

FOURIER THERMAL ANALYSIS APPLIED TO SODIUM EUTECTIC MODIFICATION OF AN ALSI7 ALLOY

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Abstract

The so-called “Fourier Thermal Analysis” (or FTA) is an evolution of the “integral thermal analysis”, which is actually used as a process control in Aluminium and cast iron foundries. It has been developed since late 80's in order to investigate nucleation and growing kinetics of the various phases in multi-component alloys. FTA is based on the evaluation of the thermal gradient in one-dimensional thermal field that arises in a cylindrical solidifying specimen.

During the last twenty years, both the traditional thermal analysis and FTA have been applied to the experimental determination of the solid fraction during solidification, in order to assess results from numerical simulation. Nevertheless, FTA has not been applied to foundry process control or optimisation.

Eutectic modification is extensively used in low-pressure permanent mould processes, in order to improve tensile properties and toughness of Al-Si alloys. The effectiveness of the treatment is subjected to the presence a minimum amount of modifying elements, such as Sr, Na or other elements. Traditional thermal analysis is useful in determining modification level of the alloy, then to control the modification treatment.

Aim of this work is to verify the potentiality of gradient-based thermal analysis method, such as FTA, in eutectic modification investigation.

An A356-type hypoeutectic Al-Si alloy has been modified with metallic sodium at four different modification levels. Two-thermocouple thermal analysis curves have been recorded, in order to perform FTA analysis. Fraction solid versus time ($f_s(t)$) and temperature ($f_s(T)$) have been determined at different modification levels.

Microstructural characterization has been made using automatic image analysis. Average values of dimension and roundness of eutectic Si have been compared to thermal analysis results.

A significant correlation between the so-called “eutectic depression” and silicon morphology has been observed. More relevant is the behaviour of the fraction solid curves, from which it is possible to note a significant delay in the start of eutectic reaction. This delay has been observed not only in time but also in temperature and fraction solid domain.

Riassunto

La “Fourier Thermal Analysis” (FTA) è una tecnica avanzata di analisi termica, sviluppata negli anni '80-'90 per determinare il calore latente rilasciato in fase di solidificazione, allo scopo di indagare le cinetiche di nucleazione ed accrescimento delle varie fasi coinvolte. I risultati delle indagini condotte con questa metodologia hanno contribuito allo sviluppo dei codici di calcolo per la modellazione dei fenomeni di solidificazione di leghe da fonderia, come le ghise e le leghe di alluminio. Non è attualmente impiegata nell'ambito della fonderia come strumento di controllo di processo o come metodo per la caratterizzazione dei fenomeni di solidificazione.

D'altra parte neanche l'analisi termica “tradizionale” viene utilizzata in modo diffuso nella fonderia di Al-Si, al contrario della fonderia di ghisa.

Scopo di questo lavoro è di verificare le potenzialità della FTA nello studio della modifica eutettica di una lega Al-Si, e più in generale nella dinamica della solidificazione delle leghe Al-Si. La modifica eutettica viene impiegata allo scopo di incrementare le caratteristiche di resilienza e resistenza a fatica delle leghe Al-Si, l'efficacia del trattamento è vincolata alla presenza di una percentuale minima di elemento modificante. L'analisi termica può essere impiegata per verificare il livello di modifica della lega, e quindi l'efficacia del trattamento.

È stata presa in considerazione una lega della classe A356, modificata con il Na, e sono state confrontate le curve $f_s(t)$ e $f_s(T)$ ottenute con diversi livelli di modifica, allo scopo di correlare le caratteristiche delle curve di frazione di fase solida rispetto al tempo ed alla temperatura con le caratteristiche microstrutturali della lega.

Sono stati riscontrati effetti della modifica sull'evoluzione nel tempo delle varie fasi, compresa la fase primaria, ricca di alluminio.

INTRODUCTION

In a foundry process, the possibility of monitoring in detail the evolution of solidification is fundamental, in order to have the correct understanding of the final microstructure and metallurgical quality of the casting. Thus, the so-called “cooling curves” (even if a more correct definition is that of “solidification and cooling curves”) are assuming an increased relevance and diffusion, both from literature and industrial application viewpoints.

A liquid metal or alloy, placed into a mould, decreases its temperature, due to the heat transfer phenomena (conduction, convection, radiation). The amount of these phenomena is dependent on various factors, including the geometry of the mould, the insulation conditions, the possible motion of the liquid, the presence of cooling devices, and so on [1-7].

Generally speaking, a temperature vs. time diagram allows the description of the thermal evolution of the metal or of the alloy. In the liquid state, the analytical description of the phenomenon is given by the equation

$$A \cdot q = V \cdot \rho \cdot c_p \cdot \frac{dT}{dt} \quad (1)$$

where V and A are, respectively, the volume and the surface of the casting, ρ and c_p are, respectively, the density and the specific heat of the material under investigation, q is the density of the thermal flow going from the metal to the mould. The term q can be evaluated, for instance, by the Fourier equation, once known the starting and contour conditions of the system. The variables T and t are, respectively, the metal temperature and the time; thus dT/dt (i.e. the derivative of temperature with respect to time) is the cooling rate of the metal [1,4-5].

