Influence of Mg and Ti on both eutectic solidification and modifying efficiency in Sr-modified Al-7Si cast alloys

L. Lattanzi, A. Fortini, M. Giovagnoli, M. Merlin

Magnesium and titanium are the main alloying elements always present in a commercial A356 alloy, and strontium is commonly added to achieve a good degree of modification of the eutectic structure. Whilst most of the studies have been focused on the role of strontium on commercial A356 alloy, little attention has been paid to understand the possible interaction of magnesium and titanium with the modifying efficiency of strontium.

In the light of these aspects, the present study is aimed at investigating the effects of magnesium and titanium on the microstructural evolution of Sr-modified Al-7Si, Al-7Si-0.4Mg and Al-7Si-0.4Mg-0.12Ti alloys. To assess the role of Sr on the eutectic solidification path, the analysis of the cooling curves combined with a quantitative microstructural evaluation of the eutectic silicon particles has been carried out. Thermal analysis results highlight how the alloys that contain magnesium show a significant decrease, higher than 5 °C, of the thermal parameters of the eutectic solidification, with respect to the Al-7Si alloy. On the other hand, titanium seems to have only a slight effect on the same solidification characteristics. Metallographic investigations and the related statistical analysis of some geometrical parameters of the silicon particles indicate that the presence of magnesium and titanium induces a variation of both dimension and morphology of the particles. As a result, these experimental findings suggest that the effect of alloying elements, such as titanium and magnesium, on the thermal parameters obtained from cooling curves has to be taken into consideration when the thermal analysis is used to assess the strontium modification efficiency.

KEYWORDS: AL-SI ALLOYS, SR MODIFICATION, THERMAL ANALYSIS, SI PARTICLES, ELEMENTS INTERACTION

INTRODUCTION

Al-Si alloys pertain to the predominant aluminium alloys used for a huge variety of automotive and aircraft cast components. This is mainly due to their low weight, good castability, low cost and favourable mechanical properties which depend on the microstructure resulting from the solidification process. In this respect, a considerable amount of studies has concerned the improvement of their characteristic by melt inoculation [1,2], by alloying [3] and by tuning the parameters of the heat treatment process [4].

In order to control the solidification behaviour of an alloy, Thermal Analysis (TA) has been proved to be an effective technique for the metal casting industry. This non-destructive and rapid on-line monitoring method enables, in fact, to evaluate the melt quality and to monitor the processing parameters prior to casting. TA can provide information about the degree of grain refinement and modification [5,6], the characteristic temperatures related to the solidification regions of both primary and eutectic phases [7,8] and the intermetallic phases formation [9].

As regards the relationship between the refinement of the eutectic silicon phase and the related changes in the cooling curves, this aspect has been extensively investigated in the literature. The depression of the eutectic growth temperature has been used to assess the modification level of the melt, thus suggesting a correlation between thermal and microstructural parameters of the eutectic phase [10]. By contrast, there is a relative paucity of scientific studies focused on the interaction between modifiers and alloying elements and its effect on TA cooling curves [11,12].

The present study sets out to experimentally investigate the influence of magnesium and titanium on the microstructural evolution of strontium modified Al-7Si, Al-7Si-0.4Mg and Al-

L. Lattanzi, A. Fortini,
M. Giovagnoli, M. Merlin
University of Ferrara, Department of Engineering (DE)
via Saragat 1, I-44122 Ferrara, Italy

7Si-0.4Mg-0.12Ti alloys. The analysis of the cooling curves and their derivatives, examined with a tailored Matlab® code, provides evidence of the role of magnesium and titanium additions. The depression of the eutectic growth temperature has been considered in the light of the microstructural investigations, conducted on the eutectic silicon particles. A comprehensive quantitative image analysis, supported by an extensive statistical approach which concerns the comparison of the distributions of equivalent diameter and roundness of the particles, clarified the mutual effect of the alloying elements.

LITERATURE SURVEY

The control of the microstructure is a key aspect to enhance mechanical properties and casting quality of aluminium alloys. Within this frame, it is well-established that the size and the morphology of the silicon particles can impair the mechanical properties of Al-Si alloys, especially ductility, due to the needle-like structure arising from nucleation and growth of the eutectic phase. As a result, the chemical modification has become a common foundry practice to promote the structural transformation of the silicon particles from a coarse plate-like structure into a fine fibrous one. The modification is commonly performed by the addition of modifying agents in the molten metal to determine changes in the growth kinetics of the eutectic phase. In recent years, strontium has become the most widely used modifying agent thanks to its good modification rate, long fading time, high recovery efficiency and ease of handling [8,13,14]. A great deal of efforts has been made to optimise the modification treatment and many studies have been addressed to investigate the microstructural changes related to strontium additions, modification level assessment and mechanical properties of strontium modified hypoeutectic Al-Si alloys [15,16].

To promote the precipitation of Mg_2Si during the heat treatment and, in turn, improve the mechanical properties of Al-Si foundry alloys, small amounts of magnesium are usually introduced. There is no dearth of experimental studies dedicated to understanding the influence of magnesium on the microstructural evolution and tensile properties of hypoeutectic Al-Si alloys. Some studies have evaluated the effects of magnesium additions on the mechanical behaviour of both unmodified and strontium modified alloys [3,17]. More recently, some studies also investigated the role played by magnesium in influencing the formation of intermetallic compounds [18,19] and the fracture behaviour [20].

