

Effect of casting and homogenizing treatment conditions on the formation of Al–Fe–Si intermetallic compounds in 6063 Al–Mg–Si alloys

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The effect of casting and homogenizing treatment conditions on the formation of several Al–Fe–Si intermetallic compounds in 6063 aluminum alloy was investigated using X-ray diffraction and transmission electron microscopy (TEM). The four kinds of alloys containing 0.1 to 0.5 mass% Fe were melted and then cooled at three different cooling rates ranging from 0.06 to 50 K/s, following the homogenization at 858 K for 54 ks and 2400 ks. The Al–Fe–Si compound particles were extracted from the alloy ingots using the thermal phenol method. The as-cast 0.1 mass% Fe ingot obtained at the casting cooling rate of 0.06 K/s had a largest amount of the β phase among the ingots investigated. When this ingot was homogenized at 858 K for 54 ks and 2400 ks, the amount of the β phase decreased, while that of the α' phase increased. On the other hand, the as-cast 0.5 mass% Fe ingot obtained at the casting cooling rate of 50 K/s had the largest amount of the α phase among the ingots investigated. When this ingot was homogenized at 858 K for 54 ks, a large amount of the α phase remained. However, the homogenization at 858 K for 2400 ks resulted in the transformation of the α phase to the α' phase. The main phase in the as-cast 0.2 mass% Fe ingot obtained at the casting cooling rate of 5 K/s, close to the industrial cooling rates, was the β phase. The β phase gradually decreased, and the relative amounts of the α and α' phases increased during homogenization at 858 K for 54 ks. Furthermore, almost all of the Al–Fe–Si intermetallic compounds were transformed into the α' phase in the ingots homogenized at 858 K for 2400 ks. © 1999 Kluwer Academic Publishers

1. Introduction

The formation of Al–Fe–Si intermetallic compounds in commercial 1000 series aluminum alloys have been studied extensively [1–4]. Depending upon the alloy composition and solidification condition, various types of the Al–Fe–Si intermetallic compounds are formed. On the other hand, for the commercial 6000 series Al–Mg–Si alloys, there are only reports that the β phase [5] formed in the as-cast ingots is transformed into the α phase [6] by applying suitable homogenizing treatments [7, 8]. The systematic studies have not been carried out of the formation of Al–Fe–Si intermetallic compounds in the commercial Al–Mg–Si alloys during casting and homogenizing.

Al–Fe–Si intermetallic compound particles in the Al–Mg–Si alloys have been identified by optical microscopy observation on the basis of the difference of colors and shapes of the intermetallic compounds in the specimens etched in a 0.5% HF solution [7, 9]. Black

and gray Al–Fe–Si particles are identified as the β and α phases, respectively. Moreover, needle or plate-like particles are identified as the β phase, while chunky, Chinese script or rounded particles are α phase. However, because more than 10 types of Al–Fe–Si intermetallic compounds have been reported [1, 10–14], it is very difficult to identify all of the compounds by this method.

In the present study, the Al–Fe–Si intermetallic compounds formed in the Al–Mg–Si alloys containing different amounts of iron have been examined using transmission electron microscopy. The influence of the casting cooling rate and homogenizing treatment condition on the type of the Al–Fe–Si intermetallic compounds formed has also been investigated.

2. Experimental procedure

Four kinds of Al–Mg–Si alloys containing 0.1, 0.2, 0.3, and 0.5% iron, based on 6063 aluminum alloy, were

TABLE I Chemical composition of specimens (mass %)

6063 alloy	Mg	Si	Fe	Cu	Ti	Mn	Cr	Zn	Al
0.1%Fe	0.49	0.43	0.09	0.002	0.001	0.001	0.000	0.001	bal.
0.2%Fe	0.49	0.42	0.18	0.001	0.001	0.001	0.000	0.001	bal.
0.3%Fe	0.49	0.42	0.33	0.001	0.001	0.000	0.000	0.002	bal.
0.5%Fe	0.52	0.40	0.50	0.002	0.000	0.003	0.000	0.001	bal.