Under the hypotheses of small variations in ρ and c_p with temperature and of $q = \text{constant}$, the cooling rate is also constant, with the cooling curve assuming a linearly decreasing aspect.

The liquid to solid transition is associated to the release of the latent heat. Consequently, equation (1) must be properly modified and becomes:

$$A \cdot q = V \cdot \rho \cdot c_p \cdot \frac{dT}{dt} - \Delta H \cdot \frac{dV^s}{dt} \quad (2)$$

where, apart from the already defined symbols, ΔH is the solidification volumetric latent heat and V^s represents the volume of already solidified metal [1,4-5].

At the end of solidification, temperature decreases again, with a different slope, due to the change in ρ and c_p values from the liquid to the solid state. These general considerations must be integrated including the role of nucleation (heterogeneous nucleation is considered) and growth mechanisms, whose effect depend specifically on the processing conditions. In particular, undercooling must be considered, being the real driving force of the whole solidification phenomenon [1]. Nucleation and growth rate can be described with specific reference to undercooling degree. Applying the continuous nucleation model, it can be written

$$N = \mu_l \cdot \Delta T^n \quad (3)$$

and

$$\frac{\partial N}{\partial t} = -n \cdot \mu_l \cdot \Delta T^{(n-1)} \cdot \frac{\partial \Delta T}{\partial t} \quad (4)$$

where N is the number of nuclei formed in the volume unit, ΔT is the undercooling, n and μ_l are the so-called nucleation parameters.

For the growth rate (V_{accr}), it can be written

$$V_{accr} = \mu_{accr} \cdot \Delta T^2 \quad (5)$$

where μ_{accr} = growth constant [1,6].

A “real” solidification curve is thus characterised by the presence of undercooling, associated with the progressive development of the latent heat, leading to the recalescence phenomenon, which is well described by the first derivative of the cooling curve (i.e. the cooling rate).

The parameters of the above equations, correlating undercooling with nucleation and growth rate, are strictly dependent on composition and technological aspects. In other terms, the evolution of solidification is strongly related with the specific properties of the cast alloy and on the foundry processing conditions adopted.

The acquisition and the analysis of the cooling and solidification curve of a cast alloy have demonstrated their industrial relevance for alloys presenting eutectic solidification, such as the Fe-C-Si (cast irons) and Al-Si systems [8-14], both in terms of process control and of microstructure understanding [11,13].

A recent development of this approach has been introduced for analysing the kinetics of nucleation and growth of eutectic systems. It is the “Fourier Thermal Analysis” approach, requiring the acquisition and the subsequent elaboration of at least two T(t) curves, as well as cylindrical or spherical crucibles [15-16].

In this paper, such an approach is developed and applied on Al-Si foundry alloys, to monitor their solidification conditions and to describe the effects of the modification stage.

FOURIER THERMAL ANALYSIS

THEORETICAL ASPECTS

The slope of the curve $T(t)$ of a generic alloy, solidifying in a thermal analysis cup, is due to two contributions: the rate of volumetric heat exchanged to the environment (H_{EXC} , [$\text{Jm}^{-3}\text{s}^{-1}$]) and the rate of volumetric latent heat released during solidification phenomena (H_{GEN} , [$\text{Jm}^{-3}\text{s}^{-1}$]). The slope of solidification curve is given by equation (6), where C_v is the volumetric heat capacity [$\text{Jm}^{-3}\text{K}^{-1}$] of the system.

$$\frac{dT}{dt} = \frac{H_{\text{EXC}}(t, T) + H_{\text{GEN}}(t, T, f_s)}{C_v(t, T, f_s)} \quad [\text{Ks}^{-1}] \quad (6)$$

H_{GEN} depends on the phase transformations that occurs during solidification, so it is influenced by the melt treatment (grain refining, eutectic modification) and also by the rate of heat extraction from the melt (the late influencing the depth of undercooling in solidification transformations).

H_{LOSS} is related to the conditions of heat exchange between the specimen and the external environment. In the so-called “Newtonian Thermal Analysis” [8,14-15], the alloy is supposed to be uniform in temperature, so that the

heat exchanged is determined only by the heat exchange at the interface between metal and the external environment.

In “Fourier Thermal Analysis”, instead, the heat exchanged is supposed to be related to temperature gradient inside the alloy. The slope of solidification curve is then related also to the thermal diffusivity α [m^2s^{-1}] of the alloy (a quantity related also to the heat conductivity of the material [15-16]) and the Laplace operator $\nabla^2 T$ [Km^{-2}], as reported by equation 7.

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T + \frac{H_{\text{GEN}}}{C_v} \quad (7)$$

In the case of a cylindrical cup, temperature gradient can be estimated by means of a two-point temperature measurement [15-16], each located to a certain radius R_i from the centre:

$$\nabla^2 T = \frac{4(T_2^2 - T_1^2)}{R_2^2 - R_1^2} \quad [^\circ\text{C/m}^2] \quad (8)$$

So that the rate of volumetric heat generated can be obtained as:

$$H_{\text{GEN}} = C_v \left(\frac{\partial T}{\partial t} - \alpha \nabla^2 T \right) \quad [\text{J/s}] \quad (9)$$

In this equation the term $\alpha \nabla^2 T$ gives the so-called “base line” for the heat measurements, i.e. the theoretical cooling curve of a material not having phase changes.

