PRACE INSTYTUTU ODLEWNICTWA
TRANSACTIONS OF FOUNDRY RESEARCH INSTITUTE

Volume LIV Year 2014 Number 1

DOI: 10.7356/iod.2014.01

Analysis of the chemical composition of AlMnFe and AlFeMnSi intermetallic phases in the interdendritic eutectics in the Al-alloys

Analiza składu chemicznego faz międzymetalicznych AlMnFe oraz AlMnFeSi w eutektykach międzydendrytycznych w stopach aluminium

Małgorzata Warmuzek

Instytut Odlewnictwa, Zespół Laboratoriów Badawczych, Laboratorium Badań Struktury i Właściwości, ul. Zakopiańska 73, 30-418 Kraków

Foundry Research Institute, Complex Research Laboratories, Laboratory of Structure and Properties, ul. Zakopiańska 73, 30-418 Kraków

E-mail: malgorzata.warmuzek@iod.krakow.pl

Streszczenie

W pracy przedstawiono prostą procedurę identyfikacji in situ *wydzieleń faz międzymetalicznych w eutektykach międzydendrytycznych w stopach AlFeMnSi do przeróbki plastycznej i odlewniczych, wraz z jej eksperymentalną weryfikacją. Na podstawie obserwacji mikroskopowych opisano, ujawnioną na zgładach międzymetalicznych, morfologię składników fazowych, występujących w tych eutektykach: A_6MnFe, α_c-AlFeMnSi, α_H-AlFeSi, β-AlFeSi. Do badań wykorzystano mikroskopy: świetlny oraz elektronowy, skaningowy. Skład chemiczny wydzieleń faz międzymetalicznych określono za pomocą punktowej mikroanalizy rentgenowskiej. Zakres zmienności składu chemicznego dla wydzieleń wybranych składników fazowych był analizowany w zależności od składu chemicznego stopu oraz cech morfologicznych mikrostruktury.*

Słowa kluczowe: stopy Al, mikrostruktura, faza międzymetaliczna, mikroanaliza rentgenowska, lokalny skład chemiczny

Abstract

In this study a simple procedure forthe in situ *identification of the intermetallic phase precipitates in the interdendritic eutectic in both wrought and cast AlFeMnSi alloys has been established and then verified by experimental results. Morphology of the phase constituents of these eutectics: A_6MnFe, α_c-AlFeMnSi, α_H-AlFeSi, β-AlFeSi, has been revealed on the metallographic microsections, observed with light and scanning electron microscopes. Chemical composition of these phase precipitates was estimated by means of point x-ray microanalysis. The homogeneity range for particular intermetallic phase precipitates, as influenced by either alloy chemical composition or microstructure morphology, was estimated.*

Key words: Al alloys, microstructure, intermetallic phase, x-ray microanalysis, local chemical composition

1. Introduction

Phase composition of the interdendritic polyphase eutectics in AlFeMnSi alloys is related to the multicomponent equilibrium diagrams, e.g., Al-Fe-Mn-Mg-Si. However, in the technical alloys, their microstructure reflects non-equilibrium effects of the technological processes. *In situ* identification of the microstructure constituents in polyphase eutectics is an important problem of both theory and practice of the Al-alloys solidification. One of the most useful analytical techniques for *in situ* microstructure examination, supplying crystal structure data, is backscattered electron diffraction (EBSD), realized in the scanning electron microscope. However, the homogeneity range of phases constituents, as affected by solidification conditions and alloy chemical composition, is an important factor of microstructure control. Chemical composition of the particular precipitate reflects alloy component`s distribution at solid/liquid interfaces on the alloy solidification path in the residual liquid. Chemical composition of the intermetallic phase is written as formula A_xB_y, of specific and repeatable value of both x and y indexes. Values of both x and y indexes are determined by alloy chemical composition and structure stabilization criteria [1,2]. Crystal lattice of the AlFeMnSi intermetallic phases retains

stability in the concentration range much more than ±1%, considered limits for intemetallic compounds [3]. Thus, the indexes in formulas estimated for intermetallic phase precipitates in the technical alloys usually are not integers. This fact is explained as caused by mutual atoms replacement. In the crystal lattice of the AlFeMnSi intermetallic phases two main sublattices have been recognized: transition metals (Fe, Mn) and Al (Al, Si). Atoms of both transition metals Fe and Mn replace each other in sites of (Fe, Mn) sublattice, while Si atoms- replace Al atoms in (Al) sublattice [4−6]. The vacances in sublattice models of some AlTMSi phases as a structure component has been included. It makes the homogeneity range of such crystals even wider [7−9].

Therefore, chemical composition of the AlFeMnSi intermetallic phases can be used as one of their specific attributes. Estimated formula $Al_{1-y}Fe_{1-x}Mn_xSi_y$ ascribed to precipitate in alloy microstructure serves as its identifier, while homogeneity range reflects alloy components influence. Nevertheless, morphological diversity and dispersion degree of the eutectic phase particles make microanalysis results evaluation difficult. Compilation of the point x-ray microanalysis results and precipitate morphology on microscope images allows us to obtain an useful tool to carry out *in situ* identification of phase constituents in polyphase alloys microregion [10,11].

