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INFLUENCE OF VANADIUM AND CHROMIUM ADDITION ON MORPHOLOGY AND COMPOSITION OF IRON BASED PHASES IN AlSi10MgMn ALLOY

Application of secondary Al-Si alloys is mostly influenced by amount of impurities. Detrimental effect of iron, as the most harmful impurity, refers mainly to morphology of iron intermetallic phases. Morphology of iron phases can be influenced by several methods from which the most common is addition of some elements. In primary alloys manganese is commonly used, but its influence is not such favourable in high iron levels because of so-called sludge phase formation. Higher iron content thus requires other alloying elements which can be vanadium, chromium or others. In this article, vanadium and mutual vanadium and chromium influence on iron phase morphology and chemical composition is analysed by optical microscopy, SEM observations and EDX analysis.

Keywords: AlSi10MgMn alloy, iron based intermetallic phase, vanadium, chromium.

1. Introduction

In recent years much effort is being expended to protect the earth's environment and one of the most desirable concepts that have been established through these developments is the recycling of waste materials. Aluminium waste must be one of the most desirable materials for recycling or re-using. This is because the energy costs involved in its production can be reduced by up to 95% by recycling Al scrap, as the production of Al from its ore, bauxite, is an energy consuming and very expensive process [1]. However, the increasing use of recycled aluminium casting alloys warrants strict process control to remove the ill effects of impurity elements [2]. From impurity elements, the most harmful is thought to be iron [3 - 5].

Presence of iron in Al-Si cast alloys is a common problem in primary alloys but it becomes more important in secondary (recycled) aluminium alloys made from scrap materials. The reason why iron has such detrimental influence is that although iron is highly soluble in liquid aluminium and its alloys, it has very little solubility in the solid (max. 0.05 wt. %) and so it tends to combine with other elements to form intermetallic phase particles of various types [5]. Intermetallic phases present in the alloys then decrease mechanical properties of the alloy and also porosity of final casting can be increased by iron phases.

A variety of Fe-rich intermetallic phases have been observed in aluminium alloys. In Al-Si-Fe system there are five main Fe-rich

phases: Al_3Fe (or $\text{Al}_{13}\text{Fe}_4$), $\alpha\text{-Al}_8\text{Fe}_2\text{Si}$ (possibly $\alpha\text{-Al}_{12}\text{Fe}_3\text{Si}_2$), $\beta\text{-Al}_5\text{FeSi}$, $\delta\text{-Al}_4\text{FeSi}_2$ and $\gamma\text{-Al}_3\text{FeSi}$ [6]. The most common intermetallic phase is $\beta\text{-Al}_5\text{FeSi}$ that is also considered to have the most detrimental effect on mechanical and foundry properties of Al-Si type alloys. The platelet-like morphology of the Al_5FeSi phase allows it to act as a stress raiser, consequently undermining the mechanical properties of the cast part, mainly tensile strength and elongation [5]. As the fraction of insoluble phase increases with increased iron content, casting properties such as fluidity and feeding characteristics are also adversely affected. Iron also lead to the formation of excessive shrinkage porosity defects in castings [7]. If Mg is present with Si, an alternative phase can form, $\pi\text{-Al}_8\text{FeMg}_3\text{Si}_6$ [5]. Phase $\pi\text{-Al}_8\text{FeMg}_3\text{Si}_6$ occurs in script-like morphology and it has a negative impact on ductile properties of Al-Si-Mg alloys [8]. For the more usual Al-Si-Mg cast alloys of modest Mn contents, the $\text{Al}_{15}(\text{Fe,Mn})_3\text{Si}_2$ phase often has an appearance of Chinese script in section, being irregular or convoluted. If Fe and Mn are sufficiently high, primary $\text{Al}_{15}(\text{Fe,Mn})_3\text{Si}_2$ phase may appear as hexagonal, star-like, or dendritic crystals.

There is still only little information about vanadium influence on iron-based intermetallic phases in aluminium alloys. In the cast 99.5 Al alloy V addition in amount of 0.1 wt. % exhibits more cubic $\alpha\text{-AlFeSi}$ phase than in V-free version in both the as-cast and homogenised conditions, although the effect became more pronounced after homogenisation [9]. Vanadium addition (0.2

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wt. %) in Al-Si cast alloys containing $3.0 \div 12.0$ wt. % of Si, $0 \div 0.4$ wt. % of Mg and $0.3 \div 2.3$ wt. % of Fe have also a beneficial influence on length of $\beta\text{-Al}_5\text{FeSi}$ but there was a negligible amount of V detected in platelets [10]. Previous work [11] shows also a beneficial influence of V addition on microstructure and mechanical properties of AlSi6Cu4 alloy but vanadium was not detected in iron intermetallic phases at all.

