Effects of Mg addition on the $Al_6(Fe,Mn)$ intermetallic compounds and the grain refinement of α-Al in Al-Fe-Mn alloys

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Abstract

The effect of Mg additions on the Fe-containing intermetallic compounds and the heterogeneous nucleation of α-Al were investigated in Al-1.4Fe-0.7Mn-*x*Mg alloys using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The experimental results show that the morphology of $Al_6(Fe,Mn)$ in eutectic structure was significantly modified from needle-like to plate-like and then dendritic with increasing Mg concentration. The effects of Mg addition on the composition and crystal structure of $Al_6(Fe,Mn)$ were also investigated. No Mg was detected in the $Al_6(Fe,Mn)$ compounds. However, clear interfacial segregation of Mg on the surface of the $Al_6(Fe,Mn)$ particles was observed. The grains of α-Al were refined with increased Mg addition. It is also found that the Mg addition in the Al alloys resulted in change to the major naturally formed oxides from Al_2O_3 to $MgAl_2O_4$, and eventually changed the heterogeneous nucleation of α-Al. The direct evidence of heterogeneous nucleation of α-Al on the naturally formed $MgAl_2O_4$ particles was observed.

Key words: Mg, $Al_6(Fe,Mn)$, α-Al, segregation, heterogeneous nucleation

1. Introduction

Aluminium alloys due to their low density were extensively used in applications where light weighting is important such as the automotive industry. Alloying elements are normally added to Al alloys to achieve the desirable properties through precipitation hardening, solid solution hardening, dispersion strengthening, grain refining or modification of metallic and intermetallic phases, suppression of grain growth at elevated temperatures, etc [1-3]. Mg addition to Al alloys is to improve low cycle fatigue resistance, corrosion resistance strengthen and harden Al alloys through solid solution and dispersion strengthening without considerable decrease in ductility. Aluminium–magnesium (Al–Mg) alloys (5000 series) are used extensively in the automotive industry due to their excellent high-strength to weight ratio, corrosion resistance, and weldability [4-5]. However, the effects of Mg on the intermetallic compounds especially the effect on the Fe-containing intermetallic compounds, and its effect on the heterogeneous nucleation of α-Al were less investigated.

Mn is usually added into Al-Mg alloys to strengthen the Al alloys. It is reported that [6-8] Mn improves ductility of aluminium alloys containing iron and silicon through modification of β-Al_5FeSi intermetallic particles from platelet to cubic form $Al_{15}(Fe,Mn)_3Si_2$. Fe as one of the un-avoidable impurities in Al alloys is easily picked up during manufacturing process of the alloy. Fe addition to Al alloys was reported to have some advantages such as improving the processing capabilities of the alloy and/or the strength of the final wrought product [3-4]. However, due to the very low solid solubility of Fe in Al, especially at the low temperatures, the main problem associated with the Fe-containing Al alloys is the Fe-rich intermetallic compounds (FIMCs) which always form as large particles and deteriorates the mechanical properties of Al alloys. However, Fe can be considered as a beneficial element to strengthen the die-cast Al-Mg and Al-Mg-Mn alloys [9].

In Al-Mn-Fe alloys, the major FIMCs is $Al_6(Fe,Mn)$ which was reported to have an orthorhombic structure [10]. As reported[9, 11], primary $Al_6(Fe,Mn)$ has a hollow needle-like morphology, and those in eutectic structures have a Chinese script morphology. Grain refinement for these FIMCs in Al alloys is very important to enhance the mechanical properties. Therefore, different methods such as deformation[12], ultrasonic processing [13], structure modification [14-16], grain refiner addition [17-19] have been used to refine the FIMCs. Some achievement has been reported. The mechanism of grain refinement by inoculation was understood as supply of potent particles for heterogeneous nucleation and alloying elements for growth restriction [20-21]. Chemical method is an effective and economic way to grain refine Al alloys during the solidification process. However, due to the limited understanding of heterogeneous nucleation of FIMCs, especially $Al_6(Fe,Mn)$, effective grain refiners for FIMCs are still not available. The recent research [21] show that the nucleation undercooling of the FIMCs is much higher than that of the pure metals such as Al and Mg.

