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POSSIBILITIES FOR ELIMINATING A LARGER AMOUNT OF IRON IN THE SECONDARY AlSi6Cu4 ALLOY WITH CHROME

MOŽNOST UPORABE KROMA ZA BOLJŠO ODSTRANITEV ŽELEZA IZ SEKUNDARNE ZLITINE AlSi6Cu4

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This paper deals with the influence of chrome on the segregation of iron-based phases. Iron is one of the most common impurities found in Al-Si alloys. It is impossible to remove iron from a melt using standard operations, but it is possible to eliminate its negative influence by adding some other elements that make the segregation of intermetallics less harmful. The experiments and the results of the analysis show a new approach to the solubility of iron-based phases when preparing a melt with a larger iron amount and the influence of nickel as an iron corrector of iron-based phases. It could be concluded that a larger amount of chrome causes the formation of sludge particles, while the shape of the iron-based phases is not altered from needles to a skeleton-like phase or Chinese script.

Keywords: secondary Al-Si-Cu based alloys, iron-based phases, thermal analysis, iron correctors, AlCr20

Članek obravnava vpliv kroma na izcejanje faz na osnovi železa. Železo je med najpogostejšimi nečistočami, ki jih lahko najdemo v zlitinah Al-Si. Z navadnimi postopki ni mogoče odstraniti železa iz taline, vendar pa je mogoče zmanjšati njegov negativni učinek z dodatkom nekaterih drugih elementov, ki povzročijo izločanje intermetalnih zlitin z manj škodljivo obliko. Izvedba eksperimentov in rezultati analize kažejo nov pogled na topnost železa med pripravo taline z večjo vsebnostjo železa in vpliv niklja kot korektorja za železo v fazah, ki vsebujejo železo. Lahko sklenemo, da večja vsebnost kroma povzroča nastanek delcev usedline, oblika faz na osnovi železa od igel do oblike okostja oziroma oblike kitajske pisave se ne obdrži.

Ključne besede: sekundarna zlitina na osnovi Al-Si-Cu, faze na osnovi železa, toplotna analiza, korektorji za železo, AlCr20

1 INTRODUCTION

Due to increased requirements on the quality of castings, the final fatigue properties and due to the pressure on the price of the final castings, it is necessary to find compromises in the casting production of secondary alloys with various impurities.[1] The basis for initiating this work was a lack of theoretical knowledge about the use of secondary Al-Si-Cu alloys with a large amount of iron and its appropriate and efficient elimination in the production of demanding castings for the automotive industry under serial conditions.

Increased amounts of iron in aluminium alloys cause intermetallic formations in various forms, affecting the final quality and durability of the castings. This adverse effect of iron greatly affects the mechanical properties of the castings.[2]

Iron cannot be removed from a melt with conventional procedures, but it is possible to eliminate its adverse effect by adding some elements, which cause the formation of iron intermetallic phases in a less adverse form. This problem was solved on the basis of the information reported in the literature, according to which a number of elements (e.g., Mn, Cr, Ni, V, Zr, Co) affect the formation of iron-based phases. However, in practice their use has not been spread or implemented.

To stimulate the segregation of intermetallics the following elements (iron correctors) are used:

Manganese – it adjusts the final strength characteristics and improves mechanical properties at elevated temperatures. An excess of manganese segregates in a needlelike shape or thickened Chinese script $Al_{15}Si_2(Fe,Mn)_3$ often having cracks. This fact causes a decrease in the mechanical properties and alloy fluidity. As a rule, manganese, together with iron, in the amount of 0.8 % improves machinability. This element is most commonly added to influence the morphology and type of segregated iron-based phases in Al-Si alloys used in a foundry. In the literature the recommended ratio of w(Fe) : w(Mn) is 0.5 to 0.65, but in serial conditions this is often insufficient. Some of the customers require the w(Mn) value to be 0.75 or 0.85 or even more, especially for demanding castings of secondary Al-Si alloys.

