The influence of Cu, Mg and Ni on the solidification and microstructure of Al-Si alloys

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Abstract. The influence of alloying elements (Cu, Mg, and Ni) on eutectic nucleation, eutectic grain morphology and the final microstructure of an Al-10Si commercial purity alloy in unmodified and Sr-modified conditions was investigated. It was found that the nucleation and eutectic grain growth morphologies of both the unmodified and Sr-modified Al-Si eutectic were significantly influenced by the addition of ternary alloying elements to a degree dependent on when the intermetallic phase formed during the solidification of the alloy with respect to the Al-Si eutectic. In cases where an intermetallic phase nucleated prior to the onset of the Al-Si eutectic reaction, the eutectic nucleation frequency was affected by changes to the available nuclei population. In cases where the intermetallic nucleated after the Al-Si eutectic, segregation of the ternary solutes in front of the Al-Si eutectic interface changed the nucleation and macroscopic growth dynamics. The changes in nucleation and growth dynamics of the Al-Si eutectic due to the presence of solute altered the morphology of the eutectic silicon considerably. This study has revealed a number of insights into the mechanisms of nucleation and growth of the Al-Si eutectic.

1. Introduction

Many commercial hypo-eutectic Al-Si alloys contain 5-12wt.%Si [1]. Cu and Mg are often added to achieve strengthening [1, 2]. Recent research has shown that changes in the nucleation frequency and macroscopic evolution of the Al-Si eutectic influence the final microstructure and formation of casting defects [3-6]. Impurity modification, alloy purity, the presence of solute and the solidification conditions are some of the factors that can influence eutectic nucleation, macroscopic growth patterns and the scale and morphology of the microstructure [7-9]. However, with the exception perhaps of the modifying elements Sr, Na and Sb, the influence of common alloying elements on eutectic nucleation and the macroscopic evolution of the eutectic phases in Al-Si alloys are relatively unexplored.

The solidification of a binary hypo-eutectic Al-Si alloy starts with the nucleation and growth of Al dendrites followed by the nucleation and growth of the Al-Si eutectic phases. It is reasonable to assume that the addition of a ternary alloying element will influence the number and distribution of nuclei present in the melt. In addition, solute pile-up ahead of both the primary Al phase and the eutectic growth interface can create constitutionally supercooled (CS) zones [10] which will influence both nucleation and growth. The purpose of this work is to investigate the influence of alloying elements (Cu, Mg and Ni) on eutectic nucleation, grain morphology and the final microstructure.
2. **Materials and experimental procedures**

Al-10Si-X (X = Cu, Mg, or Ni) unmodified and Sr-modified alloys were made from commercial purity aluminium, high purity silicon and master alloys (as indicated in Table 1).

| Alloy addition | Nominal alloy composition                        | Master alloy used                     |
|----------------|-----------------------------------------------|--------------------------------------|
| Cu             | Al-10Si-(1, 2,4,6) wt.%Cu                      | Al-33 wt.%Cu                         |
|                | Al-10Si-(1,2,4,6,8,10,15) wt.%Cu -350ppmSr     | Al-33 wt.%Cu, Al-10 wt.%Sr           |
| Mg             | Al-10Si-(0.5,1,5,2.5) wt.%Mg                   | Pure Mg (Commercial grade)           |
|                | Al-10Si-(0.5,1,5,2.5) wt.%Mg-350ppmSr          | Pure Mg, Al-10 wt.%Sr                |
| Ni             | Al-10Si-(0.5,2,5,4,5) wt.%Ni                   | Al-20 wt.%Ni                         |
|                | Al-10Si-(0.5,2,5,4,5) wt.%Ni-350ppmSr          | Al-20 wt.%Ni, Al-10 wt.%Sr           |

The alloys were melted at 760°C in an electric resistance furnace. Twenty minutes before casting, Sr if required, was added to the melt by an Al-10wt.%Sr master alloy. Samples were taken by dipping pre heated stainless steel cups into the melt. A type N thermocouple covered in a stainless steel sleeve was lowered quickly into one sample to record the temperature. The other samples were quenched into a water bath at room temperature at different times during eutectic solidification. After sectioning parallel to the vertical axis, the samples were polished using standard metallographic techniques.

