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Grain refinement of aluminium studied by use of a thermal analytical technique ☆

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Abstract

Master alloys based on the system Al–Ti–B are commonly used as grain-refining additives to aluminium castings. It has been shown in previous work that TiB_2 particles are the most common heterogeneous nucleation sites for aluminium crystals. Additions of potent nucleating particles to an aluminium melt do not, however, cause grain refinement automatically; there must be a driving force for nucleation as well as subsequent growth. The driving force at slow cooling rates can be present in the form of constitutional undercooling caused by alloying elements that do not interact with each other or the nucleating particles. The influence of hypoeutectic concentrations of silicon and iron and hypoperitectic concentrations of titanium on the α-Al grain size has been studied. It is found by use of a two-thermocouple thermal analytical technique and from studies of the microstructure that the growth-restricting effect of Fe, Si and Ti are additive at low concentrations.

The thermal analytical technique allows us to determine the point where the dendrites grow together forming a continuous network. The time lapse from nucleation to the point where the dendrites impinge on each other is used to calculate the average growth rate of the dendrites. The grain diameter is proportional to the dendrite growth rate, and once the equiaxed dendritic growth is completed, the final grain size is determined.

A deterioration in the grain-refining effect occurs at high solute concentrations. Increasing solute concentrations decreases the dendrite tip radius, counteracting the solute effect. At high solute concentrations, the dendrite tip radius eventually decreases to a critical limit where capillary effects start to become important and the growth rate increases.

Keywords: Aluminium; Dendritic growth; Grain refinement; Solute effect; TA

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1. Introduction

Inoculants in the form of master alloys are added to aluminium to promote the formation of a fine and randomly oriented equiaxed grain structure upon solidification; this is termed grain refinement. The process of grain refinement has been widely employed in the aluminium industry for many years and is a very important treatment in the casting process. A fine-grained structure can be produced by increasing the number of nucleating seeds, so that a large number of crystals are formed, which soon impinge on each other and prevent each other from further growth.

Minor additions of titanium to aluminium result in significant grain refinement. It is also known that additions containing both Ti and B yield much better grain refinement than the exclusive addition of Ti and much less master alloy is needed. Foundry alloys containing a high concentration of, for instance, Si or Cu can be successively treated with a boron addition. In industrial practice, as little addition as possible is made to keep the costs down. The minimum addition is determined by the necessity to avoid formation of twin-columnar crystals. The grains should be equiaxed and the grain boundary area large enough to withstand the thermal stress that will occur during cooling of the casting (to prevent hot tearing). The grain size required also depends on what treatment the material will undergo after the casting operation, i.e. rolling, etc.

Several theories concerning the mechanism of grain refinement by addition of ternary Al–Ti–B alloys have been proposed; many of these have been discussed by Guzowski et al. [1]. The phenomenon was scrutinised in three recent papers by Johnsson and coworkers [2–4], and the dominating mechanism was found to be that nucleation takes place heterogeneously on $(Al_{1-X}Ti_X)B_2$ particles at hypoperitectic additions of Al–Ti–B master alloys, according to the carbide–boride theory proposed by Cibula [5].

The formation of free equiaxed crystals is a result of both nucleation and growth. The presence of potent nucleating particles is not a guarantee for a fine-grained result. We also need a driving force for growth. Much of the literature about grain refinement concerns the efficiency of different nucleating particles and much less effort has been devoted to how solutes in the melt influence the structure development during solidification.

For a peritectic system like Al–Ti ($k > 1$), there will be a continuous lowering of the Ti concentration at the liquid/solid phase boundary. For a eutectic element like Si, solute atoms will pile up at the interface ($k < 1$). This diffusion process impedes growth. The grain-refining effect of an alloying element is found to depend on the constitutional factor $(k_i - 1)m_i C_0$ [4] where C_0 is the concentration, m_i is the slope of the liquidus line, and k_i is the distribution coefficient between liquid and solid of the solute element (i).

From experimental results, it has been shown that the constitutional contributions from different elements are additive at low concentrations [4] and the expression $\sum (k_i - 1)m_i C_0$ approximates to the total constitutional undercooling. The magnitude of this sum determines the diffusion profile outside the solidification front and can be termed the growth-restricting factor. At a certain addition level of nucleating particles, the grain-refining efficiency will not improve further if we increase the number of nucleants. There is a balance between the number of nucleants and the driving force for growth.

The formation of dendrite arms will make the solute redistribution easier and the solute boundary layer ahead of the front will be much thinner than in steady state growth of single crystals. The driving force for growth of the dendrites is determined by the coupling condition $\Delta T = \Delta T_c + \Delta T_t + \Delta T_r + \Delta T_k$, where ΔT_c is the undercooling at the dendrite tip due to the solute concentration difference between solid and liquid, ΔT_t is the difference in temperature between solid and liquid, ΔT_r is the temperature difference at the solid/liquid interface caused by the curvature of the tip, and ΔT_k is the kinetic undercooling for atom attachment, which can be neglected in the case of metals due to a low entropy of melting [6].