Chromium – is as an impurity in commercially available master alloys, in the range of 5 μm to 50 μm, it provides strength at room temperature and slightly increases the ductility. The presence of Cr phases $(CrFe)_4Si_4Al_{13}$ and $(CrFe)_5Si_8Al_2$ can increase the brittleness.

In the case of chromium a similar effect on the formation of the phases was observed as for manganese, but without a clear microstructural explanation. The presence of chromium, together with iron and manganese, can cause the formation of the so-called "sludge" particles.[3,4]

2 EXPERIMENTAL WORK

2.1 Experiment

For the experiments, secondary alloy AlSi6Cu4 (EN AC 45 000, A 319) was used with a specifically modified proportion of *w*(Mn) : *w*(Fe), with a value of 0.65 (**Table 1**). The AlSi6Cu4 alloy is widely spread in the aerospace and automotive industries, used for the engine components, where one of the main casting requirements is the tightness. These types of castings have good foundry properties with a limited tendency to crack formation under hot conditions; they are not prone to create concentrated shrinkages and have good machinability. The surface quality is also very good. Another advantage is the strengthening of the castings during heat treatment.[5]

Table 1: Chemical composition of AlSi6Cu4 alloy in mass fractions, *w*/%
Tabela 1: Kemijska sestava zlitine AlSi6Cu4 v masnih deležih, *w*/%

element	Si	Fe	Cu	Mn	Mg	
w/%	6.49	0.34	3.52	0.23	0.22	
element	Cr	Ni	Zn	V	Ti	Sr
w/%	0.03	0.01	0.70	0.01	0.14	<0.0001

Experimental melting was realized at the laboratory for foundry experiments at the Department of Technological Engineering at the University of Žilina. The melt was not refined, having no addition of a modifier or grain refiner. The only operations during the melt preparation were the stirring and oxide-film removal from the melt surface. The melt was poured into a metal mold with the minimum temperature of 150 °C. An alloy was prepared with an experimental procedure involving a deliberate "contamination" with an iron amount of w = 0.7 % to w = 0.8 %. The main reason for such a procedure was the fact that the increased iron amount in the alloy was close to the maximum amount allowed by the customer specification for the automotive components made from secondary alloys, type AlSi6Cu4. Normally, the maximum iron amount in such a type of alloys is from w = 0.5 % to w = 1.0 %.

An AlSi6Cu4 alloy was used as the base with the shortened chemical composition written in **Table 2** (melt no. 1).

Table 2: Chosen elements from the chemical composition of an AlSi6Cu4 alloy
Tabela 2: Izbrani elementi iz kemijske sestave zlitine AlSi6Cu4

element	Si	Fe	Mn	Ni
w/%	6.14	0.77	0.22	0.01

To stimulate the segregation of iron-based phases, master alloy AlCr20 was used. Different amounts of master alloy AlCr20 were added to the prepared alloy: 0.56 % (melt no. 2) and 0.7 % (melt no. 3).

As master alloy AlCr20 contained 0.32 % Fe, there was an increase in the iron amount in both cases (**Tables 3** and **4**).

Table 3: Chemical composition of melt no. 2 after an addition of master alloy AlCr20
Tabela 3: Kemijska sestava taline št. 2 po dodatku predzlitine AlCr20

Elem.	Si	Fe	Cu	Mn	Mg	
w/%	6.19	1.45	3.26	0.40	0.17	
Elem.	Cr	Ni	Zn	V	Ti	Sr
w/%	**2.18**	0.02	0.62	0.02	0.13	<0.0001

Table 4: Chemical composition of melt no. 3 after an addition of master alloy AlCr20
Tabela 4: Kemijska sestava taline št. 3 po dodatku predzlitine AlCr20

Elem.	Si	Fe	Cu	Mn	Mg	
w/%	6.64	1.24	3.51	0.61	0.22	
Elem.	Cr	Ni	Zn	V	Ti	Sr
w/%	**4.27**	0.01	0.35	0.01	0.12	< 0.0001

3 RESULTS AND DISCUSSION

An evaluation of the microstructures of the cast samples was made using semi-automatic light microscopy with an light microscope LEICA DMI 5000M with the LAS v4.1 program.

