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GROWTH MECHANISMS OF INTERMETALLIC PHASES IN DC CAST AA1XXX ALLOYS

X.-G. Chen

Alcan International Limited
Arvida Research and Development Centre
P.O. Box 1250, Jonquière, Canada, G7S 4K8

Abstract

In DC cast AA1xxx alloys, the presence of a fir-tree zone has long been recognized to be detrimental to the surface quality of critical sheet products. The fir-tree zone in DC cast ingots is mainly caused by a macroscopic transition between intermetallic phases. In this paper, the formation of major intermetallic phases commonly occurring in the DC ingot structure, such as Al_3Fe, Al_6Fe, Al_mFe and α-AlFeSi, is investigated by using deep-etching and SEM techniques. The three-dimensional morphologies of intermetallic particles revealed by deep-etching are presented. Based on the morphological and growth kinetic aspects, the growth mechanisms of different intermetallic phases are discussed. The nucleation behaviors of intermetallics observed by SEM are also demonstrated.

Introduction

Iron and Silicon are the most common impurities found in commercial AA1xxx aluminum alloys. It is known that iron has a high solubility in molten aluminum, but a very low one in the solid state. Therefore, almost all the iron in aluminum alloys forms intermetallic secondary phases. Silicon also has a partition coefficient of less than one and would be rejected into the liquid between dendrite arms during solidification. In combination with Si and Al, a large number of binary Al-Fe and ternary Al-Fe-Si intermetallic phases can precipitate while casting 1xxx alloys [1,2], depending on the solidification conditions and alloy chemistry. The types of intermetallic phases present in the cast structure can have a strong influence on the processing and final use properties of aluminum products.

In commercial purity alloys, the presence of the fir-tree zone has long been recognized to be detrimental to the surface quality of critical sheet products. Mainly caused by a macroscopic transition between intermetallic phases [3], the fir-tree zone is a macrodefect in the sub-surface regions of the DC cast ingot. The most commonly occurring intermetallic phases in DC cast 1xxx ingots are: monoclinic Al_3Fe (the equilibrium phase, often designated as $Al_{13}Fe_4$), orthorhombic Al_6Fe, tetragonal Al_mFe and cubic α-AlFeSi [4]. The classical fir-tree was described as a transition from metastable Al_6Fe to stable Al_3Fe during solidification. More recently, it has been established [5-7] that the fir-tree zone can result from various other combinations involving different intermetallic phases such as α-AlFeSi $\rightarrow$ Al_3Fe, α-AlFeSi $\rightarrow$ Al_6Fe, and Al_mFe $\rightarrow$ Al_6Fe. Furthermore, there is evidence that the fir-tree zone does not exclusively represent a transition from one single phase to another. In cast ingots, there is often a mixture of intermetallic phases existing on both sides of the fir-tree zone and the balance and type of phases vary across the zone. Thus, it is of considerable technological interest to control the formation of Al-Fe and Al-Fe-Si phases in the ingot cast structure in order to eliminate the fir-tree defect.

The purpose of the present work is to investigate the growth morphologies and the nucleation behaviors of the major intermetallic phases that commonly occur in the DC cast AA1xxx ingot structure. Deep-etching and SEM techniques were utilized to determine the three-dimensional morphologies of different intermetallic phases.

Experimental

Most samples were taken from commercial DC sheet ingots in the as-cast condition, and the examinations were carried out on the sub-surface region (0-60 mm from cast surface) where the fir-tree zone appears. Some samples were made by a DC Simulator in which a small cylindrical sample with a diameter of 35 mm was cast under cooling conditions similar to DC ingots. The materials investigated were DC cast commercial purity alloys. The main work was performed on the two alloy groups with the composition ranges given in Table 1. The alloys in Group A, with low Si levels, were used to study the binary Al-Fe compounds, whereas examination of the ternary α-AlFeSi phase concentrated on Group B, since the α-AlFeSi becomes one of the major intermetallic phases in the structure only at higher Si levels.

