Review, Role of L1$_2$ Modified (Al$_{1-x}$Me$_x$)$_3$Ti Intermetallic Compounds on Heterogeneous Nucleation of Alpha Aluminum Grains

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Abstract. Al$_3$Ti intermetallic compound with the tetragonal D0$_{22}$ structure undergoes a phase transformation to the high-symmetry L1$_2$ cubic structure by addition of third elements, Me. The lattice constants of some L1$_2$ modified (Al$_{1-x}$Me$_x$)$_3$Ti intermetallic compounds are closed to that of alpha aluminum. Therefore, it is expected that the addition of L1$_2$ modified (Al$_{1-x}$Me$_x$)$_3$Ti intermetallic compound particles show good grain refining performance of cast aluminum. In this paper, our recent results on novel refines containing heterogeneous nucleation site particles of L1$_2$ modified (Al$_{1-x}$Me$_x$)$_3$Ti intermetallic compounds have been reviewed.

1 INTRODUCTION

Equiaxed grain structure ensures uniform mechanical properties, reduced ingot cracking, improved feeding to eliminate shrinkage porosity, distribution of secondary phases and microporosity on a fine scale, improved machinability and cosmetic features. The grain refining inoculants commonly used in the aluminium industry are usually master alloys of Al-Ti or Al-Ti-B [1]. Grain refinement of aluminum and its alloys by the addition of Al-Ti-B refiners to liquid melt prior to casting is a common practice in order to achieve a fine equiaxed grained microstructure in a casting which otherwise solidifies usually with coarse columnar grain structure [2]. Figure 1 shows microstructural feature of Al-Ti-B refiner. As can be seen, the Al-Ti-B refiner contains TiB$_2$ heterogeneous nucleation site particles and platelet-shaped Al$_3$Ti heterogeneous nucleation site particles [3-8] with D0$_{22}$ structure ($a = 0.3851$ nm, $c = 0.8608$ nm). It is well accepted that the effective heterogeneous nucleation site particles have better lattice matching with the solidified alpha aluminium ($a = 0.4049$ nm).

It is also known that the Al$_3$Ti intermetallic compound with the tetragonal D0$_{22}$ structure can undergo a phase transformation into (Al$_{1-x}$Me$_x$)$_3$Ti intermetallic compounds with L1$_2$ cubic structure by addition of third elements of Me [9-11]. Moreover, the lattice constant of some L1$_2$ modified (Al$_{1-x}$Me$_x$)$_3$Ti intermetallic compounds is closed to that of alpha aluminum, e.x., the lattice constants of L1$_2$ modified Al$_{1-x}$Fe$_{0.5}$Ti, Al$_{1-x}$Ni$_{0.5}$Ti and Al$_{2-x}$Cu$_x$Ti intermetallic compounds are $a = 0.393$ nm, $a = 0.394$ nm and $a = 0.3927$ nm, respectively. An L1$_2$ modified Al$_{2-x}$Cu$_x$Ti intermetallic compound can be formed at the Cu/Al$_3$Ti interface in the Cu/Al$_3$Ti diffusion couple specimen heated at elevated temperature as shown in Fig. 2 [12].

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Fig. 1. SEM micrograph of Al-Ti-B refiner.

Fig. 2. Micrographs showing the interface in the Cu/Al$_3$Ti diffusion couple specimen heated at 600 °C for 4 h [12].

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Therefore, it is expected that these intermetallic compounds show good grain refining performance. In our studies [13-17], refining performance of novel refines with L12 modified Al2-xCu3-xTi, Al2-xFe3-xTi and Al2-xNi3-xTi particles are studied. In this paper, our recent results on novel refines containing heterogeneous nucleation site particles of L12 modified (Al1-xMe3)2 Ti intermetallic compounds have been reviewed.

