O F

M E T A L L U R G Y

DOI: 10.2478/amm-2014-0118

Volume 59

D. BOLIBRUCHOVÁ*, J. MACKO*, M. BRŮNA*

ELIMINATION OF NEGATIVE EFFECT OF Fe IN SECONDARY ALLOYS AISi6Cu4 (EN AC 45 000, A 319) BY NICKEL

ROLA NI W ELIMINOWANIU SZKODLIWEGO WPŁYWU FAZ ZAWIERAJĄCYCH Fe W STOPACH WTÓRNYCH AlSi6Cu4 (EN AC 45 000, A 319)

Submitted article deals with influence of iron based phases segregation by nickel, which is in literature known as iron based phases corrector. Iron is one of the most common impurities that can be found in Al-Si alloys. It is impossible to remove iron from melt by standard operations, but it is possible to eliminate iron negative effects by addition of other elements, that enables segregation of iron in form of intermetallics with less harmful effect. For melt treatment was selected an exact alloy with requested iron content - master alloy AlNi20. Influence of nickel was evaluated quantitatively by chemical analysis (solubility), thermal analysis and microstructure evaluation. Experimental results analysis shows a new view on solubility of iron based phases. It can be concluded that nickel did not influenced iron based phases (β -phases), it does not change their type into more favorable form. As an initial impulse for starting this work was insufficient theoretical knowledge of usage secondary alloys Al-Si-Cu with higher iron content and its appropriate elimination in process of castings production for automotive industry. Increased iron content in alloys causes segregation of iron phases in various shapes and types during solidification, which subsequently affects quality, soundness and lifetime of castings. Because of increased demands for casting quality, final mechanical properties and effort to reduce costs, it is necessary to look for compromises in casting production from secondary alloys with occurrence of various impurities.

Keywords: Iron based phases, thermal analysis, iron based phases correctors, nickel

Artykuł opisuje wpływ dodatku niklu do stopów wtórnych Al-Si-Cu na segregację faz zawierających żelazo, które jest jednym z najpowszechniej występujących zanieczyszczeń w tych stopach. Powszechnie wiadomo, iż nie jest możliwe usunięcie żelaza z kąpieli metalowej, natomiast można ograniczać negatywny jego wpływ poprzez związanie żelaza w fazach międzymetalicznych mniej szkodliwych niż fazy β Fe, np. w następstwie dodatku innych pierwiastków. W badaniach do obróbki kąpieli zastosowano zaprawę AlNi20 z dokładnie określoną zawartością żelaza. Oddziaływanie niklu na skład i morfologię faz żelazowych określano na drodze analizy chemicznej (badania rozpuszczalności), analizy termicznej i oceny struktury. Na podstawie wyników badań stwierdzono, iż w badanych stopach nikiel nie wywiera wpływu na zmianę składu fazy β Fe, nie zmienia również kształtu jej wydzieleń do postaci bardziej korzystnej z punktu widzenia wpływu na właściwości.

1. Introduction

Iron is one of the most common impurity, which occurs in Al-Si alloys. Iron originates in many cases directly from primary alloys. Usually iron content in commercially used alloys is not exceeding 1 wt. %. The significant degradation of mechanical properties is a negative effect of iron presence. Small amount of iron in Al alloys can influence the elongation because of segregation β -Al₅FeSi phases in needle-like shape with various length. Needles are initiators of tension, subsequently leading to crack occurrence, caused also by fragility of needles itself [1]. It is impossible to remove iron from melt by standard operations, but it is possible to eliminate iron negative effects by addition of other elements, that enables segregation of iron in form of intermetallics with less harmful effect [2]. Phase diagram Al-Fe does not have precisely determined individual sections, also reaction temperatures and phases modifications are not properly defined [3]. The most important intermetallic phases are α -AlFeSi (chinese script or fishbone shape) and β -AlFeSi (needles, or thin plate-like shapes).

In metallurgical praxis are known suitable elements (Ni, Cr, Mn, V, Co) for iron based phases correction, their usage is limited, because their effectiveness can vary and also there is not enough knowledge for their widespread application. In Al alloys that contains elements affecting iron based phases segregation, those phases are usually in chinese script shape [4].

^{*} UNIVERSITY OF ŽILINA, FACULTY OF MECHANICAL ENGINEERING, DEPARTMENT OF TECHNOLOGICAL ENGINEERING, SLOVAK REPUBLIC

2. Experimental part

2.1. Experimental material

For experiments, secondary alloy AlSi6Cu4 (EN AC 45 000, A 319) was used with specifically modified ratio Mn : Fe to value of 0.65 (TABLE 1). AlSi6Cu4 alloy has wide range of application at aerospace and automotive industry mainly for engine components, where main requirement is tightness. These type of castings needs to have good casting properties, limited inclination to cracks and shrinkage occurrence and good machinability. Surface quality is also very good. Important advantage is possibility of strengthening of casting by heat treatment [5].