The investigations on the effects of Mg as solute in Al-Mg alloys were mainly focus on the growth restriction effect. It is shown that [22] the effect of Mg solute on the grain refinement of α-Al appeared to be very complex to be accounted for by a single parameter. The effects of Mg including direct effects and indirectly effects on the oxide particles and FIMCs morphology has rarely been reported. In this study, a hypoeutectic Al-Fe-Mn alloy was designed and different Mg concentrations were added into the designed alloys to investigate such effects. The effect of Mg on the FIMCs formation and the grain refinement of α-Al in Al-1.4Fe-0.7Mn alloy were investigated using optical microscopy (OM), SEM, and TEM analysis. The study was focused on the effects of Mg on the morphology, composition and crystal structure of $Al_6(Fe,Mn)$. The native oxides were collected by pressurised melt filtration technique [23] and the effects of Mg addition

on the native oxides was examined. Heterogeneous nucleation and grain refinement of α-Al due to the Mg addition were also investigated.

2. Experimental

Al-1.4Fe-0.7Mn alloys with and without Mg addition were studied in this work. The nominal compositions of the alloys were listed in Table 1 (all compositions are in wt.% unless specified otherwise). Commercial purity Al (>99.86%), commercial purity Mg (>99.95 %), Al-20% Mn and Al-38% Fe master alloys were used to prepare the alloy with the nominal composition. The Al-1.4Fe-0.7Mn alloy was prepared before Mg addition. The pure Al, Al-Fe and Al-Mn alloys were heated in the electric resistance furnace to 750℃ and held there until molten. The molten pure Al was stirred to accelerate the melting of Al-Fe and Al-Mn master alloys. After fully molten, the alloy was held for further 30 minutes. The melt was then divided into 4 crucibles equal in weight, and then Mg was added to make the alloys with 0%, 0.5% Mg, 1% Mg and 3% Mg concentration. The pure Mg (covered in Al foil) was pre-heated at 180℃ before inserting into the Al melts. After Mg was completely molten, the melts were held for 30 minutes, and after removing of slag, cast into TP-1 mould which was preheated to 380℃ [24]. The pouring temperature was kept constant at 720℃. To investigate the effect of Mg on the in-situ oxides, a pressurised melt filtration technique was used to collect the oxide particles from Al-Fe-Mn alloys with (1 wt.% Mg) and without Mg addition. The filtration crucible was preheated to 350℃ to reduce the heat loss. Due to the heat lost during the prefilling process, the melt was held at a higher temperature of 780℃.

The TP-1 sample was sectioned in cross section at 38mm height from the bottom of the casting which has a cooling rate of 3.5K/s. The filtration materials immediately above the filter were sectioned, where the oxide particles were concentrated. Metallographic specimens were made using the standard metallographic procedures. The as-solidified microstructure of the samples was characterised using a Zeiss optical microscope fitted with the Axio Vision 4.3 image analysis system with which the volume fractions of different phases were quantified. To investigate the 3D morphology, the as-cast samples were deep-etched using an aqueous solution containing 15vol% HCl for 1-3 minutes. The grain size of the investigated alloys was observed after etching with Baker's solution. A Zeiss field emission gun (FEG) Supera 35 scanning electron microscope (SEM) was used for microstructural observation and compositional analysis with operating at an voltage of 5-20kV.

Thin foils for transmission electron microscopy (TEM) were prepared from the slices of the as-solidified samples obtained from the melt filtration which were mechanically ground and cut into 3 mm diameter discs. The discs were then manually ground to a thickness of less than 60 μm, followed by ion-beam-thinning using a Gatan precision ion polishing system (PIPS) at 2.0-5.0kV

and an incident angle of 3-6°. TEM examination was performed on a JEOL 2100F microscope equipped with EDXS facility operated at an accelerating voltage of 200kV.

