °C 20 min and (d) 1300 °C 20 min.

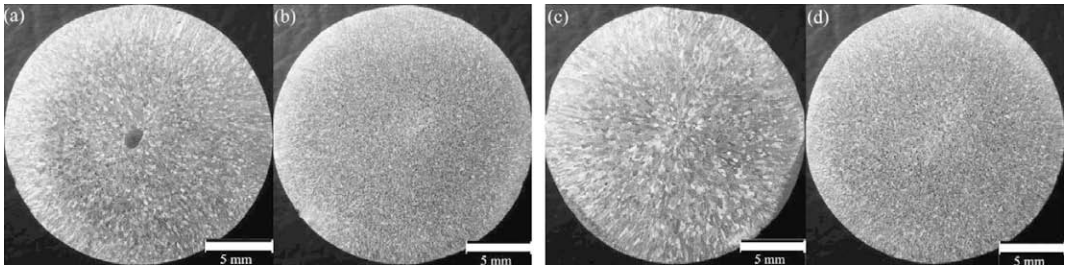


Fig. 10. Commercial pure Al including Al–%3Ti–0.60C refiner produced at: (a) 900 °C 10 min, (b) 1300 °C 10 min, (c) 900 °C 20 min and (d) 1300 °C 20 min.

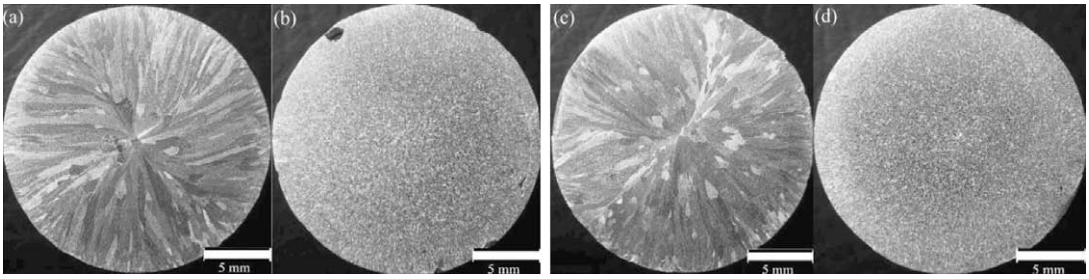


Fig. 11. Commercial pure Al including Al–3%Ti–0.75C refiner produced at: (a) 900 °C 10 min, (b) 1300 °C 10 min, (c) 900 °C 20 min, and (d) 1300 °C 20 min.

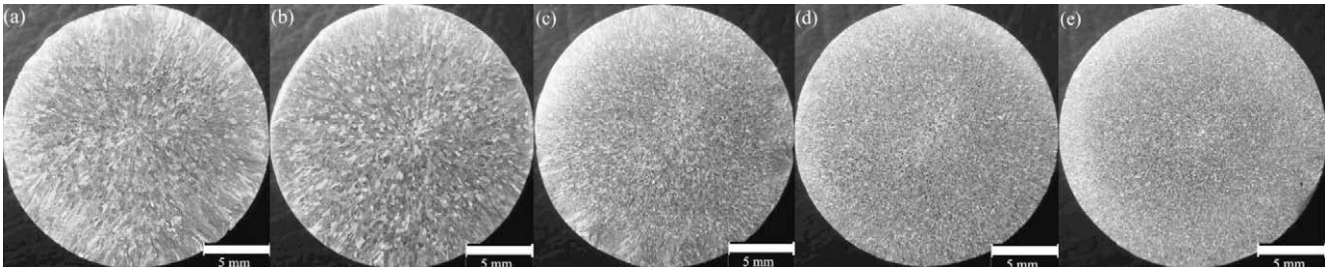


Fig. 12. one thousand three hundred 20 min grain refiners' performance comparison: (a) Al–3%Ti–0.15%C, (b) Al–3%Ti–0.30%C, (c) Al–3%Ti–0.45%C and (d) Al–3%Ti–0.60%C, and (e) Al–3%Ti–0.75%C.

