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Fazna ravnotežja v aluminijevih livarskih zlitinah v odvisnosti od vsebnosti Si in Fe

Phase Equilibrium in Aluminium Cast Alloys Depending on Si and Fe Content

POVZETEK

Železo v aluminijevih zlitinah predstavlja glavno nečistočo. V nekaterih zlitinah predstavlja železo glavni legirni element, ki poveča trdoto zlitin, a tudi povečuje krhkost. V tem delu smo preiskovali fazna ravnotežja v Al-Si livarskih zlitinah in vpliv razmerja železa in silicija (Fe/Si). Preiskovali smo tako, da smo uvajali železno žico v talino, ki je bila izdelana iz elektroliznega aluminija in zlitine AlSi12Cu(Fe) pri temperaturi 750°C in pri različnih časih raztapljanja. Za ugotavljanje značilnih temperatur procesa taljenja in strjevanja ter sproščanja toplote pri tem smo uporabili metodo simultane termične analize (STA). Z uporabo Thermo-Calc programa smo izvedli termodinamično simulacijo napovedovanja faznega ravnotežja nastalih faz železa. S programom Thermo-Calc smo izvedli tudi vrednotenje eksperimentalnih podatkov in izračunali fazne diagrame pri različnih razmerjih železa in silicija (Fe/Si).
Ključne besede: aluminijeve zlitine, termodinamika, železove faze, termična analiza

ABSTRACT

Iron in aluminium alloys presents the main impurity. At some alloys the iron presents the main alloying element, which increases the hardness of the alloys, but also increases brittleness. In this work the phase equilibrium in Al-Si cast alloys and influence of Fe/Si was investigated. Phase equilibrium was researched with the putting iron wire into the melt of electrolytic aluminium and AlSi12Cu(Fe) alloy at temperature 750°C and different dissolving times. For identifying the characteristic temperatures of the solidification and melting process with the precipitation heats was used simultaneous thermal analysis (STA). Thermodynamic modeling simulation with Thermo-Calc program was tool to predict phase equilibrium of precipitated iron phases. Evaluation of the experimental data with Thermo-Calc program were calculated phase diagrams at different Fe/Si ratio.
Key words: phase equilibrium, aluminium alloys, thermodynamics, iron phases, thermal analysis

1 Uvod

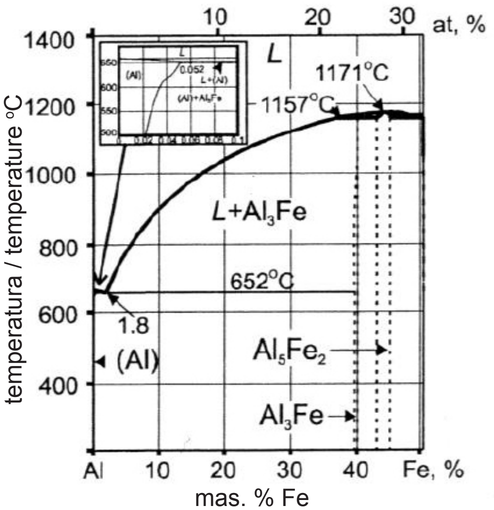
Namen naše preiskave je bil ugotoviti fazna ravnotežja v aluminijevih livarskih zlitinah v odvisnosti od vsebnosti silicija in železa. Izvedli smo preiskavo raztapljanja železove žičke v elektroliznem aluminiju in v livarski

1 Introduction

The goal of our research was to determine phase equilibria in aluminium casting alloys as a function of silicon and iron contents. The applied research method was dissolution of iron wire in the melt of zlitini AlSi12Cu(Fe), ki je vsebovala 0,8 % Fe. Preiskovo smo izvedli v elektro-uporobni peči pri temperaturi 750°C in časih raztaplanja 0, 15 in 30 minut. Opravili smo simultano termično analizo (STA) in s programom Thermo-Calc določili fazna ravnotežja.

