

DOI: 10.1515/amm-2017-0254

M. WARMUZEK*#

PRIMARY CRYSTALS OF AlFeMnSi INTERMETALLICS IN THE CAST AlSi ALLOYS

In this paper the results of the microscopic observations of the intermetallic AlFeMnSi phases crystals formed in the liquid hypo- and eutectic AlSi alloys containing transition metals 3.0 wt.% Fe and 0.1, 0.5 and 2.0 wt.% Mn were presented. The crystals morphology has been revealed on both polished and deep etched microsections. The different stages of the primary AlFeMnSi phases particles formation in the solidifying alloy and their final morphology were shown as influenced by cooling rate and alloy chemical composition.

Keywords: aluminum alloys, intermetallic, solidification, microstructure

1. Introduction

Crystals of the AlFeMnSi intermetallics are common constituents of the technical aluminum alloys microstructure, both wrought and cast [1,2]. They arise in the polyphase eutectics in a typical shape of the Chinese script. However, in some range of the chemical composition, the massive particles of the AlFeMnSi phases form directly in the liquid alloy through incongruent solidification, before α -Al solid solution crystallization begins [2-7] (Fig. 1). The long range ordering present in the crystal lattice of the intermetallic phase requires an important reconstruction of atoms configuration compared to that present previously in the liquid alloy [8]. Thus, actual morphology of AlFeMnSi pre-

cipitate formed at finite cooling rate is a result of competition between factors: internal (determined by crystal lattice ordering) and external (determined by crystal growth rate).

Usually, in slowly cooled alloys, faceted polyhedra of the α_c -AlFeMnSi phase take the habit specific for the Wulff assumptions [11]. Some examples of the morphology evolution of the ordered crystals precipitated directly from the liquid alloy were presented by Gao Tong [12] for intermetallic phase α_c -AlFeMnSi, by Li [13] for magnesium silicide Mg_2Si , and by Liu [14] for titanium nitride TiN. In the technical aluminum alloys containing transition metals, quickly cooled, especially when sludge factor SF exceeds 1 ($SF = \%Fe + 2\%Mn + 3\%Cr$), either dendrite- or star-shaped particles of the quaternary α_c -AlFeMnSi phase

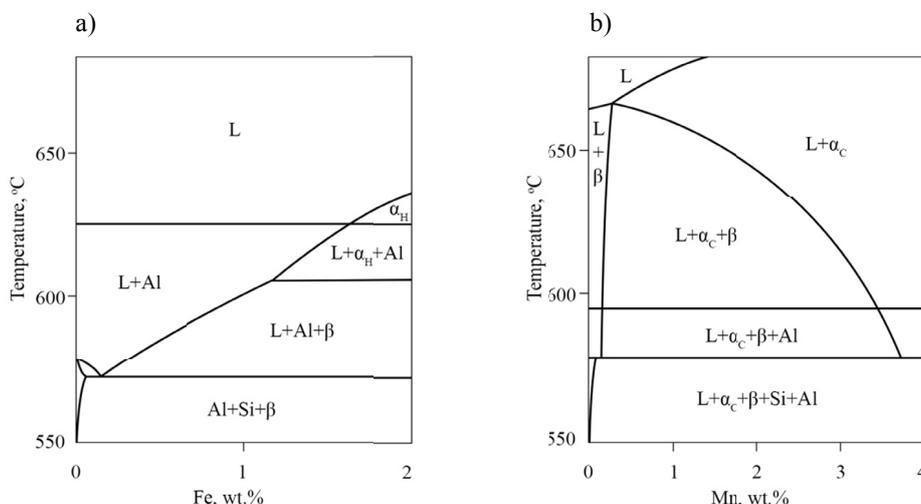


Fig. 1. Primary precipitation area of the β -AlFeSi (β), α_H -AlFeSi (α_H) and α_c -AlFeMnSi (α_c) intermetallic phases: isopleths in alloys: ternary Al-Fe-Si5 [9] (a) and quaternary Al-Fe3-Mn-Si10 [10] (b)

* FOUNDRY RESEARCH INSTITUTE, 73 ZAKOPIAŃSKA STR., 30-418 KRAKÓW, POLAND

Corresponding author: malgorzata.warmuzek@iod.krakow.pl

were also observed [4,5,15]. Nevertheless, change of shape of the AlFeMnSi primary precipitates from polyhedra to dendrites seems to be influenced not only by actual cooling rate but also by transition metals content, especially by Fe/Mn ratio [2-5].

