Decomposition of $Al_{2.7}Fe_{0.3}Ti$ in heated Al-$Al_{2.7}Fe_{0.3}Ti$ refiner fabricated by spark plasma sintering and its refining performance

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In our previous study, a novel Al-$L1_2$-type $Al_{2.7}Fe_{0.3}Ti$ refiner was fabricated by spark plasma sintering (SPS) and its refining performance was studied. It was found that $L1_2$-type $Al_{2.7}Fe_{0.3}Ti$ particles can be favorable heterogeneous nucleation sites for Al casts, since the lattice matching between $Al_{2.7}Fe_{0.3}Ti$ and Al is good. It was also found that the thermal stability of heterogeneous nucleation sites affects the grain-refining performance. In this study, the decomposition phenomena of the $Al_{2.7}Fe_{0.3}Ti$ phase in a refiner are studied by heating an Al-$Al_{2.7}Fe_{0.3}Ti$ refiner fabricated by SPS. In addition, the refining performance of a heated Al-$Al_{2.7}Fe_{0.3}Ti$ refiner is investigated.

1. Introduction

Al-Ti master alloys are added in relatively small amounts to refine the grain structure of Al and Al alloy casts. Experimental studies of the grain-refining effect show that the intermetallic phase of Al_3Ti is an extremely efficient nucleant. [1-9] One of the important issues to consider in understanding grain refinement is the potency of heterogeneous nucleation sites. It is widely accepted that an effective refiner contains heterogeneous nucleation sites having good lattice matching with the metal matrix. [10-12] It is known that Al_3Ti has a $D0_{22}$ structure and its lattice parameters are a = 0.3851 nm and c = 0.8608 nm. [13] Therefore, it is possible for an Al phase (a =0.4049 nm [14]) to nucleate on Al_3Ti particles because the lattice matching between Al_3Ti and Al is good. However, since Al_3Ti has a low-symmetry tetragonal $D0_{22}$ structure, a different crystallographic orientation relationship results in different lattice matching. [8, 15-18]

It is known that alloying with a certain amount of a transition element such as Cr, Mn, Fe, Co, Ni, Cu, or Zn causes the transformation from the $D0_{22}$-type tetragonal structure of Al_3Ti into a high-symmetry $L1_2$ cubic structure. [19-23] This transformation increases the symmetry of Al_3Ti intermetallic compounds, and therefore, the lattice matching with the metal matrix does not change from plane to plane if $D0_{22}$ modified $Al_{3-y}X_yTi$ intermetallic compounds are used as heterogeneous nucleation sites. Moreover, by changing the alloying element, the lattice constant is controllable. If a substance with better lattice matching between the substance and the solidified phase is used as a heterogeneous nucleant, it should be possible to obtain better grain-refining performance. Since gas-atomized $Al_{2.7}Fe_{0.3}Ti$ particles with an $L1_2$ structure have a lattice constant of a = 0.3925 nm, [17] better lattice matching between the substance and the solidified phase can be achieved. Then, the $Al_{2.7}Fe_{0.3}Ti$ intermetallic compound particles with the $L1_2$ structure are favorable heterogeneous nucleation sites for Al casts.

In our previous study, [17] a novel Al-$L1_2$-type $Al_{2.7}Fe_{0.3}Ti$ refiner was fabricated by spark plasma sintering (SPS) and its refining performance was studied. SPS has advantages in that sintering can be completed in a shorter time at a relatively low temperature. [24-26] It was found that the $L1_2$-type $Al_{2.7}Fe_{0.3}Ti$ particles can be favorable heterogeneous nucleation sites for Al casts since the lattice matching between $Al_{2.7}Fe_{0.3}Ti$ and Al is good. The decomposition phenomena of the $Al_{2.7}Fe_{0.3}Ti$ phase in the refiner were also observed in the

heated Al-$Al_{2.7}Fe_{0.3}Ti$ refiner. [17] It is interesting that the decomposed $Al_{2.7}Fe_{0.3}Ti$ can act as heterogeneous nucleation sites for Al casts. In this study, a detailed investigation of the decomposition phenomena of the $Al_{2.7}Fe_{0.3}Ti$ phase in the refiner is carried out by heating an Al-$Al_{2.7}Fe_{0.3}Ti$ refiner, and the refining performance of the heated Al-$Al_{2.7}Fe_{0.3}Ti$ refiner is investigated.