Table I - Chemical Compositions of the Examined Aluminum Alloys (wt %)

	Fe	Si	Cu	Mn	Mg
Group A	0.25-0.35	0.05-0.15	<0.03	<0.03	<0.03
Group B	0.30-0.40	0.25-0.35	<0.03	<0.03	<0.03

To observe the three-dimensional morphologies of intermetallic particles, a deep-etching technique was applied. The basic idea of deep-etching is to dissolve the aluminum matrix in the surface layer of a sample without disturbing the secondary phases. The procedure is quite simple: a finely ground metallographic specimen was put into a 12% HCl solution for several minutes. Under SEM (secondary electron scanning image), the phase morphology in the cast structure can be studied *in situ*.

To confirm the phase type at various positions of a sample, an intermetallic extraction method (with butanol or phenol), combined with XRD analysis for phase identification [3,8], was used.

Results

Phase Morphology

Al_3Fe

Under optical microscopy, the typical appearance of Al_3Fe is flaked and needle-like, and distributed along aluminum cell boundaries (Figure 1). Revealed by deep-etching, Figure 2 shows the three-dimensional view of Al_3Fe which is, in reality, plate-like. The Al_3Fe plate grows in a faceted manner with a preferred direction.

Sometimes in a polished section, it can be seen that a number of angular Al_3Fe particles located in the interdendritic region and their distribution seems more or less irregular. Under SEM, it appears that many fine plates tend to form a cluster. By careful observation, it is found that the Al_3Fe forms side branches on the surface of a plate at different angles and then connect each other in some extension (Figure 3). Examination, in a large number of sections, shows that the anglers between branched plates widely vary and no fixed relationships can be established.

Al_mFe

In DC ingot structures, Al_mFe is one of the frequently encountered metastable phases. It appears fibrous in a metallographic section (Figure 4), and as usual in dilute alloys, the particles locate in the cell boundaries. The SEM micrograph (Figure 5) shows Al_mFe exhibiting a fine feathery characteristic with many fibers growing in different orientations. Another SEM micrograph (Figure 6) shows a complex of Al_mFe over a few aluminum cells. The fine feathers or fibers of the Al_mFe can advance in a variety of curved forms and are able to branch frequently in order to achieve spacing adjustment and change of growth direction. Consequently, the Al_mFe connect each other in the interdendritic region over a wide range.

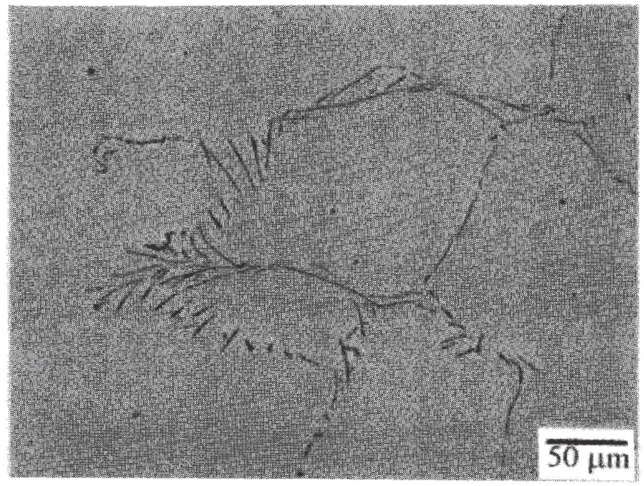

Figure 1: Photomicrograph of a DC ingot structure showing the flaked and needle-like Al_3Fe.

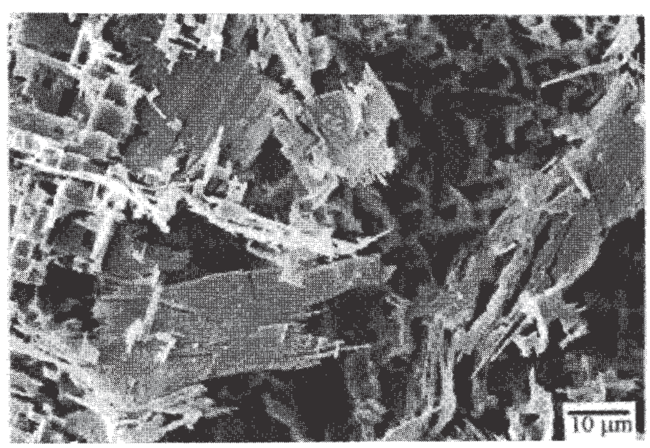

Figure 2: SEM micrograph of a deep etched sample illustrating the plate-like morphology of Al_3Fe.

