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Analysis of the distribution of transition metals and Si during primary precipitation of the intermetallic phases in Al-Mn-Si alloys*

M. Warmuzek[a], J. Sieniawski[b], K. Wicher[a], G. Mrówka[b]

[a)] Foundry Research Institute, Kraków

[b)] Rzeszów University of Technology, Rzeszów

1. INTRODUCTION

Many technological properties of the commercial aluminium alloys are due to the presence of the intermetallic phases as microstructure components. Some group of these alloys can be considered as a part of the high Al portion of the multicomponent Al-Si-TM-Cu-Mg system (where TM - transition metals) [1-3]. The phase composition of the material is some superposition of the series of binary, ternary and quaternary equilibrium diagrams. Complexity of this system causes that only the simple systems were investigated as a model of the alloy microstructure. Total amount of the intermetallic phases, containing transition metals Fe and Mn, produced in commercial alloys can be estimated as several thousands tonnes a year. The structure, morphology and thermodynamics of these phases are still examined using more and more detailed method because of their important part in the process of the optimisation of the material utility. In spite the ternary both Al-Fe-Si [1,4,5] and Al-Mn-Si [1,2,6-9] systems seem to be well known, the thermodynamic and kinetic factors forming morphology of phase precipitates should be established in more detail. The need of such investigations is particularly self-evident in case of the quaternary Al-Mn-Fe-Si system [10,11] which approximates a large number of the phase components in both commercial alloys of 3xxx series and residual liquid (interdendritic areas) in Al-Si cast alloys.
The equilibrium cubic phase α-AlMnSi arises in Al-rich alloys as a product of two invariant peritectic reactions: $L+\beta\text{-AlMnSi}\rightarrow Al_6Mn+\alpha-AlMnSi$

$$L+Al_6Mn\rightarrow Al+\alpha\text{-AlMnSi}$$

Intermetallic phases precipitated from the liquid both metastable β-AlMnSi and stable Al_6Mn form during invariant eutectic reactions. Presence of other transition element as Fe or Cr introduces the modifications, sometimes of a great importance, into precipitation processes and final morphology of the microstructure components. The effect of the Fe addition on the transformation of the metastable β-AlMnSi into stable α-AlMnSi phase has not been still determined. More data is attainable with regard to the effect of transition elements (Mn, Cr) on the phases in the Al-Fe-Si alloys, especially on the substrate and products of the reactions (phase transformations) taking part during alloy solidification [1-15]. Analysis of the

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chemical composition of α-AlMnSi phase particles precipitated from alloys of different composition [16] showed that observed differentiation concerned mainly Si and Al contents. It was assumed that this variety of Si concentration could be explained by following mechanisms of mutual substitution of the atoms in the crystal lattice [16]:

- simple one-for-one Al↔Si substitution stated in ternary phases both α_H-AlFeSi and α_C-AlMnSi
- occupation of the vacant Al lattice sites by Si (observed in Al_3Fe phase)
- Si substitution for Mn (stated in presence of Zn atoms)

The content of the transition metal Mn was rather stable as in the case of the Fe in the ternary AlFeSi phases. The Fe↔Mn substitution in the crystal lattice of the cubic quaternary phase AlFe(Mn)Si, difficult for direct observation, could be indirectly proved by relatively stable summary content. However, an addition Mn into ternary AlFeSi alloy evolved modification of the cubic AlFe(Mn) phase morphology and influenced the course of the peritectic transformation $L+Al_3Fe \rightarrow Al+AlFe(Mn)Si$ [17]. In alloys in which α-AlMn(Fe)Si phase was the primary solidifying phase the occupation of the crystal lattice by Si atoms seemed to be determined by Fe/Mn ratio. There is no data concerning the part of this factor on the course of the peritectic transformation $L+\beta\text{-AlMnSi} \rightarrow Al_6Mn+\alpha AlMnSi$.

2. EXPERIMENTAL DATA

2.1. Material for experiments

Materials for experiments were synthetic AlMn6Si3 alloys with addition of 0.5%wt and 2.0%wt Fe. Additionally 0.15%wt and 0.5%wt Cr were added into AlMn11Si3Fe0.5 alloy. The AlMn(FeCr)Si alloys were prepared from pure components: Al4N, AlSi, AlFe, AlCr master alloys and Mn. This chemical composition was chosen to examine the process of the formation of the intermetallic phases AlMnSi during the peritectic transformation $L+\beta\text{–AlMnSi} \rightarrow Al_6Mn+\alpha\text{–AlMnSi}$ in range of the silicon content lower than in previously published works [6-10]. The components were melted in the induction furnace with Ar protective atmosphere and poured into graphite crucibles. The specimens for examinations were cut from ingots obtained in this manner and examined in the as-cast state.

