

I. Naglič<sup>1</sup>, S. Ilič<sup>2</sup>, B. Markoli<sup>1</sup>, M. Dolenc<sup>3</sup>, B. Leskovar<sup>1</sup>, Ž. Filipič<sup>1</sup>, M. Perhoč<sup>1</sup>, J. Kraner<sup>1</sup>, M. Bizjak<sup>1</sup>, B. Skela<sup>1</sup>, L. Kelhar<sup>3</sup>, Š. Kozole<sup>1</sup>, D. Gerčar<sup>1</sup>, T. Ramšak<sup>1</sup>

<sup>1</sup> Univerza v Ljubljani, Naravoslovnotehniška fakulteta / University of Ljubljana, Faculty of Natural Sciences and Engineering, Aškerčeva cesta 12, 1000 Ljubljana, Slovenija / Slovenia

<sup>2</sup> Livarstvo Krim d.o.o., Dolenjska cesta 83, 1000 Ljubljana, Slovenija / Slovenia

<sup>3</sup> Mednarodna podiplomska šola Jožefa Stefana / Jožef Stefan International Postgraduate School, Jamova 39, 1000 Ljubljana, Slovenija / Slovenia

## **Modifikacija zlitine AlSi7Mg lite v peščeno formo**

## **Modification of AlSi7Mg alloy cast in to a sand mould**

### **Povzetek**

Ocenjevali smo vpliv komercialnih modifikatorjev na osnovi stroncija in natrija (SIMODAL 77) na ulitke zlitine AlSi7Mg, ulite v peščene kokile. Pripravili smo ulitke z različnimi debelinami stene ulitka z namenom ugotavljanja vpliva ohlajevalne hitrosti. Vpliv modifikacije na evtektski silicij smo ugotavljali z metodo svetlobne mikroskopije. Evtektski silicij v ulitkih zlitine AlSi7Mg z debelinami sten 10 in 20 mm je modificiran v primeru dodatka 0,3 mas. % sredstva SIMODAL 77 oziroma dodatka med 0,02 in 0,03 mas. % stroncija. Pri ulitku z debelino stene 40 mm evtektski silicij ni bil popolnoma modificiran. V primeru modifikacije s stroncijem je evtektski silicij ostal modificiran tudi po pretaljevanju zlitine. Pri modifikaciji z natrijem v obliki sredstva SIMODAL 77 pa ostane po pretaljevanju evtektski silicij nemodificiran.

**Ključne besede: aluminijeva zlitina, litje, modifikacija, mikrostruktura**

### **Abstract**

In this work the effect of commercial strontium and sodium (SIMODAL 77) modifiers in sand cast AlSi7Mg alloy were evaluated. Castings with different wall thickness were prepared to evaluate the effect of modifiers at different cooling rates. Light microscopy was used to assess the effect of eutectic silicon modification. It was found that 0.3 % (mass fraction in this article) of modifier SIMODAL 77 and between 0.02 and 0.03 % Sr effectively modified the eutectic silicon in AlSi7Mg alloy castings with wall thickness of 10 and 20 mm. Eutectic silicon was not fully modified when the wall thickness was 40 mm. Eutectic silicon remained modified after remelting in the case of strontium whilst sodium from SIMODAL 77 failed in this respect.

**Keywords: aluminium alloy, casting, modification, microstructure**

### **1 Uvod**

Zlitine na osnovi Al-Si predstavljajo veliko in pomembno skupino aluminijevih livnih zlitin.

### **1 Introduction**

Cast Al-Si alloys represent a large and important group of aluminium alloys.

Aluminij s silicijem tvori enostavni evtektski sistem z evtektsko točko pri temperaturi 577 °C in 12,6 mas. % Si. Zaradi prisotnosti magnezija v zlitini AlSi7Mg se lahko takšna zlitina dodatno utrjuje z naravnim ali umetnim staranjem [1]. V zlitinah z več kot 5 mas. % Si dosežemo izboljšanje mehanskih lastnosti z modifikacijo evtektskega silicija. Modifikacijo evtektskega silicija iz lamelne oblike do drobne globulitne oblike, lahko dosežemo z hitrim ohlajanjem ali/in z dodajanjem nekaterih elementov, kot so npr. kalcij, natrij, stroncij in antimon [2]. Modifikacija evtektika povzroči znižanje evtektске temperature in premik evtektске točke do 14,1 mas. % Si [1]. Modifikacija evtektika zviša natezno trdnost in raztezek modificiranih zlitin glede na nemodificirane [3]. Poleg izboljšanih mehanskih lastnosti zlitine kažejo tudi izboljšane livne lastnosti. Te se odražajo predvsem v hitrejšem toku taline in napajanju livne votline ter v izboljšani odpornosti proti visoko temperaturnemu pokanju [2].

Cilj dela temelji na ovrednotenju vplivov komercialnih modifikatorjev, kot sta predzlitina Al-Sr10 (z 10 mas. % Sr) in sredstvo SIMODAL 77 (natrij), pri izbrani livni temperaturi, preteku časa od dodatka modifikatorja do litja in ohlajevalni hitrosti doseženi z različnimi debelinami sten ulitka.

