# Fabrication of novel AI-L1<sub>2</sub>-type AI<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiners by spark plasma sintering and their refining performance

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Grain refinement plays a vital role in cast and wrought aluminum alloys. The grain refiners introduce particles that heterogeneously nucleate the primary alpha-aluminum. It is well known that Al<sub>3</sub>Ti particles are commonly used as heterogeneous nucleants for aluminum alloy casting. If a substance with a smaller misfit for aluminum is used as a heterogeneous nucleant, such as L1<sub>2</sub> intermetallic compounds, it should be possible to achieve a better grain refining performance. In this study, the optimum condition for a grain refiner using Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound particles with the L1<sub>2</sub> structure was investigated.

## 1. Introduction

Spark plasma sintering (SPS) simultaneously applies a pulsed current and a uniaxial pressure to punches of a mold system loaded with a mixture of powders to be sintered.<sup>1)</sup> In SPS, a high-energy, low-voltage pulsed current momentarily generates a spark plasma at extremely high and localized temperatures between the powder particles, and causes the surface of the powder particles to vaporize and melt.<sup>2)</sup> SPS has several unique and specific features. For example, SPS allows the compacted powders to be sintered at a low temperature with short heating, holding, and cooling times.<sup>3,4)</sup> Therefore, SPS has an advantage of suppressing exaggerated grain growth over conventional sintering.<sup>5)</sup> This method is usually used to fabricate hard-to-sinter materials, such as nanocrystalline materials and intermetallic compounds.<sup>4)</sup> Wu *et al.*<sup>4)</sup> have successfully fabricated transparent PbZrO<sub>3</sub> -Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> ceramics by using the SPS method. The effects of sintering conditions on the mechanical properties of biomedical porous Ti fabricated by the SPS method were studied by Hasebe *et al.*<sup>6)</sup>

Grain refinement is widely used in aluminum foundries to promote a fine equiaxed grain structure with improved mechanical and cosmetic properties.<sup>7)</sup> Al-Ti-B alloys, such as Al-3 mass% Ti-0.2 mass% B, Al-3 mass% Ti-1 mass% B, and Al-5 mass% Ti-0.2 mass% B containing Al<sub>3</sub>Ti and TiB<sub>2</sub>, are being used as grain refiners in the casting of aluminum alloys.<sup>8)</sup> It is known that Al<sub>3</sub>Ti is an excellent heterogeneous nucleant. The crystal structures of aluminum and Al<sub>3</sub>Ti phases are fcc and D0<sub>22</sub>, which are presented in Figs. 1(a) and 1(b), respectively.

If a substance with a smaller misfit for aluminum is used as a heterogeneous nucleant, it should be possible to achieve a better grain refining performance.<sup>9-12)</sup> However, not all of the candidate materials for the heterogeneous nucleants can coexist with the aluminum matrix in equilibrium. This problem could be overcome by the use of the SPS method, since sintering at a low temperature with short heating, holding, and cooling times can be achieved by this method.<sup>3,4)</sup> In this study, an L1<sub>2</sub>-type Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound, which is thermally unstable in an aluminum matrix, is used as the heterogeneous nucleant. L1<sub>2</sub>-type Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound particles are prepared by crushing of a bulk material obtained by arc melting or directly by gas atomization. Al-10 vol% L1<sub>2</sub>-type Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiners are, then, fabricated by the SPS method. The effects of the fabricated

refiners on the grain refining performance of a pure aluminum cast have been studied.

### 2. Concept of novel refiner

It is well accepted that an effective refiner should have a good lattice registry with the metal matrix.<sup>9-12)</sup> Generally, the degree of disregistry between the substrate phase and the crystalline phase,  $\delta$ , proposed by Turnbull and Vonnegut<sup>13)</sup> is used to discuss the effectiveness of heterogeneous nucleation, and it can be calculated using the following equation for an aluminum cast:

$$\delta = \frac{|a_s - a_{Al}|}{a_{Al}} \times 100\% \quad , \tag{1}$$

where  $a_s$  and  $a_{Al}$  are the lattice parameters of the substrate particles and aluminum matrix without deformation, respectively. It is believed that a good registry between the low-index planes of adjoining phases is important. Generally, when  $\delta < 5\%$ , the interface between the substrate and the matrix is coherent; when  $5\% < \delta < 25\%$ , the interface between the substrate and the matrix is partially coherent.<sup>14</sup> However, since the Al<sub>3</sub>Ti phase has a tetragonal D0<sub>22</sub> structure, as shown in Fig. 1(b), the atomic arrangement does not have exact hexagonal symmetry for {112}<sub>Al3Ti</sub> planes, and square symmetry for (100)<sub>Al3Ti</sub> and (010)<sub>Al3Ti</sub> planes. Alternatively, the plane disregistry proposed by Bramfitt<sup>15</sup> is often used.<sup>16-20</sup> The formula is given by

$$\mathcal{S}_{(hkl)_{Al}}^{(hkl)_{s}} = \frac{1}{3} \sum_{i=1}^{3} \left\{ \begin{vmatrix} d[uvw]_{s}^{i} \cos \theta - d[uvw]_{Al}^{i} \\ d[uvw]_{Al}^{i} \end{vmatrix} \times 100\% \right\} \times 100\% , \qquad (2)$$

where  $(hkl)_s$  and  $(hkl)_{Al}$  are the low-index planes of the substrate particle and Al, and  $[uvw]_s$ and  $[uvw]_{Al}$  are the low-index orientations on  $(hkl)_s$  and  $(hkl)_{Al}$ , respectively. Moreover,  $d[uvw]_s$  and  $d[uvw]_{Al}$  are the interatomic spacing distances along [uvw], and  $\theta$  is the angle between  $[uvw]_s$  and  $[uvw]_{Al}$ . The planar disregistry values between Al<sub>3</sub>Ti and aluminum are reported to be 2.17% for (112) Al<sub>3</sub>Ti // (111)Al, 2.26% for (102) Al<sub>3</sub>Ti // (101)Al, 3.96% for  $(100)_{AbTi}$  //  $(100)_{Al}$ , 4.12% for  $(110)_{AbTi}$  //  $(110)_{Al}$ , and 4.89% for  $(001)_{AbTi}$  //  $(001)_{Al}$ ,<sup>19)</sup> which are smaller than 5%. Therefore, it is possible for the aluminum phase to nucleate on Al<sub>3</sub>Ti particles on the basis of these orientation relationships.

It is reported that the refining performance of the Al-Ti alloy is strongly affected by the crystal morphologies of the Al<sub>3</sub>Ti particles.<sup>21)</sup> Arnberg *et al.*<sup>22,23)</sup> have found that Al<sub>3</sub>Ti can assume three different shapes depending on the temperature history of the master alloy, petal-like shapes, plates, and blocks. They reported that the grain refining response of the alloy depends on the morphology of the Al<sub>3</sub>Ti.<sup>21)</sup> It is also reported that the shape of Al<sub>3</sub>Ti particles in the Al-5 mass% Ti ingot are platelet-shaped,<sup>24,25)</sup> and it is known that the face of Al<sub>3</sub>Ti platelets is a (001)<sub>Al<sub>3</sub>Ti</sub> plane.<sup>26,27)</sup> Therefore, the dominant face of Al<sub>3</sub>Ti platelets is not the best plane for heterogeneous nucleation, since it has the largest planar disregistry value among the above orientation relationships. If the Al<sub>3</sub>Ti platelet within the Al-Ti alloy has a facet structure, as shown in Fig. 2(a), the area ratio of the  $\{100\}$ -type surface: {110}-type surface: (001)-type surface becomes  $12\sqrt{2} \ge t/d \ge 12 \ge t/d \ge 14$ , where t and d are the thickness and diameter of the platelets, respectively, and therefore, t/d is the aspect ratio. The area ratio is plotted against the aspect ratio t/d, and the results are shown in Fig. 2(b). As can be seen, the (001)-type surface becomes more dominant when the aspect ratio becomes smaller. The average disregistry value for the Al<sub>3</sub>Ti platelets with different aspect ratios can be calculated using the above planar disregistry values, and the results are shown in Fig. 2(c). If the Al<sub>3</sub>Ti platelet has a larger aspect ratio, the average disregistry value becomes smaller. However, the average disregistry value for the platelet with an aspect ratio of 0.08 can be estimated to be 4.8%, since the aspect ratio of the Al-5 mass% Ti alloy is reported to be  $0.08^{28}$  This value is close to 5%, beyond which the interface could not have a coherent structure.