The aim of this paper is to describe how thermal analysis can be used to study the grain-refining process during solidification of an aluminium melt and also to investigate if thermal analysis could be used as a simple tool to evaluate the grain size in an aluminium casting. The two-thermocouple thermal analysis technique developed by Bäckerud and coworkers [7,8] was employed to monitor the grain-refinement process during solidification.

2. Experimental

2.1. Materials

High-purity Al was used (>99.995 wt%, Vigeland Metal Refinery), and Fe (99.98%, Johnson-Matthey) and Si (98.4% Johnson-Matthey) in concentrations ranging up to 0.5 wt% Fe and 9 wt% Si. The melt was homogenised for 30 min before addition of the grain refiner; 450–650 g of pure Al was melted in each experiment in a resistance-heated Salamander-type crucible, which has proved to be as inert to the melt as graphite crucibles. The melt was held at 775 ± 10°C for the duration of an experiment. A grain-refining master alloy containing 4.6 wt% Ti and 0.95% B (Kawecki-Billiton Metaalindustrie) was used to supply potent nucleants. Both the boron and titanium concentrations were varied at different addition levels of the master alloy. From earlier studies [2–4] it can be concluded that the boride particles stay inert in the melt so that only the number of particles is varied. Powder X-ray diffraction revealed $TiAl_3$ and boride phase with the average composition $(Al_{0.06}Ti_{0.94})B_2$. It is assumed that all boron available is bonded in boride particles. In the discussion below, the Ti level is given as the concentration available to dissolve in the melt. The addition level varies from 0.01 to 0.07 wt%. Chemical analyses of diluted samples were in close agreement with the nominal compositions. To prevent the influence of sedimentation of particles, all grain-refining samples were taken by first stirring with a graphite rod to homogenise the melt and then pouring a sample into a small graphite mould. The graphite moulds were preheated to the same temperature as the melt, so that no nucleation occurred in the sample before the system attained thermal balance.

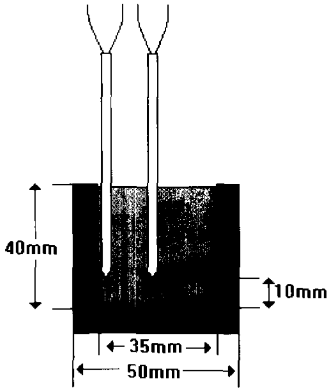

Fig. 1. The dimensions of the mould and the placement of the thermocouples therein. The sample diameter was 35 mm and the height 40 mm. Metallographic samples were taken on a horizontal section 10 mm above the bottom surface.

2.2. Thermal analysis

The solidification process of the alloys was investigated by means of a two-thermocouple thermal analysis technique [3,4,7–9]. The thermocouples were of type K (chromel–alumel, $\varnothing = 0.5$ mm). They were welded together and inserted into a double-bore tube of alumina for protection. The welded tips were covered with a thin layer of boron nitride to protect them from molten aluminium. All the thermocouples were calibrated several times against the growth temperature of pure Al (99.995%) at a cooling rate of 1°C s^{-1} until a stable output voltage was recorded. Calibration was repeated after each measurement. The sampling rate for data collection was 20 s^{-1}.

Errors in the measurements were minimised by making the wires as short as possible and reducing the number of connections between different wires to a minimum. The A/D converter was placed away from electric conductors and heat sources. The accuracy in the measurements was mainly affected by instabilities in the thermocouples and slight deviations in the cooling rate from 1°C s^{-1}. The welded tip of the thermocouples was the main source of error. The deviation in growth temperature (T_G) in 24 repeated calibrations at a cooling rate of 1°C s^{-1} was found to be $\sigma = 0.2$°C using the same pair of thermocouples.

The same pair of thermocouples were used throughout a whole series of experiments. As the calibrated thermocouples had to be used for as many experiments as possible, they had to be melted off and cleaned after each experiment. Therefore the samples for metallographic preparation had to be taken separately.

