Metallurgical and Materials Data 1, no. 3 (2023): 85-90

Publisher: Association of Metallurgical Engineers of Serbia

Metallurgical and Materials Data

www.metall-mater-data.com

Determination of optimal modifier level for eutectic silicon phase in hypoeutectic AlSi7Mg0.3Cu0.5 cast alloy

Mile Djurdjevic[1]*, Srećko Manasijević[2]

[1] *Nemak Linz GmbH, Zeppelinstrasse 24, 4030 Linz Austria*
[2] *Lola Institut Ltd., Knez Viseslava 70a, 11030 Belgrade, Serbia*

ARTICLE INFORMATION:

https://doi.org/10.56801/MMD11

Received: 28 August 2023
Accepted: 15 September 2023

Type of paper: Research paper

ABSTRACT

Silicon particles in as-cast aluminum alloys can be modified using various modifiers, with Strontium (Sr) and Sodium (Na) being the most employed in the aluminum casting sector. However, their concentration diminishes (fades) during the melting furnace process. Modifier fading within the melt can result from three principal chemical reactions: vaporization of the modifier under high vapor pressure conditions at melting temperatures, oxidation driven by a significant affinity for oxygen, or interaction with other elements in the melt leading to the formation of intermetallic compounds. Given the very low vapor pressure of both Na and Sr, their vaporization from the aluminum melt was excluded as a reason for the modifier's fading. Oxidation seems to be like the primary chemical reaction leading to the fading of Na and Sr from the aluminum melt. This study examined the effect of Sr and Na fading on the modification level of silicon particles in the AlSi7Mg0.3Cu0.5 (356) aluminum alloy. The cooling curve analysis has been utilized to quantify modifier fading. Approximately 105 ppm of Sr in the form of master alloy (AlSr10) and 67 ppm of Na in the tablet form were separately added to the melt. Both modifiers were kept in the melt for approximately 200 minutes to monitor their fading. The present paper aimed to quantify the fading of Na and Sr in an AlSi7Mg0.3Cu0.5 alloy. The depletion of modifiers (Na and Sr) while the melt is retained in a furnace can be quantitatively determined through equations derived from existing literature. The surface reaction rate constant (ks), once calculated, serves as a tool for predicting the extent of modifier loss during the melt-holding process in both industrial and laboratory furnaces.

Keywords: arsenic (V) removal, alginate, goethite, nanoparticles, composite.

1. Introduction

Various kinds of hypoeutectic Al-Si-Mg-Cu cast alloys are commonly utilized in the automotive sector, owing to their remarkable mechanical, thermo-physical, and metallurgical characteristics, alongside superior castability (Kaufman and Rooy 2005, Gruzleski and Closset 1990, Crossley and Mondolfo 1966, Sigworth 1983, Wang and Shivkumar 1995). During solidification in industrial conditions, eutectic particles without modification typically exhibit a rough, plate-like, needle-shaped silicon structure with pronounced edges, greatly diminishing the ductility of the alloy. The transformation of the silicon phase from acicular to globular morphological structure is termed as modification. The mechanical and thermo-physical properties of these alloys are enhanced through modification of the eutectic silicon particles, particularly in terms of ductility and thermal conductivity (Zamani and Seifeddine 2016, Ebhota and Jen 2017). The phenomenon of modification, initially identified by Aladar Pacz in 1921 (Aladar 1922), is evident in the transformation from angular, needle-shaped silicon phases to a fine, globular silicon structure.

Modification or control of the Al-Si eutectic can be achieved in two ways: either thermally, by applying rapid cooling, or chemically, by adding a modifier into the melt. Figure 1 illustrates the effects of both thermal and chemical approaches on the morphology and dimensions of Al-Si eutectic particles. The figure indicates that a chemical modifier significantly enhances the extent of modification more than moderate cooling rates do. In instances of high cooling rates (exceeding 50 °C/s), commonly seen in thin-walled components made through high-pressure die casting, the Al-Si eutectic structure can be effectively modified without the need for a chemical modifier. Nonetheless, heavy sections in these castings would still benefit from chemical modification.

---

* Corresponding author.
E-mail address: mile.djurdjevic@nemak.com (Mile Djurdjevic).