## 2 Eksperimentalno delo

Peščene forme za ulivanje zlitine AlSi7Mg so bile utrjene s sistemom vodnega stekla in CO<sub>2</sub>. Dimenzije ulitka z debelinami sten 10, 20 in 40 mm so prikazane na sliki 1. Taljenje zlitine je potekalo v komorni peči pri temperaturi 750 °C. Masa taline posameznem taljenju je znašala okoli 1,4 kg. Kemijska sestava komercialne zlitine, ki smo jo uporabljali, je podana v tabeli

Aluminium and silicon form a simple eutectic system with eutectic point at 12.6 % Si and 577 °C. Due to the presence of magnesium, the AlSi7Mg casting alloy can be additionally strengthened by natural or artificial aging [1]. In alloys containing 5 % Si or more a great benefit can be achieved by structural modification of eutectic lamellae. Modification of eutectic silicon from lamellar to a finer lamellar or fibrous eutectic network can be achieved by rapid cooling or/and addition of certain elements like calcium, sodium, strontium and antimony [2]. This modification causes the lowering of eutectic temperature and a shift of the eutectic point to 14.1 % Si [1]. Modification of eutectic is a great benefit since the alloys with modified eutectic silicon possess increased ultimate tensile strength and elongation compared to unmodified alloys [3]. Beside improved mechanical properties, modified alloys also display better casting performance. This is characterized by faster flow and feeding of the casting cavity and also superior resistance to elevated-temperature cracking [2].

The aim of this work was to evaluate the effect of commercial modifiers like Al-Sr10 (with 10 % Sr) and SIMODAL 77 (sodium) in selected conditions like temperature of the melt prior to casting, time after addition of the modifier and the cooling rate achieved by variations in wall thickness of the castings.

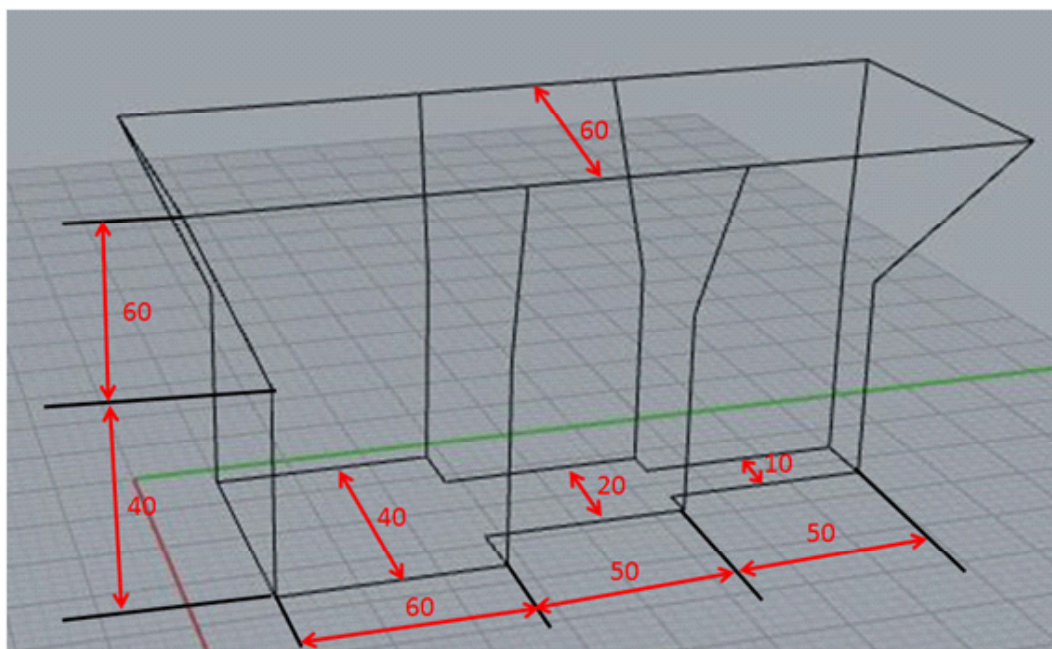
## 2 Experimental work

Sand moulds for the casting of the AlSi7Mg alloy were prepared via the sodium silicate process. Dimensions of the mould with different wall thicknesses of 10, 20 and 40 mm are presented in Figure 1. Melting of the alloy was performed in a chamber furnace at the temperature of 750 °C and weight

1. Zlitino smo ulili 15 minut po dodatku modifikatorja v talino. Kot modifikatorja smo uporabljali stroncij, v obliki predzlitine Al-Sr10 (z 10 mas. % Sr) in natrij v obliki sredstva SIMODAL 77. Pri dodajanju stroncija smo talino intenzivno mešali. V primeru dodajanja sredstva SIMODAL 77 (natrij), pa smo uporabili jekleno posodo z izvrtinami tako, da smo lahko kos tablete sredstva potopili v talino. Pretaljevanje izbranih zlitin je prav tako kot modificiranje potekalo pri temperaturi 750 °C. Talina je bila pri pretaljevanju zadržana na tej temperaturi približno 60 min in nato ulita v livno votlino.