If absence of phase changes (in liquid and solid state), thermal diffusivity α can be expressed as the ratio between the slope of $T(t)$ curve in the centre of the specimen and the Laplace operator.

$$\alpha = \frac{(\partial T / \partial t)}{\nabla^2 T} \quad (10)$$

From this equation, having a bigger diffusivity gives a bigger capacity of the material of releasing heat when subjected to the same thermal gradient.

Once known thermal diffusivity in solid and liquid state, diffusivity during solidification can be derived using a simple linear correlation [15]. An example of this approach is given by figure 1.

From the product of diffusivity and thermal gradient, a base line (or “zero line”) Z_F can be calculated and used to determine the heat released during solidification, according to (9).

In figure 2 the zero curve Z_F is plotted against the slope of solidification curve, or dT/dt .

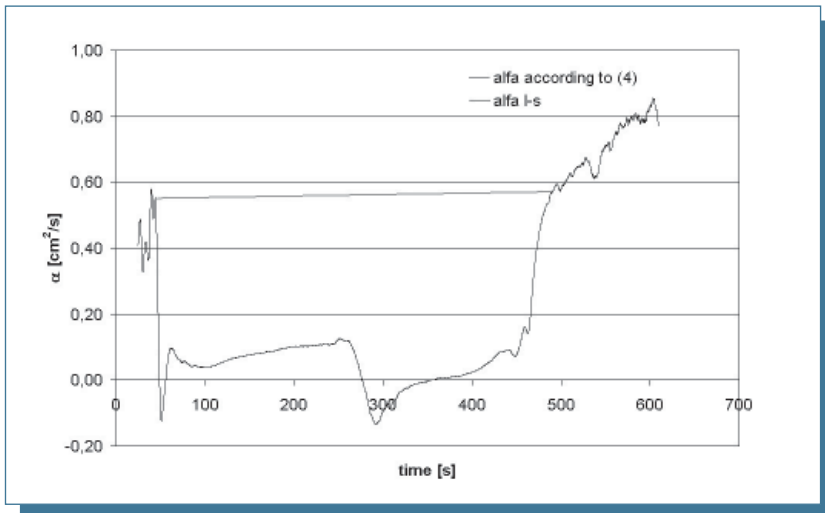


Fig. 1: thermal diffusivity as obtained from (4) (in black) and estimated inside the solidification interval (in red)

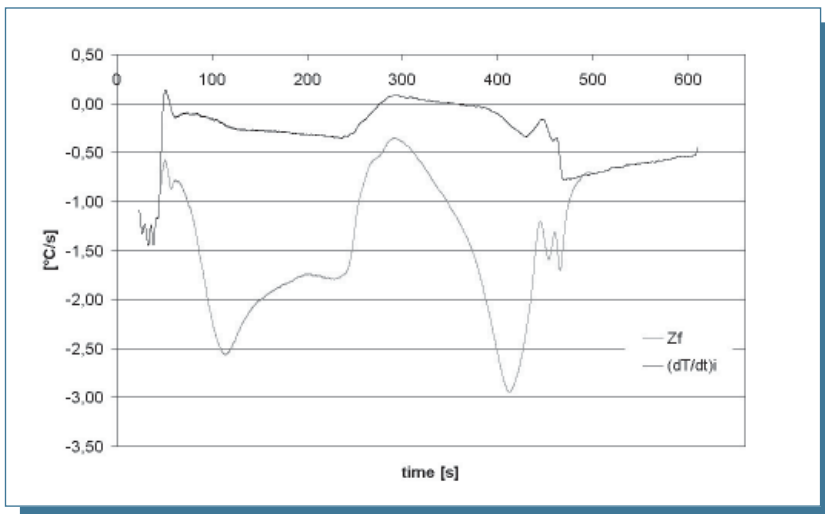


Fig. 2: first derivative of $T(t)$ curve for the central thermocouple (black) and baseline for latent heat determination (Z_F , green).

PRACTICAL APPLICATION OF FTA

The experimental set up for FTA requires only two additional features: a symmetrical cup (cylindrical or spherical) and a second thermocouple.

Once measured the two time-temperature curves ($T_{int}(t)$ e $T_{ext}(t)$), their elaboration consists in this calculation steps:

1. first derivative in the inner point
2. thermal gradient

SODIUM EUTECTIC MODIFICATION OF AN AL-SI ALLOY

Eutectic modification is one of the more effective techniques for microstructure and mechanical properties optimisation in Al-Si foundry alloys.

It consists in the addition of specific elements, or “modifying” elements (such as Na, Sr, Ca), in order to modify the structure of eutectic Si, from lamellar to fibrous and spherical. This leads to a substantial improvement in mechanical properties such as toughness and tensile strength. Other elements have been reported to have modifying properties (i.e. Ba, Y, Yb) [18-26].

