The Role of Manganese in the Alloy Based on Al-Si-Mg with Higher Iron Content

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The iron causes the formation of intermetallic phases in Al-Si alloy. These phases are most often present in the form of AlsFeSi phase platelets and degrade alloys properties, especially mechanical. By applying additive elements – correctors (e.g. Mn, Cr, V) we can achieve the change of intermetallic phases morphology to more suitable form. Presented article deals with the influence of manganese as iron corrector on AlSi7Mg0.3 alloy microstructure and length of AlsFeSi phase. The increasing the manganese content reduces the length of AlsFeSi phase, but with higher contents, mainly the skeletal formations was observed instead of the AlsFeSi phase. The evaluation of mechanical properties didn't confirmed, that the higher amount of iron in the alloy significantly decreases a mechanical properties even with the use of a corrector.

Keywords: AlSi7Mg0.3 alloy, manganese, iron intermetallic phases

1 Introduction

The usage of secondary aluminium alloys is currently increasing mainly due to cost savings and the environment factor. The secondary Al-Si alloys contain a higher iron content, which negative affect the properties. The presence of iron and other elements in the alloy causes the formation of large intermetallic phases. The rate of negative effects depends on the size, quantity, distribution and morphology of intermetallics phases. It is known that the negative impact of iron intermetallic phases is accompanied by a decrease of the elongation and tensile strength, which starts even at low amount of iron and significantly increases after exceeding critical iron content. The cause of iron intermetallic particles negative effect on the mechanical properties is fact, that it is much easier to break these particles during the tensile loading as aluminium matrix or small particles of silicon [1-3]. The critical iron content of the Al-Si alloy is directly related to the concentration of silicon in the alloy and can be calculated:

$$Fe_{krit} \approx 0,075 \text{ x (\% Si)} - 0,05$$
 (1)

After increasing the iron content above a critical level, it is necessary to consider a suitable method of its elimination. It is known several methods for elimination of iron harmful effect. By the application of the additive elements can be achieved the change of morphology from needle-like phases Al₅FeSi to the compact shape e.g. "Chinese script". In technical practice is most used elements manganese. [4-5]. The manganese is an effective element in affecting needle iron intermetallic phases. The recommended ratio of manganese addition to eliminate the harmful effects of iron, according to several authors is Mn: Fe = 1: 2 or if an iron amount exceeds a value of the mass fraction w = 0.45 %, the recommended addition of Mn should not be lower than half of the iron amount. Manganese except eliminating harmful effects of iron increases the creep resistance and heat resistance thanks to phases $Al_{20}Cu_2Mn_3$, $Al_{16}Mn_3Ni$, $Al_{12}MnCr$, $Al_{15}(FeMn)_3Si_2$ [6-8]. The manganese by the reducing the amount of β -phase (Al_5FeSi) improves the corrosion resistance of the Al-Si-Mg alloys, reduces porosity and increases the fatigue strength of castings. However, the addition of manganese to the alloy with a high content of iron and chromium can cause the formation of the "sludge phase" which is not possible to remove by conventional methods. The tendency of alloy to the formation of sludge phases depends on the content of iron, manganese and chromium and is given by "sludge" factor" (SF):

$$SF = 1x\% Fe + 2 x\% Mn + 3x \% Cr$$
 (2)

The other additive elements such as Cr, W, Ni, Be are able to eliminate the harmful effect of the phases after the addition already in a low concentrations [9-11].

2 Experiments methodology

As the experimental material was chosen AlSi7Mg0.3 alloy. The chemical composition is shown in Table. 1. The material was alloyed by AlFe10 to achieve a higher amount of iron (approximately 0.7 wt. % Fe). The manganese was added into secondary alloy in an amount of 0.2 wt. %, 0.6 wt. %, 0.8 wt. % 1.0 wt. %, 1.2 wt. %, 1.4 wt. %. The required amount of manganese was achieved by adding master alloys AlMn20. The chemical composition of the alloy with the addition of manganese is shown in Tab. 2. The experimental materials were melted in an electric resistance furnace in a graphite crucible with protective coating. The samples were poured into a metal mould preheated to a temperature of 200 ± 5 ° C at $760 \pm$ 5 ° C. The melt was not further modified, grain refined or purified. The content Ti is 0.18 wt. % and Sr is 0.015 wt. % in primary state, therefore the alloy can be considered as grain refined and modified. Basic mechanical properties (tensile strength, elongation and hardness) and microstructure of the alloy was evaluated.