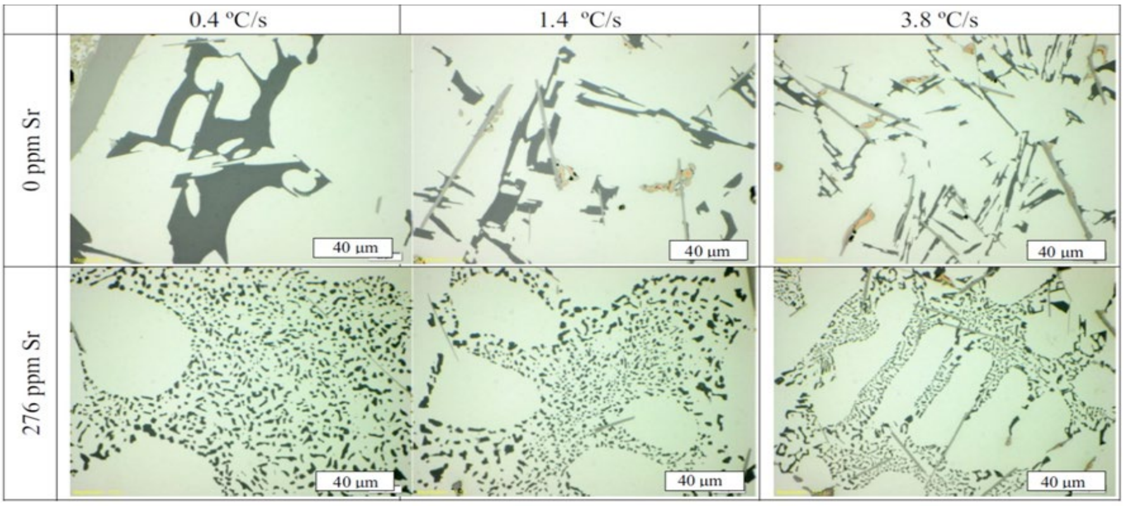

Fig. 1. Impact of cooling rates and different content of Sr on the size and shape of Al-Si eutectic particles (M. Zamani and S. Seifeddine 2016)

Several elements have been found to produce the modified fibrous structure, such as Na, K, Rb, Ce, Sr, Ca, Ba, Sb, La, Yb, Se, Cd and some others (Ebhota and Jen 2017). Among them, Sodium (Na), Strontium (Sr), and Antimony (Sb) are the most effective in creating a fine, evenly distributed, fibrous eutectic structure under industrial conditions (Gruzleski and Closset 1990, Aladar 1921, Rheinfelden Alloys Gmbh 2023, Wessen et al. 2010, Fernandez-Calvo et al. 2011, Lu et al. 2005, Wang and Gruzleski 1992, Emadi et al. 1993).

Strontium (Sr), typically used in the form of a master alloy (AlSr10), is a popular modifier in the aluminum casting industry, favored for its advantageous properties such as ease and safety of handling, durable modifying effect, smokeless addition, and moderate impact on modification. Antimony (Sb), often regarded as a permanent modifier, yields a refined flake-like eutectic structure as opposed to a fibrous one. However, Sb is not as effective as Na and Sr in achieving these modifications (Zamani and Seifeddine 2016, Ebhota and Jen 2017, Aladar 1921, Wang and Gruzleski 1992). Sodium (Na) is the strongest modifier among all previously mentioned (depresses the Al-Si eutectic growth temperature ~ 12 °C), modifying the Al-Si eutectic structure immediately after addition without incubation time (Wessen et al. 2010, Fernandez-Calvo et al. 2011, Lu et al. 2005, Emadi et al. 1993). Owing to the limited solubility of Sodium (Na) in pure Aluminum (approximately 0.01%), producing an Al-based master alloy with Na (which is typically added to the melt in the form of a flux or salt) is not feasible. Given Na's high reactivity with moisture, it is packaged in vacuum-sealed aluminum cans to reduce its exposure to air, thereby minimizing the risks of oxidation and hydrogenation.

The effectiveness of introducing a modifier into an aluminum melt can be evaluated through methods such as Optical Emission Spectroscopy (OES) analysis, thermal analysis via cooling curves, or by comparing the modified or unmodified eutectic structure against standard reference images, such as those found in AFS charts.

Under certain conditions, the levels of modifiers in the melt can diminish over time. Modifier fading can occur due to three types of chemical reactions within the melt. These include vaporization of the modifier at high vapor pressures during melting, oxidation resulting from a strong affinity for oxygen, or interactions with other elements in the melt that lead to the formation of intermetallic compounds. While the modifier remains in the melt, it exists in a chemically combined state. These chemically bound elements do not function effectively as modifiers; only the unbound, active atoms of the modifier in the liquid alloy can induce modification.

Figure 2 shows that both modifiers, Na and Sr, experience fading while being held in the melting furnace (Rheinfelden Alloys Gmbh 2023). The rate of fading for Na, at approximately 1.3 ppm per minute, is notably faster than that of Sr, which fades at a rate of 0.38 ppm per minute. This loss is evident throughout the entire duration of holding time observed.

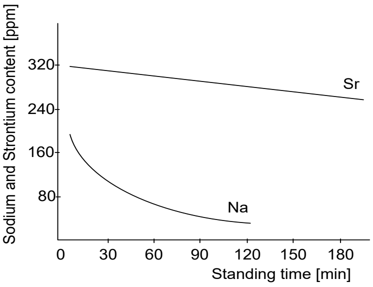

Fig. 2. Na and Sr melting loss in Silafon 13 (AlSi11) alloy (Rheinfelden Alloys Gmbh 2023)