2 LATTICE MATCHING

It is important to describe the lattice matching between heterogeneous nucleation site particles and alpha aluminum, because an effective refiner contains heterogeneous nucleation site particles with a better lattice matching with the solidified phase. One of the most famous equations is eq. (1) proposed by Turnbull and Vonnegut [18].

$$\delta = \left(\frac{a_s - a_c}{a_c}\right) \times 100 (\%) \quad (1)$$

where $\delta$ is called as disregistry between the heterogeneous nucleation site and the solidified phase, $a_s$ and $a_c$ are the lattice parameters of the heterogeneous nucleation site particles and solidified phase without deformation, respectively. However, Al6Ti has the low-symmetry tetragonal D022 structure. Therefore, eq. (1) must be modified for application to two-dimensional lattices. The plane disregistry was proposed by Bramfitt [19], and calculated by

$$\delta^{(\text{uvw})}_{(\text{hkl})} = \frac{1}{3} \sum_{\text{uvw}} \left| \frac{d[\text{uvw}]^s \cos \theta - d[\text{uvw}]^l}{d[\text{uvw}]^l} \right| \times 100 \% \quad (2)$$

where (hkl)s and (hkl)l are the low-index planes of the heterogeneous nucleation site and solidified phase, and [uvw]s and [uvw]l are the low-index orientations on (hkl)s and (hkl)l, respectively. Moreover, $d[\text{uvw}]^s$, and $d[\text{uvw}]^l$ are the interatomic spacing distances along [uvw], and $\theta$ is the angle between [uvw]s and [uvw]l.

However, it is unclear why three in-plane directions are considered when evaluating the plane disregistry. Moreover, there are some possibilities to select the third axis [15]. Kato et al. have proposed parameter M [20], which is approximately proportional to the specific misfit strain energy. In this study, parameter M defined by eq. (3) will be adopted to discuss the effective heterogeneous nucleation site [21,22].

$$M = \varepsilon_1^2 + \varepsilon_2^2 + (2/3)\varepsilon_1\varepsilon_2 \quad (3)$$

In eq. (3), $\varepsilon_1$ and $\varepsilon_2$ are the principal misfit strains calculated from the principal distortions. The parameter $M$ values of some crystallographic orientation relationships between Al6Ti and aluminum are listed in Table 1. As can be seen, different planes of Al6Ti show different parameter M values. In case of L12 modified (Al1-xMe3)2 Ti intermetallic compounds, better lattice matching between the heterogeneous nucleation site and the solidified phase can be achieved, as shown in Table 1.

Table 1. Parameter M values between heterogeneous nucleation site particles and aluminum.

| Orientation Relationship | M value  |
|--------------------------|----------|
| (100)Al/ // (100)Al     | 4.31 x 10^4 |
| (001)Al/ // (0001)Al   | 6.38 x 10^4 |
| (110)Al/ // (110)Al    | 4.31 x 10^4 |
| (112)Al/ // (111)Al   | 2.24 x 10^3 |
| (0001)Al // (111)Al   | 9.95 x 10^3 |
| (hk\ell)Al//Cu2Ti/ // (hk\ell)Al   | 2.57 x 10^3 |
| (hk\ell)Al//Fe2Ti/ // (hk\ell)Al   | 2.50 x 10^3 |
| (hk\ell)Al//Ni2Ti/ // (hk\ell)Al   | 1.93 x 10^2 |

3 EXPERIMENTAL METHODS

3.1 Fabrication of Refines

Two types of particles, i.e., prepared by mechanical crushing of bulk L12 modified (Al1-xMe3)2Ti intermetallic compounds and directly prepared by gas atomization, were used [13-17]. Hereafter, the particles prepared by the crushing of an arc melted bulk sample and prepared by the gas atomization will be denoted as “crushed particles” and “gas-atomized particles”, respectively. The bulk L12 modified (Al1-xMe3)2Ti intermetallic compound was prepared by an arc melting method under an argon atmosphere. The obtained bulk (Al1-xMe3)2Ti intermetallic compound was homogenized at elevated temperature, and then crushed into fine particles by a hammer. Both crushed and gas-atomized particles were sieved into the size of 75-150μm. The sieved (Al1-xMe3)2Ti particles are mixed with pure aluminum particles (99.99%, 106-180μm), where the volume fraction of (Al1-xMe3)2Ti particles was 10 vol%, 20 vol%, 30 vol% and 40 vol%. Sintering of the mixed powder using a spark plasma sintering (SPS) [23-25] was performed at 500 °C for 5 min under an applied stress of 45 MPa. Flow diagram for fabrication process of the refiners with L12 modified (Al1-xMe3)2Ti particles is shown in Fig. 3.