Published data of the chemical composition of AlFeMnSi intermetallic phase precipitates in the technical Al alloys are very dispersed [12−16]. Several reasons sholud be discussed: specimen preparation, limitations of spatial resolution of the x-ray microanalysis, and microstructure characteristics. The individual particles of the intermetallic phase formed in the interdendrtic area are very dispersed, so that their diameter d does not meet the size criterion $d < d_{crit}$, necessary to estimate their proper chemical composition [10]. Therefore, simultaneous excitation of the Al matrix, of unknown volume fraction, has to be considered impossible to avoid. The result of the micronalysis recorded in the chosen point on the specimen cross-section represent a microvolume of *a priori* unknown phase composition and actual heterogeneity of the particular phase crystallite. The aim of this study is to adopt, for eutectic AlFeMnSi precipitates, a composed procedure of the point microanalysis results treatment, previously elaborated for primary AlFeMnSi precipitates [10]. The result of the point the x-ray microanalysis obtained for the AlMnFeSi precipitates in the dendritic eutectics of the Al alloys were used to microstructure phase constituents identify and describe.

2. Material for examination and experiment

Material for examination were Al alloys of chemical composition present in Table 1. The AlSi6-11 alloys were analyzed in as cast state, while both AlMn1FeSi and AlMn1Mg1Fe0.5Si0.2 alloys – in the state 'frozen' from different temperatures between liquidus and solidus by fast cooling of the specimen in the ice water.

Table 1. Chemical composition of the examined alloys, wt% (Al-bal)

Tabela 1. Skład chemiczny badanych stopów, % wag. (Al-reszta)

Groupe/ Grupa	Designation / Oznaczenie	Si	Fe	Mn
Si < 1	AlMn1FeSi	0.1	0.07	1.0
	AlMn1Mg1Fe0.5Si0.2	0.2	0.5	1.0
Si6	AlSi6Fe0.5	6	0.5	–
	AlSi6Fe0.5Mn0.1	6	0.5	0.1
	AlSi6Fe0.5Mn0.5	6	0.5	0.5
Si11	AlSi11Fe0.5	11	0.5	–
	AlSi11Fe0.5Mn0.1	11	0.5	0.1
	AlSi11Fe0.5Mn0.5	11	0.5	0.5

Microstructure examinations have been carried out by means of the metallographic light microscope AxioObserver OZm on the metallographic microsections prepared in the standard way. The microstructure constituents have been revealed by chemical etching.

The chemical composition of the intermetallic phase precipitates has been estimated by means of the point x-ray microanalysis method using Link ISIS 300 microanalyser EDS connected to the scanning electron microscope, Stereoscan 420. The procedure of the standardless analysis (using standard spectra library) has been used with both FLS and ZAF corrections.

3. Results and discussion

3.1. Phase constituents in the interdendritic eutectic: α-Al + α_c-AlFeMnSi + A_6MnFe in AlSi0.1-0.2FeMn alloys

In the interdendritic eutectics in the 3xxx alloys group, two equilibrium intermetallic phases α_c-AlFeMnSi and A6MnFe crystallize. They differ in both crystal structure and chemical composition. The precipitates observed on the metallographic cross-sections represent differential morphological forms, described as: polyhedral, rods, skeletons, plates-branched, and 'Chinese scripts' [17−19] (Fig. 1).

The point microanalysis results represented the polyphase microregions α-Al, α_c-AlFeMnSi and/or A_6MnFe. Thus, only some of them can be useful to identify either the particular phase constituents or their anticipated chemical composition.