Speaking about Na modification, one of the critical aspects in the use of this element is the short fading time, after which the modifying effect disappears. Being a “temporary modification”, it has also some advantages, because:

- it does not affect significantly properties like fluidity and viscosity
- modified alloys can be recycled without additional treatments

EXPERIMENTAL SET UP

The present study has been carried out using an alloy belonging to the ENAB 42100 class (an A356 equivalent). Chemical composition of the investigated alloy is given in table 1.

A steel thermal analysis sampling cup, preheated before sampling, has been used. Thermocouples are K-type, outer diameter 1.5 mm, shielded with stainless steel (AISI 316). An additional protection

3. thermal diffusivity in liquid and solid state
4. thermal diffusivity during solidification
5. base line Z_F
6. heat released during solidification
7. fraction solid with respect to time and temperature

One of the critical aspects is the thermal diffusivity calculation. Some authors suggest evaluating diffusivity in function of fraction solid, using an iterative procedure, in which diffusivity is initially supposed to be linear function with time [15-17].

- it does not form compounds or intermetallic phases

It has been recently pointed out the up-to-dateness of sodium modification, having care that the overall process is controlled by means of suitable process control, such as thermal analysis [23]

In practice, sodium fading effect makes necessary a process control on the modification level of the melt, in order to develop a constant quality in the casting.

A traditional thermal analysis system can be useful in order to investigate on the effect of sodium and other modifying elements on the solidification mechanisms and on the final properties of the modified alloys. Traditional thermal analysis uses features of the $T(t)$ curves such as eutectic depression and recalescence, and can be used in conjunction with chemical analysis in order to characterize the melt and its modification level [12-14,17]

Fourier Thermal Analysis (FTA) has been developed in order to evaluate heat released during solidification in different cooling conditions, so to determine the dependence fraction of solid with time and temperature. The potentiality of the application of this technique to the study of eutectic modification has not yet been verified in literature, and it's the main task of this work.

The knowledge of the dependence of fraction solid with different solidification condition (heat exchange, melt treatment) is also one of the crucial points in numerical modelling of microstructure evolution. As a matter of fact, FTA has been used by different authors to characterize the various foundry alloys behaviour [2,6-7].

for thermocouple has been used, consisting in stainless steel tube (AISI 316), inner diameter 1.7 mm, thickness 0.1 mm. The distance between the inner thermocouple (T1) and the outer is 20 mm. Sampling frequency: 10 Hz.

The various step of the application of FTA are listed in the following points:

1. alloy melting and overheating (750°) in muffle furnace, addition of metallic Na, thermal analysis crucible preheating (750°C);
2. sampling of specimen M01, 5 minutes after modification
3. sampling of specimen M02, 25 minutes after modification
4. sampling of specimen M03, 45 minutes after modification

TABLE 1. CHEMICAL COMPOSITION OF THE INVESTIGATED ALLOY

Alloy type/elements	Si	Mg	Cu	Mn	Fe	Zn	Ti	Al
AlSi7MgTi	7,06	0,448	0,036	0,007	0,13	0,002	0,125	Bal

5. sampling of specimen M04, 65 minutes after modification

Traditional thermal analysis and FTA have then been performed on the recorded $T(t)$ curves. Results of the analysis have been compared to the main microstructural features of specimens:

- secondary dendrite arm spacing (SDAS) of α -phase

- average area, roundness and aspect ratio of eutectic silicon

Details on the microstructure evaluation as well as on thermal analysis are reported in the next paragraphs.

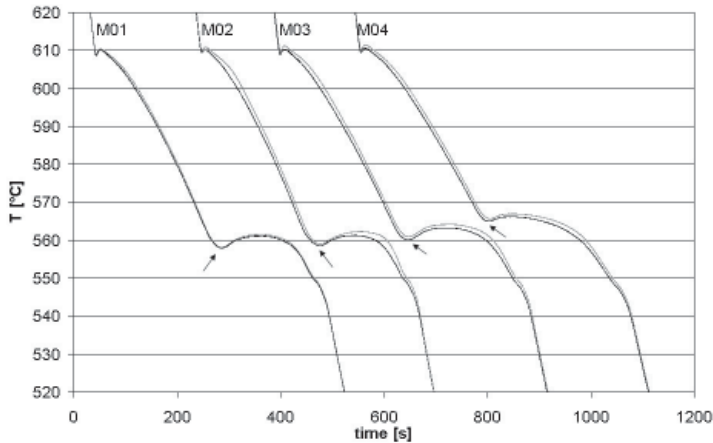


Fig. 3: $T(t)$ curves at different modification level, corresponding to specimens M01-M04.

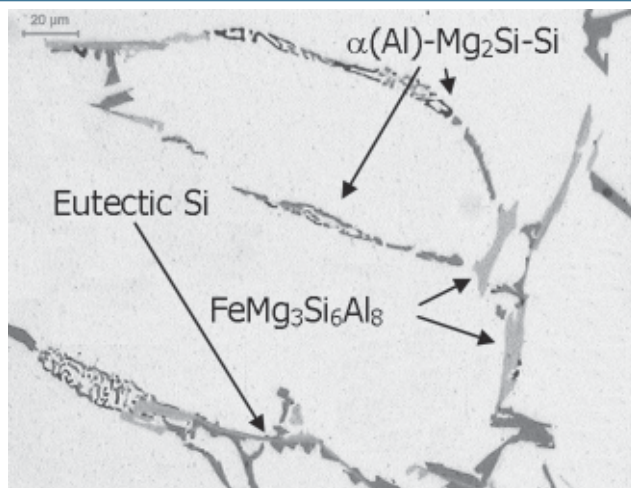


Fig. 4: microstructure of specimen M03 (200x).

