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THE IRON CORRECTORS IN Al-Si ALLOYS

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ABSTRACT: Iron is in practice present in Al-Si cast alloys as a result of using the scrap contaminated with iron and intensive dissolving of iron by melt Al-Si. The iron contents above 0.5% effects segregation of brittle and hard intermetallic phases. The decreasing of cooling rate shifts the start of needles segregation to the low iron content. Presence of iron increases hardness of alloy and decreases its corrosion resistance, fluidity and plastic properties. The influence of iron correctors (Mn, Ni, Co, Cr, Ti, V, Mo up to 0.7 %) and iron (up to 2.3 %) on the microstructure, mechanical properties and fluidity was evaluated. Cluster analysis was used for evaluation the group with the best properties. The best results of mechanical properties (Rm and A_5) were reached with Ni, Ti and V as iron modifiers. Cr and partly Mn are effective at high iron concentration. The influence of Co on the microstructure and mechanical properties is marginal.

KEYWORDS: Si alloy, iron, iron correctors, microstructure, mechanical properties

❖ INTRODUCTION

Life Cycle Assessment (LCA) is a scientific tool for the systematic evaluation of the environmental impacts of a product or service system through all stages of its life cycle “from cradle to grave” (mining and extraction of raw materials, fabrication, transportation, use and recycling/disposal). The purpose of life cycle assessment is to define the scope of all environmental impacts associated with the product during its life cycle and to identify and reduce aspects with the most significant environmental impacts. Life Cycle Assessment is intended for broad use throughout the industry with a view to assess and stimulate environmental improvement in production processes and product development. Today, life cycle assessment is increasingly developed in metallurgy. It is related to new recycling technology, metal extraction from secondary materials and to fact, that metal production belongs mostly to large environmental pollution sources [1].

This paper is aimed at the problem of recycling of Al with utilization of scrap as a material for cast Al-Si alloys. The scrap is unfortunately contaminated with iron as a rule. The fragments of iron are intensive dissolved in melt Al-Si. Iron content 0.3 ÷ 0.5 % increases strength and fluidity. Higher iron concentration increases properties at high temperatures and hardness, but decreases corrosion resistance, fluidity and plastic properties. The iron content above 0.5 % is undesirable. It supports segregation of brittle and hard intermetallic phases. Extra hazardous are long needles of $FeSiAl_5$ (β phase), overshooting Al matrix and eutectic cells. This phase affects the premature failure of the castings by notch effect. If the cooling rate decreases, the segregation of needles is shifted towards low concentration of iron [2, 3, 4]. Unwelcome side effect of casting in the chill mould (die) is soldering (sticking) between the casting and the mould. The main reason for sticking of Al alloys is the diffusion of iron from the mould into borderline of the casting, and the subsequent formation of AlFeSi phase. Reduction of the sticking can be achieved by increasing of iron content above 0.5 % [4].

A reliable and economic method of iron elimination from Al alloys has not been well-known yet in metallurgical practice. Ordinary, but in our opinion not effective solution is “dilution” of contaminated alloy with high-class Al. The negative effect of iron can be partly eliminated by superheating of the melt or by increasing of cooling rate. The construction for continual removal (continual refining) of iron from the Al-Si alloy by precipitation and sedimentation of the iron-rich intermetallic phases was presented [5]. It has been stated that there is a possibility of removing iron from an AlSi11 alloy containing 2 ÷ 3 % iron up to 0.6 % iron at one stage or at two stages by introducing an appropriate addition of manganese which affects the yield of refined melt.

Suitable iron correctors are used in metallurgical practice because of limited effectiveness of aforementioned methods. The compounds of iron correctors with Al, Si and Fe segregate in more suitable shape as needles, usually in the form of skeleton shaped „chinese script“. The corrector brings its own „added value” as a rule (e.g. Cr improves strength at indoor and higher temperatures). Co, used as iron corrector in former times is completely replaced by cheaper Mn today [3, 6].

❖ THE EFFECT OF INDIVIDUAL CORRECTORS

Co was considered be the best iron corrector in general. The recommended content 0.3 ÷ 0.45 % increases strength, resistance against the cyclic fatigue and elongation.

Mn improves strength and mechanical properties at high temperature. Excessive Mn segregates in needles and coarse „chinese script" $(Fe, Mn)_3Si_2Al_{15}$ usually with cracks. This fact results in decreasing of mechanical properties and fluidity. Mn + Fe above 0.8 % improve of workability as a rule.

