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Eprints ID: 3933

To link to this article: DOI 10.1179/174313309X380378
URL: <http://dx.doi.org/10.1179/174313309X380378>

To cite this version: Loizaga, A. and Niklas, A. and Fernandez-Calvo, A. I. and Lacaze, Jacques (2009) *Thermal analysis applied to estimation of solidification kinetics of Al-Si aluminium alloys*. International Journal of Cast Metals Research, The, vol. 22 (n° 5). pp. 345-352. ISSN 1364-0461

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Thermal analysis applied to estimation of solidification kinetics of Al–Si aluminium alloys

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Evaluation of solidification kinetics by thermal analysis is a useful tool for quality control of Al–Si melts before pouring provided it is rapid and highly reproducible. Series of thermal analysis records made with standard cups are presented that show good reproducibility. They are evaluated using a Newton's like approach to get the instantaneous heat evolution and from it solidification kinetics. An alternative way of calculating the zero line is proposed which is validated by the fact that the latent heat of solidification thus evaluated is within 5% of the value calculated from thermodynamic data. Solidification kinetics was found highly reproducible provided appropriate experimental conditions were achieved: high enough casting temperature for the cup to heat up to the metal temperature well before solidification starts; and equal and homogeneous temperatures of the metal and of the cup at any time in the temperature range used for integration.

Keywords: Thermal analysis, Al–Si alloys, Solidification kinetics, Latent heat of solidification

Introduction

In the technical literature, two main methods are used to deal with cooling curves obtained by thermal analysis (TA) that are referred to as Newton like and Fourier like. In the former, the temperature of the metal is supposed to be homogeneous at any time during cooling, heat exchange being controlled by heat transfer from the mould to the surroundings. The latter method makes use of two thermocouples that allow evaluating the slight temperature difference in the radial direction of the TA sample and from it the heat flux.

Both methods need defining a so called zero line that describes the cooling of the material if there were no phase change. Such a zero line should present a monotonous evolution because it relates directly to heat extracted out of the sample. However, in the Fourier like method, it is found that the calculated zero line closely follows the actual trends shown by the temperature differences in the material and thus presents a wavy shape when recalcification shows up because of phase transformation.^{1,2} Furthermore, the heat balance equation as used in all practicality implicitly assumes that solidification occurs homogeneously in the volume considered, i.e. the one on which temperature differences are calculated, and this appears somehow ambiguous. It was thus decided to rely on the more classical Newton

like method following the lines described in the work by Chen and Stefanescu.³ The heat balance is given as

$$-hA(T - T^\circ) = V\rho C_p \frac{dT}{dt} + \frac{dQ_L}{dt} \quad (1)$$

where V and A are the volume and the outer area of the cup, ρ and C_p are the specific mass and the specific heat of the material, h is the Newtonian heat transfer coefficient, T and T° are the temperature of the material and the outer temperature, and Q_L is the latent heat released by the sample because of solidification which is defined as a negative quantity.

For analysis of the cooling curves to be strong enough for automation, it seemed necessary to check the reproducibility of the records. The experimental methodology followed in the present work is presented in section on 'Experimental' and the results, namely the cooling curves and their derivative, in section on 'Reproducibility of thermal analysis'. The data are then processed and analysed by means of equation (1) and its derivative. An alternative method is proposed for determining the zero line the validity of which is checked by comparing the estimation of the latent heat of solidification thus obtained to thermodynamic data. Solidification kinetics deduced from this approach is then discussed.

Experimental

All experiments were performed using an alloy based on Al–7Si–0.6Mg (wt-%) with a nominal composition range listed in Table 1. Before casting the metal was refined with Ti–B master alloy and modified with Na or

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Sr, and finally degassed with nitrogen during 20 min. Recording of the cooling curves was achieved using the Thermolan–Al system⁴ with standard TA cups having a thermal modulus V/A of 0.605 cm. Temperature was recorded with a frequency of ~10 Hz. Two different sets of tests have been considered in the present study:

- (i) one ‘Sr series’ for reproducibility of the cooling curves in case of strontium modified alloy, by recording data from two standard TA cups filled at about the same time
- (ii) three ‘Na series’ for reproducibility of the cooling curves in case of sodium modified alloy, recording data from nine standard TA cups. Three cups have been filled 20 min after degassing, the next three 15 min later, and the last three after 10 more minutes while the furnace had been shut down.

Just before pouring the Al alloy into the moulds, a metal sample was taken that was analysed by inductively coupled plasma and mass spectrometry (ICPMS, PerkinElmer, Waltham, MA, USA) in the cast house. The composition of all cast alloys was checked after casting with the same method, this time in the AZTERLAN laboratory. The data obtained are listed in Table 1.

