Novel insights into kinetics of refined as cast microstructures in Al alloys

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Abstract
Structural refinement of Al alloys is by grain refinement and modification during solidification. Grain refinement is theoretically well understood as a process controlled by heterogeneous nucleation, the fulfilment of the free growth criterion and growth restriction of the formed dendrites. Thus grain refinement can be viewed as the columnar to equiaxed transition under industrial conditions. However, when detailed aspects of grain refinement are investigated in industrial practice complex interactions between alloying elements and nucleation agents as well as elements enhancing growth restriction emerge. Subsequent to grain refinement, modification in Al-Si alloys is a most important mechanism. An overview will be given on the modification mechanisms and interactions between trace alloy elements encountered during industrial casting.

Introduction

With increasing importance of structural castings made from Al alloys for light weight applications, mechanical properties as well as the ability to produce thin wall casting have to be considered. Usually Al-Si alloy are chosen because of their ability to fill intricate moulds having a high fluidity and good feeding behaviour. This is helped by the propensity of Si to expand during the last stages of solidification when the eutectic is formed. For further improvements of casting reliable properties have to be achieved in thickness sections of 3 mm and below. The question arises if current Al-Si alloys are capable to show further improvements. In particular for mass feeding thin sections a small grain size of the primary Al-phase is necessary. As a guideline, thixotropic flow of a granular system occurs when the grain size is a tenth of the wall thickness. During grain refinement of Al-Si alloys Si-poisoning occurs and the resulting grain size is in the order of 500 µm being significantly higher than that in Al-Cu alloys (200 µm). Thus with wall thicknesses approaching 3 mm and beyond, mass flow is hindered and grain refinement particularly in Al-Si alloys requires a better understanding [1].

With decreasing the volume fraction of Al-dendrites the eutectic solidification becomes increasingly dominant for the achieved mechanical properties. The naturally facetted growing Si results in a poor fracture elongation as the Si plates act as sharp

crack initiation sites. In industrial practice, Na or Sr is added to obtain a modification of the Al-Si eutectic. Subsequent heat treatments involving a solution stage result during the initial annealing period in a pinch-off of the coral-like Si structure to small Si spheres driven by Oswald ripening. The obtained microstructure exhibits a large fracture elongation making modified Al-Si alloy suitable for safety relevant castings. The modification effect of Sr and Na is believed to affect nucleation and growth of the Si. Aluminium alloys contain small amounts of 2-4 ppm of P which form with Al an AlP-compound acting as a perfect nucleation site with small lattice mismatch to Si. Sr and Na can react with P to form Na_3P and Sr_3P_2 compounds which have a lower and thus favourable enthalpy of formation than AlP. The lack of AlP compounds results in a depressed nucleation and higher nucleation undercooling detectable during thermal analysis. The subsequent growth is also affected by excess Sr and Na addition leading to a depressed growth temperature during thermal analysis. Sr and Na atoms hinder growth by the formation of multiple twins resulting in a coral- like structure. In order to achieve these twins, it is believed that atoms of a size ratio of ~ 1.6 r/R_{Si} like Sr or Na are adsorbed at the growing Si interface and force Si growth twins [2]. Other elements in particular rare earth elements show similar ratios and are found to accumulate in recycled casting alloy. For reliable modification the effect of these elements must also be understood.

In the following sections the effects of grain refinement and modification will be reviewed for Al –Si alloys.

Grain refinement in Al-Si alloys

Grain refinement is nucleation and growth restriction process which is dominated by free growth on highly efficient nucleation substrates having the same size as the critical nucleus at a given undercooling [1]. Nucleation substrates are TiB^2 particles added in the form of commercial available rods containing 5 wt. %Ti and 1 wt.% B resulting in 3.2 wt.% TiB_2 particles and 2.8 wt.% free Ti available for growth restriction. Further growth restriction is naturally occurring by alloying elements which can interact with the added Ti. The growth restriction Q is caused by the solute pile-up ahead of the dendrite tip described by the supersaturation. For low fraction solid and low solute concentrations this can be described by:

$$Q = \sum^{i} m_i(1 - k_i)C_i \qquad (1)$$

At complex alloy compositions and in particular when Al is not the primary phase Schmid-Fetzer et al. [3] have shown that the growth restriction can be described as the initial slope in the fraction solid versus temperature plot for the phase concerned according to:

$$Q_{true} = \left(\frac{\partial(\Delta T)}{\partial f_s}\right)_{f_{s\to 0}} \qquad (2)$$

