

# The effect of sodium and strontium on modification of eutectic silicon

---

**Kozina, Franjo; Zovko Brodarac, Zdenka; Tubić, Barbara; Dolić, Natalija**

*Source / Izvornik:* **51st International October Conference on Mining and Metallurgy Proceedings, 2019, 48 - 51**

**Conference paper / Rad u zborniku**

*Publication status / Verzija rada:* **Published version / Objavljena verzija rada (izdavačev PDF)**

*Permanent link / Trajna poveznica:* <https://urn.nsk.hr/urn:nbn:hr:115:166495>

*Rights / Prava:* [In copyright](#)/[Zaštićeno autorskim pravom.](#)

*Download date / Datum preuzimanja:* **2024-08-26**



SVEUČILIŠTE U ZAGREBU  
METALURŠKI FAKULTET  
UNIVERSITY OF ZAGREB  
FACULTY OF METALLURGY

*Repository / Repozitorij:*

[Repository of Faculty of Metallurgy University of Zagreb - Repository of Faculty of Metallurgy University of Zagreb](#)



DIGITALNI AKADEMSKI ARHIVI I REPOZITORIJI

## THE EFFECT OF SODIUM AND STRONTIUM ON MODIFICATION OF EUTECTIC SILICON

Franjo Kozina<sup>1</sup>, Zdenka Zovko Brodarac<sup>1</sup>, Barbara Tubić<sup>1</sup>, Natalija Dolić<sup>1</sup>

<sup>1</sup>University of Zagreb Faculty of Metallurgy, Aleja narodnih heroja 3, Sisak, Croatia, fkozin@simet.hr

### Abstract

*Modification of eutectic ( $\alpha_{Al}+\beta_{Si}$ ) is usually performed during treatment of Al-Si based alloys in order to obtain higher mechanical properties. Chemical modification is usually performed using modifying elements such as Na and Sr. The research was performed in order to estimate the efficiency of Na and Sr additions in eutectic AlSi12 alloy using chemical analysis, simple thermal analysis (STA) and metallographic analysis. The metallographic analysis revealed fully modified ( $\alpha_{Al}+\beta_{Si}$ ) eutectic microstructure in alloy treated with Na. The Sr additions widened solidification interval and, lowered the eutectic area temperatures as indicated by STA.*

**Keywords:** AlSi12, sodium, strontium, eutectic ( $\alpha_{al} + \beta_{si}$ ), modification

### 1. INTRODUCTION

Modification of eutectic ( $\alpha_{Al}+\beta_{Si}$ ) is commonly performed during treatment of aluminum-silicone (Al-Si) based foundry alloys [1]. Modification leads to a structural transformation of the eutectic  $\beta_{Si}$  phase from a coarse plate to a fine fibrous morphology [2]. This structural refinement of the inherently brittle eutectic improves mechanical properties, particularly ductility, tensile strength and elongation [3]. The fine fibrous morphology can be obtained with chemical modification or a rapid cooling rate. Although, chemical modification can be performed by addition of alkaline, alkaline earth and rare earth metals, sodium (Na) and strontium (Sr) are most frequently used in practice [4].

The modification of eutectic ( $\alpha_{Al}+\beta_{Si}$ ) through the additions of Na or Sr can be explained by their effect on  $\beta_{Si}$  phase nucleation and growth [5]. The nucleation of  $\beta_{Si}$  phase is affected by poisoning of AlP particles responsible for heterogeneous nucleation mechanism, and formation of  $Na_2P$ ,  $Sr_3P_2$  or  $Al_2Si_2Sr$  particles [6]. The reduced number of nuclei forces the eutectic transformation to higher undercooling [5]. The impurity induced twinning and restricted growth theory are two most established growth models for eutectic modification [7]. During impurity induced twinning, modifier is atomically adsorbed at the growth surfaces of  $\beta_{Si}$  phase facilitating the formation of new twins and locally enabling growth in many different directions [8]. The restricted growth theory assumes that the modifier retards  $\beta_{Si}$  phase growth by being selectively adsorbed at growing surfaces. Instead of growing fast as a plate in a few selected directions, modified  $\beta_{Si}$  phase grows isotropic in different directions [7]. Due to the increased ability of  $\beta_{Si}$  phase towards branching the decrease in undercooling is expected [9]. However, lack of undercooling reduction can occur due to Na and Sr poisoning effect. Undercooling occurs in the melt before eutectic reaction starts and modification takes place [3]. Enhanced eutectic solidification and branching of  $\beta_{Si}$  phase results in lower eutectic growth temperature [10].