Preheated graphite crucibles were used for taking samples for both thermal analysis and metallographic examination; all samples were taken as double test samples. The dimensions of the mould and the placement of the thermocouples therein are shown in Fig. 1. The graphite crucibles were placed on a 6 mm thick Fiberfrax felt and covered with a Fiberfrax lid. This set-up gave a cooling rate of

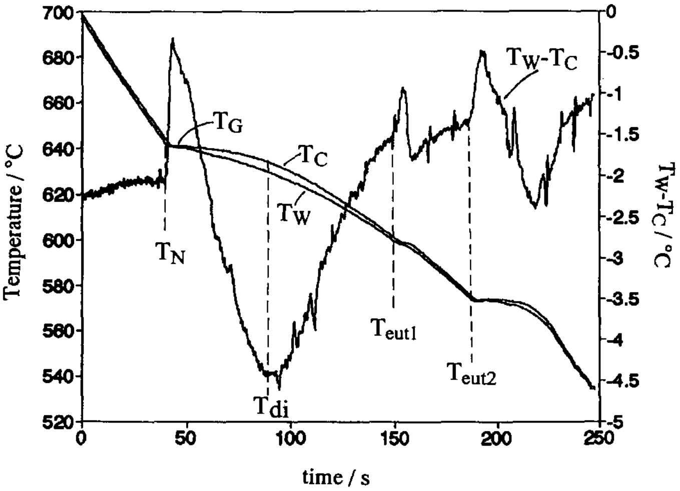

Fig. 2. Cooling curve for Al–3% Si–0.5% Fe–0.018% Ti–0.0039% B. The titanium concentration is 0.01 wt% not bonded in borides: T_C, cooling curve from the thermocouple located in the centre of the crucible; T_W, cooling curve from the thermocouple located at the wall of the crucible. The solidification path can be followed from the temperature difference curve $T_W - T_C$, which is used to define breaking points. The following breaking points are defined: T_N, nucleation temperature, read from the T_W curve; T_G, growth temperature, read from the T_C curve; T_{di}, dendrite impingement point; T_{eutl}, start of precipitation of Al_5FeSi, read from the T_W curve; T_{eut2}, start of precipitation of $Al–Si–Al_5FeSi$ eutectic, read from the T_W curve. The time lapse from T_N to T_{di} in combination with measured grain size is used to calculate the average growth rate for the dendrites.

about 1°C s^{-1} just prior to the start of solidification. Both slower and faster cooling rates have been tested, but the most reproducible results were obtained at this cooling rate. This is a reasonable cooling rate, one which would be found in many larger industrial castings. Fig. 2 shows a cooling curve with the defined breaking points marked. One thermocouple, located at the inner wall of the crucible (T_W), was used to determine the nucleation temperature (T_N). The steady-state growth temperature (T_G) was determined from the second thermocouple located at the centre of the crucible (T_C). The temperature difference curve ($\Delta T_{WC} = T_W - T_C$) was used to follow the dendritic growth and the precipitation of intermetallic phases during solidification. The time lapse from nucleation to the point where the dendrites impinge on each other was used to calculate the dendrite growth rate. The length of the dendrites was defined as half the grain diameter. Fraction solid calculations were made with a computer program developed by Tamminen [8].

2.3. Metallographic examination

Metallographic samples were taken in the same sort of graphite crucibles as the sample for thermal analysis, and they were cut at the same height from the bottom as the position of the thermocouples in order to yield directly comparable results.

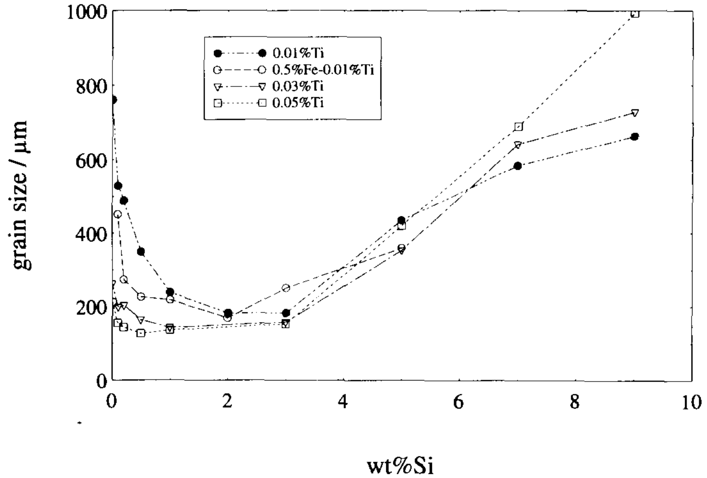

Fig. 3. A grain refinement test showing the influence of the silicon concentration on the grain size at various Ti concentrations. The cooling rate just prior to the start of solidification was 1°C s^{-1}.

Grain sizes were determined in a polarising light microscope by a line intercept method (6 non-overlapping measurements) on polished samples anodised at room temperature for 1 min in a solution of 74 ml $H_2O + 24$ ml $C_2H_5OH + 1$ ml $HF + 1$ ml HBF_4.

