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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 precipitate 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 αc-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 αc-AlFeMnSi, by Li [13] for magnesium silicide Mg2Si, 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 αc-AlFeMnSi phase

Fig. 1. Primary precipitation area of the β-AlFeSi (β), αh-AlFeSi (αh) and αc-AlFeMnSi (αc) intermetallic phases: isopleths in alloys: ternary Al-Fe-Si5 [9] (a) and quaternary Al-Fe3-Mn-Si10 [10] (b)
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 below of TL (where:
TL-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 car-
rried 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 nu-
clei 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-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 AlFe3Mn2Si11.5 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 Si, formed in the hypereutectic 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, AlFe3Mn2Si11.5 alloy) or hexadecahedron (Fig. 3d, AlFe3Mn2Si11.5 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 AlFe3Mn0.1Si6 alloy, quickly cooled and frozen at 695°C, the dendrites of the $\alpha_c$-AlFeMnSi phase replaced the polyhedra of the $\alpha_{eq}$-AlFeSi phase, equilibrium in ternary Al-Fe-Si system, precipitated previously at low cooling rate (Fig. 4). Critical Mn concentration in the AlFeMnSi alloy, necessary to make the cubic $\alpha_c$-AlFeMnSi phase of stable phase constituent and to replace an equilibrium hexagonal $\alpha_{eq}$-AlFeSi phase was reported by Munson as equal to 0.3 wt.% [18]. In this work it was stated that in the AlFe3Mn0.5Si6 alloy increase in the Mn concentration to 0.5 wt% can bring an effect such as a crystallization of the $\alpha_c$-AlFeMnSi phase polyhedra also during slow cooling. It means that addition of 0.1wt.% Mn was insufficient for cubic structure stabilization in slowly cooled AlFe3Mn0.1Si6 alloy and $\alpha_c$-AlFeMnSi phase was still its metastable micro-

![Fig. 3. Primary precipitates shape of the $\alpha_c$-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, AlFe3Mn2Si11.5 (c) and deformed hexadecahedron, AlFe3Mn2Si11.5 (d)](image-url)
structure constituent. Similar effects were noticed in the hypo-eutectic AlFeMnSi alloys examined previously in the work of Tibbals [3]. Essential effect of Mn content on stabilization of the $\alpha_{c}$-AlFeMnSi phase in the AlFeMnSi alloys was reported by Huang [19]. He noticed that morphology and phase evolution from polyhedra ($\delta$-AlFeSi) to dendrites ($\alpha_{c}$-AlFeMnSi) resulting from cooling rate increase, might be enhanced by simultaneous Mn addition (in a range of Fe/Mn = 1 → 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 AlFe3Mn0.1Si6 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 $\alpha_{c}$-AlFeMnSi to dendrites ($\alpha_{c}$-AlFeMnSi) resulting from cooling rate increase, might be enhanced by simultaneous Mn addition (in a range of Fe/Mn = 1 → 0.5).

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 $\alpha_{c}$-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 $\alpha_{c}$-AlFeMnSi phase in the quickly cooled AlFe3MnSi6 alloy, while addition at least 0.5% wt. Mn was necessary to replace the hexagonal $\alpha_{h}$-AlFeSi phase by the cubic $\alpha_{c}$-AlFeMnSi phase in the slowly cooled alloy.
2. The primary crystals of both $\alpha_{h}$-AlFeSi and $\alpha_{c}$-AlFeMnSi phases formed in the slowly cooled liquid AlFeMnSi alloys...
Fig. 5. Primary precipitates of the αc-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.

3. 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 αc-AlFeMnSi phase precipitates than that for the αH-AlFeSi phase. This effect should be confirmed in more detailed study.

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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, 33-40 (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. Neuschutz, 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).