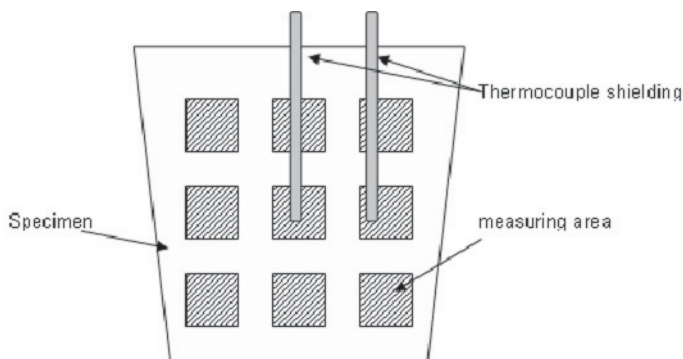


Fig. 5: position of the nine areas for metallographic investigation in the thermal analysis specimen.

RESULTS AND DISCUSSION

Traditional and Fourier thermal analysis have been applied to the specimen taken at various fading time. Results from these analyses have been compared to specimen microstructures.

Solidification curves $T(t)$ of the various specimens are reported in figure 3. Red curves refer to inner thermocouples, black curves to the outer ones.

Arrows show the effect of Na fading on eutectic depression. The minimum temperature reached during eutectic transformation gradually rises with fading time. This tendency is coherent with results reported by other authors [22, 23].

Curves have then been elaborated according to the procedure presented in previous paragraphs, in order to obtain the dependence of fraction of solid with time and temperature $f_s(t)$ e $f_s(T)$, and to evaluate the effect of Na modification on the shape of these curves.

MICROSTRUCTURAL INVESTIGATION

Microstructure of specimen named M01ÖM04 has been characterized by means of Automatic Image Analysis, in order to quantify alloy modification level in terms of average roundness and dimensions of eutectic Si. Other phases have been also identified, as reported in figure 4.

For each specimen, a total of 9 different areas have been investigated, as reported in figure 5. In each of these areas, 9 fields taken at a 500 magnification have been photographed and analysed. This procedure has been performed by means of an automatic image analysis system (LEICA QWIN), including the field individuation, data recording and analysis.

In figure 6-9, examples of microstructures taken on different specimens are presented. At higher fading times, eutectic Si grows in dimension and its shapes moves from fibrous to lamellar.

Geometric parameters of the eutectic silicon that have been investigated are: area, aspect ratio (length/width), roundness (a parameter defined inside the image analysis software, linked to

perimeter and area). Both aspect ratio and roundness are useful in describing the morphology of eutectic silicon: when they are close to unit, the eutectic is close to spherical shape. On the contrary, if their values are far from the unit, the shape of eutectic is lamellar.

Average values for the various specimens are listed in table 2. Fading of Na modification, that occurs during time, leads to the reduction in modification level. This causes the drop in roundness of eutectic silicon, and the contemporaneous increase in its size.

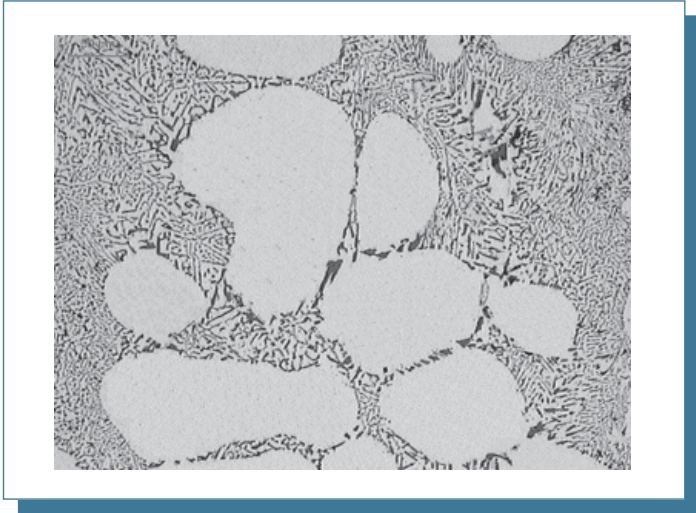


Fig. 6: specimen M01-5'.



Fig. 7: specimen M02-25'.