Although Na and Sr have similar final effect on  $\beta_{Si}$  phase, they act with different mechanism and require different processing. The Na is added to a melt in the elemental form or as a flux. The Na is easily dissolved at the temperatures above 700°C with a poor and unpredictable recovery (20-30 % of the addition) caused by high vapor pressure. The Sr, usually added via master alloy,

exhibits much higher recovery (above 90 % of the addition) and more complex dissolution characteristic. Dissolution characteristics strongly depend on the Sr content in the master alloy. Master alloys with high Sr content should be added at the lowest practical temperature, while master alloys with lower Sr content give better recovery at the higher temperatures [3].

The goal of the research is to estimate the influence of Na and Sr additions on eutectic ( $\alpha_{Al}+\beta_{Si}$ ) modification during solidification of AlSi12 alloy in a permanent steel mold. The effect of Na and Sr will be estimated using simple thermal analysis (STA) and metallography.

## 2. EXPERIMENTAL

In order to estimate the efficiency of Na and Sr, two melts were synthesized. The synthesis of the first melt began by remelting 80 kg of the AlSi12 block with the addition of fluxes. The chemical composition was amended through the additions of AlSi50%, AlTi10 and AlMn master alloys, while the grain refinement was performed using AlTiB commercial master alloys. The alloy was stirred with argon (Ar) at 780°C, and moved to the holding furnace. In the holding furnace the alloy was chemically degased. Ten minutes before casting, modification was performed by adding 0.05 kg of metallic Na packed in vacuum sealed aluminum can. The synthesized alloy was poured at 720±20°C into a permanent steel mold. During the synthesis of the second alloy, modification was performed by adding 0.23 kg of AlSr10 master alloy at 780°C before stirring with Ar. In the holding furnace alloy was chemically degased. The casting process was delayed for 20 min after modification with the melt temperature of 720±20°C.

During solidification in a permanent steel mold, the STA was performed using temperature measuring device “National Instruments” NI-9211 with NI cDAQ-9172 thermo-module and LabVIEW Full Development System software support. From the obtained cooling curves the following characteristic temperatures were identified: minimum liquidus temperature ( $T_{Lmin}$ ), maximum liquidus temperature ( $T_{Lmax}$ ), minimum eutectic temperature ( $T_{Emin}$ ), maximum eutectic temperature ( $T_{Emax}$ ) and solidus temperature ( $T_S$ ). The obtained characteristic temperatures enabled calculation of changes in liquid ( $\Delta T_L$ ) and eutectic ( $\Delta T_E$ ) temperature as well as estimation of temperature ( $\Delta T_{L-S}$ ) and time ( $\Delta t_{L-S}$ ) solidification interval.

The chemical composition was analyzed using SPECTRO MAX x LMM 04 spectrometer.

The samples for metallographic analysis were prepared using standard grinding and polishing techniques. The samples for light microscopy were etched using Keller etching solution (2.5 mL HNO<sub>3</sub> + 1.5 mL HCl + 1.0 mL HF). The samples for electron microscopy underwent caustic chemical etching consisting of etching (30 % NaOH<sub>aq</sub>) and rinsing (1 M HCl) cycles. The Olympus GX53 inverted metallographic microscope was used to perform light microscopy, while electron microscopy was done on Tescan, Vega TS 5136 MM equipped with energy dispersive spectrometer (EDS).

