

In-situ X-ray video microscopy studies of Al-Si eutectic solidification

Ragnvald H. Mathiesen¹, Lars Arnberg², Yanjun Li³, Arne K. Dahle⁴

¹Department of Physics, NTNU, N-7491 Trondheim, Norway

²Department of Material Science, NTNU, N-7491 Trondheim, Norway

³SINTEF Materials and Chemistry, N-7465 Trondheim, Norway

⁴ARC CoE for Design in Light Metals, Materials Engineering, Univ. Queensland, Brisbane Qld 4072, Australia

In-situ studies of Al-Si eutectic growth has been carried out for the first time by X-ray video microscopy during directional solidification of Al-Si-Cu alloys with and without Sr-additions. The unmodified eutectics showed distinctive non-isothermal growth dynamics, where Si-crystals attained needle-like tip morphologies and progressed under significantly higher undercooling than Al, leading to formation of an irregular eutectic with Si as the leading phase and subsequent nucleation of Al on the Si-surfaces. In the Sr-modified alloys, the eutectic reaction was found to be strongly suppressed, occurring with low nucleation frequencies at undercoolings in the range 10-18 K. In the Cu-enriched melt, the eutectic front was found to attain meso-scale interface perturbations evolving into equiaxed cellular rosettes in order to accommodate to the long-range redistribution of Cu from the composite eutectic interface. The eutectic front also attained short-range microscale interface perturbations consistent with characteristics of a fibrous Si growth, however further improvements in spatial resolution is required in order to study microscale structure formation in greater detail. Evidence was found in support of Si-nucleation occurring on potent particles suspended in the melt. Yet, both with Sr-modified and unmodified alloys, Si precipitation alone was not sufficient to facilitate the eutectic reaction, which apparently required additional undercooling for Al to form on the Si-particles. To what extent nucleation mechanisms in the Cu-enriched systems are transferable to binary or commercial Al-Si alloys remains uncertain.

Keywords: *Aluminium alloys, Al-Si eutectic solidification, radiography*

1. Introduction

Eutectic alloy systems offer specific advantages in metals such as ease of processing, isothermal or near-isothermal freezing and beneficial mechanical properties of a self-assembling composite material. Our understanding of regular eutectic solidification microstructure formation is quite far progressed. Within the operation limits of quasi-planar near-isothermal interface propagation, the pattern selection that defines the eutectic growth morphologies is fairly well described by the Jackson-Hunt model [1], and more recent extensions to this, e.g. by phase field simulations and experiments with transparent analogs, for growth behavior beyond the basic state interface stability limits [2-5]. Our understanding of irregular eutectic solidification, however, has not progressed to the same extent [6]. Presumably this can be ascribed to their substantially more complex growth behavior and conditions, which by the simultaneous progress of a faceted and a non-faceted phase, is bound to yield distinctively non-isothermal eutectic fronts [7-9], where the faceted phase tends to lead the growth [7]. Furthermore, since changes in growth direction or side branching generally is more difficult for a strongly anisotropic faceted phase compared to the typical weakly anisotropic non-faceted component, filling of space by a progressing irregular eutectic is considerably more cumbersome than for the regular systems [7].

Irregular eutectics are the backbone of two of the most common alloy systems used to produce castings, Al-Si and Fe-C. In both cases, the cast products usually contain in excess of 50% eutectic and, therefore, understanding and controlling the eutectic is an important basis for product performance optimization. Interestingly, common to both Al-Si alloys and cast irons is that trace elements can be added to produce large changes in the eutectic microstructure. The modification treatment of Al-Si alloys, typically by adding 50-300 ppm of Sr or Na, has been known for about a century. Yet, the mechanisms behind the strong element assisted eutectic refinement is still not fully understood, although recent studies point in the direction that the modifying elements strongly alters the Si- nucleation process, and thereby the formation of eutectic colonies. Retarded Si-nucleation together with potential growth restrictions imposed by impurity element rejection [10-13] has been suggested, as an alternative to impurity induced twinning [14], for being the most decisive formation mechanisms behind the typical fibrous and highly refined modified Al-Si eutectic microstructures.

