



Examination of the Eutectic Modifying Effect of Sr on an Al-Si-Mg-Cu Alloy Using Various Technological Parameters

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Abstract

With the aid of eutectic modification treatment, the precipitation of coarse lamellar eutectic silicon can be suspended during the solidification of aluminum-silicon alloys, thereby the formation of fine-grained, fibrous eutectic Si can be promoted by the addition of small amounts of modifying elements, such as Sr, to the liquid alloy. The effectiveness of this technique is, however, highly dependent on many technological factors, and the degree of modification can be lowered during the various stages of melt preparation due to the oxidation of the Sr-content of the melt. During our research, we investigated the effect of rotary degassing melt treatments coupled with the addition of three different fluxes on the degree of modification of an Al-Si-Mg-Cu casting alloy. It was also studied, that whether additional Sr alloying made before and during the melt treatments can compensate the Sr fading with time. The degree of eutectic modification was characterized by thermal analysis (TA) and the microscopic investigation of TA specimens. It was found, that by using one of the three fluxes, and by adding Sr master alloy rods before the melt treatments, better modification levels could be achieved. It was also found that the measurement of Sr-concentration by optical emission spectroscopy alone cannot be used for controlling the level of eutectic modification.

Keywords: Solidification process, Aluminum alloy, Strontium, Modification, Thermal analysis

1. Introduction

Aluminum-silicon casting alloys are extensively used in the automotive and aerospace industries for their high specific strength, excellent fluidity, good corrosion resistance and machinability [1–3]. Most commercial Al-Si alloys are hypoeutectics whose microstructure consists of primary α -Al dendrites surrounded by a eutectic phase, that contains eutectic Si particles embedded in an Al matrix [4]. The mechanical properties of these alloys are highly dependent on the size and morphology of the eutectic Si particles [5]. The structure of the Si phase can be

controlled by the addition of certain modifier elements such as Na [6], Sr [7–9], Sb [10, 11], Ca [12], Ba [12], Ce [13], La [13], Y [12], Yb [12], and by controlling the cooling rate during the solidification of the alloy [14, 15]. The addition of the mentioned elements can result in the formation of a finer lamellar or fibrous eutectic network instead of the coarse flake-like morphology of the unmodified alloy.

Nowadays, the most widely used eutectic modifier element is Sr, which can be easily added via different forms of master alloys, its loss to oxidation is relatively slow, and its application does not have such health risks as the use of Sb [5]. Despite its fading is much slower, than that of Na, Sr is a rather reactive element that

can easily form oxides or intermetallic compounds with the alloying elements of the alloy [16, 17]. In fact, in the presence of Sr, some parts of the oxide layer on the surface of the melt and the entrained oxide films inside the molten alloy gradually transform into Sr-containing oxides [18, 19]. Due to the formation of Sr-containing compounds, with time, the modifying effect on the eutectic Si is lost [20].

It is a common foundry practice, that the alloy which is used as a charge material is already alloyed with Sr by the alloy manufacturer, thus no or only minimal alloying is needed for the adjustment of the Sr-concentration, which is usually measured with optical emission spectroscopy. After melting, to remove solute hydrogen and inclusions from the melt, these liquid alloys are commonly subjected to rotary degassing and fluxing treatments. Some aspects of this practice, however, could be questioned. According to Sigworth [5], nor fluxes or reactive gases should be employed during the treatment of Sr-modified melts, as these cause accelerated Sr-loss (“burn-out”). Gyarmati et al. [21] found that the application of certain fluxes, especially those which contain a significant amount of oxidizing compounds results in a remarkable reduction of the modification rate of the eutectic Si phase. In the practice, the accelerated Sr fading caused by the melt treatments is commonly compensated with additional Sr alloying. To the authors' best knowledge, this phenomenon and the possible solutions for the consequent problems in maintaining the modifying effect of Sr are, however, had not been addressed by any other research available in the literature. Therefore, this research work aims to provide more information about the effect of different fluxes on the modifying effect of Sr. It was also investigated, that how efficiently the Sr-loss can be compensated by additional Sr alloying in the case of Al-10%Sr master alloy rod additions made before and during the melt treatments.

2. Experimental

In our research, rotary degassing melt treatments with N₂ purging gas and automatical flux dosing were carried out on an AlSi7MgCu0.5 (EN AC-45500) alloy using three different commercially available fluxes (A, B and C). The compositional ranges of the alloy are given in Table 1.

