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SOLIDIFICATION AND PRECIPITATION BEHAVIOUR IN THE AlSi9Cu3 ALLOY WITH VARIOUS Ce ADDITIONS

STRJEVANJE IN IZLOČANJE V ZLITINI ALSI9CU3 PRI RAZLIČNIH DODATKIH Ce

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The effect of Ce additions on the AlSi9Cu3 alloy was investigated using an equilibrium thermodynamic calculation, thermal analysis, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The purpose was to study the variations that occur during solidification and precipitation with different Ce additions, as well as theireffect on the mechanical properties.

The results show that Ce additions shift the temperature of the eutectic solidification (α_{Al} + Al_2Cu) and the solidus temperature to higher values. It was found that the precipitation reaction is more intense when the specimen is previously cooled with a higher cooling rate. Moreover, when the fraction of the precipitates regarding the temperature at different cooling rates was taken into account, it was found that the precipitation is faster when Ce is added and also when the specimen was cooled faster. Ce also changed the morphology of the eutectic Al_2Cu phase. Furthermore, the Ce phase was detected, indicating the Al–Ce–Cu–Si ($Al_9Ce_2Cu_5Si_3$) phase. The mechanical properties, such as hardness and tensile strength, increase with larger Ce additions.

Keywords: AlSi9Cu3 alloy, Ce addition, reaction kinetics, solidification and precipitation, mechanical properties

Vpliv dodatka Ce v zlitini AlSi9Cu3 je bil preiskan z uporabo izračuna ravnotežnega strjevanja, termične analize, diferenčne vrstične kalorimetrije (DSC) ter vrstične elektronske mikroskopije (SEM). Namen je bil preiskati spremembe, ki nastopijo pri strjevanju in izločanju v zlitini z različnimi dodatki Ce ter njegov vpliv na mehanske lastnosti.

Rezultati so pokazali, da dodatek Ce zviša temperaturo strjevanja evtektika (α_{Al}+ Al_2Cu) in solidus temperature k višjim vrednostim. Ugotovljeno je bilo, da reakcija izločanja poteče intenzivnejše, ko je vzorec predhodno ohlajen z večjo hitrostjo ohlajanja. Pri preiskavi deleža izločkov glede na različne temperature se pokaže, da poteče izločanje hitreje, ko zlitini dodamo Ce, ter prav tako, ko je vzorec predhodno hitreje ohlajen. Ce v zlitini AlSi9Cu3 spreminja tudi morfologijo evtektske faze Al_2Cu. Analizirali smo Ce fazo AlCeCuSi ($Al_9Ce_2Cu_5Si_3$). Mehanske lastnosti, kot sta trdota ter natezna trdnost, se povečujejo z dodatkom Ce v zlitini AlSi9Cu3.

Ključne besede: zlitina AlSi9Cu3, dodatek Ce, reakcijska kinetika, strjevanje ter izločanje, mehanske lastnosti

1 INTRODUCTION

Al–Si–Cu alloys are widely used for thin-wall castings[1] in automobile, aircraft and in the chemical industry. The AlSi9Cu3 alloy is a heat-treatable alloy with good castability. These alloys usually contain copper and often magnesium as the main alloying element, together with various other alloying elements or impurities, such as Fe, Mn or Cr.[2] Cu in the AlSi9Cu3 alloy reduces the corrosion resistance and improves the mechanical properties. A controlled cooling process and/or optimal alloying with Ce makes it possible to achieve suitable mechanical properties, like tensile strength and hardness. A small amount of Mg causes the formation of the Mg_2Si phase[3,4] and additionally it increases the mechanical properties in Al–Si–Cu alloys.[5,6,7,8,9] The microstructure in Al–Si alloys dictates the mechanical and technological properties of the castings. For this reason a specific microstructure and the mechanical properties must be achieved. This can be established with a smaller grain size and with a modification of the (α_{Al} + β_{Si}) eutectic and/or with high cooling rates.