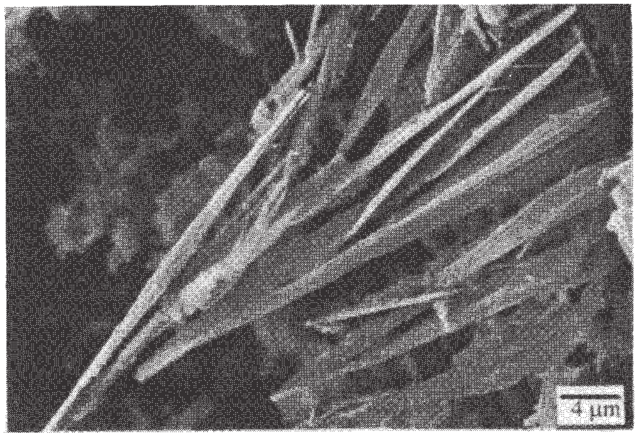

Figure 3: SEM micrograph (deep etched) showing that Al_3Fe forms side branches.

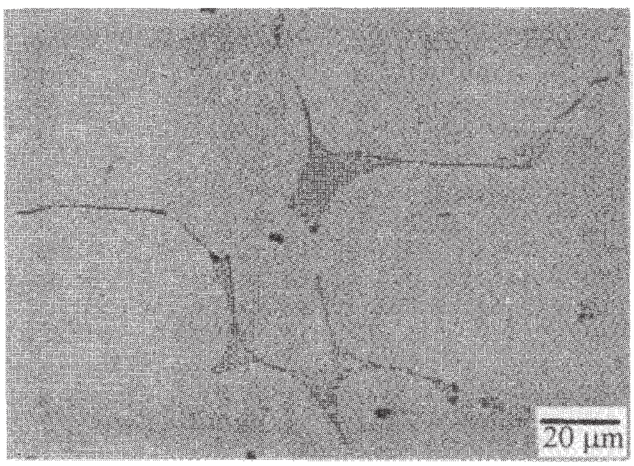

Figure 4: Photomicrograph of a DC ingot structure showing the fibrous Al_mFe.

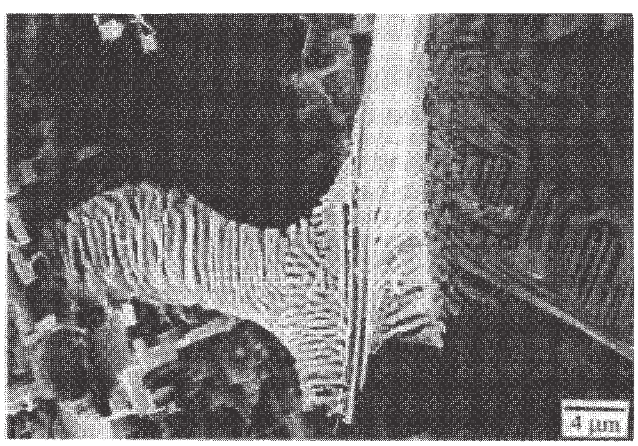

Figure 5: SEM micrograph of a deep etched sample illustrating the fine feathery characteristic of Al_mFe.

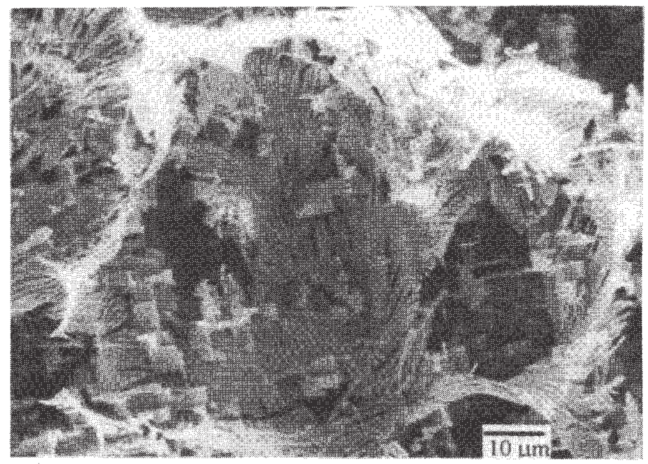

Figure 6: A complex of Al_mFe in the three-dimensional view. The fine feathers or fibers of Al_mFe can advance in a variety of curved forms and connect each other in the interdendritic region over a wide range.