Tab. 1 Chemical composition (wt.%) AlSi7Mg0.3 alloy

ALLOY	Si	Fe	Cu	Mn	Mg	Zn	Ti	Sr	Al	Mn/Fe
AlSi7Mg0.3	7.093	0.099	<0.0020	0.072	0.38	0.0054	0.18	0.015	92.14	0.73

For each alloy the critical amount of iron (1) has been calculated. The calculated critical amount of iron is given in Table 2. From caltulated values is evident, that in each sample was exceeded a critical iron content. The high iron content and addition of manganese can cause the formation sludge phases. These phases are undesirable in the structure of alloy, because of their high hardness and the

melting temperature, since they reduce the fluidity of the metal and decrease mechanical properties. The Fig. 1 presents relationship between amount of added manganese and sludge factor SF (2). Sludge factor indicates how much of these particles are formed. With the increasing amount of manganese the sludge phases formation in the a structure of alloy can be expected.

Tab. 2 Chemical con	mposition (wt.%)) AlSi7Mg0.3 alloy with	increased iron content aj	fter adding of manganese
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ALLOY/ELEMENT	Si	Fe	Cu	Mn	Mg	Zn	Ti	Sr	Al	Mn/Fe	Fecrit
AlSi7Mg0.3+0.2 wt. % Mn	7.355	0.823	<0.0020	0.309	0.396	0.0062	0.137	0.0086	90.93	0.38	0.50
AlSi7Mg0.3 + 0.6 wt. % Mn	6.916	0.753	<0.0020	0.699	0.36	0.0059	0.134	0.0043	91.1	0.93	0.47
AlSi7Mg0.3 + 0.8wt. % Mn	7.083	0.684	0.0066	0.704	0.35	0.0098	0.141	0.0077	90.98	1.03	0.48
AlSi7Mg0.3 + 1.0 wt. % Mn	6.670	0.585	0.0027	0.874	0.347	0.0035	0.139	0.011	91.34	1.49	0.45
AlSi7Mg0.3 + 1.2 wt. % Mn	6.560	0.635	0.0034	1.079	0.359	0.0049	0.139	0.0097	91.18	1.70	0.44
AlSi7Mg0.3 + 1.4 wt. % Mn	6.450	0.629	0.0036	1.232	0.354	0.0049	0.135	0.0087	91.16	1.96	0.43

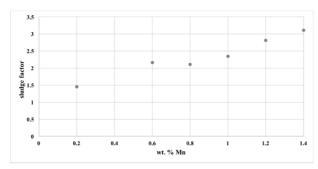


Fig. 1 The sludge factor values for individual manganese additions

3 Results

The tensile test was performed according STN 42 0310 for a maximum load of 20 kN and at a constant crosshead displacement rate of 2 mm/min and a test bar with a diameter of 10 mm. As a hardness measurement method was used method according to Brinell. The red line on graphs (Fig. 2-4) shows the minimum required values of mechanical properties for AlSi7Mg0.3 according of EN 1706.

The Fig. 2 presents relationship between tensile strength and amount of added manganese. The addition of manganese to the investigated alloy with an increased iron content in amount of 0.2 wt. % to 0.8 wt. % did not cause increase of tensile strength (Mn/Fe ranged from 0.38 to 1.03 - see Table. 2). The highest average value of tensile strength was obtained after the addition of manganese by 1.0 wt. % (Mn/Fe = 1.49), probably due to the presence of the Al₁₅(FeMn)₃Si₂ phase in the alloy microstructure. The higher additions of manganese caused decrease of tensile strength. After addition of 1.2 wt. % Mn and 1.4 wt. % Mn long skeletal and sludge phases was observed (Figure 7e, f). These particles could have caused to reduction of tensile strength in 3 %.