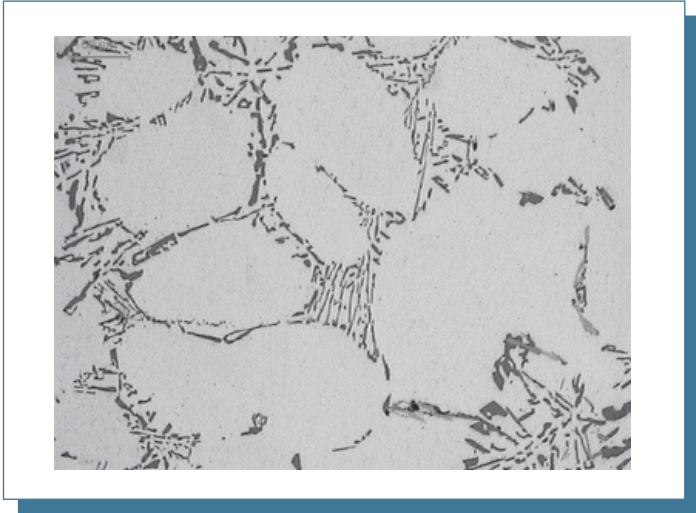


Fig. 8: specimen M03-45'.

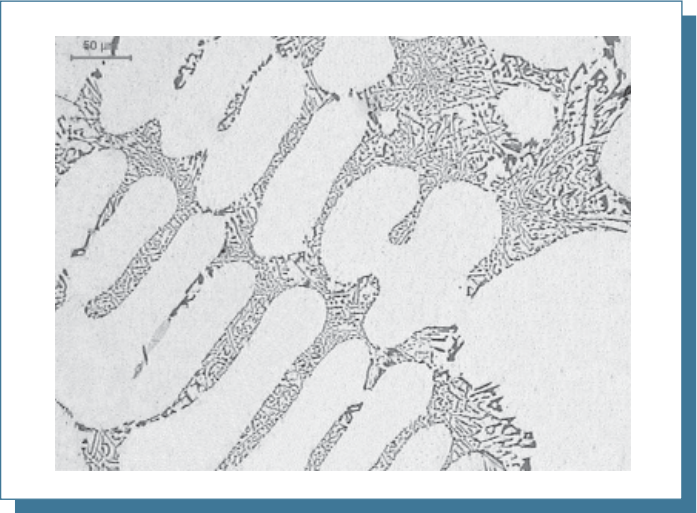


Fig. 9: specimen M04-65'.

TABLE 2. GEOMETRIC PARAMETERS OF EUTECTIC SILICON VS. SODIUM FADING TIME

	M01-5 min	M02-25 min	M03-45 min	M04-65 min
Area [mm²]	10.8	13.1	35.9	77.6
Roundness	3.3	3.6	5.8	8.4
Aspect ratio	2.5	2.4	3.2	4.3

Microstructural characterization has been completed with the measurements of the spacing

between secondary dendrite arms of Al-rich a phase. The SDAS (*Secondary Dendrite Arm Spacing*) has been evaluated in 81 different fields. Results from

TABLE 3. SDAS VARIATION WITH FADING TIME.

Specimen	time [min]	SDAS [mm]	s [mm]
M01	5	64.0	5.0
M02	25	68.0	5.5
M03	45	68.1	7.2
M04	65	68.1	4.1

these measurements are listed in table 3.

The variation of roundness and aspect ratio with fading time is presented in figure 10. The average values of both these features have a strong increase between 25 and 45 minutes, showing a decrease in modification level. After 45 minutes from the introduction of Na in the melt, the modification level reaches a critical point, from which the properties of the material are supposed to show a significant decrease.

RATE OF HEAT RELEASED VERSUS TIME

With FTA it is possible to evaluate the rate of heat released during time (or H_{GEN}), so that fraction of solid can be calculated as the fraction of heat released until that time on the total of heat released.

A visualization of the various stages of the solidification processes is then visible, as reported in figure 11, referred to 5 minutes after modification occurred. Three different areas are visible, the first one related to the primary α phase, the second one belonging to Al-Si eutectic and the third one to the secondary phases and intermetallic compounds with other alloying elements (like Mg_2Si and Fe-Mn-Mg rich phases). The area related to the last solidifying phases seems to be more evident at the highest fading times, as reported in figure 12-13. The contribution on heat generated gradually tends to get mixed up with the contribution of eutectic silicon.

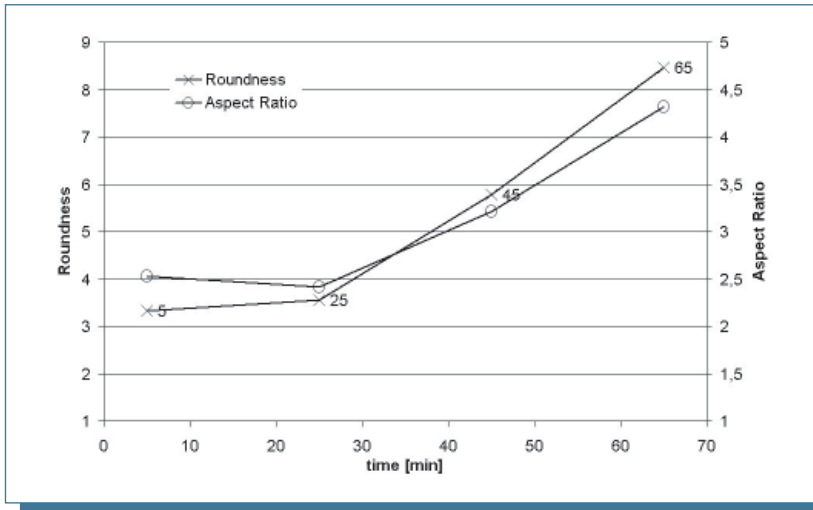


Fig. 10: variation of eutectic silicon roundness and aspect ratio for different fading time.