Al_6Fe

Al_6Fe is another metastable phase that commonly occurs in DC ingot structure. Figure 7 shows a micrograph of Al_6Fe. Its typical appearance seems to be as a flake with several short wings. In a three-dimensional view, Al_6Fe often shows a curved plate with a number of rod-like side branches (Figure 8). Observation of various samples shows that the fine branches of Al_6Fe are faceted on the micro-scale, and that Al_6Fe generally has a flexible branching ability. If the interdendritic space is large enough (at the corners of several aluminum cells), Al_6Fe's form can become quite complicated. A skeleton-like morphology is occasionally observed.

α-AlFeSi

In low Si 1xxx alloys, the common intermetallic phases are the three binary Al-Fe compounds mentioned above. With increased silicon content, the metastable α-AlFeSi becomes one of the major phases in the ingot structure. The microstructural characteristic of α-AlFeSi is the so-called "Chinese script" (Figure 9). Figure 10 shows the three-dimensional view of α-AlFeSi. It looks like a complicated dendrite form. Within a complex of the particle, some plates are large and wide, while others are small and thin. Moreover, in some plates, the small platelets can grow directly from the sides of a large plate. This arrangement and the non-uniform spacing, probably cause the script image in a metallographic section. An important feature of the α-AlFeSi, that leads to distinguish it easily from the binary Al-Fe intermetallics, is the triangular edge on the front of each plate. These plates are certainly faceted. Another interesting point is that in the edge of a parent plate, another plate can nucleate, branch and further grow in various directions. In this way the α-AlFeSi plates connect each other in the interdendritic region.

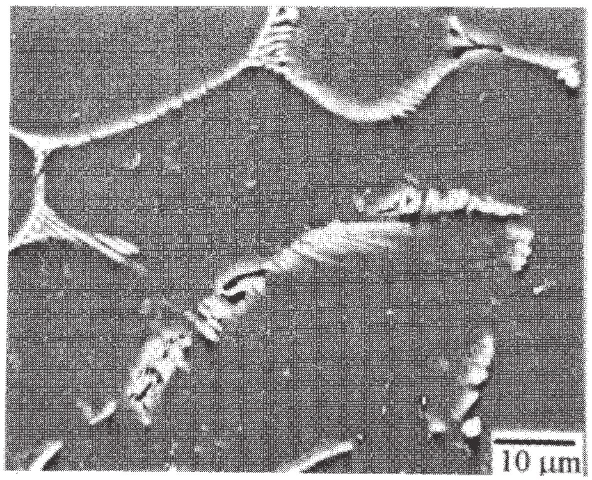

Figure 7: Micrograph of Al_6Fe in a metallographic section (SEM in backscatter mode).

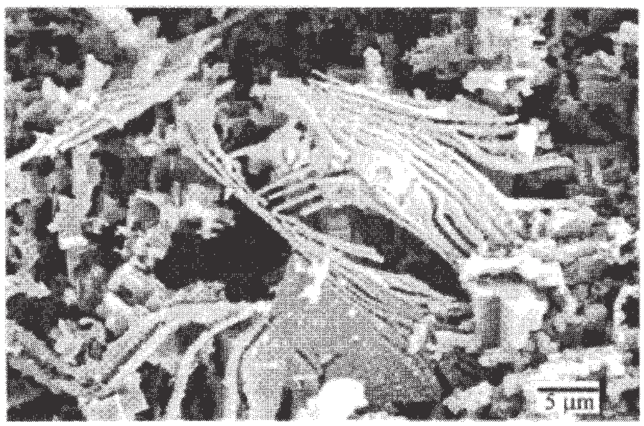

Figure 8: SEM micrograph (deep etched) showing that Al_6Fe often has a curved plate with a number of rod-like side branches.