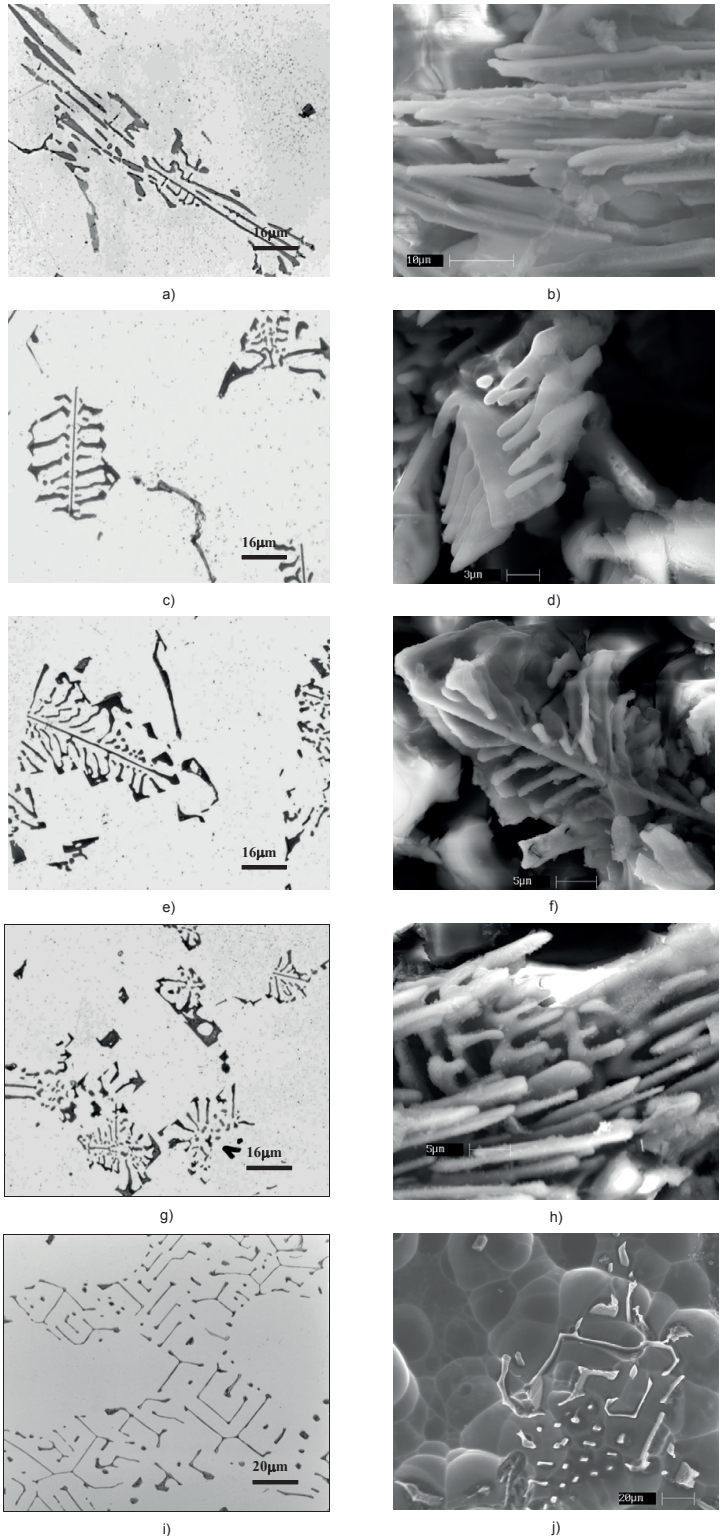

Fig. 1. Morphology of the eutectic precipitates of the intermetallic phases: AlMn1FeSi alloy, frozen at 580°C, rods of the Al_6FeMn phase (a,b) [17], AlMn1Mg1Fe0.5Si0.2 alloy, frozen at 550°C, skeleton-shaped precipitates (Al_6FeMn + α_c-AlFeMnSi) (c,d) [19], AlMn1Mg1Fe0.5Si0.2 alloy, frozen at 510°C, branched plates, (Al_6FeMn + α_c-AlFeMnSi) (e,f) [19], AlMn1Mg1Fe0.5Si0.2 alloy, frozen at 510°C, 'Chinese scripts' precipitates of α_c-AlFeMnSi phase (g,h) [19], AlMn1Mg1Fe0.5Si0.2 alloy, as-cast state, 'Chinese scripts' precipitates of α_c-AlFeMnSi phase (i,j)

Rys. 1. Morfologia eutektycznych wydzieleń faz międzymetalicznych: stop AlMn1FeSi, zamrożony 580°C, pręty fazy Al_6FeMn (a,b) [17], stop AlMn1Mg1Fe0,5Si0,2, zamrożony 550°C, wydzielenia w kształcie „szkieletów" (Al_6FeMn + α_c-AlFeMnSi) (c,d) [19], stop AlMn1Mg1Fe0,5Si0,2, zamrożony 510°C, rozgałęzione płytki (Al_6FeMn α_c-AlFeMnSi) (e,f) [19], stop AlMn1Mg1Fe0,5Si0,2, zamrożony 510°C, wydzielenia w kształcie chińskiego pisma, faza α_c-AlFeMnSi (g,h) [19], stop AlMn1Mg1Fe0,5Si0,2, stan lany, wydzielenia w kształcie chińskiego pisma, faza α_cc-AlFeMnSi (i,j)

The initial assumptions of the selection and classification of the microanalysis results have been appointed:

– free Si precipitates don`t occur in the interdendritic eutectics,
– Si, Fe, Mn solubility in the α-Al solid solution is negligible (at eutectic solidification temperature: 0.5; 0.05; 0.1 wt%, respectively).

They were established based on the analysis of the measurement series, literature data [12,20,21] and structure analysis (XRD analysis). Taking into account the assumption formulated above three-step procedure for the microanalysis results selection was established:

step I: criterion coefficient Al/[MP + Si] < 20,

step II: criterion Si > 0.5 wt%,

step III: criterion chosen value of the coefficient Al/[Fe + Mn].

The results which met step I criterion were considered as originating from microregions containing precipitates of the α_c-AlFeMnSi and/or Al_6MnFe phases. Then, they were classified according to both next criteria. The step II criterion was used to separate the results originating from microregion containing α_c-AlFeMnSi phase and Al_6MnFe phase. The step III criterion is used to identify microregions containing either stable or metastable forms of the Al_xFeMn phase (Fig. 2).

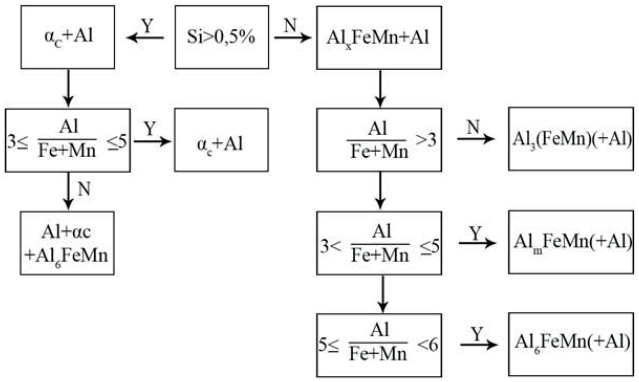

Fig. 2. Scheme of the results selection and classification procedure used to identify phase precipitates in AlMn1FeSi and AlMn1Mg1Fe0.5Si0.2 alloys

Rys. 2. Schemat blokowy procedury selekcji i klasyfikacji wyników wykorzystanych do identyfikacji wydzieleń faz w stopach AlMn1FeSi i AlMn1Mg1Fe0,5Si0,2

Chemical composition of the eutectic precipitates reflects residual liquid evolution as solidification progressed. According to the results of the frozen microstructure observations in an alloy held at 610°C/8 h and then frozen, the polyhedral particles of the Al_6FeMn phase appeared. This is not a typical form for eutectic precipitates. Formation of precipitates of this shape can be explained by holding temperature high enough to allow their lateral growth on the faceted crystallization front. Particles in the shape of rods were classified as eutectic precipitates of the Al_6FeMn phase. In the Li study [16], precipitates in the shape of rods were recognized as specific for the metastable Al_mMnFe phase in 5xxx alloys. Eutectic rods of Al_6MnFe phase contained more Fe than pre-eutectic precipitates in the form of polyhedra because they have been formed at lower temperatures in the residual liquid enriched in this element (Fig. 1a). Increase in the Fe content was caused by smaller partition coefficient value (k_{Fe} = 0.03, k_{Mn} = 0.2) and decreased volume fraction of the liquid phase.