It has been reported that Cr addition can have similar effect on iron intermetallics as Mn [12]. Chromium improves aluminium alloys strength at indoor and higher temperatures (precipitation of intermetallic compositions of Cr inhibits the growth of grains) and mildly deteriorates elongation. But the presence of Cr phases $\text{Al}_{13}(\text{CrFe})_4\text{Si}_4$ and $\text{Al}_2(\text{CrFe})_5\text{Si}_8$ can increase brittleness [10]. Cr addition leads to improvement of mechanical properties of as-cast AlSi7Mg0.3 alloy while the maximal value of tensile strength and elongation was measured at 1.0 wt. % of Cr [13 - 16].

There is no available information about the mutual V and Cr influence in Al-Si alloy. In the article, vanadium and mutual V and Cr influence on iron based intermetallics is analysed in AlSi10MgMn cast alloy by optical microscopy, SEM observations and EDX analysis.

2. Materials and methodology

Commercial AlSi10MgMn alloy was used to perform the experiments. Selected alloy was in the first step of experiments polluted by iron by addition of AlFe10 master alloy. Alloy with 0.98 wt. % of iron was obtained this way (marked as AlSi10MgMnFe1). Vanadium was added to such prepared secondary alloy in amount of 0.2 wt. % of V. Combined V and Cr influence was evaluated on the alloy prepared by chromium addition to vanadium treated alloy in the amount of 0.5 and 1.0 wt. % of Cr. Required amounts of V and Cr were added in the form of AlV10 and AlCr20 master alloys. The melts were not purified, modified or grain refined. Prepared melts were after reaching pouring temperature (760°C) poured into a permanent mould preheated to 200°C . Chemical composition of the alloys is shown in Table 1. Accurate values of Cr level in alloys with added V and Cr could not be measured due to uncommonly high Cr addition that is out of range of the used spectrometer.

Samples for metallographic observations were prepared from the castings by standard procedure containing cutting,

grinding, polishing and etching. Chemical composition of selected intermetallic particles was analysed by EDX analysis.

3. Results

Typical microstructure of AlSi10MgMn1 alloy is shown in Fig. 1. As the alloy was not modified, eutectic silicon is present in the form of platelet particles surrounded by aluminium dendrites. Significant amount of iron based intermetallics is also present in the microstructure, mostly in the form of thick needles. Position of the iron phases seems to be preferentially along the eutectic Si. Chemical analysis of the needle-like particle (Fig. 2) shows mainly the presence of Al, Si and Fe, but low amount of Mn was detected as well. Generally, it can be described as $\beta\text{-AlSiFe}$, probably Al_5FeSi .

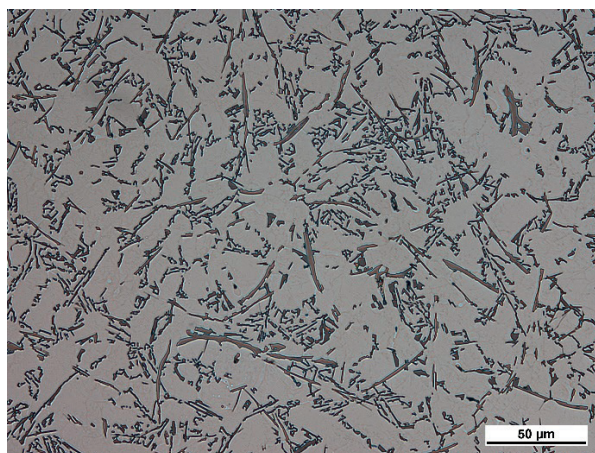


Fig. 1 Typical microstructure of AlSi10MgMnFe1 alloy, etch. 0.5% HF

Vanadium addition in amount of 0.2 wt. % leads to the formation of increased amount of script-like iron phases, but platelets were still in higher number. As it can be seen in Fig. 3, vanadium caused increasing of needle-like particles compared to AlSi10MgMnFe1 alloy but thickness was decreased. EDX analysis showed the presence of small V amount in script-like particles (Fig. 4).