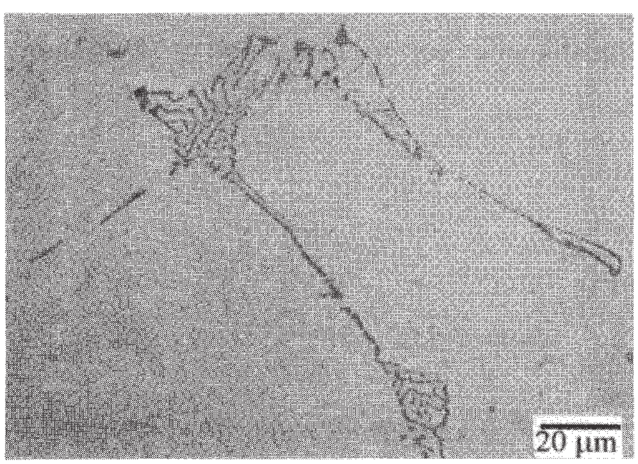

Figure 9: Photomicrograph of α-AlFeSi showing the script characteristic.

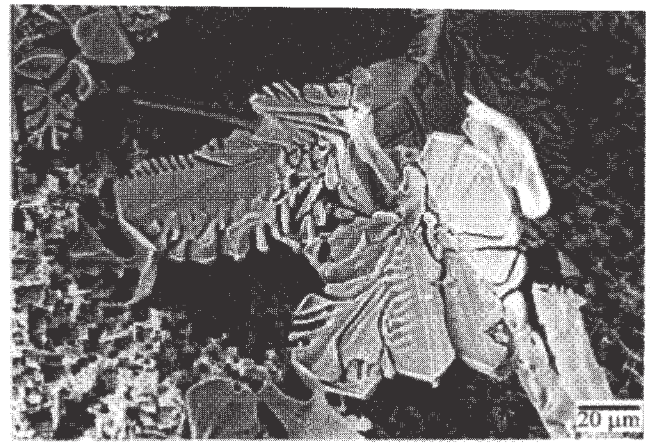

Figure 10: Three-dimensional view of α-AlFeSi in the ingot structure (SEM, deep etched).

<u>Nucleation Behavior</u>

In the deep etched samples, if an intermetallic particle is close and parallel to the cut surface, the nucleation site of the particles may occasionally be brought to light for observation.

Al_mFe

Figure 11 shows an Al_mFe growth unit and its nucleation center. It is clear to see that the Al_mFe phase grows from the center into its surroundings with numerous fine branched feathers or fibers. The site of the nucleation appears in the form of an agglomerate of a few small particles, that range from 0.2 to 1 µm. SEM-EDS (energy dispersive spectrometer) analysis indicates that these particles are a high Ti-containing compound. The crystal structure of the compound is under further investigation.

Some observations were performed in a transition region where the plate-like Al_3Fe are located on one side and the fine feathery Al_mFe on the other side. Figure 12 shows an example of how the Al_mFe nucleate and grow in this region. The appearance of the intermetallic particle here is very unique. The lower part of the particle is typically plate-like and relates to the stable Al_3Fe phase, whereas the upper part has a fine feathery characteristic and certainly belongs to the metastable Al_mFe phase. Since the Al_3Fe has a higher eutectic temperature than the Al_mFe, Al_3Fe forms first in the interdendritic liquid during the solidification and then Al_mFe follows. The evidence of the picture indicates that the Al_mFe can nucleate from the already existing Al_3Fe and then grow further.

Al_6Fe

Figure 13 shows a growth unit and its nucleation site of Al_6Fe. A small cubic particle (about 2 µm) is found in the center area of the Al_6Fe unit and from there the phase grows into its surroundings. SEM-EDS analysis indicates that the particle contains only two elements, mainly Al and a small amount of Fe. It is noted that after deep-etching, the surface of the α-Al matrix always exhibits the cubic form of its crystallographic nature. The size of these cubes ranges within a few micrometers. Considering that the central particle is α-Al and acts as an active nucleant for the Al_6Fe, it could explain that some iron is picked up by the SEM-EDS analysis, since the Al_6Fe phase would grow from certain planes of the α-Al crystal.