It is known that alloying with a certain amount of a transition element, such as chromium, manganese, iron, cobalt, nickel, copper zinc, rhodium, palladium, silver, platinum, or gold, causes the transformation from the D0<sub>22</sub>-type tetragonal structure of Al<sub>3</sub>Ti to a high-symmetry L1<sub>2</sub> cubic structure.<sup>29-33)</sup> This transformation increases the symmetry of Al<sub>3</sub>Ti intermetallic compounds. Therefore, if L1<sub>2</sub>-type intermetallic compound particles are used as heterogeneous nucleation sites, the lattice registry with the metal matrix does not change from plane to plane. Moreover, by changing the alloying

element, the lattice constant is controllable. For example, the lattice constants of Al<sub>2.5</sub>Cu<sub>0.5</sub>Ti, Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti, and Al<sub>2.75</sub>Ni<sub>0.25</sub>Ti intermetallic compounds with the Ll<sub>2</sub> structure are a = 0.3927 nm, a = 0.393 nm, and a = 0.394 nm, respectively.<sup>34</sup>) Since these values are close to that of aluminum, smaller disregistry values between these phases and aluminum can be achieved, *i.e.*, 3.03% for Al<sub>2.5</sub>Cu<sub>0.5</sub>Ti, 2.95% for Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti, and 2.71% for Al<sub>2.75</sub>Ni<sub>0.25</sub>Ti. These values are much smaller than that for platelet-shaped Al<sub>3</sub>Ti, as shown in Fig. 2(c). Therefore, it is expected that the Al<sub>2.5</sub>Cu<sub>0.5</sub>Ti, Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti, and Al<sub>2.75</sub>Ni<sub>0.25</sub>Ti intermetallic compound particles with the Ll<sub>2</sub> structure will become favorable heterogeneous nucleation sites for an aluminum cast. In this study, a grain refiner with Ll<sub>2</sub>-type Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles is examined. The aluminum-rich corner of the Al-Ti-Fe ternary equilibrium phase diagram is shown in Fig. 3.<sup>35,36</sup>) The oval region outlined by a solid line represents the extent of the Ll<sub>2</sub> phase field at 800 °C. The dotted lines separating the Ll<sub>2</sub> phase boundary from the liquid phase boundary are two-phase tie lines.

## 3. Experimental methods

The most commonly used commercial methods for making particles can be classified into those involving the chemical reduction of oxides, the mechanical crushing of brittle materials, the electrolysis of solutions, and the disintegration of melts or atomization.<sup>37)</sup> In the present work, two types of Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound particles with the L1<sub>2</sub> structure were used. One was prepared by the mechanical crushing of a bulk Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound, since it is a brittle material. The bulk Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound was prepared by an arc melting method under an argon atmosphere, as shown in Fig. 4(a). The obtained bulk Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound was homogenized at 1200 °C for 72 h, as shown in Fig. 4(b), and then crushed into fine particles by a hammer, as shown in Fig. 4(c). Hereafter, the particles prepared by the crushing of an arc melted bulk sample will be denoted as "crushed particles". Another type of L1<sub>2</sub> Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound particles was directly prepared by atomization. Because gas atomization enables greater control of various particle properties, this shows potential for mass production.<sup>38)</sup> Moreover, the production of prealloyed particles is possible with the gas atomization. In this study, the gas atomization method is, therefore, used to prepare

the L1<sub>2</sub> Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound particles, as shown in Fig.4(d). Both crushed and gas-atomized particles were sieved into the size of  $75-150 \mu m$ , as shown in Fig. 4(e). The sieved Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound particles are mixed with pure aluminum particles (99.9%, 106-180  $\mu m$ ), where the volume fraction of intermetallic compound particles was fixed to 10 vol%. Sintering of the mixed powder using an SPS apparatus (SPS-515S, SPS Syntax Inc.) was performed at 500 °C for 5 min under an applied stress of 45 MPa, as shown in Fig. 4(f). The microstructural evolution of the fabricated Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound and refiner samples was studied by scanning electron microscopy (SEM) with energy-dispersive X-ray spectromety (EDS). Phase analysis was carried out by the X-ray diffraction (XRD) technique using Cu-K $\alpha$  radiation.