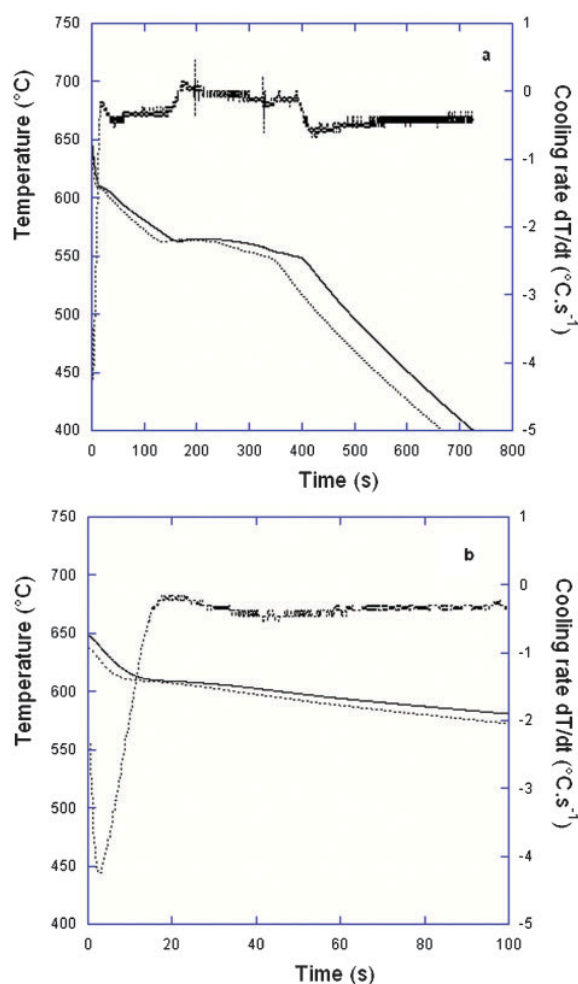
A differential thermal analysis (DTA) of the alloy was performed that is presented in the section on ‘Appendix’. The liquidus of the Sr and Na alloys was estimated at 612 and 614°C respectively, and the temperature for solidification completion at 554°C for both alloys. Taking pure aluminium as standard, an evaluation of the latent heat released during solidification was made and compared to prediction from thermodynamic calculations performed with the Thermocalc software⁵ and the COST 507 database.⁶

Reproducibility of thermal analysis

Following pouring the metal in the TA cup, the temperature of the thermocouple first increased to a maximum that depends on the initial melt temperature, and after a short while started decreasing. For every record, the origin of the time was set to zero when the maximum temperature was reached. Figure 1a compares the two cooling curves recorded during the Sr series, where it is seen that the overall solidification time may vary from one record to the other although much care was taken to ensure reproducible filling conditions. This slight difference may be due partly to the change in casting temperature and partly to some variation of the weight of metal poured in the cup.

Three thermal arrests are easily noticed on both cooling curves in Fig. 1a:

- (i) the start of solidification when (Al) dendrites begin to precipitate
- (ii) the beginning of the bulk (Al)–Si eutectic



a plot of whole records down to 400°C; b zoom on first 100 s

1 Temperature time curves recorded by standard TA analysis during Sr series and time derivative of curve showed with solid line

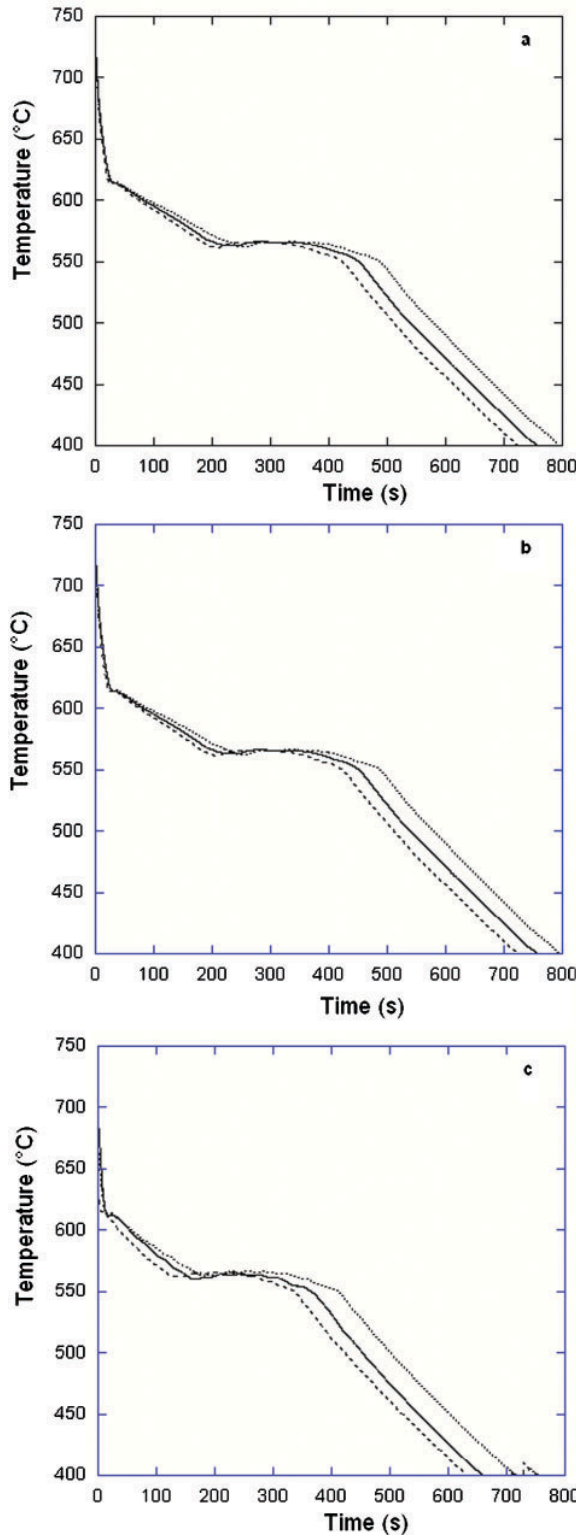
- (iii) a slightly less pronounced arrest towards the end of the eutectic plateau when minor phases precipitate.

