

The AlFeMnSi intermetallics competition in the interdendritic eutectics
in AlSi cast alloys influenced by cooling rate and transition metals content

Konkurencyjna krystalizacja faz międzymetalicznych AlFeMnSi w eutektykach
międzydendrytycznych w odlewniczych stopach AlSi – wpływ składu
i szybkości chłodzenia

Małgorzata Warmuzek¹

¹ Instytut Odlewnictwa, Zespół Laboratoriów Badawczych, Laboratorium Badań Struktury i Właściwości,
ul. Zakopiańska 73, 30-418 Kraków

¹ Foundry Research Institute, Complex of Accredited Research Laboratories, Laboratory for Structure Analysis
and Mechanical Testing, 30-418 Kraków, Poland

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

Received: 01.12.2015. Accepted in revised form: 31.03.2016.

© 2016 Instytut Odlewnictwa. All rights reserved.

DOI: 10.7356/iod.2016.02

Abstract

Microscopic observations and quantitative analysis of the microstructure image were used to analyze the solidification course and morphology evolution in polyphase eutectics in the AlSi casting alloys with transition metals Fe and Mn. The utility of the analytical test procedures was demonstrated. It was stated that their precision and repeatability should be improved. Further works on quantitative morphological coefficients used as objective discriminators of the particular morphological form of phase constituents should be continued.

Nevertheless, obtained results of the microstructure image analysis indicated that in a concentration range of transition metals: Fe 0.5–1.5 wt. % and Mn 0–0.5 wt. %, the total V_v of the eutectic intermetallics has increased with a total content of the transition metals (Fe + Mn). In both group of alloys hypo- and eutectic the final results of the competition between phases α_c -AlFeMnSi, α_H -AlFeSi and β -AlFeSi have been explained as affected by non-equilibrium microsegregation of Fe, Mn and Si in solidifying liquid, and by the actual value of the Fe/Si coefficient. Preferences for α_c -AlFeMnSi phase were reinforced by a decrease in the value of Fe/Mn coefficient.

Key words: aluminium alloys, transition metals, intermetallic phases, eutectic

Streszczenie

Obserwacje mikroskopowe oraz ilościowa analiza obrazu mikrostruktury zostały wykorzystane do analizy ścieżki krystalizacji i ewolucji morfologii wielofazowych eutektyk zawierających fazy międzymetaliczne w stopach AlSi zawierających metale przejściowe. Wykazano przydatność opracowanej procedury badawczej, jakkolwiek jej precyzja i powtarzalność będą mogły być poprawione tylko na drodze dalszych prac nad ustanowieniem obiektywnych reguł klasyfikacji opartej na ilościowym wskaźniku morfologicznym jako dyskryminatorze dla grup morfologicznych, przypisanych do składników fazowych mikrostruktury. Niemniej jednak otrzymane wyniki analizy obrazu mikrostruktury wykazały, że w zakresie stężenia 0,5–1,5% Fe i 0–0,5% Mn całkowita wartość objętości względnej V_v faz międzymetalicznych AlFeMnSi zwiększała się w miarę wzrostu zawartości metali przejściowych (Fe + Mn) w stopie. W obu grupach stopów, podeutektycznych i eutektycznych, mikrostrukturalny wynik konkurencji pomiędzy fazami α_H -AlFeSi i β -AlFeSi był uzależniony od nierównowagowej mikrosegregacji Fe, Mn i Si w cieczy resztkowej, w tym od trzeczywistych zmian wartości wskaźnika Fe/Si. Preferencje dla fazy α_c -AlFeMnSi wzmacniane były zmniejszeniem wartości wskaźnika Fe/Mn.

Słowa kluczowe: stopy aluminium, metale przejściowe, fazy międzymetaliczne, eutektyka

1. Introduction

Primary microstructure of the cast AlSi alloy, characteristic by phase composition and morphology is usually formed through a non-equilibrium sequence of invariant and polyvariant reactions depending on Si, Fe (Fig. 1a) and Mn content (Fig. 1b,c).

