Modification of AI-Si Alloys

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Keywords: eutectic, modification, strontium, nucleation, castability, porosity

Abstract

Although modification is an established technology, its mechanism of operation is still not fully understood. Recent research has shown that three different eutectic solidification mechanisms can operate in Al-Si foundry alloys. The operation of each mechanism can be controlled by altering chemical composition and casting conditions. The effects of a wide range of different potential modifier elements on the eutectic nucleation mode have been studied. It is concluded that AIP particles play a key role as nucleants for eutectic Si, and that these are removed, or rendered inactive, by the addition of modifying elements to commercial purity alloys.

1. Introduction

The eutectic reaction dominates the solidification transformation of most Al-Si foundry alloys because more than 50 vol% of the alloy is eutectic Al and Si. With its highly ordered diamond cubic crystal structure, silicon is a faceted phase, with strongly anisotropic growth. It grows predominantly in the <112> directions and is bounded by the (111) crystallographic planes [1]. Due to the difficulty in changing the growth direction, branching and termination of the plate-like silicon occurs. As a result, the Al-Si eutectic is an irregular and coupled eutectic and silicon is the leading phase in unmodified alloys. However, the silicon morphology can be changed into a refined fibrous structure through modification treatment which can improve the mechanical properties of the alloy. There are three different ways that modification can be achieved during solidification:

- 1) Quench modification involves the refinement of silicon due to high cooling rates, and thus high transformation rates. Growth rates exceeding 1mm/s have been quoted as a criterion for obtaining a quench modified eutectic microstructure [1].
- 2) Chemical modification is obtained by the addition of trace levels of certain elements. Strontium, sodium or antimony are the most common modifier elements used industrially. Addition of other alkali, alkaline earth and rare earth metals have also been reported to refine the eutectic microstructure at low cooling rates and produce a silicon morphology similar to that achieved with high cooling rates, although very limited data are available in the literature.
- 3) The third method that has recently been reported to produce a modified eutectic structure is by superheating the melt. The melt is heated from the usual pouring temperature to a temperature in the range of 850-900°C and held for a period of around 15-30 minutes, and then quickly cooled to the pouring temperature before

casting. Effective refinement has been reported and it has been suggested that presence of magnesium in the alloy is critical for the method to be effective [2].

The above three methods produce a modified silicon structure on solidification. Solution heat treatment also tends to break up and spheroidize the silicon morphology in a similar manner, but usually leading to a somewhat coarser structure.

A common problem with eutectic modification is that the porosity characteristics are changed in an undesirable manner [3]. Modification has been reported to cause a redistribution of the porosity, which is frequently, but not always, associated with an increase in the porosity level. From the literature, it appears as though the redistribution of porosity is a fundamental trait of modification, while the effect of modification on the amount of porosity may depend on the casting design and the casting conditions. This paper presents recent results of the eutectic solidification characteristics of hypoeutectic Al-Si alloys, unmodified and modified by a range of different elements.

2. Experimental Methods

Several different experimental techniques have been employed throughout the research [4-5] and these are only briefly outlined in this paper. The base metal components, usually commercial purity Al and Si, were melted in an electrical resistance furnace and kept at about 720°C. A nominal composition of Al-10wt% Si was normally used because it contains a large volume fraction of eutectic, facilitating macroscopic investigation, while still being a hypoeutectic alloy. Following stirring and surface skimming, the elements to be investigated were added. These included Sr as AlSr10 master alloy rods, Na as a Na-containing flux and other elements in elemental form. Some experiments were also conducted with ultra-high purity Al-Si alloys, using super-pure aluminium (99.999%) and solar grade silicon (99.999%), and in this case alumina crucibles were used to avoid any contamination. Thermal analysis was conducted according to the method described in detail elsewhere [4-5].

Samples were also quenched at different stages during the eutectic arrest. Samples were extracted in tapered stainless-steel cups coated with a thin layer of boron nitride. Two samples were taken in parallel by submerging the cups into the melt. The cups were placed on an insulated base, a thermocouple was positioned in the centre of one cup only, and insulation boards was placed on top of both samples. The samples were allowed to cool in air resulting in a cooling rate of the liquid just prior to nucleation of the primary aluminium of approximately 1.7 K/s, and a total solidification time of approximately 300 seconds. During solidification the cooling curve from the thermocouple was monitored on a real-time display, and the sample without a thermocouple was quenched approximately 50% of the way through the eutectic reaction. Although it is acknowledged that solidification will not proceed identically in both cups, this method prevents the thermocouple from interfering with solidification, or from damaging the microstructure during quenching.