The literature suggests that the standard concentration of Na used as a modifier in hypoeutectic Al-Si alloys typically ranges from 50 to 100 ppm (Garat et al. 1992). Similarly, a complete spectrum of modified Al-Si eutectic structures can be attained with the addition of 200 ppm Sr (Gruzleski and Closset 1990, Zamani and Seifeddine 2016, Garat et al. 1992). However, excessive quantities of Na (ranging from 180–200 ppm) might lead to over-modification of the AlSi eutectic structure, resulting in the formation of bands of primary aluminum, coarse silicon phases, and AlSiNa particles (Wessen et al. 2010, Fernandez-Calvo et al. 2011, Lu et al. 2005, Emadi et al. 1993). Added Sr levels higher than needed may exert a deleterious effect on the properties of the alloy. Two distinct phenomena are associated with Sr over-modification: coarsening of the silicon structure and appearance of Sr containing intermetallic phases (Gruzleski and Closset 1990). To obtain desired structure of Al-Si eutectic, the added amount of modifier (Sr or Na) into aluminum melt needs to be optimized. The thermal analysis (TA) technique can be readily applied to optimize the required amount of modifier. The present work used thermal (cooling curve) analysis to evaluate the efficiency of Sr and Na addition into AlSi7Mg0.3Cu0.5 melts and quantify their fading effect.

Optical Emission Spectroscopy (OES) analysis can be employed to evaluate the efficacy of chemical modification. By using OES to measure the concentrations of Sr and Na in the aluminum melt, it's possible to determine their total content. However, OES does not provide insights into their activity in the melt (for instance, the extent to which Sr or Na transforms acicular silicon particles into a more fibrous structure). Over time, the reactivity of Sr and/or Na with other elements in the melt can diminish, reducing their effectiveness as modifiers (rendering them inactive). In contrast, thermal analysis can gauge the influence of an active modifier on lowering the Al-Si eutectic temperature, offering an advantage over OES in monitoring modifier efficiency on the foundry floor.

The existing literature does not thoroughly quantify the loss of Na and Sr during the holding of aluminum melt in a furnace. This paper aims to quantify the fading of Na and Sr in an AlSi7Mg0.3Cu0.5 alloy, providing insights into which modifier fades more rapidly and which is more prone to reacting with air to form oxides. The primary hypoeutectic AlSi7Mg0.3Cu0.5 alloys were chosen for these experiments. The fading rate constants determined experimentally (loss rate constant - k and surface reaction rate constant ks) are intended to assist foundry personnel in quantifying modifier loss during melt holding in melting furnaces and in taking proactive measures to maintain an optimal amount of modifier in the aluminum melt.

2. Materials and methods

Commercial primary hypoeutectic AlSi7Mg0.3Cu0.5 aluminum alloy with chemical composition presented in Table 1 was used in this experiment.

Around 1.5 tons of the alloy were melted in an electric resistance furnace and maintained at a temperature of 730±5 °C. Initially, the melt was modified by adding Na, followed by the modification of an additional aluminum melt with Sr. Natrium was introduced into the aluminum melt using a commercial SIMODAL 77 tablet (a mixture of Na and 5–13 wt.% Si), weighing approximately 200 g, produced by Foseco. A total of 13 tablets were added to the melt to reach the desired 65 ppm of Na. Each tablet was placed on the melt surface individually before degassing and submerged using a clean, pre-warmed, perforated plunging bell. This bell was designed to position the tablets near the furnace's bottom, ensuring adequate circulation of the melt, unrestricted movement of the tablets, and efficient distribution of Na into the melt. Submersion continued until bubbling ceased before adding another tablet. After achieving the desired Na concentration, a 15-minute degassing process with nitrogen gas was performed. Subsequently, any dross on the surface of the holding furnace was meticulously removed.

For the second modification, Sr was introduced in the form of AlSr10 master alloy rods towards the end of the degassing process, targeting a Sr concentration of approximately 110 ppm in the aluminum melt. Throughout the melt holding period, no protective atmosphere was utilized. The contents of Na and Sr in the melts across both experiments are detailed in Tables 2 and 3. The concentrations of Na and Sr in the aluminum melts were monitored via OES analysis.

Table 2. Na content in the melt as a function of holding time

Na, [ppm]	65	67	63	60	57
Melt holding time, [min]	40	80	120	160	200

Table 3. Sr content in the melt as a function of holding time

Sr, [ppm]	105	104	100	98	97
Melt holding time, [min]	2	10	60	120	240

Thermal analysis (TA) was performed using a setup designed to record the cooling trajectory of a 200±10 g sample of molten alloy, tracking its temperature decrease from the molten phase (approximately 700 to 400 °C). To collect TA test samples, a cylindrical coated steel cup (50 mm in diameter and 60 mm length) was submerged in the melt for 10 seconds before being positioned on the TA apparatus. Encased in ceramic tubes, two thermocouples were automatically inserted into the cup to monitor the cooling melt's temperature. The thermocouples provided an accuracy of ±0.10 °C. Data for the TA were captured via a high-speed data acquisition system from National Instruments, connected to a personal computer.

The TA test samples, once solidified, were longitudinally sectioned and polished with a Buehler semi-automatic polisher. The ultimate stage of polishing employed a 0.05 µm colloidal silica suspension (Struers OP-U). These prepared samples were then subjected to metallographic analysis to examine the solidified structure, utilizing a light optical microscope.