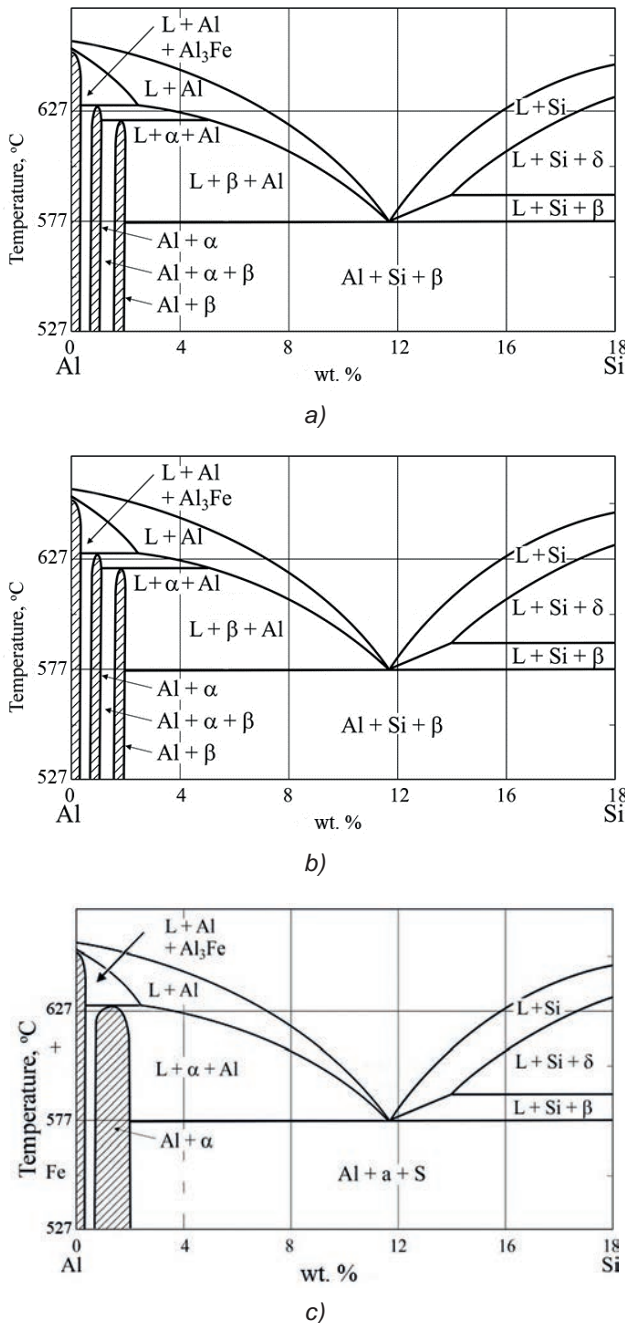


Fig. 1. Equilibrium diagram AlFe(Mn)Si; a) AlFe_{0.8}Si alloys, b) AlFe_{0.8}Mn_{0.1}Si alloys, and c) AlFe_{0.8}Mn_{0.5}Si alloys (own work, acc. to [1-6])

Rys. 1. Układ równowagi fazowej AlFe(Mn)Si; a) stopy AlFe_{0.8}Si, b) stopy AlFe_{0.8}Mn_{0.1}Si, c) stopy AlFe_{0.8}Mn_{0.5}Si (opracowanie własne wg [1-6])

Diversity of the microstructure observed in the poly-phase eutectics in the final microstructure formed in technological processes is usually explained as a result of local competition between solidifying intermetallic AlFeMnSi phases, either stable and metastable or faceted and non-faceted [7,8], influenced by alloy chemical composition and cooling rate.

The impact of the cooling rate on actual preference for nucleation (i.e. critical nucleus radius) and growth mechanism of the particular phase is very strong. As was experimentally observed in the technical AlSi cast alloys, three phases β -AlFeSi (monoclinic), α_H -AlFeSi (hexagonal) and α_C -AlFeMnSi (cubic), differing in the crystal lattice symmetry, crystallize in the interdendritic eutectic. Thus, the actual eutectic microstructure is determined by competition between these AlFeMnSi intermetallics:

- β -AlFeSi \leftrightarrow α_H -AlFeSi/ α_C -AlFeMnSi
- α_H -AlFeSi \leftrightarrow α_C -AlFeMnSi

Formation and growth of nuclei of the α_H -AlFeSi and β -AlFeSi phases are more difficult than those of the cubic α_C -AlFeMnSi phase because of more complex lattice symmetry. However, according to works [9,10], the nucleation barrier of all phases is comparable, thus, the difference in thermodynamic potential is rather small. The cooling rate (i.e. actual undercooling) was considered by Iglešis [11,12] as an important kinetic factor of phase selection β -AlFeSi vs. α -AlFeSi (Fig. 2) in ternary eutectics α -Al+Si + AlFeSi. Its impact was explained by growth mechanism specifics, determining Solid/Liquid interface morphology for each kind of the AlFeSi phase. The rough Solid/Liquid interface observed for the particle in the shape of Chinese script, i.e. α_H -AlFeSi and α_C -AlFeMnSi, privileges its growth at high undercooling, although the thermodynamical driving force might be considered comparable with that of the β -AlFeSi in a shape of needle.

The crystal lattice of the AlFeMnSi intermetallics is long range ordered. Formation of the order of atoms distribution in a long range demands diffusional displacement of atoms on a longer distance than that necessary for non-ordered solid solutions. Thus, the differential of components concentration in liquid and solid phase at Solid/Liquid interface is considered a second important factor which determines the competition results among AlFeMnSi intermetallics in polyphase eutectics. Especially, when pre-eutectic crystallization of some phase constituent takes place, e.g.:

- α -Al solid solution in hypo-eutectic alloys,
- primary, incongruent AlFeMnSi intermetallics,

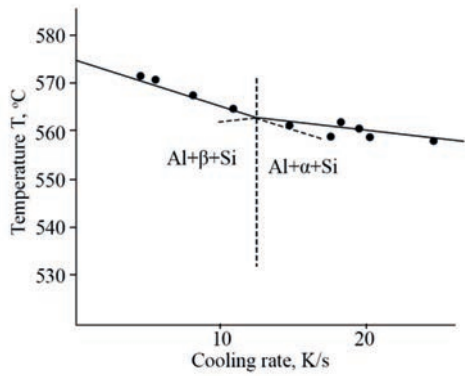


Fig. 2. Transition of stable α -Al+ β +Si to metastable α -Al+ α +Si eutectic in the AlFeSi alloys as induced by cooling rate increase [11]

Rys. 2. Wpływ szybkości chłodzenia na przemianę eutektyki stabilnej α -Al+ β +Si w metastabilną α -Al+ α +Si podczas krystalizacji stopu AlSiFe [11]

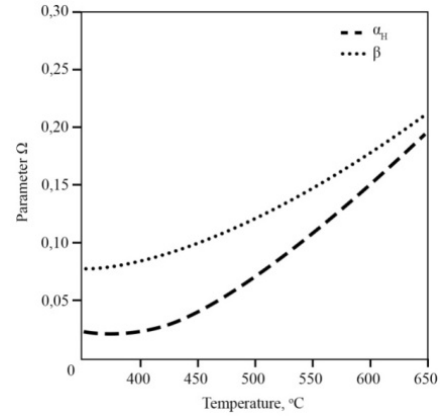
the non-equilibrium changes in the chemical composition of the solidifying liquid may appear.