2 Fazna ravnotežja pri strjevanju aluminijevih zlitin

Za študij faznih ravnotežij pri strjevanju aluminijevih zlitin se uporabljata ravnotežni fazni diagram Al-Fe in ternerni sistem Al-Fe-Si. Aluminijev kot v diagramu Al-Fe prikazuje slika 1. Topnost železa v trdnem aluminiju je pri temperaturi 652 °C zelo majhna in znaša 0,04 mas. %. Pri koncentracijah železa, ki so večje kot 10 mas.% in pri temperaturi 1158°C poteka v sistemu Al-Fe peritektska reakcija L + Al_5Fe_2 → Al_3Fe. Pri tej reakciji nastane intermetalna spojina Al_3Fe, ki vsebuje 40,7 mas.% Fe. Ta faza je krhka in nezaželena.1



Slika 1. Aluminijev kot faznega diagrama Al-Fe [1]

Figure 1. Aluminium corner of the Al-Fe phase diagram [1]

electrolytic aluminium and AlSi12Cu(Fe) alloy containing 0.8 % Fe. Experiments took place in electric resistance furnace at 750 oC. Applied dissolution times were 0, 15, and 30 min. Simultaneous thermal analysis (STA) with Thermo-Calc programme was used to determine the phase equilibria.

2 Phase equilibria in solidification of aluminium alloys

Binary Al-Fe and ternary Al-Fe-Si phase diagrams were applied for studying phase equilibria in the solidification of aluminium alloys. Aluminium corner of the Al-Fe diagram is presented in Figure 1. Iron solubility in solid aluminium is very low at 652 °C, it is only 0,04 % (mass fraction).

At iron contents higher than 10 % and at 1158 °C L + Al_5Fe_2 → Al_3Fe peritectic reaction takes place resulting the formation of intermetallic Al_3Fe compound with 40.7 % Fe. This phase is brittle and not desired.

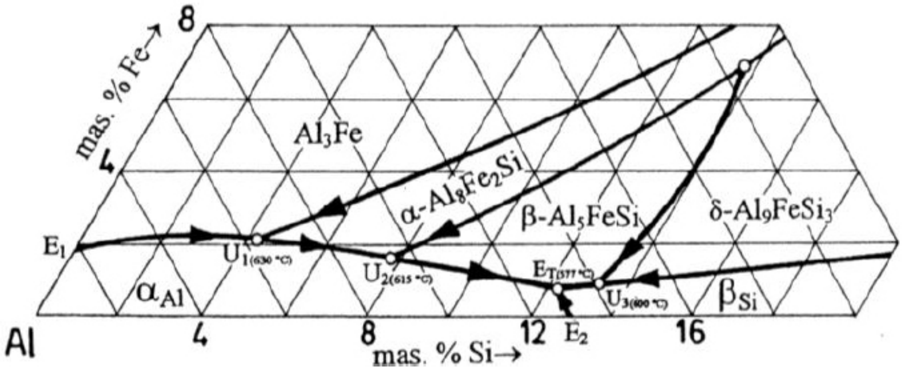
In the Al-Si casting alloys there are in presence of iron formed various equilibria and numerous phases as presented in the aluminium corner of the ternary Al-Fe-Si diagram in Figure 2.

Based on chemical composition and solidification conditions intermetallic compounds can appear already as primarily precipitated phases in the Al-Si casting alloys. Table 1 presents the intermetallic compounds with corresponding compositions that most often appear in the Al-Si casting alloys with iron.

3 Experimental

Phase equilibria were investigated with samples of electrolytic aluminium and

AlSi12Cu(Fe) casting alloy. Chemical compositions of the electrolytic aluminium and the AlSi12Cu(Fe) alloy are given in Table 2.



Slika 2. Aluminijev kot ternernega sistema Al-Fe-Si [2]

Figure 2. Aluminium corner of the ternary Al-Fe-Si diagram [2]

V Al-Si livnih zlitinah ob prisotnost železa nastanejo fazna ravnotežja in se tvorijo številne faze, ki jih prikazuje tudi aluminijev kot v ternernem faznem diagramu sistema Al-Fe-Si na sliki 2.

Samples of electrolytic aluminium and AlSi12Cu(Fe) casting alloy were melted in electrical resistance furnace with graphite crucible. Iron wire was inserted into crucible centre (Figure 3) at 750 ^{o}C and held there for 0, 15, and 30 min.

