

The Formation of Al₆(Fe, Mn) Phase in Die-Cast Al–Mg Alloys

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Abstract

In aluminium alloys, iron is a common impurity as it is unavoidably picked up in practice. The excessive Fe is strongly prone to form various intermetallic phases. These Fe-rich intermetallics are generally brittle and act as stress raisers to weaken the coherence with Al matrix, therefore decreasing elongation. However, Fe addition in Al–Mg alloys may be beneficial because of the improvement in the yield strength with the scarification of ductility of die-cast aluminium alloys. The morphology of intermetallic phases has a vital effect on the properties of aluminium alloys. In the present work, the 3D morphology of Al₆(Fe, Mn) in die-cast Al–Mg–Mn alloys with different levels of Fe contents were revealed. The formation of Al₆(Fe, Mn) was also studied through crystal features and solidification behaviours.

Keywords: Al–Mg Die-cast Al₆(FeMn) Crystal growth

Introduction

In die-cast aluminium alloys, Fe is a common deleterious impurity for elongation and is not economically removed from the melt [1–3]. Therefore the accumulation of iron has been a critical concern in recycled materials. Up to now, several methods have been invented to diminish the detrimental effect of Fe, such as melt-superheating treatment, chemical modification and rapid solidification [4–7]. Among them, Mn modification is a popular method to transform needle-like b-AlFeSi to blocky a-AlFeMnSi in Al–Si alloys. While, a-AlFeMnSi phase would forms large primary crystal and resulting in an unacceptable mechanical properties when the total amount of Mn and Fe is more than 1.5 wt%. Therefore, the application of recycled Al alloy with high Fe content is still an important concern in industry.

The obstacle of the application of recycled high-Fe Al alloy is that Fe-rich intermetallics would decrease elongation obviously. Therefore, a soft alloy matrix (such as ductile Al–Mg matrix) is necessary for high-Fe alloy. On the other side, it was found that Fe-rich phases in aluminium alloys are helpful in improving the yield strength with the scarification of ductility [8]. Besides, the addition of Mn in Al–Mg alloys can modify Al₃Fe to Al₆(Fe, Mn), and the increased cooling rate can significantly refine the Al₆(Fe, Mn) phase. It further increases the upper limit of the Fe level in aluminium alloys. Therefore, there is a potential to use Fe as a strengthening element to design an Al–Mg–Mn–Fe alloy prepared by high pressure die casting (HPDC) which has a high cooling rate among various common casting methods. The mechanical properties (especially the fracture behavior) of alloys are closed with the morphology of intermetallic phases. However, the study of Al₆(Fe, Mn) morphology and growth mechanism in Al–Mg alloys is still few. Therefore, the present works aims to reveal the 3D morphology and relative growth mechanism of Al₆(Fe, Mn) phase in Al–Mg–Mn–Fe alloys.

Experimental Methods

Commercial pure Al and Mg ingots, Al-20% Mn and Al-45% Fe master alloys (all compositions quoted in this paper are in wt% unless otherwise stated) were melted in an electric resistance furnace at 730 °C to prepare a series of Al-5 Mg-xFe-0.6Mn alloys (x = 0.5, 1.5 and 2.5). After a homogenization process for about 30 min, the melt was manually dosed and subsequently released into the shot sleeve of a FRECH 4500 kN cold chamber HPDC machine. The HPDC die and shot sleeve were preheated at about 150 °C and 100 °C, respectively. The pouring temperature was controlled at 720 °C. Al₆(Fe, Mn) particles were collected after deep-etching or completely removing the

matrix of samples by 15 vol.% HCl–distilled water solution, and then observed by a scanning electron microscope (SEM, Zeiss-Supra 35VP, Germany) equipped with an energy dispersive X-ray spectroscope (EDS) and electron back-scattered diffractor (EBSD).

Results and Discussion

The as-cast microstructures of Al-5 Mg-xFe-0.6Mn alloys ($x = 0.5, 1.5$ and 2.5) are shown in Fig. 1. As observed, the morphology, size and amount of bright Al₆(Fe, Mn) phase varies obviously with the increase of the Fe level. In the alloy with 0.5 wt% Fe, eutectic Al₆(Fe, Mn) were located at the grain boundaries and showed a lamellar morphology with some curved planes, as shown in Fig. 1a, b. When the Fe level was at 1.5 wt%, the rhombic or lath-like primary Al₆(Fe, Mn) phase was found (Fig. 1c). Meanwhile, the eutectic Al₆(Fe, Mn) intermetallics were divorced from a-Al phase and exhibited as fine lath-like or rhombic morphologies with faceted surface (Fig. 1d). When the Fe level was further increased to 2.5 wt%, both the amount and size of primary and eutectic Al₆(Fe, Mn) intermetallics were increased, while the morphology remains. What's more, it was noticed that the primary Al₆(Fe, Mn) intermetallics in the alloys with 2.5 wt% Fe have two different size ranges.