In the hypo-eutectic AlSi alloys, local deviations from the non-equilibrium composition may be caused by several factors [13–17]:

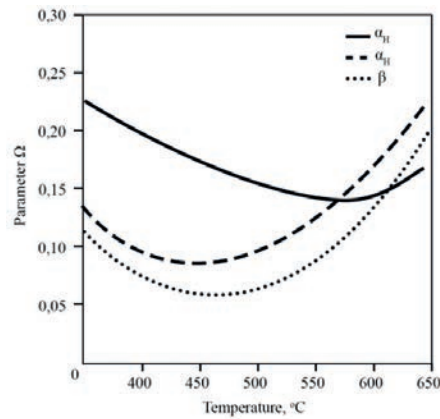
- difference in the Fe, Mn and Si solubility limit C^i in the α -Al solid solution ($C^{Mn} > C^{Si} > C^{Fe}$),
- different diffusivity of the element in liquid (this of Mn faster than that of Fe and Si),
- different back diffusion effects ($\alpha_{Si} > \alpha_{Fe} > \alpha_{Mn}$),
- dependence of the Si partition coefficient k^{Si} on alloy composition ($k^{Si} = 0.01 + 0.002(\%Si)$; $k^{Si}(AlSi6) < k^{Si}(AlSi11)$),
- decrease in Mn solubility limit in α -Al solid solution containing Fe.

The parameter Ω represents the concentration match between the liquid and solid phases [8]. Thus, the value of this parameter determines some probability of the particular phase formation in subsequent stages of the eutectic solidification. The Ω value is changing for a particular chemical composition of alloy with a change of temperature of the solidifying liquid (Fig. 3).

As an actual value of Ω depends on the partition coefficient of alloy components $k^i = C^i_S/C^i_L$ of the alloy components and their diffusivity in both phases at interface Solid/Liquid, especially in the liquid, a new kinetic preference for phase constituents might appear, independently of those determined by the initial alloy chemical composition (Fig. 4).



a)



b)

Fig. 3. Parameter Ω as affected by alloy chemical composition; a) alloy AlSi0.3Fe0.2, b) AlSi0.2Fe0.3 alloy [8]

Rys. 3. Wpływ składu chemicznego na wartość parametru Ω ; a) stop AlSi0,3Fe0,2, b) stop AlSi0,2Fe0,3 [8]

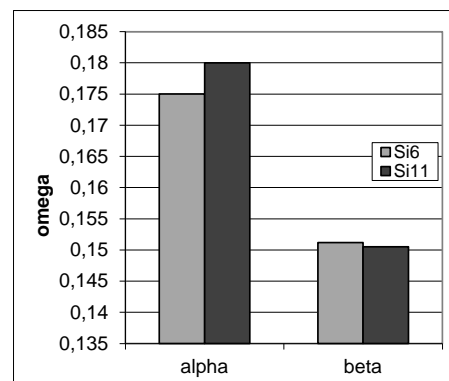


Fig. 4. Parameter Ω ($\Omega = \{(X_{Fe}^F - X_{Fe}^L)^2 + (X_{Si}^F - X_{Si}^L)\}^{1/2}$) estimated for α_H -AlFeSi (alpha) and β -AlFeSi (beta) phases, at 576°C; AlFe0.5Si6 – grey bar, AlFe0.5Si11 – black bar

Rys. 4. Parametr Ω ($\Omega = \{(X_{Fe}^F - X_{Fe}^L)^2 + (X_{Si}^F - X_{Si}^L)\}^{1/2}$) wyznaczony dla faz międzymetalicznych: α_H -AlFeSi (alfa) i β -AlFeSi (beta), temperatura 576°C; AlFe0,5Si6 – szary słupek, AlFe0,5Si11 – czarny słupek

Table 1. Chemical coefficients specific for the intermetallic phases in AlFeMnSi alloys [6]

Tabela 1. Współczynniki chemiczne charakteryzujące skład chemiczny faz międzymetalicznych w stopach AlFeMnSi [6]

Phase/Faza	(Fe+Mn)/Si		Al/(Fe+Mn)		Al/Si		Shape/Kształt
	wt. %	at. %	wt. %	at. %	wt. %	at. %	
α_c -AlFeMnSi	4.70	1.5–3.0	1.81	3.8–5.0	8.00–6.00	5.3–12.0	Chinese script / Chińskie pismo
α_H -AlFeSi	4.13	2.0	1.78	3.5–4.0	7.00–4.00	7.0–8.0	Chińskie pismo / Chinese script
β -AlFeSi	1.67	1.0	2.40	4.5–5.0	4.00	4.5–5.0	Needles/Igły
γ -AlFeSi	2.17	1.0	1.19	3.0	2.71	3.0	Needles/Igły
δ -AlFeSi	1.00	0.5–0.7	2.00	3.0–4.0	2.00	1.5–2.0	Plates/Płytki / Needles/Igły

The AlFeMnSi phases as the constituents of the polyphase eutectics (α -Al + AlFeMnSi + Si) can be also classified according to their morphological attributes into two groups: needles (β -AlFeSi) and Chinese script (α_H -AlFeSi, α_c -AlFeMnSi) [6]. Based on the morphology of particles assigned to chemical coefficients characteristic for the particular phase, estimated *in situ*, compared with those previously established (Table 1), their phase attribution could be made. It should be verified subsequently by crystal structure identification.

When each eutectic precipitate has been ascribed to a specific morphology group (Table 1), the visual effects of phase competition determining the final microstructure state could be observed on the microscopic image.

Though the eutectic crystallization course in the hypo-eutectic AlSi alloys was a subject of the research [6, 14–20], it is less identified than that in near – eutectic [3, 12, 21–26] and hyper-eutectic alloys [9, 26–28]. In this work the phase evolution of the polyphase eutectics with AlFeMnSi intermetallics was analysed in both hypo- and near – eutectic AlSi alloys in a concentration range of the transition metals complementary with that examined previously by Tibballs [29], Zakharov [27, 28], Iglessis [11, 12], Sukiennik and Flores [30, 31]. The role of some factors affecting non-equilibrium microstructural effects will be analysed and explained based on microstructure observation and quantitative image analysis.

2. Experimental

Materials for examinations were AlSi alloys with transition metals Fe and Mn (Table 2). The AlSi6-11 alloys were analyzed in as cast state after a cooling rate at 3 K/min (0.05 K/s) and 108 K/min (31 K/s). The cooling rate of 3 K/min, used in this work, was equal to that considered by Iglessis [11, 12] as critical for non-equilibrium transition β -AlFeSi (needles) \rightarrow α_c -AlFeSi (Chinese script) in the AlFeSi alloys of Fe 0.25 wt. % at least (Fig. 2).