3. Results and discussion

From a grain-refinement test with the Al–Ti–B master alloy added to Al–Si or Al–Si–Fe alloys (Fig. 3), it is clear that the alloying elements cooperate in promoting a fine-grained structure at low concentrations and that a deterioration mechanism is operative at high solute concentrations (above 3 wt% Si). An attempt was made to quantify the effect of the alloying elements. The combined effect of the alloying elements can be described by the sum of the growth restriction factors $\sum (k_i - 1)m_i C_0$ that account for the solute undercooling ΔT_c. This is based on the circumstance that k_i and m_i can be taken from the respective binary systems with

Table 1
Phase diagram parameters for the alloying elements investigated

Binary system	m_i [a]	k_i [b]	$(k_i - 1)m_i$
Al–Ti [3,10]	30.7	≈9	245.6
Al–Si [10]	−6.6	0.11	5.9
Al–Fe [11]	−3.0	0.02	2.9

[a] Slope of the liquidus line. [b] Distribution coefficient between liquid and solid in the Al–i binary system.

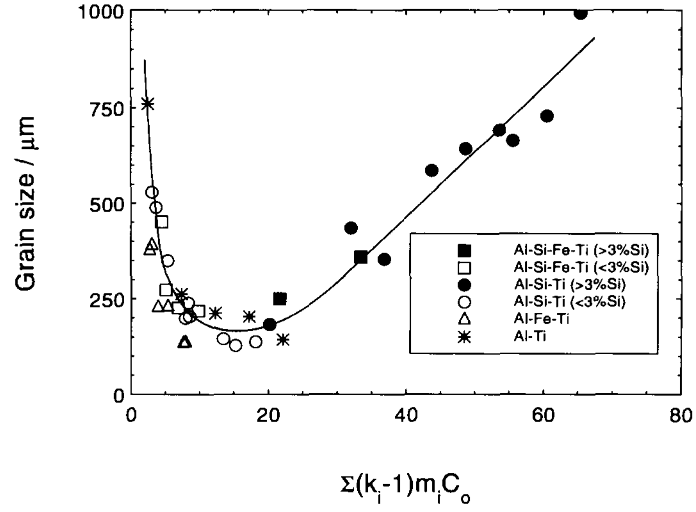

Fig. 4. The average grain size vs. the growth restriction factor (the sum of the constitutional contribution from the different alloying elements) for a number of alloy compositions.

aluminium (see Table 1). For simplicity, it was assumed that the liquidus and solidus lines are straight. It is clear that this simple factor was a major contributor to the resulting grain size for the present experimental set-up where convection could be neglected (Fig. 4).

At the dendrite impingement point, the full length of the dendrites is developed and thus the final grain size is also determined. Chai [12] studied the dendrite impingement by continuous torque measurements with a viscosimeter and noted a difference in fraction solid depending on whether the impingement point was determined by torque measurements or by thermal analysis at low solute concentrations. A larger fraction solid was measured at the impingement point with thermal analysis. This may be explained by the fact that the point determined with a viscosimeter corresponds to the point where the dendrites are grown to nearly full length but are hindered from growing together due to a diffusion field in between them (soft impingement). The solute concentration determines the shape of the dendrite tips that influence the growth rate. Low concentrations are associated with rounded tips and solutes will be pushed in front of the growing dendrite like gravel in front of a bulldozer. With increasing solute concentrations, the radius of the dendrites decreases and the bulldozing effect diminishes, and the solutes are forced to the sides. The growth rate becomes faster and the dendrites therefore collide earlier in the solidification process due to a much thinner diffusion zone. The point for dendrite impingement measured with the viscosimeter becomes more in accord with the rules from thermal analysis at increasing solute concentrations. It is the hard impingement point that we measure with the thermal analytical technique. Fig. 5 shows that the fraction solid at the impingement point decreases with increasing concentration of solute.

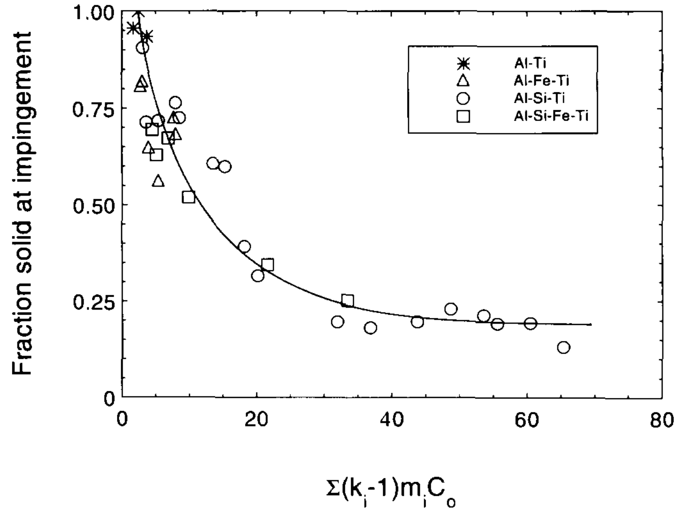

Fig. 5. The fraction solid at the dendrite impingement point (hard impingement) for a number of alloy compositions plotted against the growth restriction factor.