3. Eutectic Solidification Modes

Three different eutectic solidification modes have been identified in Al-Si alloys, as illustrated in Figure 1 together with quench micrographs supporting each illustration. The modes are:

- Mode I: nucleation adjacent to the tips of the dendrites, Figure 1a);
- Mode II: independent nucleation of eutectic grains in the interdendritic spaces, Figure 1b), and;
- Mode III: nucleation and growth opposite to the thermal gradient, Figure 1c).

Although combinations of these mechanisms may sometimes occur, the reproducibility of their response to the presence of certain elements is remarkable. Mode I eutectic solidification occurs in unmodified commercial Al-Si alloys, usually with a very high nucleation frequency. Addition of strontium promotes eutectic solidification according to Mode II, while sodium modification promotes Mode III eutectic solidification. Mode III eutectic solidification may entail nucleation according to Mode I or Mode II, but is generally observed to display the massive layer of eutectic adjacent to the walls of the casting. It is also quite possible that the operation of Mode III eutectic solidification is strongly influenced by the cooling conditions and thermal gradients of the casting, and possibly also the air gap formation characteristics in place under the governing alloy and casting conditions.



Figure 1: Illustration of the three eutectic solidification modes, with experimental evidence for their existence in the micrographs of quenched samples. a) Nucleation adjacent to the tips of the dendrites (Mode I) with a quenched micrograph from an unmodified alloy; b) Independent nucleation in the interdendritic liquid (Mode II) with a quenched micrograph of a Sr-modified alloy; and c) Eutectic growth opposite the thermal gradient (Mode III) with a quenched micrograph of a Na-modified alloy.

The dramatic difference in the spatial evolution and nucleation frequency of the eutectic becomes apparent upon quenching samples during the eutectic arrest, as shown in Figure 2 for a range of different elements. It can again be observed that the eutectic solidification is strongly dependent on the alloy composition, particularly the presence of certain elements. These differences are analysed and discussed in more detail in this paper.

Figure 2: Macrographs of aluminium-10wt% silicon samples that were quenched approximately half-way through the eutectic reaction. Eutectic that solidified prior to quenching is dark in appearance. (a) Ultra-high purity; (b) commercial purity (nucleation frequency too high to resolve the eutectic grains); (c) modified by 20 ppm sodium; (d) modified by 300 ppm strontium; (e) modified by 2400 ppm antimony.

4. Mechanism of Eutectic Solidification Mode Selection

Directional solidification studies by Heiberg et al. [6] have confirmed that a columnar-toequiaxed transition (CET) occurs for Al-Si eutectic solidification, similar to primary phase solidification. Elements that are rejected ahead of the Al-Si eutectic interface, such as Fe, Mg and Cu, are enriched in a diffusion layer ahead of the interface. This layer creates constitutional undercooling, just as it does in primary aluminium solidification. Elements that segregate more strongly have a stronger constitutional effect than those that segregate less [6]. Ternary element segregation causes the creation of a mushy zone ahead of the eutectic interface. Following Hunt's original analysis [7], nucleation can occur within this layer if there are nucleants available with sufficient potency to become active under the governing solidification conditions.

Phosphorous in the form of AIP particles is often quoted as a good nucleant for silicon. The lattice mismatch between AIP and Si is extremely small at only 0.4%. AIP is used commercially to grain refine hypereutectic AI-Si alloys. The early nucleation analysis conducted by Crosley and Mondolfo [8] also reported AIP as the nucleant for Si in commercial hypoeutectic alloys.



a)

Figure 3: a) A phosphorus-rich particle inside a polyhedral silicon crystal in a eutectic grain at the dendriteliquid interface in an unmodified 10 wt% silicon sample quenched early during eutectic solidification. The dashed lines indicate the probable outline of primary dendrites, prior to eutectic solidification and the refined eutectic is quenched liquid; b) EBSD of an unmodified AI-Si alloys showing a single crystallographic orientation of all aluminum, both primary and eutectic. The black areas are regions where insufficient crystallographic information was available.