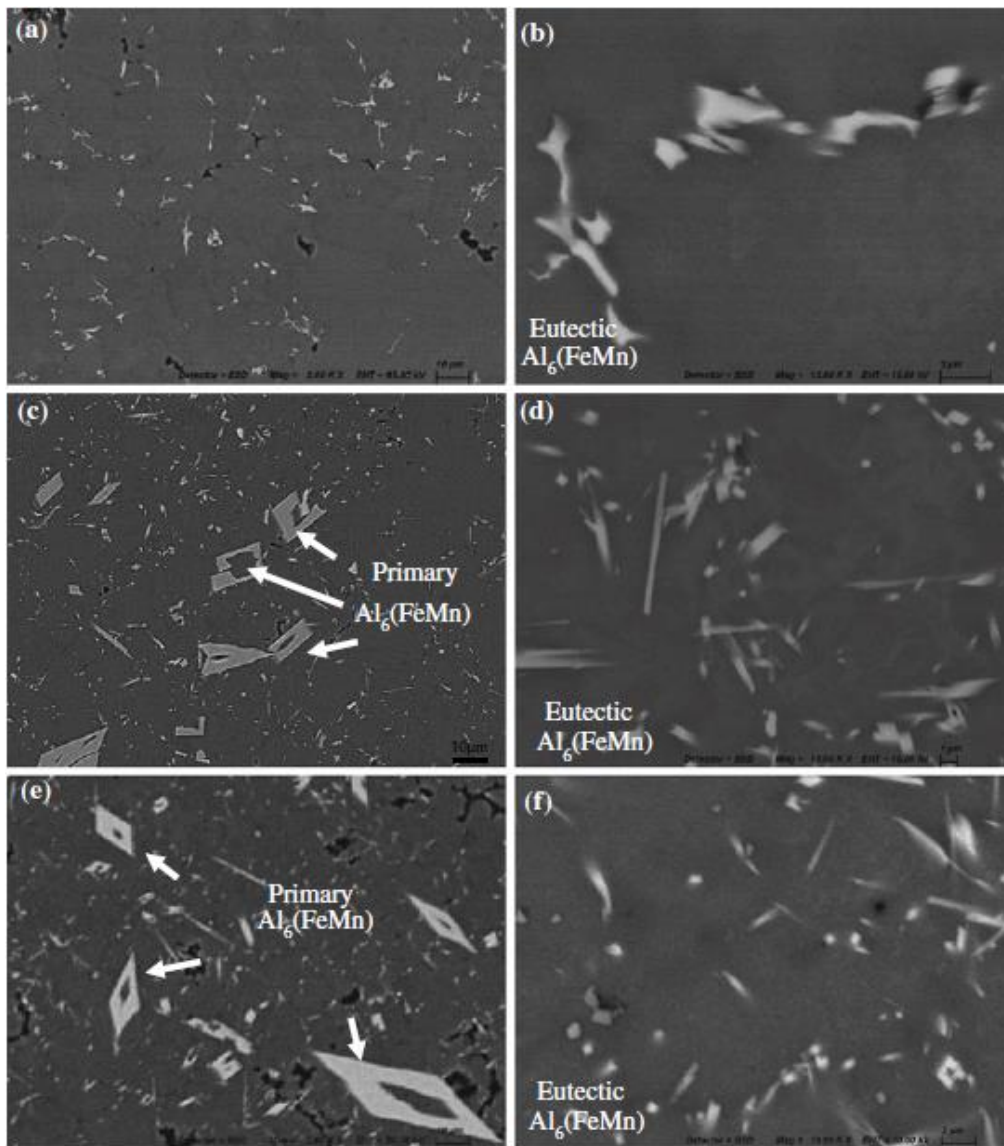


Fig. 1 Backscattered SEM micrographs showing the microstructures of the Al-5Mg-0.6Mn-xFe alloys: a, b $x = 0.5$, c, d $x = 1.5$ and e, f $x = 2.5$