Metalografski vzorci so bili odvzeti iz osrednjega dela stene ulitka debeline 10, 20 in 40 mm. Vzorci so bili nato vloženi v maso, brušeni in polirani s 3 µm diamantno pasto. Končno poliranje je potekalo s suspenzijo SiO<sub>2</sub>. Poliranju je sledilo jedkanje vzorcev z

of each batch was approximately 1.4 kg. Chemical composition of the commercial alloy which was used in this experiment is presented in Table 1. Casting of the alloy was performed 15 min. after the addition of modifier into the melt. Modifiers used in this work were strontium in the form of Al-Sr10 master alloy which contained 10.0 % Sr and sodium in the form of commercial modifying tablets SIMODAL 77. In the case of the addition of strontium, melt was mixed after the addition of master alloy. Addition of SIMODAL 77 (sodium) was carried out by a steel pot with drilled holes which was used to plunge the pieces of tablet into the melt. Remelting of some modified alloys was also performed at 750 °C and the melt was held for approximately 60 min. at that temperature before it was cast again. Metallographic samples were cut from the central region of the castings with 10,



**Slika 1:** Dimenzije ulitka z debelinami sten 10, 20 in 40 mm

**Figure 1:** Dimensions of casting with 10, 20 and 40 mm wall thickness

raztopino NaOH. Pri analizi mikrostrukture smo uporabljali svetlobni mikroskop ZEISS AXIO Imager A1m, opremljenim z digitalno kamero AxioCam ICc 3 in programsko opremo za zajemanje in obdelavo slik Axio Vision.

**Tabela 1:** Kemična sestava livne zlitine AlSi7Mg v mas. %

**Table 1:** Composition of cast AlSi7Mg alloy in % (mass fraction)

|                      | Al    | Si   | Fe   | Cu     | Mn     | Mg   | Zn   | Ti   |
|----------------------|-------|------|------|--------|--------|------|------|------|
| AlSi <sub>7</sub> Mg | 92,44 | 6,94 | 0,12 | < 0,01 | < 0,01 | 0,37 | 0,02 | 0,09 |

## 2 Rezultati in diskusija

Mikrostrukture ulitkov z debelinami sten 10, 20 in 40 mm, brez dodatka modifikatorja in z dodatkom sredstva SIMODAL 77 ter različnimi dodatki predzlitine Al-Sr10 so predstavljene na slikah 2-4. Analiza mikrostruktur je pokazala, da dodatek 0,3 mas. % sredstva SIMODAL 77 ustrezno modificira evtektik v primeru sten debeline 10 in 20 mm. Pri ulitku z debelino stene 40 mm (slika 4b) ostane evtektiski silicij še vedno deloma v obliki lamel. Sklepamo, da v takšnih primerih potrebujemo večje deleže modifikatorja za ustrezno modifikacijo evtektika.

Analize mikrostruktur ulitkov z debelino stene 10 in 20 mm so pokazale, da v primeru dodatka 0,005 mas. % Sr v obliki predzlitine Al-Sr10 evtektik ni v celoti modificiran, medtem ko je v primeru 0,01 in 0,02 mas. % Sr ta modificiran v celoti (slike 2-4). Analize mikrostruktur pri ulitkih z debelino stene 40 mm so pokazale, da v primeru dodatka 0,03 mas. % Sr v mikrostrukturi še vedno zasledimo prisotnost lamelnega evtektika (slika 4f). Prav tako lahko opazimo, da se mikrostrukturi zlitin z 0,02 in 0,03 mas. % Sr bistveno ne razlikujeta (slika 4e in 4f). Na

20 and 40 mm thick wall. Samples were mounted, ground and polished with 3  $\mu$ m diamond paste. Final polishing was done with colloidal silica. Samples were also etched with NaOH right after the polishing. Light microscopy was performed using ZEISS AXIO Imager.A1m equipped with digital camera AxioCam ICc 3 and software for digital image processing Axio Vision.

## 2 Results and Discussion

Microstructures of castings with 10, 20 and 40 mm wall thickness without the addition of modifier and with the addition of SIMODAL 77 and different additions of Al-Sr10 are presented in Figures 2-4. Microstructures reveal that the addition of 0.3 % of SIMODAL 77 (sodium) adequately modified the eutectic in the case of 10 and 20 mm thick wall while in the case of 40 mm thick wall (Figure 4b) some lamellar eutectic silicon was still present in the microstructure. This result suggests that larger quantity of modifier might be needed in cases like that.

Microstructures of castings with 10 and 20 mm wall thickness reveal that 0.005 % Sr in the form of Al-Sr10 master alloy was not sufficient to fully modify the eutectic while additions of 0.01 and 0.02 % Sr were, as presented in Figures 2-4. Microstructures in the case of the castings with 40 mm wall thickness revealed that even in the case of the addition of 0.03 % Sr lamellar eutectic was still present in the microstructure (Figure 4f). It is also obvious that microstructures of alloys with the addition of 0.02 and 0.03 % of strontium did not differ much from each other (Figure 4e and 4f). This might mean that larger quantities of modifier alone might not be sufficient to modify the eutectic silicon. It is known that strontium is effective even after several hours after it has been