Besides the benefits on mechanical properties, it has been suggested that magnesium additions up to 1 wt. % slightly increase the modification level of silicon particles [21]. Furthermore, whether sodium or strontium are not present, magnesium enables a change in morphology, from coarse lamellar to acicular, without achieving a fibrous structure though, and thus shows a weak modifying effect [11,22].

Another way to improve mechanical properties of Al-Si alloys is reducing the primary aluminium grain size. Therefore, the addition of titanium to the melt is a common foundry practice because of its potential grain refining effect [23]. Despite this, some recent works show how titanium actually refines the grains of primary aluminium phase but has no significant effect on Secondary Dendrite Arm Spacing (SDAS), thus it determines only a slight enhancement of the mechanical properties [7]. The presence of titanium also shows some influences on thermal analysis parameters. Xu et al. reported how the addition of titanium, from 0.2 wt. % to 0.8 wt. %, to an A357 alloy causes the rise of primary phase characteristic temperatures and a depression of recalescence [7]. Other works highlight how titanium can also influence the eutectic region of the cooling curve, decreasing the characteristic temperature parameters [24].

For what concerns quantitative microstructural investigations, in the last years the effect of both alloying elements and heat treatment processes have been deepened by image analysis coupled with statistical approaches. In these regards, particular attention has been paid to quantitative image analysis and silicon particle distribution. Alexopoulos et al. found a correlation between silicon particle size and average elongation, concluding that the addition of alloying elements is reflected by variations of size distribution of silicon particles [25]. Tiryakioğlu investigated solution treatments at 540 °C for different treatment durations and evaluated their effect on size and aspect ratio distributions of eutectic silicon. In particular, the reported studies find that the 3-parameter lognormal distribution provides the best fit for both equivalent diameter and aspect ratio [26]. Otherwise, a certain number of studies evaluated the effect of different grain refiners [27], alloying elements [22], combined modifying elements and solidification rate [8,28] simply considering variation in the mean values of characteristic parameters of silicon particles, coupled with their standard deviation. On the other hand, some authors considered the median values of the above-mentioned parameters, because of the large scattering of mean values [10,29]. In the present study, comparisons between Si particles parameters distributions were evaluated considering, as reported by Wilcox [30,31], the differences between the deciles of the distributions, i.e. the values that divide data into ten equal parts so that each part represents 1/10 of the population.

The analysis of the cooling curves has shown to be an effective approach to control and optimise the solidification process and TA is widely used in foundry practice to evaluate the degree of modification of hypoeutectic silicon alloys. In particular, the difference between the eutectic growth temperature of the unmodified and of the modified alloy is widely used to evaluate the modification level [9,10]. Furthermore, other temperature and time-related parameters, e.g. recalescence and duration of the eutectic plateau, have been suggested for the control of silicon modification [8,32,33]. Among the experimental variables and issues that can affect the results (e.g. possibility of comparison with the cooling curve of the unmodified melt, cooling rate variability, melt and crucible temperature stability), the interaction of alloying elements on the solidification path has not been extensively examined so far. Heusler and Schneider [11] performed a systematic investigation by means of cooling curve analysis on the influence of magnesium on the modification efficiency of sodium and strontium in an Al-11%Si alloy. Tahiri et al. [12] explored the influence of the combined addition of grain refiners and strontium on cooling curves and microstructure of the A356 alloy, reporting that the partial reaction between TiB2 and strontium would lead to a partial decrease of the modifying efficiency of strontium.

Despite the fact that the influence of alloying elements on the microstructural and mechanical features of Al-Si alloys it is well-established and TA has been gaining increasing acceptance as an effective melt quality control, few studies have been focused on the effects of chemical composition on cooling curves parameters. In particular, very little attention has been paid to the assessment of the modifying efficiency of strontium via TA with respect to the interaction of the alloying elements [11,34]. In the light of these aspects, this study examines the changes in the eutectic phase solidification of strontium modified alloys arising from magnesium and titanium additions. In an attempt to provide a quantitative evidence of the eutectic phase changes, a combined approach based on cooling curves analysis and quantitative metallographic investigation on eutectic silicon particles has been adopted.

EXPERIMENTAL PROCEDURE

Melt preparation

Three different reference alloys were prepared: Al-7Si, Al-7Si-0.4Mg and Al-7Si-0.4Mg-0.12Ti. For the Al-7Si alloy, primary aluminium ingots were melted in an electric resistance furnace and pure silicon was then added to the bath. For the Al-7Si-0.4Mg alloy, pure magnesium was also added to reach the targeted nominal content of ~ 0.4 wt. %. For the Al-7Si-0.4Mg-0.12Ti, pure magnesium and AlTi10 master alloy rods were added to reach the targeted magnesium and titanium nominal content of ~ 0.4 wt. % and ~ 0.12 wt. %, respectively. All the melts were degassed for 480 s through a rotary degasser supplied with nitrogen inert gas. The chemical composition of the reference alloys, evaluated with Optical Emission Spectrometer (OES) analysis, is reported in Tab. 1.