In our previous study, [17] superior grain-refining efficiency was also found for the refiner with gas-atomized $Al_{2.7}Fe_{0.3}Ti$ particles compared with that with crushed $Al_{2.7}Fe_{0.3}Ti$ particles. This was because the surfaces of the crushed $Al_{2.7}Fe_{0.3}Ti$ particles were covered with the retained second phase, while the second phase in the gas-atomized $Al_{2.7}Fe_{0.3}Ti$ particles was mainly located inside the particles. However, the influence of the second phase of $Al_{2.7}Fe_{0.3}Ti$ particles in a refiner on its grain-refining efficiency has not yet been studied in detail. The present paper also attempts to fill this gap by reporting a study on the effect of the second phase of $Al_{2.7}Fe_{0.3}Ti$ in a refiner on its grain-refining efficiency.

2. Experimental methods

In this study, $Al_{2.7}Fe_{0.3}Ti$ intermetallic compound particles with the $L1_2$ structure were directly prepared by gas atomization, as shown in **Fig. 1(a)**. The gas-atomized particles were sieved to obtain a particle size of 75-150 μm, as shown in **Fig. 1(b)**. The sieved $Al_{2.7}Fe_{0.3}Ti$ intermetallic compound particles were mixed with pure Al particles (99.9%, 106-180 μm), where the volume fraction of intermetallic compound particles was fixed to 10 vol%. Sintering of the mixed powder by SPS apparatus (SPS Syntax SPS-515S) was performed at 500 ºC for 5 min under an applied stress of 45 MPa, as shown in **Fig. 1(c)**.

The fabricated Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner inserted in an alumina crucible was heated to 750 ºC (higher than the melting point of Al) or 650 ºC (lower than the melting point of Al) in air, and then air-cooled, as shown in **Fig. 1(d)**. The microstructural evolution of the heated Al-$Al_{2.7}Fe_{0.3}Ti$ refiner was studied by scanning electron microscope (SEM) with an energy-dispersive X-ray spectrometry (EDS). A Rigaku RINT-2100 X-ray diffractometer with copper Kα radiation was used for phase identification.

Casting experiments were carried out to investigate the effects of preheating of the Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner. The refiner heated at 750 ºC for 300 s and 650 ºC for 24 h was used. A commercially pure Al ingot (99.99%, 148.8 g) was placed in an alumina crucible

and the temperature was increased to 750 °C using an electrical resistance furnace in argon gas, as shown in **Fig. 1(e)**. After the addition of 1.2 g of the heated refiner into the melt, the melt was stirred for 30 s with a rod, after which no further stirring was carried out. The melt was cast into a cylindrical steel mold of 45 mm inner diameter, 70 mm outer diameter, and 70 mm height, as shown in **Fig. 1(f)**, after a holding time of 0, 300, 390, 480, 600 or 900 s. A metallographic sample was horizontally cut from the bottom part (5 mm from the bottom) of each cast sample. The grain-refined samples were subjected to microscopy, and grain size analysis was carried out using the linear intercept method after etching the polished surface with a 10% hydrofluoric acid aqueous solution. The macrostructural and microstructural features of the casts were studied by optical microscopy.