After the dendritic network has developed, the dendrites thicken until the end of solidification or the start of the eutectic, if any. The time fraction for dendritic coarsening is shown in Fig. 6. At low solute concentrations, the dendrites are coarse and grow together during a late stage of the solidification process and there is only a short time left for the dendrites to coarsen. The dendrites become thinner with increasing solute concentration and they impinge at an earlier stage of the solidifi-

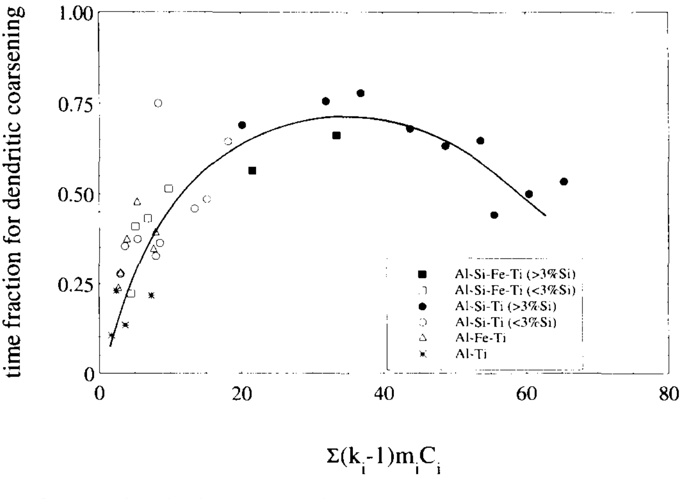

Fig. 6. The time fraction for dendritic coarsening vs. the growth restriction factor. The period of dendritic coarsening is defined as the period from dendrite impingement to the end of solidification (or start of eutectic precipitation, if any); see text for explanation.

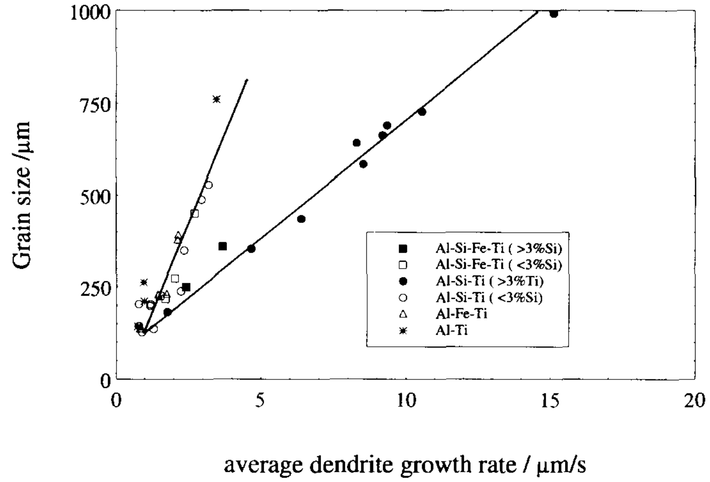

Fig. 7. The grain size was found to be proportional to the average dendrite growth rate. The growth rate is defined from the grain size and the time lapse from nucleation to the point where the α-Al dendrites impinge on each other; see definition in Fig. 2. The cooling rate just prior to the start of solidification was 1°C s^{-1}. Two relations are found depending on whether the growth is diffusion controlled (low solute concentrations) or controlled by the dendrite tip radius (high solute concentrations). The change in growth conditions occurs at about 3 wt% Si.

cation period. The time fraction for coarsening then becomes longer. With increasing solute concentration, we finally come to a point where the eutectic reaction starts closer and closer to the impingement point. The time fraction for dendritic coarsening then starts to decrease with increasing solute concentration.

A transition in the growth behaviour occurs at a silicon concentration of about 3 wt%. This can be observed from the plot of the grain size versus dendrite growth rate, see Fig. 7. The grain size is proportional to the average dendritic growth rate (v), and once the equiaxed dendritic growth is completed, the final grain size is determined.

The average dendritic growth rate v and the grain size d were found to be inversely proportional to the growth restriction factor (Eq. (1)) at low solute concentrations

$$d \propto v \propto \frac{1}{\sum (k_i - 1) m_i C_0} \tag{1}$$

The dendrite growth rate cannot be expressed by Eq. (1) at high silicon concentrations (>3 wt% Si), as shown in Fig. 8. The growth rate there starts to increase with increasing solute concentration.