Rare-earth metals, such as cerium (Ce), have been found to improve the mechanical properties of Al–Si castings by modifying their microstructure and enhancing their tensile strength[10] and ductility[11], heat resistance and extrusion behaviour.[12] It was reported that Ce-phases may act as nucleation sites for (Al) or (Si) crystals in both hypo- and hypereutectic Al-Si alloys.[13] Cerium has a high activity in an aluminium melt because of its specific electron structure. It forms a quaternary intermetallic compound with aluminium, silicon and copper and this leads to the formation of an Al–Ce–Cu–Si phase between the dendrite structure. The cerium phase acts as a barrier for dislocation movement that increases the mechanical properties of the material[14].

This paper treats the influence of Ce addition on the course of the solidification, precipitation and cooling, and also of the cooling rate, on the solidification and precipitation and on the mechanical properties of the AlSi9Cu3 alloy.

2 EXPERIMENTAL

A commercial AlSi9Cu3 alloy was melted in an electric induction furnace.Various concentrations (w(Ce) = 0, 0.01, 0.02, 0.05 and 0.1) of pure (99.9 %) Ce were added. After 10 min the melt was poured into a measuring cell with a controlled cooling system (simple thermal analysis-STA) with the purpose of recording the cooling curves at different cooling rates. A new measuring cell for the controlled cooling of specimens from the melt to low temperatures was designed in order to obtain various cooling rates. Simultaneously, the specimens for the tensile tests were also cast into a mould made according to the DIN50125 standard. The characteristic solidification temperatures were determined from the cooling curves, and the influence of Ce was defined.

Differential scanning calorimetry (DSC) using a Jupiter 449c, NETZSCH, was applied to analyse the solidification process and to determine the characteristic temperatures of single reactions and the produced or consumed enthalpies. The measurements were carried out under a protective Ar atmosphere according to the temperature program: heating rate 10 °C/min up to 710 °C → holding at 710 °C for 10 min → cooling rate 10 °C/min. Moreover, the DSC curves were plotted, the temperatures of the precipitation were marked and the formation enthalpies of the precipitates were determined. The precipitation kinetics connected to the Ce addition and the cooling rate was also determined.

Light and electron microscopy were applied to analyse the microstructures. Single microstructural phases were determined quantitatively with the system for analysing images. A quantitative analysis for the identification of the phases was performed by energy-dispersive and wave length-dispersive X-ray spectroscopy. A cerium phase was identified. The hardness was measured using a universal Brinell hardness tester and the tensile strength was defined on as-cast specimens made according to the EN 10002-1 standard using a GLEEBLE 1500D simulator of thermomechanical states.

3 RESULTS AND DISCUSSION

The chemical composition of the investigated samples is presented in **Table 1**.

From the chemical composition, equilibrium solidification and calculated equilibrium the vertical cross-section diagrams were simulated using the Thermo-Calc program TCW5 and database COST507 (**Figure 1a**). The course of the equilibrium solidification was determined (**Figure 1b**).

The equilibrium solidification of the AlSi9Cu3 alloy proceeds as follows (**Figure 1**): Si_2Ti, AlFeSi-β, primary crystals of α_{Al}, AlMnSi-α, eutectic (α_{Al} + β_{Si}) and just below the solidus temperature the Ce phase Al_8Ce. Under the solidus, the Mg_2Si and Al_2Cu-θ phase also precipitated.