Figure 1a also shows the cooling rate corresponding to the curve with the longer solidification time that has been obtained by differentiating the recorded data and then smoothing (central average on 10 measurements). Each of the three thermal arrests is associated to a peak on this latter curve. Note that the two nearly vertical lines are due to physical noise during recording. At the end of the eutectic plateau, the cooling rate decreases abruptly though it does not seem easy to ascertain when solidification stops effectively.

Figure 1b is a zoom on the first 100 s of Fig. 1a. It makes clearer the evolution of the derivative of the

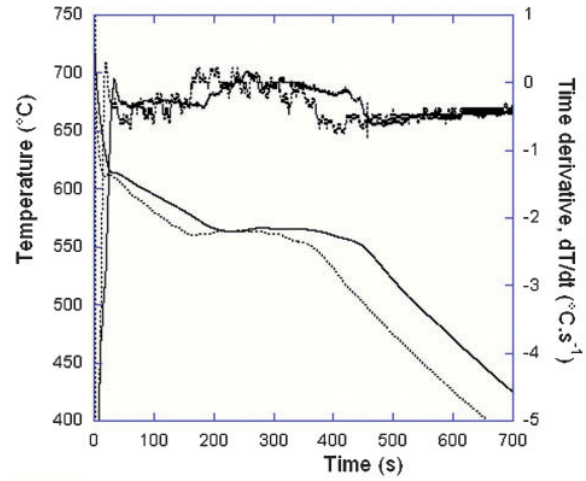
Table 1 Nominal composition of alloy Al–7Si–0.6Mg chemical analysis of casts (wt-%): accuracy of analyses is indicated by numbers between brackets for each element

	Si (0.08)	Fe (0.01)	Cu (0.01)	Mn (0.01)	Mg (0.01)	Zn (0.005)	Ti (0.007)	Na (0.003)	Sr (0.002)
Nominal composition	6.5–7.5	Max. 0.19	Max. 0.05	Max. 0.10	0.45–0.7	Max 0.07	0.08–0.25	–	–
B–Sr3	6.84	0.08	<0.01	<0.01	0.54	0.03	0.14	–	0.024
B–Na1	6.85	0.16	<0.01	0.01	0.52	<0.01	0.13	0.017	–



2 Temperature time curves recorded by standard TA analysis for three successive Na series

cooling curve that shows a minimum shortly after the temperature starts decreasing. Such a minimum was observed on all records, at a time and for a temperature that significantly varied from one record to another. It is expected to be related to the time at which the sand cup has reached the same temperature than the metal.



3 Comparison of one cooling curve and its derivative from each of first (solid line) and last (dotted line) series of Na test

Figure 2a–c shows the three series of three cooling curves recorded during the trial on sodium modified alloy. It is seen again that the overall solidification time can vary from one TA cup to another within each series. The characteristics of the curves are anyway very similar, with the average time of cooling for the first two trials being identical (Fig. 2a and b), while it is shorter for the last one (Fig. 2c) because the initial melt temperature has decreased as a consequence of the furnace shut-down. This lower initial temperature leads to much higher cooling rates of the liquid before solidification starts.

Figure 3 compares the intermediate cooling curves (shown with solid lines in Fig. 2) and their derivatives for the first and last Na series. The same features than those described for the Sr series are observed, namely that there are three thermal arrests associated to three successive solidification steps. In some cases as for the dotted curve in Fig. 3, there was some electrical disturbance that added noise to the records which is made evident on the derivative curve. It is noteworthy that the cooling rates are about equal after solidification completion, i.e. that heat exchanges are very similar at temperatures lower than $\sim 540^{\circ}\text{C}$.