The melts were then transferred to a heated ladle and kept at a temperature of 735 ± 15 °C. After the melt transfer, AlSr15 master alloy rods were added to obtain the targeted strontium content of 100 ppm. The actual strontium contents, measured with the OES, are equal to 103 ppm, 96 ppm and 100 ppm for the alloys Al-7Si, Al-7Si-0.4Mg and Al-7Si-0.4Mg-0.12Ti, respectively.

Tab. 1 – Chemical composition [wt. %] of the reference alloys

Alloy	Si	Mg	Ti	Fe	Cu	Mn	Zn	Ni	Al
Al-7Si	6.86	0.01	0.009	0.10	0.0011	0.0014	0.0010	0.0031	Bal.
Al-7Si-0.4Mg	7.16	0.37	0.012	0.11	0.0015	0.0019	0.0020	0.0026	Bal.
Al-7Si-0.4Mg-0.12Ti	7.17	0.38	0.123	0.12	0.0016	0.0020	0.0017	0.0029	Bal.

Thermal analysis

Thermal parameters of the modified alloys were evaluated by pouring the melts into a pre-heated steel cup (40 mm height, 47 mm upper diameter and 30 mm lower diameter). Cooling curves were recorded for all the samples by means of a mineral insulated K-type thermocouple (1.5 mm diameter) located in the centre of the cup, 15 mm far from the bottom. The same thermocouple was used for all tests: it was placed inside a stainless-steel sheath and then removed from solidified samples. This procedure enables a good comparison of the results obtained for each alloy. Temperature and time data were recorded at a frequency of 20 Hz by a data acquisition system (Pico Technology TC-08 Thermocouple Data Logger) linked to a personal computer, and the acquisition stopped when a temperature of 400 °C was reached during cooling.

Cooling curves and their derivatives were processed by means of a tailored Matlab® code. Experimental data processing comprised smoothing, curve fitting and plotting of the first derivative curve for the determination of the characteristic solidification temperatures. The cooling rate (CR) was evaluated in the liquid region prior to the nucleation of α-Al primary phase, in the temperature range 630 - 645 °C. The main solidification parameters of the Al-Si eutectic phase were determined, i.e. minimum temperature T_{min}, and growth temperature T_G. As displayed in Fig. 1, T_{min} is the minimum temperature prior to recalescence, T_G is the maximum temperature after T_{min} and the recalescence undercooling is defined as $\Delta T_E = T_G - T_{min}$.

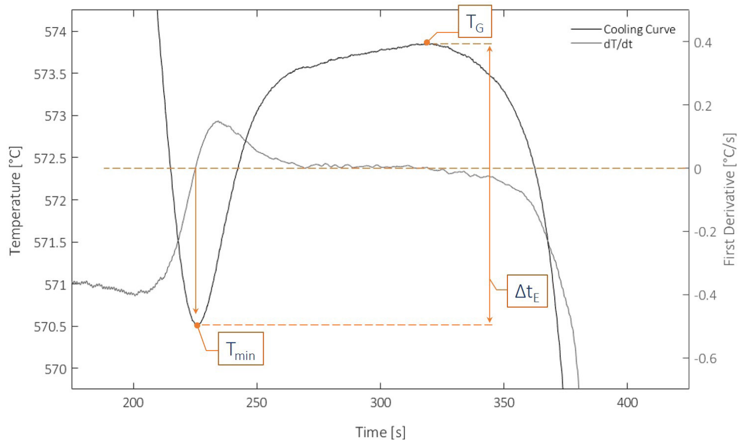


Fig. 1 – Eutectic solidification region of a cooling curve and its first derivative and related thermal parameters

ΔT_G was calculated as the difference between the growth temperature of the unmodified reference alloy ($T_{G,0}$) and the growth temperature of the alloys modified with 100 ppm of strontium. $T_{G'0}$ of the unmodified alloy was estimated by Eq. 1, proposed by Apelian et al. [35], that considers the effect of alloying elements on the eutectic growth temperature. The $T_{G,0}$ values of the reference alloys, evaluated by Eq. 1 using the chemical compositions reported in Tab. 1, are showed in Tab. 2.

$$T_{G,0} = 577 - [12.5/(\text{Si wt.\%})]*[4.43*(\text{Mg wt. \%}) + 1.43*(\text{Fe wt. \%}) + 1.93*(\text{Cu wt. \%}) + 1.7*(\text{Zn wt. \%}) + 3*(\text{Mn wt. \%}) + 4*(\text{Ni wt. \%})] \quad (1)$$

Tab. 2 – Eutectic growth temperature of the reference alloys calculated by Eq. 1

Alloy	Al-7Si	Al-7Si-0.4Mg	Al-7Si-0.4Mg-0.12Ti
$T_{G,0}$ [°C]	576.6	573.8	573.8

It has been extensively reported in the literature that the depression in eutectic growth temperature is closely linked to the Sr content in the alloy and several studies have investigated the influence of strontium content on ΔT_G [8-10, 36].