Similar with our previous result [3], the large and small primary Fe-rich intermetallics precipitated in the first solidification in shot sleeve and the secondary solidification in die cavity during cold-chamber HPDC process, respectively. It is interesting to note that both primary and eutectic have two morphologies: (1) lath/needle, (2) rhombus/dot. Besides, it was also found that almost all rhombic primary Al₆(Fe, Mn) crystals have a hollow. To further observe the morphology of the hollow primary Al₆(Fe, Mn) clearly, samples were deep-etched using a 15 vol.% HCl-distilled water solution. Figure 2 indicates that the hollow is filled by α -Al phase and has a curved, smooth surface, although Al₆(Fe, Mn) is a strong faceted crystal. It means that these surfaces are not certain exposed crystal surfaces. They formed as the results of incomplete crystal growth.

To show the 3D morphologies of Al₆(Fe, Mn) crystals, a 15 vol.% HCl water solution was applied to extract the intermetallic particles. The results shown in Figs. 3 and 4 indicate that all primary and eutectic Al₆(Fe, Mn) crystals in fact only have one 3D morphology: quadrangular prism, and the lath/needle and rhombus/dot morphology in 2D sections are just the longitudinal and cross sections of Al₆(Fe, Mn) crystals, respectively. The difference is that the primary Al₆(Fe, Mn) crystals (shown in Fig. 3) are coarse and hollow, while the eutectic Al₆(Fe, Mn) crystals (shown in Fig. 4) are thin (200–500 nm in cross section) and solid.

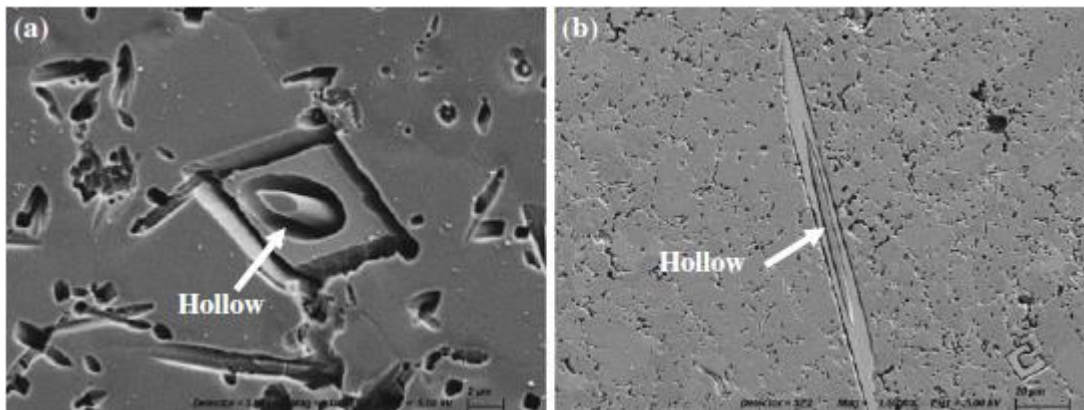


Fig. 2 SEM micrographs showing a cross and b longitudinal sections of Al₆(Fe,Mn) phase

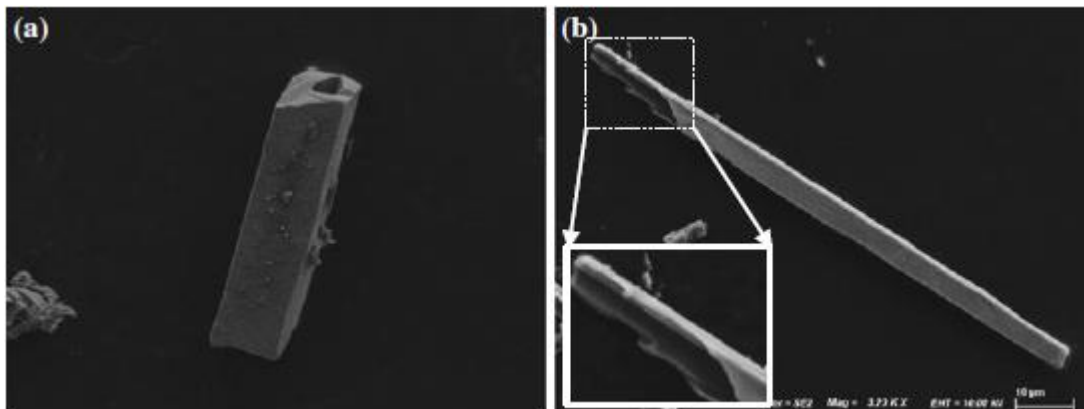


Fig. 3 SEM micrographs (a) (b) showing 3D morphology of primary Al₆(Fe, Mn) phase: a thick crystal and b a thin crystal with broken end