While in situ experimental observations in various transparent analogue systems have been invaluable in the establishment of theory and models to describe regular eutectic growth [1,4,5], only a few studies have been reported with transparent irregular eutectics [7], and their analogy to metal alloys is severely limited since system specific properties such as nucleation mechanisms, crystalline anisotropy, solid solubilities, etc. becomes far more critical under non-isothermal growth conditions. In this paper we report the first real-time studies of irregular eutectic growth in both unmodified and Sr-modified Al-Si-Cu by X-ray transmission video microscopy of directional solidification (DS) experiments in a Bridgman furnace.

2. Experiment

A challenge with Al and Si is that their K_{α} X-ray absorption edges are at too low energies to be utilized for transmission contrast with any meaningful sample thickness. Therefore, an X-ray absorbing element must be added to generate contrast at the solid-liquid interface. The contrast element addition is likely to influence the overall solidification behaviour. Moreover, since X-ray absorption contrast mainly varies as $\Delta\rho(\Delta Z)^4$, where $\Delta\rho$ is the density difference and ΔZ is the element difference, the necessity of heavier atom addition to the Al-Si alloy would also tend to alter its segregation pattern. Obviously, the contrast-aiding element should be chosen with care not to form any reaction products with the other alloy constituents at temperatures above or near the Al-, Si- and Al-Si reactions. Also, since it is of interest to study eutectic modification, it is important that the contrasting agent is not a eutectic modifier or nucleant, e.g. by forming intermetallics, or that it reacts with potent eutectic nucleant particles or modifiers. Typically, the identification of an ideal contrast element will be by trial and error. Here results are reported from the initial experiment carried out with Cu as a contrasting agent.

The alloys were prepared from high-purity Al, Cu, Si and Sr molten in an alumina crucible and then cast in an insulated bottom-chilled Cu-mould. Two alloys of eutectic composition, Al-8wt%Si-15wt%Cu (unmodified) and Al-9wt%Si-15wt%Cu-0.015wt%Sr (Sr-modified), were made. Samples were taken from the castings, prepared in 135 μm thin rectangular slices and placed inside quartz glass containers following the same procedures as in previous studies [15-17].

The experiments were carried out at beamline ID6 of the European Synchrotron Radiation Facility, where eminent conditions are available for fast real-time high-resolution X-ray absorption and phase contrast imaging. The experimental setup and procedure were identical to those used in our previous in situ studies of DS [15-17], except for the X-ray camera, which was a SensiCam QE CCD with a 1376×1040 pixel array, 12 bit dynamic range and camera read-out at 16 MHz, corresponding to a

dead time of ~ 90 ms between consecutive frames. In the experiments reported here, the camera was mounted with $10\times$ magnification optics that gave an effective pixel size of ~ 0.7 μm . The image frame grabbing rates employed were 6.25-7.15 Hz. The temperature gradient, G , imposed by the Bridgman furnace system was varied in the range 23-43 K/mm and sample translation velocity, v_s , was in the range 6-17 $\mu\text{m/s}$.

3. Results and discussion

Figure 1 shows the evolution of the eutectic in the unmodified alloy (Al-8wt%Si-15wt%Cu) in a DS-experiment with $G \parallel$ gravity, g . Although the α -Al and Si-crystals cannot be distinguished directly from the X-ray transmission contrasts, they are easily identified by large differences in growth dynamics and interface morphologies. Because this sample had already undergone three repeated cycles of solidification and re-melting prior to the particular sequence shown in Fig. 1, a negative segregation had developed in the sample region studied, altering the local composition to become hypereutectic, evidenced by the presence of two faceted primary Si-crystals. These crystals had formed at higher temperatures before appearing in the camera field of view, perhaps already inside the hot compartment of the Bridgman furnace operated at 858 K.