Thus, in the examined alloys cooled at 3 K/min, the main factor determining phase composition of the interdendritic eutectics was their chemical composition and local interatomic interactions.

Microstructure examinations have been carried out by means of the metallographic light microscope AxioObserverOZm on the metallographic microsections prepared in the standard way.

Table 2. Designation of the examined alloys accordingly to chemical composition, wt. % (Al-bal)

Tabela 2. Oznaczenia badanych stopów zgodnie z ich składem chemicznym (% wag.)

Group/Grupa	
Si6	Si11
AlSi6Fe0.5	AlSi11Fe0.5
AlSi6Fe0.5Mn0.1	AlSi11Fe0.5Mn0.1
AlSi6Fe0.5Mn0.5	AlSi11Fe0.5Mn0.5
AlSi6Fe1.5	AlSi11Fe1.5
AlSi6Fe1.5Mn0.1	AlSi11Fe1.5Mn0.1
AlSi6Fe1.5Mn0.5	AlSi11Fe1.5Mn0.5

The intermetallic phases on the microscopic images were distinguished from eutectic silicon crystals due to the visual contrast (Fig. 5) obtained by selective etching with Weck reagent. Then, their volume fraction was estimated by means of image analysis using the commercial system Aphelion 3.2. The analysis procedure was carried out in several steps: grey image conversion into a binary image, then its modification by shadow correction and contrast enhancement for analysed objects (if necessary), manual establishing and correction of the detection threshold for particular morphological class and measurements of the volume fraction of the detected objects.

The analysis was carried out for as many 30 fields of view, distributed randomly on the cross section surface at magnification 100 \times , for each examined specimen. The results of image analysis were elaborated statistically. For both morphological categories analysed in each specimen the mean value of V_v was calculated and its range of dispersion. The difference of mean value of V_v among examined specimens was evaluated by means of paired t test [32]. The null hypothesis:

V_v (needles/Ch.s) in alloy 1 = V_v (needles/Ch.s) in alloy 2 were falsified for chosen pairs of alloys.

3. Results and discussion

3.1. Microscopic observation of microstructure constituent morphology evolution

Morphology evolution occurred in the interdendritic eutectics is presented in Figure 5. In a range of concentration of the transition metals: Fe 0.5–1.5 wt. % and Mn 0–0.5 wt. %, gradual replacement of the ternary β -AlFeSi phase by ternary α_H -AlFeSi and then – quaternary α_C -AlFeMnSi phases was observed (Fig. 5).

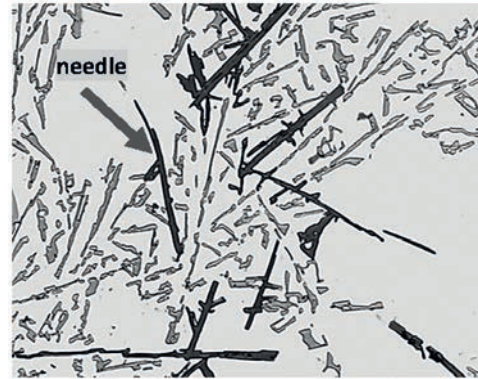
3.2. Results of the microscopic image analysis of the volume fraction of chosen microstructure constituent

The AlFeMnSi intermetallics in both morphological classes: needles and Chinese script in binary and ternary eutectics were analysed together. Results of the volume fraction measurements showed an important dispersion, which resulted from unequivocal attribution of the particular object realized by analysing the procedure in a stage of their visual discrimination and classification. It have been assumed that some objects visible on the cross-section might have originated from both morphological forms. Especially, V_v of the particles in the shape of a needle might be overestimated. Nevertheless, in most of the analysed specimens, the revealed difference in the measured volume fraction of particular particles groups was significant at a confidence level of at least 0.9 (Table 3).

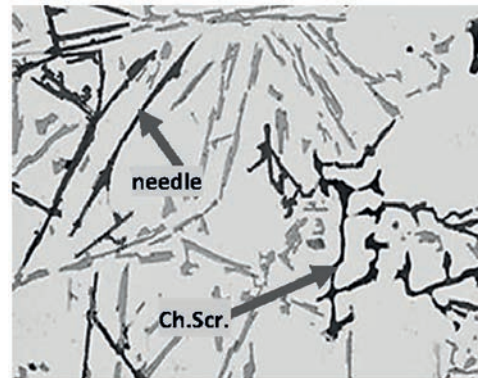
Table 3. Results of the paired t test, t value calculated based on the measurements of value of volume fraction of V_v of AlFeMnSi particles in a shape of Chinese script or needles analysed in two groups of alloys hypo-eutectic AlSi6 and eutectic AlSi11 (tabulated values: $t = 1.671$, $\alpha = 0.1$, $t = 1.296$, $\alpha = 0.2$, $t = 1.046$, $\alpha = 0.3$, for analysed number of degrees of freedom [32])

Tabela 3. Wartość t obliczona na podstawie wyników pomiarów objętości względnej V_v cząstek AlFeMnSi w kształcie chińskiego pisma lub igieł, w dwóch grupach stopów: podeutektycznych AlSi6 oraz eutektycznych AlSi11 (wartości t tablicowe dla analizowanej liczby stopni swobody $t = 1,671$, $\alpha = 0,1$, $t = 1,296$, $\alpha = 0,2$, $t = 1,046$, $\alpha = 0,3$ [32])

Alloys AlSi6 vs AlSi11 / Stopy AlSi6 vs AlSi11	t (Needles) / t (igły)	t (Chinese script) / t (chińskie pismo)
Fe0.5Mn0	1.93365	–
Fe0.5Mn0.1	1.02303	5.6701
Fe0.5Mn0.5	–	1.9975



a)



b)



c)

Fig. 5. Typical morphology of the AlFeMnSi intermetallics examined in this work; a,b) needles of phase β -AlFeSi and b) Chinese script of phases α_H -AlFeSi and b,c) α_C -AlFeMnSi, a) alloy AlFe1.5Si6, b) alloy AlFe0.5Mn0.1Si11, c) alloy AlFe0.5Mn0.5Si6, LM, etched with Weck reagent

Rys. 5. Typowa morfologia faz AlFeMnSi badanych w tej pracy; a,b) igły fazy β -AlFeSi oraz b) chińskie pismo faz α_H -AlFeSi oraz b,c) α_C -AlFeMnSi, a) stop AlFe1,5Si6, b) stop AlFe0,5Mn0,1Si11, c) stop AlFe0,5Mn0,5Si6, LM, trawiony odczynnikiem Weck

Nevertheless, taking into account the role of the analytical procedure as a source of diversity in the result of V_v measurements, some of revealed diversities might be recognized as the material effects affected by the actual solidification course.