In this work, a common effect of the Fe/Mn ratio and the cooling rate on shape and crystal structure of the primary AlFeMnSi intermetallic phases will be considered in both hypo- and eutectic AlFeMnSi alloys in a range of concentration of transition metals examined before in slowly cooled alloys in works [2,3,6,7].

2. Materials and methods

Materials for examinations were two groups of the Al-FeMnSi alloys hypoeutectic (6 wt.%Si) and eutectic (11.5 wt.%Si), each of them containing 3.0 wt.% Fe and 0.1, 0.5 and 2.0 wt.% Mn. The microstructure constituents morphology was observed in the specimens after either slow (5°C/min) or quick (116°C/min) cooling to temperature 20°C and in those held in the solid-liquid state at chosen temperature T_L (where:

T_L -alloy liquidus), and then quenched in the cold water. The alloys were quenched from the solid-liquid state after held at 665°C, 695°C and 730°C.

Microstructure observations were carried out by means of microscopes: Axioobserver Zm1 (LM) on the metallographic cross-sections prepared in the standard way, etched with reagent 1%HF in distilled water and Stereoscan 420 (SEM) on the deep etched cross sections. Phase precipitates identification was carried out by means of SAED method, using TEM Philips CM20 microscope.

3. Results and discussion

3.1. Morphology of the primary crystals of the AlFeMnSi intermetallic phases

In the examined alloys, both hypo- and eutectic, first nuclei of the AlFeMnSi intermetallics were formed before others microstructure constituents, either α -Al solid solution dendrites or (α -Al + Si) eutectic, started to grow (Fig. 2a). They have