The basis of the microstructure of the AlSi6Cu4 secondary alloy included the dendrites of solution α, the phases of Al_2Cu eutectics, cubic intermetallic phases (containing the Chinese-script or skeleton-like phases) and possibly intermetallic phases Al-Si-(Fe,Mn). The maximum allowed size of the iron-based phases with a needle-like shape is normally 100 µm. The length of the needles is documented in **Figures 1** to **3**.

Figure 1 shows the microstructure of the sample from melt no. 1 (deliberately "contaminated").

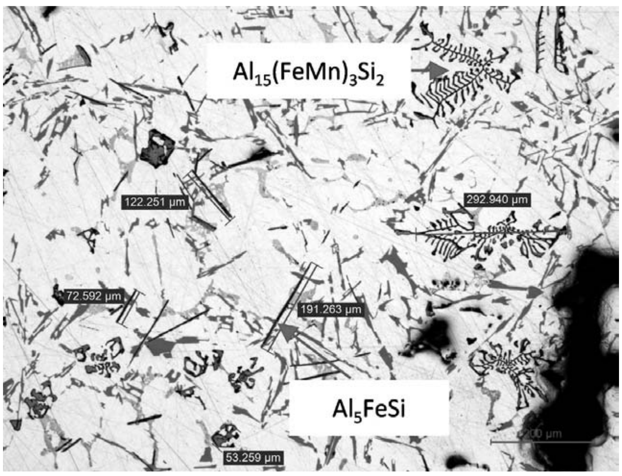

Figure 1: Light micrograph of the sample from melt no. 1 with indicated measurements of iron-based phases
Slika 1: Svetlobni posnetek vzorca iz taline št. 1 z označenimi meritvami faz na osnovi železa

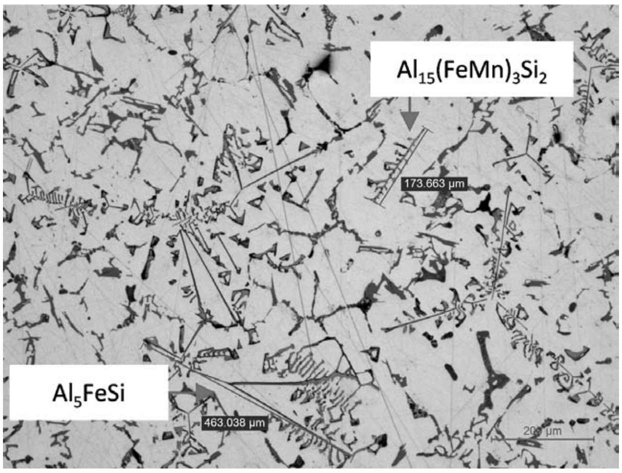

Figure 2: Light micrograph of the sample from melt no. 2 with indicated measurements of iron-based phases

Slika 2: Svetlobni posnetek vzorca iz taline št. 2 z označenimi meritvami faz na osnovi železa

Table 5: The longest lengths of iron-based phases measured during a metallographic analysis (Figures 2b, 3b, 4b)

Tabela 5: Največja izmerjena dolžina faze na osnovi železa, izmerjena pri metalografski analizi (slike 2b, 3b, 4b)

	Melt nr.	1	2	3
Length of measured phases (µm)	α-phase	293	91	744
	β-phase	122	463	–

Figure 2 shows the microstructure of the sample from melt no. 2, where melt no. 1 was taken as the base.

The AlCr20 master alloy was added to the prepared alloy (**Figure 3**). The addition ratio of 0.8 : 1 was changed so that the final amount of iron in the alloy was approximately 0.56 %. Small sludge particles are visible in the microstructure. The predominant phases are seen as skeleton-like and needle-like shapes (**Figure 2**). The length of needles is not appropriate, as it exceeds the normally allowable length of 100 µm (**Table 5**).