Cr improves strength at indoor and higher temperatures (precipitation of intermetallic compositions of Cr inhibits the growth of grains) and mildly deteriorates elongation. The presence of Cr phases $(CrFe)_4Si_4Al_{13}$ and $(CrFe)_5Si_8Al_2$ can increases brittleness [4].

Ni is infrequently recommended as iron modifier in the literary sources□□ Intermetallic compound $FeNiAl_9$ increases Rm, but also embrittlement of the castings. Simultaneous influence of Ni and Fe in Al-Si alloys with Si content above 5 % expressively decreases plasticity, fluidity and corrosion resistance□ A group of authors predicates moderate increasing of Rm and likewise elongation at indoor and elevated temperature, but only if Ni acts as an iron modifier. Otherwise its influence, first of all on the elongation is negative. Ni reduces the coefficient of thermal expansion of Al alloys as a rule. Ni and Fe together in Al-Si alloys enhance the resistance to attack of warm water or steam [7].

Ti, Zr and V (0.05 ÷ 0.15 %) and partly also Mo, Cr, Fe and Ni refine the grains of Al alloys. 0.12 ÷ 0.15 % Mo increases Rm and elongation of Al-Si alloys with iron content. V and Mo, analogous to Ni are infrequently recommended as iron modifier in the literary sources. Unfortunately only low concentrations of V (0.03 ÷ 0.05 %), Mo (0.05 ÷ 0.15 %) and Fe (1.0 %) are presented in [6]. V, Ti and partly Mo uniform the grains, increase resistance to hot tearing and decrease porosity [3,4, 5].

Additions of the iron correctors and also presence of Fe and Mg, leading to the formation of intermetallic inclusions, decrease the fluidity [4].

❖ THE EXPERIMENTAL MATERIALS AND METHODS

The basic composition of tested alloys was: 3.0 ÷ 12.0% Si, 0.0 ÷ 0.4% Mg (or 0.0 ÷ 1.0% Cu), 0.3% Fe and Al up to 100%. The atomic absorption method (spectrometer Perkin Elmer 306A) was used for chemical analysis. The alloy was melted in the graphite crucible in the electric resistance furnace. Iron (up to 2.3%) was added in the form of the master alloy AlFe9. The iron correctors up to 0.7% were added in the form of master alloys with Al. AlSiSr10 alloy (8.35% Sr) was used as Si modifier. Final Sr content (0.015 % in average) was sufficient for real modification of eutectic Si. The temperature of the casting was 760°C. The melt was cast into:

1) the chill mould for mechanical tests.
2) the steel chill mould "lyre" with six rising pipes with graduated diameter for fluidity test (Yz) [8].

The cooling rate of the castings was $18^{\circ}Cs^{-1}$. The tensile tests were carried out according to standard STN 42 0310, six specimens were used for every content of Fe and correctors. The hardness HV10 was measured according to standard ISO 6507-1. Polished metalographic samples were etched with 25% H_2SO_4 at 75°C and consequently with 0.5% HF. The morphology of eutectic Si (β phase) according to standard STN 42 0491, its interparticle spacing λ_β, dimensions and shape of intermetallic iron containing phases were evaluated. The analyzer LINK ISIS was used for analysis of the composition of intermetallic phases by EDX method.

❖ THE ANALYSIS OF THE MICROSTRUCTURE

The length of Al matrix dendrites is 50 μm in average and width is 10÷34 μm. Eutectic Si (β phase) is segregated in globular particles (1÷5 μm), the interparticle spacing λ_β is 1.0÷1.75 μm. The length of rare needles of eutectic Si does not exceed 10 μm. The eutectic Si was completely modified.

MICROSTRUCTURE WITHOUT IRON CORRECTOR

<1.0 % Fe: Rare grey – rusty needles of intermetallic α phase (Fe_2SiAl_8) segregated in eutectic cells (length 5÷20 μm and width <3 μm). Higher concentration of iron results in segregation of sheaf - shaped clusters of needles with the length < 100 μm, above all in dendrites of Al matrix.

1.0 ÷ 1.6 % Fe: High density (network) of thin traversing needles (length about 50 μm). Long needles of intermetallic β phase $(FeSiAl_5)$, overshooting eutectic cells and dendrites of Al matrix with length up to 700 μm segregate at Fe > 1.6 %.