Chemical compositions of prepared alloys in wt. %

Table 1

Alloy	Si	Mg	Mn	Fe	Ti	Zn	Cu	V	Cr	Al
AlSi10MgMn	10.220	0.277	0.108	0.448	0.046	0.029	0.047	0.010	0.006	rest
AlSi10MgMnFe1	9.73	0.313	0.118	0.980	0.041	0.026	0.048	0.009	0.037	rest
AlSi10MgMnFe1 + 0.2 wt. % V	9.133	0.265	0.116	1.588	0.034	0.026	0.046	0.216	0.166	rest
AlSi10MgMnFe1 + 0.2 wt. % V + 1.0 wt. % Cr	8.996	0.291	0.119	1.446	0.033	0.029	0.047	0.139	>0.480	rest
AlSi10MgMnFe1 + 0.2 wt. % V + 0.5 wt. % Cr	8.539	0.290	0.098	1.182	0.031	0.028	0.053	0.135	>0.480	rest

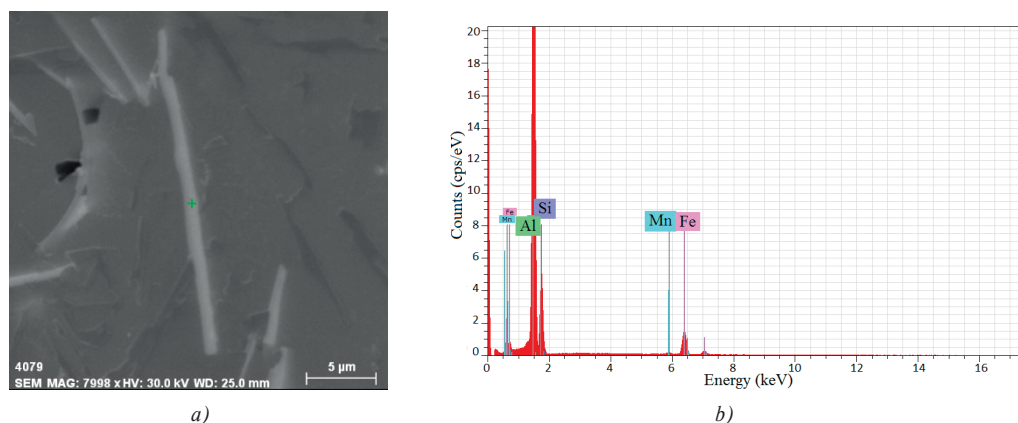


Fig. 2 EDX analysis of needle-like phase in AlSi10MgMnFe1 alloy: a) SEM image of analysed place, b) EDX spectrum

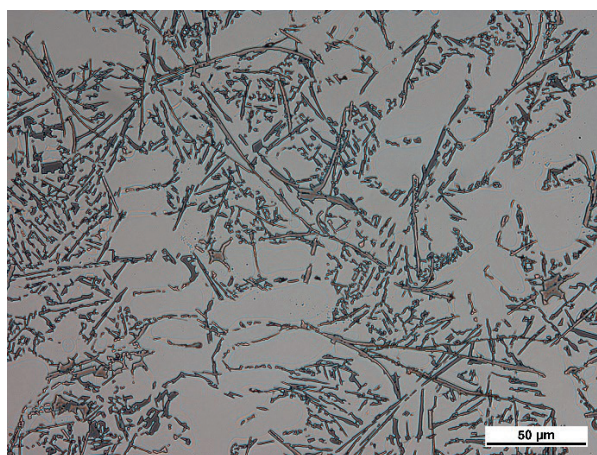


Fig. 3 Typical microstructure of AlSi10MgMnFe1 alloy with 0.2 wt. % of V, etch. 0.5% HF