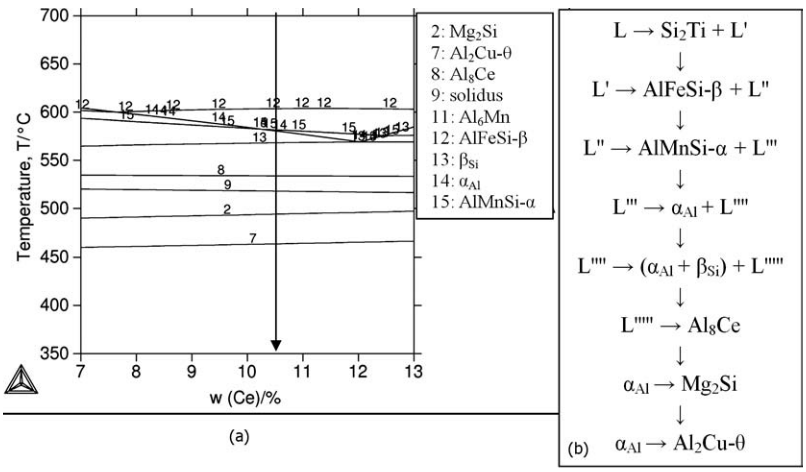


Figure 1: Equilibrium phase diagram (a) and schematic representation of equilibrium solidification of AlSi9Cu3 alloy (b) with w = 0.02 % Ce
Slika 1: Ravnotežni fazni diagram (a) ter shematski prikaz ravnotežnega strjevanja zlitine AlSi9Cu3 (b) z w = 0,02 % Ce

Table 1: Chemical composition of AlSi9Cu3 alloy, w/%
Tabela 1: Kemijska sestava zlitine AlSi9Cu3, w/%

Specimen	Mg	Mn	Cu	Ti	Fe	Si	Ce (nominal)	Ce (actual)	Al
AlSi9Cu3	0.35	0.242	2.61	0.04	0.694	10.72	0		rest
AlSi9Cu3 + 0.01 % Ce	0.34	0.27	2.55	0.04	0.75	10.60	0.01		rest
AlSi9Cu3 + 0.02 % Ce	0.35	0.29	2.685	0.04	0.80	10.66		0.015	rest
AlSi9Cu3 + 0.05 % Ce	0.32	0.29	2.565	0.04	0.81	10.59		0.043	rest

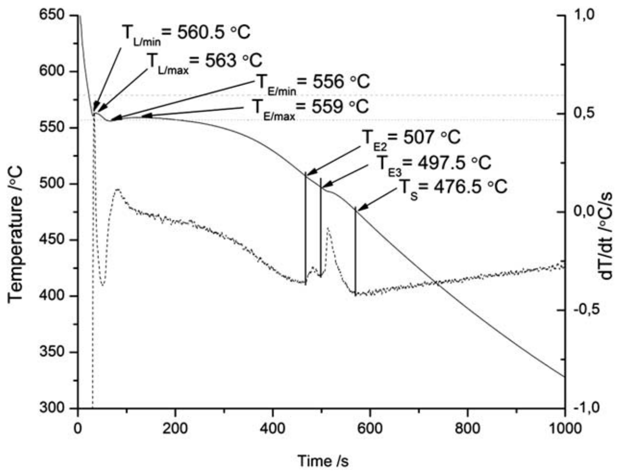


Figure 2: Cooling curve and differential cooling curve of AlSi9Cu3 alloy with w = 0.02 % Ce and with the theoretical calculated equilibrium liquidus and eutectic temperature (horizontal line)

Slika 2: Ohlajevalna in diferencirana ohlajevalna krivulja zlitine AlSi9Cu3 z w = 0,02 % Ce ter z vrisanima teoretično izračunanima ravnotežno likvidus in evtektsko temperaturo (vodoravne črte)

Figure 2 shows a typical cooling curve together with a differential cooling curve of the investigated AlSi9Cu3 alloy with 0.02 % Ce. The characteristic solidification temperatures were determined in all the specimens with various Ce additions (**Table 2**). The striped line indicates the theoretical, with the Thermo-Calc calculated, liquidus temperature calculated from the chemical composition:

$$T_{\text{L teor.}} = 656.38468 - 6.78571 \cdot w(\text{Si}) - 1.42857 \cdot w(\text{Cu}) + 1.34798 \cdot 10–10 \cdot w(\text{Fe}) - 1.04224 \cdot 10–10 \cdot w(\text{Mn}) - 3.15848 \cdot w(\text{Mg}) - 2.24953 \cdot w(\text{Zn})$$