The segregation of sheaf – shaped clusters and dense network of needles depends on the concentration of iron. It is not expressively affected by iron correctors.

Mn: <1.0 % Fe: The needles of α phase (length <20 μm) are in eutectic cells independently of Mn content. Their number increases with increasing Fe content, they create sheaf – shaped clusters also in Al matrix. Grey – rusty skeleton – shaped formations „chinese script" $(FeMn)_3Si_2Al_{15}$ and star shape particles (both < 80 μm) appear if Mn > 0.4% especially in eutectic cells. The length of β phase needles is < 800 μm at 0.2 % Mn – 2 % Fe or < 500 μm at 0.4 % Mn - 1.7% Fe and 0.7 % Mn - 1.7 % Fe.

Cr: < 1.0 % Fe: Grey – rusty needles of intermetallic phase < 10 μm, containing 63.7% Al -17.7% Si – 0.6 % Cr – 14.4% Fe are in eutectic cells at 0.2% Cr. The contents 0.4% Fe and 0.7% Cr results in segregation the clusters (□□□< 200 μm) of globular or elliptic particles (□ about 10 μm). If Fe > 1.0 % sheaf - shaped clusters together with clusters of globular, elliptic and angular - vertebra shaped particles (as a segmented backbone - 0.4% Cr) or fishbone particles (0.7% Cr) appear. The additional increasing of the Fe effects in segregation of dense network of needles with the length about 50 μm and long overshooting needles containing 67.0% Al – 13.3% Si – 0.6% Cr – 19.2% Fe, partly fallen to chains of angular (vertebra shaped) particles. The ultimate length of overshooting needles is 300 μm (0.2 % Cr – 1.5 % Fe), 500 μm (0.4 % Cr – 1.9 % Fe) and 100 μm (0.7 % Cr – 1.4 % Fe) [9].

Co: < 1.0 % Fe: Needles of intermetallic phase < 20 μm containing 70.1 % Al – 21.0 % Si – 4.5 % Co – 4.7 % Fe in eutectic cells. Skeleton shaped particles < 50 μm segregate at 0.7 % Co. The ultimate length of overshooting needles, containing 63.9 % Al – 11.5% Si – 5.4 % Co – 19.2 % Fe is 700 μm (0.2 % Co – 1.7% Fe), 500 μm (0.4 % Co – 1.8 % Fe) and 900 μm (0.7% Co – 1.8 % Fe) [10].

Ni: < 1.0 % Fe: Needles of intermetallic phase < 15 μm containing 70.9 % Al – 11.5 % Si – 2.5% Ni – 15.2% Fe in eutectic cells and rare skeleton shaped particles at 0.4 or 0.7 % Ni. The ultimate length of overshooting needles containing 61.0% Al – 11.8% Si – 1.5% Ni – 25.7% Fe is 600 μm (0.2 % Ni – 2.5 % Fe), 200 μm (0.4% Ni – 1.7% Fe), 300 μm (0.7 % Ni – 2.0% Fe) or 1200 μm (0.7% Ni – 2.5% Fe). The skeleton – shaped particles are rare [11].

Mo: <1.0 % Fe: Sporadic rusty – grey needles of intermetallic phase with length < 20μm in eutectic cells. The length and number of the needles increases with increasing of Fe content. Simultaneously segregate the clusters of globular, elliptic and rare skeleton shaped particles containing 5.2÷5.6% Mo; 20.1÷24.4 % Fe; 8.2÷1.4 % Si, Al the rest, with □□< 30 μm. The length of β needles is about 200 μm (1.5 % Fe), their ultimate length not exceeds 600 μm (1.8% Fe). The concentration of Mo in skeleton shaped particles not exceeds 0.2%, their density and dimensions increase (up to 50 μm) with increasing of Fe and Mo content.

V: <1.0% Fe: The needles of intermetallic phase (Al_2SiAl_8 with 0.1% V) long < 20 μm in eutectic cells. The length of β needles is < 200 μm at 1.8% Fe and < 800 μm at 2.3% Fe. The content of V in β needles is negligible.

Ti: <1.0% Fe: The needles of intermetallic phase with length <5 μm can be seen in eutectic cells. The segregation of globular clusters (□□about 10μm) was observed at higher concentrations of Ti and above 0.5% Fe. The length of β needles is < 300 μm at 1.7% Fe and < 700μm at 2.0% Fe. The content of Ti in the α and β needles is not expressive (tenths %) with exception of rare needles similar to β phase with about 30% Ti [12].