Image analysis and statistical evaluation

Samples from TA were sectioned transversely to the axis of the thermocouple and prepared using standard metallographic procedures. Quantitative Image Analysis (IA) was performed by means of a Leica DMi8 A optical microscope, equipped with Leica Application Suite 4.9 image analysis software. The investigated area was a square of 4 mm² chosen close to the centre of the sample surface (i.e. close to the tip of the thermocouple) and included enough silicon particles to be representative of the entire sample. Indeed, in accordance with the BS ISO 13322-1:2014, a preliminary study was conducted to determine the minimum number of particles to investigate. The analysis of 400 micrographs enabled to trustworthy identify the distribution of geometrical parameters for the entire population. The minimum number of particles needed was calculated according to Eq. 2:

$$n^* = \alpha^2 u^2 s^2 (2 \cdot (\beta + 0.5 \cdot \alpha)^2 s^2 + 1) \cdot \delta^{-2} \quad (2)$$

where α and β are constants defined from the geometrical parameter to be measured, *s* is the standard deviation of the population geometrical parameter, δ is the % relative error (fixed to 5 %), u is an intermediate parameter of 1.96 for a given probability of 95 %. The resulting n* of 3000 particles ensures a negligible variability of geometrical features of Si particles. To ensure the suitability of the employed optical magnification and the sufficient number of pixel for the smallest particle to be measured, a minimum threshold of 15 pixels was fixed within the IA software in order to obtain the required accuracy of measurement. In the present study, 5 composite images were considered for each specimen. Each composite image was made up of 25 micrographs, taken at a magnification of 500 ×, and comprised an investigation area of about 1920000 mm^2. The described method ensured the analysis of a suitable number of particles, i.e. comprised within the range of 6000 - 10000 particles. Equivalent Diameter ($ED = (4A/\pi^{0.5})$) and Roundness ($R = A\pi/4p^2$) of eutectic silicon particles were statistically analysed by means of a customised Matlab® code. In particular, distribution fitting was performed on ED and R of eutectic silicon particles and the 3-parameters lognormal distribution resulted to be the best fit to the experimental data, since it was the distribution with the lowest Anderson-Darling statistic (AD) value.

Usually, the effect of different chemical compositions on the eutectic microstructure of Al-Si alloys is evaluated by comparing the mean values of some geometrical and morphological parameters of Si particles and considering the standard deviation of data, for example by a Student's t-test. However, it is worth noting that a simple comparison of means would be poorly efficient with distributions that exhibit a similar central tendency and, in general, it would not be able to catch modification of spread and shape of distribution due to 'treatment' effect. For these reasons, comparisons between distributions of silicon particle parameters were evaluated considering the differences of deciles of the distributions themselves, according to the work of Wilcox [30,31]. Deciles were calculated using the Harrell-Davis (HD) quantile estimator [37], which is the weighted average of all the order statistics (Eq. 3):

$$Q_P = \sum_{i=1}^{n} W_{n,i} X_{(i)} \qquad (3)$$

where $X_{(i)}$ is the *i*-th order statistic of the sample and $W_{n,i}$ is the weighting function of the i-th term and it derives from a beta cumulative distribution function. The HD estimator enables, in combination with a bootstrap estimation of the standard error of deciles, to derive the confidence intervals of the difference between deciles of two groups. The bootstrap estimation is a resampling method that relies on random sampling with replacement from an approximating distribution. The confidence level for hypothesis testing to evaluate if decile differences are statistically significant was fixed to 95 %. Multiple comparisons were necessary to perform a set of statistical inferences simultaneously, one for each decile. Nevertheless, when performing multiple comparisons, the probability of incorrect rejection increases with increasing number of comparisons. Thus, the method used to evaluate the rate of Type I errors in null hypothesis testing, when conducting multiple comparisons, was the False Discovery Rate (FDR) and it was controlled by the Benjamini-Hochberg procedure [38]. This procedure controls the FDR so that the confidence level could be maintained around 5 % across the nine confidence intervals.

RESULTS AND DISCUSSION

TA curves and parameters

Figure 2 compares the cooling curves, restricted to the Al-Si eutectic formation, of the investigated alloys with a strontium content of 100 ppm. The horizontal lines at 576.6 °C and 573.8 °C represent the $T_{G',0}$ evaluated by Eq. 1, as reported in Tab. 2. It can be observed in Fig. 2 that in the Al-7Si alloy strontium determines a decrease of the eutectic T_G of about 2.8 °C. What stands out in Fig. 2 is that the addition of magnesium leads to a significant decrease of both minimum and growth temperatures during the Al-Si eutectic solidification, of about 8 °C. The presence of titanium seems to have a slightly similar effect on the cooling curve since it determines a further slight decrease of T_{min}. What can be concluded from these cooling curves is that magnesium and titanium additions appear to not produce an adverse effect on the strontium modification performance since they do not determine a rise of both minimum and growth temperatures of the eutectic solidification.

Table 3 reports the principal thermal parameters of the eutectic solidification in the strontium modified investigated alloys. From the data, it can be seen that the depression of TG related to the presence of magnesium and titanium, also depicted in Fig. 2, is reflected in increased values of ΔT_G for the Al-7Si-0.4Mg and Al-7Si-0.4Mg-0.12Ti alloys. The Al-7Si alloy modified with 100 ppm of strontium displays a ΔT_G of 2.8 °C, whilst the alloys containing magnesium and titanium show a significantly higher ΔT_G, of about 7.8 °C. Changes in the recalescence undercooling, defined as $\Delta T_E = T_G - T_{min}$, also occur, since the alloying elements seem to have an influence also on T_{min}. As illustrated in Tab. 3, for the Al-7Si alloy ΔT_E has a value of about 3.2 °C but it decreases to 2-2.3 °C in presence of magnesium and of both magnesium and titanium.