The eutectic solidification mode of commercial unmodified alloys in Figure 1a suggests that the eutectic nucleates adjacent to the tips of the dendrites. It is believed that the nucleation of silicon occurs on AIP particles that are located adjacent to the tips of the dendrites, as indicated in Figure 3a). These are readily available as the phosphorous level of most commercial alloys is in the range of 10-20 ppm, and because the particles are small and unwetted by AI they are most likely pushed ahead of the evolving dendrites. EBSD analyses have shown that the crystallographic orientation of eutectic aluminium is

identical to that of the surrounding dendrite arms – See Figure 3b). This indicates that the eutectic aluminium has nucleated epitaxially on the dendrites, rather than on the silicon. This dual nucleation mechanism suggests that the nucleation of silicon is the critical step and that the aluminium is a better nucleant for eutectic aluminium than the silicon. However, subsequent to the nucleation of the eutectic phases, the eutectic grows with a typical coupled interface, i.e. Al and Si growing side-by-side, with the typically quite rough interface observed in unmodified commercial alloys. It is therefore likely that there are no common preferred crystallographic relationships between eutectic aluminium and silicon.

The role of phosphorous in eutectic nucleation is evident when comparing the eutectic solidification modes in the commercial purity alloy (Figure 2b) to the ultra-high purity alloy (Figure 2a). There is a dramatic decrease in eutectic nucleation frequency on increasing the purity. The nucleation mode appears more like Mode II in the ultra-pure alloy. The high purity alloy is virtually phosphorous free and therefore the nucleation frequency of silicon is significantly reduced.

The addition of modifying elements to the commercial purity alloy changes the eutectic solidification mode into Mode II or Mode III, or a combination of these. It is likely that the mechanism involves deactivation of the AIP particles, possibly by the formation of intermetallic phases on the AIP, rendering them inactive as potent nucleants for Si, resulting in a significant reduction of nucleation frequency. For example, in the case of Sr the intermetallics could be AISiSr or AISr phases [8]. Similar effects are also expected to occur with Na and Sb additions, and therefore Mode III solidification could be a special case where most nucleants within the bulk of the samples are inactive and therefore the eutectic cannot nucleate ahead of the main interface.

Large, globular eutectic grains are formed when Mode II eutectic solidification occurs [4]. The solid/liquid interface is quite smooth as often reported in the literature, and the grains therefore appear close to spherical in the cross section. EBSD analysis has shown that eutectic aluminium within these grains displays a sub-structure with multiple areas of different crystallographic orientation. The number and size of aluminium sub-grains within each eutectic grain has been found to vary significantly depending on modifier addition level and solidification conditions. An illustration of eutectic grains and subgrains is shown in Figure 5. The mechanism responsible for the formation of subgrains is still not understood, but may be a result of re-nucleation of aluminium on silicon during eutectic growth.



Figure 5: An illustration of eutectic grains and subgrains in Sr-modified alloys. EBSD maps are shown on the left. To the right is a model illustrating the difference between a eutectic grain (sectioned), (i), and its subgrains (ii). Based on Hogan [9].

5. Eutectic Growth

In recent years, the most well-known model to explain chemical modification relates to the growth of eutectic silicon. Lu and Hellawell [1] suggested that atoms of the modifier are absorbed onto the growth steps of the silicon solid-liquid interface creating a twin plane reentrant edge (TPRE). This is called impurity induced twinning. It has been calculated that a growth twin is formed at the interface when the atomic radius of the element relative to that of silicon (r/r_{Si}) exceeds 1.652. Because the elements causing modification, including Sr, Na, Sb, Ba, Ca, Y, and rare earth elements (eg. La, Ce, Pr and Nd), all have an atomic radius ratio close to 1.65, the theory is generally well accepted. However, recent studies [10-12] have questioned the validity of this model because the results have not confirmed a higher density of twins in modified eutectic silicon. More work is needed in this area.

A second effect on eutectic growth that has been proposed is that the eutectic growth rate is a function of the solid/liquid interface area [13], ie. at a constant transformation rate, a larger interface will grow more slowly than a small interface. Therefore, the eutectic growth rate with Mode II and Mode III eutectic solidification is expected to be much higher than for Mode I eutectics. A refinement of the eutectic spacing is expected to accompany an increased growth rate.

6. Conclusions

The eutectic in Al-Si alloys may evolve with widely different spatial distributions and is significantly affected by trace levels of several elements, particularly those known to also affect eutectic silicon morphology (modifiers). The morphology of eutectic silicon is not directly related to either the thermal parameters of the eutectic or the eutectic solidification mode . Furthermore, it is suggested that the silicon morphology is not only controlled by the TPRE effect, but also by the growth rate of the eutectic grains, which is a function of the nucleation frequency (which is controlled by composition). The eutectic solidification mode and the resulting spatial distribution of growing eutectic grains have a controlling impact on the permeability of the mushy zone during the last critical stages of solidification, and therefore porosity formation in Al-Si alloys.

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