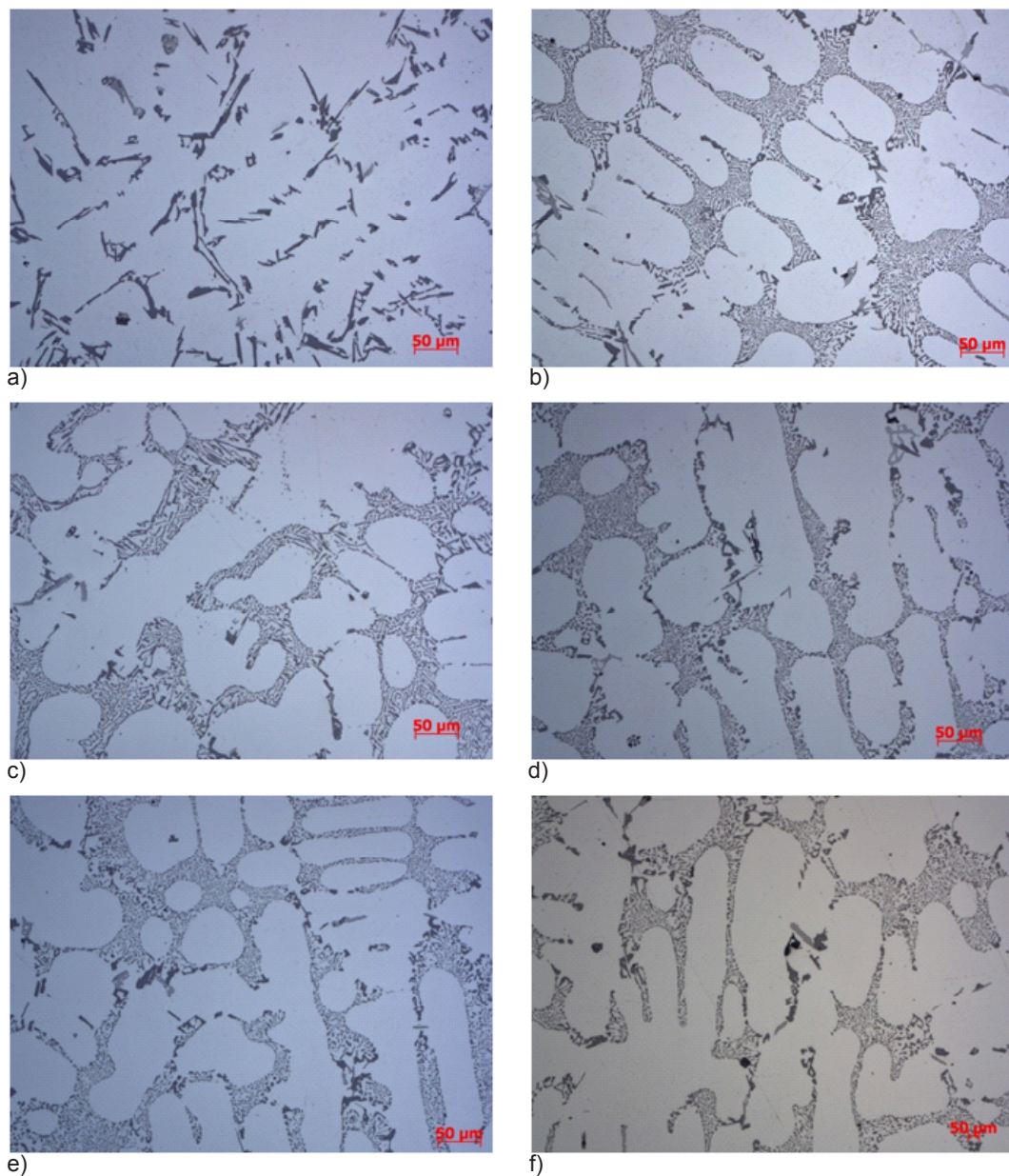
podlagi tega lahko sklepamo, da z dodatki večjega deleža modifikatorja verjetno tudi ne bomo ustrezno modificirali evtektkega silicija. Znano je, da je stroncij kot modifikator učinkovit še več ur po dodatku v talino. Njegova učinkovitost v odvisnosti od časa po dodatku v talino narašča še 6 h [3]. Glede na to, da smo zlitino ulivali 15 min po dodatku modifikatorja, obstaja verjetnost, da bi daljši časi zadrževanja taline po dodatku večjih deležev stroncija lahko vodili do bolj učinkovite modifikacije. Obstajajo tudi predzlitine s 5 mas. % Sr in 3,5 mas. % Sr. Predzlitine z manjšim deležem stroncija so lahko bolj učinkovite v primeru kratkih časov po dodatku modifikatorja v talino, ker so verjetno delci s stroncijem bogate intermetalne faze v teh zlitinah manjši. Dokazano je bilo, da je modifikator Al-Sr10 v obliki žice z manjšimi delci intermetalnih faz  $Al_4Sr$  učinkovitejši pri krajših časih po dodatku sredstva v talino kot modifikator Al-Sr10 v obliki blokov, kjer so intermetalne faze  $Al_4Sr$  večje [4]. Delci intermetalne faze  $Al_4Sr$  v modifikatorju se morajo raztopiti v talini zlitine, kar je predpogoj za učinkovitost modifikatorja. Večji delci se za razliko od manjših raztapljajo dlje časa. Stroncij, raztopljen v talini, se mora enakomerno porazdeliti po talini, kar omogoča učinkovito modifikacijo evtektkega silicija. Zelo pomembno je zato tudi mešanje taline, ki poleg tega tudi prepreči kopičenje stroncija v bližini raztapljajoče intermetalne faze  $Al_4Sr$ , kar bi lahko povzročilo počasnejše raztapljanje te faze.