TABLE 1 Chemical composition of AlSi6Cu4 alloy

| element | Si | Fe | Cu | Mn | Mg | Cr | Ni | Zn |
|---------|-------|-------|--------|--------|-------|--------|-------|--------|
| wt. % | 6.49 | 0.342 | 3.524 | 0.229 | 0.223 | 0.0257 | 0.014 | 0.703 |
| element | Ti | Zr | Bi | Ca | V | Pb | Sn | Sb |
| wt. % | 0.144 | 0.007 | 0.0006 | 0.0011 | 0.01 | 0.038 | 0.004 | 0.0037 |

2.2. Experimental casts

An experimental casts were executed at Department of technological engineering laboratory at University of Žilina. Alloy preparation was performed in graphite melting furnace, which has been treated by refractory coating. For melting was used resistance furnace T15V, managed by PID controller CAL 3200. Melt temperature did not exceed $750\pm5^{\circ}$ C, it has been monitored by submersible pyrometer DMT 1550 with

thermocouple NiCr – Ni. Melt was not refined and without addition of modificator or grain refiner. The only operations during melt preparation made were stirring and oxide film removal from melt surface. Melt was poured into metal mold with minimal temperature of 150° C. An alloy had been prepared by experimental procedure (deliberately "contaminated") by iron content 0.7 to 0.8 wt. %. The main reason was to increase iron content in alloy, which approaches the maximal allowed content by customer specification for automotive components (made from secondary alloys AlSi6Cu4). Regularly the maximal iron content in such type of alloys is from 0.5 to 1.0%.

As a basic material was used aluminium alloy AlSi6Cu4 with shortened chemical composition written in TABLE 2 (melt nr. 1).

TABLE 2 Chosen elements from chemical composition of an alloyAlSi6Cu4

| element | Si | Fe | Mn | Ni | |
|---------|------|-------|-------|-------|--|
| wt.% | 6.14 | 0.769 | 0.221 | 0.014 | |

To influence the segregation of iron based phases a master alloy AlNi20 was used. Into prepared alloy different amounts of master alloy AlNi20 had been added 0.5% (melt nr. 2), 1.0% (melt nr. 3), 1.5% (melt nr. 4). Final chemical composition of individual melts are in following tables (TABLE 3, 4 and 5). By observing the chemical composition of individual alloys it is visible that with addition of high amount of master alloy AlNi20 (0.5%; 1.0%; 1.5% of nickel) is not always possible to achieve higher concentrations of added elements, even with the adequate melting temperature, holding temperature ($750\pm5^{\circ}$ C) and with correct holding time (20 to 25 min.).

TABLE 3

Si Fe Ni element Cu Mn Mg Cr Zn 6.33 0.832 0.224 0.025 wt. % 3.484 0.181 0.135 0.659 В element Be Bi Ca Cd Co Li Na 0.0001 0.0002 0.0005 < 0.000 < 0.0001 wt. % 0.0006 0.0005 < 0.0001 element Р Pb Sb Sn Sr V Zr Ti < 0.0005 0.04 < 0.0004 0.005 < 0.0001 0.0095 0.007 0.135 wt. %

Chemical composition of melt 2 after addition of master alloy AlNi20 (0.5 %)

| Chemical composition of melt 3 after addition of master alloy AlNi20 (1 | .0 %) | |
|---|-------|--|
|---|-------|--|

| alamant | Si | Ea | Cu | Ma | Ma | C. | Ni | 7 |
|---------|----------|--------|----------|--------|----------|---------|----------|----------|
| element | 51 | Fe | Cu | Mn | Mg | Cr | INI | Zn |
| wt. % | 5.99 | 0.832 | 3.209 | 0.229 | 0.187 | 0.026 | 0.233 | 0.63 |
| element | В | Be | Bi | Ca | Cd | Co | Li | Na |
| wt. % | 0.0006 | 0.0001 | 0.0005 | 0.0003 | 0.0004 | < 0.000 | < 0.0001 | < 0.0001 |
| element | Р | Pb | Sb | Sn | Sr | V | Zr | Ti |
| wt. % | < 0.0005 | 0.036 | < 0.0004 | 0.004 | < 0.0001 | 0.01028 | 0.007 | 0.158 |

TABLE 4

TABLE 5

Chemical composition of melt 4 after addition of master alloy AlNi20 (1.5 %)

| element | Si | Fe | Cu | Mn | Mg | Cr | Ni | Zn |
|---------|----------|--------|--------|--------|----------|---------|----------|----------|
| wt. % | 6.21 | 0.685 | 3.37 | 0.199 | 0.207 | 0.022 | 0.376 | 0.642 |
| element | В | Be | Bi | Ca | Cd | Co | Li | Na |
| wt. % | 0.0005 | 0.0001 | 0.0005 | 0.0004 | 0.0005 | 0.000 | < 0.0001 | < 0.0001 |
| element | Р | Pb | Sb | Sn | Sr | V | Zr | Ti |
| wt. % | < 0.0005 | 0.038 | 0.0008 | 0.004 | < 0.0001 | 0.00909 | 0.007 | 0.139 |

2.3. Metallographic evaluation of samples and EDX phases analysis

Microstructure evaluation of casted samples was made by semiautomatic light microscopy with optical microscope LEICA DMI 5000M using LAS v4.1 program.

