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FORMATION OF AlFeSi PHASE IN AlSi12 ALLOY WITH Ce ADDITION

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Preliminary Note – Prethodno priopćenje

The influence of cerium addition on the solidification sequence and microstructure constituents of the Al-Si alloys with 12,6 mass % Si was examined. The solidification was analyzed by a simple thermal analysis. The microstructures were examined with conventional light and scanning electron microscopy. Ternary AlSiCe phase was formed in the Al-Si alloys with added cerium during the solidification process. AlSiCe and β-AlFeSi phases solidified together in the region that solidified the last. Cerium addition influenced on the morphology of the α-AlFeSi phase solidification.

Key words: Al-Si alloys, cerium, β-AlFeSi phase

Obrazovanje faze AlFeSi u slitini AlSi12 sa dodatkom cera. Ispitan je utjecaj dodatka cera na tijek skrućivanja i oblikovanje mikrostrukture u Al-Si slitini s 12,6 mas. % Si. Skrućivanje je praćeno s jednostavnom toplinskom analizom. Mikrostrukture su kvantificirane pomoću svjetlosnog i elektronskog mikroskopa. Pri skrućivanju Al-Si slitine sa dodatkom Ce, obrazuju se faze Al-SiCe, AlSiCe te β-AlFeSi, koje se skrućivaju zajedno u završnom području skrućivanja. Dodatak Ce utječe na morfologiju skrućivanja faze α-AlFeSi.

Ključne riječi: Al-Si slitine, cer, AlFeSi- β faza

INTRODUCTION

Iron represents main impurity element in aluminium alloys that arises during manufacturing of primary aluminium via the Bayer Process and the Hall-Héroult electrolytic reduction process. Another source of iron in aluminium can be scrap of metallurgical aluminium [1].

In some alloys iron is added as an alloying element to increase hardness but it also increases the brittleness of the alloy.

Solubility of iron in solid aluminium is very low and amounts 0,04 mass % at 625 °C [2]. Therefore iron forms intermetallic phases. Depending on the chemical composition and solidifications conditions the microstructure of Al-Si alloys the following intermetallic phases can contain: α-Al_8Fe_2Si, β-Al_5FeSi and δ-Al_9FeSi_2 as primary crystallized phases.

Most often precipitated phase in Al-Si alloys is the β-Al_5FeSi. Table 1 shows typical phases with iron and other alloying elements in Al-Si alloys and Figure 1 some micrographs of iron containing phases. β- Al_5FeSi phase has negative influence on the mechanical properties. Needles of these phase has notch effect in the microstructure. Along β-Al_5FeSi needles cracks can appear (Figure 2) [3].

Reference [4] reported that with increasing cerium content in in-situ Mg_2Si/Al-Si-Cu composite, the morphology of primary Mg_2Si particles changed from dendritic to polygonal shape. The eutectic Mg_2Si phase changed from flake-like to chrysanthemum-like. Cerium addition have also influence on the solidification of primary β_{Si} and on (α_{Al} + β_{Si}) eutectic. The refinement of primary β_{Si} and of (α_{Al} + β_{Si}) eutectic with cerium addition can be achieved [5].

Voncina [6] reported that the morphology of eutectic Al_2Cu-θ phase changed from »crumbled« to fully form with addition of 0,05 mass % Ce to the AlSi10Cu3 alloy.

EXPERIMENTAL

Basic alloys with 12,6 mass % Si were prepared by mixing hypereutectic Al-Si alloy with 26 mass % Si and 99,7 % pure Al.

Alloys were prepared by melting in an electric resistance furnace in graphite crucible with capacity of 1 kg. Cerium was added as 99,9 % pure metal. Cerium was added to melt at 750 °C. After manual stirring, slag removing and holding time of 20 minutes, melts were cast into sand measuring cells for the simple thermal analysis.

Using Thermo-Calc program all the thermodynamically possible equilibrium phases that can exist at defined conditions were calculated and equilibrium binary phase diagrams were constructed. Data base COST 507 was used for the equilibrium calculations. With this program composition of microstructure constituents could be predicted.