3. Results and discussion

3.1 Microstructure of heated Al-$Al_{2.7}Fe_{0.3}Ti$ refiner

The microstructure of the fabricated Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner before heating is shown in **Fig. 2(a)**. It can be seen from this figure that spherical particles fabricated by gas atomization are successfully embedded homogeneously in the Al matrix. The magnified microstructure of the novel refiner is shown in **Fig. 2(a')**. It can be observed that the gas-atomized particles consist of two phases, i.e., a gray phase with the stoichiometric chemical composition of $Al_{2.7}Fe_{0.3}Ti$ and a mesh-shaped white Fe-rich second phase. Another notable feature observed in **Fig. 2(a')** is that no reaction between the $Al_{2.7}Fe_{0.3}Ti$ intermetallic compound and the Al matrix occurs at the interface, even though the refiner is fabricated by a sintering route. It can be concluded that the $Al_{2.7}Fe_{0.3}Ti$ intermetallic compound particles can be successfully embedded in an Al matrix by SPS without any reaction.

Although the micrographs of the refiner heated at 750 °C for 90 s are not presented here, no notable difference in microstructure between the unheated refiner and the refiner heated at 750 °C for 90 s is recognized, and the spherical particles still keep their original shape. It is also found that the particles have the stoichiometric composition of $Al_{2.7}Fe_{0.3}Ti$. Therefore, no significant reaction occurs upon heating for a shorter period and the $L1_2$-type stoichiometric $Al_{2.7}Fe_{0.3}Ti$ particles are still retained in the refiner.

However, prolonged heating causes microstructural evolution. **Figures 2(b) and 2(b')** show SEM micrographs of the refiner heated at 750 °C for 300 s. As can be seen from these figures, the particles in the refiner heated at 750 °C for 300 s have a core and mantle

microstructure. The thickness of the mantle in the heated refiner increases and the size of the core decreases upon further heating, as shown in **Figs. 2(c) and 2(c')**, which are observed for the refiner heated at 750 °C for 510 s. The results of the compositional analysis of the refiner in **Fig. 2(b')** by EDS are shown in **Table I**. The chemical compositions of the matrix region, *i.e.*, point 1, and core region, *i.e.*, points 4 and 5, are almost pure Al and a Ti-rich $Al_{2.7}Fe_{0.3}Ti$ phase, respectively. On the other hand, the mantle region, *i.e.*, points 2 and 3, does not have such chemical compositions. Similar EDS results are obtained for the refiner heated at 750 °C for 510 s, although the data are not presented here. [17] Thus, partial decomposition of the $Al_{2.7}Fe_{0.3}Ti$ phase occurs in the refiner heated at 750 °C for 300 and 510 s.

On the other hand, the microstructure of the refiner heated at 750 °C for 930 s shows firework-shaped and fibrous particles, instead of spherical particles, as shown in **Fig. 2(d).** The magnified microstructure shown in **Fig. 2(d')** reveals that the firework-shaped particles consist of small blocky particles. The blocky and fibrous particles are identified by EDS analysis to be Al_3Ti and Al_3Fe, respectively. Thus, complete decomposition of the $Al_{2.7}Fe_{0.3}Ti$ phase into Al_3Ti and Al_3Fe phases occurs. It is reported that the shape of the Al_3Fe intermetallic compound appearing in the Al-Fe binary alloy changes upon processing, and granular, rectangular, barlike bulky, sticklike, bulky sharp-edged, and fibrous particles can exist. [27] Moreover, it is reported that the morphology of Al_3Ti particles is related to the temperature of the molten Al. Blocky Al_3Ti is obtained at a low temperature (< 850 °C) and needle plate/strip Al_3Ti can be obtained at a high melting temperature (higher than 1000 °C). [28] Moreover, fine granular Al_3Ti is observed at a relatively low processing temperature, while coarse platelet like particles of Al_3Ti can be achieved at high casting temperatures in Al-Al_3Ti functionally graded materials processed by the reaction centrifugal mixed-powder method. [29] Since heating is carried out at a low temperature (750 °C), the Al_3Ti phase has a blocky shape, as shown in Fig. 2(d'). Therefore, the shapes observed in this study do not contradict the results observed for Al-Fe and Al-Ti binary alloys.