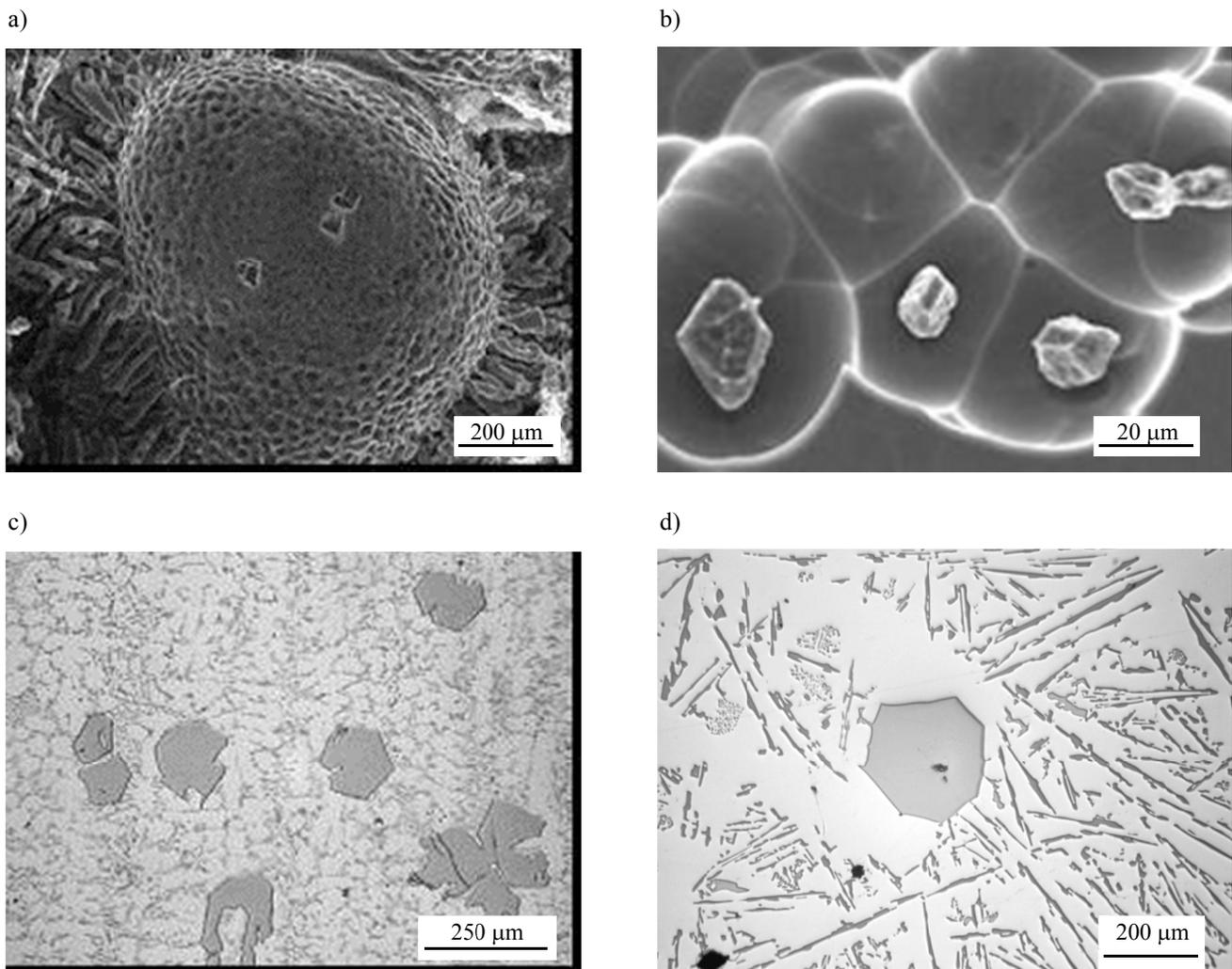


Fig. 2. The α_c -AlFeMnSi phase precipitates at subsequent stages of crystallization in the AlFe3Mn2Si11.5 alloy; nuclei frozen at α -Al dendrite surface at 730°C, SEM (a), faceted polyhedra at first stage of growth, specimen frozen at 730°C, SEM (b), polyhedra developed in the liquid alloy after held at 730°C/6h, then frozen, LM (c), and in the specimen cooled slowly (5°C/min) from the liquid state to 20°C, LM (d)

taken a shape of the faceted polyhedra, as it is visible in the AlFe₃Mn₂Si_{11.5} alloy (Fig. 2b), that developed over time of specimen holding at a temperature 730°C in the different geometric forms (Fig. 2c). Afterwards, after slow cooling to room temperature, the AlFeMnSi intermetallics have taken a shape of the large faceted particles (Fig. 2d).

Faceted octahedra formed in the AlFe₃Mn₂Si₆ alloy (Fig. 3a) were similar to those of the Si₃, formed in the hyper-eutectic AlSi alloys [16,17]. It might be assumed that they were limited with close packed {111} planes, typical for the many others cubic crystals. However, different geometric forms were also observed: deformed octahedron connected with cube (Fig. 3b, AlFe₃Mn₂Si₆ alloy), dodecahedron (Fig. 3c, AlFe₃Mn₂Si_{11.5} alloy) or hexadecahedron (Fig. 3d, AlFe₃Mn₂Si_{11.5} alloy), similar to those presented in works [6,12]. Observed derogation from the regular shape can be explained by local fluctuations in both concentration and temperature fields at solid-liquid interface during crystal growth from the liquid alloy.