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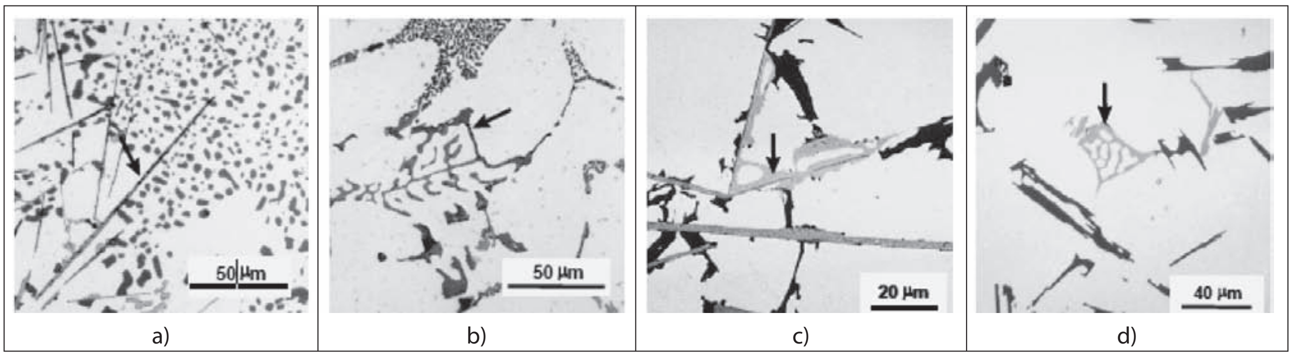


Figure 1 Photomicrographs of iron-containing intermetallic phases in Al-5%Si-1%Cu-0,5%Mg-(Fe) alloys: β-Al_5FeSi plateles (a), script-like α-Al_8Fe_2Si (b), π-phase growing from β (c), script-like π-phase (d). [1]

Table 1 **Binary and multi-component phases with iron and other alloying elements. [7]**

Phase	Chemical composition / mass %
$Al_{13}Fe_4$ (Al_3Fe)	Fe: 33,9-37,8 Si: 0,8-2,9
Al_6Fe	Fe: 25,6-28,0
β-Al_5FeSi	Fe: 23,5-30,0 Si 12,0-18,9
β-$Al_{4,5}FeSi$ ($Al_9Fe_2Si_2$)	Fe: 27,0-28,0 Si 14,0-15,0
γ-Al_3FeSi	Fe: 33,0-38,0 Si: 13,0-18,5
δ-Al_9FeSi_3	Fe: 15,0-25,4 Si: 20,0-25,5
α-Al_8Fe_2Si	Fe: 28,2-31,6 Si: 7,9-10,5
$Al_9Fe_{0,84}Mn_{2,16}Si$	Fe: 10,7; Si: 6,44 Mn: 27,2
π-$Al_8Si_6Mg_3Fe$	Fe: 8,0; Si: 25,0-33,8; Mg:13,0-16,0
α-Al_{12-15}(Fe, Mn, Me)$_3Si_{1-2}$ Me=(Cr,Cu)	Fe: 8,6-30,7; Si: 4,5-12,5; Mn: 0,52-14,0; Cu: to 7,5; Cr: to 14,4
α-Al_{12-25}(Fe,Me)$_{2-3}Si_{2-4}$, Me=(Mn,Cr,Cu,Co,Ni)	Fe: 6,3-25,2; Si: 4,6-10,0; Mn: to 13,1; Cu: to 13,0; Cr: to 14,4; Co: to 20,1; Ni: to 26,8

Thermal analysis is an excellent tool for the determination of the characteristic temperatures, fractions of solids, and of latent heat in the solidification process.

Samples for microstructural analysis with light and electron microscope were prepared by standard methods of grinding, polishing and final etching.

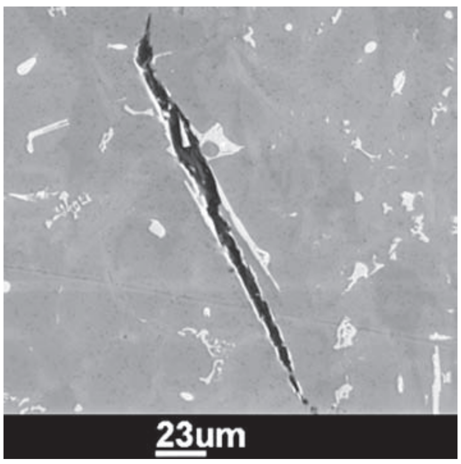


Figure 2 Crack along Al_5FeSi-β needle. [8]

RESULTS AND DISCUSSION

Basic AlSi12 alloy was chemically analyzed using specimens of simple thermal analyses. Table 2 show chemical composition of examined alloy.