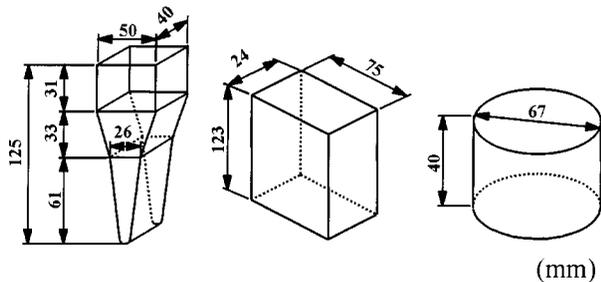


Figure 1 Schematic representation of the ingots.

prepared. The chemical compositions of the alloys are given in Table I. They were prepared by melting in air using 99.99% pure aluminum ingots, 99.9% pure magnesium ingots, 99.9% pure silicon ingots, and Al-48.1-51.3%Fe alloys. The casting was carried out at three different cooling rates. Slowly solidified ingots were prepared by furnace cooling in the cylindrical crucible furnace with an internal diameter of 67 mm. The ingots obtained were 40 mm in length. The center parts of the ingots (25 mm in length) were used as specimens by cutting off both of the sides. The ingots prepared at the intermediate cooling rate were cast into the permanent mold with a bottom area of 24×75 mm and with a height of 123 mm. The top and bottom 20 mm in length of the ingots were cut off, and the remaining was used as specimens. Rapidly solidified ingots were prepared by casting into V-shaped copper mold, and the tip of the ingots (about 15 mm in length) was used. Schematic representation of each ingot is shown in Fig. 1. About 10 g of specimens was used for homogenizing treatment. The specimens were heated at a rate of 1 K/s to 858 K and maintained at this temperature for 54 ks or 2400 ks in air.

The surface of the specimens was observed by optical microscopy after electropolishing. The Al-Fe-Si intermetallic compound particles formed were extracted from the matrix using the thermal phenol method. The structure of the extracted particles was identified by using a Rigaku RINT 1100 X-ray diffractometer with $\text{CuK}\alpha$ radiation and a TOPCON Co. LTD EM002B transmission electron microscope (TEM) equipped with EDAX facilities. The extracted particles were taken on carbon-coated grids for TEM observation and on glass plates for X-ray measurement.

3. Results

The microstructures of the as-cast 0.3%Fe alloy ingots obtained at the three different cooling rates are shown in Fig. 2. The intermetallic compound particles, observed as dark contrast, are coarse in the slowly solidified ingot