## 3. RESULTS AND DISCUSSION

The results of chemical analysis are given in Table 1.

Table 1. Chemical composition of the synthesized alloys

Melt	Chemical composition, mas. %									
	Al	Si	Fe	Cu	Mn	Mg	Ni	Ti	Na	Sr
1 <sup>st</sup>	87.3	12.180	0.1160	0.0039	0.2040	0.0041	0.0024	0.0840	0.0120	0.0001
2 <sup>nd</sup>	87.3	12.200	0.1170	0.0016	0.2010	0.0057	0.0033	0.0810	0.0040	0.0018

The chemical composition of synthesized alloys is in accordance with EN AC 44100 for eutectic AlSi12 alloy. Based on the results, solidification sequence of both alloys began with transformation  $L \rightarrow \alpha_{Al} + (\alpha_{Al}+\beta_{Si})$  followed by solidification of eutectic ( $\alpha_{Al}+\beta_{Si}$ ).

The recorded cooling curves are given in Figure 1. The changes in eutectic temperatures as well as  $T_L$  and  $T_S$  are given in Table 2.

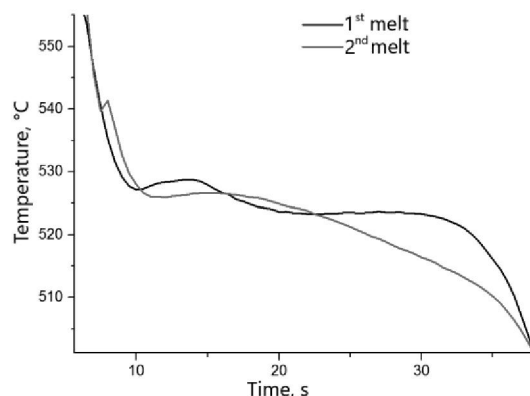


Table 2. Characteristic temperatures identified from the cooling curve given in Figure 1

Metl	$T_L$ , °C	$T_{Emin}$ , °C	$T_{Emax}$ , °C
1 <sup>st</sup>	578.73	527.23	527.75
2 <sup>nd</sup>	598.57	525.92	526.58

$\Delta T_{E_2}$ , °C	$T_{S_2}$ , °C	$\Delta T_{L-S_2}$ , °C	$\Delta t_{L-S_2}$ , °C
0.52	523.39	55.34	23.5
0.66	510.16	88.41	35.0

Figure 1. Cooling curves of 1<sup>st</sup> and 2<sup>nd</sup> synthesized alloys

The cooling curves of 1<sup>st</sup> and 2<sup>nd</sup> melt indicate a similar behaviour in eutectic region characterised by undercooling and following recalcescence.

The solidification of the 1<sup>st</sup> melt began at  $T_L$  of 578.73°C. Nucleation of eutectic ( $\alpha_{Al} + \beta_{Si}$ ) started at  $T_{Emin}$  of 527.23°C followed by the increase of the eutectic growth temperature to  $T_{Emax}$  (527.75°C). Nucleation of eutectic caused recalcescence  $\Delta T_E$  of 0.52°C. Solidification ended at  $T_S$  of 523.39°C with cooling rate of 2.35°C/s. Solidification sequence of the 2<sup>nd</sup> melt began at  $T_L$  of 598.57°C followed by reaction at  $T_{Emin}$  of 525.92°C and recalcescence  $\Delta T_E$  of 0.66°C. Solidification ended at  $T_S$  of 510.16°C with cooling rate of 2.53°C/s. Compared to Na, Sr additions widened solidification interval and lowered the temperatures of eutectic reaction and growth.

Microstructure of 1<sup>st</sup> and 2<sup>nd</sup> melt at magnification of 200 X is given in Figure 2.