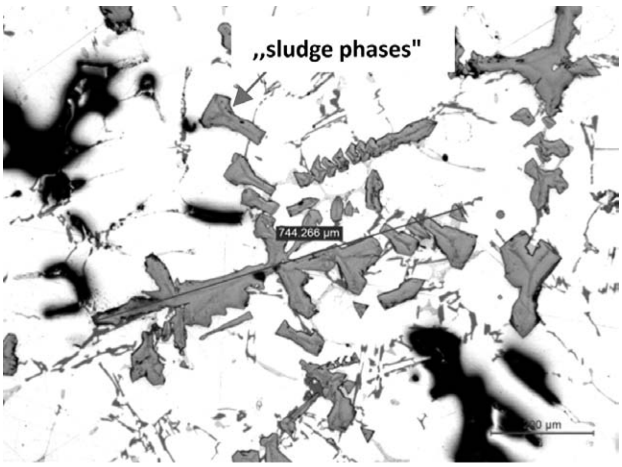

Figure 3: Light micrograph of the sample from melt no. 3 with indicated measurements of iron-based phases

Slika 3: Svetlobni posnetek vzorca iz taline št. 3 z označenimi meritvami faz na osnovi železa

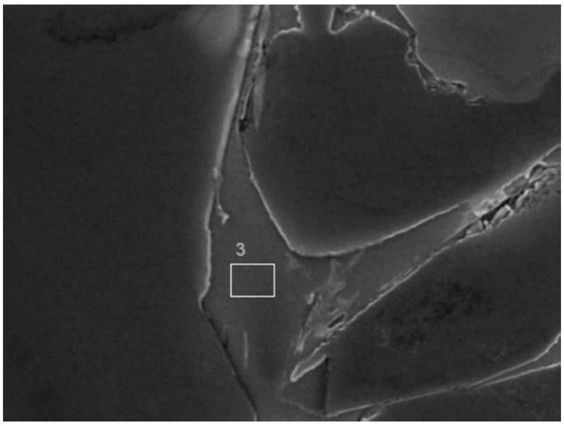

Figure 4: SEM micrograph of the sample from melt no. 3 with indicated EDX measurement of iron-based α-phase (chemical composition in mass fractions: *w*(Al) = 59.31 %, *w*(Si) = 9.25 %, *w*(Cr) = 13.71 %, *w*(Mn) = 5.03 %, *w*(Fe) = 11.17 %, *w*(Cu) = 1.54 %)

Slika 4: SEM-posnetek vzorca iz taline št. 3 z označenim mestom EDS-analize α-faze na osnovi železa (kemijska sestava v masnih deležih: *w*(Al) = 59,31 %, *w*(Si) = 9,25 %, *w*(Cr) = 13,71 %, *w*(Mn) = 5,03 %, *w*(Fe) = 11,17 %, *w*(Cu) = 1,54 %)

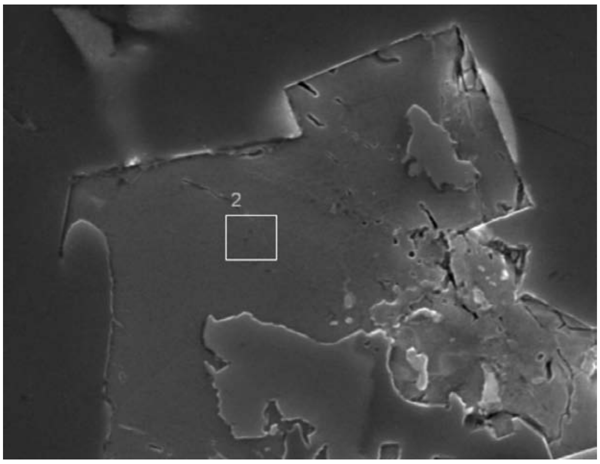

Figure 5: SEM micrograph of the sample from melt no. 3 with indicated EDX measurement of sludge particles (chemical composition in mass fractions: *w*(Al) = 50.13 %, *w*(Si) = 9.14 %, *w*(Cr) = 18.37 %, *w*(Mn) = 6.68 %, *w*(Fe) = 13.81 %, *w*(Cu) = 1.87 %)

Slika 5: SEM-posnetek vzorca iz taline št. 3 z označenim mestom EDS-analize delcev usedline (kemijska sestava v masnih deležih: *w*(Al) = 50,13 %, *w*(Si) = 9,14 %, *w*(Cr) = 18,37 %, *w*(Mn) = 6,68 %, *w*(Fe) = 13,81 %, *w*(Cu) = 1,87 %)

Figure 3 shows the microstructure of melt no. 3, which was also based on melt no. 1.