The X-ray diffraction (XRD) patterns of the heated Al-$Al_{2.7}Fe_{0.3}Ti$ refiner are shown in **Fig. 3**. The XRD measurements show the presence of $L1_2$-type $Al_{2.7}Fe_{0.3}Ti$ along with α-Al in the refiner heated for a shorter time, as shown in Figs. 3(a) and 3(b). For the refiner heated at 750 °C for 510 s, a newly formed Al_3Ti phase is detected from its diffraction peaks,

as shown in Fig. 3(c). This means that decomposition occurs and the new phase forms upon heating, which is in good agreement with the result of the SEM observation shown in Figs. 2(C) and 2(c) and the EDS analysis. On the basis of the results of XRD shown in Fig. 3(d) and the EDS analysis, it is clear that the complete decomposition of the $Al_{2.7}Fe_{0.3}Ti$ phase into Al_3Ti and Al_3Fe phases occurs upon longer heating in the liquid state.

Figures 4(a) - 4(c) show the microstructures of the Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner heated at 650 °C for 3, 6 and 24 h, respectively. XRD profiles of the refiner heated at 650 °C for 3, 6 and 24 h are shown in **Figs. 5(a) - 5(c)**, respectively. Figures 4(a) and 5(a) reveal that heating at 650 °C for 3 h causes the complete decomposition of the $Al_{2.7}Fe_{0.3}Ti$ phase into Al_3Ti and Al_3Fe phases. These Al_3Ti and Al_3Fe phases are stable at 650 °C, as shown in Figs. 4(b), 4(c), 5(b), and 5(c). Even in the solid state, the $Al_{2.7}Fe_{0.3}Ti$ phase in the Al matrix decomposes into Al_3Ti and Al_3Fe phases upon heating.

It is important to note that the addition of a commercial Al-Ti-B refiner with Al_3Ti and TiB_2 particles negatively affects the mechanical properties of casts. Agglomerations of TiB_2 cause quality problems with the end product in certain applications since TiB_2 particles are much harder than Al. On the other hand, $Al_{2.7}Fe_{0.3}Ti$ particles in the novel Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner can decompose into Al_3Ti and Al_3Fe in the melt and do not remain in the cast. This is one of the merits of the novel refiner.

3.2 Grain-refining performance of heated refiner

Using the heated refiner containing Al_3Ti and Al_3Fe phases obtained by heating at 650 °C for 24 h, the grain-refining performance is studied. The result is shown in **Fig. 6(a)**. For comparison, the macrostructures of an unrefined pure Al cast and an Al cast refined by an unheated Al-$Al_{2.7}Fe_{0.3}Ti$ refiner are shown in **Figs. 6(b) and 6(c)**, respectively. [17] The holding time for Figs. 6(a) and 6(c) is 600 s. The Al cast without the refiner has coarse and inhomogeneous grains, as shown in Fig. 6(b), and the average grain size is about 3690 μm. [17] On the other hand, the grain size is smaller in the Al cast with the heated refiner, although the macrostructure retains a columnar structure in the outer region of the cast, as shown in Fig. 6(a). By comparing the macrostructures shown in Figs. 6(a) and 6(b), one can recognize that the heated refiner containing Al_3Ti and Al_3Fe phases still has grain-refining efficiency. However, since the grain size of the cast refined by the unheated refiner is

smaller than that of the cast refined by the heated refiner, the grain-refining efficiency of the heated refiner is lower than that of the unheated refiner. This is direct evidence of the efficacy of the $Al_{2.7}Fe_{0.3}Ti$ phase in the refiner, and the $L1_2$-type $Al_{2.7}Fe_{0.3}Ti$ particles are favorable heterogeneous nucleation sites for Al casts.

If the above discussion is true, partially decomposed $Al_{2.7}Fe_{0.3}Ti$ particles should show intermediate grain-refining performance between those of undecomposed and completely decomposed $Al_{2.7}Fe_{0.3}Ti$ particles (Al_3Ti and Al_3Fe particles). Next, the grain-refining performance of the heated refiner containing partially decomposed $Al_{2.7}Fe_{0.3}Ti$ particles with the core and mantle structure is investigated. For this purpose, the refiner heated at 750 °C for 300 s is used.