Tabela 1. Intermetalne spojine v Al-Si zlitinah z železom [3]

Table 1. Intermetallic compounds in the Al-Si alloys with iron [3]

Faza / Phase	Kemijska sestava / Chemical composition (mass fraction %)
$Al_{13}Fe_4$ (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: up to 7,5, Cr: do 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: do 13,1; Cu: up to 13,0, Cr: up to 14,4; Co: up to 20,1; Ni: up to 26,8
$Al_{19}Fe_4MnSi_2$	Fe: 19,2; Si: 8,3; Mn: 7,8; Cu:2,5; Cr: 0,2

Tabela 2. Kemijska sestava preiskovanih vzorcev v mas.%

Table 2. Chemical compositions of investigated samples in % (mass fraction)

	Si	Fe	Cu	Mn	Mg	Zn	Al
Elektrolizni Al	0,041	0,1497	<0,0008	<0,0001	0,0011	0,0098	ostalo
AlSi12Cu(Fe).	11,5584	0,8292	0,7159	0,1915	0,0546	0,4673	ostalo

Glede na kemijsko sestavo in pogoje strjevanja lahko v livarskih Al-Si zlitinah z železom pričakujemo intermetalne spojine že kot primarno izločene faze. Tabela 1 prikazuje intermetalne spojine s kemijskimi sestavami, ki se najpogosteje pojavljajo v Al-Si livnih zlitinah z železom.

3 Eksperimentalni del

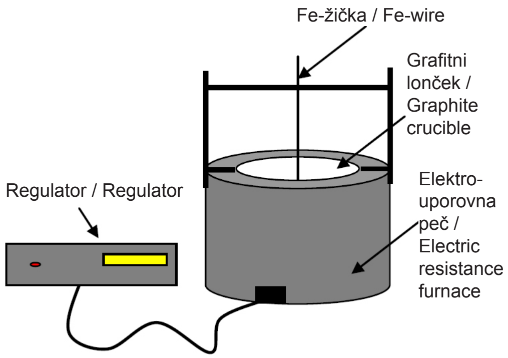
Fazna ravnotežja smo preiskovali v vzorcih iz elektroliznega aluminija in iz livarske zlitine AlSi12Cu(Fe). Kemijska sestava elektroliznega aluminija in livarske zlitine AlSi12Cu(Fe) je prikazana v tabeli 2.

Vzorce elektroliznega aluminija in livarske zlitine AlSi12Cu(Fe) smo stalili v elektro- uporovni peči z grafitnim lončkom. Pri temperaturi taline 750°C smo na sredino lončka (slika 3) vstavili železno žičko in jo v njej držali 0, 15 in 30 minut.

Ohlajene vzorce smo vzdolžno razrezali ob Fe-žički. Analizirali smo vsebnost železa v aluminiju in livarski zlitini AlSi12Cu(Fe) v oddaljenosti 1 do 9 mm od žičke. Rezultate so zbrali v diagramu vsebnost Fe v odvisnosti od oddaljenosti od žičke. Z računalniško simulacijo Thermo-Calc smo določili fazna ravnotežja v livarski zlitini AlSi12Cu(Fe) z 0,8 % Fe. Vzorce livarske zlitine AlSi12Cu(Fe) smo preiskali tudi s simultano termično analizo (STA) na aparaturi STA 449 firme NETZSCH. Vzorce smo segreli do temperature 720 °C s hitrostjo 10 K/min v zaščitni atmosferi argona in jih nato z isto hitrostjo ohladili do sobne temperature.