Na sliki 5 so predstavljene mikrostrukture ulitkov zlitine AlSi7Mg z debelino stene 10 mm brez dodatka modifikatorja in z dodatkom 0,02 mas. % Sr in 0,3 mas. % sredstva SIMODAL 77. Na tej sliki sta predstavljeni tudi mikrostrukture prej omenjenih zlitin (z dodatkom stroncija in sredstva SIMODAL 77) po pretaljevanju. Analiza mikrostrukture kaže, da

added to the molten alloy. Effect of strontium is still increasing six hours after the addition of modifier [3]. As our alloys were cast only 15 min. after the addition of modifier, longer times after the addition of larger quantities of strontium would most likely lead to a more pronounced modification. It should also be mentioned that master alloys with lower content of strontium, like master alloys with 5 and 3.5 % are also available in the market. Those might be more effective even at short times after the addition of modifier since particles of strontium-rich intermetallic phases within those modifiers probably have smaller mean diameter. It was already demonstrated that Al-Sr10 master alloy is more effective at short times when added as wire (smaller  $Al_4Sr$  phases) than in the form of ingot as  $Al_4Sr$  phases are larger [4]. For the effectiveness of these master alloys intermetallic particles present in these alloys must dissolve in the molten Al-based alloy. Larger particles need more time to dissolve than the smaller ones. Strontium from dissolved  $Al_4Sr$  phase for instance should also be evenly distributed in the melt to enable effective modification of eutectic silicon. Consequently mixing of the melt is also of a great importance since it prevents local build-ups of strontium in the vicinity of the dissolving  $Al_4Sr$  phase which in turn slows down its dissolution.

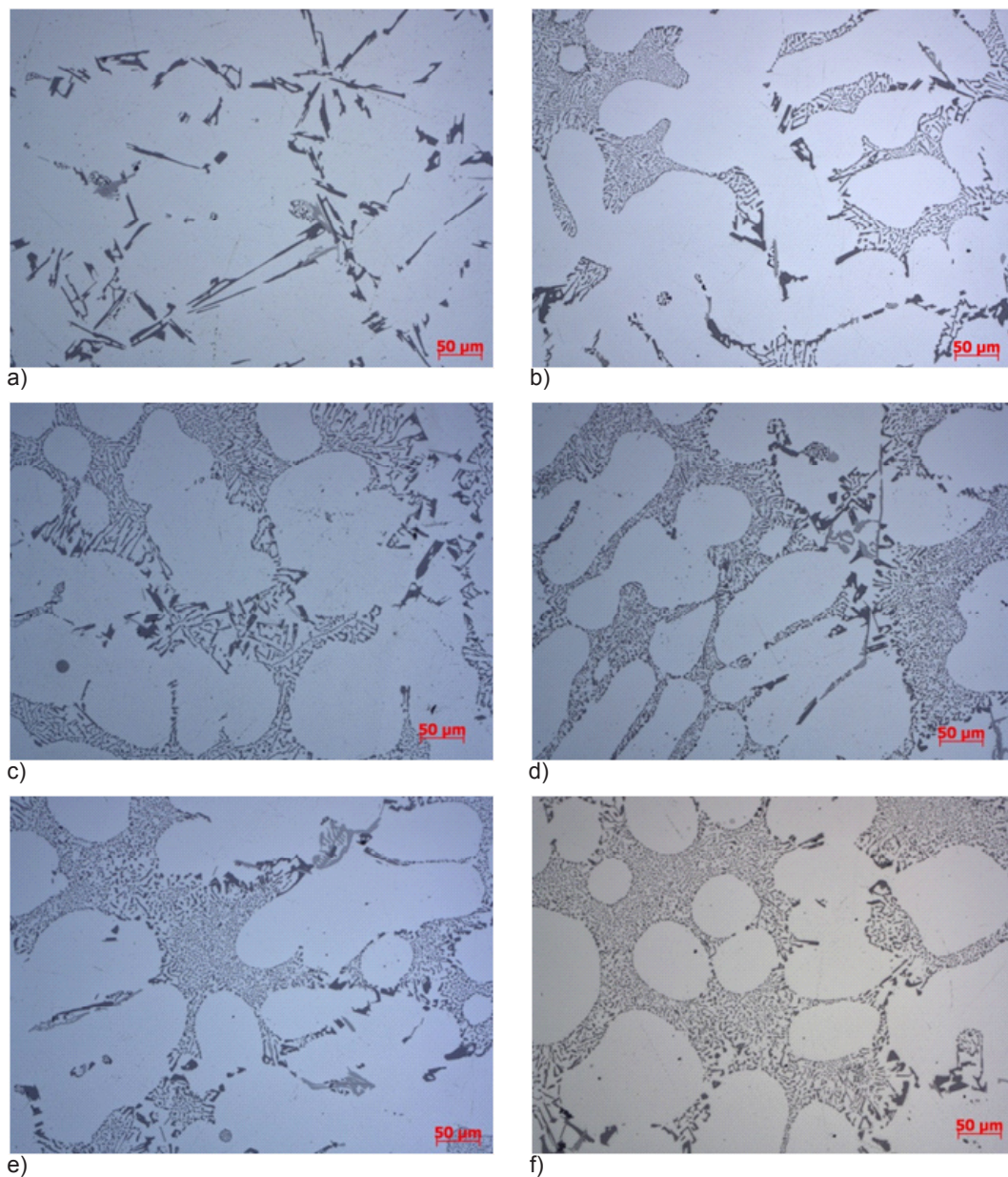
Figure 5 has the microstructures of casting with wall thickness 10 mm of alloy AlSi7Mg without and with the addition of 0.02 % Sr and 0.3 % of SIMODAL 77. Microstructures of remelted samples containing strontium and sodium (SIMODAL 77) are also presented in this figure. Microstructure revealed that remelting of strontium-modified AlSi7Mg alloy did not affect the modification effect. Microstructure of remelted sample previously modified with strontium (Figure 5d) is similar to the one before remelting (Figure 5b). Remelting of