As for the obstruction of segregation or growth of β phase needles, the significant effect was observed for V, Cr, Co, Mn and Ni, fig. 1. Figure 2 illustrates the influence of iron and correctors (0.2% for Mo, and 0.4 for the rest, 9.0 ÷ 11.0% Si and 0.2 % Mg) on the ultimate tensile strength Rm. The value decreases with increased iron content. The most significant effect for this increasing removal was attained if Ni, Ti and if appropriate V (reduced size of experiments) and Cr (for higher iron contents) were used. For "classic" correctors Mn and Co the values of Rm were lower than they without corrector. The influence of the correctors on the elongation A_5 (the values of reduction of area Z were low, difficult measurable and so uncertain) are similar to Rm as can be seen on fig. 3. The exception is positive influence of Mn at higher Fe concentrations. The hardness increases with increasing of the content of correctors and iron. The most significant effect has Mg, as far as correctors Cr, Mn and Ti. The correctors and iron reduce fluidity of Al-Si alloy. The most significant is influence of Co and V. Negative effect of Fe is partly obstructed by Mn, fig. 4.

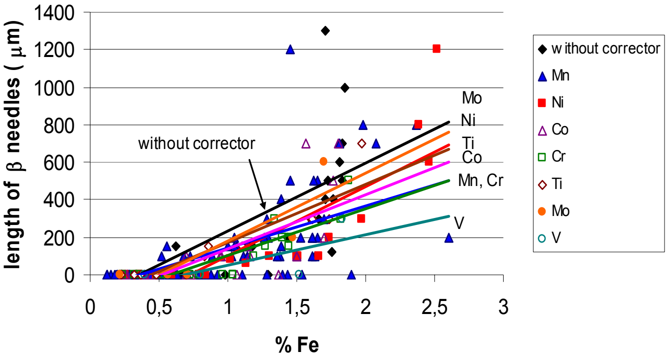

Figure 1. The segregation of the needles of β phase

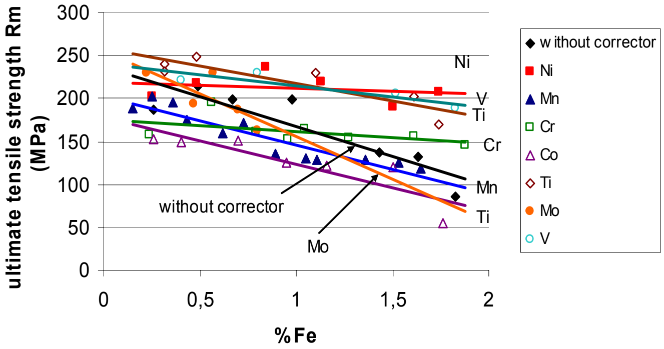

Figure 2. The influence of Fe and the correctors on Rm

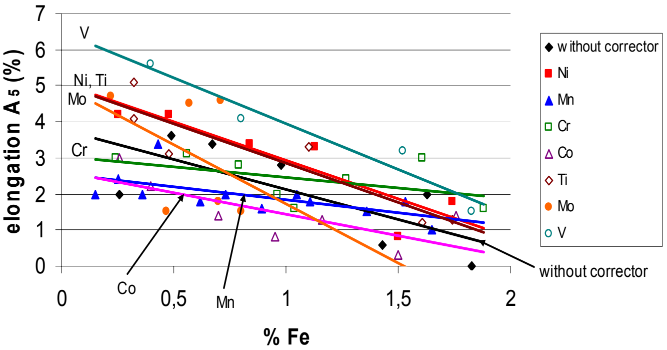

Figure 3. The influence of Fe and the correctors on A_5

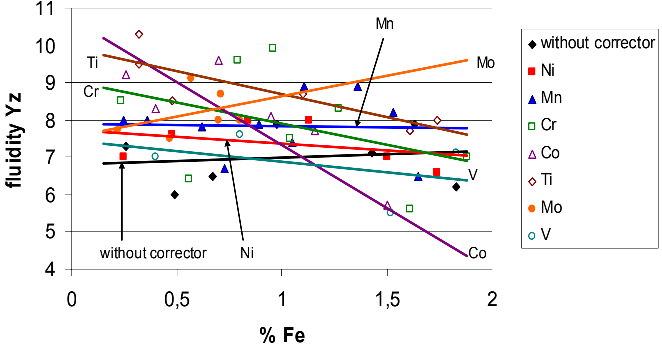

Figure 4. The influence of Fe and the correctors on the fluidity

❖ THE CLUSTER ANALYSIS

Cluster analysis was used for selection of concentration of correctors, Si and Fe, resulting in optimal values of strength, plasticity and fluidity.

