Eutectic morphology evolution and Sr-modification in Al-Si based alloys studied by 3D phase-field simulation coupled to Calphad data

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Abstract. The mechanical properties of Al-Si cast alloys are mainly controlled by the morphology of the eutectic silicon. Phase-field simulations were carried out to study the evolution of the multidimensional branched eutectic structures in 3D. Coupling to a Calphad database provided thermodynamic data for the multicomponent multiphase Al-Si-Sr-P system. A major challenge was to model the effect of the trace element Sr. Minor amounts of Sr are known to modify the silicon morphology from coarse flakes to fine coral-like fibers. However, the underlying mechanisms are still not fully understood. Two different in literature most discussed mechanisms were modelled: a) an effect of Sr on the growth kinetics of eutectic silicon and b) the formation of Al$_2$Si$_2$Sr on AlP particles, which consumes most potent nucleation sites and forces eutectic silicon to form with lower frequency and higher undercooling. The phase-field simulations only revealed a successful modification of the eutectic morphology when both effects acted in combination. Only in this case a clear depression of the eutectic temperature was observed. The required phase formation sequence L→ fcc-(Al)→ AlP→ Al$_2$Si$_2$Sr→ (Si) determines critical values for the Sr and P content.

1. Introduction

Hypoeutectic Al-Si alloys offer excellent casting characteristics, good ductility and corrosion resistance. A drawback is the coarse flaky morphology of the unmodified eutectic (Si) phase which deteriorates the mechanical properties and favors cracking [1]. Minor Sr addition of the order of 100-400 ppm is known to significantly improve the properties by modifying the (Si) morphology to refined fibers. Despite the technical experience with Sr modification, the underlying mechanisms by which Sr affects the eutectic morphology are still controversially discussed as reviewed in [2-3]. The most-widely accepted theory is that adsorbed Sr atoms hinder the growth of (Si) in the preferred growth direction and trigger multidirectional twinning. [4, 5]. Another well-approved hypothesis is that Al$_2$Si$_2$Sr precipitates neutralize the fine dispersed AlP particles as nucleation sites for (Si), thus reducing its nucleation frequency [6, 7]. We considered both hypotheses in our phase-field model and performed 3D microstructure simulations to test which of both aspects dominates the modification of the eutectic structure. As basis for our phase-field study we chose the prototypic cast alloy AlSi7 whose solidified structure consists of roughly 50% fcc-(Al)-(Si) eutectic. Simulations were run for varied P and Sr levels based on thermodynamic data evaluated from a recently new assessed Calphad database for the Al-Si-P-Sr system [8, 9].
Microstructure simulation were run using the multicomponent multiphase-field model by Eiken et al. [10] as implemented in the software MICRESS® [11]. Mobility correction and anti-trapping are formulated in the thin interface limit [12] and profile specific FD-correction terms minimize the numerical discretization error [13]. The size of the 3D calculation domain was set to 140 µm x 40 µm x 100 µm with a grid resolution of Δx=0.4 µm, revealing 8.75 million numerical cells. The multiple phase-field equations described the evolution of the phases: liquid, fcc-(Al), (Si), AlP and Al$_2$Si$_2$Sr based on the phase-specific interfacial energies: $\sigma_{L/fcc}^0 = 0.165$ Jm$^{-2}$ [14], $\sigma_{L/(Si)}^0 = 0.352$ Jm$^{-2}$ [14], $\sigma_{L/AlP}^0 = 0.1$ Jm$^{-2}$, $\sigma_{L/Al2Si2Sr}^{fcc} = 0.2$ Jm$^{-2}$, $\sigma_{fcc/fcc}^0 = 0.15$ Jm$^{-2}$, $\sigma_{fcc/(Si)}^0 = 0.38$ Jm$^{-2}$. Solute redistribution and diffusion was solved for the components Si, P and Sr applying Arrhenius functions for the temperature dependent diffusion coefficients, preprocessed from the mobility database TC-MobAl1[15]: $D_{0}^{Si,fcc} = 1.34 \times 10^{-7}$ m$^2$s$^{-1}$, $Q_{Si,fcc} = 3 \times 10^{4}$ Jmol$^{-1}$, $D_{0}^{Si,fcc} = 0.89 \times 10^{-4}$ m$^2$s$^{-1}$, $Q_{Si,fcc} = 1.36 \times 10^{4}$ Jmol$^{-1}$, $D_{0}^{Sr,L} = 1.3 \times 10^{-7}$ m$^2$s$^{-1}$, $Q_{Sr,L} = 3 \times 10^{3}$ Jmol$^{-1}$. Diffusion coefficients of P were estimated to be equal to those of Sr, as no specific data was available. Since the heat diffusion length was large compared to the domain size, the temperature could be assumed to be homogeneous. The temperature evolution with time was calculated from the balance of heat extraction and growth-related latent heat release averaged over the calculation domain [16]. The simulation started at a temperature of T = 615 °C from 100% liquid phase with a constant heat extraction rate of $q = 1.8 \times 10^{5}$ Js$^{-1}$m$^{-3}$. All thermodynamic quantities such as driving forces, local undercooling, interface concentrations, heat capacity and enthalpy were evaluated as function of local composition and actual temperature from a Calphad dataset for the Al-Si-Sr-P system [9, 15], as illustrated in Fig. 1.