3.2 Refining Performance

To evaluate the grain refinement performance of the fabricated refiners containing L12 modified (Al1-xMe3)2Ti heterogeneous nucleation site particles, following casting experiments were conducted. Commercially pure aluminum ingot (99.99%, 148.8 g for 10 vol% refiner, 149.4 g for 20 vol% refiner, 149.6 g for 30 vol% refiner, and 149.7 g for 40 vol% refiner) was melted in an alumina crucible using the electrical resistance furnace at 750 °C in argon gas atmosphere. The mass fractions of the refiners as additives were 0.8%, 0.4%, 0.27% and 0.2% for the 10, 20, 30, and 40 vol% refiners, respectively, so that the total amount of
L12 modified (Al1−xMex)3Ti particles within the melt was the same. After the addition of the refiner into the melt, the melt was stirred with a rod for 30 s, after which no further stirring was carried out. The melt was cast into a cylindrical steel mold of 45mm inner diameter, 70mm outer diameter, and 70mm height after a holding time. Here, the holding time is the time interval from when the stirring was finished to when the melt was cast into the mold. The classical metallographic route was used to prepare the samples for microstructural analysis. The specimen for grain structure examination was horizontally cut from the bottom part (5 mm from the bottom) of each cast sample. The macrostructural and microstructural features of the casts were studied by optical microscopy or scanning electron microscopy after etching the polished surface with a 10% hydrofluoric acid aqueous solution. Flow diagram of grain refining performance test is summarized in Fig. 4.

Fig. 3. Flow diagram for fabrication process of the refiners with L12 modified (Al1−xMex)3Ti particles.

Fig. 4. Flow diagram for casting experiment of the refiners with L12 modified (Al1−xMex)3Ti particles.

4 RESULTS AND DISCUSSION

4.1 Refined by Al-10 vol%Al2.7Fe0.3Ti

The SEM photomicrographs of Al-10 vol% Al2.7Fe0.3Ti refiners with homogenized crushed particles and gas-atomized particles are shown in Figs. 5 (a) and (b), respectively [13]. It is seen that reaction between the Al2.7Fe0.3Ti intermetallic compound and the aluminum matrix is not found at the interface, even though the refiners were fabricated by the sintering route. However, heating of Al-10 vol% Al2.7Fe0.3Ti refiners with gas-atomized particles at 750°C for 300s causes microstructural evolution, as shown in Fig. 5 (c) [14]. The particles in the heated Al-10 vol% Al2.7Fe0.3Ti refiners with gas-atomized particles have a core and mantle microstructure, and the chemical compositions of the core region and mantle region are a titanium rich Al2.7Fe0.3Ti phase and Al3(Ti,Fe), respectively.

It is also visible from cross-sectional observations of gas-atomized particles (Fig. 5 (b)) that the gas-atomized particles contain a mesh-shaped secondary phase. However, such secondary phase is not found in the inside of the crushed particle as shown in Fig. 5 (a). Instead, secondary phase was found on the surface of
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. Anyway, it can be concluded that the L12 modified Al23Fe0.5Ti intermetallic compound particles can be successfully embedded in the aluminum matrix by SPS without any reaction.