Analysis of cooling curves

Assuming that Newton like heat transfer applies, the coefficient h in equation (1), or equivalently the coefficient $B = \frac{hA}{V\rho C_p}$, may be estimated by fitting the zero line when there is no phase change, i.e. at temperatures either higher or lower than the solidification interval. In that case, Q_L is set to zero in equation (1) that now writes

$$V\rho C_p \frac{dT}{dt} = -hA(T - T^{\circ}) \quad (2)$$

Equation (2) may then be integrated as³

$$\begin{aligned} T &= T^{\circ} + (T_{\text{ini}} - T^{\circ}) \exp \left[-\frac{hA}{V\rho C_p} (t - t_{\text{ini}}) \right] \\ &= T^{\circ} + (T_{\text{ini}} - T^{\circ}) \exp[-B(t - t_{\text{ini}})] \end{aligned} \quad (3)$$

where T_{ini} and t_{ini} are any selected metal temperature and associated time.

As seen in Fig. 1, the cooling rate of the metal is about -4 and -0.55 K s^{-1} at respectively 640 and 540°C. For these temperatures and the associated times, and with $V/A=0.00605 \text{ m}$, $\rho=2660 \text{ kg m}^{-3}$ for solid Al-Si alloy, $C_p=1000 \text{ J kg}^{-1} \text{ K}^{-1}$, it is found through equation (2) that $h \approx 105 \text{ W m}^{-2} \text{ K}^{-1}$ and $h \approx 14 \text{ W m}^{-2} \text{ K}^{-1}$ for the high and low temperature ranges respectively. This significant change may be tentatively related to the formation of an air gap between the solidifying metal and the cup because of solidification shrinkage.

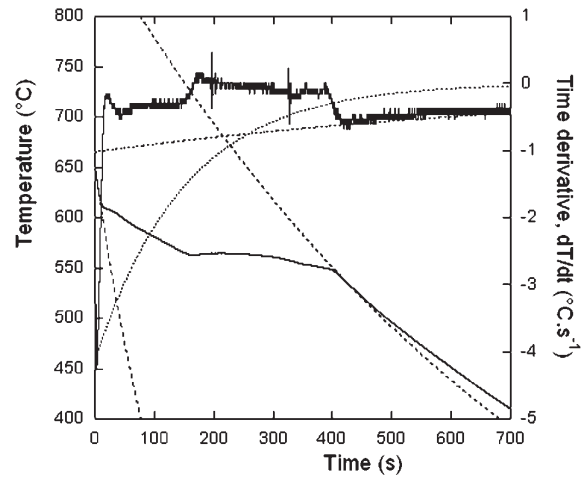
At this stage, it is possible to check if the single thermocouple technique (Newton type analysis) is such that the Biot number of a standard TA cup sample does not exceed 0.1 which is the necessary condition if one wants to consider that the temperature differences in the metal are negligible. The Biot number is given as $Bi=h\lambda/k$ where λ is the conduction length (half the size of the cup, i.e. $\sim 0.02 \text{ m}$), k is heat conductivity ($k \approx 100 \text{ W m}^{-1} \text{ K}^{-1}$) and h is the average heat transfer coefficient.⁷ With the above data, the Biot number is 0.02 in the high temperature range and 0.003 in the low temperature one, i.e. in both cases below the critical value.

In order to model the zero line before solidification starts, it was first thought that the minimum of the derivative curve could give the reference point for estimating B . It turned out however that when the corresponding temperature was much higher than the liquidus of the alloy, then the calculated curve did not follow the experimental one down to the start of solidification. It was thus decided to use the point when the temperature was closest to 635°C (i.e. $\sim 20^\circ\text{C}$ above the liquidus), except when the minimum of the derivative appeared at a lower temperature in which case it was selected. The time t_{ini} , the temperature T_{ini} and the cooling rate $V_{r,ini}$ corresponding to the selected initial point are listed in Table 2. The corresponding value of B for the high temperature range B_{ini} was obtained using the derivative of equation (3) that reads³

$$\frac{dT}{dt} = -(T_{ini} - T^0)B \exp[-B(t - t_{ini})] \quad (4)$$

For $t=t_{ini}$, this gives $\frac{dT}{dt}|_{t_{ini}} = -(T_{ini} - T^0)B_{ini}$. The values of B_{ini} obtained with T^0 equal to 25°C are given in Table 2.