In addition, Bäckerud [9] suggested that due to the orthorhombic crystal structure of Al_6Fe, the low lattice disregistry can be well fitted between Al_6Fe and α-Al. Thus, it is reasonable to suppose that the nucleation site discovered in Figure 13 is α-Al.

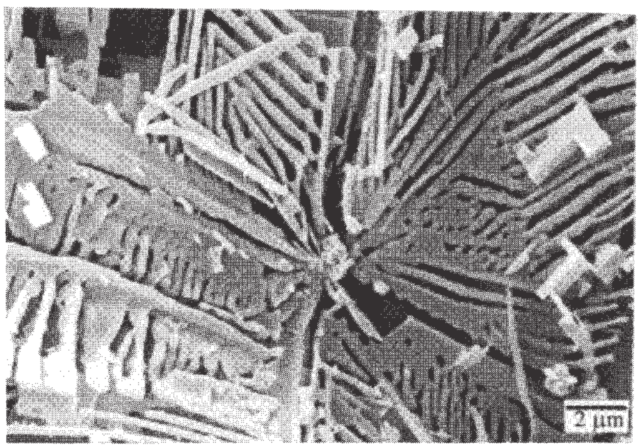

Figure 11: Nucleation center of Al_mFe in the ingot structure.

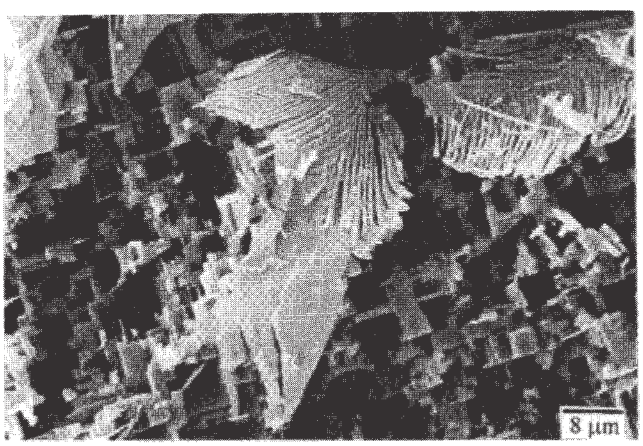

Figure 12: SEM micrograph (deep etched) showing the transition of Al_mFe from Al_3Fe.

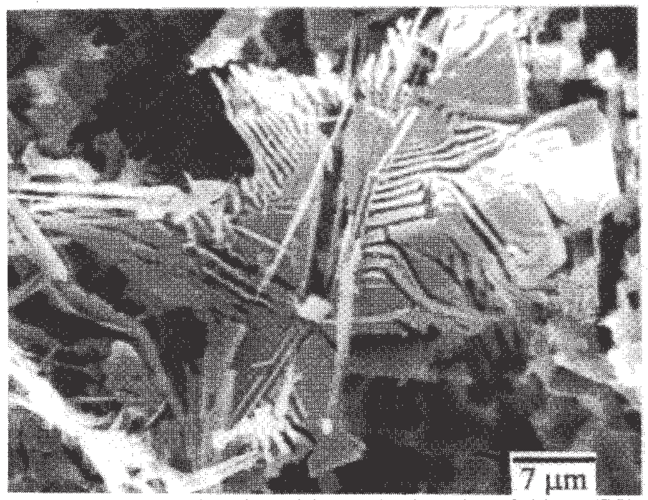

Figure 13: A growth unit and its nucleation site of Al_6Fe (SEM, deep etched).

Discussion

In the binary Al-Fe system, Al_3Fe is the only existing equilibrium phase. The entropy of fusion for Al_3Fe is greater than 2 and it therefore tends towards faceted growth [10]. In DC casting at low cooling rates, Al_3Fe grows as individual faceted plates with a preferred direction in the remaining eutectic liquid between α-Al dendrites. The faceted plates are usually straight and unrelated. In this case, repeated nucleation is the only way for Al_3Fe to maintain the continuity of the phase precipitation as solidification proceeds. At higher cooling rates, Al_3Fe begins to branch, probably caused by twin or crystal faults [10]. Side plates can form on the surface of a parent plate through different angles. The branching permits the spacing adjustment between plates and a change of growth direction, although the branching ability of Al_3Fe is somewhat limited in this way, less repeated nucleation is needed to allow continuous growth.