![Crushed Al23Fe0.5Ti Particle](image1)

![Gas-Atomized Al23Fe0.5Ti Particle](image2)

![Al23Cu0.5Ti Refiner](image3)

By using the Al-10 vol% Al23Fe0.5Ti refiners with homogenized crushed particles and gas-atomized particles, the casting experiments are carried out, and the results are shown in Figs. 6 (b) and (c), respectively [13]. A photomicrograph taken before addition is shown in Fig. 6 (a). It is seen from Figs. 6 (a) to (c) that the higher grain refining efficiency is found for the refiner with gas-atomized particles compared with the refiner with homogenized crushed particles. This is because the secondary phase in the gas-atomized particles is mainly located inside the particles, while that in the crushed particles located on the surface of the particles, which may lead to large parameter value of heterogeneous nucleation site particles.

The lattice matching between the particles and the solidified phase is critical to the effectiveness of the heterogeneous nucleation site. To discuss the effects of the lattice matching on the grain refining performance, the grain refining performance of the unhomogenized crushed refiner with a certain amount of the secondary phase on the surface of particles and heated gas-atomized refiner with partially decomposed Al23Fe0.5Ti particles are studied. The results are also shown in Figs. 6 (d) and (e), respectively [14]. As can be seen, the grain-refining efficiency of the unhomogenized crushed refiner or heated gas-atomized refiner is inferior to that of the homogenized crushed refine or unheated refiner, respectively. This is because the surfaces of the unhomogenized crushed particles and heated particles are covered with secondary phase and mantle phases, which may have a lower lattice matching. Different refining performance characteristics appeared for refiners with different phases, even though the chemical compositions of the refiners themselves were the same.

![Grain refining performance test results of the Al-10 vol% Al23Fe0.5Ti refiner](image4)

**4.2 Refined by Al-(10-40)vol%Al23Cu0.5Ti**

SEM micrographs of the Al-10vol%, 20 vol%, 30 vol% and 40 vol% Al23Cu0.5Ti refiners with gas-atomized particles are shown in Figs. 7 (a) to (d), respectively [16]. Spherical shaped gas-atomized particles are homogeneously distributed in the aluminum matrix, even when there is a high volume fraction of refiner. The SPS process thus successfully produced fully dense refiners consisting of a high volume fraction of Al23Cu0.5Ti particles embedded in the aluminum matrix.
The refiners containing different amounts of heterogeneous nucleation site particles showed differences in the grain refining performance with the holding time, even though the total amount of Al$_2$Cu$_3$Ti particles within the melt was the same. The best holding times for the 10 vol%, 20 vol%, 30 vol%, and 40 vol% atomization refiners were determined to be 300 s, 420 s, 540 s and 600 s, respectively. The results of grain refinement performance tests for the 10 vol%, 20 vol%, 30 vol% and 40 vol% atomization refiners with holding times of 300 s, 420 s, 540 s and 600 s are shown in Figs. 8 (a) to (d), respectively [16]. Longer holding time is required to achieve a uniform dispersion of Al$_2$Cu$_3$Ti particles in the melt for the refiners with high volume fraction of heterogeneous nucleation site particles. In this way, fading of the grain refinement effect occurs slower when the volume fraction of heterogeneous nucleation site particles increased.

4.3 Refined by Al-10 vol%Al$_2$Ni$_{0.3}$Ti

The minimum grain size can be achieved for the cast refined by the Al-10 vol% Al$_2$Ni$_{0.3}$Ti refiner after the holding time of 690 s, as shown in Fig. 9 (a) [15]. This size is about one ninth that of the unrefined cast. However, a lower grain refinement efficiency is found for the Al-10 vol% Al$_2$Ni$_{0.3}$Ti refiner than for the Al-10 vol% Al$_2$Fe$_{0.3}$Ti refiner shown in Fig. 6 (c). This phenomenon cannot be explained by simple lattice matching between the heterogeneous nucleation site and the solidified phase, since the $M$ value between Al$_2$Ni$_{0.3}$Ti and aluminum, $M = 1.93 \times 10^3$, is smaller than that between Al$_2$Fe$_{0.3}$Ti and aluminum, $2.50 \times 10^3$.