To simulate cooling of the TA cups after solidification completion, the reference point was always selected when the experimental temperature reached 540°C. The



4 Example of one experimental cooling curve and its derivative (solid lines) and two reference curves for cooling without phase change (interrupted lines) calculated above liquidus and below solidus: derivatives of curves are also drawn with dotted lines

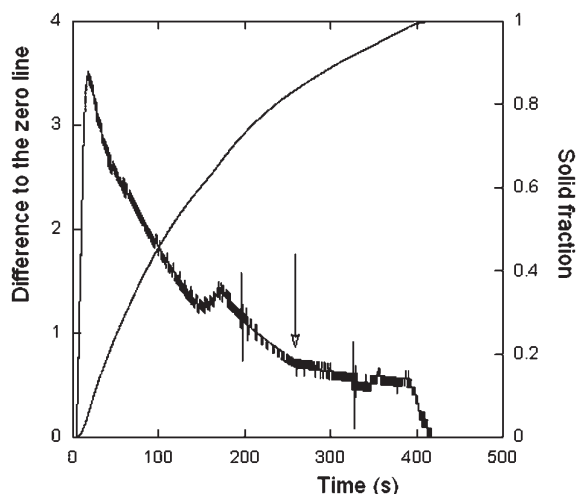
values t_{540} and the estimated values of B_{540} obtained with T^0 again set at 25°C are also listed in Table 2 and can be introduced in equation (3) to simulate the cooling curves after solidification. Figure 4 compares the calculations made to the experimental cooling curve corresponding to the first record of the Sr series. The derivatives of the calculated curves have been also drawn and it is seen that they differ significantly from each other in the solidification interval, in agreement with the very different h values evaluated above.

Latent heat of solidification and solidification kinetics

The significant change in the h (or B) value upon solidification, as shown in Fig. 4, suggested using the two derivative curves to define the zero line, changing from one to the other when they intersect. The difference between the experimental derivative and the zero line thus determined may then be integrated and should equal L/C_p according to Chen and Stefanescu.³ The values of L were evaluated with C_p set to $1000 \text{ kJ kg}^{-1} \text{ K}^{-1}$, as listed in Table 2. It is seen that the estimated L values vary significantly, from 471 to 562 kJ kg^{-1} . However, if one excludes the data obtained from the third series of the Na test, that were performed with a melt at quite low casting temperature, the

Table 2 Thermal analysis parameters determined from cooling curves recorded during Sr test and Na test

	$V_{r,ini}, \text{K s}^{-1}$	$T_{ini}, ^\circ\text{C}$	t_{ini}, s	B_{ini}, s^{-1}	$V_{r,540}, \text{K s}^{-1}$	t_{540}, s	B_{540}, s^{-1}	$L, \text{J kg}^{-1}$
Sr	-4.01	635.0	3.72	0.00660	-0.61	417.2	0.0012	510
	-4.62	627.9	2.64	0.00766	-0.53	360.6	0.0010	486
	-3.045	635.1	17.28	0.00500	-0.61	469.3	0.0012	484
	-2.826	635.1	17.04	0.00463	-0.62	505.6	0.0012	495
	-3.326	635.0	14.40	0.00545	-0.66	441.4	0.0013	492
	-3.030	634.9	17.28	0.00497	-0.68	469.3	0.0013	494
Na	-2.879	635.2	16.92	0.00472	-0.61	505.6	0.0012	499
	-3.258	635.2	14.28	0.00534	-0.68	441.4	0.0013	488
	-5.455	635.2	7.68	0.00894	-0.61	385.6	0.0012	537
	-4.773	634.8	5.64	0.00782	-0.682	428.9	0.0013	562
	-4.243	623.8	2.40	0.00709	-0.53	353.3	0.0010	471



variations are limited between 484 and 510 kJ kg⁻¹. It may be suggested that the large difference between the third series of the Na test and the first two relates to the low temperature of casting, and thus to the fact that the temperature was not yet homogeneous in the system formed by the metal and cup when solidification started. In well controlled experiments, the approach proposed to define the zero line give results that appear highly reproducible.

The average value of the solidification enthalpy at ~500 kJ kg⁻¹ is 15% higher than the value estimated from DTA experiments and by thermodynamic calculations under equilibrium, but only 5% higher than the values obtained from thermodynamic calculations assuming Scheil's model solidification (*see* the section on 'Appendix'). Such differences seem representative of the best capabilities of the methods as illustrated by the works of Chen and Stefanescu on cast iron³ and Barlow and Stefanescu on Al–Si alloys.⁸

The cumulative curve obtained by integrating the difference between the zero line and the experimental derivative may then be normalised to give the evolution of solid fraction, assuming the molar (or weight) enthalpy of transformation is the same for primary and eutectic reaction. Figure 5 shows together the evolution of this difference and the estimated change of the solid fraction in the case of the first casting of the Sr test the cooling curve of which was shown in Fig. 1. On the difference curve, the main peak is due to primary deposition of (Al) dendrites with an abrupt increase at the onset of solidification. The peak associated to the (Al)–Si eutectic is also clearly distinguished, while the last thermal arrest nearby the end of the eutectic plateau is hardly seen. It is interesting to note that this last arrest does not lead to any strong slope change on the solid fraction curve that appears anyway quite smooth along the whole solidification range.