2.1 Modelling of heterogeneous nucleation

An embedded model for heterogeneous nucleation generates new seeds at particular nucleation sites when the local undercooling, as function of composition and temperature, reaches a critical value [16]. In the present simulations, fcc-(Al) nucleates as primary phase with a critical undercooling of $\Delta T_{fcc} = 2$°C in one of the domain corners. Later, it nucleates again as eutectic phase on the (Si) surface. Finely dispersed AlP particles nucleate with a critical undercooling of $\Delta T_{AlP} = 2$°C and a minimal distance of $\Delta x = 20$µm on randomly distributed sites in the melt. The growing AlP particles in turn represent polar sites for nucleation of the phases (Si) and Al$_2$Si$_2$Sr. The required undercooling is evaluated according to the free growth concept for heterogeneous nucleation as function of the particle size by

$$\Delta T_{a} = 2\sigma_{aL}^{0}/(\Delta S_{aL} r_{AlP}) \quad { with } \quad r_{AlP} = \frac{1}{\sqrt{4\phi_{AlP}/(3\pi)}} \Delta x,$$

where $\sigma_{aL}^{0}$ denotes the mean surface energy and $\Delta S_{aL}$ the enthalpy of fusion of the nucleating phase $a$, which may be either (Si) or Al$_2$Si$_2$Sr. The particle radius $r_{AlP}$ is evaluated under assumption of spherical geometry from the local phase fraction $\phi_{AlP}$ as long as it is too small to be accurately resolved on the numerical grid. Whether (Si) or Al$_2$Si$_2$Sr nucleates on a particular AlP particle depends on which of the phases first reaches the required undercooling. In the absence of free AlP particles (Si) can alternatively nucleate on another single nucleation site when it reaches a higher undercooling of $\Delta T_{(Si)} = 10$°C.

2.2 Modelling of anisotropy and effects of Sr on (Si)-growth kinetics

The interfacial properties of the solid phases against the liquid were modelled anisotropic under consideration of their specific lattice symmetry, e.g. the interfacial energy of fcc-(Al) was modelled by a standard weak cubic anisotropy function with a coefficients of $\delta_s = 0.02$ and the interfacial mobility
with a coefficient of $\delta_n = 0.05$. Of greater significance for the evolution of the eutectic structure is the faceted growth of (Si), which is governed by the slowest-growing and lowest-energy $\{111\}$-facets. We adopted the modelling of the faceted (Si)-mobility $\mu_{\text{Si}}$ from [17] and used the same, but reciprocal, anisotropy function $a_{\text{Si}}(\theta)$ to model the interfacial stiffness $\sigma^*$.

$$\mu(\theta) = \mu^0 \cdot a(\theta) \text{ and } \sigma^*(\theta) = \sigma^0 \cdot a(\theta)^{-1}$$

with $a(\theta) = \delta_n + (1-\delta_n) \cdot |\tan \theta| \cdot \tanh (|\tan \theta|^{\frac{1}{2}})$ and $\theta = \arccos (\vec{n} \cdot \vec{f}_{\text{n}})$. \(\theta\) denotes the angle between the interfacial normal vector and the nearest $\{111\}$-facet vector $\vec{f}_{\text{n}}$. The direct modelling of the interfacial stiffness $\sigma^*$ instead of the interface energy $\sigma$ avoids negative values in forbidden growth directions.