**Slika 2:** Mikrostruktura zlitine AlSi7Mg z debelino stene 10 mm a) brez in z dodatkom b) 0,3 mas. % sredstva SIMODAL 77, c) 0.005 mas. % Sr, d) 0.01 mas. % Sr, e) 0.02 mas. % Sr in f) 0.03 mas. % Sr v obliki predzlitine Al-Sr10

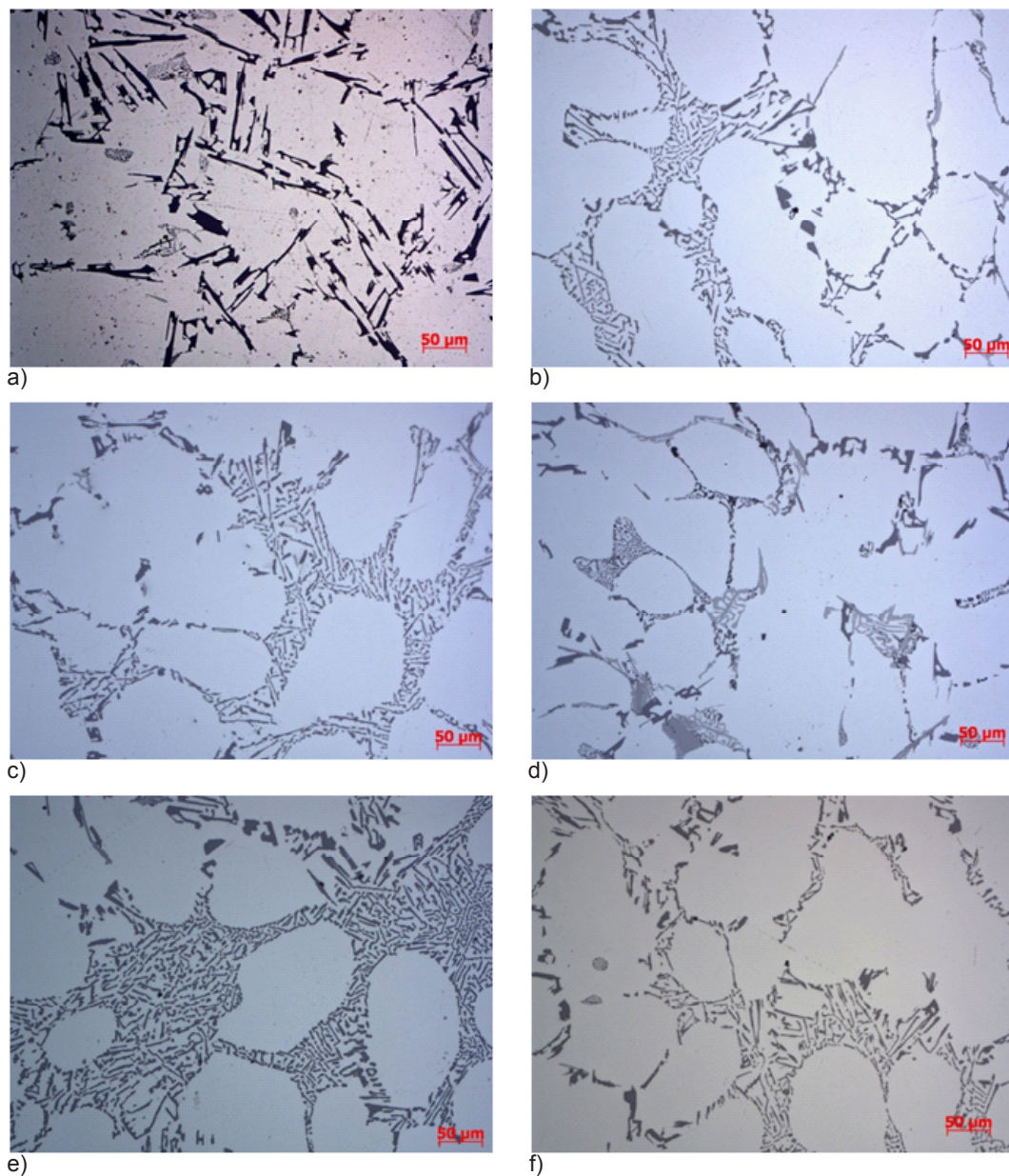
**Figure 2:** Microstructure of AlSi7Mg alloy with 10 mm wall a) without and with addition of b) 0.3 % of SIMODAL 77, c) 0.005 % Sr, d) 0.01 % Sr, e) 0.02 % Sr and f) 0.03 % Sr in the form of Al-Sr10 master alloy