Macrographs of Al casts refined using the refiner heated at 750 °C for 300 s are shown in **Fig. 7**, where holding times in (a) to (f) are 0, 300, 390, 480, 600, and 900 s, respectively. Significant modification of the microstructure from a coarse columnar structure to a fine equiaxed one is achieved in the cast at a holding time of 600 s. Reduced grain-refining performance (fading) is found when the holding time becomes 900 s. The comparison of Figs. 6 and 7(e) shows that the grain-refining efficiency of the refiner with partially decomposed particles is clearly superior to that of the refiner with completely decomposed particles, but almost the same as those with undecomposed particles.

To discuss the above phenomena, quantitative analysis of the average grain size is carried out and the results are shown in **Fig. 8** as a function of holding time. The results of casts refined by the unheated refiner are also shown in this figure. [17] As can be seen in this figure, the grain-refining efficiency of the heated refiner is inferior to that of the unheated refiner. This is because the surfaces of the heated particles are covered with a core structure, which may have a higher interfacial energy. In the case of the heated refiner, the grain-refining performance starts to decrease after a holding time of 600 s. This situation is the same as in the case of the unheated refiner, as shown in Fig. 8. However, as can be seen, the fading phenomenon occurs more rapidly for the heated refiner. Upon holding the Al melt at 750 °C after the addition of the refiner, the $Al_{2.7}Fe_{0.3}Ti$ particles start dissolving in the melt as they are not stable in the Al matrix. Owing to the dissolution, the size of the particles decreases, and the decrease is more significant for the partially decomposed particles. This may be the reason for the rapid deterioration in performance (fading

phenomenon) for the heated refiner.

3.3 Effects of second phase in $Al_{2.7}Fe_{0.3}Ti$ on grain-refining performance

To refine a material via heterogeneous nucleation, the lattice mismatch between the nucleating substrate and the solid matrix is critical to the effectiveness of the substrate. In our previous study, [17] it was found that $L1_2$-type $Al_{2.7}Fe_{0.3}Ti$ particles with good lattice matching between the nucleating substrate and the solid matrix can act as effective heterogeneous nucleation sites for primary Al in the solidification. In this study, inferior grain-refining performance is found for the heated Al-$Al_{2.7}Fe_{0.3}Ti$ refiner with decomposed $Al_{2.7}Fe_{0.3}Ti$ particles. This means that refiners with different phases should have different refining performance characteristics, even though the chemical compositions of the refiners themselves are the same. Superior grain-refining efficiency is also found for the refiner with gas-atomized particles to the refiner with crushed particles since the surfaces of the crushed particles are covered with the retained second phase, while the second phase in the gas-atomized particles is mainly located inside the particles. [17] Therefore, it is expected that the second phase in $Al_{2.7}Fe_{0.3}Ti$ will strongly affect the grain-refining performance.

Next, the effects of the second phase in $Al_{2.7}Fe_{0.3}Ti$ on the grain-refining performance are studied. However, it is not easy to control the amount of the second phase in the gas-atomized $Al_{2.7}Fe_{0.3}Ti$ particles by controlling the process parameters. Moreover, elimination of the second phase from the bulk $Al_{2.7}Fe_{0.3}Ti$ needs an extremely long heat treatment for homogenization even at an elevated temperature. Alternatively, in this study, the grain-refining performance of the Al-$Al_{2.7}Fe_{0.3}Ti$ refiner with a certain amount of the second phase is therefore studied.