The dotted line in **Figure 2** indicates the theoretically calculated eutectic temperature calculated from the chemical composition:

$$T_{\text{Eteor.}} = 574.2834 - 0.57134 \cdot w(\text{Si}) - 2.57143 \cdot w(\text{Cu}) - 3 \cdot w(\text{Fe}) - 1.14639 \cdot 10^{-10} \cdot w(\text{Mn}) - 5.73489 \cdot w(\text{Mg}) - 1.38954 \cdot w(\text{Zn})$$

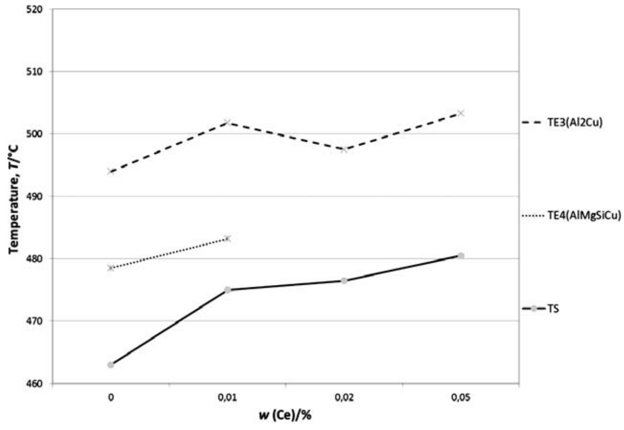
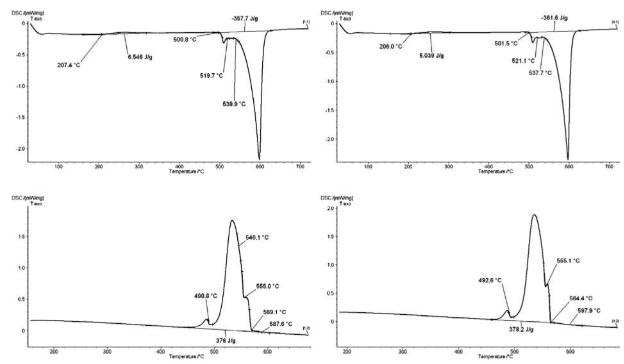


Figure 3: Comparison of some characteristic solidification temperatures for AlSi9Cu3 alloy with respect to Ce addition

Slika 3: Primerjava nekaterih karakterističnih temperature pri strjevanju zlitine AlSi9Cu3 glede na dodatek Ce



a) b)

Figure 4: Heating and cooling DCS curves of AlSi9Cu3 alloy without Ce (a) and with w = 0.02 % Ce (b)

Slika 4: Segrevalne in ohlajevalne DSC-krivulje zlitine AlSi9Cu3 brez Ce (a) in z w = 0,02 % Ce (b)

Table 2 and **Figure 3** represent the characteristic solidification temperatures with respect to the Ce addition. The temperature of the eutectic solidification (α_{Al} + Al_2Cu) and the solidus temperature shift to higher temperatures. The temperature of the eutectic solidification (α_{Al} + AlCuMgSi) could not be detected when larger

Table 2: Characteristic solidification temperatures for AlSi9Cu3 after STA

Tabela 2: Značilne temperature strjevanja zlitine AlSi9Cu3 po STA

w(Ce)/%	T_{Lteor}/°C	$T_{\text{L/min}}$/°C	$T_{\text{L/max}}$/°C	$\Delta T_{\text{L p.}}$/°C	$\Delta T_{\text{L r.}}$/°C
0	578.8	561	564	17.81	3
0.01	579.7	562	566.8	17.71	4.8
0.02	579.1	560.5	563	18.6	2.5
0.05	579.9	563.7	565.9	16.1	2.2