A commercially pure aluminum ingot (99.99%, 148.8 g) was melted in an electrical resistance furnace using an alumina crucible at 750 °C under an argon gas atmosphere, as shown in Fig. 5(a). After the addition of 1.2 g of refiner into the melt, the melt was homogenized for 30 s by mechanical stirring and it was held for a certain time at 750 °C (hereafter, holding time), and then poured into a steel mold with 45 mm inner diameter, 70 mm outer diameter, and 70 mm height, as shown in Fig. 5(b). For grain size analysis, each cast sample was sectioned horizontally at a fixed distance of 5 mm from the bottom, as shown in Fig. 5(c). The grain refined samples were subjected to microscopy and grain size analysis was carried out using the mean linear intercept method after etching the polished surface with a 10% hydrofluoric acid aqueous solution, as shown in Fig. 5(d). The microstructural characterization has been carried out by optical microscopy (OM) and SEM.

#### 4. Results and discussion

## 4.1 Al2.7Fe0.3Ti intermetallic compound prepared by arc melting

Figures 6(a) and 6(b) show the XRD patterns of the arc-melted Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti sample before and after the homogenization treatment, respectively. X-ray analysis shows the peak pattern of L1<sub>2</sub>-type Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti. The lattice constant of the homogenized sample shown in Fig. 6(b) is a = 0.3927 nm. This value is in agreement with the reported value.<sup>34</sup>) It is also shown that some unidentified peaks appeared in both samples, but the unidentified peaks were decreased by the homogenization treatment.

The SEM photomicrographs of the arc-melted Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound

samples before and after the homogenization treatment are shown in Figs. 7(a) and 7(b), respectively. It is clear that none of the samples are single-phase materials. The microstructures of the samples consist of a matrix and a second phase, even in the case of the homogenized sample. The chemical composition of the matrix part of each sample was studied by EDS and found to be 62.7 at.% Al, 8.9 at.% Fe, and 28.4 at.% Ti for point 1, and 63.0 at.% Al, 8.9 at.% Fe, and 28.2 at.% Ti for point 3. On the other hand, the chemical compositions of points 2 and 4 were found to be 64.5 at.% Al, 28.4 at.% Fe, and 7.0 at.% Ti, and 63.5 at.% Al, 14.9 at.% Fe, and 21.6 at.% Ti, respectively. Since the stoichiometric composition of the Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound phase is 67.5 at.% Al, 7.5 at.% Fe, and 25 at.% Ti, the matrix has a Ti-rich composition, while the second phase has an Fe-rich composition. It is emphasized that the second phase observed in the as-cast sample cannot be eliminated by the homogenization treatment at 1200 °C for 72 h.

The bulk-shaped Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound was crushed into fine particles by a hammer after the homogenization treatment, and the crushed particles are shown in Fig. 8. It is seen from this figure that the crushed particles have a granular shape. Although the stoichiometric composition of the Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound phase is found for points 1 and 3, the chemical compositions of points 2, 4 and 5 are found to be 28.1 at.% Al, 19.3 at.% Fe, and 52.7 at.% Ti, 13.7 at.% Al, 24.4 at.% Fe, and 61.9 at.% Ti, and 21.9 at.% Al, 57.0 at.% Fe, and 21.2 at.% Ti, respectively. This is because, during the crushing of the bulk-shaped sample by a hammer, fragmentation may occur across the second phase, consequently the surfaces of the crushed particles are covered by the second phase.