Table 1.
Chemical composition of the alloy used for the experiments (wt%)

Si	Fe	Cu	Mn	Mg	Ti	Sr
6.5 -	< 0.2	0.45 -	< 0.1	0.36 -	< 0.2	0.017 -
7.5		0.58		0.45		0.030

The melting of the alloy was conducted in a stack smelter. After melting, the liquid metal was transported by a transport ladle to a resistance heated holding furnace where the melt treatments were performed. In each cycle, 400 g of flux was added to the melt. The treatment parameters were the same in each case. Each flux was used in 6 treatment cycles. The N₂ gas flow rate was 20 L/min; the rotor rotational speed was 500 RPM during vortex formation and 250 RPM in the degassing phase. The treatment time was 10 minutes in each case. The molten metal temperature in the holding furnace was maintained between

725 °C and 750 °C. To improve the modification of the eutectic Si phase and to compensate for the Sr-loss during the process, Al-10%Sr master alloy rods were added to the molten alloy. For each flux, in the case of 3 treatment cycles, the master alloy additions were carried out immediately before the treatment, while during 3 additional cycles, the master alloy rods were added 9 minutes after the treatments had been started (as it is illustrated in Fig. 1.). The quantity of the treated melt in each cycle was approx. 1000 kg. The 9th minute of the treatment was chosen because 9 minutes is a sufficiently long time for effective degassing, while after the addition of the master alloy, a further mixing can take place to ensure homogeneous distribution of the Sr in the melt. Depending on the initial chemical composition of the melt, which was determined with optical emission spectroscopy, 2 or 3 Al-10% Sr master alloy rods weighing app. 200 g were added to the melt, to increase the Sr content of the alloy within the range of Sr-concentrations given in Table 1. A 15 minute long resting time followed each melt treatment.

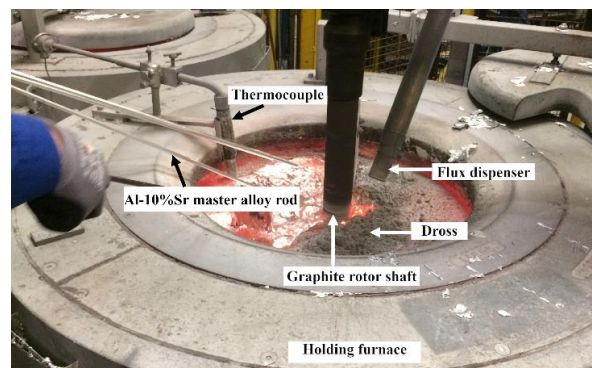


Fig. 1. Master alloy addition during melt treatment

Fig. 2. shows the stereomicroscopic images of the fluxes used during our experiments. It can be seen that flux A and B are granular, while C is a fine-grained powder-like flux. The chemical composition of the three fluxes was determined with a Rigaku MiniFlexII, Desktop X-ray Diffractometer.

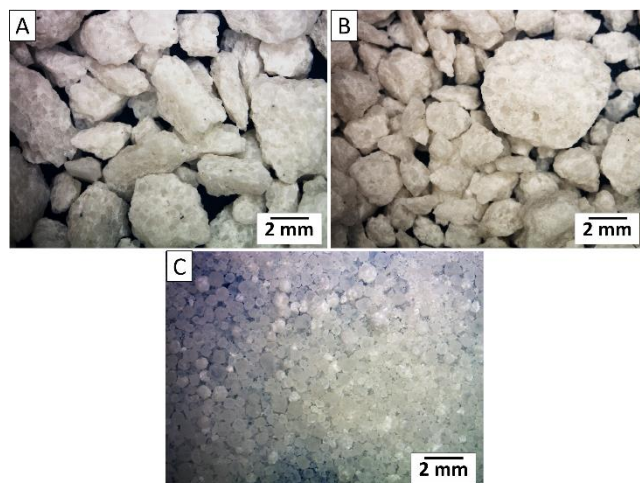


Fig. 2. Stereomicroscopic images of the fluxes at 6.5x magnification

To quantify the efficiency of the compensation of the Sr-loss during the treatments by the addition of master alloy rods, a so-called Sr-utilization parameter (Sr_{util}) had been evaluated by the following equation:

$$Sr_{util} = \frac{Sr_{diff}}{Sr_{added}} \cdot 100 \quad (1)$$

where Sr_{util} is the degree of compensation of the Sr-loss by additional alloying [%], Sr_{added} is the quantity of Sr added with the alloying rods [ppm] and Sr_{diff} is the difference between the Sr-concentration of the melt evaluated before (Sr_{start}) and after the treatment and after the 15-minute long resting period (Sr_{finish}) [ppm]:

$$Sr_{diff} = Sr_{finish} - Sr_{start} \quad (2)$$

During the different sampling stages, the Sr-concentration of the melt was evaluated with optical emission spectroscopy of separately cast test pieces.