w (Ce)/%	$T_{\text{Eteor.}}$ /°C	$T_{\text{E/min}}$ /°C	$T_{\text{E/max}}$ /°C	$\Delta T_{\text{E p.}}$ /°C	$\Delta T_{\text{E r.}}$ /°C	$T_{\text{E2(Mg2Si)}}$ /°C	$T_{\text{E3(Al2Cu)}}$ /°C	$T_{\text{E4(AlCuMgSi)}}$ /°C	T_{S} /°C
0	557.4	556.5	559	0.9	2.5	512	494	478.5	463
0.01	557.5	563.9	564.7	–6.4	0.8	520.1	501.8	483.2	475
0.02	556.9	556	559	0.9	3	507	497.5		476.5
0.05	557.4	563.4	564.4	–6.0	1	523.2	503.3		480.5

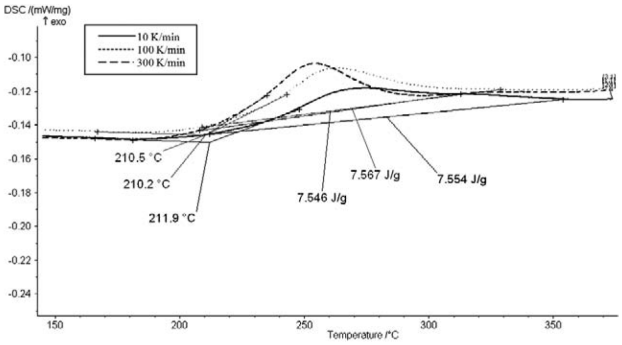


Figure 5: DSC curves of the precipitation region of AlSi9Cu3 alloy at different cooling rates
Slika 5: DSC-krivulje s področja izločanja zlitine AlSi9Cu3 pri različnih hitrostih ohlajanja

concentrations of Ce were added, presumably because these elements combined with Ce.

The DSC analysis was made on all the specimens after the STA. From the heating (**Figure 4a**) and cooling (**Figure 4b**), all the characteristic temperatures during heating/cooling were determined, including the melting/solidification and precipitation enthalpies with various Ce additions.

When the precipitation kinetics was investigated, it was found that the precipitation reaction is more intense when the specimen is previously cooled faster (**Figure 5**). This is a consequence of a more supersaturated solid solution. Moreover, when the fraction of the precipitates regarding the temperature at different cooling rates was taken into account, it was found that the precipitation ki-

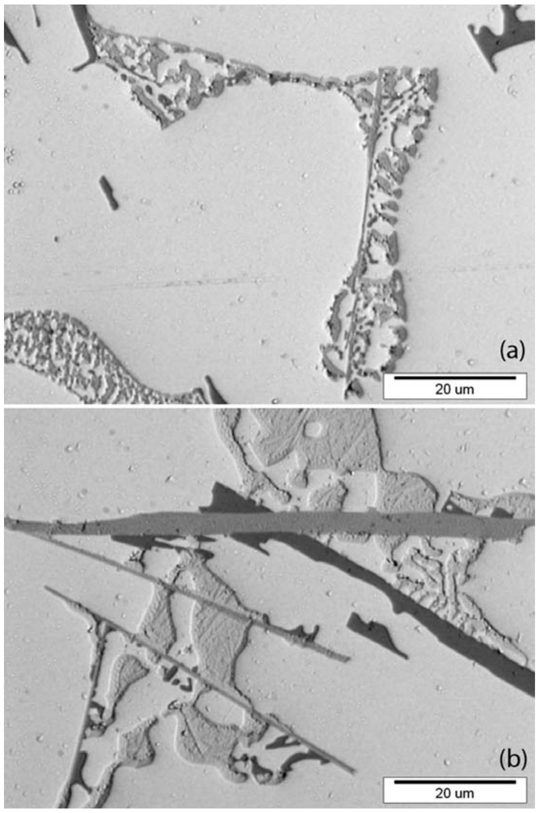


Figure 7: Microstructure of Al_2Cu phase without Ce (a) and with w = 0.05 % Ce (b)
Slika 7: Mikrostrukturni posnetek faze Al_2Cu brez Ce (a) in z w = 0,05 % Ce (b)

