





# Effects of combined additions of Sr and AlTiB grain refiners in hypoeutectic Al–Si foundry alloys

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#### Abstract

Strontium is the most widely used and a very effective element for modifying the morphology of eutectic silicon, while Ti and B are commonly present in the commercial grain refiners used for Al–Si alloys. Systematic studies on the effects of combined additions of Sr and different AlTiB grain refiners on the Al+Si eutectic and primary aluminium solidification have been performed. While slight coarsening of both eutectic Si and primary aluminium grains occurs during holding, no obvious interactions are observed between Sr and AlTiB grain refiners when the addition level of grain refiners is low. As a result, a well-modified and grain refined structure was obtained. However, strong negative interactions between Sr and Al1.5Ti1.5B were observed as the addition level of the grain refiner increases. It was found that these interactions have a much more profound impact on the eutectic solidification than the primary Al solidification. The melt treated with combined additions of Sr and Al1.5Ti1.5B still shows good grain refinement efficiency even after losing its modification completely. The mechanism responsible for such negative interactions is further discussed.

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#### 1. Introduction

The Al–Si alloy system, characterized by high specific strength, excellent corrosion resistance, sound castability as well as good thermal and electrical conductivities, is widely used to replace the traditional materials in the areas of transportation, packaging, construction, and machinery to achieve greater weight reduction. It constitutes about 85–90% of aluminium cast parts produced. However, eutectic Si in untreated Al–Si foundry alloys is often very coarse, leading to poor mechanical properties, particularly ductility. It has long been known that the mechanical properties of Al–Si foundry alloys are heavily influenced by the morphology of eutectic Si. Changing the morphology of eutectic Si from its original coarse acicular structure to a less harmful, finer fibrous structure, known as eutectic modification, leads to a significant improvement in mechanical properties of Al–Si alloy castings.

Modification of eutectic Si is usually accomplished by adding certain modifying elements, or chemical modifiers [1–5]. Alternatively, a refined Si morphology can be achieved in casting processes where the cooling rate is high [2,3], but in such a case uniformity is only achieved if the complete casting solidifies at a high cooling rate. Strontium is used commercially to treat hypoeutectic Al–Si foundry alloys in order to refine and modify the eutectic Si from a coarse acicular to a fine fibrous morphology. However, Sr addition has been reported to promote the columnar growth of primary Al dendrites, which is deleterious to the mechanical properties of alloys [6,7]. Therefore, subsequent grain refinement of primary Al dendrites becomes a necessary step to further materialize the beneficial effects of eutectic modification on properties.

Grain refinement is standard practice for commercial wrought aluminium alloys to achieve fine equiaxed aluminium grains. In addition to superior mechanical properties, fine equiaxed grain structures are expected to lead to uniform distribution of secondary phases and micro-porosity in castings, consequently resulting in good surface finish, resistance to hot tearing and machinability. It can be achieved by different means: fast cool-

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ing, heterogeneous nucleation, solute addition, melt agitation, etc. Due to their simplicity and efficiency, solute addition and heterogeneous nucleation, usually in combination, have become common industrial practice. The well known Al5Ti1B master alloy was developed based on this mechanism, containing Al3Ti particles which dissolve quickly to release strongly segregating Ti into the melt and also potent TiB<sub>2</sub> nucleant particles. While this grain refiner is extremely effective for wrought alloys, it is not as effective in foundry alloys. Foundry alloys are already rich in solute and thus do not require the solute effect from dissolving Al<sub>3</sub>Ti, and it has been reported that the TiB<sub>2</sub> particles are rendered less potent in Al-Si foundry alloys due to the formation of TiSi compounds on the surface of TiB<sub>2</sub> particles in the presence of high Si in the melts [8]. A new type of grain refining master alloy with a Ti:B weight ratio close to or below 2.2, corresponding to the stoichiometric value of TiB<sub>2</sub>, such as Al1.5Ti1.5B and Al1.2Ti0.5B, were hence developed to eliminate Al<sub>3</sub>Ti particles in the master alloys. The excess B in the master alloy can react with Ti in the melt to form TiB2, thus providing additional potential nucleant parti-

Recent work on the combined additions of Sr and Al–B master alloys [7,9,10] and of Sr and Al5Ti1B master alloy [6] has suggested negative interactions between Sr and grain refiners added. The grain refiners reportedly reduce the strontium available for modification, i.e. extra Sr is required to neutralise this poisoning effect. However, the impact of such interactions on primary Al solidification was not reported. The mechanisms for such negative interactions are not fully understood either. This paper documents the experimental work and results aimed at determining the effects and mechanisms of Sr and AlTiB interactions in an Al–10Si–0.35Mg alloy.