In Figure 1 it can be observed that, as the eutectic front reaches the upper primary Si-crystal from above the field of view, new non-faceted Al-crystals start to nucleate at the interfaces of the primary Si-crystals and proceeds to grow dendritically into the intercolonial melt. This is consistent with the observation of halo formation of α -Al surrounding primary silicon crystals in Al-Si alloys, and confirms that Si is a viable nucleant for α -Al [18,19]. Nevertheless, it is worth noticing that in other locations the eutectic front has already progressed further to higher temperatures, evidenced by the Al-dendrite tip to the left located further ahead into the melt region. Evidently, the presence of Si is not in itself sufficient to initiate the eutectic reaction when the eutectic temperature is reached. Additional undercooling seems to be required for Al to start forming on the preexisting Si crystal, and apparently the required undercooling can be provided locally by the solute boundary of the dendrite approaching from above. Further on in the image sequence, new Si-needles are seen to form at irregular intervals and shoot off quickly in different directions. From video analysis the initial growth velocities of the Si-needles are found to be up to 5 times higher than the Al-dendrite tip velocities, which again is about $-2 v_s$. The Si-needles always appear in the vicinity of the α -Al dendrites, but it is not possible to determine directly from the images whether the Si-needles really are new crystals or if they have orientation relationships with pre-existing needles or the primary Si crystals. In principle they may nucleate directly on the α -Al at adequately high undercooling, and they were never observed to nucleate separately from established colonies in the $G \parallel g$ DS-configuration. However, since these alloys were made from high purity base materials, they potentially contain a lower number of heterogeneous substrates than what would be the case with commercial purity variants. The number of Si needles that appear in this and similar sequences with the unmodified alloys is notable, despite the limited field of view and relatively short time it takes for the non-isothermal front to progress beyond it. Studies have shown that eutectic silicon in unmodified Al-Si alloys exhibit a large degree of interconnectivity in the as-cast microstructure, suggesting branching to be an important part of the Si growth mechanism [14,19].

Other striking features are the disordered nature of the eutectic growth in this alloy, as well as the highly irregular morphology of the solid liquid interface, including the liquid pockets surrounding the Al-Si eutectic colonies which remain open as solidification progresses. Clearly, these features are not well governed for by current irregular eutectic growth models [7-9], where silicon crystals should be leading a massive eutectic interface. The open pockets stems from the pronounced ternary alloy