4. Material effects discussion

4.1. The results of the total volume fraction estimation of the AlFeMnSi intermetallics

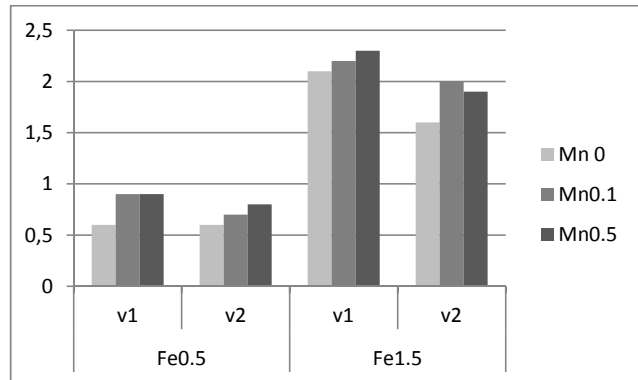
Based on the obtained results, it was stated that the total volume fraction V_v of the AlFeMnSi intermetallics depended on the total content of the transition metals, i.e. wt. % [Mn + Fe] in the alloy. It was in accordance with the general trend revealed also by visual observation results. A cooling rate increase was a second important factor determining the total volume of the AlFeMnSi intermetallics (Fig. 6). Shabestari and Gruzleski [22,23] showed that due to a tenfold increase in the cooling rate above 1 K/s, in the eutectic AlSi alloy with Fe 0.4–1.2 wt. % and Mn 0.3 wt. %, almost a hundredfold decrease in the intermetallics volume fraction took place (Fig. 7). In the range of lower cooling rate (<1 K/s) the effect of its change was less important. It was quite difficult to make an exact comparison between experimental results of previous works and those of the present work because of very strong sensitivity of results on the other interactions between atoms of different elements (Table 4).

However, it was stated that an increase in the cooling rate from 0.05 K/s up to 31 K/s resulted in a decrease of total V_v of about 10% (eutectic alloys) and 25% (hypo-eutectic alloys). This effect might be assigned to the "solute trapping effect" [33] resulting from retention of some non-equilibrium amounts of the alloy components in the α -Al solid solution, which started to grow, first of all as Mn atoms, and then, to a lesser extent as Fe and Si.

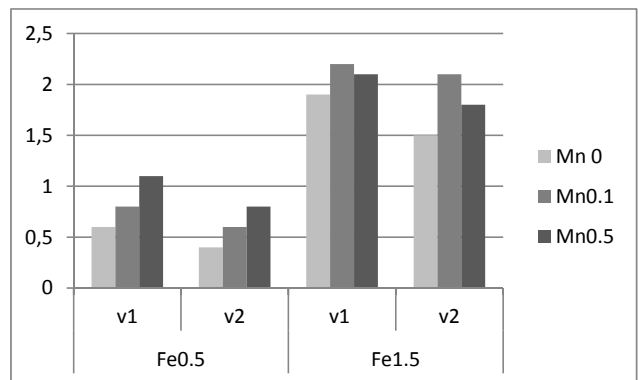
4.2. Results of the V_v estimation of the eutectic precipitates of the AlFeMnSi intermetallics

The evolution of the volume fraction and morphology of the eutectic intermetallics observed in the examined alloys (Fig. 8) can be explained by changes in the local preferences for α_c -AlFeMnSi, α_H -AlFeSi phase or β -AlFeSi phases induced by transition metals content, either summary (Fe + Mn) or ratio (Fe + Mn)/Si, and subsequent non-equilibrium modification of the chemical composition of the eutectic liquid by effects activated as alloy crystallization proceeded. Previously, it was stated empirically [23,26] that the influence of both metals Fe and Mn is similar. An increase in Fe or Mn concentration in 0.1 wt. % caused an increase in V_v of about 0.2%. In the hypo-eutectic AlFe0.5-1.5Si6 alloys examined in this work, volume fraction V_v of the β -AlFeSi phase (needles) increased fourfold with an increase in the Fe content from 0.5 to 1.5 wt. %, so the microstructural effect was more important.

Some specific microstructural phenomena might be ascribed to phase reactions occurring on the solidification path of the particular alloy.



a)



b)

Fig. 6. Volume fraction V_v of the intermetallics in polyphase eutectics as affected by cooling rate v ($v_1 = 0.05$ K/s and $v_2 = 31$ K/s) in the examined a) hypoeutectic alloys and b) eutectic alloys

Rys. 6. Objętość właściwa V_v faz międzymetalicznych w eutektyce wielofazowej w badanych stopach, wpływ szybkości chłodzenia v ($v_1 = 0,05$ K/s and $v_2 = 31$ K/s), a) stopy podeutektyczne oraz b) stopy eutektyczne

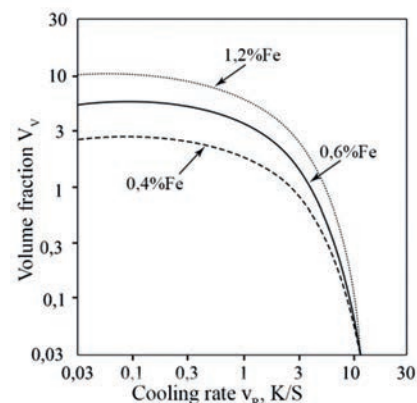


Fig. 7. Volume fraction V_v of the intermetallics in polyphase eutectics in cast AlFeMn0.3Si11 alloy as affected by Fe content and cooling rate [23]