The simple attribution of the skeleton-shaped precipitates and branched plates according to both established criteria for chemical coefficient Al/(Fe + Mn) and (% Si) became impossible. The Si content in the skeleton-like precipitates did not cross the criterion value for Al_6FeMn phase while value of the coefficient Al/[Fe + Mn] = 4-5, was lower than that acceptable for it. Although Si content noticed in the branched plates crossed the limit established for Al_mFeMn phase, the value of the coefficient (Mn + Fe)/Si was higher than that assumed as typical for α_c-AlMnFeSi phase. This effect can reflect unfinished stage of the peritectic transformation L + $Al_6FeMn \rightarrow \alpha_c$-AlMnFeSi at L/$Al_6Mn$ interface [17, 22]. Measured value of the Si and (Mn + Fe) concentrations in the skeleton- and plate-shaped precipitates was averaged for three-phase microregion: Al_6MnFe (high (Fe + Mn), low Si) + α_c-AlMnFeSi (high (Fe+Mn), high Si) + α-Al (no Si, Fe, Mn).

'Chinese scripts' morphology is typical for the eutectic precipitates of the α_c-AlMnFeSi phase in all aluminum alloys. In comparison to the Al_6FeMn phase, the α_c-AlMnFeSi phase precipitates are characterized by higher Si contents. Particles in the shape of 'Chinese scripts' started to form when the liquid phase became enriched in Si to a sufficient degree to attain the chemical composition of the eutectic point. Since the Si concentration noticed in the particles in the 'Chinese scripts' shape crossed its solubility in the Al_6MnFe phase, all of them were assigned to the α_c-AlMnFeSi phase.

The intermetallic phase precipitation sequence and particle morphology evolution on the solidification path has been revealed on the basis of the observations of the microstructure state 'frozen' at several temperatures chosen in a range liquidus – solidus.

The solidification path of the residual liquid in the interdendritic microregions of the 3xxx group of Al alloys is presented in the Table 2.

Table 2. Morphology of eutectic precipitates of the intermetallic phases in Al1MnFeSi and Al1Mn1Mg0.5Fe0.2Si alloys [13,14,16−19]

Tabela 2. Morfologia eutektycznych wydzieleń faz międzymetalicznych w stopach Al1MnFeSi i Al1Mn1Mg0,5Fe0,2Si [13,14,16−19]

Alloy/Stop	Morphology/ Morfologia	Temperature, °C / Temperatura, °C	I criterion Si, wt% / I kryterium Si, % wag.	II criterion Al/(Fe + Mn) / II kryterium Al/(Fe + Mn)	Intermetallic phase IM (+α-Al) / Faza międzymetaliczna FM (+α-Al)
AlMn1FeSi, AlMn1Mg1Fe0.5Si0.2	Polyhedra Pre-eutectic / Wielościany pre-eutektyczne	> 600	–	3−6	Al_nFeMn 3 < n < 6
AlMn1FeSi, AlMn1Mg1Fe0.5Si0.2	Rods eutectic / Pręty eutektyczne	600−580	–	3−6	Al_nFeMn 3 < n < 6
AlMn1FeSi, AlMn1Mg1Fe0.5Si0.2	Skeletons (Peritectic) / Szkielety (perytektyczne)	580	(Si)	3−5	$Al_nFeMn(3 < n < 6)$ + α_c-AlMnFeSi
AlMn1FeSi, AlMn1Mg1Fe0.5Si0.2	Branched plate (Peritectic) / Rozgałęzione płytki (perytektyczne)	580−555	(Si)	3−5	$Al_nFeMn(3 < n < 6)$ + α_c-AlMnFeSi
AlMn1FeSi, AlMn1Mg1Fe0.5Si0.2	'Chinese scripts' Eutectic / „Chińskie pismo" eutektyczne	< 555 As-cast	Si	3−5	α_c-AlMnFeSi

3.2. Morphological characteristics of the eutectic precipitates of the α_c-AlFeMnSi, α_H-AlFeSi, and β-AlFeSi phases in AlSi6-11FeMn alloys

The AlFeMnSi intermetallic phases reported in the interdendritic eutectics in the cast AlSi6-11Fe0.5Mn0-0.5 alloys differ in their crystal structure and chemical composition. In the equilibrium state, three intermetallic phases, α_H-AlFeSi, β-AlFeSi (in ternary Al-Fe-Si equilibrium diagram), and α_c-AlFeMnSi (in quaternary Al-Fe-Mn-Si equilibrium diagram), can crystallize in the interdendritic eutectics. In alloys solidifying under industrial conditions, the concentration limits of the particular equilibrium phase are shifted, so that non-equilibrium phases can also form (Table 3 – see page 8).

Taking into account the precipitate morphology revealed by the deep etching technique, observed in the scanning electron microscope (Fig. 3a,c), each eutectic precipitate of a specific shape can be assigned to one of the particular groups: 'needles' and 'Chinese scripts'. Thus, visual features of the precipitates observed on the metallographic cross-sections can be considered sufficient to distinguish two morphological groups (Table 3). Apparently, they were easily differentiated by visual analysis on the metallographic cross-sections (Fig. 3b,d).