One possible drawback of the adopted method could have been that the change from one base line to the other led to the appearance of an artificial effect on the

difference curve, and thus on the solid fraction evolution. The record shown in Fig. 5 was selected because the change from the upper to the lower temperature base line is located at about one third of the eutectic plateau, and should thus be clearly visible if it affected in any significant way the estimated evolution of the solid fraction. The location of the change is indicated with the arrow in Fig. 5, and it is seen that it does in fact lead to a very slight slope change of the difference curve but does not at all affect the calculated evolution of the solid fraction.

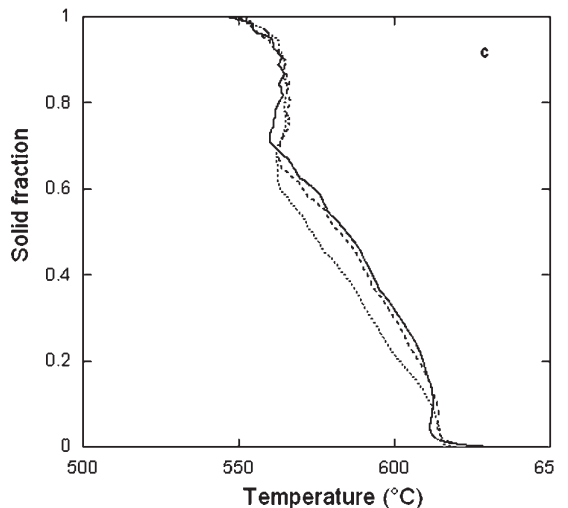
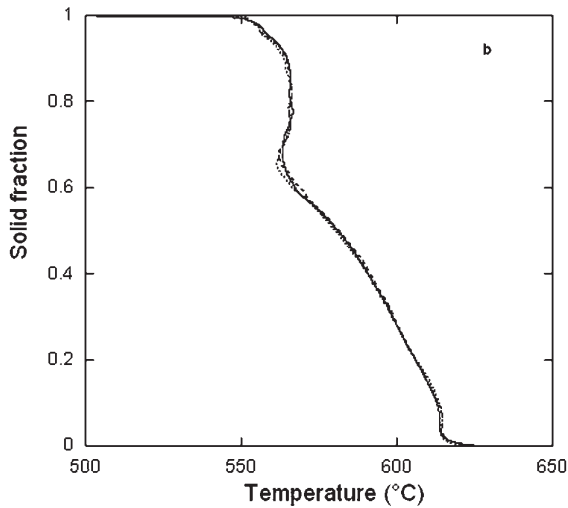
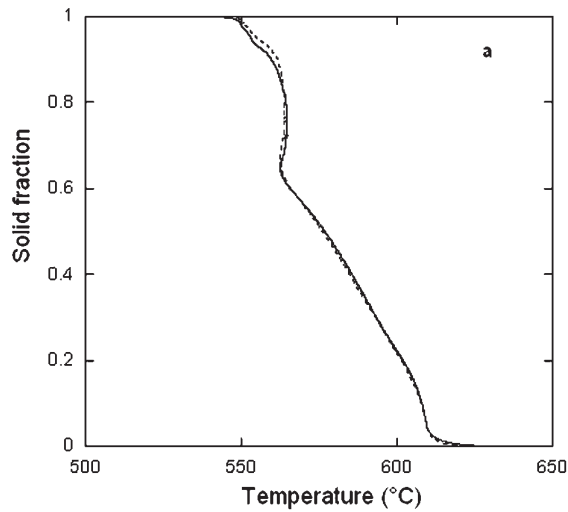
Figure 6a–c shows the evolution of the solid fraction versus metal temperature for the Sr test and the first and last series of the Na test. Figure 6a and b shows that the curves are nearly superimposed thus illustrating the high reproducibility of the procedure for solid fraction evaluation. The same similarities were observed on the curves calculated from the second series of the Na test. On the contrary, Fig. 6c shows that the records in the third series of the Na test were carried out under inappropriate conditions that led not only to poor determination of the solidification enthalpy as mentioned earlier but also to large uncertainties in solid fraction estimates.

It may be noted however on the curves in Fig. 6 that there is an apparent slow increase in the solid fraction before the actual onset of solidification. This is an artefact linked to the choice of the reference temperature considered for simulating high temperature cooling, and this artefact could be avoided by selecting a start temperature closer to the actual liquidus temperature of the alloy. The discrepancy thus induced is in fact very limited and was not considered as having any relevance in the present work. It could be easily possible to renormalise the curve by considering that the actual start of solidification relates to a slope of the curve higher than a minimum threshold value.