## 4.2 Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound prepared by gas atomization

The XRD pattern of Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles prepared by gas atomization is shown in Fig. 9. X-ray analysis shows the peak pattern of L1<sub>2</sub>-type Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti with the lattice constant of a = 0.3925 nm, which is also in agreement with the reported value.<sup>34)</sup> It is also shown that no evidence for a large amount of second phase is observed.

A SEM photomicrograph of  $Al_{2.7}Fe_{0.3}Ti$  particles prepared by gas atomization is shown in Fig. 10. As shown in Fig. 10, most of the particles are spherical or nearly spherical, and some satellites are found around the main particles. A dendrite structure is also observed on the surface. The chemical compositions of points 1 and 2, analyzed by EDS, are 68.0 at.% Al, 9.9 at% Fe, and 22.2 at.% Ti, and 64.5 at.% Al, 9.6 at.% Fe, and 25.9 at.% Ti, respectively. In this manner, the spherical and stoichiometric  $Al_{2.7}Fe_{0.3}Ti$  particles with the L1<sub>2</sub> structure could be directly prepared by gas atomization.

#### 4.3 Al-L12-type Al2.7 Fe0.3 Ti refiners fabricated by SPS

The crushed and gas-atomized Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles with the L1<sub>2</sub> structure have lattice constants of a = 0.3927 nm and a = 0.3925 nm, respectively. From these lattice constants, the disregistry value of the Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound with the L1<sub>2</sub> structure for all planes is estimated to be 3.02 or 3.07%, which is smaller than that of platelet-shaped Al<sub>3</sub>Ti. Therefore, it is expected that both prepared Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound particles with the L1<sub>2</sub> structure will become favorable heterogeneous nucleation sites for an aluminum cast. With the above in mind, Al-L1<sub>2</sub>-type Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiners are fabricated by the SPS method, and the effects of the fabricated refiners on the grain refining performance of a pure aluminum cast are studied.

Figures 11(a) and 11(b) show the XRD patterns of the fabricated novel refiners with crushed and gas-atomized Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles, respectively. The X-ray diffraction studies have shown the presence of an L1<sub>2</sub>-type intermetallic compound phase along with aluminum in the refiners, although large peaks of aluminum are found in these figures. Hence, the L1<sub>2</sub>-type intermetallic compound phase does not change into other phases during the sintering.

Figures 12(a) and 12(b) show the microstructures of the fabricated novel refiners with crushed and gas-atomized L1<sub>2</sub>-type  $Al_{2.7}Fe_{0.3}Ti$  particles, respectively. It is seen from these figures that the granular or spherical particles are successfully embedded within the aluminum matrix homogeneously, which can be achieved by the SPS method.

The magnified microstructures of crushed and gas-atomized particles in the novel refiners are shown in Figs. 13(a) and 13(b), respectively. It is visible from cross-sectional observations that the gas-atomized particles contain a mesh-shaped second phase, while no such second phase is found in the crushed particles. This may be evidence of the fragmentation behavior of the arc-melted intermetallic compound sample, caused by crushing with a hammer. Namely, fragmentation occurs across the secondary phase, and as a result, the secondary phase exists not in the inside of the crushed particle but on its

surface. EDS analysis indicates that the concentration of aluminum in the matrix (points 1 and 3) is more than 99.6 at.%, while the chemical compositions of points 2, 4, and 5 are 62.3 at.% Al, 10.9 at.% Fe, and 26.9 at.% Ti, 64.4 at.% Al, 9.2 at.% Fe, and 26.4 at.% Ti, and 61.1 at.% Al, 23.2 at.% Fe, and 15.7 at.% Ti, respectively. The chemical composition of the secondary phase observed in the gas-atomized particles is similar to that in the arc-melted sample, *i.e.*, crushed particles. Another notable feature observed in Fig. 13 is that no reaction between the Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound and the aluminum matrix is found at the interface, even though the refiners were fabricated by the sintering route. It can be concluded that the Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound particles can be successfully embedded in the aluminum matrix by SPS without any reaction.