2.2 Examinations of microstructure and chemical composition of the phase precipitates

The microstructure of the alloys was observed on the metallographic microsections etched with reagent: solution of 1%HF in distilled water. The microscopic observations were carried out by means of the metallographic light microscope Neophot 32 and scanning electron microscope Stereoscan 420. The chemical composition of the phase components was estimated by X-ray microanalysis method using EDS microanalyser with ISIS 300 system coupled to SEM S420.

3. RESULTS OF EXAMINATIONS

3.1. Microstructure of the examined alloys

Microstructure of the examined alloys is presented in Figs.1-3. One can see that the peritectic transformation occurred in the investigated range of alloy composition, but equilibrium microstructure state was not achieved. In alloy AlSi3Mn6 the primary precipitates of the β–AlMnSi phase were covered with a product of the peritectic transformation in shape of the layer of α-AlMnSi phase. These processes advanced as Fe was added into alloy. In Figs. 2a,b there are visible changes of the profile of the α-AlMnSi/ α-Al interface due to Fe

addition. Irregular profile of the interface in the ternary Al-Mn-Si alloy (Fig.1b) became transformed into Chinese script when 0.5%Fe was added (Fig.2a) and then (in alloy containing 2.0%Fe) the contours of the polyhedra of the new phase started to be visible (Fig.2b). Isolated Chinese script precipitates present in all the examined alloys were constituents of the polyphase eutectic: Al+α -AlMn(Fe)Si+Si, solidifying in the residual liquid. Chromium addition stimulated the characteristic dendrite morphology of the intermetallic α-AlMn(FeCr)Si phase (Fig.3a) and an appearance of its separated polyhedra. The primary phase β-AlMnSi was covered with the peritectic phase layer of the characteristic "polygonal"profile (Fig.3b,c).

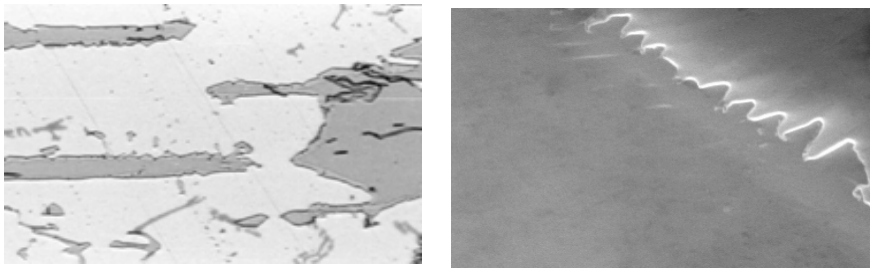

Fig.1. Microstructure of AlSi3Mn6 alloy; a/ LM, mag.1000x, b/ SEM, mag.10000x

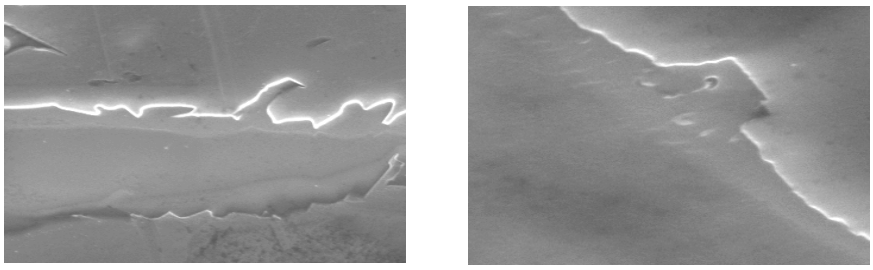

Fig.2. Microstructure of AlSi3Mn6Fe alloy, SEM; a/ AlSi3Mn6Fe0.5, mag.4000x, b/ AlSi3Mn6Fe2.0, mag.4000x