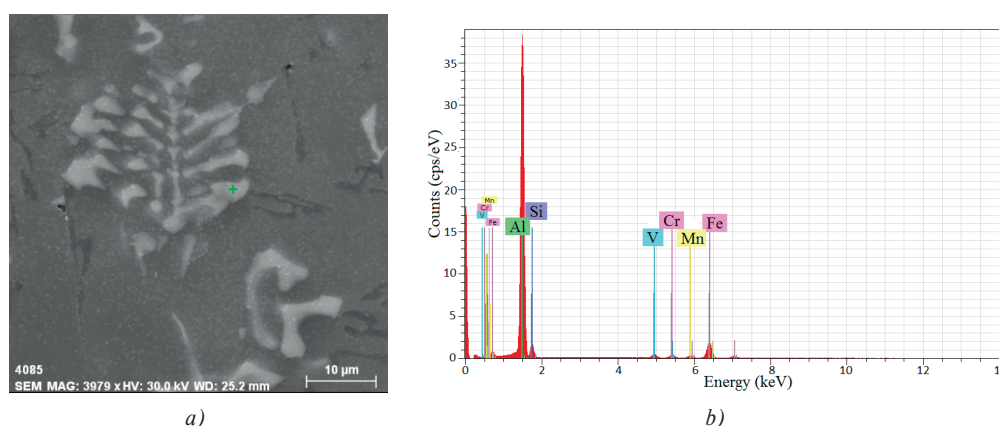


Fig. 4 EDX analysis of script-like phase in AlSi10MgMnFe1 alloy with 0.2 wt. % of V: a) SEM image of analysed place, b) EDX spectrum

Mutual V and Cr addition leads to the formation of so called “sludge phases”. Amount of sludge phases increased with Cr addition, lower amount was present after addition of 0.5 wt. % of Cr (Fig. 5) and higher in the alloy with 1.0 wt. % of Cr (Fig. 6). Size and amount of needle-like particle was after the V and Cr

addition decreased but the formation of sludge phases is thought to be even more deleterious compared to needles or script-like particles. This is due to its high melting point, high specific gravity and hardness which causes the increasing wear of melting devices and deteriorating of the alloy machinability [14]. Except of this,

once the sludge phase is formed, it cannot be removed from alloy by further re-melting or refining process. Chemical composition of script-like phase present in alloy with 0.5 wt. % Cr addition shows presence of both V and Cr in analysed place (Fig. 7) while

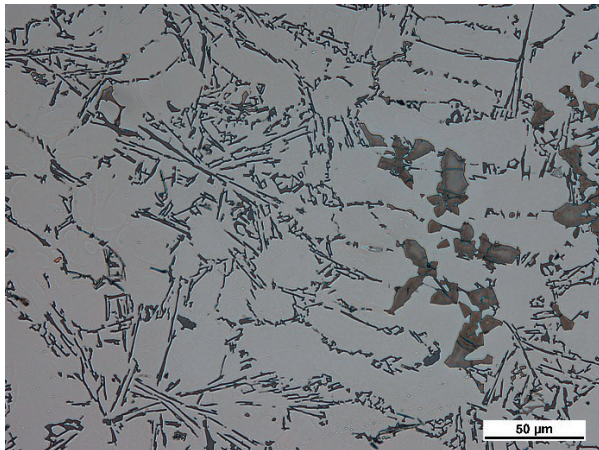


Fig. 5 Typical microstructure of AlSi10MgMnFe1 alloy with 0.2 wt. % of V and 0.5 wt. % of Cr, etch. 0.5% HF

in alloy with 1.0 wt. % of Cr only chromium was detected (Fig. 8). Moreover, the amount of Cr was lower in a script-like phase after higher chromium addition.

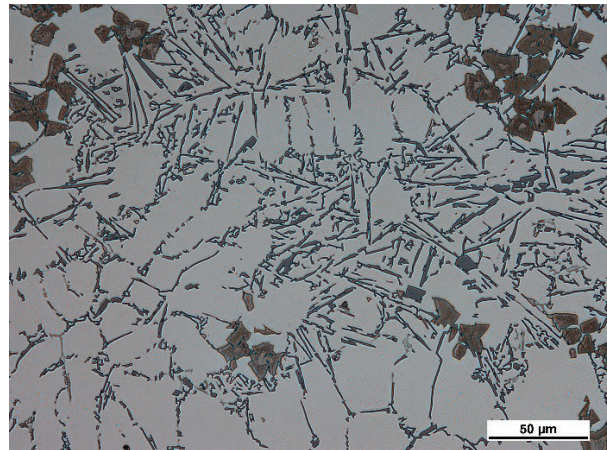
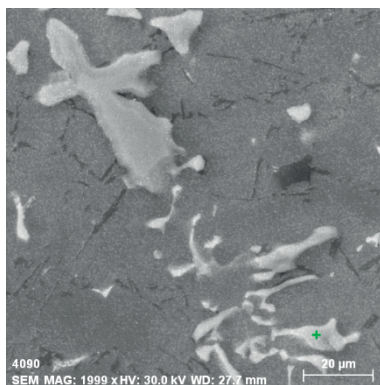
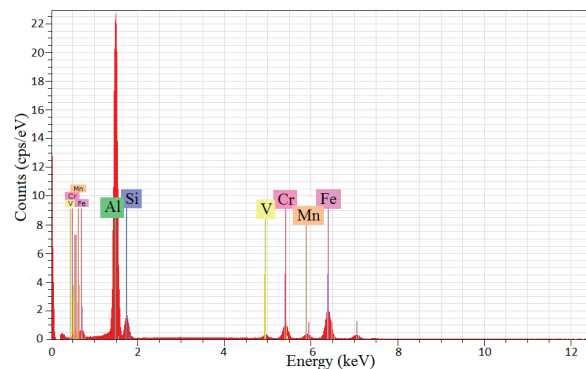