3. Results

Fig.1 shows the optical microstructure of Al-1.4Fe-0.7Mn-*x*Mg alloys solidified at 3.5K/s without Mg (Fig.1a), with 1% Mg (Fig.1b) and 3% Mg (Fig.1c) addition. It is demonstrated that all the alloys were solidified with primary α-Al and binary eutectic (Al_6(Fe,Mn) + α-Al). The eutectic spacing, Table 2, between the eutectic-Al_6(Fe,Mn) increases with increased Mg concentration. The morphology of Al_6(Fe,Mn) in eutectic structure changes from needle-like (Fig.1a) to Chinese script (Fig.1c) when Mg concentration increased from 0 to 3wt.%.

The details of the 3D morphology of the Al_6(Fe,Mn) in Al-1.4Fe-0.7Mn-*x*Mg alloys were examined by dissolving the Al matrix, Fig.2. Fig.2a shows that the morphology of the eutectic-Al_6(Fe,Mn) in Mg-free Al-Fe-Mn alloy is the need-like. Fig.2b shows that, with 1wt.% Mg addition, the eutectic-Al_6(Fe,Mn) becomes plate-like in Al-1.4Fe-0.7Mn-1.0Mg alloy. These plate-like Al_6(Fe,Mn) particles have branches at the edge, which is reminiscent of leaves. Fig.2c shows that the plate-like Al_6(Fe,Mn) in Al-1.4Fe-0.7Mn-3.0Mg alloy are coarser and thicker when Mg concentration increased to 3wt.%. The branches of the Al_6(Fe,Mn) crystals also becomes coarser and thicker, which present like trees.

The optical microstructure following Bakers reagent etching, Fig.3, of as-cast alloys shows that the grain size of α-Al decreases with increased Mg addition. The columnar α-Al grains on the edge of the sample almost eliminated when the Mg addition increases to 3wt.%. The quantified average grain size of α-Al for the alloys were measured and shown in Table 2. It shows that the grain size of α-Al in Al-1.4Fe-0.7Mn decreases from 954±106μm to 594±41μm when the Mg concentration increased from 0 to 3wt.%. However, the eutectic spacing in the inter-dendritic zone of α-Al increases with the increasing Mg addition as shown in Table 2.

TEM examination was conducted on the Al_6(Fe,Mn) in the Al-Fe-Mn alloys with different Mg additions. Table 3 gives the experimentally measured composition of the eutectic Al_6(Fe,Mn) phase in the alloys containing different Mg contents using TEM-EDX spectra. Every such measurement was carried out on more than 10 particles in each alloy and the average value was taken. It is shown that, although the concentration of (Fe+Mn) in Al_6(Fe,Mn) crystals increases with the increasing Mg addition, the variation is very small. Most importantly, no Mg was detected from all of these Al_6(Fe,Mn) particles. The experimentally measured lattice parameters, Table 4, of Al_6(Fe,Mn) in Al-1.4Fe-0.7Mn-*x*Mg alloys were list and compared with that of the reported Al_6Fe [27] and Al_6Mn [28]. It shows that the lattice parameter ***a*** decreases slightly in the Al-1.4Fe-0.7Mn-*x*Mg alloys with the increasing Mg concentration.

It was found that the $Al_6(Fe,Mn)$ particles in all studied alloys are {1 1 0} faceted, independent of the Mg addition. One of the examples is shown in Fig.4. The bright field TEM image in Fig.4a shows the eutectic $Al_6(Fe,Mn)$ in Al-1.4Fe-0.7Mn alloy. The corresponding high-resolution TEM (HRTEM) image from the interface of α-Al/$Al_6(Fe,Mn)$ when viewed along the [1 1 0] zone direction of $Al_6(Fe,Mn)$ was shown in Fig.4b. It shows that the $Al_6(Fe,Mn)$ is {1 1 0} faceted.