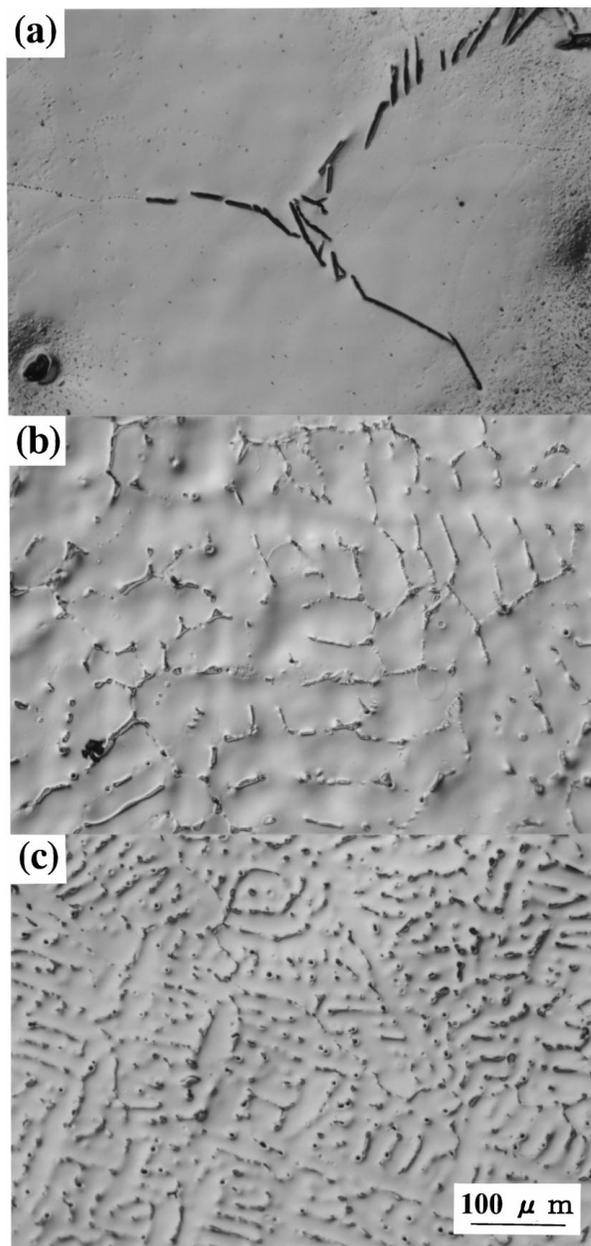


Figure 2 Optical micrographs of the 0.3%Fe as-cast ingots solidified at (a) slow, (b) intermediate, and (c) fast cooling rates.

(Fig. 2a). Their particles and the Al-dendrite cell size (DCS) became smaller as the cooling rate increased. The similar changes in the microstructures were observed irrespective of iron content (0.1~0.5%).

The precise cooling rate of the ingots was measured by using thermocouples. The cooling rates of the ingots solidified at slow, and intermediate cooling rates were about 0.06 and 5 K/s, respectively. The cooling rate of the fast solidified ingots could not be measured because the cooling rate was too fast.

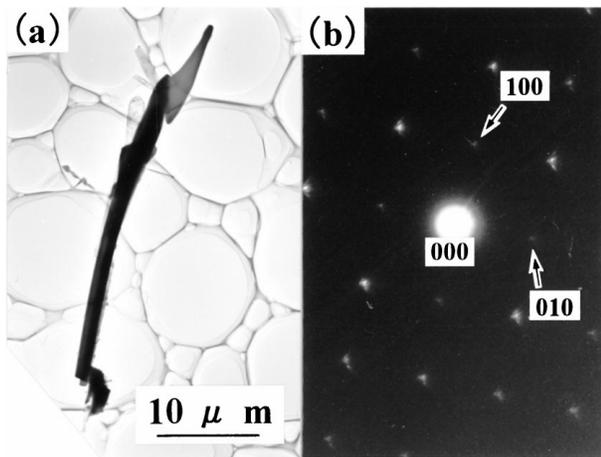


Figure 3 The results of TEM observation of an intermetallic compound particle extracted from the as-cast ingot at the cooling rate of 0.06 K/s. The particle is supported on a microgrid. (a) Bright field image and (b) selected area diffraction pattern. Beam // [001] of monoclinic β -AlFeSi.

The relationship between a secondary dendrite arm spacing (DAS) and cooling rate was reported to be expressed as follows [15]:

$$d = 85R^{-0.38} \quad (1)$$

where d is DAS and R is cooling rate. In order to determine the cooling rate of the fast solidified V-shaped ingots, the secondary dendrite arm spacing (DAS) was used to measure. To obtain the accurate DAS, the observation of the grains with an identical orientation is required, but the grains observed were randomly oriented. Thus, the accurate DAS was not measured. However, the same relationship between DCS and cooling rate as that between the DAS and cooling rate (Equation 1) for the ingots solidified at slow and intermediate cooling rate was found. By applying this relationship between DAS and cooling rate to the fast solidified ingot, the cooling rate of the V-shaped ingots was estimated to be about 50 K/s.