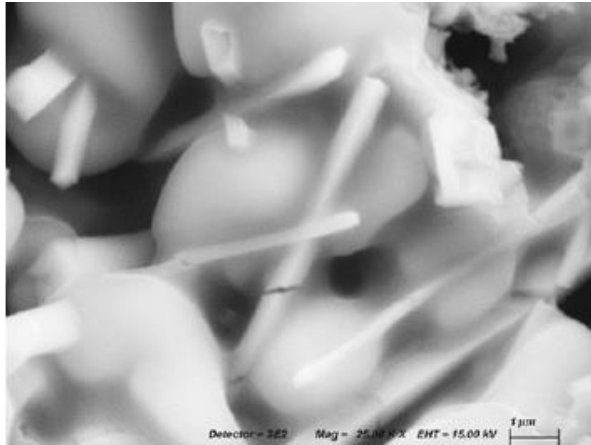


Fig. 4 SEM micrographs showing 3D morphology of eutectic Al₆(Fe,Mn) phase

The Bravais-Friedel-Donnay-Harker (BFDH) law is a well-accepted method to predict the possible exposed crystal faces. Al₆(Fe, Mn) has a Cmc₂m (63) space group and an orthorhombic structure ($a = 0.7498$ nm, $b = 0.6495$ nm, $c = 0.8837$ nm) [10]. According to the BFDH law, the 2 most possible exposed face are closed packed {100} and {002} faces. For orthorhombic crystal, the {110} only contains 4 (-110), $(1-10)$ and $(-1-10)$ faces, which form four side faces of an enclosed geometrical rhombic prism. While, {002} contains (112) and $(00-2)$ faces, forming the top and bottom face of rhombic prism. Therefore, it can be speculated that the rhombic Al₆(Fe, Mn) is bounded by four {110} and two {002} faces.

The growth process of a prism Al₆(Fe, Mn) crystal in Al–Mg–Mn–Fe melt can be described as follows. With the decrease of melt temperature, the atomic cluster becomes bigger and bigger, then forms crystal seeds. When the seed crystal grows and exceeds a critical size, it becomes unstable and grows rapidly along its first preferential growth directions ($[001]$, $[100]$ and $[010]$). At almost same time, new secondary branches generate on the first branches and grow between the first branches and finally fill these making Al₆(Fe, Mn) crystal having a small prism morphology ($\{110\} + \{002\}$) with a strong intrinsic faceting feature.

In the following growth stage, the rapid growth of {002}, which has a higher growth rate than {110} according to BFDH law, would elongate Al₆(Fe, Mn) prism, making it have a lath-like (primary phase) or needle-like (eutectic phase) morphology. The hollows inside Al₆(Fe, Mn) crystal are also formed in the following process due to volume-diffusion. Compared with the diffusion in the side {110} faces, the diffusion in the central area of the faster growing {002} faces is relatively difficult. Therefore, the supplement of solute atoms and the ejection of impurities expelled from {002} faces are relatively slow. It will retard the growth in the central areas of the {002} faces, leading to the formation of hollows inside the primary Al₆(Fe, Mn) prism. On the other hand, the volume diffusion is not a decisive factor for small eutectic Al₆(Fe, Mn) crystals, so eutectic Al₆(Fe, Mn) crystals remain solid.

Conclusions

In the present work, the 3D morphology and formation mechanism of Al₆(Fe, Mn) phase in HPDC Al–Mg–Mn–Fe alloys were revealed. It was found that eutectic Al₆(Fe, Mn)

in 0.5 Fe wt% alloy is the only Fe-rich phase and has an irregular morphology. As the Fe level increased to 1.5 wt% and 2.5 wt%, both primary and eutectic Al₆(Fe, Mn) have a rhombic prism morphology which is bound by four {110} and two {002} faces. While, primary Al₆(Fe, Mn) phase has inside hollows, the eutectic phase is small and solid. In the late stage of crystal growth, volume-diffusion restrains the growth of the central areas of two {002} faces, leading to the formation of

hollows inside the primary Al₆(Fe, Mn) phase. The small eutectic Al₆(Fe, Mn) phase is not affected by volume diffusion and remains solid.

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