4 Rezultati in diskusija

Na sliki 4 so rezultati koncentracijskega diagrama raztapljanja železa v odvisnosti od oddaljenosti od Fe-žičke pri temperaturi



Slika 3. Skica naprave

Figure 3. Scheme of apparatus

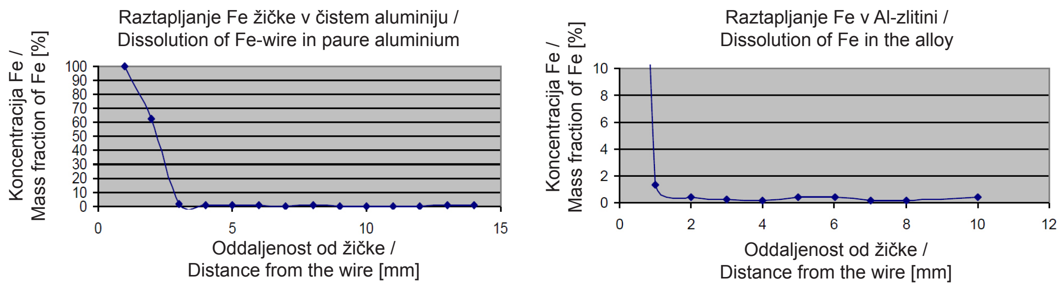
Cooled samples were cut longitudinally along the Fe wire. Iron contents in aluminium and AlSi12Cu(Fe) alloy were analysed at distances 1 to 9 mm. Results are collected in the diagram iron content - distance from iron wire.

Thermo-Calc computer simulation was applied to determine phase equilibria in the AlSi12Cu(Fe) casting alloy with 0.8 % Fe. Samples of the AlSi12Cu(Fe) alloy were investigated also with the simultaneous thermal analysis (STA) using STA 449 apparatus of Netzsch company. Samples were heated to 720 ^{o}C with heating rate 10 K/min in protective atmosphere of argon and then they were cooled with the same rate to room temperature.

4 Results and Discussion

Figure 4 presents results of content measurements at distances 3 mm and 9 mm from the wire during the iron dissolution for 30 min at 750 ^{o}C. Iron content drop was observed in the electrolytic aluminium as well as in the AlSi12Cu(Fe) casting alloy.

Phase equilibrium was predicted applying Thermo-Calc thermodynamic simulation programme. Phase equilibria in the AlSi12Cu(Fe) alloy were determined

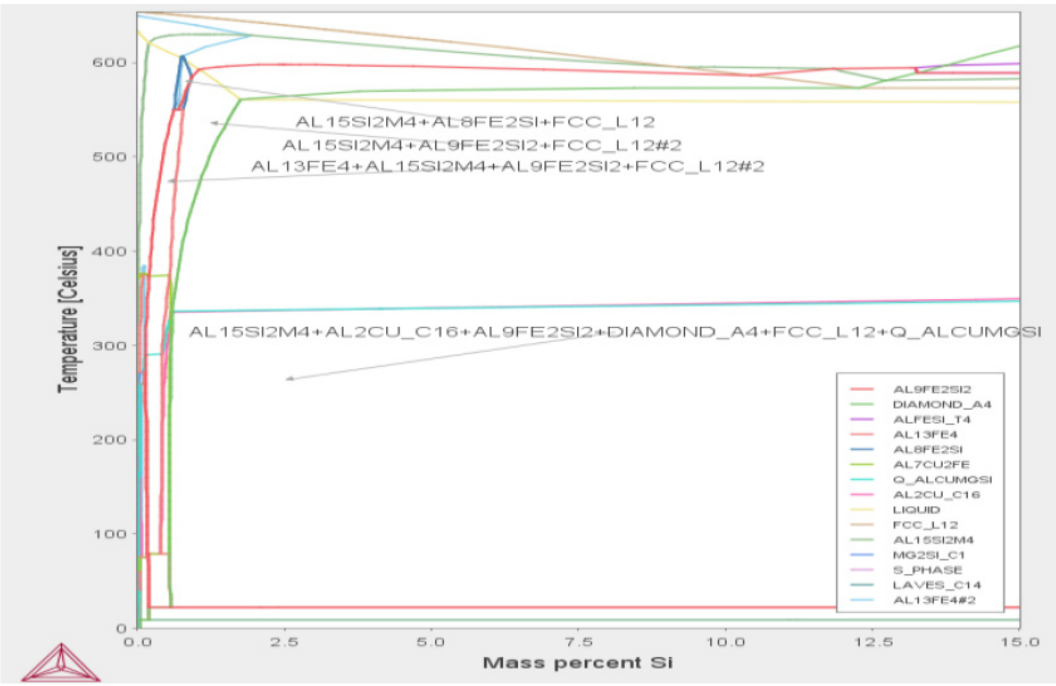


Slika 4. Koncentracijski diagram raztapljanja Fe-žičke pri 750 °C in času 30 min v čistem aluminiju in livarski zlitini AlSi12Cu(Fe) na oddaljenosti 3 in 9 mm od žičke