(Fig. 12). Increasing TiC amount can be the main reason for this situation. However, at grain refiner production small inefficiencies occured in carbon addition.

4. Conclusions

In the present work, Al–Ti–C Grain refiners were produced by adding elemental carbon to Al–Ti master alloys and the grain refiner performances were compared. By this method, effective grain refinement production is possible and conclusions are summarized:

- It is possible to produce Al–Ti–C grain refiners with the addition of elemental carbon.
- Al_3Ti and TiC were detected as effective phases in grain refinement process.
- Refiners produced at 1300 °C had relatively good performance when compared to 900 °C productions by the presence of high amounts of Al_3Ti and TiC phases.
- In Al–Ti–C refiners produced at 1300 °C, grain size decreased as the carbon content increased.
- At grain refiner production step, holding time for 10 min and 20 min had no clear effect to grain refiner performance.
- Al–3%Ti–0.60%C and Al–3%Ti–0.75%C compositions produced at 1300 °C were determined as the most effective grain refiners.

Acknowledgements

This study was supported by YTU-BAPK under Grant No.: 28-07-02-02.

References

[1] Birol Y. Grain refining efficiency of Al–Ti–C alloys. J Alloys Compd 2006;422:128–31.
[2] Limmaneevichitr C, Eidhed W. Fading mechanism of grain refinement of aluminium–silicon with Al–Ti–B grain refiners. Mater Sci Eng A 2003;349:197–206.
[3] Iqbal N, Dijk NHV, Offerman SE, Moret MP, Katgerman L, Kearley GJ. Nucleation kinetics during the solidification of aluminium alloys. J Non-Cryst Solids 2007;353:3640–3.
[4] Kashyap KT, Chandrashekar T. Effects and mechanisms of grain refinement in aluminium alloys. Bull Mater Sci 2001;24(4):345–53.

[5] Limmaneevichitr C, Eidhed W. Novel technique for grain refinement in aluminium casting by Al–Ti–B powder injection. Mater Sci Eng A 2003;355:174–9.
[6] Birol Y. Effect of the salt addition practice on the grain refining efficiency of Al–Ti–B master alloys. J Alloys Compd 2006;420:207–12.
[7] Kearns MA, Thistlethwaite SR, Cooper PS. Recent advantages in understanding the mechanism of aluminium grain refinement by TiBAl master alloys. In: TMS 125th annual meeting, 4–8 February 1996; California.
[8] Moldovan P, Popescu G. The grain refinement of 6063 aluminium using Al–5Ti–1B and Al–3Ti–0.15C grain refiners. JOM 2004;56(11):59.
[9] Yu L, Liu X. The relationship between viscosity and refinement efficiency of pure aluminium by Al–Ti–B refiner. J Alloys Compd 2006;425:245–50.
[10] Chandrashekar T, Muralidhara MK, Kashyap KT, Rao RP. Effect of growth resricting factor on grain refinement of aluminium alloys. Int J Adv Manuf Techol 2007.
[11] Naglic I, Smolej A, Dobersek M, Mrvar P. The influence of TiB_2 particles on the effectiveness of Al–3Ti–0.15C grain refiner. Mater Charact 2008.
[12] Kumar VGS, Murty BS, Chakraborty M. Development of Al–Ti–C grain refiners and study of their grain refining efficiency on Al and Al–7Si alloy. J Alloys Compd 2005;396:143–50.
[13] Birol Y. In situ synthesis of Al–TiC_p composites by reacting K_2TiF_6 and particulate graphite in molten aluminium. J Alloys Compd 2006.
[14] Ding H, Liu X, Yu L, Zhao G. The influence of forming process on the distribution and morphologies of TiC in Al–Ti–C master alloys. Scripta Mater 2007;57:575–8.
[15] Kerti I. Production of TiC reinforced – aluminium composites with the addition of elemental carbon. Mater Lett 2005;59:3795–800.
[16] Sato K, Flemings CM. Grain refining of Al–4.5Cu alloy by adding an Al–30TiC master alloy. Metall Mater Trans A 1998;29a(June):707.