Rys. 7. Objętość właściwa V_v faz międzymetalicznych w eutektyce wielofazowej w stopach AlFeMn0.3Si11, wpływ zawartości żelaza oraz szybkości chłodzenia [23]

Table 4. Volume fraction V_v of AlFeMnSi intermetallics estimated in cast AISi alloys

Tabela 4. Objętość właściwa faz V_v międzymetalicznych AlFeMnSi wyznaczona w odlewniczych stopach AISi

Alloy/Stop	Volume fraction V_v , % / Objętość właściwa faz V_v , %		Ref.
	Needles/Igły	Chinese script / Chińskie pismo	
AlSi Fe0.4Mn0.1		0.01	[22]
AlSiFe0.4Mn0.5		0.60	
AlSiFe1.2Mn.0.1		0.60	
AlSiFe1.2Mn0.5		1.88	
AlSi13Fe0.4	–	0.10	[23]
AlSi13Fe0.8	1.50	2.50	
AlSi13Fe1.2	4.50	2.20	
AlSi9Fe1,0Mn0.3	2.70	0.80	[19]
AlSi10-12Fe0.4Mn0.5	–	4.00	[24]
AlSi10-12Fe0.4Mn0.7		4.20	
AlSi7Fe0.7Mn0.5	0.87	3.25	[16]
AlSi6Fe0.5	3.30	–	[20]

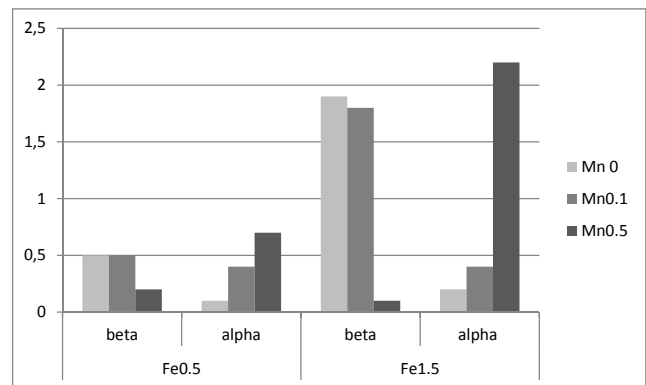
When α -Al dendrites started to grow, a step change appeared in the content of the Fe, Mn and Si in the residual liquid. Alloy components insoluble in the α -Al solid solution, i.e. Fe and Si, were gathering in the residual liquid consequently increasing its supersaturation.

In the hypo-eutectic AlFe0.5-1.5Mn0.1Si6 alloys, at the time of the eutectic reactions commencement, volume fraction V_v of the α -Al solid solution was equal to about 40% and then increased to 65% at the end of solidification. However, because of the difference in the Fe and Si solubility limits in the α -Al solid solution, the relative supersaturation with Fe and impoverishment in Si have taken place in the residual liquid. Thus, the Fe/Si value relatively increased which made Ω parameter in the residual liquid more favourable for α_H -AlFeSi and/or α_c -AlFeMnSi phases.

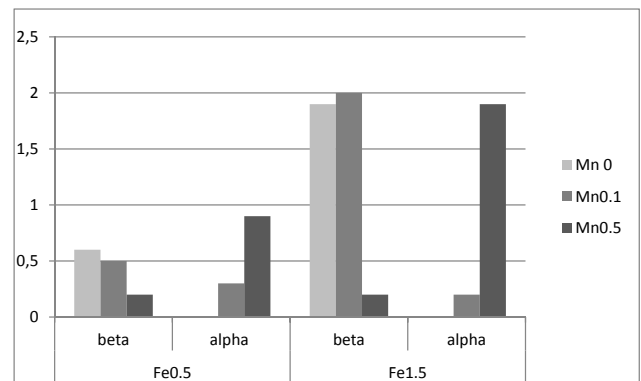
In the examined eutectic AlFe0.5-1.5Mn0.1Si11 alloys, the eutectic started to solidify in liquid of almost equilibrium composition. At the start of eutectic reactions, the V_v of the α -Al solid solution has achieved a value equal to about 10%.

The increase in value of Fe/Si in the eutectic alloys also may occur because of the Si partition coefficient increase, but the non-equilibrium preference for the α_H -AlFeSi phase was not revealed. The volume fraction of the precipitates in the shape of Chinese script in this group of alloys was less than that in the hypo-eutectic alloys, and particles in this shape have appeared in the presence of 0.1 wt. % Mn, while in hypo-eutectic alloys traces of Chinese script were evident already in manganese free alloys.

In alloys containing Mn 0.5 wt. %, the competition between two phases of α_H -AlFeSi and α_c -AlFeMnSi, both in the shape of Chinese script and β -AlFeSi phase in the shape of needles was observed and then analysed.



a)



b)

Fig. 8. Volume fraction V_v of the particular intermetallics (alpha – Chinese script, beta – needles) in polyphase eutectics as affected by examined alloy composition; a) hypoeutectic alloys and b) eutectic alloys

Rys. 8. Objętość właściwa V_v faz międzymetalicznych (alfa – chińskie pismo, beta – igły) w eutektyce wielofazowej w zależności od składu chemicznego stopu; a) stopy podeutektyczne oraz b) stopy eutektyczne

The larger volume fraction of the Chinese script in the eutectic alloys containing 0.5 wt. % Mn than that in the hypo-eutectic alloys was explained by the preference for α_c -AlFeMnSi phase induced by Fe/Mn value decrease.

Solubility of Mn in α -Al solid solution at eutectic temperature is quite large, thus some number of Mn atoms have been incorporated into the α -Al dendrites. In the hypo-eutectic AlSi6 alloys, because of the limited efficiency of the Mn back diffusion, Mn atoms remained in the α -Al solid solution during cooling of the alloy. Thus, an actual Fe/Mn value in the interdendritic liquid was greater than that equilibrium. This relative increase in Fe/Mn value resulted from non-equilibrium Mn microsegregation has worsened the local conditions for α_c -AlFeMnSi phase formation in the hypo-eutectic AlSi6 alloys.