ΔT_G has been often used as an index to be correlated with the modification level [9,10,39]. In fact, it has been reported that modifying agents like sodium and strontium increase twinning density of eutectic silicon and thus allow silicon itself to branch more easily and to form fibrous particles rather than flakes or lamellae [40].

At the same time, strontium addition seems to deactivate some favourable sites for the nucleation of eutectic phase, typically AlP nuclei, which are located at the tips of primary aluminium dendrites or in the interdendritic space [40-42]. Therefore, eutectic cells require a higher degree of undercooling to nucleate, and this leads to the depression of both nucleation and growth eutectic temperatures [40,42]. These considerations clarify the common use of ΔT_G as an indicator of strontium modification efficiency.

Figures 3a, 3b and 3c depict the microstructures of the three reference alloys modified with 100 ppm of strontium. Comparing the three microstructures, it can be observed that strontium addition to Al-7Si alloy (Fig. 3a) determines a fully modified eutectic morphology, with fine silicon particles. For what concerns the Al-7Si-0.4Mg (Fig. 3b), the simultaneous presence of magnesium and strontium leads to a partially modified eutectic structure, characterised by regions with coarse silicon particles and other regions with silicon particles that show a fine morphology. The titanium presence in the Al-7Si-0.4Mg-0.12Ti (Fig. 3c) does not determine a significant variation of the microstructure already observed in the alloy with sole magnesium.

It has been reported that an increase of ΔT_G is a representative index of the goodness of the strontium modification treatment. For this reason, one could be induced to conclude, from the cooling curves displayed in Fig. 2 and data showed in Tab. 3, that magnesium additions determine a better modification than the one obtained with strontium. Nevertheless, this could be a misled observation, because it does not take into account the effect of every single alloying element on the cooling curves. In fact, previous studies [11,22,24] reported that the effect of alloying elements on the eutectic temperatures has to be considered when the thermal analysis is used to assess and control the efficiency of a modification treatment. Heusler and Schneider [11] affirmed that the effect of magnesium content is difficult to determine and it cannot be easily correlated with the observed microstructure in an Al-7Si alloy. A similar conclusion is reported by Joenoes and Gruzleski [22], who found that magnesium reduces the degree of microstructure homogeneity despite it determines a decrease of eutectic minimum and growth temperatures. Magnesium alone neither clearly refines nor coarsens eutectic silicon particles in an Al-7Si alloy. Furthermore, magnesium has a negative effect on strontium modification since it changes the eutectic morphology from a fully modified to a partially modified one. For what concerns titanium, Golbahar et al. [24] reported that eutectic growth temperature in a strontium modified A356 alloy is decreased due to titanium additions and thus it does not affect the strontium modification performance.

According to the above-reported observations, the effect of alloying elements on both cooling curves and microstructural features cannot be overlooked. In an attempt to further investigate and provide a quantitative evaluation of the role played by alloying elements on microstructure, a detailed analysis of silicon particle geometrical parameters has been carried out.

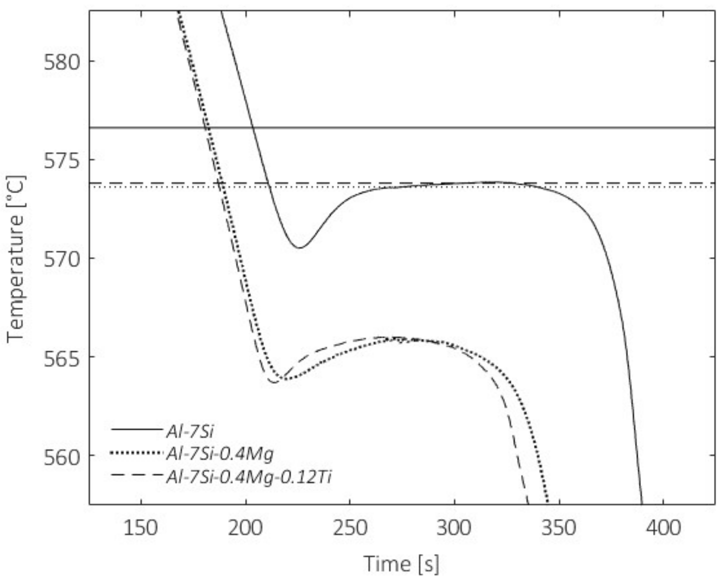


Fig. 2 – Cooling curves, restricted to the eutectic solidification region, of the investigated alloys modified with 100 ppm of strontium. The horizontal lines represent the $T_{G,0}$ values related to each alloy

Tab. 3 – Eutectic thermal parameters [°C] of the alloys modified with 100 ppm of strontium

Alloy	T_{min}	T_G	$\Delta T_E = T_G - T_{min}$	$\Delta T_G = T_{G,0} - T_G$
Al-7Si	570.5	573.8	3.3	2.8
Al-7Si-0.4Mg	563.9	566.0	2.1	7.8
Al-7Si-0.4Mg-0.12Ti	563.7	566.0	2.3	7.7