The slight increase of elongation after addition of 0.6 wt. % Mn is observed (Fig. 3). On the contrary, the ad-

dition of 0.8 wt. % Mn caused a slight decrease of elongation. The addition of manganese to the alloy of 1.0 wt. % caused an increase of elongation as well as tensile strength. In the case of addition of 1.2 wt.% and 1.4 wt. % manganese to the alloy, result was an decrease of elongation. The difference between the highest and lowest value reached of elongation was 0.67, a decrease of 30 %.

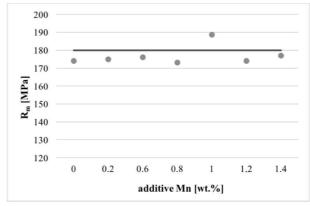


Fig. 2 Results of tensile strength of AlSi7Mg0.3 alloy with increased iron content with different additive of manganese

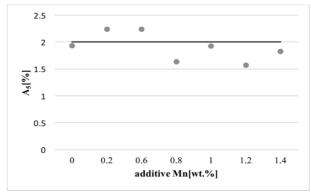


Fig. 3 Results of elongation of AlSi7Mg0.3 alloy with increased iron content with different additive of manganese

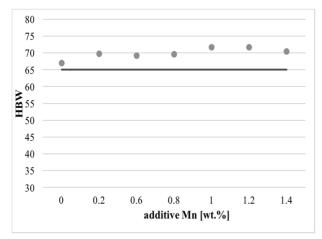
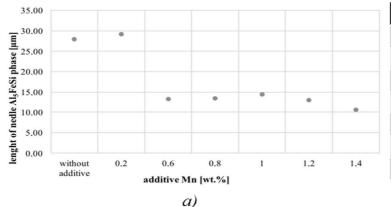


Fig. 4 Results of Brinell hardness of AlSi7Mg0.3 alloy with increased iron content with different additive of manganese

The measurements of hardness showed that by increasing the manganese content in the alloy with higher content of iron leads to a slight increase of hardness in average of 30 %. The highest value of hardness was achieved after the addition 1,2 wt. Mn – 71,6 HBW and 1,4 wt. % Mn – 72 HBW (Fig. 4). Higher hardness can be caused by the presence of sludge formations in the structure of alloys, that exhibit hardness 800-1000 HV, but also iron phases which are distributed in the structure of the alloy. The difference between the minimal value HBW in cast state and lowest reached value is 3 %.

The influence of manganese in the AlSi7Mg0.3 alloy with increased iron content was investigated for purpose to describe a change in the shape of iron-based intermetallic phases after the addition of manganese. The measurements of length needle-like phases by 500 × magnification was performed. The Fig. 5a) presents relationship between measured values length of iron-based intermetallic phases and amount of added of manganese.

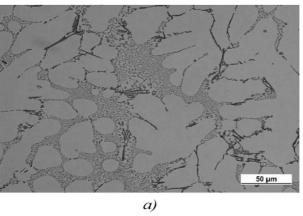


Additive of Mn [wt. %]/actual amount of Mn in the alloy	Length of needle Al ₅ FeSi phase [μm]
0	27.97
0.2	29,19
0.6	13.32
8.0	13.44
1	14.17
1,2	13,03
1.4	10.53
	5)

Fig. 5 a) The results measuremed of length Al₅FeSi phase after adding manganese, b) The results of length Al₅FeSi phase

The addition 0.2 wt. % Mn did not caused the length decrease of the Al5FeSi phase (Fig. 7a). The length decrease of the Al₅FeSi by higher amount of Mn was observed. Manganese addition in amount of 0.6 wt. % caused the length decreasing of the Al₅FeSi by more than half (Fig. 7b). The higher additions of Mn doesn't have significant effect to decreasing the length of the Al₅FeSi phase (Fig. 5b)

The Fig. 6 a) presents the typical microstructure



AlSi7Mg0.3 alloy. The microstructure is formed by α -phase dendrites, silicon eutectic and iron based intermetallic phases excluded in the form of Chinese script small particles. In the microstructure of alloy with increased amount of iron 0.7 wt. % (Fig. 6 b), but without added manganese are mostly iron based particles in the form of Al₅FeSi needles. In brackets is shown the actual amount of Mn in the alloy from Tab. 2.