Figure 4. Content diagram of Fe wire dissolution for 30 min at 750 °C in pure aluminium and in the AlSi12Cu(Fe) alloy at distances 3 and 9 mm from the wire

750 °C in času raztapljanja 30 min na oddaljenosti 3 mm in 9 mm. Viden je padec koncentracije Fe tako za čisti aluminij, kot tudi za livarsko zlitino AlSi12Cu(Fe).

Z uporabo Thermo-Calc programa smo izvedli termodinamično simulacijo and isopleth phase diagram was plotted. It is presented in Figure 5. The diagram shows the presence of $Al_{13}Fe_4(Al_3Fe)$ iron phase and the presence of Al_8Fe_2Si, $Al_9Fe_2Si_2$, $Al_{15}Si_2M_4$ and Al_2Cu phases. All these phases were formed in the content



Slika 5. Izopletni diagram faznih ravnotežij v livarski zlitini AlSi12Cu(Fe)

Figure 5. Isopleth diagram of phase equilibria in the AlSi12Cu(Fe) casting alloy

napovedovanja faznega ravnotežja. Določili smo fazna ravnotežja v zlitini AlSi12Cu(Fe) ter izrisali izopletni fazni diagram, ki je na sliki 5. Iz diagrama je razvidno, da so prisotne železove faze $Al_{13}Fe_4$ (Al_3Fe) in faze v obliki Al_8Fe_2Si, $Al_9Fe_2Si_2$, $Al_{15}Si_2M_4$ in Al_2Cu faza. Vse faze so nastale v koncentracijskem območju do 2,5% Si in razmerja železa in silicija (Fe/Si)=0,33.

Za vzorce livarske zlitine AlSi12Cu(Fe) smo opravili tudi simultano termično analizo. Slika 6 prikazuje primerjavo segrevalnih krivulj livarske zlitine AlSi12Cu(Fe) in toplot, ki se pri taljenju porabljajo. Pri daljšem času držanja Fe-žičke pri 750 °C, so nižje likvidus temperature, višje pa so temperature taljenja evtektika. To je bila posledica povečanja deleža železa v zlitini (0 min - rdeča; 15 min - zelena; 30 min - modra).

Temperature začetka taljenja, taljenja evtektika in njihove toplote so v tabeli 3.

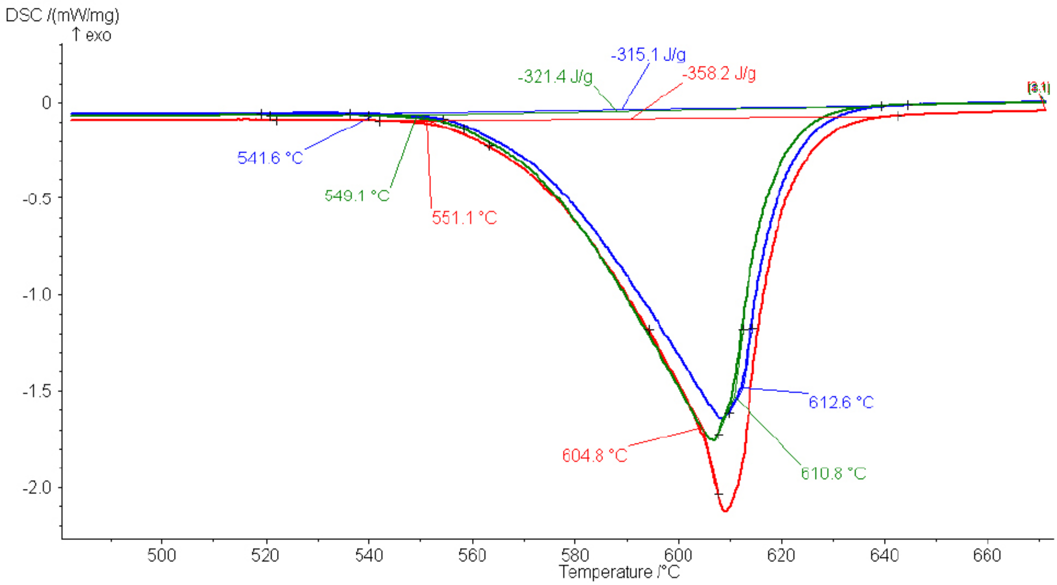
Slika 7 prikazuje primerjavo ohlajevalnih krivulj v livarski zlitini AlSi12Cu(Fe). Iz krivulj lahko opazimo, da so temperature