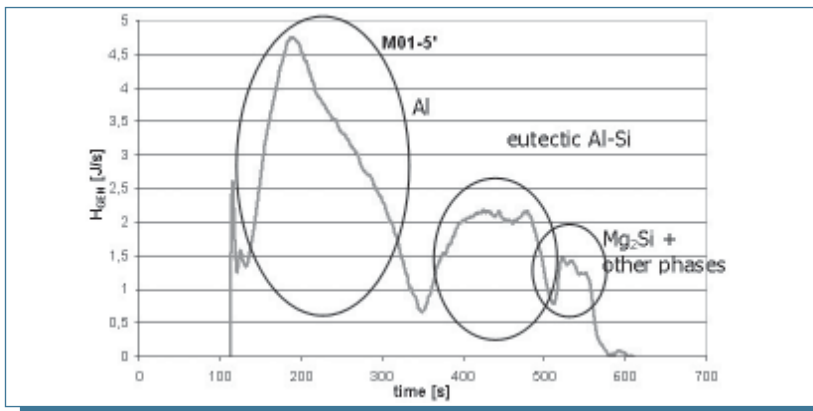


Fig. 11: latent heat released vs. time, 5 min. after modification, specimen M01.

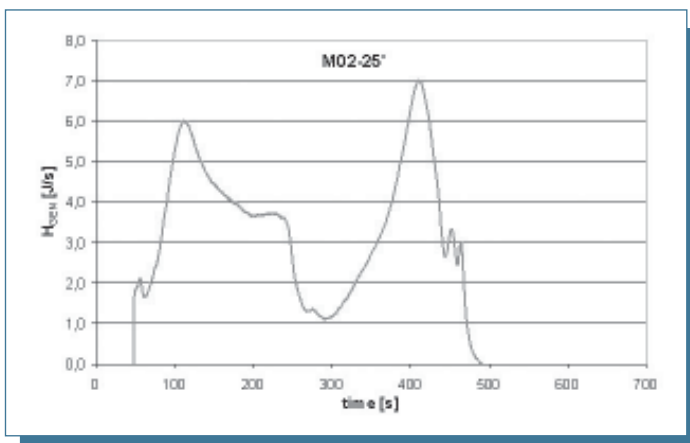


Fig. 12: latent heat released vs. time, 25 min. after modification, specimen M02.

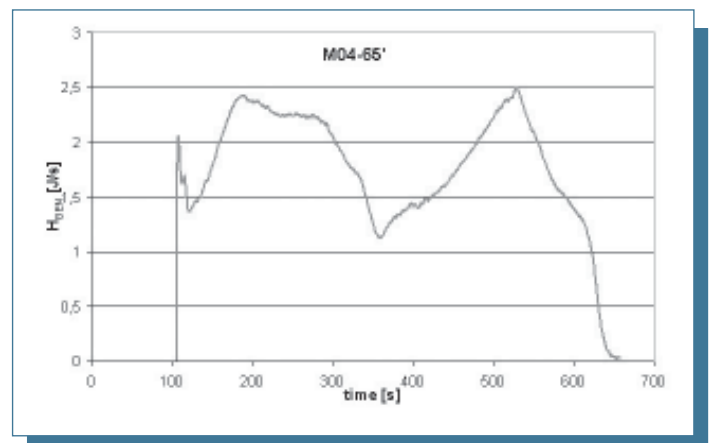


Fig. 13: latent heat released vs. time, 65 min. after modification, specimen M04.

RATE OF HEAT RELEASED VERSUS SOLID FRACTION

Latent heat released can be compared to fraction of solid, in order to free the results from time

dependence. In this way it's possible to compare results obtained in different cooling conditions.

From figures 14-15 it is evident the shift in the initial point for eutectic reactions, which is moving towards lower fraction of solid.

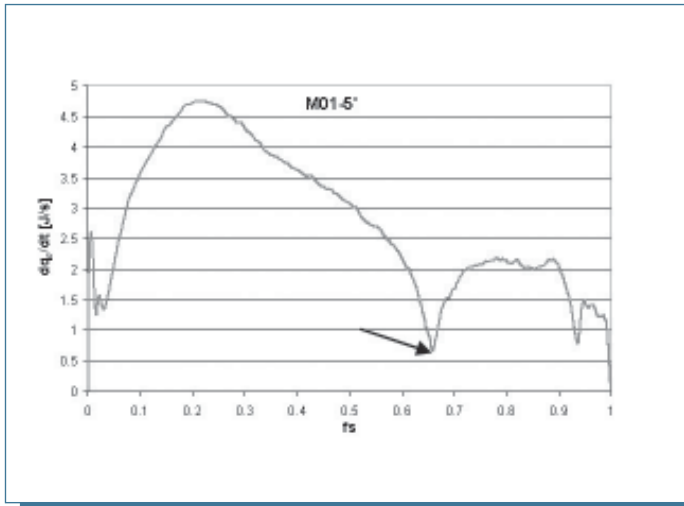


Fig. 14: latent heat released vs. solid fraction, 5 min. after modification, specimen M01.