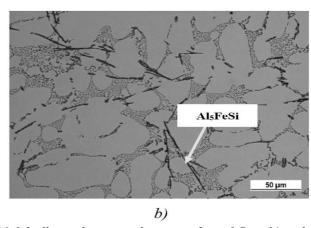


Fig. 6 a) Typical microstructure AlSi7Mg0,3 alloy, b) AlSi7Mg0,3 alloy with increased amount of iron 0.7 wt. %, etch. 0,5 % HF

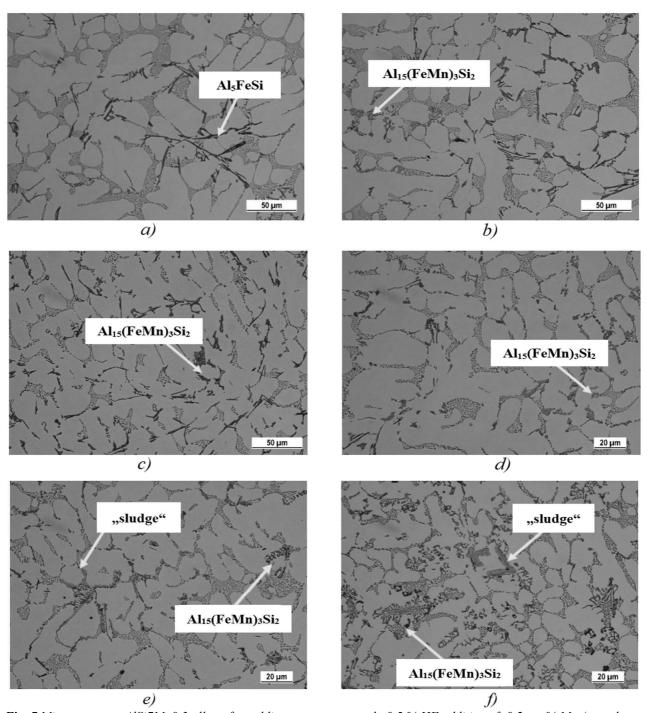
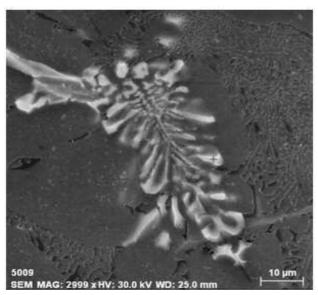


Fig. 7 Microstructure AlSi7Mg0,3 alloy after adding manganese, etch. 0.5 % HF additive of: 0,2 wt. % Mn (actual content 0,309 wt.% Mn), b) 0,6 wt. % Mn (actual content 0,699 wt. % Mn), c) 0,8 wt.% Mn (actual content 0,704 wt. % Mn), d) 1,0 wt. % Mn (actual content 0,874 hm. % Mn), e) 1,2 wt. % Mn (actual content 1,079 wt. % Mn), f) 1,4 wt. %Mn (actual content 1,232 hm. % Mn)

Manganese addition in amount of 0.2 wt. % into alloy with increased iron content didn't lead to change of morphology needle phase of Al_5FeSi to the less harmful shape of skeleton particles or Chinese script. In the structure of the alloy were located Al_5FeSi phase in the form of thin needles (Fig. 7a). The smaller skeletal particles began to appear after addition of 0.6 and 0.8 wt. % Mn, but the predominant representation had intermetallic phases based on iron, probably small Al_5FeSi phases evenly distributed in the aluminium matrix (Fig. 7b and 7c). EDX analysis of the skeleton particles of

Al₁₅(Fe,Mn)₃Si₂ phase is shown in Fig. 8. More of skeleton formations probably of Al₁₅(FeMn)₃Si₂ phase mostly in interdendritic areas after addition of 1.0 wt. % Mn was observed (Fig. 7d).

When increasing the content (1.2 and 1.4 wt. % Mn), probably needle Al₅FeSi phase in the alloy structure was observed. The structure was predominantly formed of small skeletal crystals or long skeletons in the case of addition of 1.4 wt. % Mn. The presence of significant amounts of manganese caused the formation of sludge formations (Fig. 7e and 7f).