In the AlFeMnSi11 alloys at eutectic temperature, Mn content in the liquid solidifying was almost the same as in the whole alloy volume on average because it was not previously gathered in the solid α -Al. Thus, Fe/Mn value in the solidifying liquid was less than that in AlSi6 alloys of the same Fe and Mn contents. Additionally, contrary to Fe and Si, Mn partition coefficient k^{Mn} depends on the actual temperature. In a temperature range of 600–570°C, the value of k^{Mn} , is reduced from 0.32 to 0.22. It means that Mn concentration gradient in the liquid alloy gradually increased and the Fe/Mn value decreased. It has promoted the α_c -AlFeMnSi phase formation as well.

Thus, the preferences for α_c -AlFeMnSi phase in polyphase eutectics α -Al + Si + AlFeMnSi observed in the AlSi11FeMn alloys resulted from local composition of the liquid at the Solid/Liquid interface, relatively enriched in Mn and relatively depleted in Si.

5. Summary conclusions

The conclusions based on the results obtained in this work, concern microstructure image analysis procedure and microstructure effects of morphology evolution of the polyphase eutectics phase constituents:

1. The modified procedure of quantitative analysis of the microstructure images was applied for description of the phase composition in polyphase eutectics in the AlSi casting alloys. The proposed idea of morphological classification of phase components was recognized as useful in revealing and analysing AlFeMnSi intermetallics in particular.
2. It was shown that the manual detection threshold allowed for the satisfactory repeatability, but with quite a large dispersion of the results. The automatic classifiers of local morphological forms of the microstructure constituents should be the subject of further works.
3. In a concentration range: Fe 0.5–1.5 wt. % and Mn 0–0.5 wt. %, the total V_v of the eutectic intermetallics increased with an increase in the total content of the transition metals. As the intermetallics of binary and ternary eutectics were analysed together, this increase resulted mainly from the appearance of the binary eutectic on the solidification path (Fe wt. 1.5%, Mn wt. 0.5%). In alloys with a small content of Mn (0–0.1 wt. %) the final result of the competition α_H -AlFeSi and β -AlFeSi was affected by the actual value of the Fe/Si ratio in the solidifying liquid. With an increase in the (Fe)/Si value, preference for α_H -AlFeSi phase appeared. In the alloys containing 0.5 wt. % Mn an increase in the (Fe + Mn)/Si value promoted the α_c -AlFeMnSi phase formation.
4. In the hypo-eutectic alloys in a concentration range: Fe 0.5–1.5 wt. % and Mn 0–0.1 wt. %, due to an increase in the value of the coefficient Fe/Si, the competition β -AlFeSi vs α_H -AlFeSi appeared and developed in the interdendritic eutectics. The preference for the α_H -AlFeSi in the shape of Chinese script was revealed as the estimated volume fraction of this phase in the hypo-eutectic alloys was higher than that in the eutectic: $V_v^{Al6} > V_v^{Al11}$.
5. In the eutectic AlSi11 alloys in a concentration range: Fe 0.5–1.5 wt. % and Mn 0.5 wt. %, the total V_v of the eutectic intermetallics was greater than that in the hypo-eutectic AlSi6 alloys, especially due to the enhanced preference for α_c -AlFeMnSi phase formation.
6. A different impact of both transition metals Fe and Mn on V_v of intermetallics formed in the eutectics was revealed. The increase of the Mn content in a range of 0–0.5 wt. % only slightly influenced the total V_v , while, the Fe addition induced a strong increase in the total V_v of the AlFeMnSi intermetallics. In a range of 0.5–1.5 wt. % Fe, V_v increased twofold.

Acknowledgments

This work was realized with the financial support of FRI under projects No. 4007/00 (2014) and No. 5008/00 (2015).

References

1. Du Y., Y.A. Chang, Shuhong Liu, Baiyun Huang, F.-Y. Xie, Ying Yang, S.-L. Chen. 2005. "Thermodynamic description of the Al-Fe-Mg-Mn-Si system and investigation of microstructure and microsegregation during