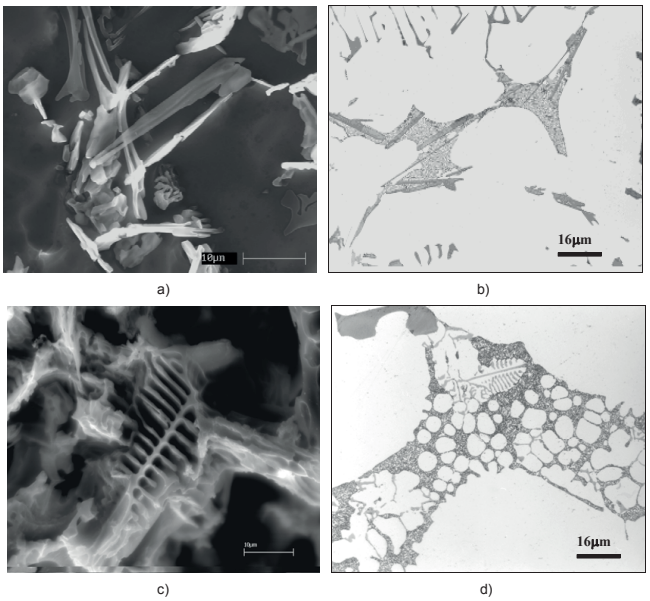

Fig. 3. Microstructure of the AlSiFeMn alloy frozen from the liquid state, above the ternary eutectic temperature. Morphology of the intermetallic phase precipitates, needle-shaped particles of the β-AlFeSi phase (a,b) and 'Chinese scripts' precipitate of the α_c-AlFeMnSi phase (c,d)

Rys. 3. Mikrostruktura stopu AlSiFeMn zamrożonego ze stanu ciekłego, z temperatury wyższej od temperatury początku krystalizacji eutektyki potrójnej. Morfologia wydzieleń fazy międzymetalicznej, „igły" fazy β-AlFeSi (a,b) oraz wydzielenie „chińskiego pisma" fazy α_c-AlFeMnSi (c,d)

Table 3. Morphology of the phase precipitates in the interdendritic eutectics in the AlSi6-11Fe0.5 Mn0-0.5 alloys [15,20,23]

Tabela 3. Morfologia wydzieleń faz międzymetalicznych w międzydendrytycznych eutektykach w stopach AlSi6-11Fe0,5 Mn0-0,5 [15,20,23]

Morphology of precipitate / Morfologia wydzielenia	**Alloy state / Stan stopu**	**Phase group / Grupa faz**	
		Ternary equilibrium system Al-Fe-Si / Trójskładnikowy układ równowagi fazowej Al-Fe-Si	**Quaternary equilibrium system Al-Fe-Mn-Si (Mn > 0.3 wt%) / Czteroskładnikowy układ równowagi fazowej Al-Fe-Mn-Si (Mn > 0,3 wt%)**
Chinese scripts/ Chińskie pismo	Equilibrium/Równowagowy	α_H-AlFeSi	α_c-AlFeMnSi
	Non-equilibrium/ Nierównowagowy	α_c-AlFeSi	α_H-AlFe(Mn)Si
Needle/Igła	Equilibrium/Równowagowy	β-AlFeSi	–
	Non-equilibrium/ Nierównowagowy	δ-AlFeSi, γ-AlFeSi	β-AlFe(Mn)Si, δ-AlFe(Mn)Si, γ-AlFe(Mn)Si

Table 4. Chemical coefficients specific for the intermetallic phases in AlFeMnSi alloys [7−9,24−27]

Tabela 4. Charakterystyczne współczynniki chemiczne dla faz międzymetalicznych w stopach AlFeMnSi [7−9,24−27]

Phase/Faza	**(Fe + Mn)/Si**		**Al/(Fe + Mn)**		**Al/Si**	
	wt%	**at.%**	**wt%**	**at.%**	**wt%**	**at.%**
α_c-AlFeMnSi	4.70	1.5−3	1.81	3.8−5	8−6	5.3−12
α_H-AlFeSi	4.13	2	1.78	3.5−4	7−4	7−8
β-AlFeSi	1.67	1	2.40	4.5−5	4.0	4.5−5
γ-AlFeSi	2.17	1	1.19	3	2.71	3
δ-AlFeSi	1.0	0.5−0.7	2.0	3−4	2.0	1.5−2

3.3. Estimation of the chemical composition of the eutectic precipitates as a support tool of its phase attribution

Non-equilibrium alloy solidification conditions result in deviations from the typical morphology and chemical composition of the phase constituents. The complicated 3D morphology of the 'Chinese scripts' precipitates introduces some additional uncertainty to the microstructure morphology descriptions, observed on the plane (2D) cross section especially when true precipitate shape (3D) is unknown.

In the alloys containing > 1% Si, in the interdendritic eutectics, besides the AlFeMnSi phase particles, pure Si precipitates are always present. Their size and morphology are comparable to other eutectic constituents. This fact should be taken into account when an attempt is made to use an estimation of the local chemical composition of the microregions for intermetallic phases identifications. Two initial assumptions had to be established:

– Si, Mn and Fe do not dissolve in the α-Al solid solution,
– Al, Mn and Fe do not dissolve in the Si eutectic precipitates.

To choose the results of the point microanalysis proper for the further phase identification, two chemical coefficients were chosen as selection criteria:

– Al/Si > 1.5,
– (Fe + Mn)/Si > 0.5.

Chemical coefficients, defined as particular components concentration ratio were assumed as the possible attributes of the specific phase precipitate.

The limits for each chemical coefficient characteristic for the specific AlFeMnSi phase (Table 4) were estimated on the basis of the stoichiometric formulas, given in literature [7−9,20,24−27].