Cluster analysis is a method of unsupervised learning, and a common technique for statistical data analysis. Cluster analysis is the assignment of a set of observations into subsets (called clusters) so that observations in the same cluster are similar in some sense.

Some authors consider that cluster analysis is a type of uncontrolled classification [13].

The similarity of two elements is determined with measuring of their distance. Cluster analysis can be divided according to the method of identifying clusters to:

☐ partitioning clustering methods
☐ hierarchical clustering methods
☐ fuzzy clustering methods

In this work we used for cluster analysis an agglomerative hierarchical clustering method. The hierarchical clustering method creates a nested sequence of clusters for one cluster to *N* clusters for a data matrix with *N* data points. The Agglomerative hierarchical method starts with each data point as a separate cluster and merges them into successively larger clusters.

The results of hierarchical clustering are usually presented in a large dendrogram. As we stated the similarity between clusters are measured with the distance. For the results of analysis is very important select the right measure of distance. For our type of data we chose the correlation measure. The mathematical formulation of our distance measure is for data matrix X = {x_{ij}} the formula (1).

$$1-\frac{\sum_{i=1}^{n}(x_{ij}-\bar{x}_j)(x_{ik}-\bar{x}_k)}{\sqrt{\sum_{i=1}^{n}(x_{ij}-\bar{x}_j)^2}\sqrt{\sum_{i=1}^{n}(x_{ik}-\bar{x}_k)^2}} \tag{1}$$

The algorithm of Agglomerative hierarchical clustering is following [14]:

1. Compute the proximity of matrix
2. Repeat
3. Merge the closest two clusters
4. Update the proximity matrix to reflect the proximity between the new cluster and the original clusters.
5. Until only one cluster remains

In our work was the result of repeating steps 3 and 4 recorded in tree like structure - dendogram. But for the high complexity of this dendogram we can’t publish it here. The important question in hierarchical clustering is which level of dendogram will be chose as result. In our work we used a special algorithm for determination of dendogram result level. The algorithm is a special application of multiscale bootstrap resampling algorithm. The result this algorithm are two parameters for each cluster on each level of dendogram. The first is Approximately Unbiased and second Bootstrap Probability. These two parameters are in range form 0 to 1 and say how strong is this cluster support with data. For more information about this algorithm we recommend [15]. For computing the cluster analysis we used special statistical software – R. R is a GNU project for Statistical Computing platform. For result processing and creation of graphs we used Microsoft Excel 2003.

Table 1. The composition for maximal values

	value	Fe	Si	Mg	Cu	Mn	Ni	Co	Cr	Ti	Mo	V
Rm	188 MPa	0.68	7.60	0.21	0.12	0.24	0.07	0	0.01	0.03	0	0.01
A_5	9.82 %	0.40	5.68	0.14	0	0.88	0	0	0.03	0	0	0
Z	9.85 %	0.30	8.35	0.22	0.25	0.19	0	0	0	0.10	0	0.03
HV10	81 HV10	0.89	8.80	0.22	0.15	0.19	0.04	0.04	0.04	0.02	0	0.00
Y_z	7.32	0.87	9.21	0.21	0.13	0.17	0.05	0.05	0.05	0.02	0	0

The cluster analysis divided each of observed mechanical properties (Rm, A_5, Y, HV10 and Y_z) into levels (four as a rule) with growing value. Equivalent concentration of chemical elements was associated to every group. The composition of the groups with the best properties is in tab. 1.

❖ CONCLUSIONS

1. The iron correctors except for Co shorten the length of β needles in compare with the alloy without corrector. Cr, Mn and Vanadium have the most significant effect. The segmentation of β needles and creation of skeleton – shaped particles were not observed when Ni was used, but improvement of mechanical properties was observed.
2. The best results of mechanical properties (Rm and A_5) were reached with Ni, Ti and V. Cr and partly Mn are effective at high iron concentrations.
3. The hardness increases with increasing of the content of correctors and iron. The most significant effect has Mg, as far as correctors Cr, Mn and Ti.
4. The fluidity is negative effected by Fe, V and Co, certain improvement effects Mo.

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