A special issue of eutectic (Si) in Al-Si is that internal twinning plays an important role and can be affected by Sr-addition. (Si)-flakes commonly consist of multiple parallel twins, i.e. the crystal orientation is repeatedly mirrored back and forth with respect to the same (111)-twin plane. This arrangement is particularly stable in unmodified Al-Si-alloys due to the twin-plane re-entrant edge mechanism (TPRE), which favors growth in $\langle 112 \rangle$-directions parallel to the (111)-twin plane [3, 5]. To consider the internal twinning in our simulations, we developed an effective anisotropy function which features not only the $\{111\}$-facets of the original crystal, but additionally the mirrored $\{111\}$-facets of the potential twin crystals. The potency for twinning in one or multiple directions can be adjusted by the choice of the facet coefficients. Table 1 gives the facet vectors and the sets of facet coefficients used in this study. Set 1 reflects the standard growth mode according to the TPRE mechanism. It favors twinning with respect to a single (111)-plane and promotes growth in the six $\langle 112 \rangle$-directions within this plane. Set 2 models the Sr-modified growth kinetics. It is assumed that adsorbed Sr atoms at the (Si)-surface hinder growth in the preferred $\langle 112 \rangle$-direction and promote frequent multidirectional twinning with respect to all four potential twin $\{111\}$-planes [3-5]. In this study, Set 2 is applied to model the interface mobility in all Sr-containing alloys, independent of the precise Sr concentration. The reference mobility value was defined as $10^{-13} \text{m}^4 \text{J}^{-1} \text{s}^{-1}$ in both cases. The interfacial stiffness remained unaffected by the Sr addition. Fig. 1 illustrates the two different faceted anisotropies for (Si).

**Figure 1** The MICRESS® software simulates nucleation and growth of the multiple solid phases as well as growth-related solute redistribution and latent heat release. Thermodynamic data is evaluated from a CALPHAD database as function of local composition. A dedicated effective anisotropy function models the impact of strontium on the (Si)/liquid interface kinetics due to impurity induced twinning.
Table 1: Facet vectors and coefficients defined in the effective anisotropy function for eutectic (Si)

| j | x | y | z | δ_i (Set 1) | δ_i (Set 2) |
|---|---|---|---|-------------|-------------|
| 1 | 1 | 1 | 1 | 0.001       | 0.4         |
| 1 | 1 | -1| 1 | 0.6         | 0.4         |
| 1 | 1 | -1| -1| 0.6         | 0.4         |
| 1 | 1 | 1 | -1| 0.8         | 0.4         |
| 1 | 1 | 5 | -1| 0.8         | 0.4         |
| 1 | 1 | 5 | 1  | 0.8         | 0.4         |
| 5 | 1 | 1 | 5  | 1          | 0.4         |
| 1 | 5 | 1 | 1  | 0.4         | 0.4         |
| 1 | 5 | 1 | 5  | 0.4         | 0.4         |
| 5 | 1 | 1 | 1  | 0.4         | 0.4         |
| 1 | 1 | 5 | 1  | 0.4         | 0.4         |
| 1 | 1 | 1 | 5  | 0.4         | 0.4         |

3. Simulated morphology evolution

The following three simulations with varying strontium levels are representative for different modes of eutectic solidification in hypoeutectic Al-Si cast alloys:

3.1 Simulation of AlSi7 + 5 ppm P without Sr addition

The first simulation example illustrates unmodified solidification of the hypoeutectic AlSi7 without Sr addition. Phosphorus has been considered as unavoidable trace element. The P level of 5 ppm was selected as typical value within the purity range of a commercial alloy. Figure 2a shows the microstructure shortly before onset of the eutectic growth. Small AlP particles have already formed in the melt, especially in the vicinity of primary fcc-(Al) where the P content is highest due to segregation. These AlP particles act as inoculants and trigger frequent nucleation of eutectic (Si). During the initial decoupled growth (Si) evolves as blocky polyhedrons, forming the centers of the numerous eutectic cells (Figure 2b). When the blocky (Si) is almost completely encapsulated by either primary or newly nucleated fcc-(Al), it starts to branch. Both phases then grow in a coupled eutectic mode until end of solidification. Figures 2c and 2d illustrate the evolution of the coarse flaky (Si) morphology around the blocky centers, which is characteristic for unmodified eutectic growth.

3.2 Simulation of AlSi7 + 5 ppm P + 50 ppm Sr

The second simulation represents an example of unsuccessful modification due to insufficient Sr addition. The effect of strontium on the interface kinetics of the eutectic (Si) has been modeled by using the modified anisotropy coefficients (Set 2) given in table 1. The simulation results in figures 3a-d reveal that the mere modification of the interface kinetics is not sufficient to achieve a modification of the resulting eutectic morphology. Due to the low Sr content, Al2Si2Sr does not become stable early enough to compete with (Si) on the potent nucleation sites. Despite the altered interface kinetics no significant refinement or structural modification can be observed. The temperature curves in section 4 will show that the kinetic growth undercooling is too low to activate the Sr-induced twinning.

3.3 Simulation of AlSi7 + 5 ppm P + 100 ppm Sr

The last simulation example eventually describes successful eutectic modification. It points out that a refined fibrous (Si) structure is only obtained when Sr affects both, growth and nucleation of the (Si) phase. All process conditions are identically adopted from the previous simulation and also the effect of strontium on the (Si) growth kinetics is modelled in exactly the same way. The only difference to the previous simulation is that the Sr level is increased to 100 ppm. This causes Al2Si2Sr to become stable prior to (Si) and thus to first nucleate on the AlP particles as shown by figure 4a. It is emphasized that the nucleation sequence has not been given as input, but results from evaluation of the local undercooling evaluated from the thermodynamic database as function of composition. Due to the fact that the Al2Si2Sr precipitates have already occupied all potent nucleation before onset of the eutectic growth, (Si) nucleates retarded on the single alternative nucleation site. Because of the high undercooling, eutectic fcc-(Al) directly nucleates on its surface (figure 4b) and both phases than grow in coupled eutectic mode. Figures 4c and 4d illustrate the refined coral-like growth of the (Si) fibers, which is characteristic for Sr-modified eutectic growth.

Figures 5a-c give the (Si) morphologies after 70s in comparison for the three different Sr levels.
Figure 2 Simulation of unmodified eutectic solidification for AlSi7 + 5 ppm P. (Si) nucleates on numerous AlP particles. It becomes encased by fcc-(Al) and branches during coupled eutectic growth.

Figure 3 Simulation of unsuccessful eutectic modification for AlSi7 + 5 ppm P + 50 ppm Sr. The Al$_2$Si$_2$Sr phase does not become stable early enough to prevent nucleation of (Si) on AlP particles.
**Figure 4** Simulation of successful eutectic modification for AlSi7 +5 ppmP +100 ppm Sr. Fibrous coral-like growth is obtained when Sr affects both nucleation and growth of the (Si) phase.

**Figure 5** Comparison of the (Si) morphologies at t= 70s simulated for three different Sr levels. The unmodified structure is characterized by multiple eutectic cells with blocky (Si) centers and coarse flaky (Si) branches. The structure obtained for 50 ppm is almost identical, only the shape of the blocky cell centers exhibits a slightly different shape. The increased Sr level of 100 ppm eventually revealed the targeted modification towards coral-like (Si)-growth with refined fibrous morphology.
3. Discussion of the simulated temperature curves

The modification of the eutectic structure was found to be correlated to a change in the temperature evolution. Figure 6 shows the simulated temperature curves for the previously described examples in comparison. Identically in all three simulations, the temperature continuously decreases during the primary growth of fcc-(Al). Differences start with the onset of the eutectic transition: The first example of unmodified eutectic solidification without Sr addition yields a relative low eutectic nucleation undercooling due to the fact that (Si) forms on potent AlP inoculants. Latent heat release then leads to recalescence. During coupled eutectic growth, the temperature remains almost constant, as the heat extraction is completely compensated by latent heat release. Eventually, on completion of the eutectic solidification, the latent heat release stops and the temperature rapidly drops according to the heat extraction rate.