### 2. Experimental

#### 2.1. Melt preparation

An Al-10Si-0.35Mg ternary alloy was selected as a base alloy in order to achieve a microstructure with a high volume fraction of eutectic. Magnesium was added to provide ternary segregation effects. The base alloy melt was prepared from commercial purity aluminium, silicon and magnesium in an induction furnace and then transferred to an electric resistance furnace, which was held at 730 °C. Upon thermal equilibrium, the melt was further alloyed using Al10Sr and AlTiB (Al5Ti1B or Al1.5Ti1.5B) master alloys. A weighed Al10Sr rod was added into the molten base alloy to ensure that the Sr level in the melt reached about 350 ppm. After being held for 10 min for homogenization, the Sr-modified melt was further treated by adding different amounts of AlTiB master alloy. All master alloys were dried in an oven at 300 °C and then wrapped in aluminium foil before addition to ensure that they dissolved properly and evenly throughout the melt. It should be emphasised that some of the addition levels of grain refiners used in this research were much higher than those used industrially. Nevertheless, this will help to assess and understand the interactions between Sr and the grain refiners.

#### 2.2. Thermal analysis

To determine the solidification behaviour of both base and treated alloys, thermal analysis was performed approximately 10 min after each addition of AlTiB master alloys, or at a predetermined interval while the treated melt was held. For comparison, thermal analysis was also performed on the base alloy and the Sr-treated melt. It was performed using a preheated graphite crucible with a centrally located Type N thermocouple. The facility was carefully calibrated just prior to testing using high-purity aluminium to achieve a standard deviation below 0.5 °C for the characteristic temperatures. Since only the temperature differences, i.e.  $\Delta T$ , are used for discussion in most cases in this paper, an even better accuracy is expected. The cooling rate in the liquid just prior to nucleation of primary aluminium was about 1 °C/s. Based on the thermal analysis, the characteristic temperatures,  $T_N$ ,  $T_{Min}$  and  $T_G$ , for both the primary Al and the eutectic solidification are readily determined.

#### 2.3. Sample characterization

Samples for chemical analysis were collected immediately after thermal analysis and analysed using an optical emission spectrometer. Fully solidified thermal analysis samples were sectioned horizontally at the level of the thermocouple. These samples were mounted in resin and prepared using a standard procedure with a final polishing stage of 0.05 µm colloidal silica suspension. The micrographs were taken in the median region of the section, 10 mm away from the bottom of the samples, in the unetched condition. Samples from the bottom of the melts at the end of holding were also collected and examined chemically and microscopically to determine the possible formation of heavy dense compounds between Sr and the AlTiB grain refiners during melt holding. While all polished samples were evaluated in an optical microscope, selected samples were also examined by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

#### 3. Results and discussion

3.1. Microstructures and fading behaviour of AlTiB master alloys

#### 3.1.1. Microstructures

In Fig. 1, two other phases in addition to the Al matrix can be observed in the AlTiB master alloys; one is dark grey and very coarse and the other is light grey and extremely fine. According to the X-ray diffraction spectra in Fig. 2, the coarse dark grey particles are believed to be Al<sub>3</sub>Ti and the fine light grey particles are boride particles, mainly TiB<sub>2</sub>. While Al5Ti1B was found to contain both TiB<sub>2</sub> and Al<sub>3</sub>Ti particles, only fine boride particles were observed in the Al1.5Ti1.5B master alloy, as shown in Figs. 1 and 2. Since there is an excess amount of B in the latter, it is believed to contain mixed borides  $(Al_X, Ti_{(1-X)})B_2$  particles. This is in agreement with the results reported in the literature [11].

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