Although this is not the aim of the present work, it is of interest to compare the evolution of the solid fraction with temperature for both alloys, as shown in Fig. 7. It is seen that primary deposition of the (Al) primary phase is nearly identical for both alloys, though at slightly higher temperature for the alloy modified with Na than for the other one because of the higher liquidus temperature. While the eutectic (Al)–Si reaction starts at the same temperature for both alloys, it is seen that the eutectic plateau is at slightly higher temperature after modification with Na than after modification with Sr. A more complete description of these aspects of the thermal analysis of the solidification of Sr and Na modified Al–Si alloys will be given elsewhere.

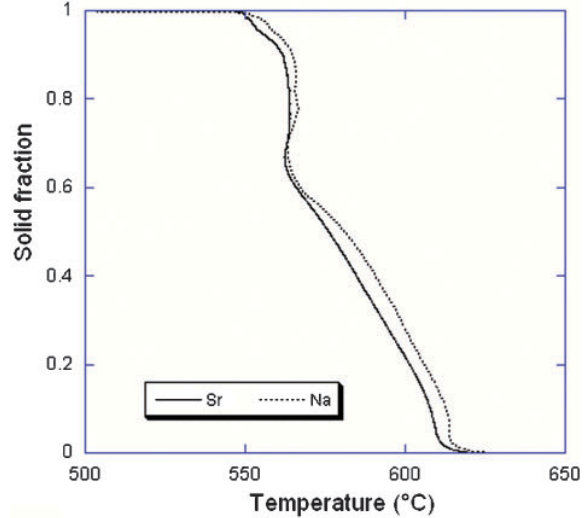
Discussion

The problem of selecting a convenient zero line has often been stressed and a review of different approaches, for both Newtonian and Fourier like description of heat exchanges has been made by Barlow and Stefanescu.⁸ The possibility of considering two zero lines, the one estimated from above the liquidus and the one deduced from below the solidus, was proposed long ago by Ekpoom and Heine.⁹ In this work, a linear interpolation between both zero lines was then made for the solidification range. The same approach was adopted by Barlow and Stefanescu⁸ in their three heat transfer



6 Evolution of solid fraction as estimated from cooling records of *a* Sr test and from *b* first and *c* third series of Na test

coefficients method. Although this method is straightforward and allows handling any case of change of the heat transfer conditions, there is no reason to think that the heat transfer coefficient varies so simply in the solidification range.



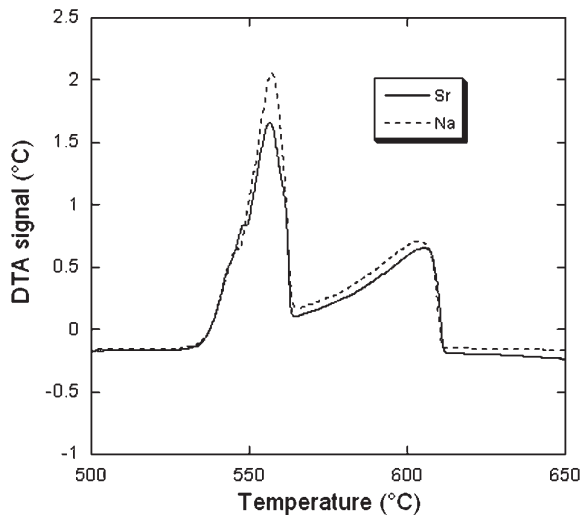
7 Comparison of solidification kinetics of Al-Si alloy after modification with Sr (solid line) and Na (dotted line)

In a recent work, Gibbs and Mendez expressed C_p in equation (1) as a weighted average of the liquid and solid heat capacities.¹⁰ They then proposed an explicit scheme for deducing the evolution of the solid fraction from cooling records which adjust iteratively the heat transfer coefficient until the appropriate value has been found. The zero line is in fact implicitly defined in this procedure that works only if there is no change in the heat transfer coefficient between liquid and solid cooling. As mentioned previously, it was considered that the huge change in the cooling rate observed in the present study should rather relate to a change in the boundary conditions induced by solidification shrinkage. In such a case, the change in C_p between solid and liquid, which is anyway limited in the case of Al-Si alloys, is of minor importance while the achievement of homogeneous temperature distribution during cooling and solidification appeared essential.

Conclusions

Series of cooling curves recorded by standard TA cups have shown good reproducibility in terms of solidification temperatures and times. It was noted that the cooling rate was much lower after solidification than before, and that this could not be dealt with by considering change in specific heat. A Newtonian like description of heat exchange during solidification of the cups was performed assuming a change of the zero line from the one calculated from liquid cooling to the one calculated during solid state cooling. The appropriateness of the method seems to be ascertained by the fact that the estimated latent heat values agree within 5% with thermodynamic calculations performed assuming Scheil's model for solidification. From the evaluation of the instantaneous latent heat evolved, solidification kinetics could be deduced. Reproducible results were achieved when appropriate experimental conditions are fulfilled.