The AlCr20 master alloy was added to the prepared alloy. The addition ratio of 1 : 1 was changed so that the final amount of iron in the alloy was approximately 0.7 %. The influence of chromium on the formation of sludge particles with large dimensions is visible in the microstructure.

The impact of these particles was also observed due to the reduced values of ductility during the static tensile test (due to a limited scope of this article, they are not reported in detail).

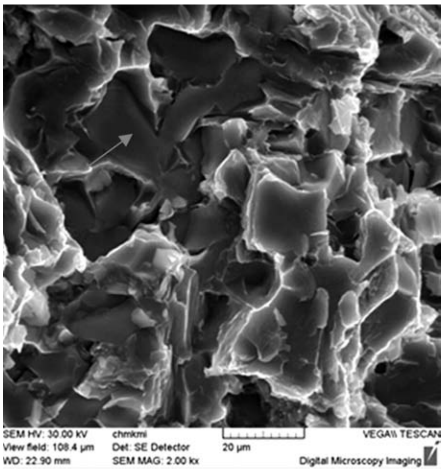

Figure 6: SEM micrograph of the sample from melt no. 3 with indicated EDX measurement of fracture area of tensile-test specimen (chemical composition in mass fractions: *w*(Al) = 56.57 %, *w*(Si) = 8.77 %, *w*(Cr) = 17.28 %, *w*(Mn) = 5.72 %, *w*(Fe) = 11.67 %)

Slika 6: SEM-posnetek vzorca iz taline št. 3 z označenim mestom EDS-analize na prelomni površini vzorca po nateznem preizkusu (kemijska sestava v masnih deležih: *w*(Al) = 56,57 %, *w*(Si) = 8,77 %, *w*(Cr) = 17,28 %, *w*(Mn) = 5,72 %, *w*(Fe) = 11,67 %)

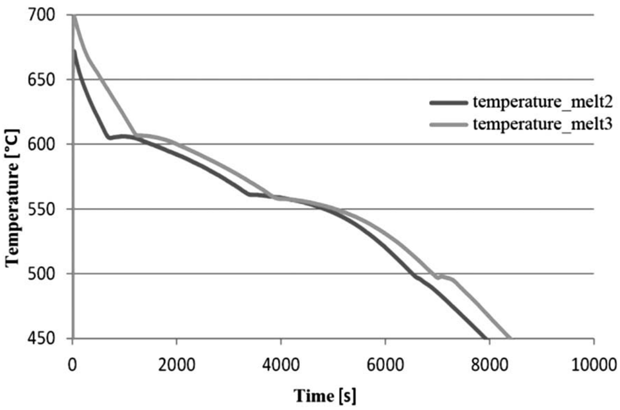

Figure 7: Cooling curves of melts 2 and 3 after the additions of various amounts of master alloy AlCr20

Slika 7: Potek ohlajevalnih krivulj talin 2 in 3 po dodani različni količini predzlitine AlCr20

The lengths of the needles are not appropriate because they exceed by several fold the allowable length of 100 μm (**Table 5**).

In the microstructure (**Figure 3**) we can see large particles and their clusters, which were analyzed with an EDX analysis. With the results of the chemical analysis we indentified a larger amount of Cr. On this sample we found intermetallic phases, which were not observed in the microstructure of melt no. 2, where the AlCr20 master alloy was also used, though in a smaller amount. The particles analyzed with the EDX analysis had a chemical composition based on Al-Si-(CrFe) (**Figures 4** and **5**).