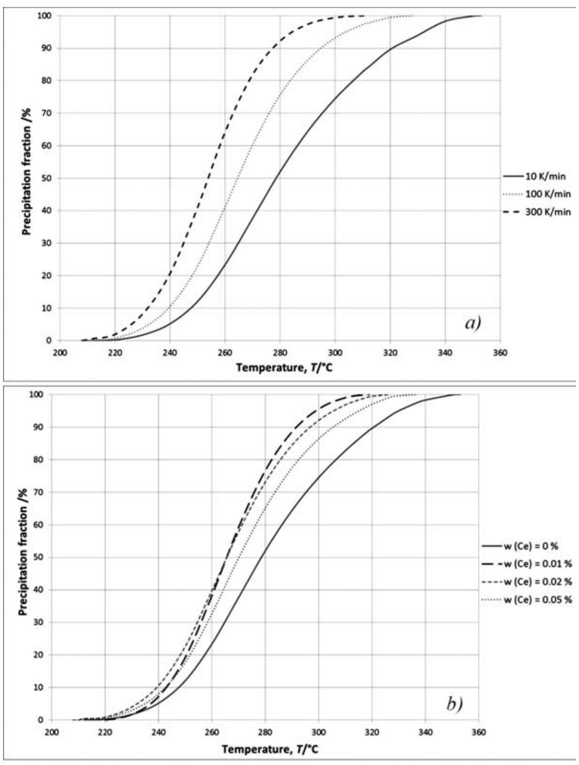


Figure 6: Fraction of Al_2Cu precipitates with respect to the temperature in the AlSi9Cu3 alloy at various cooling rates (a) and at various concentrations of Ce (b)
Slika 6: Delež izločkov Al_2Cu v odvisnosti od temperature v zlitini AlSi9Cu3 po različnih hitrostih ohlajanja (a) ter pri različnih koncentracijah Ce (b)

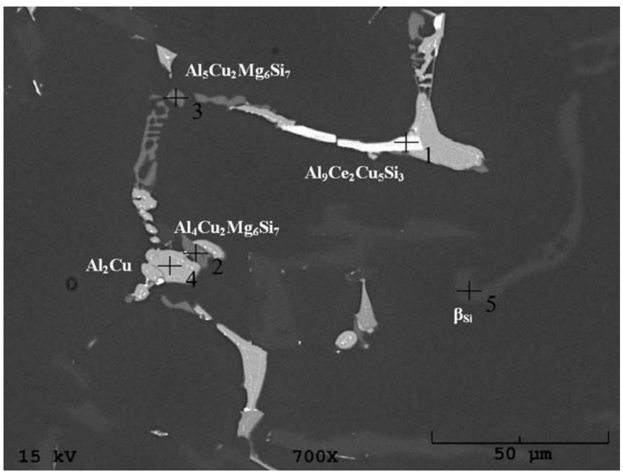


Figure 8: Microstructure (SEM) of AlSi9Cu3 + 0.02 % Ce with EDS analysis
Slika 8: Mikrostruktura (SEM) zlitine AlSi9Cu3 + 0,02 % Ce z EDS-analizo