Thermal analysis data was used in combination with the optical micrographs to observe the evolution of different phases during solidification. Quantitative metallographic studies were performed to understand the influence of increasing additions of each alloying element on the Al-Si eutectic nucleation frequency. The Sr-modified eutectic grain growth morphology was studied using the micrographs obtained from quenched samples using a stereo microscope. In unmodified samples the total number of Si -particles/m² of sample was used to approximate the nucleation frequency of the eutectic grains. In the Sr-modified alloys, eutectic grains were counted from the macrographs.

3. **Results and discussion**

3.1 **Eutectic nucleation**

The area density of eutectic grains in unmodified and Sr-modified alloy quenched samples are plotted against the solute content in figure 1 in which a considerable amount of scatter can be observed. In the case of Al-10Si-1.5Mg, Al-10Si-1.5, 2.5Ni and Al-10Si-8, 10, 15Cu samples counting the eutectic grain size was not possible due to the complex interface morphology of the eutectic grains as shown in figure 2(b) for example.

From figure 1, it can be observed that in the case of Cu additions the eutectic nucleation frequency steadily increased with an increase in the solute content with the exception of some minor variations. In the case of Mg additions the eutectic nucleation frequency increased up to 0.5wt.% in the case of unmodified alloys and 1.5wt.% in the case of Sr-modified alloys and then decreased as the solute addition increased further. In the case of Ni additions to the unmodified Al-10Si alloy, the eutectic nucleation frequency increased. Where as in the case of Sr-modified alloy the eutectic nucleation frequency slightly increased at 0.5wt.% Ni addition level and then decreased.

The different effects of the various elements at different concentrations can be rationalised by considering the solidification path of each alloy. As we observe the solidification path of the Al-10Si-X (X = Cu, Mg, or Ni) alloys using the thermal analysis curves and optical micrographs, it is
observed that the addition of a ternary alloying element resulted in the formation of an intermetallic phase for all compositions. When the intermetallic nucleated before the Al-Si eutectic reaction (circled data points in figure 1), the Al-Si eutectic nucleation frequency decreased in the unmodified and Sr-modified conditions, relative to samples with lower additions of the same elements. If the formation of the intermetallic phase occurred after the Al-Si eutectic, the ternary alloy addition resulted in an increase in the eutectic nucleation frequency in unmodified and Sr-modified alloys.

In commercial purity unmodified alloys there is an abundance of AlP particles [11-14]. These particles are considered highly potent with respect to their ability to nucleate polyhedral silicon particles, which then initiate the formation of the eutectic grains. In cases where the ternary alloying elements result in the formation of intermetallic phases before the Al-Si eutectic forms, they can interact with the available nuclei population and hence change the eutectic nucleation frequency. In this case, it is important to consider the nucleation mechanism of these intermetallics and their ability to nucleate the Al-Si eutectic. It is worth noting that for the Mg and Ni additions, when intermetallic formation occurred prior to the Al-Si eutectic solidifying nucleation frequency decreased in both the unmodified or Sr-modified conditions. This may indicate that AlP is the most potent nucleant for the Al-Si eutectic but that none of these intermetallics (Mg$_2$Si and Al$_3$Ni) were able to nucleate the Al-Si eutectic efficiently.

When an alloying element added to the Al-Si alloy is not involved in any solidification reactions prior to formation of the Al-Si eutectic, the rejected solute from both the eutectic constituents accumulates ahead of the interface as the eutectic grain is growing. Due to this solute segregation ahead of the eutectic interface the equilibrium melting point of the liquid changes locally. The actual temperature of the melt is less than the equilibrium liquidus temperature and, hence, the melt in this boundary layer is constitutionally supercooled [10]. In addition to the changes in the equilibrium liquidus temperature other changes might be expected. These include variations in the surface tension which can influence the wetting of nuclei present in the boundary layer and the melt, and changes to the chemical driving force for nucleation [15]. As such, significant changes can be expected in the nucleation behaviour due to solute segregation.