Fig. 3a shows a TEM image of a coarse stick-like Al-Fe-Si compound particle of 40 μm in length extracted from the 0.1%Fe alloy ingot solidified at the cooling rate of 0.06 K/s. The selected area diffraction pattern (SADP) shown in Fig. 3b corresponds to the pattern of the β Al-Fe-Si phase (monoclinic: $a = b = 0.612$ nm, $c = 4.15$ nm, $\beta = 91^\circ$). The incident electron beam direction is parallel to [001]. In the slowly solidified ingots, many intermetallic compound particles were very coarse. Thus, SADP could not be obtained from most of intermetallic compounds, and only a few intermetallic compounds were identified from SADP. Among fifteen intermetallic compound particles observed in the slowly solidified 0.1%Fe ingot, fourteen particles, corresponding to about 93% of the intermetallic compounds, were identified as the β phase, that is, about 93% of Al-Fe-Si intermetallic compounds were the β phase. This percentage was largest among the as-cast ingots examined in this study. This also agrees very well with the results of X-ray investigation. In the slowly solidified ingots, a large amount of the binary Mg-Si intermetallic compound particles, as well as the Al-Fe-Si compound particles, were also observed by TEM.

Fig. 4a shows a TEM image of an intermetallic compound particle extracted from the 0.1%Fe ingot solidified at cooling rate of 0.06 K/s and homogenized at 858 K for 2400 ks. This faceted Al-Fe-Si compound particle is about 10 μm in width and 50 μm in length, and is identified as the α' phase (hexagonal: $a = 1.23$ nm, $c = 2.62$ nm) from the SADP. Many intermetallic compounds in this phase were identified as the α' phase. Fig. 5 shows the change in the relative frequency of Al-Fe-Si phases in the slowly solidified 0.1%Fe ingot with time of homogenizing treatment at 858 K. It is found that the β phase transforms into the α' phase in the slowly solidified ingots during homogenization.

Fig. 6 shows the changes in the relative frequency of Al-Fe-Si phases in the 0.2%Fe ingot solidified at

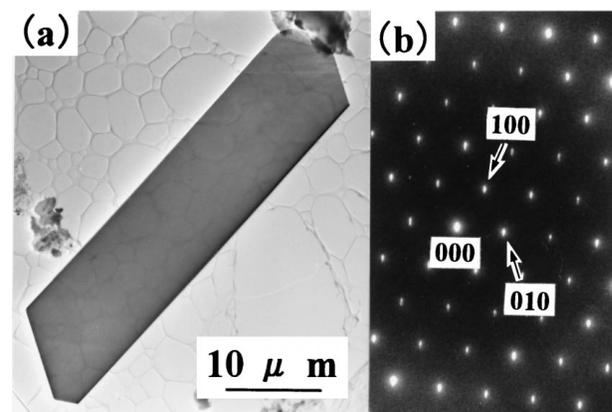


Figure 4 The results of TEM observation of an α' -AlFeSi particle extracted from the 0.1%Fe ingot solidified at the casting cooling rate of 0.06 K/s and homogenized at 858 K for 2400 ks. (a) Bright field image and (b) selected area diffraction pattern. Beam // [001] of the α' phase.

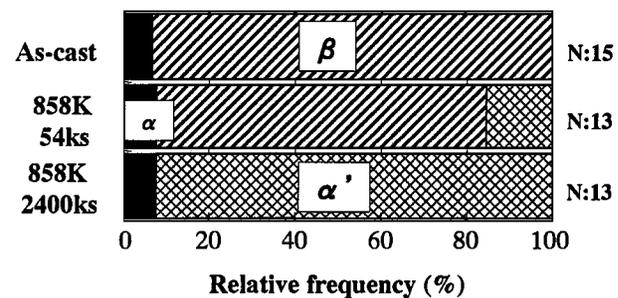


Figure 5 Change in the relative frequency of Al-Fe-Si intermetallic compounds in the 0.1%Fe ingots at the casting cooling rate of 0.06 K/s with homogenizing time. N : total number of the particles observed.