3. Results and discussion

The TA technique, in conjunction with OES analysis, has been utilized in this study to analyze the effect of Sr and Na fading on the characteristic AlSi eutectic growth temperature of the AlSi7Mg0.3Cu0.5 alloy. As indicated in Figure 3, varying contents of strontium (105 ppm) and sodium (67 ppm) significantly altered the shape of the cooling curves by lowering their eutectic growth temperatures.

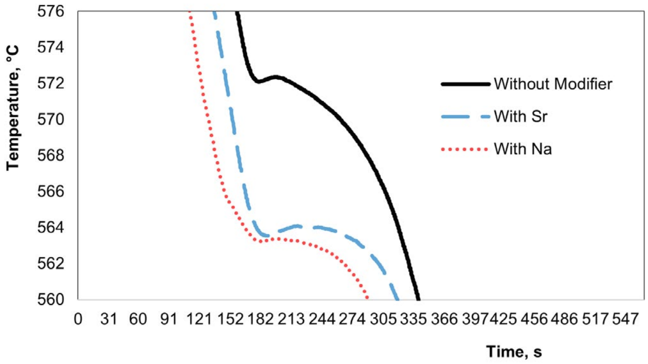

Fig. 3. The Al-Si eutectic section of the cooling curves of AlSi7Mg0.3Cu0.5 alloy. One cooling curve illustrates the shape of Al-Si eutectic region without addition of modifier, while two others show the shape of Al-Si eutectic regions modify with strontium (105 ppm) and sodium (67 ppm).

According to previous knowledge and foundry experience, Na more significantly depresses the Al-Si eutectic growth temperature than Sr. Immediately after Na addition, the Al-Si eutectic growth (plateau) temperature (TAlSi E, G) dropped from 572.5 °C to its lower value of 563.5 °C (by 67 ppm Na), reducing the AlSi growth temperature by almost 9 °C. The addition of Sr lowered the Al-Si E, G growth temperature to 564.2°C, decreasing the Al-Si growth temperature by 8.3 °C. The depression of the Al-Si eutectic growth temperature (plateau temperature) has been used in this study as a parameter to correlate with the fading of Sr and/or Na during melt holding in the melting furnace. The fading of modifiers (Na and Sr) added to the AlSi7Mg0.3Cu0.5 alloy during various melt holding times is presented in Figure 4. In both trials, the furnace capacity was the same: 1500 kg.

Samples of the melt for Na-modifier analysis were collected from the melting furnace every 40 minutes over a 200-minute holding period. Meanwhile, five samples for Sr-modifier analysis were taken at different intervals throughout a 240-minute holding period. The concentration of both modifiers showed a gradual decline as the holding time increased, exhibiting nearly the same pattern of fading behavior.

According to earlier literature (Gruzleski and Closset 1990, Rheinfelden Alloys Gmbh 2023, Grand 1952, Eguiskiza et al. 2015), Na is expected to have a higher rate of loss compared to Sr. Recently, some studies in the literature (Djurdjevic et al. 2022) have presented different findings regarding Na fading, indicating its moderate loss during melt holding.

Table 1. The chemical composition of the primary AlSi7Mg0.3Cu0.5 aluminum alloy was determined using OES analysis.

Alloy	Chemical Compositions (wt. %)									
	Si	Fe	Cu	Mn	Mg	Zn	Ti	Sr	P	Na
AlSi7Cu0.5Mg	7.30	0.12	0.48	0.06	0.38	0.07	0.12	0.0000	0.0015	0.0000

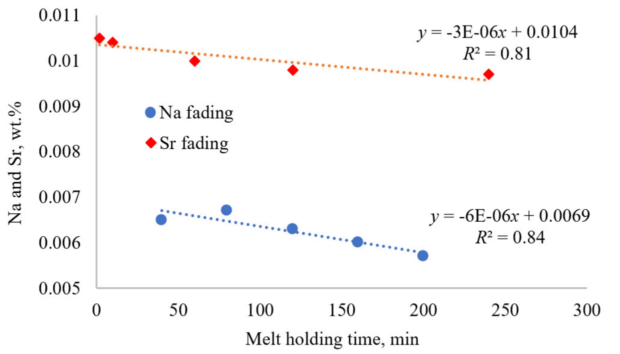

Fig. 4. Fading of Na and Sr during holding in the AlSi7Mg0.3Cu0.5 aluminum melt

Our industrial experiments, as depicted in Figure 4, verified the recent findings of moderate fading for the two modifiers under investigation. Once the desired levels of Sr and Na were reached (105 ppm for Sr and 65 ppm for Na), we observed that over the following 250 minutes, Na exhibited a marginally greater loss than Sr. Specifically, Na decreased by 10 ppm, whereas Sr diminished by 8 ppm. Despite this reduction, the remaining concentrations of both modifiers were still within the recommended levels for the Al-Si7Mg0.3Cu0.5 alloy, ensuring effective modification of silicon particles. The fading rates for Na and Sr can be inferred from the slopes of the linear trends presented in Figure 4. The rate of Sr fading was calculated at $3x10^{-6}$ wt.%/min, with Na's fading rate being slightly higher at $5x10^{-6}$ wt.%/min.