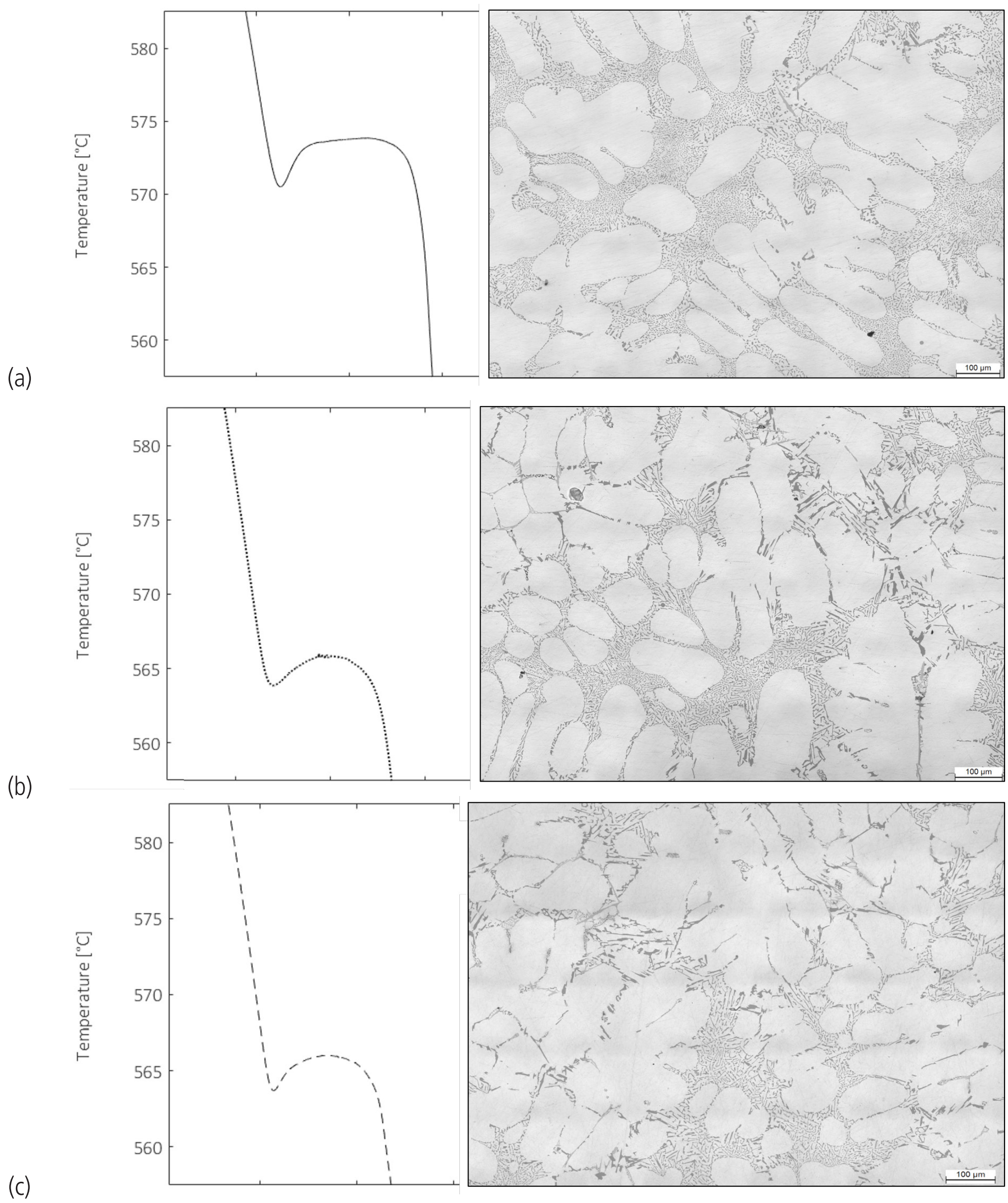


Fig. 3 – Comparison of microstructures of the three different alloys with 100 ppm of strontium: a) Al-7Si; b) Al-7Si-0.4Mg; c) Al-7Si-0.4Mg-0.12Ti

Silicon particles

Figure 4a represents the 3-parameters log-normal distributions related to the dimensional parameter Equivalent Diameter of eutectic silicon particles, for the investigated alloys, with the addition of 100 ppm of strontium. It can be observed that all distributions are located in a range of very small values of equivalent diameter. In addition, the peak of the curves, that corresponds to the maximum probability density of the selected parameter, is always located in the range between 2 ÷ 3 μm. These observations seem to be in line with the fact that addition of 100 ppm of strontium induces a good degree of modification for all the analysed alloys and thus reduces silicon particle dimension. Nevertheless, the distribution related to the binary Al-7Si alloy clearly shows a higher peak and, consequently, a lower right tail when compared to the other distributions. The presence of magnesium leads to a decrease of the maximum value of the distribution and an increase of the right tail. Further, the addition of titanium seems to enhance this effect. These qualitative observations suggest that the presence of both magnesium and titanium induces some modification on the dimension of eutectic silicon particles.

