Vanadium Influence On Iron Based Intermetallic Phases In AlSi6Cu4 Alloy

Negative effect of iron in Al-Si alloys mostly refers with iron based intermetallic phases, especially Al$_5$FeSi phases. These phases are present in platelet-like forms, which sharp edges are considered as main cracks initiators and also as contributors of porosity formation. In recent times, addition of some elements, for example Mn, Co, Cr, Ni, V, is used to reduce influence of iron. Influence of vanadium in aluminium AlSi6Cu4 alloy with intentionally increased iron content is presented in this article. Vanadium amount has been graduated and chemical composition of alloy has been analysed by spectral analysis. Vanadium influence on microstructural changes was evaluated by microstructural analysis and some of intermetallic particles were reviewed by EDX analysis.

Keywords: AlSi6Cu4 alloy, iron correction, vanadium, iron based phases

1. Introduction

Improving the properties of cast non-ferrous alloys has been recently focused mainly on developing the theory and practice of structure refinement, e.g. [1, 2, 3], on modification of chemical composition as well as melt purification from detrimental impurities. The latter has a key importance when melting secondary alloys.

Using of secondary (recycled) aluminium alloy contribute to decrease production costs in every branch of industry. The biggest disadvantage of secondary alloys using is presence of elevated amount of iron. In Al-Si based aluminium alloys is the high iron amount connected with elongation and also tensile strength decreasing [4, 5]. Even at lower amount of iron, its negative effects are observed, although the most detrimental effect occurs after exceeding the critical iron level. The critical iron level present in the alloy is directly related with Si amount and it can be calculated according to relation (1) [5].

$$Fe_{crit} \approx 0.075x (\text{wt.\%Si}) - 0.05 \ (\text{wt.\%}) \ (1)$$

The detrimental iron effect in Al-Si alloys consists in formation of hard and brittle intermetallic phases [6], for example Al$_3$FeSi and Al$_{15}$(FeMn)$_3$Si$_2$. The reason that are intermetallic particles containing Fe detrimental to mechanical properties of alloy is that they are much more easily fractured under tensile load than aluminium matrix or the small silicon particles (if modified). Micro-cracks tend to initiate at these particles and they provide easy pathways for macro-cracks to propagate through [4].

Different iron solubility in liquid and solid aluminium could lead to combine with other elements and to form intermetallic phases. In Al-Si alloys are mostly present intermetallic phases Al$_3$Fe$_2$Si (known as $\alpha$-phases) and Al$_3$FeSi (known as $\beta$-phases). Al$_3$FeSi phase of the iron phases occurs most frequently at the higher content of Fe (0.5 to 1.2 wt. %). This higher content can significantly affect the mechanical properties such as reducing the tensile strength, ductility and fracture toughness. It also reduces the fatigue life of castings [5, 7]; the existence of long platelet-like formations of Al$_3$FeSi phase support the initiation of fatigue cracks and increases the porosity. In the presence of Mn in Al-Si alloys dominant phase that forms is Al$_{15}$(FeMn)$_3$Si$_2$, with convoluted structure, on metallographic sample observed as “Chinese script”. It was found out, that platelets of Al$_3$FeSi phases are much more susceptible to contravention and connection into cracks like particles of Chinese script phase Al$_{15}$(FeMn)$_3$Si$_2$. This observation led to adding the iron correctors into Al-Si alloys with medium and higher Fe content [4].
The most known iron corrector in aluminium alloys is Mn that not only decreases the detrimental iron effect but also through the different phases increases creep resistance and heat resistance. The recommended Mn addition to negative effect of iron correction varies in amount greater than half of the Fe content. Sometimes the Mn addition in the alloy with high amount of Fe and Cr can cause formation negative so called “sludge” phases that cannot be removed from final alloy. Tendency of formation “sludge” phases in alloy depends on the content of Fe, Mn and Cr and it can be calculated according to so called “sludge factor” (SF) [5]:

\[
SF = 1\% Fe + 2\% Mn + 3\% Cr
\]  

(2)

Between other used correctors belongs Co, Cr and Be [8]. By the lower additions of elements such as Ni, Ti, V and Mo there were also discovered beneficial effects to decreasing influence of iron [9].