Based on equilibrium thermodynamic calculations with Thermo-Calc program, solidification of the AlSi12 alloy should commence with precipitation of the Si_2Ti phase and then continue with the solidification of primary silicon followed by solidification of the ($\alpha_{Al} + \beta_{Si}$) eutectic, β-AlFeSi phase and α-AlMnSi phase.

Table 2 **Chemical composition of examined alloys.**

	Element / mass %							
Alloy	Si	Fe	Mn	Mg	Cu	Ti	Ce	Al
AlSi12	12,89	0,122	0,003	0,001	0,001	0,006	1,035	rest

Solidification of the alloys with 1 mass % Ce should be characterized by simultaneous solidification of β-AlFeSi and $Al_{11}Ce_3$ phases. Phases like Mg_2Si, Al_6Mn and Al_2Cu-θ should precipitate at lower temperatures. The presence of these phases however is not very likely since the contents of copper, manganese and magnesium are well below the solubility in the α_{Al} matrix.. Figure 3 shows calculated equilibrium phase diagram of Al-Si alloy without (a) and with 1 mass % Ce (b).

Figure 4 presents results of simple thermal analysis. Solidification of the AlSi12 alloy (Figure 4 a) commenced with precipitation of primary β_{Si} silicon phase at 580 °C and it progressed with formation of the (α_{Al} + β_{Si}) eutectic at 572 °C. Eutectic recalescence was 4 °C. At 565 °C the AlFeSi phase solidified. Solidification was completed at 555 °C. When cerium was added, solidification commenced at 570 °C with formation of the (α_{Al} + β_{Si}) eutectic (Figure 4 b). Eutectic recalescence was 4,5 °C. Solidification was completed at 554,5 °C.

Figure 5 a presents microstructure of the AlSi12 alloy. Microstructural components are the (α_{Al} + β_{Si}) eutectic and the β_{Si} primary silicon phase. Size of primary β_{Si} particles were between 20 – 46 µm. Addition of cerium (Figure 5b) coarsened the (α_{Al} + β_{Si}) eutectic. Primary β_{Si} particles are the same size as in the pure AlSi12 alloy. There was also an intermetallic phase present, which is supposed to be cerium-rich phase.

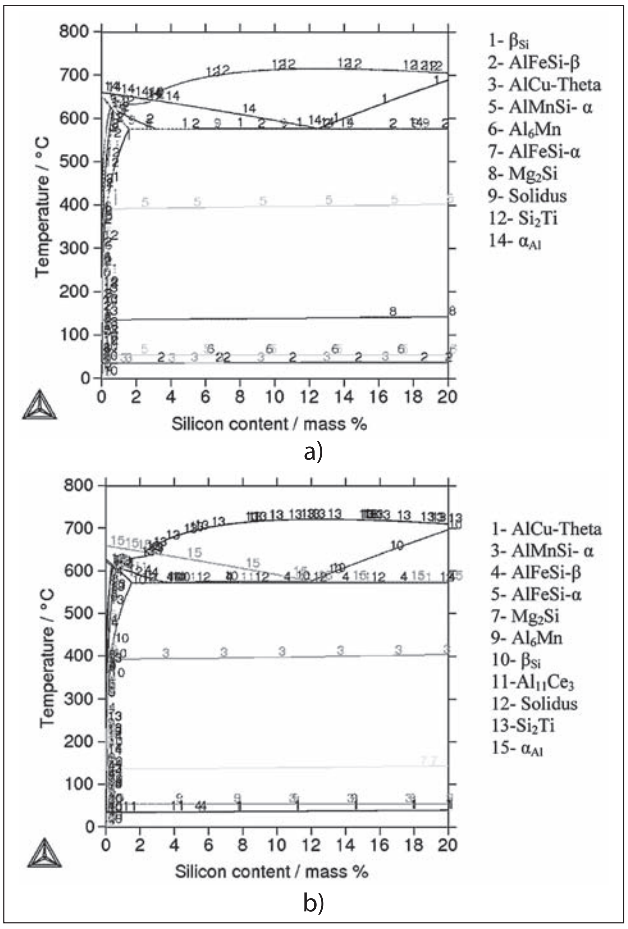


Figure 3 Equilibrium phase diagram of Al-Si alloy without (a) and with 1 mass % Ce (b).