Figure 4b illustrates the quantitative comparison between the distributions depicted in Fig. 4a. The trend with solid circles shows the differences between the deciles of the distribution related to Al-7Si-0.4Mg alloys with respect to the deciles of the distribution related to Al-7Si alloy, assumed as the reference. Likewise, the trend with solid squares represents the same differences related to Al-7Si-0.4Mg-0.12Ti alloy. These values are plotted as a function of Al-7Si alloy deciles.

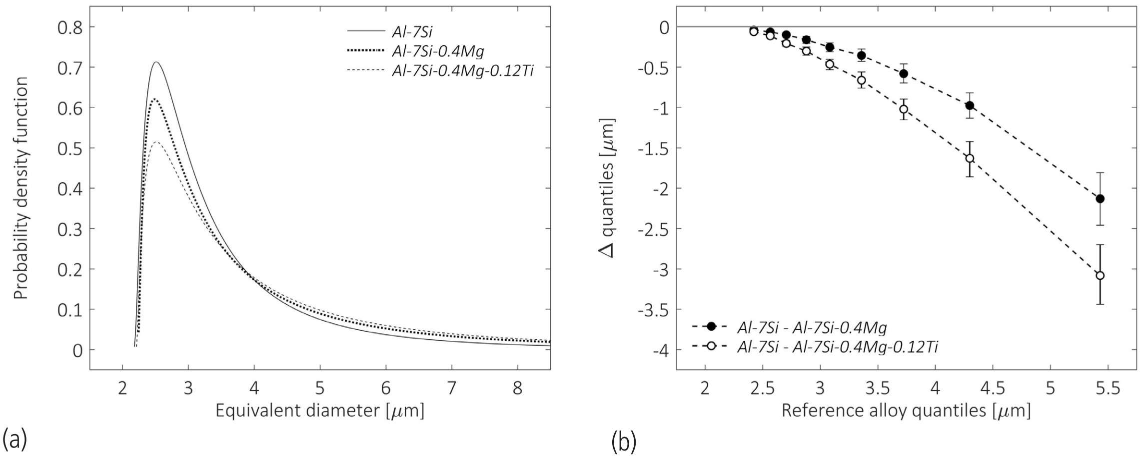
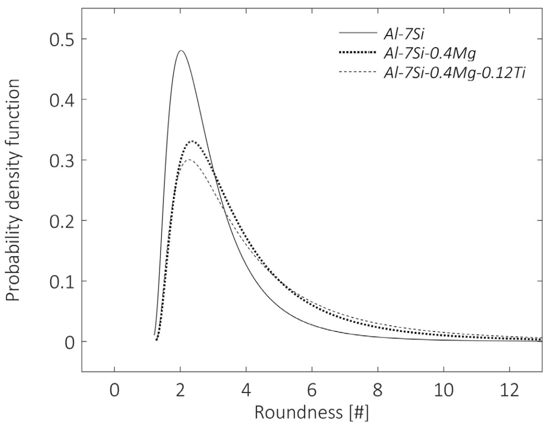


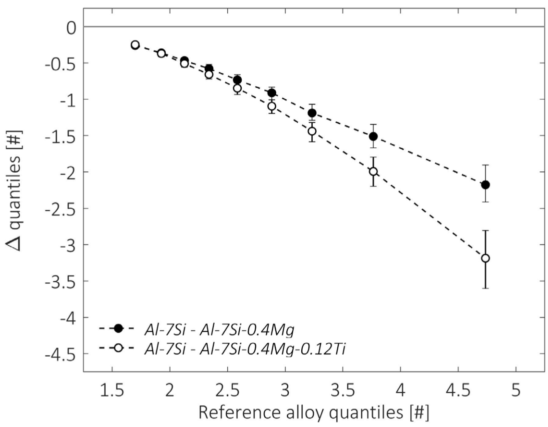
Fig. 4 – a) Distributions of equivalent diameter for the alloys with 100 ppm of Sr; b) Comparison of distributions, Al-7Si taken as reference alloy

It is noteworthy to observe that differences are negative for both the represented curves. This means that all deciles for alloys with sole magnesium and with both magnesium and titanium additions are shifted toward slightly higher values of equivalent diameters, with respect to the binary alloy. Furthermore, the reported trends reveal that each decile difference is statistically significant, as it can be observed in Fig. 4b, since neither of the confidence intervals overlaps the zero line. It is worth to note that the differences of first deciles, although statistically significant, are very close to zero for both the represented trends. Instead, the absolute value of the differences increases to 2 ÷ 3 μm for the last deciles. This increasing trend is directly linked to the modification of the distribution spread and, in particular, it explains the decreased distribution peak and the increased size of the right tail observed with the addition on magnesium and titanium to the binary alloy. The quasi-zero values of the first decile differences in Fig. 4b reflect the fact that the probability of finding particles with a small size (2 - 2.5 μm, corresponding to first deciles values) in the microstructure is quite the same for the three investigated alloys. This observation is in line with the knowledge reported in the literature that an amount of 100 ppm of strontium is enough to achieve a good degree of modification of silicon particles [8]. On the other hand, the increased value of last deciles suggests that there is a higher probability of finding also particles with a larger size in the alloy containing sole magnesium and even more in the alloy containing both magnesium and titanium, with respect to the binary Al-7Si alloy. As a result, a loss of microstructure homogeneity, depicted in the microstructures of Fig. 3a, 3b and 3c and reported in the literature [22], can be related to a decreased efficiency of the strontium modification treatment.