interval up to 2.5 % Si and at iron/silicon ratio (Fe/Si) = 0.33.

Samples of the AlSi12Cu(Fe) casting alloy were analysed also with the simultaneous thermal analysis. Figure 6 gives comparison of heating curves of the alloy and of heats consumed in melting the alloys. After longer times of holding iron wire in the melt at 750 °C lower liquidus temperatures and higher temperatures of melting of eutectic were obtained. This was consequence of higher iron content in the alloy (0 min - red, 15 min - green, 30 min blue).

Temperatures of the beginning of the alloy melting, of melting of eutectic, and the consumed heats are presented in Table 3.

Figure 7 presents comparison of the cooling curves of the AlSi12Cu(Fe) casting alloy. Curves indicate that the temperatures of the beginning of primary solidification and of solidification of eutectic are similar. With longer holding times of iron wire in the melt at 750 °C liberated heat in solidification was



Slika 6. Primerjava segrevalnih krivulj v livarski zlitini AlSi12Cu(Fe)

Figure 6. Comparison of heating curves of the AlSi12Cu(Fe) casting alloy

Tabela 3. Temperature začetka taljenja in toplote pri taljenju livarske zlitine

Table 3. Temperatures of the beginning of the AlSi12Cu(Fe) casting alloy melting and the consumed heats

	0 min	15 min	30 min
Začetek taljenja / Beginning of melting	551,1 °C	549,1 °C	541,6 °C
Taljenje evtektika Melting of eutectic	604,8 °C	610,8 °C	612,6 °C
Porabljena toplota / Consumed heat	-358,2 J/g	-321,4 J/g	-315,1 J/g

začetka primarnega strjevanja in strjevanja evtektika podobne. Z daljšim časom držanja Fe-žičke v talini na temperaturi 750°C se je sprostilo manj toplote pri strjevanju. Tabela 4 prikazuje temperature primarnega strjevanja, strjevanja evtektika in toplot, ki se pri strjevanju sprostile za livarsko zlitino AlSi12Cu(Fe).

4 Zaključki

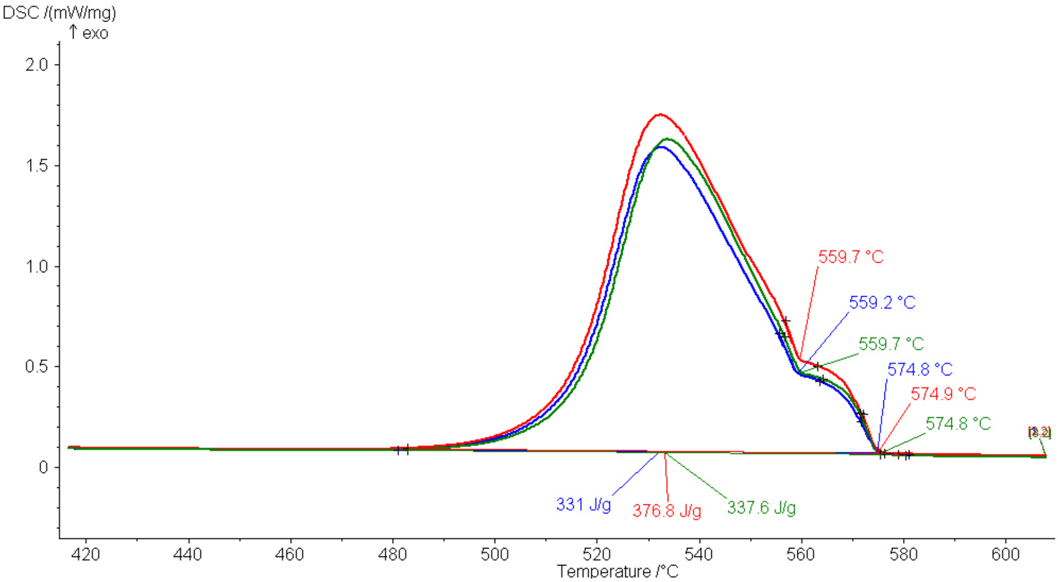
Namen naše preiskave je bil ugotoviti fazna ravnotežja v aluminijevih livarskih zlitinah v odvisnosti od vsebnosti silicija in železa.