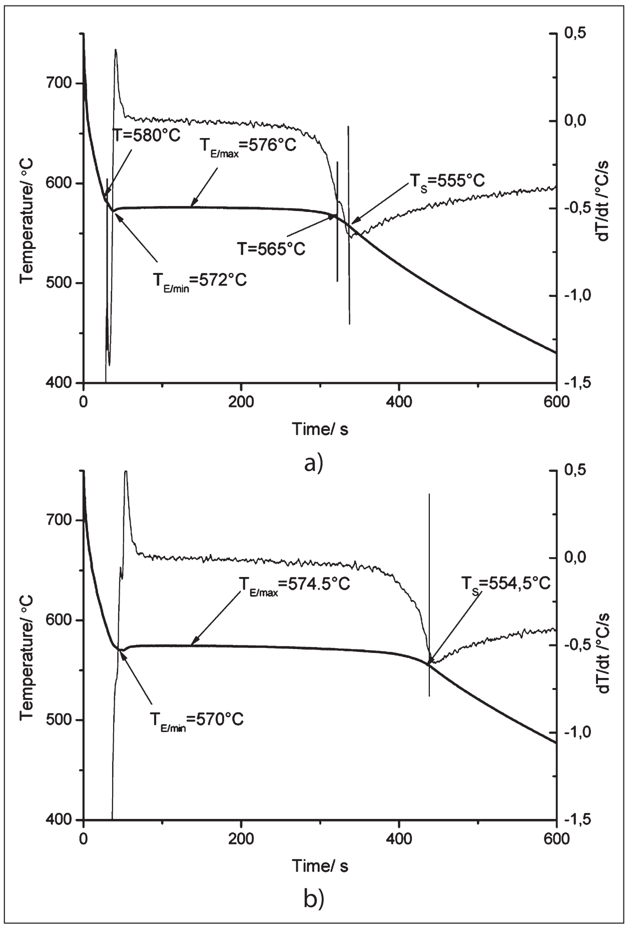
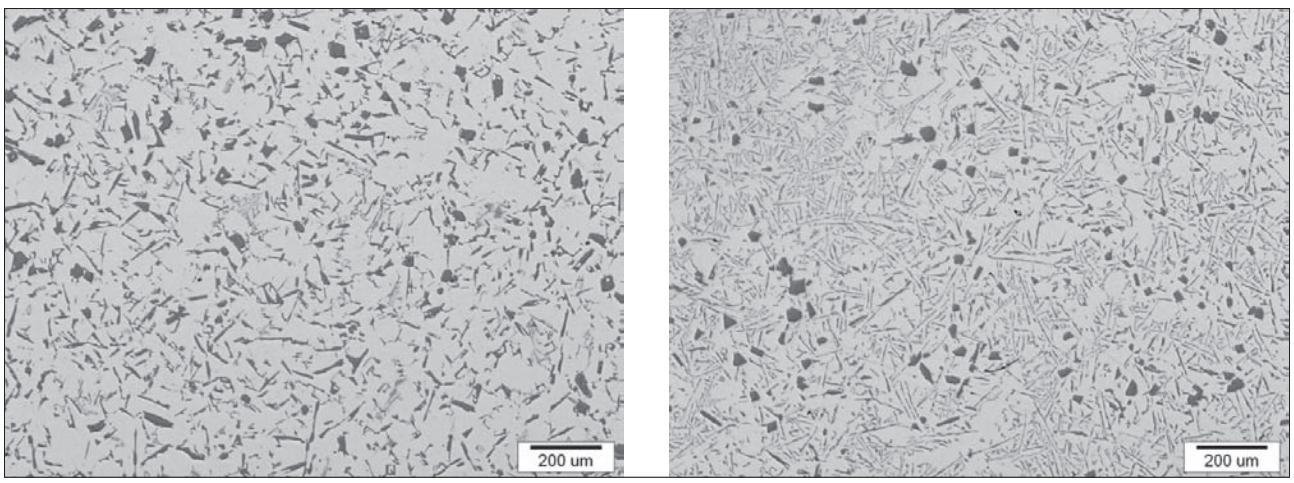


Figure 4 Cooling curves of AlSi12 alloy (a), AlSi12 alloy with additions of Ce (b).

Cerium addition also influenced precipitation of the AlFeSi phase. Solidification temperature of the AlFeSi phase was detected at the end of solidification process on the DTA cooling curves. In the alloy with 1 mass % Ce no peak for the AlFeSi phase was observed. Figures 6a and b show detailed cooling curves of the AlSi12 alloy (a) and the alloy with 1 mass % Ce (b). Solidification of the AlFeSi phase in the last solidification sequence was evidently detected in Figure 6 a, while cooling curve of the alloy with 1 mass % did not exhibit it. This could be explained by the solidification of iron phase together with cerium phase at the end of the solidification of ($\alpha_{Al} + \beta_{Si}$) eutectic.