#### 4.4 Grain refining performance of AI-L12-type AI2.7Fe0.3Ti refiners

By using the novel Al-10 vol% L1<sub>2</sub>-type Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiners, the grain refining performance was studied, and results are shown in Figs. 14 and 15. Figures 14(b)-14(f) show the macrostructures of the aluminum cast refined by a refiner with crushed particles, where the holding times are 0, 300, 600, 900, and 1200 s, respectively. For comparison, the macrograph of an unrefined pure aluminum sample cast is also shown in Fig. 14(a). The aluminum cast without a refiner has coarse and inhomogeneous grains, as shown in Fig. 14(a), and the average grain size is about 3690  $\mu$ m. In contrast, the average grain size is smaller and the grains are more homogeneous in the aluminum cast with the Al-L1<sub>2</sub>-type Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti grain refiner, although the columnar microstructure remains in the outer region of the cast. In this manner, the L1<sub>2</sub> type Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles can become favorable heterogeneous nucleation sites for the aluminum cast.

The photomacrographs of an aluminum grain refined by the fabricated refiner containing gas-atomized particles are shown in Fig. 15. The holding times shown in Figs. 15(a)-15(h) are 0, 120, 210, 300, 390, 600, 900, and 1200 s, respectively. A comparison of Figs. 14 and 15 shows that the grain refining efficiency of the refiner with gas-atomized particles is clearly superior to that with crushed particles. 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. Fading in the grain refinement performance was noted after a holding time of 900 s.

Quantitative analysis of the average grain size is carried out and the results are shown in Fig. 16 as a function of holding time. As shown in Fig. 16, again we can say that the superior grain refining efficiency is found for the refiner with gas-atomized particles compared with the refiner with crushed particles. This is because the surfaces of the crushed particles are covered by the retained secondary phase, which may lead to worse disregistry, while in the case of the gas-atomized particles, the secondary phase is mainly located inside the particles. The grain size of the sample cast with the refiner reaches a minimum at 600 s and then has an ascending trend with holding time. The chemical compositions of Al-10 vol% Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti and molten aluminum with refiners used in this study are Al-0.82 at.% Fe-2.73 at.% Ti and Al-0.0064 at.% Fe-0.021 at.% Ti, respectively. Therefore, the Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound phase cannot exist within the aluminum matrix in equilibrium, and this may result in the fading behavior.

#### 4.5 Aging of Al-10 vol% Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiner

To discuss the above fading behavior, the Al-10 vol% Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiner with gas-atomized particles (1.2 g) is heated at 750 °C under ambient atmosphere, and then air-cooled. Figure 17 shows SEM micrographs of the refiner heat-treated (aged) at 750 °C for 90 s. As seen, the spherical particles keep their original shape. The chemical compositions of points 1, 2, and 3 are 62.0 at.% Al, 7.9 at.% Fe, and 30.2 at.% Ti, 62.2 at.% Al, 14.2 at.% Fe, and 23.2 at.% Ti, and 64.8 at.% Al, 8.2 at.% Fe, and 27.1 at.% Ti, respectively, while point 4 is pure aluminum. Although some scatter was found for the chemical composition of particles, the particles still have a stoichiometric composition of Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti. No notable reaction could be observed by heating for 90 s, and the L1<sub>2</sub>-type stoichiometric Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles still remain within the refiner.

Prolonged heat treatment causes the microstructural evolution. SEM micrographs of the refiner heat-treated at 750 °C for 510 s are shown in Fig. 18. As can be seen from this figure, the particles have a core and mantle microstructure. The chemical compositions of the core regions, *i.e.*, points 1 and 5, are 63.2 at.% Al, 10.6 at.% Fe, and 26.2 at.% Ti, and 65.3 at.% Al, 8.5 at.% Fe, and 26.2 at.% Ti, respectively. Therefore, the core region still keeps a stoichiometric  $Al_{2.7}Fe_{0.3}Ti$  phase. It is worth mentioning here that the mantle region is not a stoichiometric  $Al_{2.7}Fe_{0.3}Ti$  phase, and that the chemical