1. The casting temperature is high enough for the cup to heat up to the metal temperature well before solidification starts.



8 Differential thermal analysis records obtained upon cooling at 5 K min^{-1} of each of Sr and Na modified alloys investigated in present study

2. The temperatures of the metal and of the cup are equal and homogeneous at any time in the temperature range used for calculation.

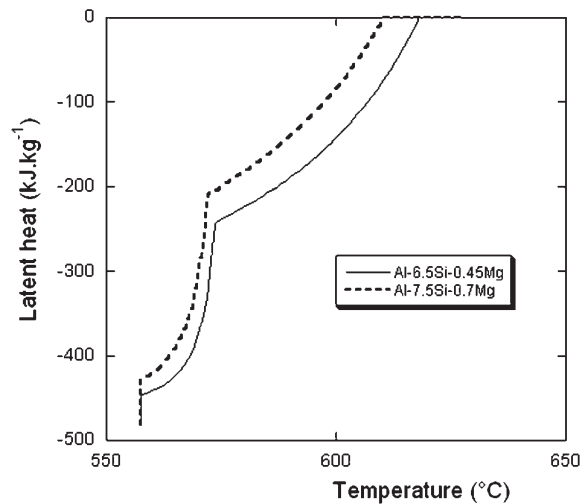
Appendix

Differential thermal analysis experiments were performed using a SETARAM SETSYS apparatus to evaluate the liquidus temperature and the end of solidification temperature of the alloys. For that purpose, heating and cooling at different scanning rates ($5\text{--}20 \text{ K min}^{-1}$) were performed. The experiments were carried out with samples being all $\sim 3.9 \text{ mm}$ in diameter and 2 mm in height, i.e. having about the same weight and undergoing similar heat transfer conditions. Figure 8 shows the records obtained on the two Al–Si alloys, where it is seen that they give highly similar DTA traces with two main peaks related respectively to (Al) primary deposition and (Al)–Si eutectic, and a shallow peak at lower temperature. This latter peak may be attributed to the formation of magnesium rich phases, either Mg_2Si and/or $\text{Al}_5\text{Mg}_3\text{FeSi}_6$.^{11,12}

The temperature for the end of fusion and end of solidification were plotted versus the scanning rate. The actual temperatures are deemed to be given as the extrapolated values at zero scanning rate. It was found that the liquidus temperature of the Sr and Na alloys should be about 612 and 614°C respectively, while the temperature for the end of solidification would be the same at 554°C . It should be noted however that the actual end of solidification of the alloys appeared sensitive to the cooling rate, e.g. because of solid state

Table 3 Area of DTA peaks recorded at 5 K min^{-1} , initial mass of sample and latent heat of transformation of alloys evaluated using value for pure Al as reference

Sample	Area of the peak, K s^{-1}	Mass of the sample, g	Latent heat, kJ kg^{-1}
Pure Al	512	0.0618	
Sr modified alloy	668	0.0745	420
Na modified alloy	730	0.0766	446



9 Evolution with temperature of enthalpy of Al-6.5Si-0.45Mg and Al-7.5Si-0.7Mg alloys calculated assuming Scheil's solidification model

back diffusion of solutes, and the actual temperature for solidification completion was observed to be $< 554^\circ\text{C}$ at $\sim 545^\circ\text{C}$. A detailed account of these results will be given elsewhere.

In order to evaluate the solidification enthalpy, similar samples of pure aluminium were submitted to a run at a cooling rate of 5 K min^{-1} . The DTA signal recorded with the SETARAM apparatus is expressed in microvolts. Once converted in Celsius, and after removing of the base line, the DTA peaks were integrated. The values obtained are listed in Table 3 where is also given the initial mass of the samples that was measured with a Sartorius precision balance. Using a value of 388 kJ kg^{-1} for pure aluminium, estimates of the latent heat of solidification of the alloys could be obtained that are given in Table 3. An average of 433 kJ kg^{-1} is thus obtained.

Using the Thermo-Calc⁵ software and the COST-2 database,⁶ a value of 440 J kg^{-1} is calculated for equilibrium solidification. Using the Scheil's model with the appropriate module of Thermo-Calc, the change of enthalpy by mass showed in Fig. 9 were calculated for two compositions close to the extreme of the composition ranges listed in Table 1 (Al-6.5Si-0.45Mg and Al-7.5Si-0.7Mg alloys). The enthalpy related to solidification is then predicted to change from about 480 to 486 kJ kg^{-1} from the former to the latter alloy.

Acknowledgement

This paper is based on work supported by the Spanish Industry Ministry, PROFIT program (contract no. FIT-030000-2007-70).

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