Since strontium modification induces a variation not only on the size of the silicon particles but also on their morphology, a single geometrical parameter is not sufficient to understand its overall effect. Thus, the dimensionless parameter Roundness has been also evaluated. The 3-parameters log-normal distributions for the roundness of the analysed alloys are reported in Fig. 5a. Similarly to Fig. 4a, it shows that the distribution related to the binary Al-7Si alloy appears to be again the one characterised by the maximum value of probability density and the minimum spread, whilst the other distributions exhibit a larger dispersion of data and a taller right tail. Figure 5b reports the comparison between decile differences for the alloy with magnesium and titanium addition with respect to the base Al-7Si alloy.



(a)



(b)

Fig. 5 – a) Distributions of roundness for the alloys with 100 ppm of Sr; b) Comparison of distributions, Al-7Si taken as reference alloy

As previously observed for equivalent diameter, the higher differences are related to the last deciles, whilst for the first deciles differences are close to the zero line. These results suggest that, despite no confidence interval intersects the zero line, there are only slight differences between first deciles. In other words, a large number of particles with low Roundness, i.e. with a shape similar to the circular one, is present in all three alloys. Nevertheless, the addition of magnesium causes the distribution to become flatter and the right tail of the distribution to become taller. Therefore, considering its effect on microstructures showed in Fig. 3a, 3b and 3c, magnesium increases the number of silicon particles which exhibit high roundness values and thus reduces the modification efficiency of strontium, causing the retention of a lamellar silicon structure rather than the formation of a fibrous one. A slightly further deterioration of the eutectic silicon modification level is achieved with the addition of titanium to the alloy with magnesium.

The poisoning effect of magnesium on the strontium modification treatment is in good agreement with literature. Some authors [22] reported that magnesium additions to an Al-7Si alloy cause the eutectic silicon morphology to become progressively less modified, as the magnesium content increases. The result is an increased value of geometrical and morphological parameters, i.e. perimeter and aspect ratio respectively, in comparison with the alloy without magnesium. Furthermore, the final microstructure is characterised by a mixture of fibrous, lamellar and acicular silicon particles. This loss of homogeneity of eutectic silicon morphology is linked to higher values of standard deviation for silicon particles descriptors parameters. The same authors suggest that a possible explanation for this poisoning effect is the reaction of magnesium with strontium that leads to the formation of a complex intermetallic compound, with formula $Mg_2Sr(Si_3Al_4)$. The formation of this intermetallic compound, which occurs at a temperature higher than the eutectic one, reduces the total amount of strontium available for the eutectic silicon modification.

In summary, these statistical outcomes are consistent with the observations arisen from the microstructural investigation, showing that magnesium and titanium affect the efficiency of the strontium modification treatment.

CONCLUSIVE OBSERVATIONS

The present study was carried out with the aim of deepening the interaction between magnesium and titanium, the main alloying elements of Al-7Si alloy, and strontium, one of the most commonly employed modifying agents. According to the experimental findings, the following conclusions can be drawn:

- Cooling curves related to the investigated alloys, i.e. Al-7Si, Al-7Si-0.4Mg and Al-7Si-0.4Mg-0.12Ti, modified with 100 ppm of strontium revealed that magnesium determines a substantial decrease of both T_{min} and T_G of the eutectic solidification. Furthermore, titanium addition also seems to have a slightly similar effect on the eutectic temperatures.
- Microstructural observations showed that strontium determines a fine and fibrous morphology of eutectic silicon particles and thus a fully modified microstructure. The presence of magnesium leads to a partially modified eutectic structure and, further, titanium does not determine a significant variation of the microstructure already observed in the alloy with sole magnesium.
- Statistical analysis of geometrical parameters of the eutectic silicon particles, i.e. Equivalent Diameter and Roundness, indicated that in both cases data were fitted with a 3-parameters log-normal distribution. The binary Al-7Si alloy shows the higher peak in comparison with the other alloys. The comparison of distributions, performed by quantiles comparison, revealed

that the presence of magnesium leads to a decrease of the maximum values of the distribution and the further addition of titanium seems to enhance this effect. These results show that the presence of both magnesium and titanium induces a variation of the dimension of eutectic silicon particles.
In summary, these results could suggest that the ΔT_G parameter should be used cautiously for the assessment of the modification level when comparing different alloys, since each alloying element could have a certain influence on its numerical value and thus could conduce to a misled interpretation of the efficiency of the modification treatment. Nevertheless, thermal analysis is a valuable on-line instrument to control liquid alloy treatments, forasmuch as microstructural evaluation is operator dependent and requires time-consuming preparation techniques. For this reason, it is important to improve the reliability of thermal analysis technique and it would be helpful to develop a reference database of thermal parameters, established from a large number of experimental investigations on melts with different alloying elements. In this way, the effect of each alloying element on cooling curves could be then easily tracked and a better correlation between thermal parameters and modification efficiency could be obtained.

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