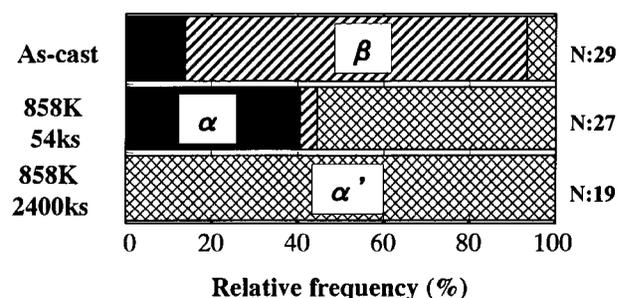


Figure 6 Change in the relative frequency of Al-Fe-Si intermetallic compounds in the 0.2%Fe ingots at the casting cooling rate of 5 K/s with homogenizing time. N : total number of the particles observed.

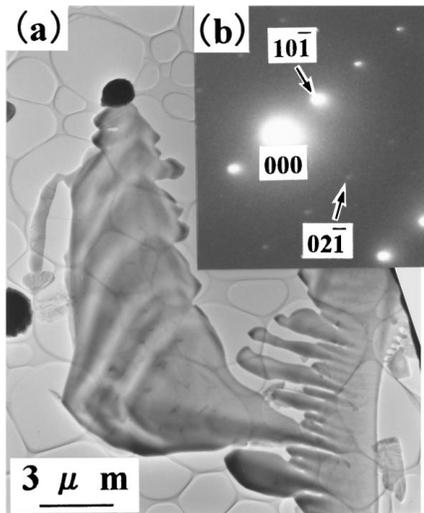


Figure 7 The results of TEM observation of an α -AlFeSi particle extracted from the 0.5%Fe alloy ingot at the casting cooling rate of 50 K/s. (a) Bright field image and (b) selected area diffraction pattern. Beam // [212] of simple cubic.

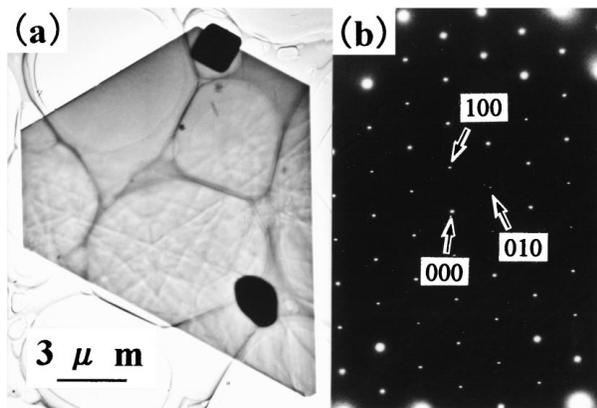


Figure 8 The results of TEM observation of an α' -AlFeSi particle extracted from the 0.5%Fe as-cast ingot homogenized at 858 K for 2400 ks at the casting cooling rate of 50 K/s. (a) Bright field image and (b) selected area diffraction pattern. Beam // [001] of the α' -AlFeSi.

the cooling rate of 5 K/s, with time of homogenizing treatment at 858 K. The solidified condition of this ingot is very similar to that of the commercial aluminum alloys. In the as-cast ingot, the relative frequency of β phase is about 80%. The amount of β phase gradually decreases and those of the α phase (cubic: $a = 1.252$ nm or $a = 1.256$ nm) and α' phase increases after homogenizing for 54 ks. Further prolonged homogenizing treatment, that is, 2400 ks treatment, leads to the almost complete transformation of the α and β phases into the α' phase. Fig. 7a shows a TEM image of the α phase extracted from the fast solidified 0.5%Fe ingot without homogenizing treatment. Among the twenty-seven Al-Fe-Si compound particles observed, there is only the α phase with Chinese script morphology [16]. The relative frequency of α phase in this ingot is the highest among all the as-cast ingots. Fig. 8a shows a TEM image of an intermetallic compound particle extracted from the fast solidified 0.5%Fe ingot homogenized at 858 K for 2400 ks. This faceted polygonal Al-Fe-Si compound particle of about 15 μm in length is identified as the α' phase.

