Effects of Mn on the crystal structure of $\alpha$-Al(Mn,Fe)Si particles in A356 alloys

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Abstract

In a commercial Al-7.0Si-0.38Mg cast alloy (A356) with 0.20 wt% Fe, added Mn modifies acicular $\beta$-Al$_5$FeSi particles to less acicular $\alpha$-Al(Mn,Fe)Si in both crystallization and precipitation conditions. The crystal structure of $\alpha$-Al(Mn,Fe)Si changes from body-centered cubic (bcc) / simple cubic (sc) to Pm3 structures in response to an increase in the bulk Mn content of the alloy. The $\alpha$-Al(Mn,Fe)Si particles (50–200 nm) precipitate during solution treatment and their precipitation temperature is about 485 °C in the as-cast condition.

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1. Introduction

The presence of the Fe impurity in the cast Al–Si–Mg alloys enables the crystallization of acicular $\beta$-Al$_5$FeSi during solidification, even though the Fe content is extremely low in a melt [1,2], and its presence severely lowers the dynamic fracture toughness of the alloy [3]. Since the morphology of $\beta$-Al$_5$FeSi mainly depends on the cooling rate of the melt [4], permanent mould casting or high-pressure die-casting has been used in order to modify the shape of $\beta$-Al$_5$FeSi. However, a chemical modification method is preferred for widespread application of the alloy, irrespective of casting methods. Thus, alloying elements such as Mn, Cr, Mo and Be have been used to replace the acicular $\beta$-phase with $\alpha$-Al(Mn,Fe)Si which has granular or skeleton (or Chinese script) morphology [5–9].

On the other hand, the crystal structure of $\alpha$-Al(Mn,Fe)Si has been studied in the wrought aluminum alloys, not in cast alloys, with respect to precipitates [10–12]. It is suggested isomorphous to $\alpha$-AlMnSi (simple cubic, sc) with a Pm3 space group [10] or $\alpha$-AlFeSi (body-centered cubic, bcc) with a disordered Im3 space group [11]. And, the crystal structure of the precipitated $\alpha$-Al(Mn,Fe)Si depends on the Mn/Fe ratio [12]. However, the crystal structure of coarse $\alpha$-Al(Mn,Fe)Si formed during solidification has not been examined thoroughly in the cast Al alloys.

Therefore, in this study, the crystal structure and morphology of crystallized $\alpha$-Al(Mn,Fe)Si particles during solidification, in response to the Mn addition, are investigated using a commercial Al–Si–Mg cast alloy (A356) with a high Fe content of 0.20 wt%. And, the precipitation behavior of $\alpha$-Al(Mn,Fe)Si particles is also explored.

2. Experimental procedures

The commercial A356 cast alloy (Al-7.0Si-0.38Mg) was used as a base material. To induce the crystallization of $\beta$-Al$_5$FeSi during solidification, an alloying element Fe of 0.20 wt% Fe was added. Four different alloys containing 0, 0.07, 0.13 and 0.20 Mn in wt%, respectively, were used. All alloys were melted in an electric furnace at 750–760 °C, and then at 740 °C, poured into a Y-block permanent mould preheated to 280 °C. The Y-block has a shape of 300 mm in height, 30 mm in thickness and 250 mm in width. Samples

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were cut within 2 cm from the bottom of the ingots. The T6-heat treatment (solution treatment at 555 °C for 10 h followed by water quenching, then held at room temperature for 12 h, and finally aged at 160 °C for 6 h) was performed.

The crystal structure of the α-Al(Mn,Fe)Si particles was analyzed by selected area diffraction pattern (SADP) in a transmission electron microscopy (TEM) (PHILIPS CM 20, 300 kV) equipped with energy dispersed X-ray spectrometer (EDX). Microstructural observation and chemical composition analysis were performed at 160 kV. Specimens for SADP were polished on an emery paper to thickness of 200μm firstly, then worked by jet polisher (STRUERS Tenupol-3) using etching agent of HClO₄:CH₃OH = 1:9. Microstructures were observed by scanning electron microscopy (SEM) (PHILIPS-XL30SFEG) and optical microscopy (OM). The differential scanning calorimetry (DSC) (TAINST Q-10) analysis with a scanning rate of 3 °C/min was carried out to examine the precipitation temperature and amount of each particle. The equilibrium phase diagram and the solidification path of the A356-0.20Fe-X(Mn) alloys were calculated using the Thermo-Calc thermodynamic program of version Q [13] and the Al commercial database [14].