compositions of points 2, 4 and 6 are 73.2 at.% Al, 7.4 at.% Fe, and 19.4 at.% Ti, 78.8 at.% Al, 4.5 at.% Fe, and 16.7 at.% Ti, and 74.2 at.% Al, 6.0 at.% Fe, and 19.8 at.% Ti, respectively, while the chemical composition of point 7 is 74.7 at.% Al, 1.3 at.% Fe, and 24.0 at.% Ti, which can be identified as Al<sub>3</sub>Ti. On the other hand, since the chemical compositions of points 3 and 8 are 99.7 at.% Al and 0.3 at.% Ti, and 99.8 at.% Al and 0.2 at.% Ti, respectively, the matrix is  $\alpha$ -Al. In this manner, the decomposition of the Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti phase is notable.

Further heat treatment causes the complete decomposition of the  $Al_{2.7}Fe_{0.3}Ti$  phase. Figure 19 shows SEM micrographs of the refiner after heat treatment at 750 °C for 1 h. The chemical compositions are 76.7 at.% Al, 0.4 at.% Fe, and 22.9 at.% Ti for point 1, 79.3 at.% Al and 20.7 at.% Fe for point 2, and 73.6 at.% Al and 26.4 at.% Fe for point 3, while point 4 is pure aluminum. Judging from the Gibbs phase rule (if the number of components is three, and the number of phases is four, the system is invariant), the Al-20 at.% Ti phase found here may metastable. Therefore, the  $Al_{2.7}Fe_{0.3}Ti$  phase is decomposed into  $Al_3Ti$  and  $Al_3Fe$  during the heat treatment. It is reported that the shape of the  $Al_3Fe$  intermetallic compound that appeared in the Al-Fe binary alloy changes with processing, and there are granular, rectangular, barlike bulky, sticklike, bulky sharp edge, or fibrous particles.<sup>39)</sup> In this study, two-dimensionally fibrous particles, similar to a binary alloy, are observed in the heat-treated Al-Ti-Fe ternary alloy.

#### 4.6 Grain refining performance of Al- Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiner with smaller particles

It is well accepted that the number of heterogeneous nucleation sites strongly affects the grain refining performance, and a larger number results in a better grain refining performance.<sup>18,40)</sup> However, on the other hand, it is expected that worse grain refining performance will appear in the Al-Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiner with smaller particles. This is because the easier decomposition of Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles occurs for smaller particles with a larger interface area, which accelerates the fading behavior. The grain refining performance of the Al-Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiner with smaller particles is, therefore, studied.

The Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles used here were prepared by gas atomization. After sieving into 32-75  $\mu$ m, the Al-10 vol% Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiner with smaller particles was fabricated by SPS. The grain refining performance of the fabricated refiner with smaller particles was

also studied in the same manner as previous experiments.

Photomacrographs of casts refined by the Al-10 vol%  $Al_{2.7}Fe_{0.3}Ti$  refiner after holding times of 0, 120, 300, 390, 480, and 600 s are shown in Figs. 20(a)-20(f), respectively. As seen, limited grain refining performance could be observed for the Al-10 vol%  $Al_{2.7}Fe_{0.3}Ti$  refiner with smaller particles. The average grain sizes of casts with holding times of 0, 120, 300, 390, 480, and 600 sec are 1159, 1025, 1224, 889, 750, and 1116 µm, respectively. The fading starts after the holding time of 480 s, which is earlier than that in the case of larger particles. Therefore, it can be concluded that the thermal stability of the heterogeneous nucleation site is another issue that affects the grain refining performance.

## 5. Conclusions

Novel refiners, in which L1<sub>2</sub>-type Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles are dispersed, have been fabricated by spark plasma sintering (SPS) in this work. The Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles were prepared by crushing of a bulk intermetallic compound or gas atomization. The obtained results are summarized as follows.

1) Spherical and stoichiometric  $Al_{2.7}Fe_{0.3}Ti$  particles with a highly symmetric  $L1_2$  structure could be directly prepared by gas atomization.

2) Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound particles can be successfully embedded in an aluminum matrix by SPS without any reaction or transformation.