Next, the thermal stability of the Al$_2$Ni$_{0.3}$Ti phase in the Al-10 vol% Al$_2$Ni$_{0.3}$Ti refiner was investigated. For this purpose, the Al-10 vol% Al$_2$Ni$_{0.3}$Ti refiner was heated at 750 °C for 300 s, and result is shown in Fig. 9 (b) [15]. It is seen that heating for a short time causes the decomposition of the Al$_2$Ni$_{0.3}$Ti phase into Al$_1$Ti and Al$_1$Ni phases. On the other hand, in the case of the heated Al-10 vol% Al$_2$Ni$_{0.3}$Ti refiner, the particles have a core and mantle microstructure as shown in Fig. 5 (c), and the chemical composition of the core region is still Al$_2$Fe$_{0.3}$Ti phase. By comparing the decomposition phenomena in the Al-10 vol% Al$_2$Ni$_{0.3}$Ti and Al-10 vol% Al$_2$Fe$_{0.3}$Ti refiners, it is found that the thermal stability of the Al$_2$Ni$_{0.3}$Ti phase in the refiner is lower than that of the Al$_2$Fe$_{0.3}$Ti phase. This may be the reason for the relatively lower grain refinement performance of the Al-10 vol% Al$_2$Ni$_{0.3}$Ti refiner. In this way, the thermal stability of the heterogeneous nucleation site also affects the grain refinement performance.

![Fig. 7. SEM micrographs of fabricated (a) Al-10vol%, (b) 20 vol%, (c) 30 vol% and (d) 40 vol% Al$_2$Cu$_3$Ti refiners with gas-atomized particles [16].](image)

![Fig. 8. Macrostructures of aluminum casts refined with (a) Al-10vol%, (b) 20 vol%, (c) 30 vol% and (d) 40 vol% Al$_2$Cu$_3$Ti refiners with gas-atomized particles by hold times of 300 s, 420 s, 540 s and 600 s, respectively [16]. The levels of addition were 0.8%, 0.4%, 0.27% and 0.2% for the 0, 20, 30, and 40 vol% atomization refiners, respectively, so that the total amount of Al$_2$Cu$_3$Ti particles within the melt was the same.](image)

![Fig. 9. (a) Grain refinement performance test result of the Al-10 vol% Al$_2$Ni$_{0.3}$Ti refiner after holding time of 690 s. (b) Microstructure of Al-10 vol% Al$_2$Ni$_{0.3}$Ti refiner heated at 750 °C for 300 s [15].](image)
5 CONCLUSIONS

In this paper, the role of L12 modified (Al1−xMe3)yTi phases on the heterogeneous nucleation of alpha aluminum primary crystal was reviewed. The refiners with L12 modified (Al1−xMe3)yTi particles prepared by gas atomization or crushing were fabricated by SPS. The results are summarized as follows.

1) L12 modified (Al1−xMe3)yTi particles can be prepared by mechanical crushing of bulk L12 modified (Al1−xMe3)yTi intermetallic compounds and directly prepared by gas atomization. The L12 modified (Al1−xMe3)yTi particles embedded in an aluminum matrix do not react with aluminium nor transformation into stable phases during sintering.

2) The aluminum cast without the refiner has coarse and inhomogeneous grains. On the other hand, the grain size is smaller in the aluminum cast with the Al-(Al1−xMe3)yTi refiners. Therefore, L12 modified (Al1−xMe3)yTi particles can act as effective heterogeneous nucleation sites for primary aluminum in the solidification process.

3) Different refining performance characteristics appeared for refiners with different phases, even though the chemical compositions of the refiners themselves were the same. This is because the lattice matching between heterogeneous nucleation site particles and solidified aluminum is critical to obtain finer grain structures for aluminum casts.

4) Although L12 modified Al27Ni37Ti phase has small M value, the grain refinement performance of Al-10 vol% Al27Ni37Ti refiner is relatively weaker than expected. This is because the Al-10 vol% Al27Ni37Ti refiner does not have a high thermal stability. The thermal stability of the heterogeneous nucleation site also affects the grain refinement performance.

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