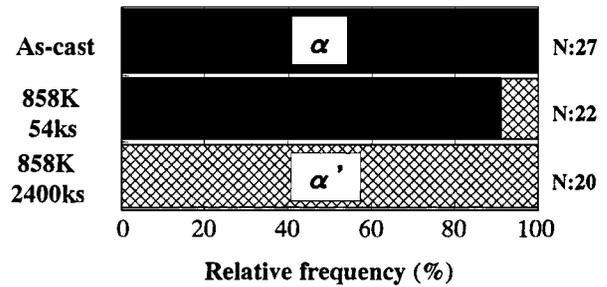


Figure 9 Change in the relative frequency of Al-Fe-Si intermetallic compounds in the 0.5%Fe ingots at the casting cooling rate of 50 K/s with homogenizing time. N : total number of the particles observed.

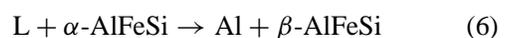
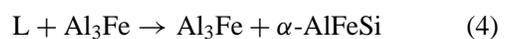
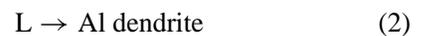
Fig. 9 shows the changes in the relative frequency of Al-Fe-Si phases in the fast solidified 0.5%Fe ingot with a homogenizing time at 858 K. A large amount of the α phase remained in the homogenized ingot at 858 K for 54 ks, similar to the as-cast ingot. However, the main Al-Fe-Si intermetallic compounds change from the α phase to the α' phase in the ingot homogenized at 858 K for 2400 ks, similar to the ingots solidified at the slow and intermediate cooling rates.

Fig. 10 shows the schematic views of the changes in the Al-Fe-Si intermetallic compounds in the as-cast and homogenized ingots with the cooling rate and the iron content. It was reported that the β phase formed in the as-cast ingots transformed into the α phase by suitable homogenizing treatment in 6000 series aluminum alloys [7, 8]. In the present study, it was found that the α phase increased when the ingots solidified at the cooling rate of 5 K/s were homogenized at 858 K for 5 ks. However, irrespective of Fe content and casting cooling rates, almost all of the Al-Fe-Si intermetallic compound particles were identified as the α' phase after homogenizing at 858 K for 2400 ks. This result is different from the previous report [7, 8].

4. Discussion

It was reported that the α phase was formed in the Al-Si-Fe alloys solidified at a fast cooling rate, while the β phase was formed in the Al-Mg-Si alloys solidified at a fast cooling rate. However, the α phase was formed in the present Al-Mg-Si alloys solidified at the fast cooling rate of 50 K/s, irrespective of Fe content, as shown in Fig. 10.

The formation of the Al-Fe-Si phases during solidification of 6000 series alloys has been reported to take place through the following reactions [16~18]:



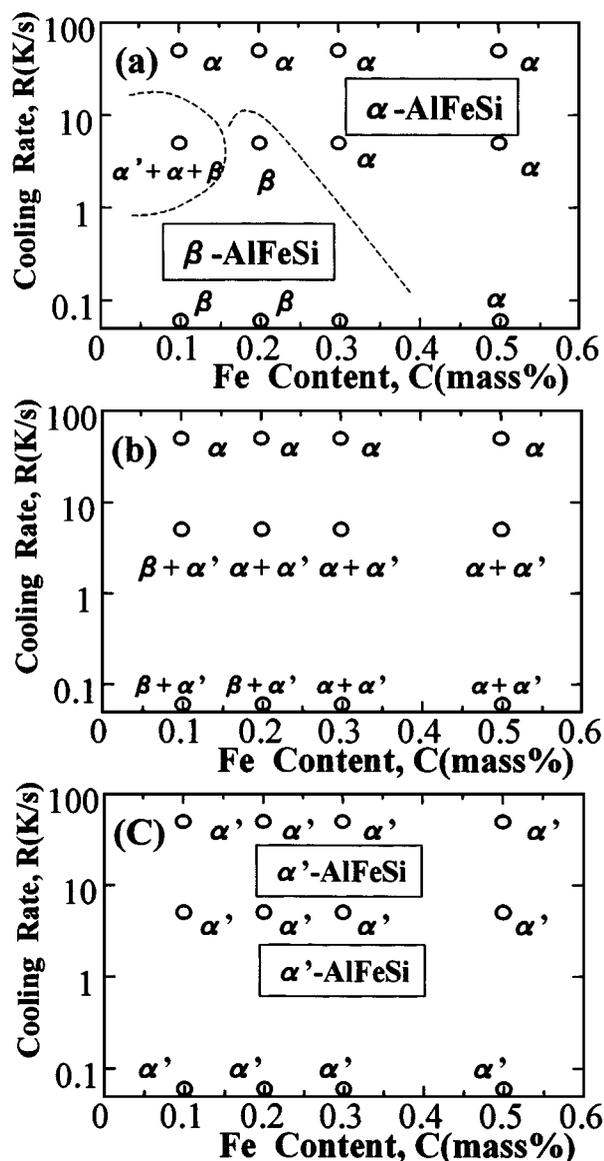


Figure 10 Schematic view of the change in the relative amounts of the Al-Fe-Si intermetallic compounds in the ingots (a) as-cast, (b) homogenized at 858 K for 54 ks, and (c) for 2400 ks as a function of casting cooling rate and Fe content.

From these equations, the α and β phases were formed from the liquid phase. However, in the case of the industrial fast cooling rate (10 – 20 K/s), the β phase was predominantly formed in the billets solidified at the fast cooling rate [16, 18]. This was explained as follows: the formation of eutectic with high concentrations of alloying elements and impurities decreased the liquid temperature owing to supercooling phenomenon; and aluminium, silicon, and the β -AlFeSi phase precipitated in the finally solidified regions (Equation 8) at the eutectic temperature of 858 or 851 K. In particular, Mulazimoglu *et al.* [16] suggested that almost all of the Al-Fe-Si intermetallic compounds were nucleated as the β phase directly in the liquid phase because the extremely thin α phase particles were easily decomposed to the β phase. In accord with this explanation, the β phase should be more easily formed, and the α phase should not be formed at the faster cooling rate of 50 K/s. Additionally, the α phase is expected to be present without decomposition in the more slowly cast

ingots. However, the predominant phase in the present ingots solidified at the cooling rate of 50 K/s is the α phase, as shown in Fig. 8. Also, a large amount of the β phase is observed in the 0.1%Fe ingot solidified at the cooling rate of 0.06 K/s. Therefore, it is difficult to explain the present results by applying the previous interpretation.

The formation of the α and β phases in the present study is explained well by using the equilibrium phase diagram of the solid phases, not of the liquid phases, which has been often used. The equilibrium phase diagram is used a vertical sectional view of the Al-Fe-Si ternary alloy phase diagram [19]. For the alloy composition of Al-0.4%Si-0.1%Fe without magnesium, only the solid phases are present in equilibrium at and below 900 K. When the liquid phase of this composition is cooled, the solid phases appear in the order of Al + α -AlFeSi phase, Al + β -AlFeSi phase, and Al + β -AlFeSi phase + Si. Therefore, the formation of the α phase in the fast solidified ingots can be explained by considering that no further reaction of Al + α phase formed from liquid phase occurs during casting. Similarly, the formation of the β phase in the slowly solidified ingots can be explained by the solid state reaction of Al + α phase to Al + β phase. It can also be explained by the facts that a large amount of the α phase with a Chinese script morphology is formed at the fast casting cooling rate of 50 K/s, and that the β phase with the same morphology and size as the α phase is also formed in the 0.2%Fe ingot solidified at the casting cooling rate of 5 K/s.