3.2. Evolution of the AlFeMnSi intermetallics morphology as affected by Mn content in alloy

Chemical composition of AlFeMnSi alloy, especially Mn content has an important impact on a final effect of microstructure evolution: intermetallic AlFeMnSi phases crystal lattice and morphology of their primary particles [2-5,15]. In this work, it was noticed that in the AlFe₃Mn_{0.1}Si₆ alloy, quickly cooled and frozen at 695°C, the dendrites of the α_c -AlFeMnSi phase replaced the polyhedra of the α_H -AlFeSi phase, equilibrium in ternary Al-FeSi system, precipitated previously at low cooling rate (Fig. 4). Critical Mn concentration in the AlFeMnSi alloy, necessary to make the cubic α_c -AlFeMnSi phase of stable phase constituent and to replace an equilibrium hexagonal α_H -AlFeSi phase was reported by Munson as equal to 0.3 wt.% [18]. In this work it was stated that in the AlFe₃Mn_{0.5}Si₆ alloy increase in the Mn concentration to 0.5 wt% can bring an effect such as a crystallization of the α_c -AlFeMnSi phase polyhedra also during slow cooling. It means that addition of 0.1wt.% Mn was insufficient for cubic structure stabilization in slowly cooled AlFe₃Mn_{0.1}Si₆ alloy and α_c -AlFeMnSi phase was still its metastable micro-