The results which meet simultaneously both criteria were considered as originating from the biphase microvolume α-Al + IM (IM – Intermetallic phase). Then, the calculated value of the chemical coefficients were compared to the standard values, established for particular AlFeMnSi phases (Table 4 – see above).

Because of the spatial complexity of the precipitates in a shape of the 'Chinese scripts', some of their cross-sections can be recognized as representatives of the needle shaped group. Calculation of the value of (Fe + Mn)/Si coefficient can improve the *in situ*

phase identification, regardless of the actual shape of the particular precipitate visible on the metallographic cross-section (Table 5). If for elongated particles, representing on the cross section segments of the 'Chinese scripts' precipitate, the calculated value of (Fe + Mn)/Si is > 5, its wrong attribution to the needle -shaped phase group can be eliminated.

Table 5. Chemical coefficient (Fe + Mn)/Si as a discriminator between precipitates in the shape of the 'Chinese scripts' (IM = α_c-AlFeMnSi, α_H-AlFeSi) and needle-shaped (IM = β-AlFeSi, γ-AlFeSi, δ-AlFeSi)

Tabela 5. Współczynnik chemiczny (Fe+Mn)/Si jako dyskryminator wydzieleń w kształcie „chińskiego pisma" (FM = α_c-AlFeMnSi, α_H-AlFeSi) i wydzieleń w kształcie igieł (FM = β-AlFeSi, γ-AlFeSi, δ-AlFeSi)

(Fe + Mn)/Si	Result/Wynik: α-Al + IM
> 0.5	β-AlFeSi, γ-AlFeSi, δ-AlFeSi, α_c-AlFeMnSi, α_H-AlFeSi
> 1.0	α_c-AlFeMnSi, α_H-AlFeSi

The other two chemical coefficients can be used to make phase attribution more precise (Tables 6 and 7). The chemical coefficient Al/Si permits discrimination between groups of phases of high and low Si content (Table 6). Its value strongly depends on the phase composition of the microregion (3D) analyzed in fact, it means the specimen zone recorded x-ray lines were excited in as the α_H-AlFeSi and α_c-AlFeMnSi intermetallic phase volume fraction in the analyzed zone approaches 1, the value of the Al/Si coefficient crosses successive discrimination thresholds (5 and 8, respectively).

Table 6. Chemical coefficient Al/Si as a discriminator between intermetallic phases: IM = β-AlFeSi, γ-AlFeSi, δ-AlFeSi, α_c-AlFeMnSi and α_H-AlFeSi

Tabela 6. Współczynnik chemiczny Al/Si jako dyskryminator wydzieleń faz międzymetalicznych: FM = β-AlFeSi, γ-AlFeSi, δ-AlFeSi, α_c-AlFeMnSi i α_H-AlFeSi

Al/Si	Result/Wynik: α-Al + IM
> 1.5	β-AlFeSi, γ-AlFeSi, δ-AlFeSi, α_c-AlFeMnSi, α_H-AlFeSi
> 2.0	β-AlFeSi, γ-AlFeSi, α_c-AlFeMnSi, α_H-AlFeSi
> 3.0	β-AlFeSi, α_c-AlFeMnSi, α_H-AlFeSi
> 5.0	α_c-AlFeMnSi, α_H-AlFeSi
> 8.0	α_c-AlFeMnSi

The set of results obtained for both examined alloy groups: hypo-eutectic AlSi6Fe0.5Mn0.1-0.5 and eutectic AlSi11Fe0.5Mn0.1-0.5 have been shown in Figure 4. Taking into account the established limits of the chemical coefficients (Fe + Mn)/Si and Al/Si, the probable presence of the β-AlFeSi, α_H-AlFeSi, α_c-AlFeMnSi phases can be assumed. However, homogeneity ranges for only two phases, β-AlFeSi (Al/Si < 5, (Fe + Mn)/Si < 1) and α_c-AlFeMnSi (Al/Si > 8, (Fe + Mn)/Si > 1) have been recognized unequivocally. The limits of these coefficients for α_H-AlFeSi phase coincide with those for the other phases.

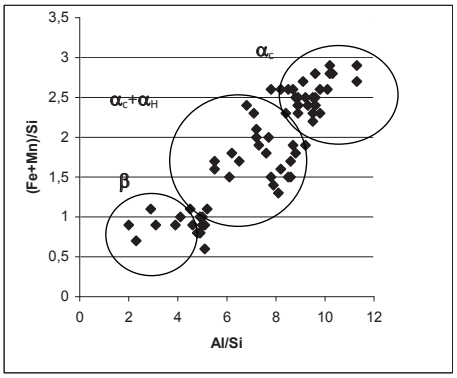

Fig. 4. The heterogeneity of the chemical composition of the eutectic precipitates of the intermetallic phases in hypo-eutectic AlSi6Fe0.5Mn0.1-0.5 and eutectic AlSi11Fe0.5Mn0.1-0.5

Rys. 4. Zakres zmienności składu chemicznego w eutektycznych wydzieleniach faz międzymetalicznych w stopach podeutektycznych AlSi6Fe0,5Mn0,1-0,5 i eutektycznych AlSi11Fe0,5Mn0,1-0,5

Compilation of two chemical coefficients Al/(Fe + Mn) and Al/Si permits discrimination between precipitates of the α_c-AlFeMnSi, α_H-AlFeSi phases in a shape of well defined 'Chinese scripts' (Fig. 5).