Eq. (1) is only valid if α-Al is the only phase precipitating before the dendrites impinge on each other. The term pertaining to Fe in the expression for the growth restriction factor is low and gives only a minor contribution to the final sum. For iron concentrations higher than 0.5 wt%, the phase $FeAl_3$ may start to precipitate

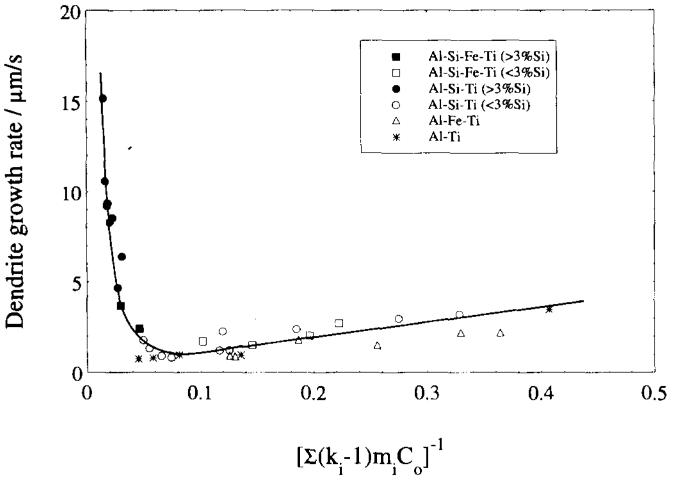

Fig. 8. Dendrite growth rate vs. the reciprocal of the growth restriction factor. At low solute concentrations the relation is linear and the growth rate is diffusion controlled. At high solute concentrations the growth becomes controlled by capillary effects due to the decreasing dendrite tip radius. At such high solute concentrations, the relation between growth rate and the reciprocal of the growth restricting factor is no longer linear.

before the α-Al dendrite impingement point. This will cause a slight deviation from the relation in Eq. (1) and due to this fact Fe concentrations higher than 0.5 wt% are not used in this study.

It is not likely that the deterioration effect at high silicon concentrations is due to a reaction between silicon and boride particles or between silicon and dissolved boron, because the addition of boron to a high-silicon-content hypoeutectic Al–Si melt has been reported to be very efficient [13–16], and the contact time after addition of the Al–Ti–B master alloy does not seem to influence the results. An interaction between Si and Ti may occur, but no intermetallic phase containing both Si and Ti has been observed. The present Ti concentrations (0.01–0.09 wt%) are also too low for $TiAl_3$ to survive in the melt; this phase is known to dissolve some silicon [17,18].

It seems reasonable to explain the deterioration by a curvature effect due to increasing growth rate with decreasing dendrite tip radius, which occurs at increasing concentrations of alloying elements. At a certain small radius, a transition occurs from diffusion-controlled growth to growth controlled by curvature of the dendrite. A sharper tip can grow more rapidly because it can reject solute more effectively [6]. In the competition between nucleation and growth, growth becomes the winner at a certain concentration: the radius effect results in a faster growth rate and a change in the dendrite morphology.

The thermal analysis measurements show that nucleation takes place at a temperature higher than the growth temperature at low Si concentrations (see Fig. 9) and that the steady-state-growth temperature increases relatively to T_N with

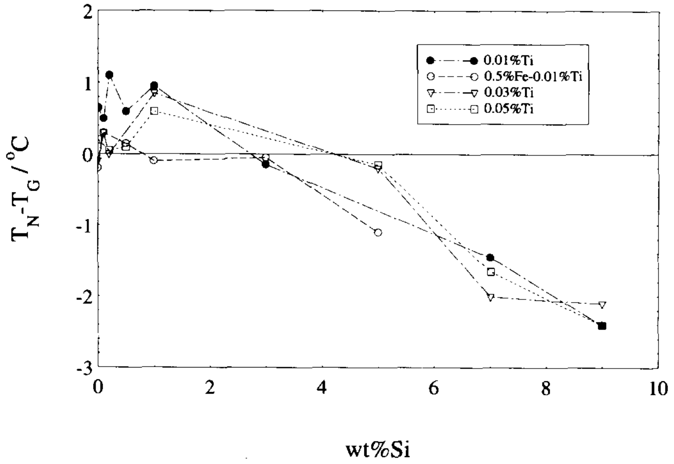

Fig. 9. Nucleation temperatures (T_N) minus growth temperatures (T_G) for various Ti concentrations plotted versus the Si concentration. At low Si concentrations, nucleation takes place at a higher temperature than the growth temperature, while at higher Si concentrations the reverse is true. The effect is thought to depend on more heat being released per unit time at the beginning of solidification, due to the faster growth rate for high-Si alloys. The cooling rate just prior to the start of solidification was 1°C s^{-1}.

increasing Si concentrations. It seems reasonable to explain the transition as follows: at high Si concentrations, the α-Al dendrites start to grow with higher speed than at low Si concentrations soon after they are nucleated due to a larger driving force for growth, resulting in more heat per unit time being released at the beginning of solidification.