Fig. 6 Typical microstructure of AlSi10MgMnFe1 alloy with 0.2 wt. % of V and 1.0 wt. % of Cr, etch. 0.5% HF

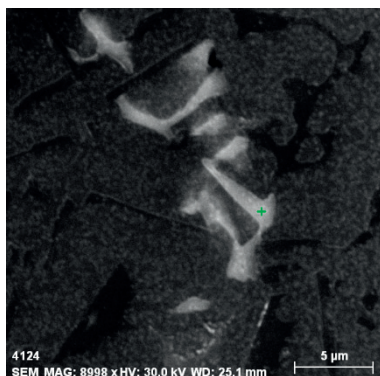


a)

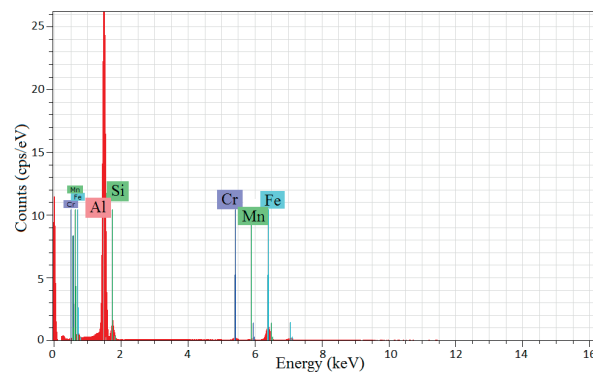


b)

Fig. 7 EDX analysis of script-like phase in AlSi10MgMnFe1 alloy with 0.2 wt. % of V and 0.5 wt. % of Cr: a) SEM image of analysed place, b) EDX spectrum



a)



b)

Fig. 8 EDX analysis of script-like phase in AlSi10MgMnFe1 alloy with 0.2 wt. % of V and 1.0 wt. % of Cr: a) SEM image of analysed place, b) EDX spectrum

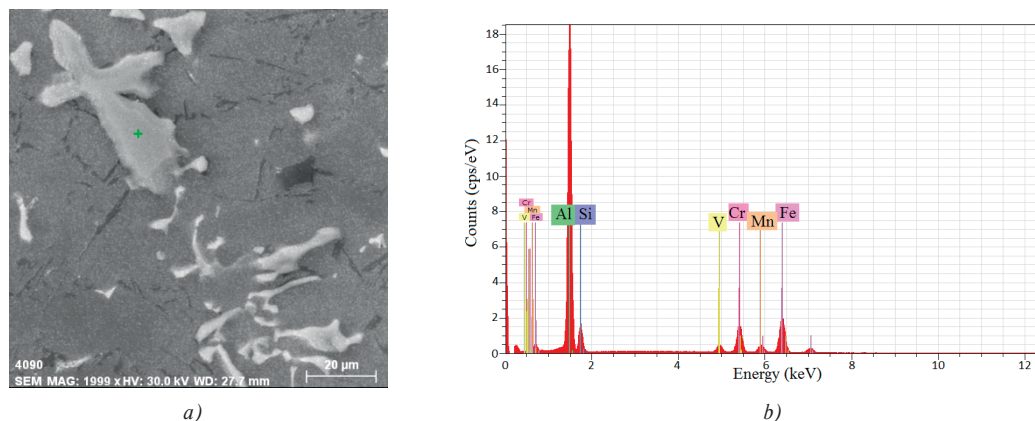


Fig. 9 EDX analysis of sludge phase in AlSi10MgMnFe1 alloy with 0.2 wt. % of V and 0.5 wt. % of Cr: a) SEM image of analysed place, b) EDX spectrum