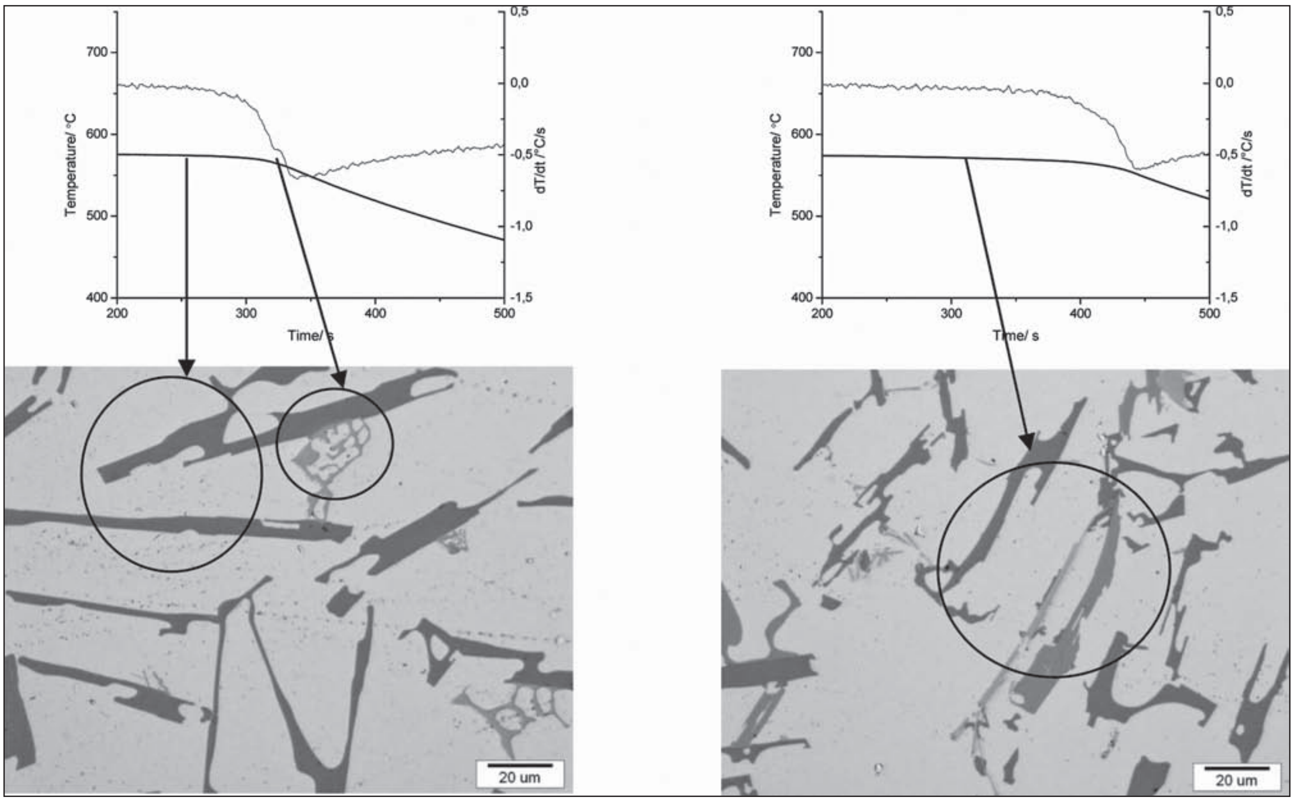
Figure 6 a presents microstructure of the AlSi12 with AlFeSi phase, and Figure 6 b microstructure of the alloy with 1 mass % Ce with evidence that AlFeSi phase solidified simultaneously with the AlSiCe phase.

Figure 7 a presents SEM micrograph of the AlSi12 alloy together with EDS analyses of existing phases. All phases i.e. β_{Si}, α_{Al} and AlFeSi were analyzed. AlFeSi phase was present in two different modifications. AlFeSi phase occurred in the alloys without Ce addition as



a) b)

Figure 5 Microstructures of AlSi12 alloy (a), and with additions of Ce (b).



a) b)

Figure 6 Cooling curve and microstructure of AlSi12 alloy (a) and alloy with 1 mass % Ce (b).

AlFeSi-α phase. This phase, cited in reference [9], named also Fe_2SiAl_5 or $Fe_3Si_2Al_{12}$ phase containing 30 –33 mass % Fe and 6 – 12 mass % Si and appeared in the microstructure resembling Chinese script.