3) The L1<sub>2</sub>-type Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles can become favorable heterogeneous nucleation sites for the aluminum cast, since the disregistry between Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti and aluminum is small.

4) Superior grain refining efficiency is found in the refiner with gas-atomized particles compared with the refiner with crushed particles, since the surfaces of crushed particles are covered by the retained second phase, while the second phase in gas-atomized particles is mainly located inside the particles.

5) The thermal stability of the heterogeneous nucleation site is another issue that affects the grain refining performance.

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## **Figure Captions**



**Fig. 1.** (Color online) Schematic illustrations of Al with fcc structure (a), Al<sub>3</sub>Ti with  $D0_{22}$  structure (b), and Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti with L1<sub>2</sub> structure (c).



**Fig. 2.** (Color online) Model structure of Al<sub>3</sub>Ti platelet (a), area ratio (b), and average disregistry value (c) as a function of aspect ratio of Al<sub>3</sub>Ti platelet.



Fig. 3. (Color online) Aluminum-rich corner of Al-Ti-Fe ternary equilibrium phase diagram.<sup>35,36)</sup>



**Fig. 4.** (Color online) Flow diagram for fabrication process of novel refiner with L1<sub>2</sub>-type Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti intermetallic compound particles.



Fig. 5. (Color online) Flow diagram of grain refining performance test.



**Fig. 6.** (Color online) XRD profiles of arc-melted Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti samples before (a) and after (b) homogenization treatment.



**Fig. 7.** (Color online) SEM photomicrographs of  $Al_{2.7}Fe_{0.3}Ti$  samples prepared by arc melting before homogenization treatment (a) and after homogenization treatment (b).



**Fig. 8.** (Color online) SEM photomicrograph of crushed  $Al_{2.7}Fe_{0.3}Ti$  particles prepared from arc-melted bulk sample.



**Fig. 9.** (Color online) XRD profile of gas-atomized Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles.



**Fig. 10.** (Color online) SEM photomicrograph showing gas-atomized Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles.



**Fig. 11.** (Color online) XRD profiles of Al-10 vol% Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiners with crushed particles (a) and gas-atomized particles (b).



**Fig. 12.** (Black and White) SEM photomicrographs showing Al-10 vol%  $Al_{2.7}Fe_{0.3}Ti$  refiners with crushed particles (a) and gas-atomized particles (b).



**Fig. 13.** (Color online) Magnified SEM microstructures of crushed particle (a) and gas-atomized particle (b) in novel Al-10 vol%  $Al_{2.7}Fe_{0.3}Ti$  refiners.



**Fig. 14.** (Black and White) Grain refining performance test results of the novel Al-10 vol%  $Al_{2.7}Fe_{0.3}Ti$  refiner with crushed particles after holding times of 0 (b), 300 (c), 600 (d), 900 (e), and 1200 (f) s. A photomacrograph taken before addition (a) is also shown.



**Fig. 15.** (Black and White) Grain refining performance test results of the novel Al-10 vol%  $Al_{2.7}Fe_{0.3}Ti$  refiner with gas-atomized particles after holding times of 0 (a), 120 (b), 210 (c), 300 (d), 390 (e), 600 (f), 900 (g), and 1200 (h) s.



**Fig. 16.** (Color online) Average grain size of the samples with different holding times after addition of novel Al-10 vol% Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiners.



**Fig. 17.** (Color online) SEM microstructures of Al-10 vol% Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiner with gasatomized particles heat-treated at 750 °C for 90 s.



**Fig. 18.** (Color online) SEM microstructures of Al-10 vol% Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiner with gas-atomized particles heat-treated at 750 °C for 510 s.



**Fig. 19.** (Color online) SEM microstructures of Al-10 vol% Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiner with gas-atomized particles heat-treated at 750 °C for 1 h.



**Fig. 20** (Black and White) Photomacrographs of casts refined by the Al-10 vol% Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti refiner after holding times of 0 (a), 120 (b), 300 (c), 390 (d), 480 (e), and 600 (f) s. Al<sub>2.7</sub>Fe<sub>0.3</sub>Ti particles were prepared by gas atomization and then sieved into the size range of 32-75  $\mu$ m.