The bulk $Al_{2.7}Fe_{0.3}Ti$ intermetallic compound is prepared by arc melting in argon. SEM microphotographs of an unhomogenized $Al_{2.7}Fe_{0.3}Ti$ sample prepared by arc melting are shown in **Fig. 9**. It is clear that the microstructure of the unhomogenized sample consists of a matrix and a second phase. The chemical compositions at points 1 to 4 are listed in **Table II**. Point 2, in the matrix region, shows the stoichiometric composition of $Al_{2.7}Fe_{0.3}Ti$, while point 4 shows the stoichiometric composition of Al_3Ti. On the other hand, the chemical compositions at points 2 and 3 are found to be neither $Al_{2.7}Fe_{0.3}Ti$ nor Al_3Ti. A certain amount of the second phase is thus formed in the unhomogenized sample.

The volume fraction of the second phase in the homogenized sample used in the previous study [17] was 6.2 vol%, while that in the unhomogenized sample used in this study is 11.1 vol%.

The unhomogenized sample is crushed into fine particles by a hammer. After sieving to obtain a particle size of 75-150 μm, an Al-10 vol%$Al_{2.7}Fe_{0.3}Ti$ refiner is fabricated by SPS in the same manner as in previous experiments. Hereafter, the refiner fabricated with unhomogenized particles with a large amount of the second phase will be denoted as the "unhomogenized refiner", whereas the refiner fabricated with homogenized particles with a small amount of the second phase studied in the previous study [17] will be denoted as the "homogenized refiner".

The typical microstructure of the unhomogenized refiner is shown in **Fig. 10**. It is observable from this figure that the crushed particles have a granular shape and contain some of the second phase. The results of EDS analysis shown in **Table III** and the XRD profile shown in **Fig. 11** indicate that the Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner with a certain amount of the second phase can be fabricated by the above process.

The grain-refining performance of the fabricated unhomogenized refiner with a certain amount of the second phase is studied in the same manner as in previous experiments. Macrophotographs of casts refined by the unhomogenized Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner after holding times of 0, 600 and 1200 s are shown in **Figs. 12(a) - 12(c)**, respectively. Limited grain-refining performance can be observed for the unhomogenized Al-10 vol%$Al_{2.7}Fe_{0.3}Ti$ refiner.

The average grain size of each cast is evaluated and the results are plotted against the holding time in **Fig. 13**. For comparison, the average grain size of the Al cast refined by the homogenized refiner is also shown in this figure. [17] Lower grain-refining performance is found for the Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner with a certain amount of the second phase. Again, different refining performance characteristics appear for refiners with different phases, even though the chemical compositions of the refiners themselves are the same. It can be concluded that $Al_{2.7}Fe_{0.3}Ti$ particles with an $L1_2$ structure can act as effective heterogeneous nucleation sites for primary Al in the solidification.

4. Conclusions

A novel refiner, in which $L1_2$-type $Al_{2.7}Fe_{0.3}Ti$ particles are dispersed, has been fabricated by spark plasma sintering (SPS). The decomposition phenomena of the $Al_{2.7}Fe_{0.3}Ti$ phase in the refiner and the refining performance of the heated Al-$Al_{2.7}Fe_{0.3}Ti$ refiner were investigated. In addition, the grain-refining performance of an Al-$Al_{2.7}Fe_{0.3}Ti$ refiner with a certain amount of the second phase was also studied. The obtained results are summarized as follows.

1) The particles in the refiner heated under relatively weak conditions have a core and mantle microstructure. The chemical composition of the core region is Ti-rich $Al_{2.7}Fe_{0.3}Ti$. The thickness of the mantle increases and the size of the core decreases upon further heating.

2) The particles in the refiner heated under relatively strong conditions have firework-shaped particles consisting of small blocky Al_3Ti and fibrous Al_3Fe particles. Complete decomposition of the $Al_{2.7}Fe_{0.3}Ti$ phase occurs upon heating under relatively strong conditions.

3) Using the heated refiner containing Al_3Ti and Al_3Fe phases and partially decomposed particles with a core and mantle microstructure, the grain-refining performance was studied. It was found that the grain-refining efficiency of the refiner with partially decomposed particles is clearly superior to that of the refiner with completely decomposed particles, but inferior to that of the unheated refiner.