Figures 5 and 6 display the typical as-cast eutectic microstructure of the AlSi7Mg0.3Cu0.5 alloy, both without and with a modifier. The Al-Si eutectic microstructure appears in the form of large, needle-like particles with sharp edges. Figure 5 shows the microstructural changes occurring with the decrease in Sr content due to fading, while Figure 6 illustrates the alterations in the shape and size of Al-Si eutectic phases caused by Na fading. Both micrographs reveal the development of coarse silicon eutectic particles during modifier fading. The Al-Si eutectic structure modified with Na is characterized by smaller, fully spheroidized silicon particles. In contrast, the silicon particles modified with Sr are less spheroidized and slightly coarser. Based on cooling curve analysis (indicating a depression of the Al-Si growth temperature for both modifiers of > 8°C) and metallographic analysis (as shown in Figures 5 and 6), all observed structures can be considered modified.

Drawing from the literature (Gruzleski and Closset 1990, (Fernandez-Calvo et al. 2011, Lu, Nogita, and Dahle 2005, Wang and Gruzleski 1992, Emadi et al. 1993, Garat et al. 1992, Grand 1952, Eguiskiza et al. 2015, Djurdjevic et al. 2022) and the findings illustrated in Figures 4–6, it is evident that Sr and Na diminish in presence within the aluminum melt. As discussed in the introduction of this paper, various studies (Gruzleski and Closset 1990, Crosley and Mondolfo 1966, Rheinfelden Alloys Gmbh & Co. KG, Fernandez-Calvo et al. 2011, Emadi et al. 1993, Eguiskiza et al. 2015, Djurdjevic et al. 2022) have identified vaporization and oxidation as the primary chemical reactions leading to the fading of modifiers.

As reported by Gruzleski and other researchers (Gruzleski and Closset 1990, Granger 1988), at 730 °C, the vapor pressures of Sr and Na are 10-3 and 0.2 atm, respectively, indicating that Na has a 200-fold higher vapor pressure than Sr. However, recent studies by G.K. Sigworth (Sigworth 2021, Sigworth 2000) have revealed that the vapor pressure of Na, for the reaction Na (wt.%) = Na (vapor), is significantly lower, amounting to 0.005 atmospheres (at a melting temperature of 730 °C and a Na content in the melt of 60 ppm), thus aligning more closely with that of Sr.

Vapor pressure for Na has been calculated applying equation (1) (Sigworth 2000).

$$\ln K_1 = \ln\left[\frac{P_{Na}}{\%_{Na}}\right] = \frac{-64.140+62.428T}{RT} = \frac{-7715}{T} + 7.509 \qquad 1$$

The very low vapor pressures of Na and Sr do not account for their evaporation from the aluminum melt. Thus, oxidation is identified as the primary chemical reaction responsible for the loss of Na and Sr from the aluminum melt during its retention in the melting furnace. This assumption is supported by a laboratory investigation conducted by T.I. Sigfusson et al. (Sigfussen and Pensaert 1994), which demonstrated that Na, when dissolved in aluminum melt, promotes oxide formation on the melt's surface. The decrease of modifiers (Na and Sr) during melt holding in an industrial furnace can be quantified using equations (2) and (3).

Equation (2) taken from Gobrecht (Gobrecht 1978) has been used to calculate modifier loss rate constant k, while Equation (3) taken from literature (Williams et.al. 2000) has been used to calculate the empirical surface reaction rate constant (k_s).

$$C = C_0 \exp(kt) \qquad 2$$

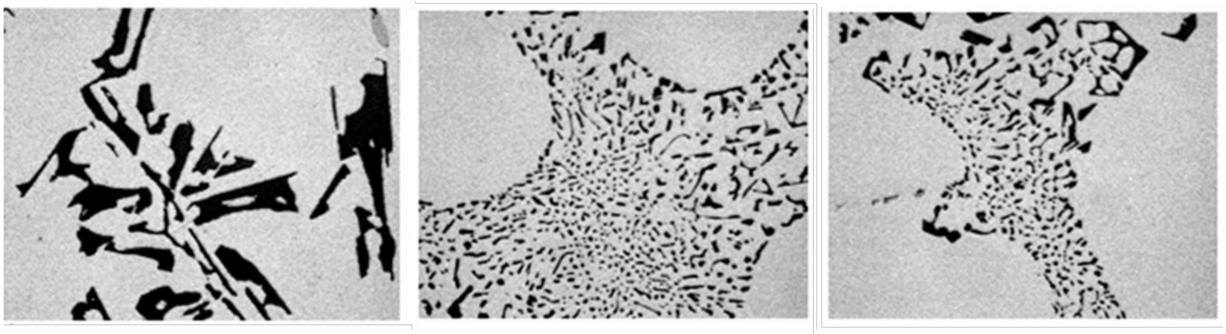

Fig. 5. Effect of Sr addition on the eutectic structure of an AlSi7Mg0.3Cu0.5 alloy a) without Sr, b) 105 ppm and c) 97 ppm.