- directional solidification of an Al-Fe-Mg-Mn-Si alloy". *Zeitschrift für Metallkunde* 96 (12) : 1351–1362.
2. Belov, N.A., D.M. Eskin, A.A. Aksenov. 2005. *Multicomponent phase diagrams: applications for commercial aluminium alloys*. Elsevier.
 3. Liu Z.K., Y.A. Chang. 1999. "Thermodynamic assessment of the Al-Fe-Si system". *Metallurgical and Materials Transactions A* 30 (4) : 1081–1098.
 4. Tamminen J. 1988. *Thermal analysis for investigation of solidification mechanism in metals and alloys*. *Chemical Communications*, No. 2. University of Stockholm.
 5. Warmuzek M., Z. Lech, G. Sęk-Sas. 2002. „Ewolucja mikrostrukturalna w obecności metali przejściowych (Fe, Mn, Cr) w stopach Al-Si". *Biuletyn Instytutu Odlewnictwa* 4 (6) : 4–11.
 6. Warmuzek M. 2014. "Analysis of the chemical composition of AlMnFe and AlFeMnSi intermetallic phases in the interdendritic eutectics in the Al alloys". *Prace Instytutu Odlewnictwa* 54 (1) : 3–12.
 7. Perepezko J.H., D.R. Allen. 1996. "Kinetic Competition in Undercooled Liquid Alloys". *Materials Research Society Proceedings* 398 : 1–12.
 8. Malakhov D.V., D. Pnahi, M. Gallernaut. 2010. "On the formation of intermetallics in the rapidly solidifying Al-Fe-Si alloys". *Calphad*, 34 (2) : 159–166.
 9. Dons A.L. 1991. "Simulation of solidification – a short cut to a better phase diagram for Al-Mg-Fe-Si alloys". *Zeitschrift für Metallkunde* 52 : 684–688.
 10. Dons A.L. 1985. "AlFeSi particles in industrial cast aluminium alloys". *Zeitschrift für Metallkunde* 76 : 609–612.
 11. Igléssis J., C. Frantz, M. Gantois. 1977. «Conditions de formation des phases fer dans les alliages Aluminium – Silicium de pureté commerciale». *Mémoires Scientifiques de la Revue de Métallurgie* 74 (4) : 237–242.
 12. Igléssis J., C. Frantz, M. Gantois. 1978. «La croissance par propagation de plans de macles des composés eutectiques dans le système Al-Fe-Si». *Mémoires Scientifiques de la Revue de Métallurgie* 75 : 93–100.
 13. Yang Bing Jiang, D.M. Stefanescu, J. Leon-Torres. 2001. "Modeling of microstructural evolution with tracking of equiaxed grain movement for multicomponent Al-Si Alloy". *Metallurgical and Materials Transactions A* 32 (12) : 3065–3076.
 14. Lee S., B. Kim, S. Lee. 2011. "Prediction of solidification paths in Al-Fe-Si ternary system and experimental verification: Part I: Fe containing hypoeutectic Al-Si alloys". *Materials Transactions* 52 (6) : 1053–1062.
 15. Gorny A., J. Manickaraj, Z. Cai, S. Shankar. 2013. "Evolution Fe based intermetallic phases, in Al-Si hypoeutectic casting alloys. Influence of the Si and Fe concentrations, and solidification rate". *Journal of Alloys and Compounds* 577 : 103–124.
 16. Belmares-Perales S., M. Castro-Román, M. Herrera-Trejo, L.E. Ramírez-Vidaurri. 2008. "Effect of cooling rate and Fe/Mn weight ratio on volume fractions of α -AlFeSi and β -AlFeSi phases in Al-7.3Si-3.5Cu alloy". *METALS AND MATERIALS International*, 14 (3) : 307–414.
 17. Belmares-Perales S., A.A. Zaldivar-Cadena. 2010. "Addition of iron for removal of the β -AlFeSi intermetallic by refining of α -AlFeSi phase in an Al-7.5Si-3.6Cu alloy". *Materials Science and Engineering B* 174 (1–3) : 191–195.
 18. Kim H.Y., T.Y. Park, S.W. Han, H.M. Lee. 2006. "Effects of Mn on the crystal structure of α -Al(Mn,Fe)Si particles in 356 alloys". *Journal of Crystal Growth* 291 (1) : 207–211.
 19. Reza Ghomashchi M. 1987. "Intermetallic compounds in an Al-Si alloy used in high pressure die-casting". *Zeitschrift für Metallkunde* 79 : 784–787.
 20. Khalifa W., F.H. Samuel, J.E. Gruzleski. 2003. "Iron intermetallic phases in the Al corner of the Al-Fe-Si system". *Metallurgical and Materials Transactions A* 34 (3) : 807–825.
 21. Lee S., B. Kim, S. Lee. 2011. "Prediction of solidification paths in Al-Si-Fe ternary system and experimental verification: Part II. Fe containing eutectic Al-Si alloys". *Materials Transactions* 52 (6) : 1308–1315.
 22. Shabestari S.G. 2004. "The effect of iron and manganese on the formation of intermetallic compounds in aluminum–silicon alloys". *Materials Science and Engineering A*, 383 (2) : 289–298.
 23. Shabestari S.G., Gruzleski J.E. 1994. "The effect of solidification condition and chemistry on the formation and morphology of complex intermetallic compounds in aluminium–silicon alloys". *Cast Metals* 6 : 217–224.
 24. Ma Z., E. Samuel, A.M.A. Mohamed, A.M. Samuel, F.H. Samuel, H.W. Doty. 2010. "Parameters controlling the microstructure of Al-11Si-2.5Cu-Mg alloys". *Materials and Design* 31 (2) : 902–912.
 25. Cao X., J. Campbell. 2004. "The solidification characteristics of Fe-rich intermetallics in Al-11.5Si-0.4Mg cast alloys". *Metallurgical and Materials Transactions A* 35 : 1425–1435.
 26. Abou Khatwa M.K., D.V. Malakhov. 2006. "On the thermodynamic stability of intermetallic phases in the AA6111 aluminium alloy". *Computer Coupling of Phase Diagrams and Thermochemistry Calphad* 30 (2) : 159–170.
 27. Zakharov A.M., I.T. Gulcyn, A.A. Arnold, J.A. Macenko. 1998. „Fazovyje ravnovesia v systemie Al-Si-Fe-Mn w intervale koncentracji 10-14%Si, 0-3%Fe i 0-4%Mn". *Izv. VUZ., Cvetn. Met.* (4) : 89–94.
 28. Zakharov A.M., I.T. Gulcyn, A.A. Arnold, J.A. Macenko. 1989. „Secenia izotermiceskich tetraedrov sistemy Al-Si-Fe-Mn pri 10-14%Si, (do 3%Fe i 4%Mn)". *Izv. VUZ., Cvetn. Met.* (4) : 78–81.
 29. Tibballs J.E., L.A. Horst, C.J. Simensen. 2001. "Precipitation of α -Al(Fe,Mn)Si from the melt". *Journal of Materials Science* 36 : 937–941.
 30. Flores-Valdes A., M. Sukiennik, A.H. Castillejos-E., F.A. Acosta-G., J.C. Escobedo-B. 1998. "A kinetic study on the nucleation and growth of Al₈FeMnSi₂ intermetallic compound for aluminum scrap purification". *Intermetallics* 6 (3) : 217–227.

31. Flores-Valdés A., M. Sukiennik, A.H. Castillejos-Esco-bar, M. Méndez-Nonell, F.A. Acosta-González. 1996. "Experimental determination of the standard formation functions of AlFeMnSi intermetallic phase". *Archives of Metallurgy* 41 : 293–309.
32. Volk W. *Statystyka stosowana dla inżynierów*. 1973. Warszawa: Wydawnictwa Naukowo-Techniczne.
33. Aziz M.J. 1982. "Model for solute redistribution during rapid solidification". *Journal of Applied Physics* 53 (2) : 1158–1168.