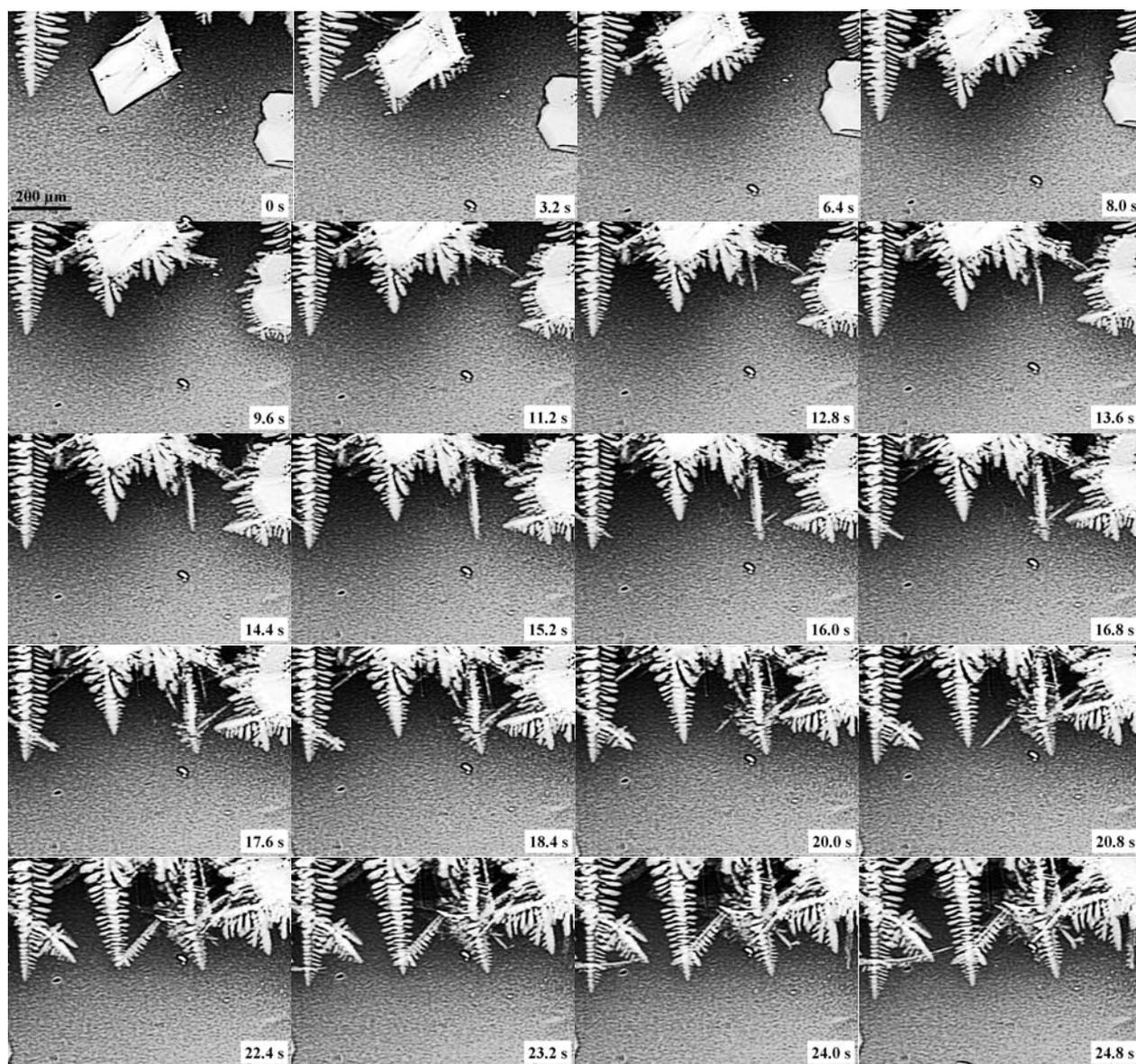


Figure 1. Unmodified eutectic microstructure formation during DS \parallel g of Al-Si-Cu alloy. $G = 23.0$ K/mm, $v_s = 17 \mu\text{m/s}$, $\Delta t = 160$ ms. Times given in the images are relative to the first frame of the figure (0 s)

composition, where the remaining melt gradually enriches from hypoeutectic to eutectic Al-Cu as the Al-Si eutectic mush cools down. Eventually, the final liquid solidifies into a regular lamellar Al-Al₂Cu eutectic, evidenced by post-experiment metallographic investigations.

Figure 2 shows images taken with the Sr-modified sample for DS with $G \parallel g$. The first inset image is a montage taken from five frames of the video sequence by following a particular image region over a period of roughly 10 s. A black arrow can be seen pointing at a $\sim 10 \mu\text{m}$ particle in horizontal motion towards the α -Al dendrite on the left. In the final frame, at $t = -3.78$ s, the particle has reached a position inside the box region fixed over a particular dendrite side branch in all the five frames. The next frame, at $t = 0$ s, is when eutectic nucleation can be confirmed by visual examination of full resolution images. The box region is drawn over the same side branch as in the 5-frame montage of suspended particle motion ahead of the nucleation event. The eutectic nucleation undercooling is estimated ~ 16 K relative to the Al-Si eutectic reaction in Al-9wt%Si-15wt%Cu. This estimate is based on G and the α -Al dendrite tip undercooling, after having confirmed later by in situ monitoring,