reduced. Table 4 presents temperatures of primary solidification, solidification of eutectic and liberated solidification heats for the AlSi12Cu(Fe) casting alloy.

4 Conclusions

The goal of research was to determine phase equilibria in aluminium casting alloys depending on the silicon and iron contents. The following conclusions can be made:

1. $Al_{13}Fe_4$ (Al_3Fe) phase and phases in form of Al_8Fe_2Si, $Al_9Fe_2Si_2$, $Al_{15}Si_2M_4$ next to Al_2Cu phase are present. Formation



Slika 7. Primerjava ohlajevalnih krivulj v livarski zlitini AlSi12Cu(Fe)

Figure 7. Comparison of cooling curves of the AlSi12Cu(Fe) casting alloy

Tabela 4. Temperature začetka strjevanja in strjevanja evtektika ter sproščene toplote livarske zlitine AlSi12Cu(Fe)

Table 4. Temperatures of the beginning of solidification of the alloy, solidification of eutectic, and liberated heats of the AlSi12Cu(Fe) casting alloy

	0 min	15 min	30 min
Začetek strjevanja / Beginning of solidification	574,9 °C	574,8 °C	574,8 °C
Taljenje evtektika / Solidification of eutectic	559,7 °C	559,7 °C	559,2°C
Sproščena toplota / Liberated heat	376,8 J/g	337,6 J/g	331 J/g

S preiskavami smo prišli do naslednjih zaključkov:

1. Da so prisotne železove faze $Al_{13}Fe_4$ (Al_3Fe) in faze v obliki Al_8Fe_2Si, $Al_9Fe_2Si_2$, $Al_{15}Si_2M_4$ in Al_2Cu faza. Nastanek faz v livarski zlitini $AlSi_{12}Cu(Fe)$ je potekal do deleža 2,5% Si in pri razmerju železa in silicija (Fe/Si) = 0,33.
2. Iz koncentracijskih profilov raztapljanja železa je razvidno, da koncentracija železa pada z oddaljenostjo od žičke. Najvišjo koncentracijo železa smo dobili z raztapljanjem žičke pri 750°C in času 30 minut. Krivulja se je izravnala na oddaljenosti 4 mm od žičke.
3. S simultano termično analizo livarske zlitine AlSi12Cu(Fe) smo ugotovili, da se z večanjem deleža železa v zlitini znižuje temperatura tališča, temperatura tališča evtektika pa se zvišuje, pri čemer se zniža tudi toplota, ki se porablja pri taljenju.

of these phases in the AlSiCu(Fe) alloy took place in content interval up to silicon fraction of 2.5 % and at the silicon/iron ratio (Fe/Si) = 0.33.

2. Content profiles of iron dissolution showed that the iron content reduced with the distance from the iron wire. The highest content by dissolving iron wire obtained for 30 min at 750 ^{o}C. The curve flattened at the distance of 4 mm from the wire.
3. Simultaneous thermal analysis of the AlSi12Cu(Fe) alloy showed that increased fraction of iron in the alloy reduced melting point of alloy while melting point of eutectic was increased. Heat consumed for melting was reduced too.

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