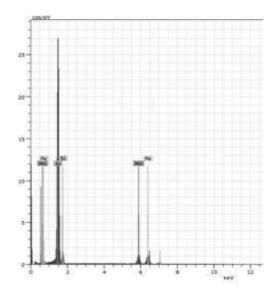


Fig. 8 EDX analysis of skeletol phases in AlSi7Mg0.3 alloy with 0.7 wt. % Fe and 0.6 wt. % Mn

4 Conclusions

The adding of manganese into alloy lead the slight decrease of tensile strength, elongation and the slight increase of hardness. The higher addition of Mn promote to shorten length of needle Al₅FeSi phase. The additions of Mn (1,2 wt. % a 1,4 wt.%) with higher additions (1.2 wt. % and 1.4 wt. % Mn) and the Al₅FeSi phase is probably replaced by the Al₁₅(FeMn)₃Si₂ phase in the form of skeleton formations. The evaluation of mechanical properties didn't support the opinion, that the higher amount of iron in the alloy significant decrease of mechanical properties even with the use of a corrector. By evaluating the mechanical characteristic wasn't clear support for the opinion that the higher the amount of iron in the alloy examined significantly reduces the mechanical properties even with the use of a corrector. We can conclude that manganese has a significant effect on elimination harmful iron phases.

References

- [1] TAYLOR, J.A. 2012. Iron-containing intermetallic phase in Al-Si based casting alloys. In: *Procedia Materials Science*. 2012. Vol 1, pp. 19-33.
- [2] TILLOVÁ, E. CHALUPOVÁ, M. 2009. *Štruktúrna analýza zliatin Al-Si*. EDIS Žilina. 2009. 191 s. ISBN 978-80-554-0088-4
- [3] DINNIS, C. M. et al., 2005. As-cast morphology of iron-intermetallics in Al-Si foundry alloys, Scripta Materialia 53 (8), pp. 955-958.
- [4] BELOV N. A., A. A. AKSENOV, D. G. ESKIN 2002.: *Iron in aluminium alloys*, Taylor & Francis, 343s, ISBN 0-415-27352-8

- [5] MEŠKO, J. ZRAK, A. MULCZYK, K. -TOFIL, S. 2014.: Microstructure analysis of welded joints after laser welding. In: Manufacturing Technology, Vol. 14, No. 3, pp. 355 - 359, ISSN 1213-2489.
- [6] PASTIRČÁK, R. 2014.: Effect of low pressure application during solidification on microstructure of AlSi alloys. In: *Manufacturing Technology*. ISSN 1213-2489. Vol. 14, No. 3 (2014), p. 397-402.
- [7] BRŮNA, M., KUCHARČÍK, L. 2013.: Prediction of the Porosity of Al Alloys. In: *Manufacturing Technology*. ISSN 1213-2489. Vol. 13, No. 3, pp. 296-302.
- [8] BOLIBRUCHOVÁ, D., ŽIHALOVÁ, M. 2013.: Possibilities of iron elimination in aluminium alloys by vanadium. In: *Manufacturing Technology*, ISSN 1213-2489, Vol. 13, No. 3, pp. 289-296.
- [9] ZHANG A KOL. (2013).: Effect of the Mn/Fe ratio and cooling rate on the modification of Fe intermetallic compounds in cast A356 based alloy with different Fe contents. Materials Transactions.
- [10] KUCHARÍKOVÁ, L. TILLOVÁ, E. BELAN, J. UHRIČÍK, M. 2015.: The Effect of Casting Technology on Fe Intermetallic Phases in Al-Si Cast Alloys. In: Manufacturing Technology. ISSN 1213-2489. Vol. 15, No. 4 (2015), p. 567-571.
- [11] SLÁDEK, A., PASTIRČÁK, R., BRŮNA, M., REMIŠOVÁ, A. 2017.: New Application in Technological Preparations for Investment Casting Production in Aircraft Industry. In: *Manufacturing Technology*. ISSN 1213-2489. Vol. 17, No. 4 (2017), p. 842-847.

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