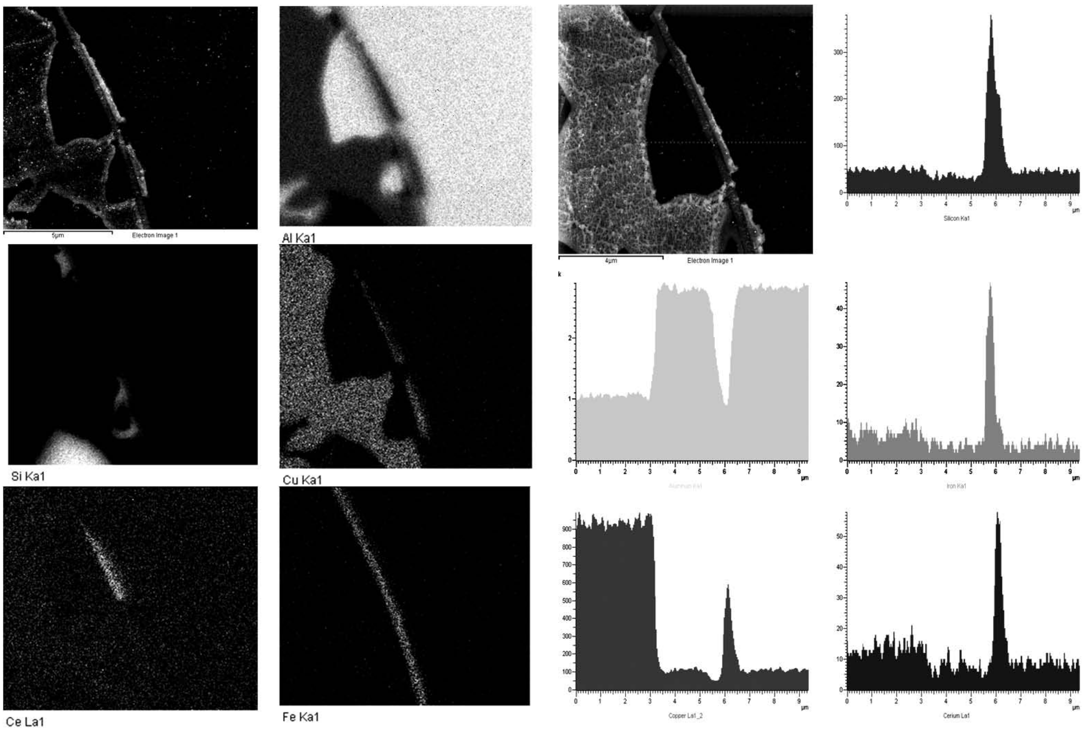


Figure 9: Mapping (a) and line analyses (b) of (α_{Al} + Al_2Cu) eutectic in AlSi9Cu3 alloy with w = 0.02 % Ce
Slika 9: Površinska porazdelitev elementov ter linijska analiza (b) evtektske faze (α_{Al} + Al_2Cu) v zlitini AlSi9Cu3 z w = 0,02 % Ce

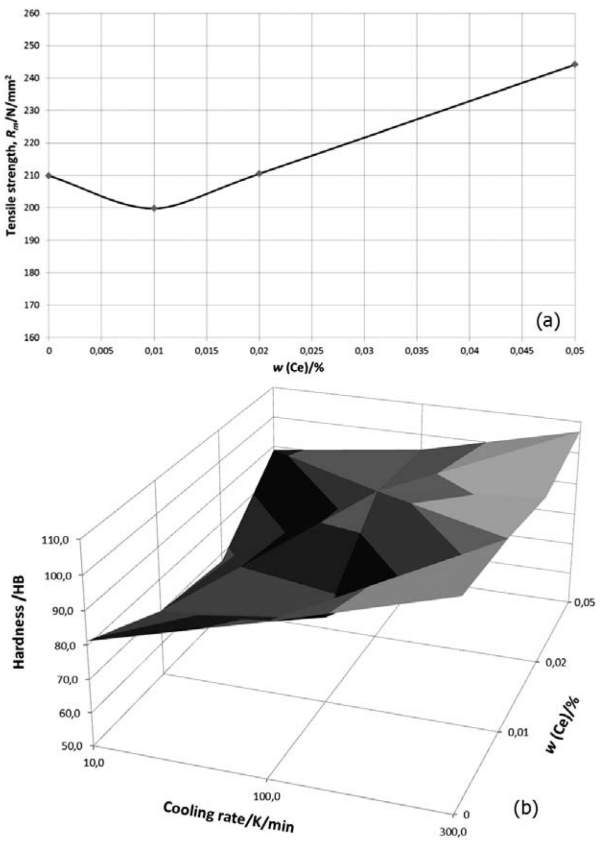


Figure 10: Tensile strength (a) and hardness (b) of AlSi9Cu3 alloy for various Ce additions
Slika 10: Natezna trdnost (a) ter trdota (b) zlitine AlSi9Cu3 pri različnih koncentracijah Ce