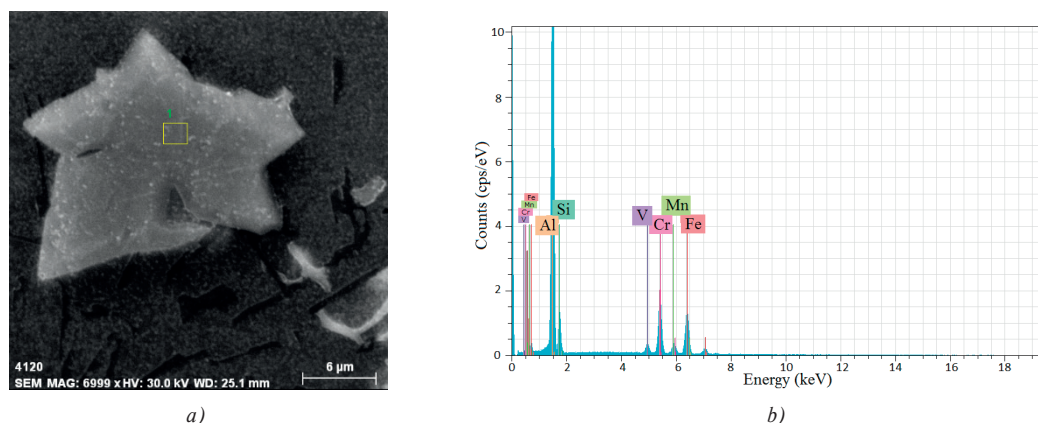


Fig. 10 EDX analysis of sludge phase in AlSi10MgMnFe1 alloy with 0.2 wt. % of V and 1.0 wt. % of Cr: a) SEM image of analysed place, b) EDX spectrum

Sludge phase chemical observations in both Cr treated alloys (Fig. 9 and 10) show presence of Al, Si, Fe, Cr, Mn and V. Amount of Cr in sludge phase seems to be higher with increasing Cr addition.

4. Discussion

Iron addition in the amount of 0.98 wt. % in AlSi10MgMn alloy leads to formation of thick needle like intermetallic phases β -AlFeSi. Manganese neutralisation effect on iron in such alloy composition is then insufficient because the Mn to Fe ratio is only 0.12 (recommended value 0.5 [5, 7 and 14]). Vanadium influence as the iron corrector was analysed in addition of 0.2 wt. % V. Formation of higher amount of script-like phases was observed. Vanadium also caused change of the needle-like length and thickness. Length of the phases rises in disagreement with the literature [10 and 11], but thickness was reduced. Some needle-like phases have a curved shape (Fig. 3) what might be probably the result of the accidental mechanical hindrance to

the straightening action which was observed by other authors [7] and it might be a sign of higher strength of these phases against the loading. Vanadium presence was detected in script-like phases together with Al, Si, Fe, Mn and Cr. Number of needle-like particles rapidly decreased after mutual V and Cr addition but a high amount of sludge phases were observed. The formation of this kind of particles had been observed by many authors [11, 13 and 14] and it is thought to be detrimental to mechanical, foundry properties and machinability of the alloy [14]. Influence of sludge phases on mechanical properties of Al-Si-Mg alloys is still not clear and in spite of the presence of sludge phases in AlSi7Mg0.3 alloy the tensile properties can increase as it has been shown in [13]. EDX analysis in alloys shows decreasing of V level present in script-like phases with alloys after Cr addition. Vanadium and also chromium level rises in the sludge phases with increasing of the Cr addition. It is possible that not only Cr, Mn and Fe are sludge forming elements, but also V belongs to that group at its higher levels.

5. Conclusions

Influence of V and mutual V and Cr addition in AlSi10MgMn alloy were analysed by optical microscopy, SEM observations and EDX analysis. Following conclusions can be drawn from the results:

- (1) Detrimental iron effect in the AlSi10MgMn alloy leads to formation of thick platelets of Al₅FeSi (probably Al₅FeSi) phase placed mainly near the eutectic Si.
- (2) Vanadium has an influence on the formation of higher amount of script-like phases and it acts like an iron corrector.

Also thickness of the needle-like particles was reduced by V addition but the length of needles increased.

- (3) Cr in amount of 0.5 and 1.0 wt. % leads to the formation of sludge phases which might deteriorate mechanical properties of alloy. More sludge phases formed at higher Cr level.
- (4) Sludge phases also contain certain amount of V that might be also a sludge formation element when the content of Fe, Mn and Cr exceeds a critical value.
- (5) Vanadium addition in amount of 0.2 wt. % has the most beneficial effect on morphology and chemical composition of iron intermetallics.

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