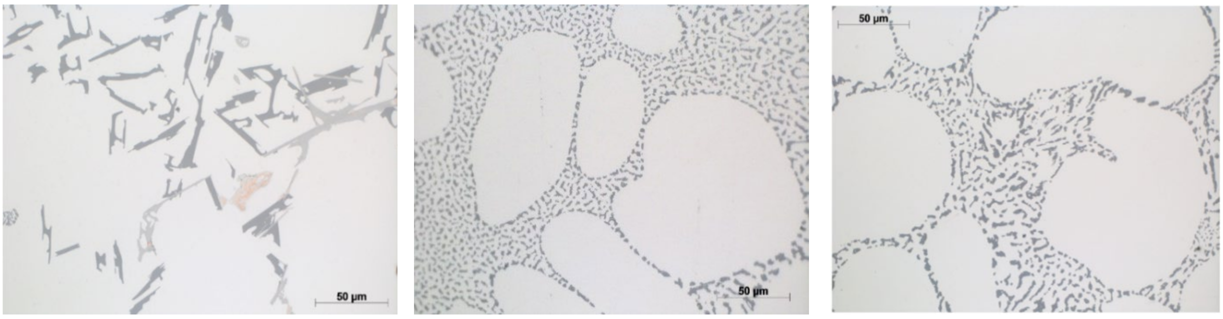

Fig. 6. Effect of Na addition on the eutectic structure of an AlSi7Mg0.3Cu0.5 alloy a) without Na, b) 67 ppm Na and c) 57 ppm Na.

Where:

C - is the concentration of element (Na or Sr) with time (wt.%)

C_0 - is the beginning concentration of element (Na or Sr) at zero time (wt.%)

k - is the Na/Sr loss rate constant (h^{-1})

t - is the melt holding time (hours)

$$\frac{C}{C_0} = e^{-\frac{k_s \rho A_s}{M}} * t \qquad 3$$

Where:

k_s - is the rate constant for the surface reaction (m/s) ρ - is the density of liquid aluminum melt (kg/m^3) A_s - is the surface area of the melt/air interface (m^2) M - is the mass of molten metal in the furnace (kg) t - is the melt holding time (sec)

The results obtained applying equations (2) and (3) for two trials presented in Figure 4 with Na and Sr as modifier are presented in Table 4.

Table 4. Calculated Na and Sr loss rate constant (k) and surface reaction rate constant (k_s) for the same alloy (AlSi7Mg0.3Cu0.5) under industrial conditions (holding furnace capacity 1500 kg and diameter ~ 1 m).

Parameter	AlSi7Mg0.3Cu0.5 (Holding furnace capacity 1500 kg)	
	Modifier Na	Modifier Sr
k, [h-1]	0.0394	0.0198
ks, [m/s]	3.42x10-5	1.72x10-5

Based on the data presented in Table 4, the loss rate constant (k) for Na and Sr from the industrial furnace over an approximately 4-hour holding period was comparatively low. Natrium exhibited a loss rate constant that was twice as high as that of Sr, aligning with expectations and corroborating prior findings (Gruzleski and Closset 1990, Rheinfelden Alloys Gmbh 2023, Wessen et al. 2010, Fernandez-Calvo et al. 2011, Lu et al. 2005, Wang and Gruzleski 1992, Emadi et al. 1993, Garat et al. 1992, Grand 1952, Eguiskiza et al. 2015, Djurdjevic et al. 2022).

The calculated outcomes reveal that the rate constants (ks) for the surface reactions of Na and Sr are comparable. Natrium demonstrates a marginally greater rate of elimination from the aluminum melt ($3.42x10^{-5}$) relative to Sr's rate of removal ($1.72x10^{-5}$). This observation is anticipated and consistent with prior data in the literature, as indicated by Table 5 (Eguiskiza et al. 2015) and Table 6 (Williams et al. 2000).

Table 5. Sr loss rate constant (k) and surface reaction rate constant (k_s) calculated for A356, A319, A360 and A413 aluminum alloys (Eguiskiza et al. 2015)

	A356 High Sr (4 kg)	A356 Medium Sr (4 kg)	A356 Low Sr (4 kg)	A360, A413 High Sr Gobrecht (Gobrecht 1978)		
				3 kg	10 kg	30 kg
k, (h-1)	0.13	0.31	0.12	0.22–1.19	0.07–0.08	0.03–0.04
ks, (m/s)	$2.96x10^{-6}$	$7.71x10^{-6}$	$5.42x10^{-6}$	-	-	-

Table 6. Calculated average surface reaction rate constant (ks) for alkali metal removal during furnace hold (mass of metal was 11.35 t and surface area of furnace was 12.6 m^2)