The main drawback of Sr level determination with optical emission spectroscopy is, that the results do not give information about the form of the Sr in the melt. As a result of Sr fading, Sr can be present in the form of such compounds that do not participate in the eutectic modification process. However, with the aid of thermal analysis, the quantity of "active" Sr which causes eutectic modification can be easily evaluated [5]. The eutectic growth temperature ($T_{E,G}^{Al-Si}$ [°C]) which can be determined from the cooling curve and its first derivative with respect to time (Fig. 3.), provides adequate information about the eutectic modification level of the alloy. As a result of Sr addition, the solidification of the Al-Si eutectic phase begins at a lower temperature with larger undercooling. As a consequence, the eutectic nucleation temperature (T_{NUC}^{Al-Si} [°C]) and the eutectic growth temperature ($T_{E,G}^{Al-Si}$ [°C]) is lowered. The difference between the eutectic growth temperature of an unmodified and a modified alloy ($\Delta T_{E,G}^{Al-Si}$ [°C]) is directly related to the eutectic modification level of the given alloy [20, 22].

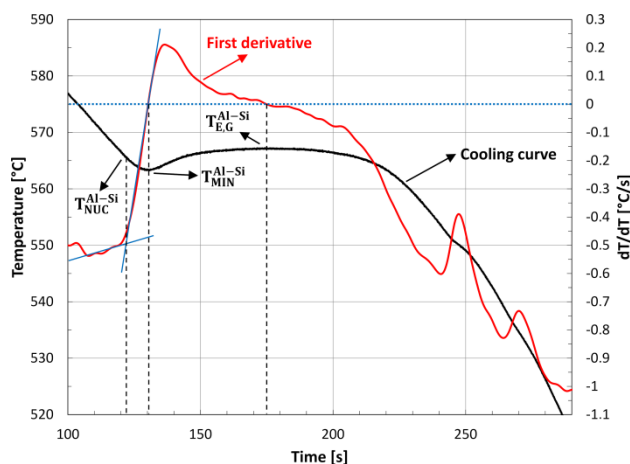


Fig. 3. The determination of $T_{E,G}^{Al-Si}$ using the cooling curve and its first derivative

During the experiments, thermal analysis tests were executed before and after the melt treatments, following the resting period, as well as approximately 1 hour after the treatments, when the majority of the melt (about 800 kg) had been taken to casting and only a lesser quantity of melt remained in the crucible. The samples were taken by pouring the aluminum melt into a cylindrical steel cup (40 mm in diameter, 40 mm deep), equipped with a K-type thermocouple (Ni-Cr-Ni), which was protected by a stainless steel sheath. The thermal analysis test cup was preheated to 200 °C. The average weight of the TA test samples was 110 ± 10 g. The data for thermal analysis were collected by a data acquisition system linked to a personal computer. The temperatures between 700 °C and 400 °C were recorded for all the experiments. The change in eutectic growth temperature ($\Delta T_{E,G}^{Al-Si}$ [°C]) was calculated using Eq. 3:

$$\Delta T_{E,G}^{Al-Si} = T_{E,G,Unmodified}^{Al-Si} - T_{E,G,Modified}^{Al-Si} \quad (3)$$

where $T_{E,G,Modified}^{Al-Si}$ [°C] is the eutectic growth temperature of the modified alloy determined from the cooling curve and its first derivative, $T_{E,G,Unmodified}^{Al-Si}$ [°C] is the eutectic growth temperature of the unmodified alloy determined from the chemical composition of the alloy using the following equation [9, 20]:

$$T_{E,G,Unmodified}^{Al-Si} = 577 - \frac{12.5}{Si} (4.43Mg + 1.43Fe + 1.93Cu + 1.7Zn + 3.0Mn + 4.0Ni) \quad (4)$$

where Si, Mg, Fe, Cu, Zn, Mn, and Ni are the concentration of the indicated elements in weight percent. The effect of melt treatments on the eutectic modification level was evaluated by the comparison of the changes in the values of $\Delta T_{E,G}^{Al-Si}$ caused by melt treatments with different fluxes:

$$\Delta T_{E,G,Change}^{Al-Si} = \Delta T_{E,G,2}^{Al-Si} - \Delta T_{E,G,1}^{Al-Si} \quad (5)$$

where $\Delta T_{E,G,Change}^{Al-Si}$ [°C] is the change in $\Delta T_{E,G}^{Al-Si}$ values caused by the melt treatment, $\Delta T_{E,G,2}^{Al-Si}$ [°C] and $\Delta T_{E,G,1}^{Al-Si}$ [°C] are the $\Delta T_{E,G}^{Al-Si}$ values determined after and before the melt treatment, respectively.

Representative samples were extracted from the TA specimens and were ground with SiC grinding paper with grit sizes of 80, 120, 240, 320, 500, 800, and 1200. Then, the samples were polished with 3 μm polishing slurry and 1 μm polishing paste. After cleaning with distilled water and ethanol, the surfaces of the sectioned samples were examined with a light microscope, and micrographs were taken at a magnification of 100X.

3. Results and discussion

The compounds identified during the X-ray powder diffraction of the fluxes are listed in Table 2. Based on the results, the chemical composition of fluxes A and B are similar, as they both contain NaCl, Na₂SO₄, and CaF₂. Besides that, flux B also has KCl which is frequently used together with NaCl as a carrier material, because they form a eutectic with a relatively low

eutectic temperature of 657 °C [23], which provides low melting temperature to the mixture. In all fluxes, CaF₂ is used as a surfactant, which can alter interfacial energies between the inclusions, the molten flux, and the liquid alloy. Besides CaF₂, flux C also contains K₂SiF₆ which can dissolve Al₂O₃ and in this way, can remove oxide inclusions from the melt [24, 25]. Na₂SO₄ serves as an oxidizing agent in the fluxes, as Na₂SO₄ reacts with molten Al in an exothermic reaction [26]. Flux C also contains a rather complex compound whose function cannot be identified based on the literature. It is important to notice, that each flux contains oxygen-bearing compounds, which act as oxidizing agents and in this way, they can cause accelerated Sr-fading [21].

Table 2.
Components of the fluxes

Flux	Identified compounds
A	NaCl, Na ₂ SO ₄ , CaF ₂
B	KCl, NaCl, Na ₂ SO ₄ , CaF ₂
C	KCl, K ₂ SiF ₆ , CaF ₂ , Ca ₃ Al ₂ Si ₃ O ₁₂ , Li _{3,85} Na _{4,15} (AlSi ₄) ₆ Cl ₂

Fig 4. presents the results of Sr-content evaluation by optical emission spectroscopy.

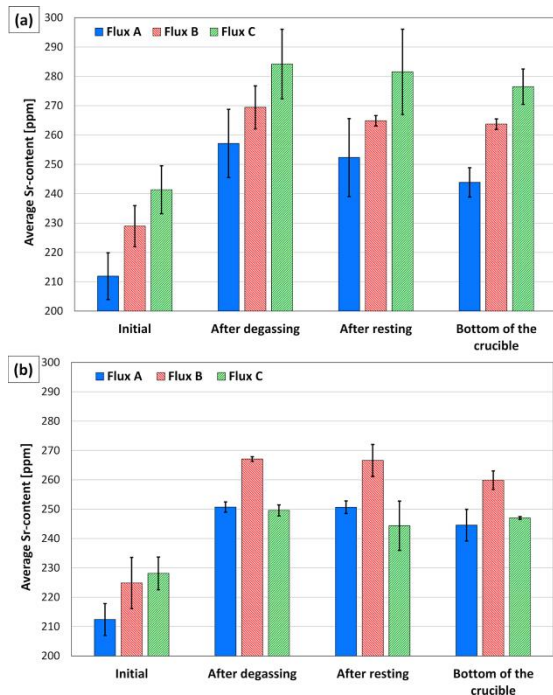


Fig. 4. Variation of the Sr-content during melt preparation in the case of master alloy addition (a) before and (b) during the melt treatments

It can be observed in Fig. 4, that most of the average Sr-content values are significantly higher if the Sr master alloy addition was made before the treatments. A rather momentous difference can be observed between the values obtained when flux C was applied, which is mostly due to the fact, that during three

cycles, when this flux was used, and the alloying was made during the treatments, only 40 ppm of Sr was added. In each case, the addition of the master alloy rods resulted in higher Sr-content, which slightly decreased with time. The Sr-utilization values calculated with equation (1) are shown in Table 3. As can be seen, the Sr_{util} results are close to each other (approx. 60-70 %) with one exception: in the cases when only 40 ppm of Sr was added, the utilization value is only approximately 40 %.