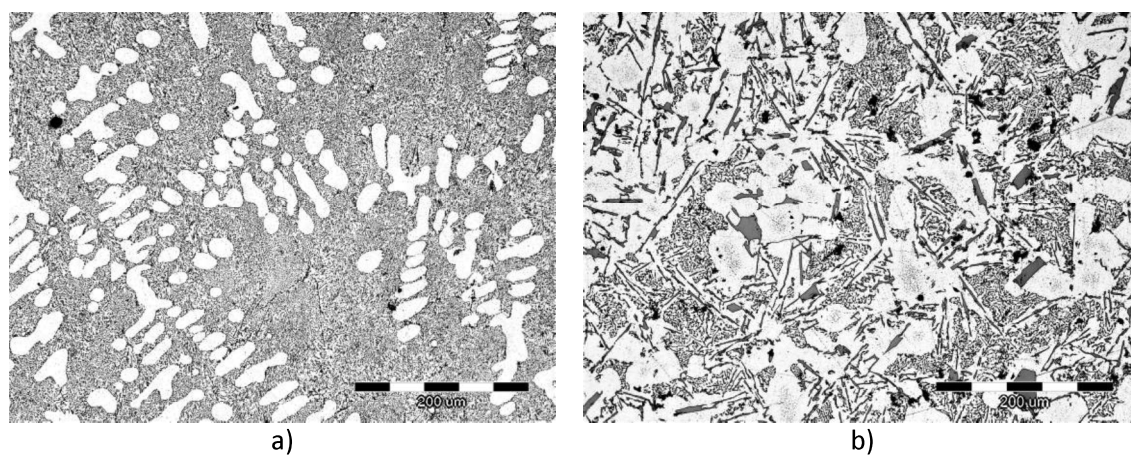


Figure 2. Microstructure of: a) 1<sup>st</sup> melt modified with Na, b) 2<sup>nd</sup> melt modified with Sr

Microstructure of the 1<sup>st</sup> melt consists of primary  $\alpha_{Al}$  dendritic network and fully modified fiber eutectic ( $\alpha_{Al} + \beta_{Si}$ ). Microstructure of 2<sup>nd</sup> melt, modified with Sr consists from primary  $\alpha_{Al}$  dendrites, with plates of primary  $\beta_{Si}$  and unmodified lamellar eutectic  $\beta_{Si}$  phase in interdendritic spaces and finally surrounded by modified fibrous eutectic  $\beta_{Si}$  phase.

The Scanning Electron Image (SEI) and following EDS analysis for synthesized alloys are given in Figure 3. The Na and Sr exhibit different distribution behaviour, as indicated by EDS analysis. Compared to Sr (0.42 mas.%), Na exhibits higher solid solubility in  $\alpha_{Al}$  dendrites (1.47 mas.%).