The basis of AlSi6Cu4 microstructure is composed by dendrites of solution α , phases of Al₂Cu eutectics, cubic intermetallic phases (contains chinese script or fishbone like phases) and possibly intermetallic phases containing Al-Si-(Fe,Mn). Maximal allowed size of iron based phases (requested by customer) is usually 100 μ m in needlelike shape.

At (Fig. 1) is shown microstructure of sample from melt nr. 1. On observed microstructure can be seen iron basis phases with needle like shape and fishbone intermetallics. Iron based phases with fishbone like shape were analyzed by EDX analysis (Fig. 2).



Fig. 1. Microstructure of melt nr. 1 - measurement of iron based phases



Fig. 2. EDX analysis of α -phases from melt nr. 1

As a result from EDX analysis of chemical composition can be concluded, that phases contain sufficient manganese amount, that assists to form fishbone like shape phases (α -phase).

Microstructure of a sample from melt nr. 2 (addition of 0.5 wt. % AlNi20) is on Fig. 3. On microstructure can be seen thin long needles of iron based phases. Length of needles is documented on Fig. 3b. Needle like shaped intermetallic phases were analyzed by EDX analysis (Fig. 4). Length of needle-like shape phases based on iron is multiple times bigger than standardly allowed 100 μ m (Fig. 4).



Fig. 3. Microstructure of sample from melt nr. 2 – measurement of iron based phases



Fig. 4. EDX analysis of β -phase from melt nr. 2 with area of analysis

Microstructure of a sample from melt nr. 3 (addition of 1.0 wt. % AlNi20) is on Fig. 5. On microstructure can be seen sludge phases, needle like and fishbone like shapes of intermetallic phases. Most of the needles has length smaller than $100 \,\mu$ m, but in microstructure are also needles that exceed this value.

TABLE 6 The longest measured length of iron based phases measured on metallographic analysis (Fig. 2b, 4b, 6b, 8b)

| Melt nr. | 1. | 2. | 3. | 4. | |
|------------------------------|-----------------|--------|--------|--------|--------|
| Length of measured phases | α -phase | 292.94 | 91.36 | - | 176.85 |
| (μ m) | β -phase | 122.25 | 646.04 | 255.09 | 421.46 |

An EDX analysis have been performed on thickened particle (Fig. 6). It is necessary to point out, that in observed particles no nickel was found and sludge phases were confirmed.

Microstructure of a sample from melt nr. 4 (addition of 1.5 wt. % AlNi20) is shown on Fig. 7. On microstructure can be seen a visible thicker needle like phases compared to melts nr. 2 and nr. 3. Length of phases is also bigger.



Fig. 5. Microstructure of sample from melt nr. 3 – measurement of iron based phases



Fig. 6. EDX analysis of coarsen α -phases on sample from melt nr. 3



Fig. 7. Microstructure of sample from melt nr. 4 – measurement of iron based phases

2.4. Thermal analysis

Thermal analysis record from melts nr. 2 to nr. 4 is shown on Fig. 8. Cooling curve shows peak before eutectic reaction that is in area where β -phases are segregated in needle like shape. In the graph of first derivation (Fig. 9) are visible β -phases segregation in comparison to melts, which corresponds to microstructure of analyzed samples.

Addition of nickel into alloy with higher iron content decreases its liquidus temperature, also increases temperature of primary undercooling, temperature of eutectic reaction and solidus temperature.



Fig. 8. Cooling curves graph from melts nr. 2 to 4 after addition of various amount of master alloy AlNi20



Fig. 9. Comparison of first derivation in area of segregation iron based phases from melts nr. 2 to 4 after addition of various amount of master alloy AlNi20

3. Conclusion

The goal of the submited article was to identify effect of master alloy AlNi20 on secondary alloy AlSi6Cu4. Based on the achieved results, it is not possible to conclude that nickel is iron based phases segregation corrector. It is possible to conclude that high nickel content has detrimental influence on microstructure – creation of thickened and long iron based β -phases in needle like shape, and occurrence of thickened iron based α -phases. Based on the results of microstructure and evaluation of iron based phases after addition of iron corrector (nickel) the change of shape of segregated phases from

Acknowledgements

This work was created in framework of the grant project VEGA č. 1/0363/13. The authors would like to thank the Grant Agency for support.

Received: 10 January 2014.

REFERENCES

- [1] W. K a h l i f a, Role inclusions in the precipitation of α aluminium and Fe-intermetallistics in aluminium rich corner of the Al-Si-Fe ternary system (2003).
- [2] N. Tenekedjiev, H. Mulazimoglu, B. Closset, Microstructures and thermal analysis of strontium treated aluminium-silicon alloys (1995).
- [3] Š. Michna et al., Encyclopedia of Aluminium, Adin s.r.o. (2005).
- [4] R. Pastirčák, D. Urgela, In: Quo vadis foundry III, Ecological aspects of metallurgy and foundry, 148-152 (2010).
- [5] R. Pastirčák, A. Sládek, I. Vaško, Technological engineering. – ISSN 1336-5967. Roč. 4, č. 1, 8-9 (2007).