The Q_{true} value can be obtained from commercially available soft-ware programs calculating the thermodynamic equilibria in alloy systems. In **Figure 1** the Q true values for Al are plotted for different Ti additions over the Si content for Al-Si-Ti alloys. It is clear from the graph that above 3-4 wt. % Si the addition of Ti has negligible effect on the overall growth restriction. Therefore, for commercial reasons alone the addition of Ti would not be advisable in Al-Si alloys as no increase in growth restriction can be achieved. Furthermore, the work by Schmid-Fetzer and co-authors on the Al-Si-Ti phase diagram [4] has also shown that Al is not the primary phase but a complex $Al_5Si_{14}Ti_7$ τ_1-phase as shown in **Figure 2**. The appearance of the τ_1 phase coincides with an increase of grain size with Si content and the onset of the Si-poisoning phenomenon at 3-4 wt.% Si. Indeed, it was shown by McKay and co-workers [5-7] that TiB_2 can be totally encapsulated by an Al-Si-Ti phase making the surrounded TiB_2 particle ineffective for the nucleation of Al directly. Interestingly, the τ_1 phase itself can form Al by a complex peritectic reaction, although no comparable grain size to e.g. in Al-Cu alloys is obtained. The existence of the τ_1 phase may explain why different grain refiner additions in Al-Si alloys always result in similar grain sizes, suggesting that these particles nucleate first the τ_1 phase and have subsequently no additional growth restriction as seen in **Figure 1**. As Ti addition does not increase growth restriction significantly over that by the Al-Si alloy itself, it is interesting to note in **Figure 2** that with decreasing Ti content below ~ 0.01 wt.% the τ_1 phase disappears and this would facilitate nucleation on TiB_2 particles. Improved grain refinement was reported for the addition of AlB_2 particles which extract Ti from the alloy to form the thermodynamically more stable TiB_2 and thereby creating effective particles and reduce the Ti content outside the stable phase field of the τ_1 phase. Therefore, for industrial applications the Ti content particular in recycled alloy needs to be tightly controlled.

Modification in Al-Si alloys

In **Figure 3** a high resolution transmission electron micrographs (HRTEM) of a modified Si particle is shown in an Al-5Si wt.% alloy in the as cast condition with 200 ppm Sr addition [8]. The Si particle is tilted to the <110> direction so that columns of atoms are visible. Within the arrangements of atoms twins are clearly visible on the {111}Si plane resulting in twins with a symmetry axis in the <112>Si direction. Interestingly, at the intersection of twin planes it was possible to detect Sr atoms by scanning transmission electron microscopy (STEM) with energy dispersive X-ray analysis (EDX). This shows clearly that Sr adsorbs at the growing interface of the Si crystal and forces a growth twin. Sr as modification agent has therefore a multiple role to play. Firstly, Sr interacts with AlP to form Sr_2P_3 thereby increasing nucleation undercooling and secondly, to introduce twins by segregation or adsorption on the surface of the growing Si crystal, which hinders growth and leads to a high growth undercooling during thermal analysis.

In contrast, in **Figure 4** a Si crystal is shown in the as cast condition with 6100 ppm Yb addition. Yb has a similar atomic ratio to Si of 1.6 and is expected to induce modification [2,9]. Rare earth elements are also expected to exhibit very stable compounds with P. Thus modification would be expected. However, although large undercoolings are observed in Al-5wt.%Si alloy with up to 6100ppmYb a truly modified structure is not observed. However, Si crystals appear refined with more Si-crystals per unit volume. The crystals appear still facetted and no clear multiple twins can be observed in the TEM picture in **Figure 4**. This suggests that Yb can refine and effect the nucleation of Si via the equilibrium between AlP and YbP. However, Yb does not tend to modify or lead to the formation of a twined network within a Si crystal. Although Yb has a low solubility in Si, similar to Sr, and both will be segregated ahead of the growing Si interface, it appears that atomic species such as Sr and Na can be adsorbed at the Si interface rather than only be segregated. This adsorption and incorporation in the growing interface facilitates the formation of growth twins by multiple twinning and the formation of coral-like Si structures which are subsequently suited to be formed to spheres by solution heat treatment.

Conclusions

I. Grain refinement of Al alloys must take into consideration the true growth restriction factor
II. During grain refinement attention must be paid to the true primary phase
III. In Al-Si alloys Ti addition has negligible effect above 3 wt.% Si on growth restriction
IV. In Al-Si alloys above 3 wt.% Si the τ_1 phase is the primary phase with even little Ti addition
V. For successful grain refinement in A-Si alloys the Ti concentration must be lowered drastically
VI. During modification Sr and Na play a multiple role in reducing AlP and facilitating multiple twinning
VII. The critical atomic size ratio is not sufficient to elucidate modification of Si crystals by multiple twinning.