Figure 6 shows the fracture surface of the sample from melt no. 3. On this fracture surface we found a considerable amount of oxides and a brittle fracture in

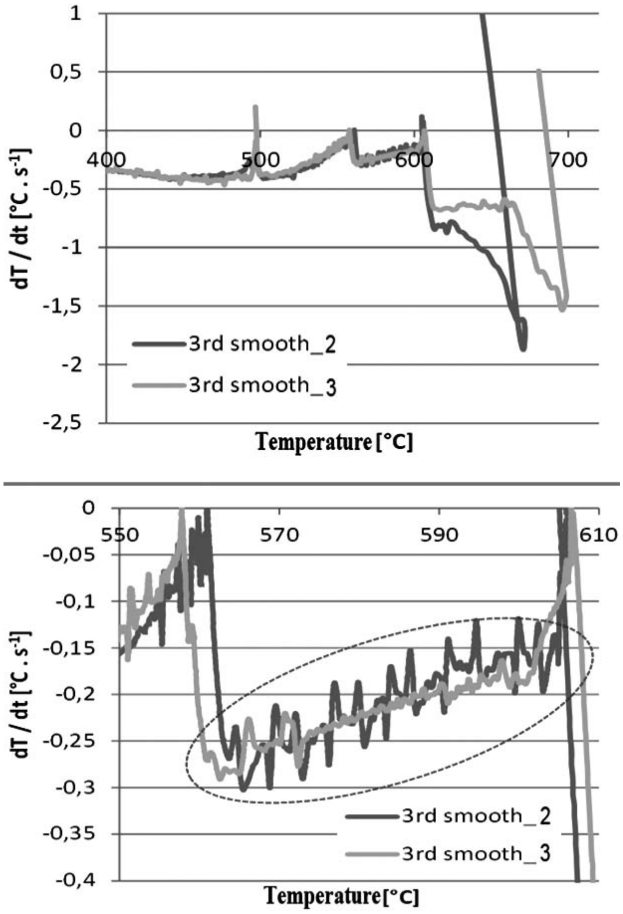

Figure 8: Comparison of first derivations in the area of segregation of iron-based phases from melts no. 2 and 3

Slika 8: Primerjava prvega odvoda s področja izločanja faz na osnovi železa iz talin št. 2 in 3

the area of the iron-rich phase. On the fracture surface we also performed an EDX analysis of the phase, on which the brittle fracture occurred. This phase can be chemically described as phase Al-Si-(CrFe)-Mn.[6]

The thermal-analysis records for melts no. 2 and 3 are presented in **Figure 7**. The graph shows the difference in the temperature at the beginning of the process (approximately 30 °C). When evaluating the solidification curves we could not observe the exclusion of iron-based β-phases, therefore, the first derivations of the curves were made according to the solidification time and both derivations were three times refined using the method of moving averages (**Figure 8**). In this figure you can see the area where the precipitation of iron-based phases occurs; these phases are affected by chrome.

In the graph we can see the influence of different amounts of Cr in the alloy and their influence on the temperature of the primary crystallization and also on the temperature of the eutectic reaction. At the same time we can see that in this area there is an exclusion of iron-based phases, affected by chromium. From the thermal analysis we can conclude that a chrome addition to the alloy with a larger iron amount decreases the liquidus temperature and increases the temperature of the eutectic reaction and the solidus temperature.

4 CONCLUSION

The goal of this research was to identify the effect of master alloy AlCr20 on the secondary AlSi6Cu4 alloy. Is it possible to conclude that a large chromium amount has a detrimental influence on the microstructure – the occurrence of very thick and long iron-based β-phases in a needle-like shape and the presence of very thick iron-based α-phases. According to the results of a microstructural analysis and an evaluation of the iron-based phases after an addition of iron corrector (chromium), there was no change in the shape of the segregated phases from needles to fishbone or Chinese script that lead to more favorable mechanical properties. Another research will be carried out to realize the experimental work, which will focus on determining the appropriate ratio of w(Cr) : w(Fe) and the influence of other elements on the secondary Al-Si-Cu alloy, used for demanding casting in the automotive industry.

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