Our observation in the ingot structure shows that Al_mFe has fine feathery morphology and excellent branching ability. The edge of the fine branches, particularly at the growth front where it contacts with liquid, is round. Although no data of the entropy of fusion for Al_mFe is available, from the morphological viewpoint, it is obvious that the growth of Al_mFe is non-faceted.

In contrast to Al_mFe, the initial morphology of Al_6Fe is still plate-like, which can be clearly seen from a growth unit with its initial point (Fig. 13). As the growth progresses, the rod-like or feathery branches appear and go further. However, the front edge of the rod-like Al_6Fe is still faceted. This was also observed by Adam and Hogen in 2-4% Fe aluminum alloys [11]. The entropy of fusion for Al_6Fe was reported to be around 2 [9,11]. It can therefore be concluded that the growth manner of Al_6Fe is between faceted and non-faceted. With an increase in cooling rate, the tendency to non-faceted growth increases, resulting in the dominant rod-like growth of Al_6Fe. Similar to the analysis of Al_6Fe, the growth of α-AlFeSi in the dilute Al-Fe-Si alloys is also between faceted and non-faceted, but is more likely to be in the faceted direction.
Since all four intermetallics have distinct morphologies and different growth modes, the growth kinetic of each intermetallic

phase is quite different. Al_3Fe has the slowest growth kinetic associated with its faceted and relatively rigid growth mode, whereas Al_mFe exhibits the highest growth kinetic due to its non-faceted manner and excellent branching ability, providing a great growth advantage at high cooling rates (growth rates). The Al_6Fe and α-AlFeSi represent intermediate cases because of their transitional position between faceted and non-faceted.

The nucleation process and subsequent growth of individual intermetallics will control the phase selection, and thereby determine the fir-tree zone present in the ingot structure. The nucleation process is mainly dependent on the thermodynamic factor and the effectiveness of heterogeneous nucleants. The thermodynamic driving force for the formation of stable Al_3Fe is always greater than that for the metastable phases, in a descending order of Al_3Fe, Al_6Fe and Al_mFe, since Al_3Fe has a higher eutectic temperature than Al_6Fe and Al_mFe. Although one phase may be favored thermodynamically over another phase, the potential nucleants for both phases could change the competition. For example, it is often seen in DC ingots that Al_mFe exists together with Al_3Fe or even becomes the dominant phase in the shell zone where the cooling rate is the lowest in the sub-surface region of ingots. It is believed that efficient nucleants for Al_mFe, as discovered in the present work, play an important role in promoting Al_mFe in the shell zone.

On the other hand, the subsequent growth process is determined by local solidification conditions and growth modes of intermetallics. In general, as the cooling rate (growth rate) increases, the Al_3Fe will be replaced by the Al_6Fe and be further taken over by Al_mFe in the binary Al-Fe system. The growth mode of individual intermetallics will aid in understanding the phase selection during solidification. However, in dilute alloys, the eutectic reaction for formation of intermetallics takes place only in the last less than 10% of the remaining liquid. The local solidification conditions of the rest of the interdendritic liquid, particularly in the sub-surface region of ingots where the cooling rate and growth rate change dramatically, are often not available in detail, since the widely employed cell size and cooling rate measurements reflect mainly the primary α-Al growth. As a result, studies of the phase selection in DC ingots related to the fir-tree defect have still been qualitative in nature.

Summary

In the present study, the growth morphologies of the four intermetallic phases, Al_3Fe, Al_6Fe, Al_mFe and α-AlFeSi, were investigated in DC cast AA1xxx alloys. The two-dimensional image of intermetallics in a metallographic section and the three-dimensional view revealed by deep-etching were presented. It was found that all four intermetallic phases have distinct morphologies and growth kinetics. Based on the morphological and growth kinetic aspects, the characteristics and growth mechanisms of each phase in DC ingots were discussed.

The nucleation behaviors of some intermetallics were also studied. The heterogeneous nucleants of individual intermetallic phases could play an important role in the control of phase selections.

Acknowledgments

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