Although the Mg does not partition into the $Al_6(Fe,Mn)$, the interfacial segregation of Mg was observed discontinuously at the surface of $Al_6(Fe,Mn)$. Such Mg segregation on the $Al_6(Fe,Mn)$ surface is a common phenomenon in all of the examined particles in the Al-Fe-Mn-Mg alloys. Detailed examination on the Mg segregation was carried out and the results are presented in Fig.5 and Table 5. One such example is shown in Fig.5. The bright monolayer at the surface of the $Al_6(Fe,Mn)$ particle was observed using the bright field TEM image, Figs.5a and b. The composition variation from $Al_6(Fe,Mn)$ particle, Al/$Al_6(Fe,Mn)$ interface to the Al matrix was measured, Table 5. Fig.5b shows three phases at the interface which indicates an irregular Mg segregation morphology on the surface of $Al_6(Fe,Mn)$ particle. It is demonstrated that the brighter layers between the α-Al and the $Al_6(Fe,Mn)$ contains much higher Mg than the $Al_6(Fe,Mn)$ particle and the Al matrix, Table 5. The HRTEM image, Fig.5c, shows clearly that when viewed along the [1 0 1] zone direction of $Al_6(Fe,Mn)$ the Mg-rich segregation which has a thickness about 6-10nm is off the zone direction. Although the interface between $Al_6(Fe,Mn)$ and Mg-rich monolayer is not faceted, no obvious transition area can be observed between them. However, at the interface between α-Al and the Mg-rich monolayer, there exists a large transition area. When view along the [3 2 0] zone direction of Mg-rich layers, the HRTEM at the interface, Fig.5d, presents that both the connected α-Al and $Al_6(Fe,Mn)$ are off zone direction. The Mg-rich segregation phase was viewed along different zone directions. One of the Fourier fast transformation (FFT) pattern from the Mg-rich layers was shown in Fig.5e. The schematic indexed FFT pattern of Fig.5e is shown in Fig.5f which demonstrates that the Mg-rich phase is likely to be$Al_{12}Mg_{17}$ phase viewed along its [3 2 0] zone direction. No well-defined orientation relationship was observed between the α-Al and $Al_{12}Mg_{17}$, and between $Al_{12}Mg_{17}$ and $Al_6(Fe,Mn)$.

The native oxides in the Al-1.4Fe-0.7Mn and Al-1.4Fe-0.7Mn-3.0Mg alloys collected using the pressurised melt filtration technique were examined using SEM and TEM analysis. The SEM images, Fig.6, present different type of native oxides in Mg-free and Mg-containing Al-1.4Fe-0.7Mn alloys. The native oxides in the Mg-free Al-Fe-Mn alloys, Fig.6a, have a long needle-like morphology. The SEM-EDX spectra from these native oxides, Fig.6c, demonstrates that they contain Al and O only. These oxides were identified as Al_2O_3 and have thickness less than 50nm and length ranged from 10-100 nm. The native oxides in the Al-1.4Fe-0.7Mn-3.0Mg alloy, Fig.6b, have different size ranges which varies from 100-200 nm to a few μm. The SEM-EDX spectra from these native oxides, Fig.6d, demonstrates that they contains Al, Mg and O. These oxides were identified as $MgAl_2O_4$ later by TEM analysis.

To investigate the mechanism of grain refinement of the α-Al by the Mg addition, the relationship between α-Al and the native $MgAl_2O_4$ particles was investigated using TEM analysis. The TEM

examination at the interface between α-Al and $MgAl_2O_4$ indicates that most of the $MgAl_2O_4$ particles do not have well-defined orientation relationship (OR) with the adjacent α-Al. However, a well-defined OR between α-Al and $MgAl_2O_4$ particle was experimentally observed when the $MgAl_2O_4$ particle was embedded in α-Al. One of the examples was shown in Fig.7. This HRTEM image shows the interface between α-Al and $MgAl_2O_4$ when the incident electron beam is parallel to both the [1 1 0] zone direction of $MgAl_2O_4$ (lower part) and α-Al (upper part).This suggests an orientation relationship (OR) between α-Al and $MgAl_2O_4$: $(\bar{1}\,1\,\bar{1})$ α-Al // $(\bar{1}\,1\,\bar{1})$ $MgAl_2O_4$ and [1 1 0]α-Al // [1 1 0] $MgAl_2O_4$.