3. Results and discussion

3.1. Morphology and crystallization sequence of α-Al(Mn,Fe)Si

As shown in Fig. 1(a), the long and needle-type β-Al₃FeSi particles are crystallized in A356-0.20Fe without Mn. With the addition of Mn from 0.07 to 0.20 wt%, the needle-type β-Al₃FeSi particles were replaced by rod-type or skeleton α-Al(Mn,Fe)Si, which is clearly seen in Fig. 1(b)–(d). According to previous studies [5,6,8,15], the morphology of α-Al(Mn,Fe)Si changed with the cooling rate and the amount of Si and Mn. For example, the low cooling rate and the high Si content favored complicated Chinese script α-Al(Mn,Fe)Si [5,6,8,15]. In this study, only Mn played a role in affecting the morphology of α-Al(Mn,Fe)Si because the cooling rate and the Si content were maintained in the same condition. With the addition of 0.07 or 0.13 Mn, the needle-type β-Al₃FeSi particles are modified to rod-like α-Al(Mn,Fe)Si (see Figs. 1(b) and (c)). The β-Al₃FeSi was replaced by the α-Al(Mn,Fe)Si with a skeleton shape in the A356-0.20Fe-0.20Mn alloy (Fig. 1(d)).

The increased Mn content in an A356 alloy enlarges a gap between the onset crystallization temperature of α-Al(Mn,Fe)Si and the eutectic temperature of Si [16]. The equilibrium phase diagram of A356-0.20Fe with the amount of Mn was shown in Fig. 2(a), which reveals that the onset crystallization temperature of α-Al(Mn,Fe)Si, denoted by the line B, is depressed below the eutectic temperature, marked by the line Si, as the Mn content decreases. And, the calculated solidification sequence shows that the depression comes from the decreased Mn content (see Fig. 2(b)–(d)). The rod-like α-Al(Mn,Fe)Si particles in the eutectic Si zone or along the dendrite arm boundaries shown in Figs. 1(b) and (c) can be interpreted from the lower onset temperature and the resultant insufficient solidification time. Figs. 2(b) and (c) clearly manifest that the α-Al(Mn,Fe)Si particles crystallizes later at lower temperature than the eutectic Si particle during cooling of A356-0.20Fe-0.07Mn and A356-0.20Fe-0.13Mn. However, in the case of A356-0.20Fe-0.20Mn, the α-Al(Mn,Fe)Si can grow sufficiently into a skeleton shape because it can form at higher temperature than the eutectic Si particles and thus coarse skeleton-type α-Al(Mn,Fe)Si particles can crystallize as shown in Fig. 1(d).

3.2. Effect of Mn affecting the structure of crystallized α-Al(Mn,Fe)Si

Concerning the crystal structure of α-Al(Mn,Fe)Si, the precipitating phase has been mostly studied in wrought alloys. It was reported that the increase of Mn in α-Al(Mn,Fe)Si changes its crystal structure from disordered Im3 to ordered Pm3 [11,17] and the crystal structure is also dependent on the heat treat conditions [12,18]. However, in the present study, the coarse α-Al(Mn,Fe)Si particles crystallized during solidification were investigated, and since the heat-treatment was fixed to the T6 condition, the Mn/Fe ratio needs to be considered.