It is apparent that the temperature curve does not change, when the Sr-addition is insufficient, while the successful modification by 100 ppm Sr yields clearly decreased temperatures, both during eutectic nucleation and growth. This is in agreement with the empirical observation that the depression of the eutectic temperature is a major indicator for successful modification. In fact, the simulations give evidence that the increased growth undercooling is an indispensable prerequisite for eutectic modification. While the thermodynamic impact of Sr on the eutectic temperature is completely negligible, the altered nucleation was found to be the dominating factor. An inverse correlation between growth undercooling and nucleation frequency was observed: When (Si) nucleates with high frequency on AlP, the individual eutectic cells grow relatively slow, i.e. with low undercooling close to local thermodynamic equilibrium. The growth process is in this case controlled by diffusion, and the interface kinetics – no matter if modified or not – are of minor significance.

This is different in the example with an increased Sr content of 100 ppm, where Al$_2$Si$_2$Sr successfully blocks the AlP particles and (Si) nucleates with higher undercooling on the alternative site. Since the single eutectic cell has to grow much faster than multiple cells in order to release the same amount of latent heat, the kinetic undercooling is increased and the process is shifted to interface-control. This brings the Sr modified interface kinetics into effect: The reduced mobility further amplifies the initial depression of the eutectic temperature which leads to a general refinement, while the Sr-induced twinning modifies the (Si) morphology to multidirectionally-branched fibers.

![Figure 6](image_url)

**Figure 6** Simulated temperature curves for AlSi7 + 5ppm P with different Sr levels.

In agreement with experimental observations, successful modification of the eutectic morphology reveals an increased nucleation undercooling and a depression of the eutectic temperature.
3. Conclusions

The phase-field method was successfully applied to reproduce both unmodified and Sr-modified eutectic solidification of AlSi7. A major issue had been to bridge the gap from the internal Sr-affected twinning to the outer faceted growth and branching behavior of the eutectic (Si). This problem was solved by formulation of effective anisotropy functions which implicitly account for the mirrored twin facets. The twinning potential in different directions was adjusted by the choice of the facet parameters. Alloys without Sr additions were modelled with standard one-directional twinning and preferred growth in six coplanar <112>-directions according to the TPRE mechanism. Applied in simulation of AlSi7 + 5 ppm P this reproduced a coarse blocky and flaky eutectic structure, characteristic for unmodified eutectic growth.

A second set of coefficients was defined to model Sr-induced multi-directional twinning with uniform, but reduced amplitudes in all possible <112>-directions. The altered interface mobility was applied to all Sr containing alloys, but only showed an effect above a critical Sr-level of about 80 ppm. In simulations on AlSi7 + 5 ppm P with subcritical Sr levels, the eutectic (Si) nucleates with high frequency on AlP particles and then evolves diffusion-controlled close to local equilibrium. In the absence of kinetic growth undercooling, the altered interface kinetics does not become effective and thus no modification of the eutectic structure is obtained. This is different for AlSi7 + 5 ppm P with supercritical Sr addition where Al2Si2Sr forms prior to (Si) and blocks the AlP particles. (Si) nucleates under this condition with increased undercooling and reduced frequency, and then evolves interface-controlled with high velocity. The Sr-altered interface kinetics, once brought into effect, further amplifies the depression of the eutectic temperature and eventually results in the refined coral-like fibrous growth, characteristic for Sr-modification. From these results, it can be concluded that the effects of Sr on both nucleation and growth of eutectic (Si) have to be considered to efficiently control Sr-modification in hypoeutectic Al-Si alloys.

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