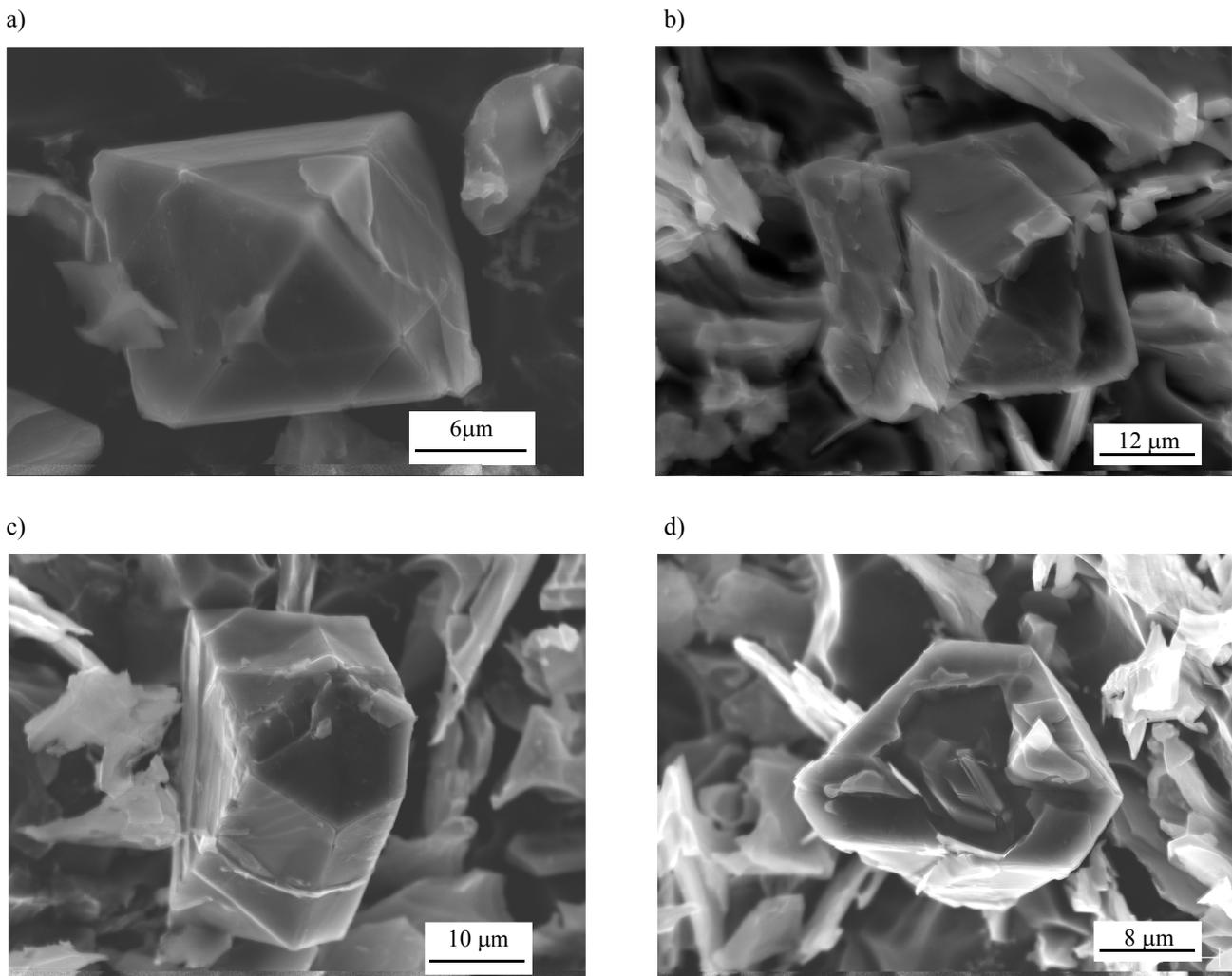


Fig. 3. Primary precipitates shape of the α_c -AlFeMnSi phase as affected by instability in the local kinetics of growth at solid/liquid interface, slow cooling (5°C/min) from liquid state to 20°C, SEM; equilibrium octahedron, AlFe₃Mn₂Si₆, (a), octahedron with cube, AlFe₃Mn₂Si₆ (b), dodecahedron, AlFe₃Mn₂Si_{11.5} (c) and deformed hexadecahedron, AlFe₃Mn₂Si_{11.5} (d)