References

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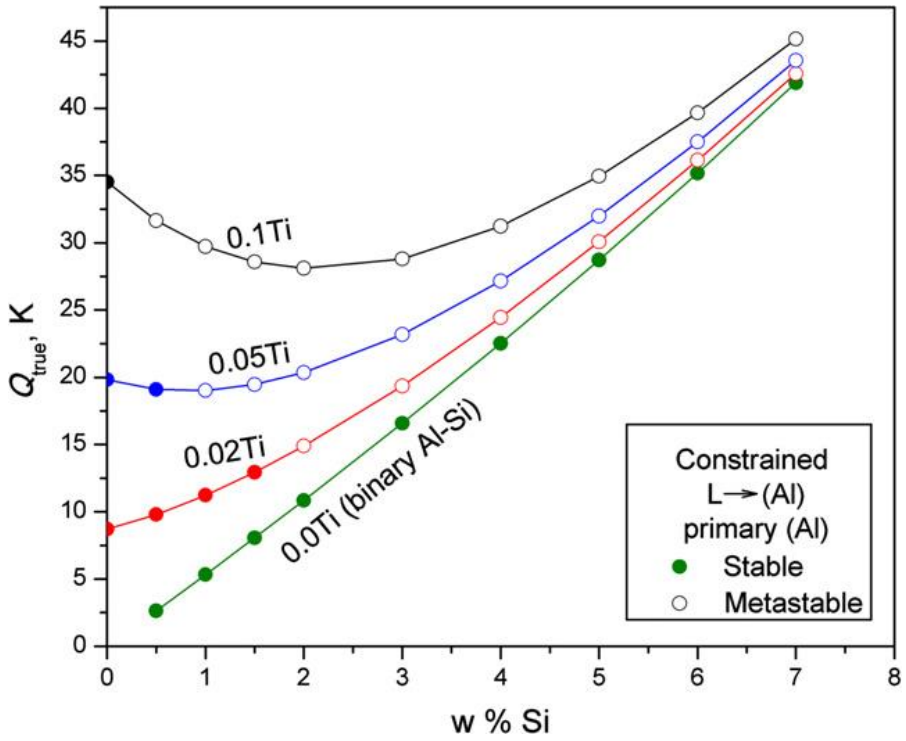

Figure 1: Caculated Q_{true} values using the metastable liquidus line for Al [3].

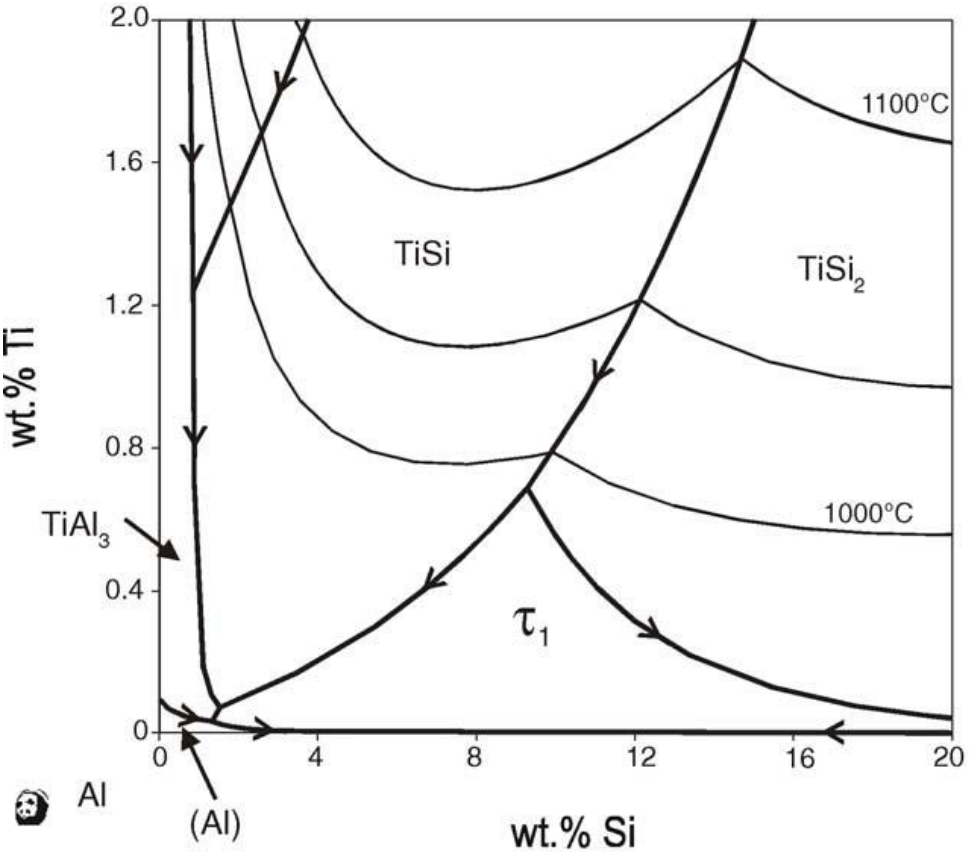

Figure 2: Calculated phase diagram of the Al-Si-Ti system showing the liquidus projection and the dominance of the τ_1 phase in the Al-rich part [4].