Easton et al. [16] proposed that the presence of a CS zone ahead of a primary phase can promote a wave of nucleation events ahead of the interface. In the case of unmodified Al-Si eutectic in the presence of highly potent nuclei, nucleation events readily occur ahead of the growing interface of existing eutectic grains leading to a high density of eutectic grains throughout the casting. Hence, the presence of ternary segregating elements has a relatively minor effect on the eutectic grain density in the unmodified alloys.

The addition of eutectic modifiers to Al-Si alloys significantly decreases the density and potency of the nuclei of the eutectic grains. The addition of Sr deactivates the AlP particles probably due to the nucleation of Sr-intermetallics on AlP [11, 17], which significantly reduces the potency of the nucleant particles. Thus, more CS is needed to activate these nuclei. The presence of a ternary segregating solute can provide CS ahead of the eutectic grain-liquid interface and, therefore, increase the number of eutectic grains. Despite this increase in the number of grains with increasing ternary element concentration the number of grains is significantly less than for the unmodified alloys.
3.2 Macroscopic growth
The abundant nucleation in unmodified alloys influenced the eutectic growth in two ways. For a given rate of heat extraction the interface growth rate will be low due to the presence of more solid-liquid interfacial area. In addition, as the eutectic grains are much closer to each other their solute diffusion fields quickly overlap decreasing the available driving force for growth. For Al-Si binary alloys this solidification condition leads to many small discrete eutectic grains with an irregular interface structure and it is very difficult to observe the influence of ternary alloying elements on their macroscopic growth morphology. This remains an area that needs more research.

In the case of the Sr-modified eutectic, it was observed that the effect of ternary alloying elements on eutectic macroscopic growth was dependent on when intermetallic evolution occurs. When the intermetallic is formed before the Al-Si eutectic nucleation commenced, the intermetallic influence d the eutectic interface growth by acting as a physical barrier for eutectic growth. In this case, the intermetallic phase morphology was found to be vital.

In cases where the Al-Si eutectic nucleated before the intermetallic, it was observed that at low solute addition levels the spherical morphology of the eutectic interface slightly destabilised late in solidification. As the solute addition level increased the interface destabilised sooner. Further increases in solute concentration result in eutectic grains with a dendritic morphology as shown in figure 2 which shows the macrostructure of quenched samples of Al-10Si-0.5Mg-350Sr (figure 2a) and Al-10Si-1.5Mg-350Sr (figure 2b) alloys. During eutectic solidification a diffusion layer forms due to the rejection of ternary elements at the eutectic grain-liquid interface. A CS zone can then form immediately ahead of the advancing interface and perturbations eventually grow into the CS zone. With the increase in addition of a ternary segregating element the increase in the amount of CS on one hand destabilised the eutectic interface. On the other hand, it increases the eutectic nucleation frequency which in turn decreases the interface velocity contributing towards stability of the eutectic-liquid interface. However, the results from this research that the interface destabilises earlier with an increase in the concentration of ternary alloy additions, suggests that the increase in the amount of CS ahead of the interface and its contribution towards interface destabilisation is dominant.
3.3 Eutectic microstructure

The changes in nucleation frequency and the growth morphology of the eutectic grains affected the morphology of eutectic Si. In the cases where the Al-Si eutectic nucleation frequency decreased due to the addition of solute (Mg with concentration high enough to form pre-eutectic intermetallics), the final eutectic silicon morphology changed from flake-like to a mixture of flake-like and fibrous silicon as shown in figure 3. Figure 3 shows the micrographs and macrographs of unmodified quenched samples of Al-10Si-0.5Mg (figure 3a) and Al-10Si-2.5Mg (figure 3b) alloys.