Because the ingots used in the present study contain 0.5% magnesium, silicon in the Al + β phase + Si phases formed at and below about 673 K is expected to react with magnesium, forming a Mg_2Si intermetallic compound. In fact, in this study Mg-Si binary intermetallic compounds are observed in all of the slowly solidified as-cast ingots.

The decrease in the iron content from 0.5 to 0.1% in the slowly solidified as-cast ingots results in the increase in the relative amount of the β phase. Similar results were reported previously [20]. This suggests that the temperature range forming the β phase is extended with a decrease in the iron content at and below 773 K. These results cannot be explained by the previous interpretation mentioned above [16~18]. However, the results can be explained by considering that the Al-Fe-Si intermetallic compound phases formed in the as-cast ingots are determined by the competition of the cooling rate and the rate of solid state reaction. When the casting cooling rate is fast, the α phase remains the same due to fast cooling before the solid state transformation of the α phase into the β phase occurs. At the slow casting cooling rate, such transformation occurs during casting, and hence, the relative amount of the β phase becomes high.

In accord with the equilibrium phase diagram, the homogenizing treatment at 858 K should lead to the formation of Al + α phase. However, the Al-Fe-Si phase observed after homogenizing for 2400 ks is the α' phase. Hoier *et al.* also reported the formation of the α' phase in the Al-0.5 mass% Mg-0.6 mass% Si-0.2

mass% Fe alloy homogenized at 853 K for 86.4 ks [21]. They suggested the transformation of the β phase formed in the as-cast ingot into the α' phase during homogenizing. They did not observe the formation of the α phase, and explained this fact by the high purity of the iron-containing alloy, which was almost free from impurities such as manganese. In the present study, high purity alloys were used. However, about 40% of the Al-Fe-Si intermetallic compounds in the 0.2%Fe ingot solidified at the intermediate cooling rate and homogenized at 858 K for 54 ks is the α phase (Fig. 9), although the composition of the ingots and the casting and homogenizing treatments in the present study are slightly different.

If the α' phase is a stable one at the homogenizing temperature, the α' phase present in the as-cast ingots should be formed by the transformation of a part of the α phase into the α' phase during solidification. The absence of the α' phase in the ingots solidified at the cooling rate of 50 K/s is due to too-fast cooling rate to transform the α phase into the α' phase. Thus, all of the α phase formed in the ingots remains without further transformation.

5. Conclusions

The effects of casting and homogenizing treatment conditions on the formation of Al-Fe-Si intermetallic compounds in 6063 Al-Mg-Si alloys have been examined using TEM observation. The following conclusions are drawn.

1. The main phase in the 0.1 mass% Fe as-cast ingot at the casting cooling rate of 0.06 K/s is the β phase, while the main phase in this ingot homogenized at 858 K for 2400 ks changes into the α' phase.

2. The main phase in the 0.5 mass% Fe as-cast ingot at the casting cooling rate of 50 K/s is the α phase, while the main phase in this ingot homogenized at 858 K for 2400 ks changes into the α' phase similar to the slowly solidified ingot.

3. The main phase in the 0.2 mass% Fe as-cast ingot at the casting cooling rate of 5 K/s, close to the industrial cooling rates, is the β phase. The β phase gradually

decreases and the relative frequency of the α phase increases from 10% to 40% in homogenizing at 858 K for 54 ks, in good agreement with the previous report. However, the relative frequency of the α' phase also increases to 50% in the homogenized ingot. Furthermore, almost all of the Al-Fe-Si intermetallic compounds are transformed into the α' phase in the ingot homogenized at 858 K for 2400 ks.

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