netics is faster when Ce is added (**Figure 6a**) and also when the specimen was cooled faster (**Figure 6b**).

When the microstructure was investigated, no influence on the size and distribution of the microstructure components was detected, only the morphology of the Al_2Cu phase changed. In the alloy without Ce, the eutectic phase Al_2Cu appears to be "crumbled" (**Figure 7a**), but when Ce was added the Al_2Cu phase was fully formed (**Figure 7b**).

Besides the usual phases that occur in these types of alloys, the Ce phase was also detected with the EDS analyser, indicating the Al–Ce–Cu–Si (calculated stoichiometry was $Al_9Ce_2Cu_5Si_3$, **Figure 8**) phase. This phase forms in a needle shape. To establish what happens with the Al_2Cu, mapping (**Figure 9a**) and line analyses (**Figure 9b**) through the Al_2Cu were made. It was proved that the Ce is bound to the Al_2Cu eutectic phase.

The tensile strength and Brinell hardness of the AlSi9Cu3 alloy with respect to Ce are presented in **Figure 10a and 10b**. The tensile strength for a small amount of Ce is slightly reduced and at a higher concentration of Ce it is increased, probably because of the modified Al_2Cu eutectic phase. The hardness due to the Ce addition was investigated for different cooling rates. For the smaller cooling rate (10 K/min) the hardness slightly decreased when 0.01 % Ce was added to the alloy, but it increased as well as the tensile strength for higher Ce additions. With higher cooling rates the hardness increased because the influence of the Ce was reduced.

4 CONCLUSION

The effects of Ce content on the solidification sequence, microstructure and mechanical properties of the AlSi9Cu3 alloy were investigated. Moreover, the reaction kinetics of the precipitation in the AlSi9Cu3 alloy was studied also. The results can be summarized as follows:

The equilibrium solidification of the AlSi9Cu3 alloy proceeds as follows: Si_2Ti, AlFeSi-β, primary crystals of α_{Al}, AlMnSi-α, eutectic ($\alpha_{Al} + \beta_{Si}$) and just below the solidus temperature the Ce phase Al_8Ce is precipitated. Below the solidus the Mg_2Si and Al_2Cu-θ phases are precipitated also. The data base should be complemented with multicomponent phases with Ce.

The temperature of the eutectic solidification (α_{Al} + Al_2Cu) and the solidus temperature are shifted to higher temperatures with the addition of Ce. The temperature of the eutectic solidification (α_{Al} + AlCuMgSi) could not be detected when greater concentrations of Ce were added.

When the precipitation kinetics was investigated it was found that the precipitation reaction is more intense for the specimen that was previously cooled faster. Moreover, when the fraction of the precipitates depending on the temperature at different cooling rates was taken into account, it was found that the precipitation is faster when Ce is added and also when the specimen was cooled faster.

Ce changed the morphology of the eutectic Al_2Cu phase with building into the Al_2Cu phase. Furthermore, the Ce phase was detected, indicating the Al–Ce–Cu–Si ($Al_9Ce_2Cu_5Si_3$) phase. This phase forms in a needle shape.

The tensile strength and the hardness vs. slower cooling for a small amount of Ce were slightly reduced. However, they were increased when a greater concentration of Ce is added, probably because of the modification of the Al_2Cu eutectic phase. With higher cooling rates the hardness increased and the influence of Ce is reduced.

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