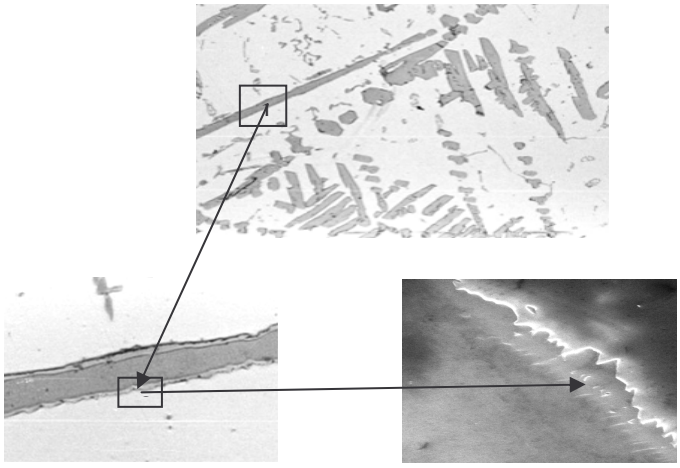

Fig.3. Microstructure of the AlSi3Mn6Fe0.5Cr0.1 alloy, a/ LM, mag. 200x, b/ microregion 1, LM. mag. 1000x, c/ microregion 2, SEM. mag. 4000x

3.2. Results of the X-ray microanalysis

Results of the estimation of the chemical composition of the phase components of the examined alloys allowed distinguishing three groups of the precipitates: primary precipitates

(lower Si), secondary precipitates - peritectic phase (higher Si) and precipitates in the residual liquid regions (higher both Si and Fe).

The maps of distribution of the alloy components in the three-phase microregion (Fig.4a) show the central microregion containing mainly Mn (Fig.4c) and Si (Fig.4d), surrounded with the layer enriched in Fe (Fig.4b) and Si (Fig.4d). The contour of the layer enriched in Fe (Fig.4b) corresponded to the peritectic transformation product (Fig.4a), while the Si distribution map (Fig. 4d) showed the presence of the larger region enriched in this element. The differentiation in the Si and Fe contents between primary and peritectic phase was clearly visible in the concentration maps. The differentiation in the Mn content in these phases was not very clearly revealed (Fig.4c) on the Mn distribution map; nevertheless it was detected and estimated by means of the point analysis. The summary amount of the transition metals in the primary phase β-AlMnSi was about 38%wt. (Fig.5a,b) whilst the Si content was estimated as equal 5.6%wt. The peritectic phase α-AlMnSi contained of 31%wt. of the Mn (+Fe) and higher amount of Si (6-7.5%wt in average). The transition metals summary content corresponding to the previously established limits of the Mn was considered the criterion of these phases identification together with the solidification sequence, revealed on the metallographic microsections (Figs.1-3,4a). The Fe content detected in the primary phase was lower than in the peritectic phase. It was stated that the precipitates forming in the successive stages of the alloy solidification (also in the residual liquid) were enriched in this element (Fig.5b). Chromium was almost entirely cumulated in both primary (0.6%wt) and peritectic (0.4%wt) phases. It was not detected in the particles precipitated in the residual liquid. Silicon concentration in the AlMnSi phases particles was influenced by alloy composition (Table 1, Fig.6) especially in the α-AlMnSi. In Fig.6 the dependence of the Si concentration in the intermetallic phases, primary (β) and peritectic (α), on the Si content in alloy was shown.

Table 1. Chemical composition of the intermetallic phases

%Fe(wt) in alloy		0.5	2.0
Mn/Fe in alloy		10	2.5
Mn/Fe in phase	primary	44	5.2
	peritectic	31	4.5
% (wt)Si in phase	primary	5.7	5.6
	peritectic	7.7	6.3

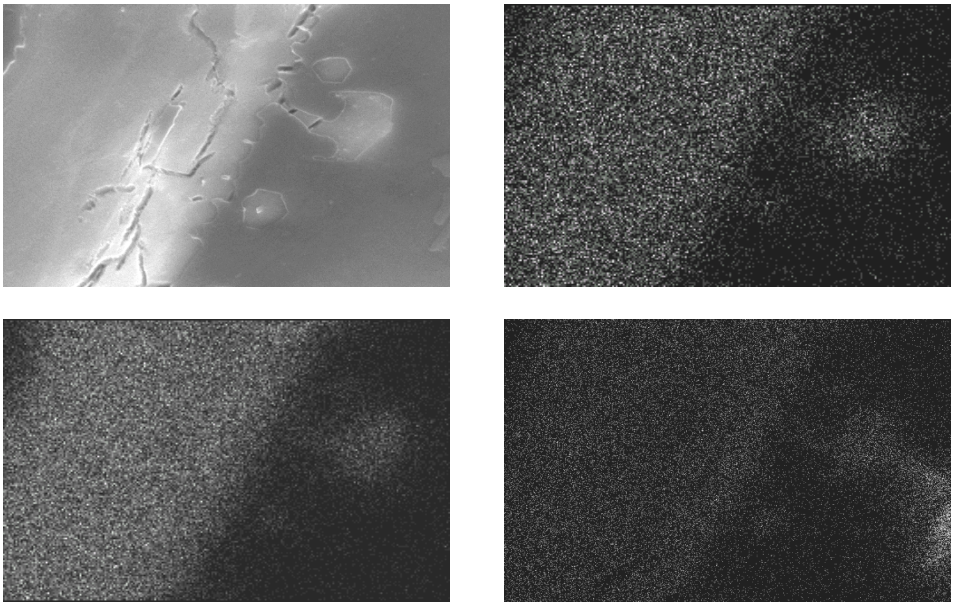

Fig. 4. Microstructure of AlSi3Mn11Fe2.0 alloy; a/ SEM, mag.8500x, b/ map of distribution of Fe, c/ map of distribution of Mn, d/ map of distribution of Si