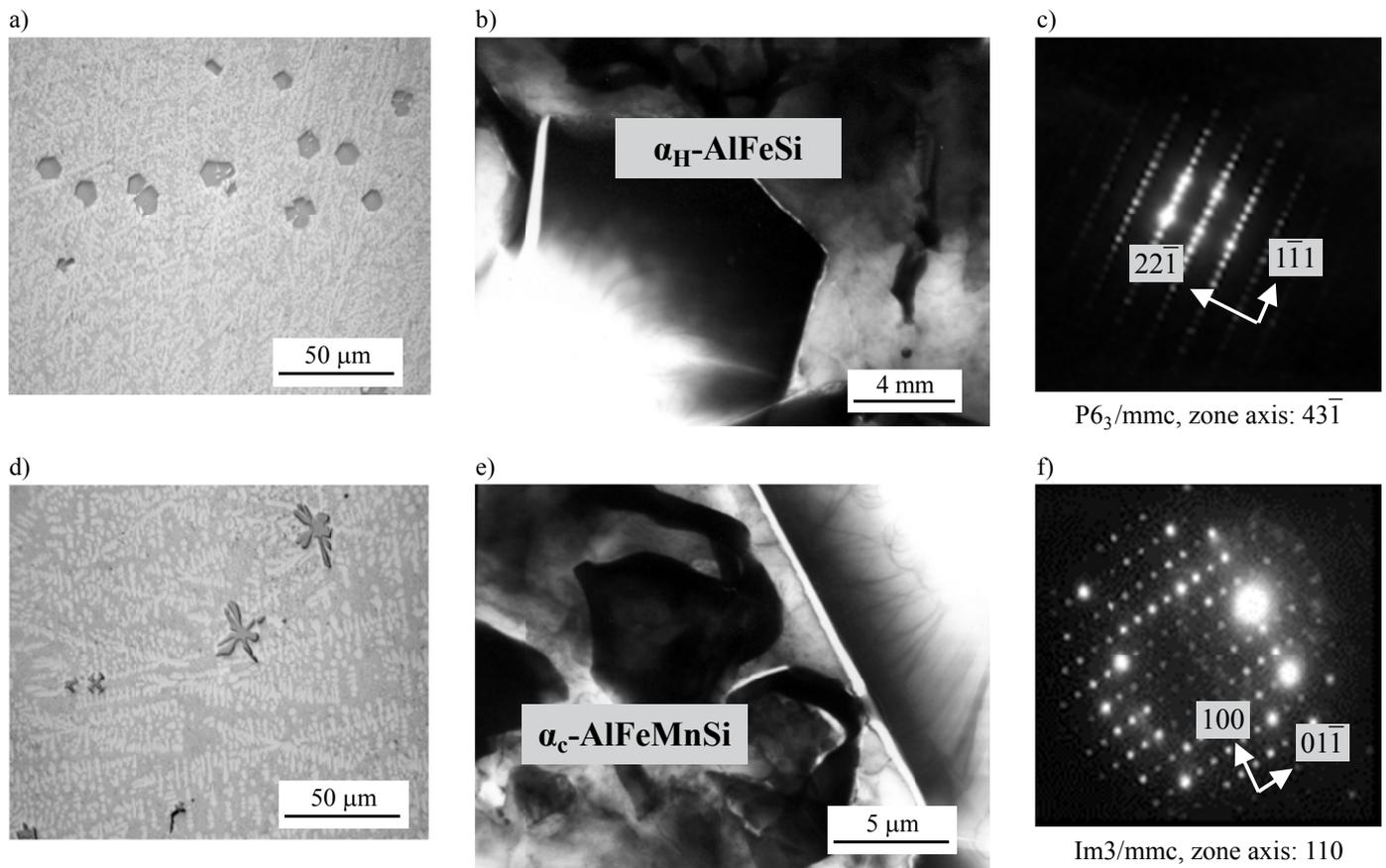


Fig. 4. Primary precipitates of the intermetallic phases, AlFe₃Mn_{0.1} Si₆ alloy; α_{H} -AlFeSi phase, slow cooling from liquid state, quenching at 695°C, LM (a), TEM (b) [6], SAE diffraction pattern (c) [6], α_{c} -AlFeMnSi phase, quick cooling from liquid state, quenching at 695°C, LM (d), TEM (e), SAE diffraction pattern (f)

structure constituent. Similar effects were noticed in the hypoeutectic AlFeMnSi alloys examined previously in the work of Tibbals [3]. Essential effect of Mn content on stabilization of the α_{c} -AlFeMnSi phase in the AlFeMnSi alloys was reported by Huang [19]. He noticed that morphology and phase evolution from polyhedra (δ -AlFeSi) to dendrites (α_{c} -AlFeMnSi) resulting from cooling rate increase, might be enhanced by simultaneous Mn addition (in a range of Fe/Mn = 1 \rightarrow 0.5).

3.3. Evolution of the AlFeMnSi intermetallics morphology as affected by cooling rate

As the results obtained in this work show, an increase in the cooling rate has resulted in the change of the shape of the primary precipitates of the AlFeMnSi intermetallic phases formed in the examined alloys. An example of this evolution results observed in the AlFe₃Mn₂Si_{11.5} alloy is present in Fig. 5. An increase in cooling rate from 5 to 116°C/min caused change of the primary particles shape of the α_{c} -AlFeMnSi phase from faceted polyhedra (Fig. 3c,d) to dendrites (Fig. 5). Similar morphology of the AlFeMnSi intermetallics was frequently described in numerous technical Al-Si alloys, e.g. in works [4,5,15]. Nevertheless, observed evolution of the morphology probably does not result directly from simultaneous change in the growth mechanism.

Interface seemed to be rough when the whole particle is observed at rather low magnification (Fig. 5a,c,d, LM), while observations carried out at higher magnification revealed on a local scale the small facets (Fig. 5b, SEM). The observed crystal surface has been considered as consisting of numerous faceted terraces defined by chosen crystallographic planes, similarly to those reported for Si, while their walls vertical had not any specific orientation. At high cooling rate, more developed, rough solid/liquid interface seemed to be more advantageous to join the new atoms to the crystal of the α_{c} -AlFeMnSi phase. This morphological phenomenon, might be explained by general assumptions of Perpendicular Macroscopic Growth theory, describing evolution of the eutectic silicon crystals morphology, subjected to chemical modification [20].