**Slika 3:** Mikrostruktura zlitine AlSi7Mg z debelino stene 20 mm a) brez in z dodatkom b) 0,3 mas. % sredstva SIMODAL 77, c) 0.005 mas. % Sr, d) 0.01 mas. % Sr, e) 0.02 mas. % Sr in f) 0.03 mas. % Sr v obliki predzlitine Al-Sr10

**Figure 3:** Microstructure of AlSi7Mg alloy with 20 mm wall a) without and with addition of b) 0.3 % of SIMODAL 77, c) 0.005 % Sr, d) 0.01 % Sr, e) 0.02 % Sr and f) 0.03 % Sr in the form of Al-Sr10 master alloy

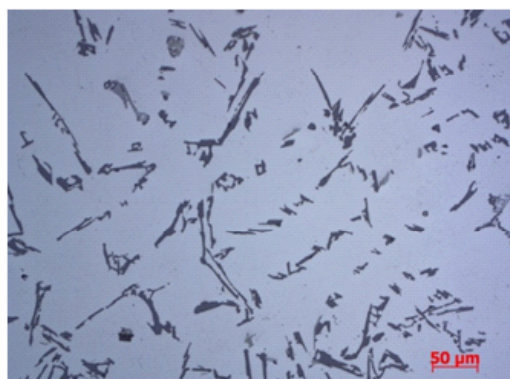




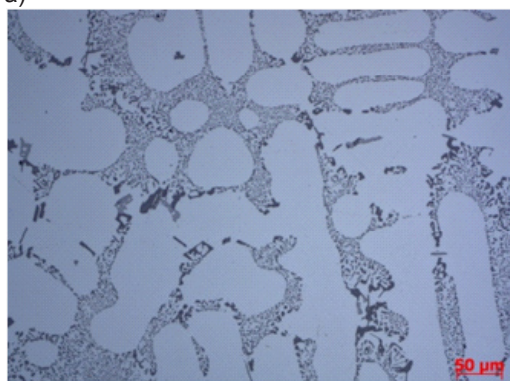
**Slika 4:** Mikrostruktura zlitine AlSi7Mg z debelino stene 40 mm a) brez in z dodatkom b) 0,3 mas. % sredstva SIMODAL 77, c) 0.005 mas. % Sr, d) 0.01 mas. % Sr, e) 0.02 mas. % Sr in f) 0.03 mas. % Sr v obliki predzlitine Al-Sr10

**Figure 4:** Microstructure of AlSi7Mg alloy with 40 mm wall a) without and with addition of b) 0.3 % of SIMODAL 77, c) 0.005 % Sr, d) 0.01 % Sr, e) 0.02 % Sr and f) 0.03 % Sr in the form of Al-Sr10 master alloy

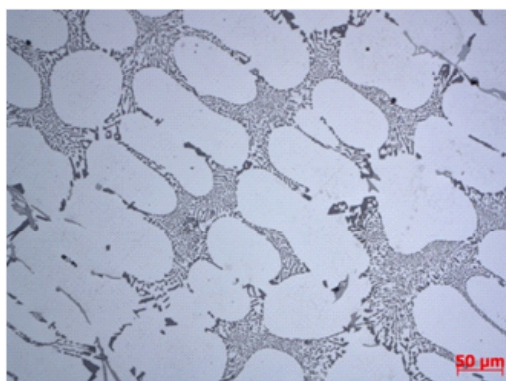




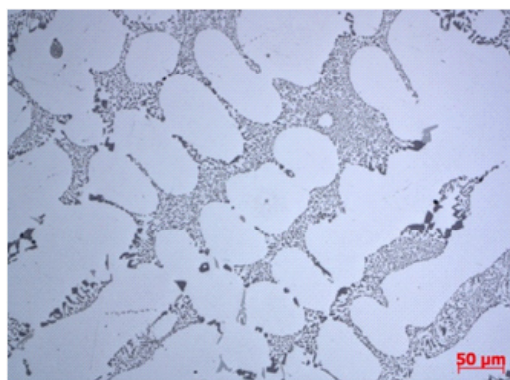
a)



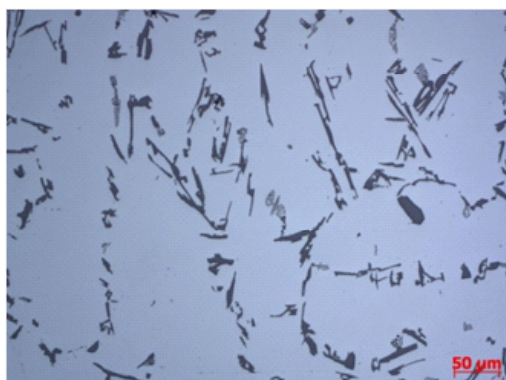
b)



c)



d)



e)

**Slika 5:** Mikrostruktura zlitine AlSi7Mg z debelino stene 10 mm a) brez dodatka modifikatorja in b) z dodatkom 0,02 mas. % Sr, c) z dodatkom 0,3 mas. % sredstva SIMODAL 77 ter d) po pretaljevanju zlitine z dodatkom 0,02 mas. % Sr in e) po pretaljevanju zlitine z dodatkom 0,3 mas. % sredstva SIMODAL 77