Table 3.

Parameters and results of the calculation of Sr-utilization

	Flux	Sr _{start} [ppm]	Sr _{added} [ppm]	Sr _{finish} [ppm]	Sr _{diff} [ppm]	Sr _{util} [%]
Al-10%Sr was added before the treatment	A	211.90 ± 7.96	60	253.33 ± 13.29	41.43	69.05
	B	228.97 ± 6.98	60	264.87 ± 1.78	35.90	59.83
	C	241.37 ± 8.17	60	281.53 ± 14.53	40.16	66.94
Al-10%Sr was added during the treatment	A	212.43 ± 5.42	60	250.67 ± 2.15	38.24	63.73
	B	224.87 ± 8.72	60	266.60 ± 5.47	41.73	69.55
	C	228.13 ± 5.57	40	244.37 ± 8.39	16.24	40.59

Fig. 5. shows the average $\Delta T_{E,G}^{Al-Si}$ values evaluated with the aid of thermal analysis during the different stages of melt preparation.

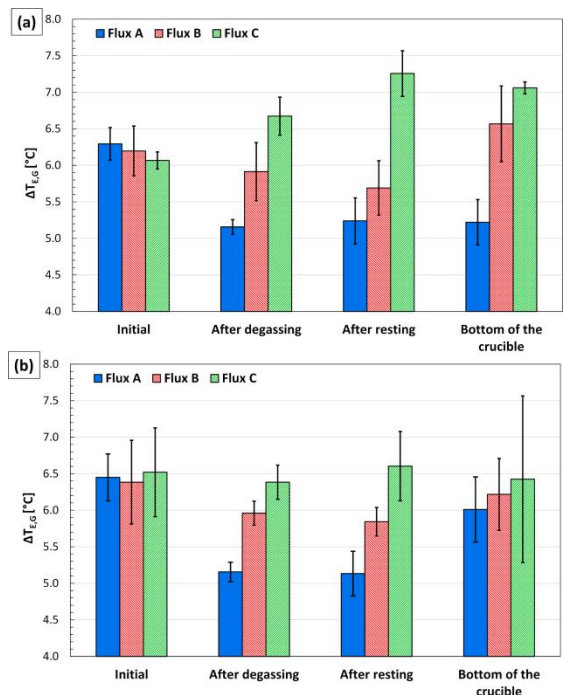


Fig. 5. Variation of the eutectic undercooling during melt preparation in the case of master alloy addition (a) before and (b) in the 9th minute of the melt treatments

As can be seen in Fig. 5, the highest $\Delta T_{E,G}^{Al-Si}$ results were achieved when flux C was used and the master alloy addition was made before the treatments. Regardless of the timing of the Al-10%Sr alloying rod additions, when flux A and B was used, despite the higher average Sr-contents after degassing, the eutectic undercooling values were lowered during the melt treatments and higher $\Delta T_{E,G}^{Al-Si}$ values could be only evaluated in the case of melts retained at the bottom of the crucible. This indicates that when these fluxes were used, the Sr-fading could not be compensated by the additional alloying rods and that, the melt in the bottom of the crucible was enriched in “active” Sr which causes eutectic modification. Fig. 6. shows the average change of the $\Delta T_{E,G}^{Al-Si}$ values due to the melt treatments and resting. The interpretation of the data presented in the figure can be made as follows: if the change in $\Delta T_{E,G}^{Al-Si}$ is positive, the degree of modification is increased, and when $\Delta T_{E,G}^{Al-Si}$ is decreased, the modification level is lowered by the melt treatments.