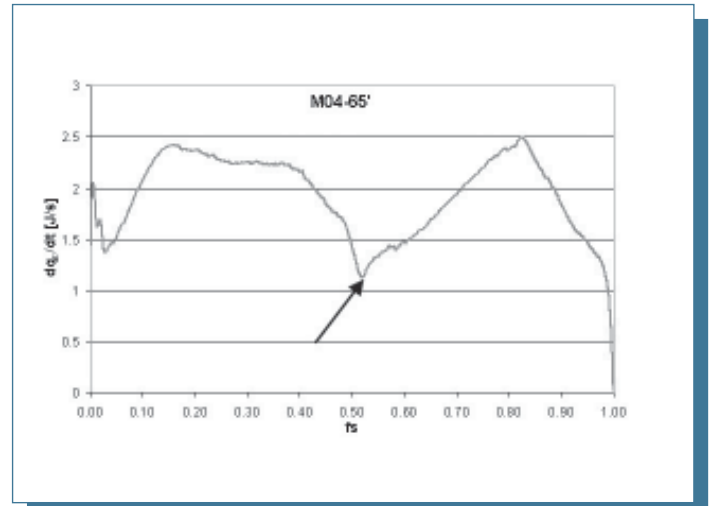


Fig. 15: latent heat released vs. solid fraction, 65 min. after modification, specimen M04.

FRACTION OF SOLID VERSUS TEMPERATURE

Fraction of solid f_s , as measured by means of FTA, can be plotted against the temperature measured in the centre of the thermal analysis cup. The effect of modification on transformation kinetics is then visible in the curve $f_s(T)$.

Figure 16 collects the various $f_s(T)$ curves for specimens M01-M04. Starting point for eutectic reaction is identified with the minimum point of $f_s(T)$ curves.

Not only modification shifts this point to lower temperatures (as shown also from traditional thermal analysis), but also seems to shift the fraction of solid of this point to higher values. In other terms, eutectic reaction starts at lower temperatures, when a higher quantity of Aluminium rich α -phase has been already formed.

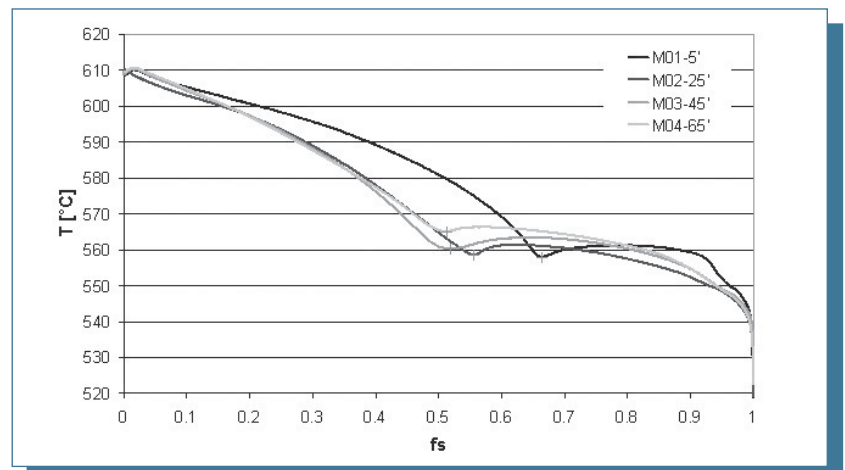


Fig. 16: solid fraction vs. temperature, at various fading time.

TABLE 4. VARIATION OF EUTECTIC START WITH FADING TIME.

Specimen	Fading time [min]	f_s at start of eutectic reaction	T at start of eutectic reaction [°C]
M01	5'	0.66	558.0
M02	25'	0.55	558.5
M03	45'	0.52	560.1
M04	65'	0.51	565.0

Data regarding the shift of the eutectic start point are listed in table 4.

The presence of sodium in the melt seems to influence also the primary solidification, not only the eutectic formation.

CONCLUSIONS

The so-called Fourier Thermal Analysis (FTA) has been used to monitor the effect of modification on the evolution of solid fraction during solidification of an A356 Al-Si alloy.

The latent heat released during solidification has been measured, and from that the solid fraction has been obtained during the various stages of solidification. The evolution of solid fraction in temperature (the $f_s(T)$ curves) has been found to be the most effective in evaluating the effect of melt treatment on the solidification phenomena.

Solid fraction curves $f_s(T)$ have been obtained at different modification levels, showing significant effects of the sodium modification level on the starting point of formation of eutectic phases.

These results confirm the feasibility of using FTA as an experimental method for evaluating $f_s(T)$ curves in different melt treatment conditions, in particular regarding eutectic modification. These curves can be used also as input parameters for numerical modelling of microstructure formation in foundry alloys.

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