**Figure 5:** Microstructure of of AlSi7Mg alloy with 10 mm wall a) without the addition of modifier and b) after the addition of 0.02 % Sr, c) after the addition of 0.3 % of SIMODAL 77 and d) after remelting of sample with the addition of 0.02 % Sr and e) after remelting of sample with the addition of 0.3 % of SIMODAL 77

pretaljevanje zlitine AlSi7Mg, modificirane s stroncijem (slika 5d), nima vpliva na modifikacijo. Mikrostruktura pretaljene zlitine z dodatkom stroncija je enaka mikrostrukturi zlitine pred pretaljevanjem (slika 5b). Mikrostruktura pretaljene zlitine modificirane z natrijem (SIMODAL 77) kaže, da je učinek modifikacije po pretaljevanju izgubil (slika 5e). Najverjetnejši razlog za izgubo učinka je nizko vrelišče natrija, ki ima pri temperaturi 892 °C parcialni tlak 105 Pa [5]. Mikrostruktura pretaljenega vzorca modificiranega z natrijem je popolnoma enaka mikrostrukturi vzorca brez dodatka modifikatorja (slika 5a). Na podlagi tega lahko sklepamo, da v primeru recikliranja zlitin s stroncijem, dodatno modificiranje ni potrebno. Pri pretaljevanju zlitin modificiranih z natrijem, pa potrebujemo enako količino modifikatorja, kot pri nemodificirani zlitini, da dosežemo popolno modifikacijo evtektškega silicija.

### 3 Zaključki

Ugotovljeno je bilo, da 0,3 mas. % sredstva SIMODAL 77 učinkovito modificira evtektski silicij v ulitkih zlitine AlSi7Mg s stenami debelin 10 in 20 mm. V primeru ulitka z debelino stene 40 mm pa v mikrostrukturi še vedno opazimo lamelni evtektik. Mikrostrukture ulitkov zlitine AlSi7Mg z debelinami sten 10 in 20 mm so pokazale, da je za učinkovito modifikacijo evtektškega silicija zadosten dodatek med 0,01 in 0,02 mas. % Sr. Pri ulitku z debelino stene 40 mm, pa tudi 0,03 mas. % Sr ni dovolj za popolno modifikacijo evtektškega silicija. Učinek modifikacije ulitkov zlitine AlSi7Mg modificirane s sredstvom SIMODAL 77 (natrij) po pretaljevanju popolnoma izgine. Pri modificiranju ulitkov zlitine AlSi7Mg s stroncijem pa učinek po pretaljevanju ostane nespremenjen. Natrij je po pretaljevanju

the sample with the addition of SIMODAL 77, which contained sodium as modifier revealed that the effect of modification was completely lost after remelting (Figure 5e). Most probable reason for this is its low boiling point with partial pressure of 105 Pa at 892 °C [5]. Microstructure of remelted sample modified with sodium is comparable to the one without the addition of modifier (Figure 5a). This suggests that in the case of recycling of strontium modified material no additional modifier is needed. During the remelting of material originally modified with sodium the same amount of sodium containing modifier is needed to induce the modification of eutectic silicon.

### 3 Conclusions

It was found that 0.3 % of modifier SIMODAL 77 effectively modifies the eutectic silicon in AlSi7Mg alloy castings with wall thickness of 10 and 20 mm. In the case of 40 mm wall thickness lamellar eutectic is still present in the microstructure. Microstructures of AlSi7Mg alloys with the addition of strontium revealed that 0.01 and 0.02 wt. % Sr is sufficient to eliminate the lamellar eutectic silicon in the case of the 10 and 20 mm wall thickness. In the case of the casting with wall thickness 40 mm 0.03 % Sr is not enough to fully modify the microstructure. Remelting of AlSi7Mg alloys with the addition of strontium and SIMODAL 77 (sodium) revealed that modification effect is in the case of SIMODAL 77 completely lost while in the case of the strontium the effect remained unchanged. Sodium is ineffective due to its low evaporation temperature and inability to form intermetallic phases with aluminium and silicon.

neučinkovit kot modifikator zaradi nizke temperature vrelišča in nezmožnosti tvorbe intermetalnih faz z aluminijem in silicijem.

### Zahvala

Avtorji se zahvaljujejo Javnemu skladu Republike Slovenije za razvoj kadrov in štipendij za finančno podporo tega dela v okviru razpisa »Po kreativni poti do praktičnega znanja«.

### Acknowledgements

Authors would like to acknowledge the financial support of Slovene Human Resources and Scholarship Fund under the call »Po kreativni poti do praktičnega znanja«.

### Literatura / References

- [1] Springer Handbook of Condensed Matter and Materials Data, W. Martienssen and H. Warlimont (Eds.), Springer Berlin Heidelberg 2005
- [2] ASM Handbook, Vol. 2, Properties and Selection: Nonferrous Alloys and Special-Purpose Materials, K. M. Zwilsky and E. L. Langer, ASM International, 1992
- [3] ASM Handbook, Vol. 15, Casting, D.M. Stefanescu, ASM International, 1992
- [4] B. Stunova and M. Lunak, Al<sub>4</sub>Sr particle sizes and morphology influence on modification of Al-Si alloys. 19th International Conference on Metallurgy and Materials, Roznov pod Radhostem, Czech Republic, 2010
- [5] ASM Handbook, Vol. 4, Heat Treating, S. M. Copley and E. L. Langer, ASM International, 1991