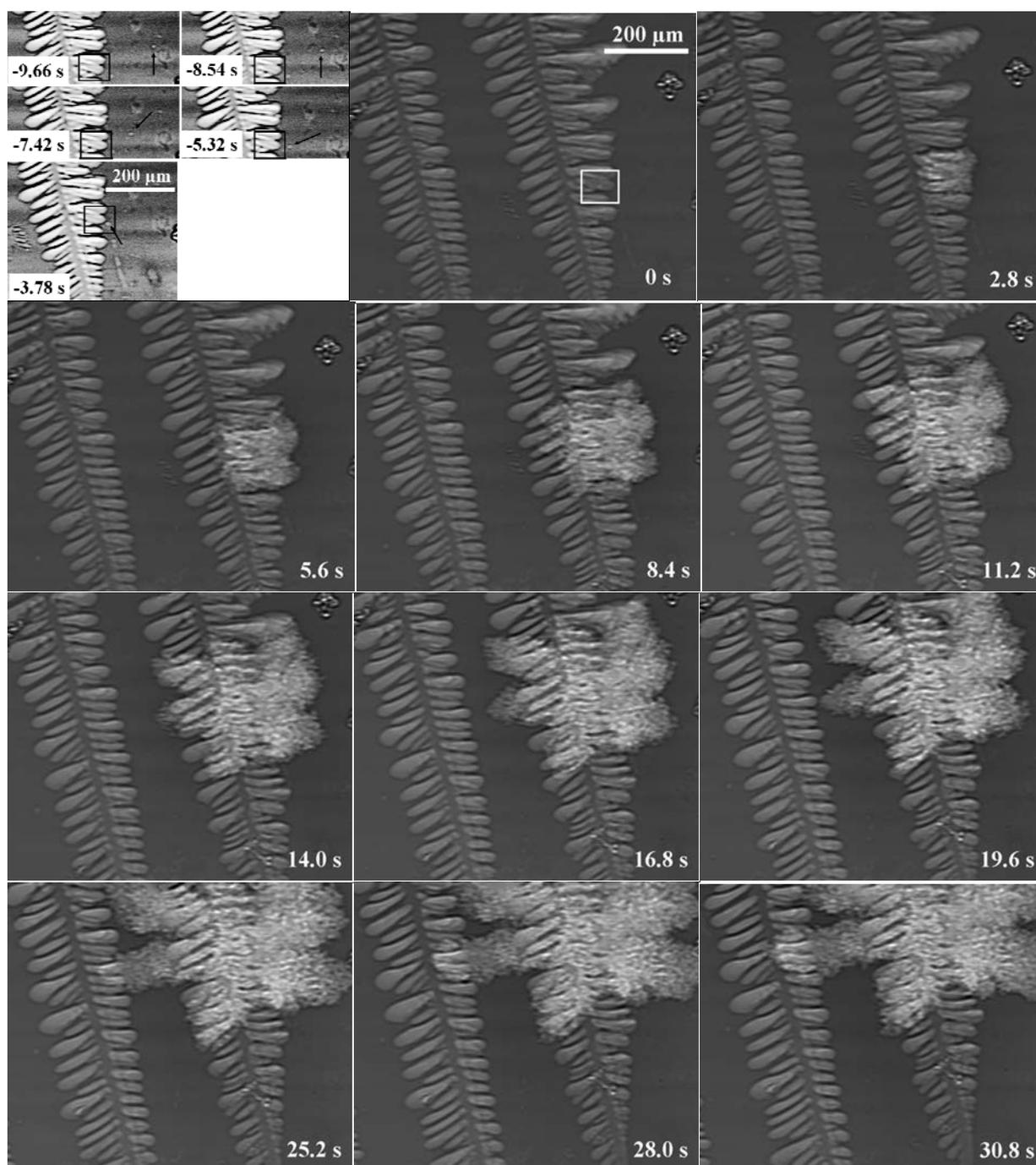


Figure 2. Sr-modified eutectic microstructure nucleation and growth during DS \parallel \mathbf{g} of Al-Si-Cu-Sr alloy. $G = 18.4$ K/mm, $v_s = 10.5$ $\mu\text{m/s}$, $\Delta t = 140$ ms. Times given in the images are relative to the first frame of the figure (0 s).

with the sample motion stopped, that the latter indeed grows with tip undercooling relative to the nominal eutectic reaction temperature for this alloy constitution. In the following images, a fine coral-like modified eutectic colony is seen to form, evolving into a six-folded equiaxed cellular rosette. The cellular branches propagate with closely steady tip velocities $\sim v_s = 11.4$ $\mu\text{m/s}$ and quite uniform in all directions. The rosette spreads quite evenly over the surface of the columnar α -Al dendrite and into the intercolumnar melt regions, eventually bridging over to the nearest neighbor columnar dendrite.