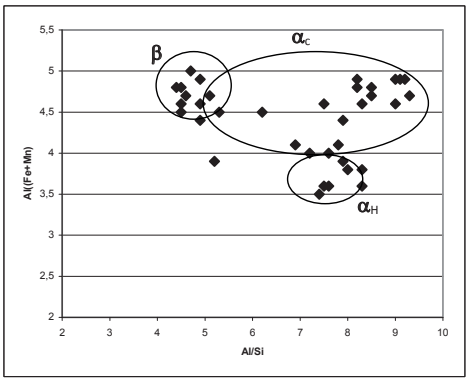

Fig. 5. The heterogeneity of the chemical composition of the eutectic precipitates of the intermetallic phases in hypo-eutectic AlSi6Fe0.5Mn0.1-0.5 and eutectic AlSi11Fe0.5Mn0.1-0.5

Rys. 5. Zakres zmienności składu chemicznego w eutektycznych wydzieleniach faz międzymetalicznych w stopach podeutektycznych AlSi6Fe0,5Mn0,1-0,5 i eutektycznych AlSi11Fe0,5Mn0,1-0,5

Table 7. Chemical coefficient Al/(Fe + Mn) as a discriminator between precipitates of the intermetallic phases: IM = β-AlFeSi, γ-AlFeSi, δ-AlFeSi, α_c-AlFeMnSi and α_H-AlFeSi

Tabela 7. Współczynnik chemiczny Al/(Fe + Mn) jako dyskryminator wydzieleń faz międzymetalicznych: FM = β-AlFeSi, γ-AlFeSi, δ-AlFeSi, α_c-AlFeMnSi i α_H-AlFeSi

Al/(Fe+Mn)	Result/Wynik: α-Al + IM
> 1.5	β-AlFeSi, γ-AlFeSi, δ-AlFeSi, α_c-AlFeMnSi, α_H-AlFeSi
> 3.0	β-AlFeSi, δ-AlFeSi, α_c-AlFeMnSi, α_H-AlFeSi
> 4.0	β-AlFeSi, α_c-AlFeMnSi

The precipitates in the shape of the chinese scripts which are characterized by a value of the Al(Fe + Mn) coefficient < 4 can be assigned to the α_H-AlFeSi phase.

3.4. Chemical composition of the intermetallic phases in quaternary AlFeMnSi alloys

In AlFeMnSi alloys, Mn can dissolve not only in the α-Al solid solution but also in the precipitates of the intermetallic phases. The Mn/Fe ratio represents the number of Mn atoms dissolved in the actually phase precipitate. Its value reflects Mn → Fe replacements range in the transition metals sublattice in the crystal of the AlFeMnSi phases. The upper limit of concentration of dissolved Mn in both phases β-AlFe(Mn)Si and α_H-AlFe(Mn)Si formed in the interdendritic eutectics in quaternary AlFeMnSi alloy has been reported to be very low [12,20,25]. The solubility limit of Mn in the primary precipitates of the β-AlFeSi phase is also low and does not exceed 0.5 wt% [20]. According to Munson [27], the solubility limit of Mn in the α_H-AlFeSi precipitates is about 1.3 wt% (0.6 at.%). Thus, each result of the point x-ray microanalysis for Mn < 1.3% comes from precipitate of one of three phases β-AlFeSi, α_H-AlFeSi or α_c-AlFeMnSi. The result for Mn > 1.3 wt% comes only from the α_c-AlFeMnSi phase precipitate. Taking into account that lower limit of Mn concentration in the α_c-AlFeMnSi phase has not been established more exactly than % Mn > 0, two overlapped discrimination rules for polyphase (α-Al + IM) microregions containing the quaternary AlFeMnSi phases were established:

– Mn/Fe ≥ 0-analyzed microvolume contains precipitates of the phases β-AlFeSi, α_H-AlFeSi or α_c-AlFeMnSi,
– Mn/Fe > 0-analyzed microvolume contains only precipitates of the phase α_c-AlFeMnSi.

On the basis of the undefined upper limits of Fe solubility, the homogeneity range of the precipitates of the intermetallic phases β-AlFeSi, α_H-AlFeSi or α_c-AlFeMnSi, analyzed in both hypo-eutectic AlSi6Fe0.5Mn0-0.5 and eutectic AlSi11Fe0.5Mn0-0.5 alloys, were estimated (Fig. 6).

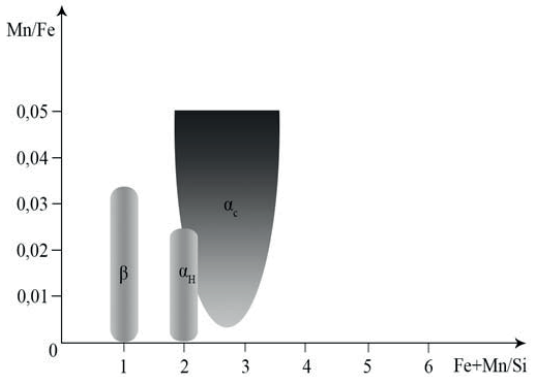

Fig. 6. Homogeneity range of the intermetallic phases precipitated in interdendritic eutectics in the AlSi6-11 Fe0.5Mn0-0.5 alloys

Rys. 6. Zakresy graniczne stężenia składników w wydzieleniach faz międzymetalicznych w międzydendrytycznych eutektykach w stopach AlSi6-11 Fe0,5Mn0-0,5

Estimated morphology map (needles and 'Chinese scripts') estimated for both hypo- and eutectic alloys represent satisfying correlation between visual and chemical classifications of the phase precipitates (Fig. 7). Initial selection and classification of the results of the point microanalysis have been carried out, using the criteria described for the chemical coefficients.