One can see that the trend stated in the high Si alloys [5-7,9,16] can be extended for alloys of lower Si content, examined in the present work and reported in [17]. It corresponds with an assumption that Si atoms occupy the vacancies in the lattice before replacing Al atoms.

The very initial results obtained in this work show that Si content is rather stable in the primary phase (Fig.6, Table 1) while Si concentration in the peritectic phase seems to be influenced by the Fe content in alloy.

In the examined alloys the equilibrium state was not achieved, so simple explanation of this relationships could not be presented. First of all some increase in the density of the phase takes place when a heavier Fe atoms substitute for Mn in the lattice. However others factors should be taken into account such as changing value of the electron concentration e/a when Fe atoms were building in the crystal lattice. Moreover the important decrease in the volume of the unit cell when one Fe atom was build in [16] could be explained by an increase in the vacancy number. The occupation of these vacant lattice sites by large Si atoms might be difficult and then its content in the α -AlMnSi phase particles would be reduced.

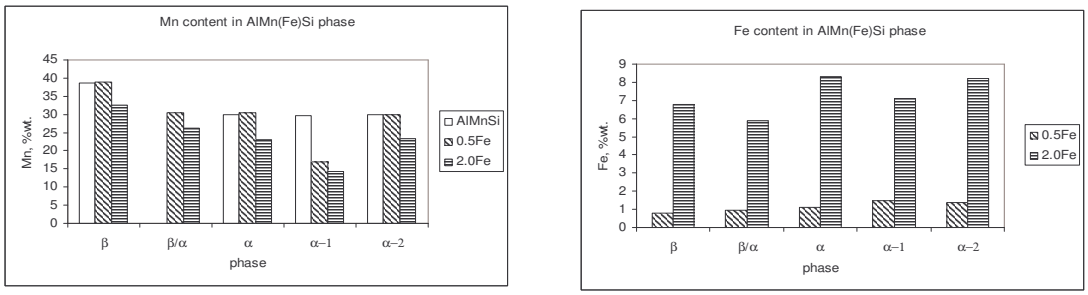

Fig.5. Concentration of the transition metals Mn and Fe in the intermetallic phases α -AlMnSi and β -AlMnSi in dependence on Fe content in the alloy (α–1 Chinese script, α–2 separate polyhedron)

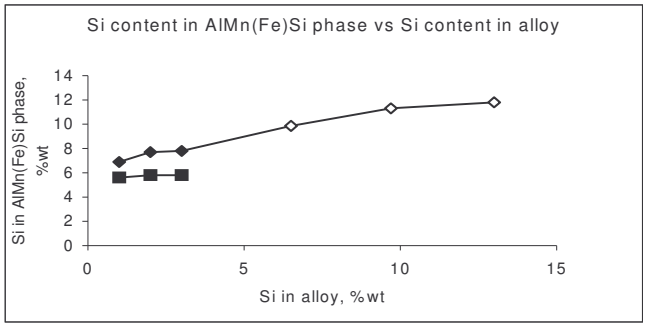

Fig.6. Si concentration in intermetallic phase in dependence on Si content in alloy Al-Mn-Si ◇- phase α, acc. to [9,16]◆ - phase α, acc.to present work, ■- phase β, acc. to present work.

4. CONCLUSIONS

- In the examined alloys the stable phase α–AlMn(FeCr)Si has formed during peritectic transformation from primary metastable high-temperature phase: L+β-AlMnSi→α–AlMnSi and in the residual liquid as a constituent of polyphase eutectic.
- The transition metals Fe and Cr added into ternary Al-Mn-Si alloy were gathered mainly in the stable α–AlMnSi phase. The Fe concentration in this phase was higher as the temperature of its formation was lower, i. e. an increase in the Fe content was observed in the eutectic precipitate of the α–AlMnSi phase.

- Concentration of Si in the α–AlMnSi phase was influenced by the content in the alloy of both Si and Fe.

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