For the concentrations investigated in the system Al–Si–Fe–Ti, the deterioration is mainly an effect of Si and approximately independent of the Fe concentration. At such a high Si concentration where the tip radius effect has started to become an important driving force for growth, an addition of Ti will increase the growth rate of the dendrites and thus cause a larger grain size, see Fig. 8. This seems to be the reason why an addition of B or an Al–Ti–B master alloy with a Ti/B ratio not above the stoichiometric ratio required to form TiB_2 gives a more fine-grained cast structure than a hypoperitectic addition of an over-stoichiometric Al–Ti–B alloy, as described in the literature [13–16].

To explain the growth behaviour over the whole concentration interval we must take into account the effects of the cooling rate, the constitutional undercooling and the dendrite tip radius. Fig. 10 shows how the average growth rate (and grain size) varies over the concentration range. At very low solute concentrations, we have columnar grains with fast growing thermal dendrites. At a sufficiently high solute concentration, the solute gradient ahead of the dendrite tip causes a constitutional undercooling that is high enough for the columnar-to-equiaxed transition. The growth becomes diffusion controlled and the growth rate decreases substantially. Increasing the solute concentration decreases the dendrite tip radius, counteracting

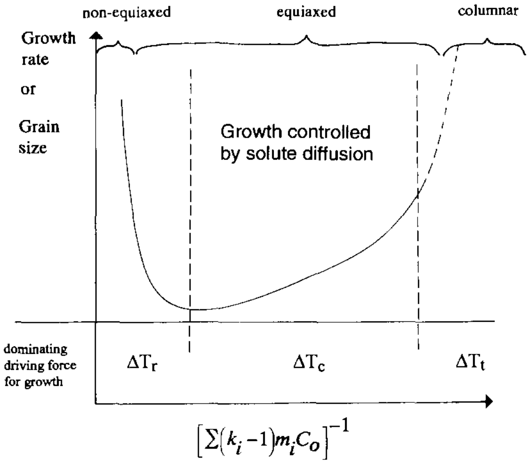

Fig. 10. A sketch showing how the average dendritic growth rate (and grain size) varies over the composition range. The solute concentration increases to the left in the figure. It is assumed that the alloys contain a dispersion of potent nucleating particles that can become active at a large enough undercooling. At low solute concentrations, the cast structure will become columnar and the growth is controlled by thermal conditions. Increasing the solute concentration will decrease the growth rate and cause a transition to diffusion-controlled equiaxed growth. Increasing solute concentrations will decrease the dendrite tip radius, counteracting the solute effect and at a certain small radius the capillary effects start to become important and the growth rate increases.

the solute effect. At high solute concentrations, the dendrite tip radius eventually decreases to a critical limit where capillary effects start to become important and the growth rate increases. This interpretation is in good agreement with theoretical studies of dendritic growth, see, for example, Kurz and Fisher [6] and Rappaz [19].

Titanium is the element that has the largest effect per wt% added in restricting the growth rate and promoting a fine-grained structure of nucleated α-Al; other elements have markedly lower effects. According to the discussion above, it is not possible to grain-refine all kinds of aluminium alloys merely by adding potent nucleating particles because the constitutional contribution may not be high enough. To such alloys, it is necessary to add titanium in excess compared to the amount contained in the nucleating boride particles. However, problems may occur if the alloy contains elements like Zr and Cr that interact with Ti also at low concentrations [4].

The thermal analytical technique used in this paper is simple and quick to use. It should therefore be of great interest if the method could be used as a tool to control the final grain size in a casting.

It is indicated in Fig. 11 that a fraction solid at impingement of between 0.3 and 0.7 predicts a fine-grained structure. Fig. 12 is a plot of the grain size versus the temperature decrease per unit time $\Delta T_{\mathrm{di}}/\Delta t_{\mathrm{di}}$ during dendritic growth. The quotient increases with increasing temperature interval for dendritic growth and, thus, with increasing solute concentration. At a low value of $\Delta T_{\mathrm{di}}/\Delta t_{\mathrm{di}}$, the solute concentra-