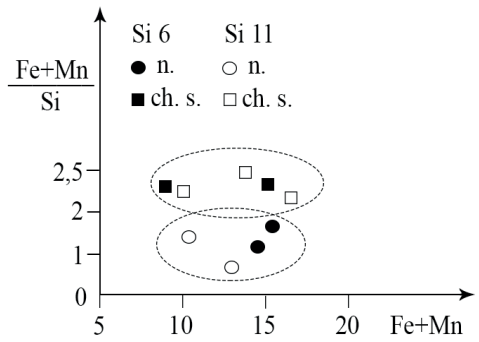

Fig. 7. Comparison of results of the visual and analytical classification of the intermetallic phase precipitates observed in the microstructure image in interdendritic eutectics in the AlSi6-11 Fe0.5Mn0.1-0.5 alloys

Rys. 7. Porównanie wyników wizualnej i analitycznej klasyfikacji wydzieleń faz międzymetalicznych obserwowanych w międzydendrytycznych eutektykach w stopach AlSi6-11 Fe0,5Mn0,1-0,5

Usually, the value of the Mn/Fe ratio in the precipitates formed in the eutectics is lower than that in the alloy (Fig. 7), since it reflects the component`s distribution between the liquid and solid phases on the

solidification path. The significant dispersion of the Mn/Fe ratio value has been noticed in the 'Chinese scripts' precipitates in both AlSi6Fe0.5Mn0.5 and AlS11Fe0.5Mn0.5 alloys. Comparison of the calculated value of the coefficients Mn/Fe in phase and Mn/Fe in alloy reveals two clusters of precipitates (Fig. 8). Average values of the Mn/Fe ratio for 'Chinese scripts' precipitates in these clusters differed significantly. It indicates two classes of eutectic precipitates. In the AlSi6Fe0.5Mn0.5 and AlS11Fe0.5Mn0.5 alloys, a sequence of eutectic reactions: α-Al + α_c-AlFeMnSi (bivariant at 648−573°C) and α-Al + α_c-AlFeMnSi + Si (monovariant at 575−573°C) occurs on the solidification path [20]. Chemical composition of the liquid phase changes in the temperature range (from 2.0% Fe, 0.35% Mn at 648°C to 0.6% Fe and 0.2% Mn at 573°C). Therefore, when the temperature decreases, a total excess of the Fe content has to be remove from the residual liquid and gathered in the α_c-AlFeMnSi phase precipitates. Distribution of the alloy components between α-Al solid solution and liquid is continued even after the eutectic reactions start, until exhaustion of the residual liquid. Thus, alloy components are concentrated in the decreasing liquid volume. Partition coefficient of Mn is higher than that of Fe, thus Mn concentration in the liquid increase relatively slower. Therefore, the α_c-AlFeMnSi phase precipitates are gradually enriched in Fe.

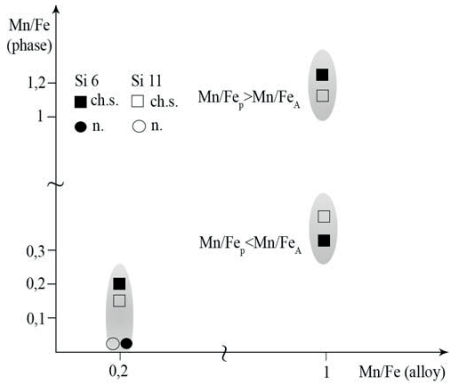

Fig. 8. Distribution of Fe and Mn in the eutectic precipitates of the AlMnFeSi phases in both AlSi6Fe0.5Mn0.5 and AlSi11Fe0.5Mn0.5 alloys as compared with alloy composition

Rys. 8. Rozkład stężenia Fe i Mn w eutektycznych wydzieleniach faz międzymetalicznych AlMnFeSi w stopach AlSi6Fe0,5Mn0,5 i AlSi11Fe0,5Mn0,5, w porównaniu ze składem chemicznym stopu

4. Conclusions

1. The results of the x-ray point microanalysis combined with the microscopical observations can be used as an effective tool for *in situ* discrimination and identification of the intermetallic phase precipitates formed in the interdendritic eutectics in the AlFeMnSi alloys. Although the phase composition of the polyphase microregions can be verified on the basis of the Al-Fe-Mn-Si equilibrium diagram, the actual microstructural constituent characteristic is influenced by both non-equlibrium factors and other alloying elements effects.
2. Established critical limits of the chemical coefficient characterizing the homogeneity range of the AlFeMnSi intermetallic phases precipitates support their *in situ* distinction regardless of their actual cross-section shape:

a) estimated limits of (Fe + Mn)/Si chemical coefficient value can be used as a discriminators for two groups of phases:
   – β-AlFeSi, γ-AlFeSi, δ-AlFeSi (needle-shaped in 3D) and
   – α_c-AlFeMnSi, α_H-AlFeSi ('Chinese scripts'-shaped in 3D),

   regardless of their actual shape visible on the cross-section, in both ternary AlFeSi and quaternary AlFeMnSi alloys,

b) estimated limits of Mn/Fe ratio and those of two other chemical coefficients, (Mn + Fe)/Si and Al/Si permit distinction between eutectic precipitates of the phases β-AlFeSi and α_c-AlFeMnSi, α-AlFeSi phases,

c) estimated limits of Al/(Fe + Mn) chemical coefficient value can be used for distinction between:

– precipitates of two phases: Al_6FeMn and α_c-AlFeMnSi in the interdendritic eutectics in the of 3xxx alloy group,

– precipitates of two phases: α_c-AlFeMnSi, α_H-AlFeSi in the shape of 'Chinese scripts' well defined, in the interdendritic eutectics in the cast AlSi alloys.

Acknowledgments

This work has been carried out with the financial support of Polish Ministry of Science and Higher Education under FRI project No. 3601/00

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