Element	Li	Ca	Na
ks, [m/s]	$2.4x10^{-5}$	$2.4x10^{-5}$	$2.3x10^{-5}$

The loss rate constants (k) for Na and Sr, as shown in Table 4, are an order of magnitude lower compared to those listed in Table 5. This discrepancy confirms that the size of the melting furnace significantly impacts the loss rate constant (k). Consequently, modifier fading in a smaller melting furnace (as noted in Table 5: k=0.31 for a furnace capacity of 4 kg with a medium Sr concentration of 113 ppm) is fifteen times greater than in a larger melting furnace (Table 4: k=0.0198 for a furnace capacity of 1500 kg with a medium Sr concentration of 105 ppm). As J. Gobrecht (Gobrecht 1978) mentions, factors such as the size of the melting furnace, the temperature of the melt bath (with higher temperatures leading to quicker fading), movement within the bath (which accelerates fading), and the ratio of bath surface area to volume (with smaller ratios leading to less fading) all influence the rate at which modifiers in aluminum melts fade. However, it's challenging to isolate and assess the relative impact of each reaction (such as oxidation with other elements and vaporization during the casting process) and process parameters (including melt temperature, degassing time, furnace capacity, and melt surface area). Thus, an attempt should be made to estimate and quantify modifier fading under both industrial and laboratory conditions using a straightforward method.

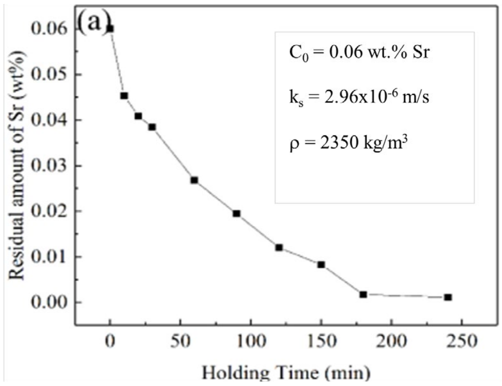

Fig. 7. The residual amount of Sr as function of the melt holding time (Zhang et al. 2019)

The previously determined loss rate constant (k) and surface reaction rate constant (k_s) offer a method for quickly estimating the fading of Na and Sr under production and/or experimental settings. The applicability of these constants for quantifying modifier fading is validated through literature data (Zhang et al. 2019). Figure 7 presents experimental findings on the fading of Sr during its retention in a small laboratory furnace (with a surface area of approximately 0.015 m^2). A total of 1.5 kg of the A356 (Al-Si7Mg) alloy was melted at 750 °C, with 0.06 wt.% Sr introduced into the melt and maintained for 240 minutes. The initial sample for chemical analysis was collected 30 minutes following the addition of Sr, with subsequent samples gathered at 30-minute intervals.

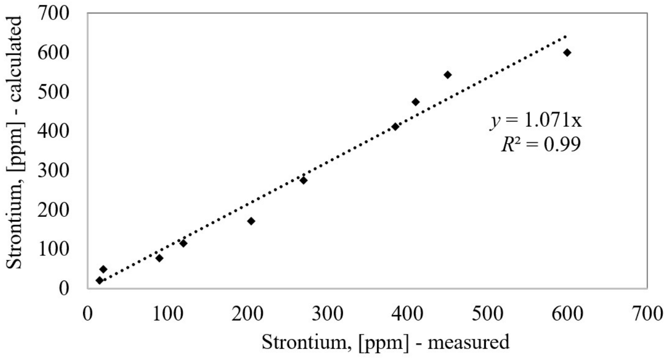

Fig. 8. Comparison of calculated and measured values for Sr during melt holding in the laboratory furnace for period of 4 hours

Applying equation (3) and utilizing the surface reaction rate constant (k_s) from Table 5 for high Sr content ($k_s = 2.96x10^{-6}$), the corresponding Sr concentration (C) during the holding time can be calculated. Figure 8 illustrates a plot of the calculated values for Sr fading versus their experimentally determined counterparts. The calculated values for Sr fading demonstrate a high level of reliability ($R^2 = 0.99$). Thus, the experimentally determined surface reaction rate constant (k_s) enables foundry personnel to accurately predict the removal rate of modifiers from the aluminum melt over various holding periods.

4. Conclusion

Several experiments were conducted to observe the effects of Sr and Na fading under industrial conditions and to determine their optimal levels for the investigated AlSi7Mg0.3Cu0.5 alloy. It was found that both modifiers (Sr and Na) fade moderately under industrial conditions, more slowly than what is suggested in the literature. Oxidation has been identified as a major reason for the fading of modifiers. The reduction in modifier concentration during melt holding was mathematically quantified through the surface reaction rate constant (k_s), determined from the experiments. This research demonstrates that a straightforward analytical method enables foundry personnel to measure the depletion of modifiers during melt holding and establish an adequate time window for casting. This ensures the maintenance of an optimal concentration of the necessary refining element in the holding furnace at all times.

Acknowledgment

We want to thank Serbia's Ministry of Science, Technological Development, and Innovation (Contract ID: 451-03-47/2023-01/200066) for financing and supporting the successful cooperation between Lola Institute Ltd and Nemak Europe.

References

Aladar, P. United States Patent 1387900, August 16, 1921.