Presence of vanadium in aluminium alloys supports grain refinement from the content 0.05 to 0.15 wt. % [10]. Addition of 0.2 wt. % of V in the alloy with high Fe content has beneficial influence on mechanical properties, specifically to increase tensile strength, elongation and even hardness [11]. At the same value of vanadium addition length of platelets particles Al<sub>5</sub>FeSi phase was decreased [11].

2. Experimental part

Experimental part is focused on analyse the possibilities of vanadium use as an iron corrector in secondary aluminium alloy AlSi6Cu4 [12]. The real chemical composition of used alloy obtained by spectral analysis is presented in Tab. 1.

| Element | Si (wt. %) | Fe (wt. %) | Cu (wt. %) | Mn (wt. %) | Mg (wt. %) | Cr (wt. %) |
|---------|------------|------------|------------|------------|------------|------------|
| Amount  | 6.43       | 0.34       | 3.43       | 0.232      | 0.229      | 0.03       |

| Element | Ni (wt. %) | Zn (wt. %) | Be (wt. %) | Ca (wt. %) | Cd (wt. %) | Li (wt. %) |
|---------|------------|------------|------------|------------|------------|------------|
| Amount  | 0.01       | 0.70       | 0.0001     | 0.0014     | 0.0004     | <0.0001    |

| Element | Na (wt. %) | P (wt. %) | Pb (wt. %) | Sr (wt. %) | Ti (wt. %) | Al (wt. %) |
|---------|------------|-----------|------------|------------|------------|------------|
| Amount  | 0.0004     | <0.0005   | 0.04       | <0.0001    | 0.16       | rest       |

The alloy was alloyed by master alloy AlFe10 to obtain the higher Fe amount. After controlled pollution of alloy to value approximately 0.75 wt. % of Fe, melts were realised, at which alloy was alloyed by vanadium. The amount of added vanadium was ranked by 0.5 wt. %. In this way alloys with addition 0.5, 1, 1.5 and 2 wt. % of V were obtained.

On casted samples evaluation of chemical composition, microstructure and EDX analysis was realised to review vanadium influence on structure of material.

The evaluation of alloys chemical composition was realised by spectral analysis. Presence of vanadium was not verified, however changes in chemical content of some elements with the increasing amount of V has been detected (Fig. 1). In Fig. 1a, decrease of Si amount by 0.99 wt. % between the melt without vanadium and melt with 2.0 wt. % of V addition is observed. Measured value represented 15.3 % percentage decrease of Si amount. Decrease of Cu amount was also detected (Fig. 1b) between first and last melt with percentage decrease 13.7 %. The most significant decrease was found out in case of Ti (Fig. 1c) where decrease of 0.12 wt. % of V amount represented 75 % decrease compared to first melt.

From obtained values of chemical composition the critical amount of iron was calculated according to relation (1) with results presented in Tab. 2. The real Fe content in all samples exceeds value of critical amount of iron according to chemical composition of used alloy.

| Melt No. | Critical amount of iron | Real iron content |
|----------|-------------------------|-------------------|
| Fe<sub>crit</sub> (wt. %) | Fe content (wt. %) |
| 1        | 0.43                    | 0.75              |
| 2        | 0.42                    | 0.77              |
| 3        | 0.40                    | 0.75              |
| 4        | 0.37                    | 0.72              |
| 5        | 0.36                    | 0.73              |

At higher levels of Fe, Mn and Cr formation of “sludge phases” can be expected that existence is objectionable. The values of “sludge factor” for individual melts are shown in Fig. 2.