In our case this phase contained 33 mass % Fe and 9 mass % Si.

SEM micrograph of the AlSi12 alloy with addition of 1 mass % Ce and corresponding analysis of the cerium-rich phase are shown in Figure 7 b. Cerium-rich phase was composed of Al, Si and Ce and it was determined as AlSiCe phase. Corresponding to the work of Zerechnyuk and Altunina [10,11] that reported the existence of AlSiCe phase with composition of $Al_{35}Si_{45}Ce_{20}$ (at. %) in the alloys containing from 0 to 33 at. % Ce, our examined phase consisted of Al ~ 34 %, Si ~ 39 % and Ce ~ 27 % (at. %) [12].

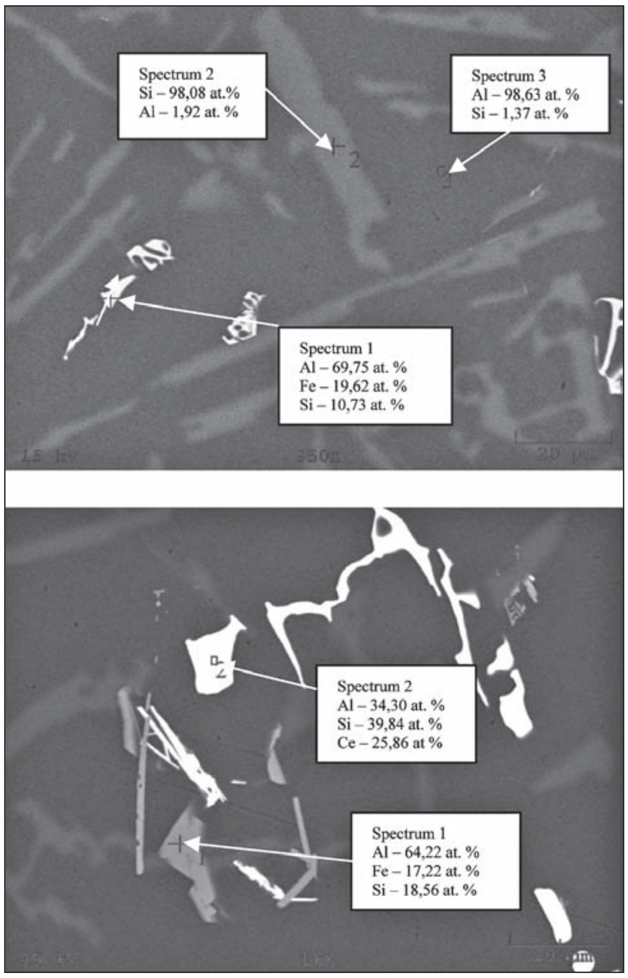


Figure 7 SEM micrograph of the AlSi12 alloy without (a) and with addition of Ce (b).

CONCLUSIONS

The following conclusions can be made from the results of this work:

It was found that simulation of equilibrium solidification of the alloy with 1 mass % Ce indicated that $Al_{11}Ce_3$ cerium phase which was the only cerium-rich phase that was enclosed in the database of Thermo-Calc program solidified simultaneously with the β-AlFeSi phase and it appeared in the region that solidified the last. References on the other hand gave evidence that solidifying phase was not $Al_{11}Ce_3$ but AlSiCe that was actually not enclosed in the applied database. Such solidification course was confirmed also by the simple thermal analysis. Solidification of single phases can be determined from differential cooling curves. Cooling curves of alloys with cerium additions differ from other cooling curves. In the region of final solidification, peak on differential cooling curve as indication of the AlFeSi solidification accompanied with solidification of cerium-rich phase did not appear.

Addition of cerium to eutectic Al-Si alloy lengthened solidification times. When cerium was added to alloy, the amount of silicon phase was reduced and new AlSiCe phase appeared. This most probably caused longer solidification time.

AlSiCe phase (Al: 34 at. %, Si: 40 at. %, Ce: 26 at. %) was formed in the Al-Si alloys with added cerium during the solidification process. Needles and polyhedral shapes were characteristic for the solidified AlSiCe phase.

Cerium addition influenced the α-AlFeSi phase formed in solidification. This phase initial appearing as Chinese script was changed into β-AlFeSi phase in form of needles. AlSiCe and β-AlFeSi phases solidified together in the region that solidified the last.

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Note: The responsible person for English language is prof. dr. Andrej Paulin.