Using the SADP analysis in this study, although it was not shown here, the needle-type particles appearing in Fig. 1(a) were identified as the monoclinic β-Al₃FeSi, whose lattice parameter was \(a = b = 0.612 \text{ nm}, \ c = 4.15 \text{ nm}\).
and $\gamma = 91^\circ$, which agreed with results of a previous study \cite{11}. The bright field (BF) TEM image of rod-type particles in A356-0.20Fe-0.07Mn and its SADP are shown in Fig. 3, which show a stripe pattern. Based on the indexed SADP the $\alpha$-Al(Mn, Fe)Si is found to compose of two kinds of crystal structures. Lattice parameters obtained in Figs. 3(b) and (c) are $1.250 \pm 0.02$ nm and $1.22 \pm 0.02$ nm, respectively. They are consistent with the lattice parameters of the bcc (Im3) and sc (Pm3) structures. This implies that a rod-type $\alpha$-Al(Mn, Fe)Si particle consists of several regions containing bcc $\alpha$-AlFeSi and sc $\alpha$-AlMnSi, and these layers independently contribute to SADP.

Considering the different space group of $\alpha$-AlFeSi and $\alpha$-AlMnSi phases, it is suggested that a relatively low Mn content in 0.07 wt% partially changes the crystal structure of the $\alpha$-Al(Mn, Fe)Si from bcc Im3 to sc Pm3. Or, two types of the $\alpha$-Al(Mn, Fe)Si grow independently in accordance with a different Mn content in the retained liquid melt. The stripe pattern of Fig. 3(a) accompanies the different chemical reaction nature of bcc and sc layers to agent for jet-polishing. The bcc/sc composite structure has a crystallographic orientation relationship as follows: 

$$ \langle 0 \bar{1} 1 \rangle_{\text{BCC}}//\langle 1 \bar{3} 9 \rangle_{\text{SC}}. $$

Fig. 2. (a) The equilibrium phase diagram of A356-0.20Fe with the amount of Mn. The Scheil mode solidification sequence of (b) A356-0.20Fe-0.07Mn, (c) A356-0.20Fe-0.13Mn and (d) A356-0.20Fe-0.20Mn alloys, which were obtained by Thermo-Calc. (Liq* in (a) means the solidification end temperature).

Fig. 3. (a) TEM BF image and (b,c) SADP showing a bcc/sc dual crystal structure in a rod-like $\alpha$-Al(Mn,Fe)Si observed in A356-0.20Fe-0.07Mn alloy.
On the other hand, the diffraction pattern of the skeleton-type \(\alpha\)-Al(Mn,Fe)Si observed in the A356-0.20Fe-0.20Mn alloy is different. While the BF image of the \(\alpha\)-Al(Mn,Fe)Si is shown in Fig. 4(a), the SADP shows a \(Pm\overline{3}\) structure with a lattice parameter of 1.24 \pm 0.02 nm in Fig. 4(b). The diffraction spots indicated by circles signify an ordered structure [17] in a \(Pm\overline{3}\) structure. Similar ordering is also observed in A356-0.20Fe-0.13Mn alloy, as shown in Fig. 4(c, d).

In case of precipitated \(\alpha\)-Al(Mn,Fe)Si, it was reported that the disorder–order transition accompanies a change in the ratio of Mn/Fe caused by heat treatment and diffusion of Mn [12], and the diffuse scattering in the diffraction pattern would occur during the transition process [17]. However, such a diffused pattern for precipitated \(\alpha\)-Al(Mn,Fe)Si was not observed in the crystallized \(\alpha\)-Al(Mn,Fe)Si of this study. As a result, the Mn diffusion during heat treatment (T6) is not a main reason for disorder–order transition of the crystallized \(\alpha\)-Al(Mn,Fe)Si and other factors seems to play roles.