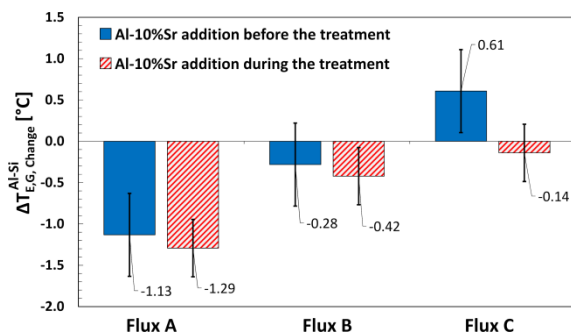


Fig. 6. The average change in the $\Delta T_{E,G}^{Al-Si}$ values

Based on Fig. 6, the modification level increased only in the case of flux C, when the master alloy addition was performed before the treatment. Regardless of the type of flux, less negative changes in the $\Delta T_{E,G}^{Al-Si}$ values were attainable when the alloying rods were added before the treatment, which indicates that better eutectic modification can be achieved by this timing of addition. It can be seen in Fig. 6, the most advantageous changes in $\Delta T_{E,G}^{Al-Si}$ results were attainable with the application of flux C, which indicates that the level of eutectic modification is more sustainable when this flux is used.

Fig. 7 compares the average Sr-content and average $\Delta T_{E,G}^{Al-Si}$ values evaluated during the experiments with representative micrographs of the TA specimens. The results indicate that while the Sr-content can vary from approx. 212 ppm to 270 ppm, the eutectic undercooling remains the same or can be even lower at higher Sr-concentrations. Higher average $\Delta T_{E,G}^{Al-Si}$ results could be only evaluated at Sr levels of about 280 ppm. Based on the microscopic inspection of the TA specimens, in most cases, the level of the eutectic modification was the same and can be categorized as mostly modified (#4 based on the modification rating system of the American Foundry Society [5]). A slightly worse modification level could be observed (transitional lamellar (#3)) when the $\Delta T_{E,G}^{Al-Si}$ values were close to 5 °C. As there is no direct relationship between the amount of Sr and the $\Delta T_{E,G}^{Al-Si}$

results, it is evident, that in foundry practice the level of eutectic modification cannot be controlled by the measurement of Sr-concentration with optical emission spectroscopy. As in most cases, mostly modified (#4), and in some cases, transitional lamellar (#3) ratings could be evaluated regardless of the stage of the melt preparation and the type of flux used, the solidified microstructure is only moderately sensitive to the technological changes made during the experiments and the small variations in the degree of eutectic undercooling.

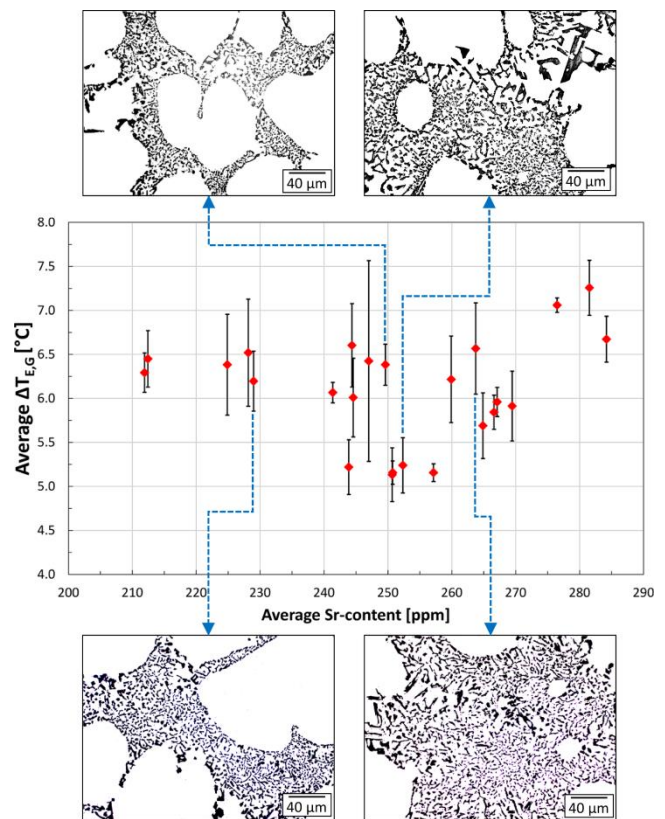


Fig. 7. The comparison of average $\Delta T_{E,G}^{Al-Si}$ and Sr-content results

4. Conclusions

Based on the results of the present research, the following conclusions can be drawn:

- the highest $\Delta T_{E,G}^{Al-Si}$ results were achieved when flux C was used and the master alloy additions were made before the treatments,
- the same level of eutectic modification could be achieved regardless of the Sr-concentration at Sr levels between 212 and 270 ppm,
- in foundry practice, besides Sr content evaluation with optical emission spectroscopy, thermal analysis is also needed for adequate control of the eutectic modification level.

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