From measured values, it can be decided that the alloy with the highest addition of V has the lowest tendency to form “sludge phases”. Cast samples were prepared by standard metallographic procedure to microstructural analysis focused on describing iron based intermetallic phases presented in alloy. Microstructure of alloy was formed by dendrites of aluminium α-phase, eutectic silicon and intermetallic phases. Whereas the alloy includes a significant Cu content, Al-Cu based phases were observed in the alloy. Moreover significant amount of iron based intermetallic phases were present which distinguished by shape, but particularly by length of needle-like phases.
In alloy microstructure with high amount of iron, but without added vanadium (Fig. 3a), especially skeleton-like particles of $\text{Al}_{15}(\text{FeMn})_3\text{Si}_2$ phase were also presented in spite of high iron level. The cause of skeleton-like phases instead needle-like phases formation was relatively high Mn content in alloy.

With vanadium addition larger amount platelet-like iron phases $\text{Al}_5\text{FeSi}$ began to exist in alloy microstructure. On microstructural samples, length of individual needles visible on microstructure scans was measured at 500x magnification. The average length of needle-like particles was 39.47 $\mu$m on sample with 0.5 wt. % of added V (Fig. 3b). With the increasing of V addition to 1 wt. %, decrease of average needles length to value of 34.23 $\mu$m was discovered. Place of platelet-like particles was not balanced in observed places, but places with higher needles level (Fig. 3c) as well as places without iron phases presence occurred. Microstructure of sample with 1.5 wt. % of added V (Fig. 3d) contained platelet-like iron phases, but also skeleton-like structures were present in lower amount. The needle-like particles on sample reached lower average value again (33.98 $\mu$m). After adding 2 wt. % of V, needle-like phases and atypical phases (Fig. 3e) occurs in microstructure. Average length of needle-like phases represented the lowest value from all evaluated samples, 31.44 $\mu$m. By examination of individual samples microstructure, forming of until now unexplored atypical irregular form phases was observed at higher vanadium addition.

Whereas presence of vanadium was not detected in individual samples through spectral analysis, EDX analysis of chosen areas of microstructure was performed, in an effort to confirm vanadium presence in alloy. Based on EDX analyses made at individual points, vanadium presence was not confirmed [12], therefore linear EDX analysis, that covers larger area of sample, was realised. Fig. 4 shows measured values of chemical elements content. From figure is obvious that either this way vanadium content in alloy was not detected. Insufficient display resolution of used method, but also analysing of small area might be a cause.

### 3. Discussion

Presence of vanadium in alloy was not confirmed by spectral analysis of chemical composition. Insufficient calibration or incorrect adjustment of device used for vanadium analysing might be a reason. Spectral analysis pointed at still unexplained decrease of some elements (Si, Cu, Ti) content after vanadium adding to alloy. One of possible explanations is combination of elements to intermetallic phases (for example atypical phase Fig. 3e), unevenly distributed in examined sample volume.

Influence of vanadium to microstructural changes was also marked. Iron-based phases in alloy without added V microstructure had mostly skeleton-like shape (Chinese script). After vanadium addition, needles of $\text{Al}_5\text{FeSi}$ phase in a higher amount occurred, along with them skeleton-like phases were still present. High number of skeleton-like phases was caused by significant manganese content in cast samples. Length of individual needle-like structures was reduced as amount of added vanadium increase. Unknown phases of irregular form were detected in microstructure at higher vanadium addition.

In an effort to determine a form, in which vanadium in such alloy exists, EDX analysis of chemical composition proceeded. After EDX analyses focused to single point was not vanadium presence confirmed, hence linear EDX analysis was performed that takes greater measured area. By this method...
vanadium was not discovered either. The reasons can be insufficient examination of vanadium presence in used alloy but also relatively small investigated area by EDX analysis.

### 4. Conclusions

Beneficial influence of vanadium adding to AlSi6Cu4 alloy on intermetallic phases has been determined by performed experiments. Vanadium addition evoked shortening of Fe-based needle-like particles length. Effect of vanadium as iron corrector has been approved by measures even at its higher amount.

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