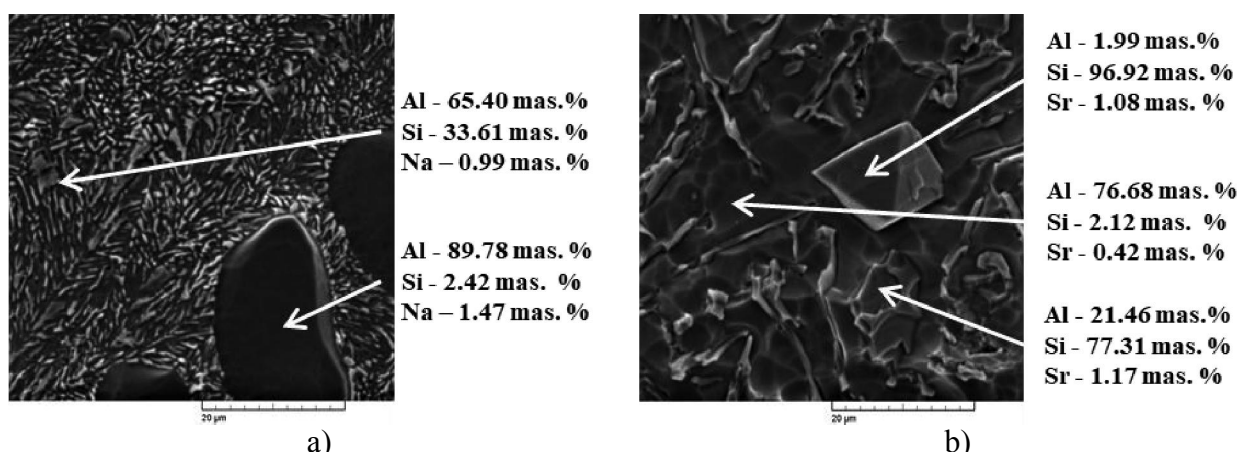


Figure 3. SEI and following EDS analysis for a) 1<sup>st</sup> melt modified with Na, b) 2<sup>nd</sup> melt modified with Sr. The highest amounts of Sr was measured at the unmodified eutectic  $\beta_{Si}$  phase (1.17 mas. %).

#### 4. CONCLUSION

The influence of Na and Sr addition on eutectic ( $\alpha_{Al}+\beta_{Si}$ ) modification was analyzed. Based on the results of STA, Sr additions widened solidification interval and lowered temperatures of eutectic reaction and growth. However, results of metallographic analysis indicated full eutectic ( $\alpha_{Al}+\beta_{Si}$ ) modification only in Na modified melts. Microstructure of Sr modified melts consisted of plates of primary  $\beta_{Si}$  phase and partially modified eutectic ( $\alpha_{Al}+\beta_{Si}$ ). The influence of Sr on solidification interval and characteristic temperatures results from insufficient branching at eutectic  $\beta_{Si}$  phase growth surfaces, despite high Sr content detected in unmodified eutectic  $\beta_{Si}$  phase (1.17 mas. %).

#### ACKNOWLEDGEMENTS

*Investigations were performed within the research topic "Design and Characterization of Innovative Engineering Alloys", Code: FPI-124-2019-ZZB funded by University of Zagreb within the Framework of Financial Support of Research, scientific-research project within Croatian-Slovenian collaboration "Design and Characterization of Innovative Aluminum - Magnesium - Lithium alloy (2018-2019) funded by Ministry of Science and Education and infrastructural scientific project: Center for Foundry Technology, Code: KK.01.1.1.02.0020 funded by European Regional Development Fund, Operational programme Competitiveness and cohesion 2014 - 2020.*

#### REFERENCES

- [1] A. K. Dahle, K. Nogita, S. D. McDonald, C. Dinnis, L. Lu., *Materials Science and Engineering*, 413-414 (1) A (2005) 243-248.
- [2] K. Nogita, S. D. McDonald, A. K. Dahle., *Materials Transactions*, 45 (2) (2004) 323-326.
- [3] S. Hegde, K. N. Prabhu., *Journal of Materials Science*, 43 (2008) 3009-3027.
- [4] J. H. Li, X. D. Wang, T. H. Ludwig, Y. Tsunekawa, L. Arnberg, J. Z. Jiang, P. Schumacher., *Acta Materialia*, 84 (1) (2015) 153-163.
- [5] J. H. Li, J. Barrirero, M. Engstler, H. Aboufadel, F. Mucklich, P. Schumacher., *Metallurgical and Materials Transactions A*, 46 A (2015), 1300-1311.
- [6] M. Zarif, B. McKay, P. Schumacher., *Metallurgical and Materials Transactions A*, 42 A (2011) 1684-1691.
- [7] M. Timpel, N. Wanderka, R. Schlesiger, T. Yamamoto, N. Lazarev, D. Isheim, G. Schmitz, S. Matsumura, J. Banhart., *Acta Materialia*, 60 (2012) 3920-3928.
- [8] S. Lu, A. Hellawell., *Metallurgical Transactions A*, 18 A (1987) 1721-1733.
- [9] S. C. Food, J. D. Hunt., *Metal Science*, 15 (1981) 287-293.
- [10] S. Farahany, A. Ourdjini, M. H. Idris., *Journal of Thermal Analysis and Calorimetry*, 109 (2012) 105-111.