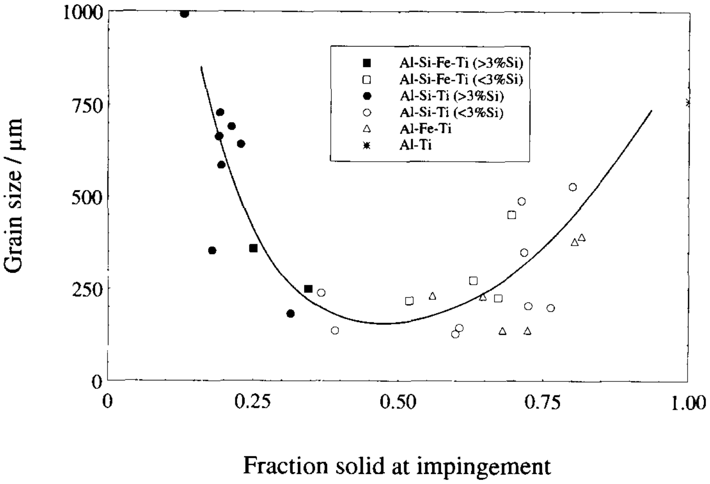

Fig. 11. An attempt to relate grain size to thermal analysis data. It can be seen that a fraction solid at impingement between 0.3 and 0.7 indicates a fine-grained solidification structure.

tion is not high enough to impede the growth rate to form a fine-grained equiaxed cast structure. At high values of the quotient, the solute concentration is so high that capillary effects are more important than solute effects and the grain size coarsens again. A value of $\Delta T_{\mathrm{di}}/\Delta t_{\mathrm{di}}$ in the range 0.1–0.2°C s^{-1} indicates a

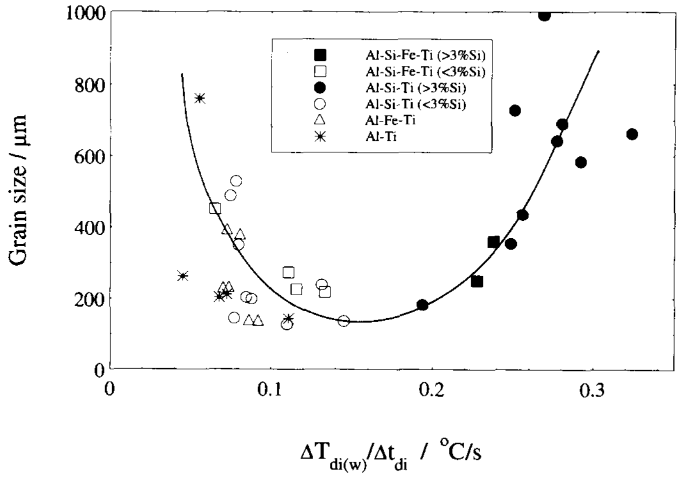

Fig. 12. The temperature interval for solidification will influence the rate of temperature lowering during the dendritic growth. $\Delta T_{\mathrm{di(w)}} = T_{\mathrm{N}} - T_{\mathrm{di(wall)}}$; Δt_{di} is the time for dendritic growth. At a low value of the quotient $\Delta T_{\mathrm{di(w)}}/\Delta t_{\mathrm{di}}$, the solute concentration is not high enough to impede the growth rate to form a fine-grained equiaxed cast structure. At high values of the quotient $\Delta T_{\mathrm{di(w)}}/\Delta t_{\mathrm{di}}$, the solute concentration is so high that capillary effects are more important than solute effects and the grain size becomes coarse again. A value of $\Delta T_{\mathrm{di(w)}}/\Delta t_{\mathrm{di}}$ in the range 0.1–0.2°C s^{-1} indicates a fine-grained structure.

fine-grained structure for a cooling rate of 1°C s^{-1} just prior to the start of solidification.

A combination of relations such as those in Figs. 11 and 12 may be used to control the grain size in a casting. The results are interesting because only relative temperatures are used so that a careful calibration of thermocouples is not required, unlike when absolute temperatures are measured.

4. Conclusions

The dendritic growth during solidification of an aluminium casting can be studied by use of thermal analysis; the two-thermocouple thermal analysis technique allows us to determine the point where the dendrites grow together forming a continuous network.

The equiaxed grain size is proportional to the average growth rate of the dendrites. The growth-restricting effect of the different alloying elements, Fe, Si and Ti, are additive at low concentrations. During diffusion-controlled growth, the grain size and the dendritic growth rate are inversely proportional to the growth-restricting factor, $\sum(k_i - 1)m_i C_0$, which is obtained by using data from the respective binary phase diagrams with aluminium. Silicon has a stronger effect than iron in reducing the grain size at low concentrations due to the larger growth-restricting factor.

A deterioration in the grain-refining effect occurs at high solute concentrations. This effect starts to develop at about 3 wt% Si. The effect seems to be a result of decreasing dendrite tip radius. A sharper tip can reject solute more effectively, and this will lower the efficiency of the addition of an Al–Ti–B grain refiner compared to the addition to pure aluminium.

Some indications are found that it is possible to process the thermal analysis data in order to use the technique as a tool to control the grain size in a casting.

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