4. Conclusions

1. Addition of 0.1wt.% Mn was recognized as sufficient for crystallization of the α_{c} -AlFeMnSi phase in the quickly cooled AlFe₃MnSi₆ alloy, while addition at least 0.5% wt. Mn was necessary to replace the hexagonal α_{H} -AlFeSi phase by the cubic α_{c} -AlFeMnSi phase in the slowly cooled alloy.
2. The primary crystals of both α_{H} -AlFeSi and α_{c} -AlFeMnSi phases formed in the slowly cooled liquid AlFeMnSi alloys

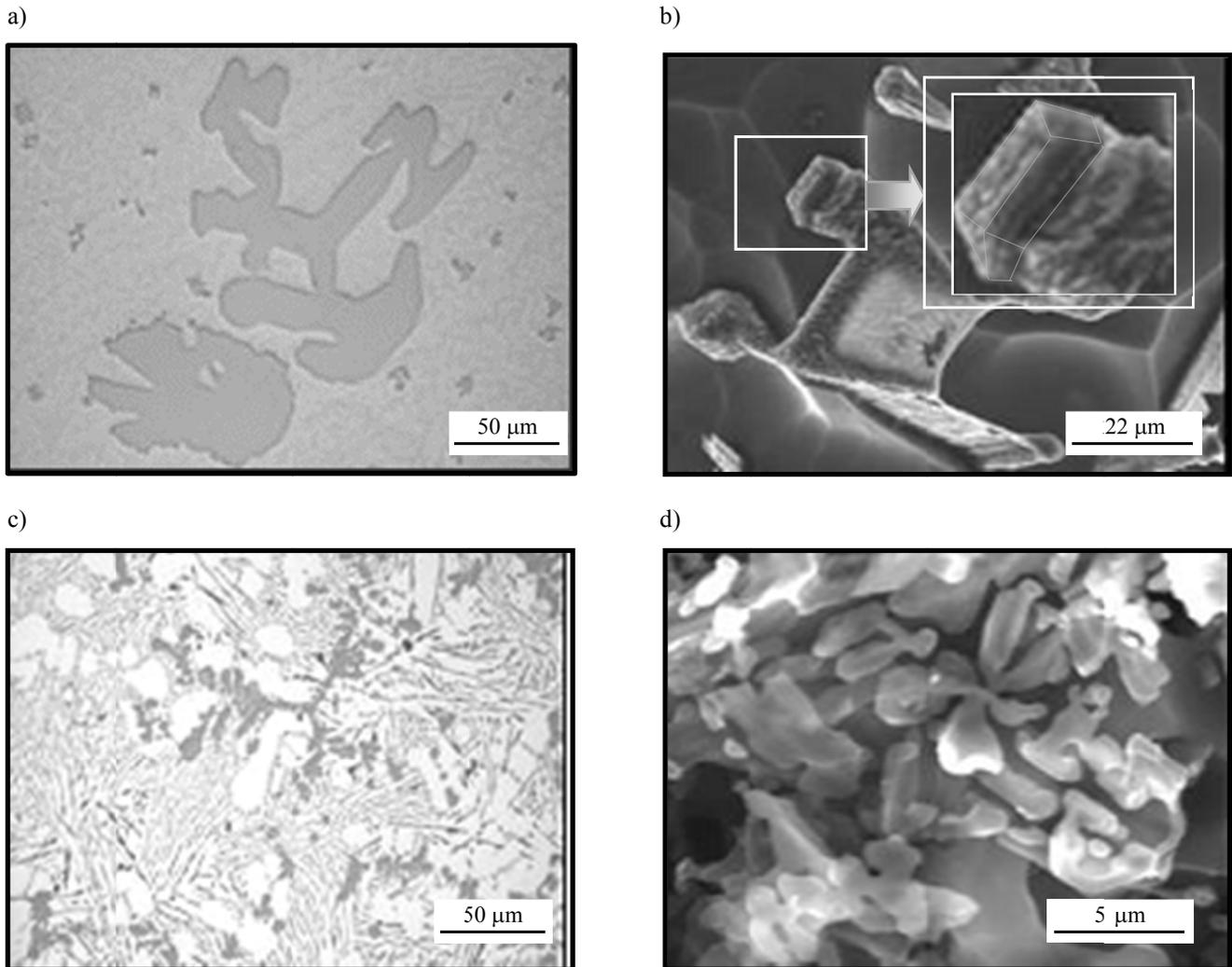


Fig. 5. Primary precipitates of the α_c -AlFeMnSi phase in the shape of dendrite, AlFe3Mn2Si11.5; quick cooling (5°C/min) from liquid state to 665°C, held by 2 h and then quenching, LM (a), SEM (b), quick cooling (116°C/min) from liquid state to 20°C, LM (c), SEM (d)

have taken a shape of the faceted polyhedra, of habit subordinated to the local preferences for the crystallographic planes growth.