Crosley, Phillip Bernard, and L. F. Mondolfo. "The modification of aluminum-silicon alloys." Mod Cast 49, no. 3 (1966): 99-100.

Djurdjevic, M.B., S. Manasijevic, and M. Ponjavic. "Fading of Strontium in AlSi7Cu0.5Mg Alloy Studied Using Thermal Analysis Technique." International Journal of Metal Casting, doi:10.1007/s40962-022-00916-4, 2022.

Ebhota, W., and T.C. Jen. "Effects of Modification Techniques on Mechanical Properties of Al-Si Cast Alloys." In Aluminium Alloys - Recent Trends in Processing, Characterization, Mechanical Behavior and Applications. Published by INTECH Open Science, 2017, 59-80.

Eguiskiza, S., A. Niklas, A.I.F. Calvo, F. Santos, and M.B. Djurdjevic. "Study of Strontium Fading in Al-Si-Mg and Al-Si-Mg-Cu Alloy by Thermal Analysis." International Journal of Metalcasting 9(3) (2015): 43-50.

Emadi, D., J.E. Gruzleski, and J.M. Toguri. "The Effect of Na and Sr Modification on Surface Tension and Volumetric Shrinkage of A356 Alloy and Their Influence on Porosity Formation." Metallurgical Transaction B 24 (1993): 1055-1063.

Fernandez-Calvo, A.I., A. Niklas, A. Loizaga, and M. Perez. "Assessment of Sodium Modification Treatment of A357 Aluminum Alloy by Thermal Analysis." Proceedings of the European Conference on Aluminum Alloys, Bremen, Germany, October 5-7, 2011, 35-37.

Garat, M., G. Laslaz, S. Jacob, P. Meyer, P.H. Guerin, and R. Adam. "State of the Art Use of Sb, Na and Sr Modified Al-Si Casting Alloys." AFS Trans 146 (1992): 821-832.

Gobrecht, J. "**Über** den Einfluss von Zusatzelementen auf die Dauer der Veredelungswirkung von Na und Sr in Aluminum-Silicium Gusslegierungen." Giesserei 65(7) (1978): 158-164.

Grand, L. "The Modification of Aluminum-Silicon Alloys." Revue de l'Aluminum 29 (1952): 5-15.

Granger, D. "Solidification of eutectic alloys: aluminum-silicon alloys." ASM Handbook. 15 (1988): 159-168.

Gruzleski, John E., and Bernard M. Closset. "The treatment of liquid aluminum-silicon alloys." (No Title) (1990).

Kaufman, John Gilbert, and Elwin L. Rooy. Aluminum alloy castings: properties, processes, and applications. Asm International, 2004.

Lu, L., K. Nogita, and A. Dahle. "Combining Sr and Na Additions in Hypoeutectic Al-Si Foundry Alloys." Material Science Engineering A 399 (2005): 244-253.

Rheinfelden Alloys Gmbh & Co. KG. Hüttenaluminium-Gusslegierungen: RHEINFELDEN ALLOYS, GRUPPE DREI, www.rast-bs.de/images/content/technikerschule/Linksammlung/RHEINFELDEN-ALLOYS_Gusslegierungen_2010.pdf, Accessed September 10, 2023

Sigfussen, T.I., and S. Pensaert. "A New Method for Analyzing Sodium Content of Aluminium Melts." Light Metals, 765-769, 1994.

Sigworth, G. K. "Theoretical and practical aspects of the modification of Al-Si alloys." AFS Trans 91, no. 715.2 (1983).

Sigworth, G.K. "Refining of Secondary Aluminum: Important Chemical Factors." Journal of Metals 73(9) (2021): 2594-2602.

Sigworth, G.K. "Removal of Alkali Metals from Aluminum: A Thermodynamic Analysis." Aluminum Transaction 2(1) (2000): 81-89.

Wang, L., and S. Shivkumar. "Strontium Modification of Aluminum Alloy Casting in the Expendable Pattern Casting Process." Journal of Material Science 30 (1995): 1584-1594.

Wang, W., and J.E. Gruzleski. "Antimony-Modifier Interactions in Aluminum Foundry Melts-Part 1 Antimony-Strontium Interaction." Cast Metals 5 (1992): 20-28.

Wessen, M., N.E. Andersson, and O. Granath. "Effect of Sodium Modification on Microstructure and Mechanical Properties of Thick-Walled AlSi6Cu2.5 Rheocast Component." Transaction Nonferrous Metals Society of China 20 (2010): 1643-1648.

Williams, E.M., T.H. Williams, R.W. McCarthy, and S.A. Levy. "Removal of Alkali Metals from Aluminum." Light Metals, 2000, 785-794.

Zamani, M., and S. Seifeddine. "Determination of Optimum Sr Level for Eutectic Si Modification in Al-Si Cast Alloys Using Thermal Analysis and Tensile Properties." International Journal of Metal Casting 10 (2016): 457-465.

Zhang, W., S. Ma, Z. Wei, and P. Bai. "The Relationship between Residual Amount of Sr and Morphology of Eutectic Si Phase in A356 Alloy." Materials 12(19) (2019): 3222.