4) Inferior grain-refining performance was also found for the Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner with a certain amount of the second phase. Different refining performance characteristics appeared for refiners with different phases, even though the chemical compositions of the refiners themselves were the same.

5) It can be concluded that $Al_{2.7}Fe_{0.3}Ti$ particles with an $L1_2$ structure can act as effective heterogeneous nucleation sites for primary Al in the solidification.

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Figure Captions

Fig. 1. (Color online) Flow diagram of experimental procedure.

Fig. 2. (Color online) SEM microstructures of Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner heated at 750 °C. The heating times are (a) and (a') 0, (b) and (b') 300, (c) and (c') 510, and (d) and (d') 930 s.

Fig. 3. (Color online) XRD profiles of Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner heated at 750 °C. The heating times for (a) - (d) are 90, 300, 510, and 3600 s, respectively.

Fig. 4. (Color online) SEM microstructures of Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner heated at 650 °C. The heating times are (a) and (a') 3, (b) and (b') 6, and (c) and (c') 24 h.

Fig. 5. (Color online) XRD profiles of Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner heated at 650 °C. The heating times for (a) - (c) are 3, 6, and 24 h, respectively.

Fig. 6. Macrographs of Al casts. (a) Refined by the heated refiner containing Al_3Ti and Al_3Fe phases obtained by heating at 650 °C for 24 h, (b) without refiner [17] and (c) refined by unheated Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner. [17] The holding time for (a) and (c) is 600 s.

Fig. 7. Grain-refining performance test results of the heated Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner after holding times of (a) 0, (b) 300, (c) 390, (d) 480, (e) 600, and (f) 900 s. Heating is carried out at 750 °C for 300 s.

Fig. 8. (Color online) Average grain size of the samples with different holding times after addition of heated and unheated Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiners Heating is carried out at 750 °C for 300 s. The original data for the unheated Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner appeared in Ref. 17.

Fig. 9. (Color online) SEM microphotographs of unhomogenized $Al_{2.7}Fe_{0.3}Ti$ sample prepared by arc melting.

Fig. 10. (Black and white) SEM microphotographs showing unhomogenized Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner.

Fig. 11. (Color online) XRD profile of unhomogenized refiner showing the existence of the Al_3Ti phase as well as the $Al_{2.7}Fe_{0.3}Ti$ phase in an Al matrix.

Fig. 12. (Black and white) Grain-refining performance test results of unhomogenized Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner after holding times of (a) 0, (b) 600, and (c) 1200 s.

Fig. 13. (Color online) Effects of the second phase formed in the $Al_{2.7}Fe_{0.3}Ti$ particles on the grain-refining performance of homogenized and unhomogenized Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiners with crashed particles. The volume fractions of the second phase in the homogenized and unhomogenized samples are 6.2 and 11.1 vol%, respectively. The original data for the homogenized Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner appeared in Ref. 17.

Table I. EDS analysis results of the Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner heated at 750 °C for 300 s shown in Fig. 2(b) (unit: mol%).

	Al	Fe	Ti
1 (Matrix)	100.0	0.0	0.0
2 (Mantle region)	74.7	5.3	20.0
3 (Mantle region)	73.6	5.7	20.7
4 (Core region)	65.1	7.1	27.8
5 (Core region)	64.0	7.0	29.0

Table II. EDS analysis results of the unhomogenized $Al_{2.7}Fe_{0.3}Ti$ intermetallic compound shown in Fig. 9(b) (unit: mol%).

	Al	Fe	Ti
1	61.1	21.1	17.8
2	55.6	21.1	23.3
3	71.6	0.4	28.0
4	66.4	7.5	26.1

Table III. EDS analysis results of the unhomogenized Al-10 vol% $Al_{2.7}Fe_{0.3}Ti$ refiner shown in Fig. 10(b) (unit: mol%).

	Al	Fe	Ti
1	100.0	0.0	0.0
2	64.0	8.2	27.8
3	99.6	0.0	0.4
4	74.3	0.3	25.4
5	22.1	0.0	77.9