- The precipitates in a shape of dendrites formed in the quickly cooled alloys can be considered as the effect of change of the growth front morphology. With an increase in the cooling rate, the AlFeMnSi crystals interface becomes rough on a macroscopic scale. This change of the interface morphology facilitates to create more sites suitable to atom built into the crystal. The tendency to change of the interface morphology was observed stronger for α_c -AlFeMnSi phase precipitates than that for the α_H -AlFeSi phase. This effect should be confirmed in more detailed study.

Acknowledgments

This work was carried out with a financial support of the Polish Ministry of Science and Higher Education under grant nr TO8B 032 17. Author wishes to thank Prof. J. Morgiel from IMIM PAN in Kraków for support in SAED analysis in TEM.

REFERENCES

- [1] M. Warmuzek, A. Gazda, *J. An. At. Spectrom.* **14**, 422-8 (1999).
- [2] M. Warmuzek, W. Ratuszek, G. Sęk-Sas, *Mater. Charact.* **54**, 31-40 (2004).
- [3] J.E. Tibballs, L.A. Horst, C.J. Simensen, *J. Mater. Sci.* **36**, 937-41 (2002).
- [4] S.G. Shabestari, J.E. Gruzleski, *Met. and Mat. Trans. A* **26A**, 999-1006 (1995).
- [5] D.A. Granger, *AFS Trans.* **99**, 379-383 (1991).
- [6] M. Warmuzek, *Trans. of the Foundry Research Institute* **55**, 51-60 (2015).
- [7] B. Onderka, M. Sukiennik, K. Fitzner, *Arch. Metall.* **45**, 119-132 (2000).
- [8] K.A. Jackson, *Interface Science* **10**, 159-69 (2002).
- [9] N.A. Belov, D.M. Eskin, A.A. Aksenov, *Multicomponent phase diagrams: applications for commercial aluminum alloys*, Elsevier, Oxford 2005.
- [10] E. Balitchev, T. Jantzen, I. Hurtado, D. Neuschütz, *Computer Coupling of Phase Diagrams and Thermochemistry* **27**, 275-8 (2003).

- [11] I. Sunagawa, *Forma, Review*. **14**, 149-166 (1999).
- [12] T. Gao, Y. Wu, Ch. Li, X. Liu, *Mater. Let.* **110**, 191-4 (2013).
- [13] C. Li, Y. Wu, H. Li, X. Liu, *Acta Mater.* **59**, 1058-67 (2011).
- [14] G. Liu, K. Chen, H. Zhou, J. Tian, C. Pereira, J.F. Ferreira, *Crystal Growth & Design*. **6**, 2404-11 (2006).
- [15] S.G. Shabestari, *Mater. Sci. Eng. A* **383A**, 289-98 (2004).
- [16] H. Singh, A.M. Gokhale, A. Tewari, S. Zhanga, Y. Maoa, *Scripta Mater.* **61**, 441-4 (2009).
- [17] C.L. Xu, H.Y. Wang, C. Liu C, Q.C. Jiang, *J. Crystal Growth* **29**, 540-7 (2006).
- [18] D.J. Munson, *J. Inst. Metals*. **95**, 217-9 (1967).
- [19] H.J. Huang, Y.H. Cai, H. Cui, J.F. Huang, J.P. He, J.S. Zhang, *Mater. Sci. Eng. A*. **502**, 118-25 (2009).
- [20] J.M. Dowling, J.M. Corbet, W. Kerr, *J. Mater. Sci.* **22**, 4504-13 (1987).