The Mn/Fe ratio of the crystallized \(\alpha\)-Al(Mn,Fe)Si keeps almost the same values in an alloy. The mean values of the ratio obtained from EDX are 0.11, 0.66 and 5.1 in A356-0.20Fe-0.07Mn, A356-0.20Fe-0.13Mn and A356-0.20Fe-0.20Mn alloys, respectively. In this study, the crystal structure of the crystallized \(\alpha\)-Al(Mn,Fe)Si varied from the bcc/sc dual structure to the \(Pm\overline{3}\) structure with increasing the Mn/Fe ratio. The Mn/Fe ratio of 0.11 refers to the bcc/sc dual structure, and the Mn/Fe ratio of 0.66 and 5.1 results in the \(Pm\overline{3}\) structure. Therefore, the ratio of Mn/Fe for the disorder–order change lies in 0.11–0.66. And since crystal structure of all the \(\alpha\)-Al(Mn,Fe)Si particle strongly depends on the Mn content in the bulk alloy, it is highly likely that the crystal structure of \(\alpha\)-Al(Mn,Fe)Si is already determined by the bulk Mn content after solidification, not after the T6 heat treatment.

3.3. Effect of Mn on precipitation of \(\alpha\)-Al(Mn,Fe)Si

After solution treatment, many \(\alpha\)-Al(Mn,Fe)Si particles precipitated, apart from the crystallized \(\alpha\)-Al(Mn,Fe)Si mentioned above. Fig. 5(a) shows the DSC result of the as cast and heat treated A356-0.20Fe-0.20Mn alloy. The peaks at lower temperatures correspond to formation of \(\beta''\), \(\beta'\) and \(\beta\) (Mg,Fe) phases [19,20] while the \(\alpha\)-Al(Mn,Fe)-Si particles are precipitated at higher temperatures around 485°C. The exothermic heat (J/g) formed during precipitation of \(\alpha\)-Al(Mn,Fe)Si corresponds to its peak area and a large number in J/g means much precipitation of \(\alpha\)-Al(Mn,Fe)Si. After solution treatment, the precipitated...
a amount of $\beta''$, $\beta'$ and $\beta$(Mg$_2$Si) phases became larger than that of the as-cast alloy probably because Mg and Si are fully dissolved in the matrix during solution treatment. On the other hand, the amount of $\alpha$-Al(Mn,Fe)Si precipitates is smaller after the solution treatment because a lot of precipitates must have already formed during the solution treatment at 535 $^\circ$C for 10 h. Likewise, the precipitation temperature is slightly shifted to higher temperature of 487 $^\circ$C. The solution treatment in the T6 heat treatment seems to act as an aging process of the $\alpha$-Al(Mn,Fe)Si precipitates. The granular $\alpha$-Al(Mn,Fe)Si particles in Fig. 5(b), whose size ranges from 50 to 200 nm, are precipitated in A356-0.20Fe-0.20Mn. The mean ratio of Mn/Fe in the $\alpha$-Al(Mn,Fe)Si precipitates of Fig. 5(b) is around 1.5 and their SADP reveals that the Pm3 structure with a lattice parameter of $a = 12.3$ nm has already proceeded. It implies that the Mn/Fe ratio of 1.5 is sufficient to make Pm3 $\alpha$-Al(Mn,Fe)Si precipitates in the T6 heat treatment condition for the A356-0.20Fe-0.20Mn alloy. It is consistent with the result of Fig. 4 that the Pm3 structure appears with Mn/Fe higher than 0.66 in the crystallized $\alpha$-Al(Mn,Fe)Si particle.

4. Summary

The effect of the addition of Mn to A356 alloyed with 0.20 wt% Fe was studied with a focus on the crystal structure and morphology of the Al(Mn,Fe)Si particles after T6 heat treatment. With the addition of 0.07 or 0.13Mn, the needle-type $\beta$-Al$_5$FeSi was replaced with rod-like $\alpha$-Al(Mn,Fe)Si, and with skeleton shape in A356-0.20Fe-0.20Mn. The $\alpha$-Al(Mn,Fe)Si particle is found to have a bcc/sc dual crystal structure or just Pm3 structure depending on the Mn/Fe ratio which is determined by the Mn content in bulk. The critical Mn/Fe value for disorder–order transition of crystallized $\alpha$-Al(Mn,Fe)Si lies within 0.11–0.66. The solution treatment in T6 heat treatment seems to act as an aging process of the $\alpha$-Al(Mn,Fe)Si precipitates, whose crystal structure is Pm3.

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References