The modified eutectic growth shown in Fig. 2 was confirmed by very similar observations from five additional DS sequences collected with the same alloy. In all events of Sr-modified eutectic nucleation within the camera field of view, it appeared in the immediate vicinity of the α -Al surfaces. From the sequence illustrated in Fig. 2, the particle shown in motion at $t < 0$ s is assumed to be a Si-crystal which has formed on a potent inoculant suspended in the melt, and then grown to a size of ~ 10 μm . Presumably, the horizontal motion is caused by thermo-solutal convection at the scale of the full sample size, verified to occur quite frequently with these experiments in the $G \parallel g$ DS configuration [16, 20]. Just as for the unmodified alloy sequence in Fig. 1, this is taken to support the statement that nucleation or presence of Si could be inadequate to facilitate the eutectic reaction, and that additional undercooling beyond Si-formation may be required. However, this is a quite surprising result for the Sr-modified system, since it to our knowledge has been assumed more or less exclusively in previous studies that the eutectic reaction occur as soon as Si-crystals are able to form [6, 10-14]. Despite the novel result, the main influence of Sr on eutectic nucleation remains unaltered, namely to initiate precipitation of intermetallic phases considerably less potent for Si nucleation than those that would form with impurity level constituents in its absence. Post-experimental metallography of another sample solidified with the same parameters in the same furnace reveal a fibrous Al-Si eutectic very similar to those found in modified binaries[11], with the exception of a few tiny Al_2Cu fibers that may have formed in open liquid channels with trapped solute or by back-diffusion of Cu from α -Al upon cooling to room temperature. Finally, the reason for the Mullis-Sekerka type instabilities to form at the modified eutectic interface is a discrepancy between the short wavelength periodic Cu redistribution profile along the fibrous Al-Si composite interface, and the long range diffusion field of rejected Cu building up parallel to its growth direction. The long range boundary layer builds up gradually as the Al-Si eutectic evolves, since Cu solubility is about zero in Si and only 4-5wt% in Al over the full freezing range of the ternary alloy.

References

- [1] K. A. Jackson and J. D. Hunt: *Trans. Metall. Soc. AIME* 236 (1966) 1129-1142.
- [2] A. Karma and A. Sarkissian: *Met. Mat. Trans* 27A (1996) 635-656.
- [3] A. Parisi and M. Plapp: *Acta Mater.* 56 (2008) 1348-1357
- [4] M. Ginibre, S. Akamatsu and G. Faivre: *Phys. Rev. E* 56 (1997) 780-796
- [5] S. Akamatsu, S. Bottin-Rousseau and G. Faivre: *Phys. Rev. Lett.* 93 (2004) Art. no. 175701.
- [6] M. Asta, et al: *Acta Mater.* 57 (2009) 941-971.
- [7] D. J. Fischer and W. Kurz: *Acta Metall.* 28 (1980), 777-794.
- [8] P. Magnin and W. Kurz: *Acta Metall.* 35 (1987) 1119-1128.
- [9] E. Guzik and D. Kopyciński: *Metall. Mater. Trans.* 37A (2006) 3057-3067.
- [10] A.K. Dahle, et al. : *Mat. Sci. Eng. A* 413-414 (2005) 243-248.
- [11] A.K. Dahle, et al : *Met. Mat. Trans.* 32A (2001) 949-960.
- [12] S.D. McDonald, K. Nogita, A.K. Dahle: *Acta Mater.* 52 (2004) 4273-4280.
- [13] Y.H. Cho, H.-C. Lee, K.H. Oh, and A.K. Dahle: *Met. Mat. Trans* 39A (2008) 2435-2448.
- [14] S.Z. Lu and A. Hellewell: *Met. Trans* 18A (1987), 1721-1733.
- [15] R. H. Mathiesen, et al.: *Met. Mat. Trans.* 33B (2002) 613-623.
- [16] R. H. Mathiesen and L. Arnberg: *Acta Mater.* 53 (2005) 947-956.
- [17] R. H. Mathiesen, et al.: *Met. Mat. Trans.* 37A (2006) 2515-2524.
- [18] M. Shamsuzzoha and L.M. Hogan: *J. Cryst. Growth* 76 (1986) 429-439.
- [19] C.M. Dinnis, A.K. Dahle and J.A. Taylor: *Mater. Sci. Eng. A* 392 (2005) 440-448.
- [20] P. Delaleau, C. Beckermann, R. H. Mathiesen and L. Arnberg: *ISIJ Intl.* 50 (2010), accepted.