With an increase in the Al-Si eutectic nucleation frequency, for example the case of Cu additions to Sr-modified alloys, the silicon morphology changed from completely fibrous to a mixture of flake-like and fibrous morphologies as shown in figure 4. Figure 4 shows the micrographs and macrographs of the Al-10Si-2Cu-350Sr (figure 4a) and Al-10Si-8Cu-350Sr (figure 4b) alloy samples.

The origin of the morphological change from flake-like to fibrous Si with the addition of eutectic modifiers is not fully understood. Studies have generally focused either on the effect of modifiers on the nuclei [11, 18-22] or on the effect of modifiers on the eutectic Si growth [23-26]. However, it is likely that a modifier element has a combined effect on both the nucleation and the growth of the eutectic Si.

Most faceted phases, including Si, can undergo a roughening transition (faceted to non-faceted) when the driving force for growth or the interface growth velocity increases [27]. Apart from twinning [23, 28] it is believed that the driving force ahead of the solidifying interface and the growth velocity of the interface controls the Si morphology [20]. These two parameters change during the solidification of a particular alloy and they are also influenced by the changes in the nucleation and macroscopic growth modes that are caused by the addition of a ternary alloying element. The relative impact of these two factors is difficult to separate due to the complex interactions between them.
This work has shown that CS plays an important role in each step of the solidification of Al-Si alloys from nucleation and eutectic grain growth to the degree of modification of the Si phase. First, CS promotes the nucleation of eutectic grains throughout the casting. Second, increasing the amount of CS causes destabilisation of the eutectic grain interface from spherical to dendritic. Third, the growth rate of the eutectic grain interface is controlled by the amount of CS developed between the eutectic grains. The growth rate is initially high when the grain spacing is large as a higher amount of CS can be sustained over longer distances before the diffusion fields overlap decreasing the amount of CS and thus the growth velocity, causing a transition from fibrous to flake-like Si (dependent on the concentration of modifier). The interdependence between eutectic nucleation and growth influences the final eutectic microstructure. It is important to take factors such as the solidification conditions, nuclei population, macroscopic growth mode and intermetallic evolution into consideration when predicting the final eutectic microstructure of a commercial foundry alloy.

4. Conclusions

- The addition of a ternary alloying element (Cu, Mg, and Ni) to an Al-10Si alloy influences the eutectic nucleation frequency, growth morphology and the final alloy microstructure considerably.
- When the addition of a ternary element resulted in the nucleation of an intermetallic phase as the primary phase or as a binary eutectic phase prior to Si nucleation, there is a decrease in the eutectic nucleation frequency both in unmodified and Sr-modified conditions probably due to a change in the nuclei population.
- Presence of a constitutionally undercooled zone ahead of the eutectic interface does not result in major changes in the unmodified eutectic nucleation frequency due to the presence of a high number of potent nuclei (probably AlP). In Sr-modified Al-Si alloys where the eutectic nucleation frequency is very low compared to the unmodified alloy, the addition of solute (even 1 wt.% of Cu) results in increased nucleation. Further increases in the solute content results in an increase in the number of eutectic grains and a decrease in their size. This important result indicates that the basic principles relating to the effect of solute on grain refining can be extended to eutectic growth as well.
- In Sr-modified alloys solute pile-up ahead of the eutectic interface (due to the presence of ternary alloying element) influences the eutectic macroscopic growth morphology significantly. After a critical value of solute addition a dendritic growth pattern emerged in the eutectic (i.e. the eutectic grains developed primary arms).
- It follows that the eutectic silicon morphology depends both on eutectic nucleation and growth dynamics and the influence of solute must be considered.

Figure 4. Influence of the copper concentration on the morphological transition of the eutectic Si in eutectic cells of samples with (a) 2 wt.% Cu and (b) 8 wt.% Cu. The insets show the macrographs.
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