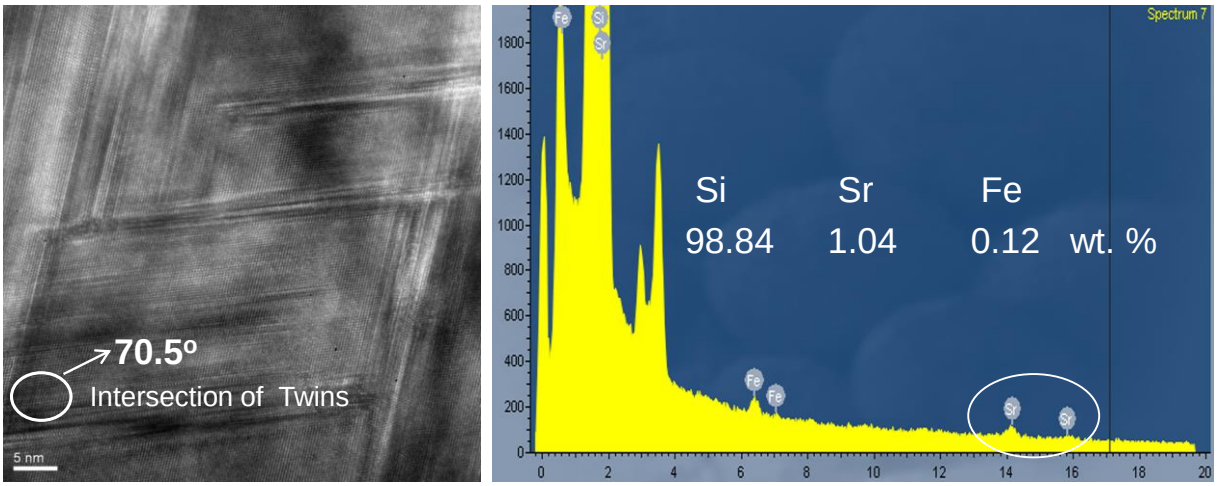

Figure 3: Multiple twinned Si particle in a Sr modified Al-5 wt.% alloy tilted to the <110> zone axis showing Sr at the re-entrant edge [8].

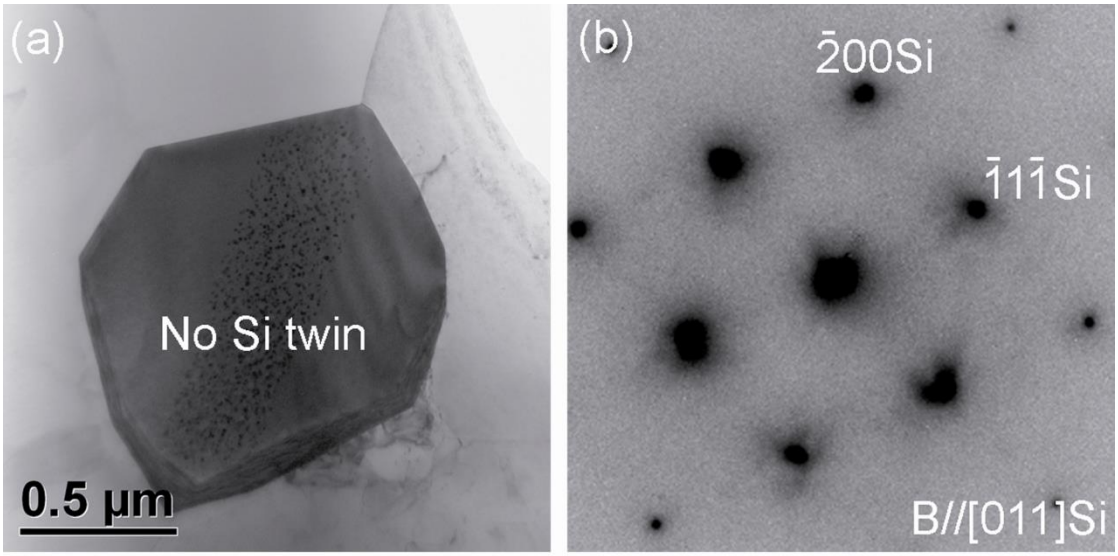

Figure 4: TEM bright field image (a) and the corresponding SADP (b) of the faceted Si phase in commercial purity Al-5Si-6100 ppm Yb alloy. No clear Si twin was observed [9].