4. Discussion

The experimental results (Fig.1) indicated that the Al-1.45Fe-0.7Mn alloys with and without Mg addition were solidified with primary α-Al, and binary eutectic (BE) structure (Al_6(Fe,Mn)+ α-Al) at 3.5K/s. There are two main effects of Mg addition in Al-Fe-Mn alloys. The first one is the grain refinement of α-Al. The second one is the effect on the morphology of BE-Al_6(Fe,Mn). The mechanism of grain refinement of α-Al by Mg addition can be understood from two part. The first one is the effect of Mg solute growth restriction. The second one is enhancing heterogeneous nucleation of α-Al by changing the native oxide from not potent Al_2O_3 to $MgAl_2O_4$.

As shown, the investigated alloys are hypoeutectic Al-Mg alloys which solidified forming primary α-Al and eutectic (FIMCs+α-Al). Mg did not partition into the FIMCs changing the chemistry. Therefore, the effects of solute Mg on the grain refinement in these alloys are similar to that of any Al-Mg alloy. The grain restriction of Mg on the α-Al grains has been investigated by calculating the Q values [22]. It shows that [22] it is fair to conclude that the solute effect depends on the system and appears to be too complex to be accounted for by a single parameter. In this study, we found some growth restriction effects of Mg solute on the α-Al grain size variation. However, the refinement caused by the change of the oxide on the heterogeneous nucleation which related to the final grain refinement has never been reported and need to be considered as an important factor.

The as-cast results, Fig.3, showed a clear grain refinement of α-Al in Al-1.4Fe-0.7Mn alloy with Mg addition. Further study showed that the Mg addition not only refined the α-Al grains and the eutectic spacing, but also changed the major native oxide type from Al_2O_3 to $MgAl_2O_4$, which changed the potency of the nucleated substrates for the primary α-Al. Direct evidence showing the heterogeneous nucleation of α-Al on native $MgAl_2O_4$ was observed using TEM analysis. The experimental results revealed that the native $MgAl_2O_4$ is more potent than Al_2O_3 for the heterogeneous nucleation of α-Al.

The experimental results also indicated that the Mg addition can indirectly change the morphology of FIMCs by grain refining the α-Al and changing the inter-dendritic spacing of α-Al. It is reported that [29-30] the grain refinement of primary α-Al grains in Al alloys by adding grain refiner such as Al-5Ti-1B, can change/refine the following eutectic intermetallic compounds morphology.

Therefore, the similar contribution of the grain refinement of α-Al in this study on the morphology transition of BE- Al_6(Fe,Mn) need to be considered.

The other effects of Mg on the morphology transition of BE-Al_6(Fe,Mn) in Al-1.45Fe-0.7Mn-*x*Mg can be discussed from the crystal structure and the Mg segregation on Al_6(Fe,Mn) surface. The 3D morphology of the BE-Al_6(Fe,Mn), Fig.2, indicated that the morphology of Al_6(Fe,Mn) was modified from need-like to plate-like and to Chinese script by different amounts of Mg addition. However, the TEM-EDXS results from the Al_6(Fe,Mn), Table 3, showed that the Mg did not partition into the Al_6(Fe,Mn) but segregated on the surface of the Al_6(Fe,Mn), Table 5. The Mg segregation at the α-Al/Al_6(Fe,Mn) interface results in the likely formation of $Al_{12}Mg_{17}$ phase with a thickness of a few nano-meters. These evidence indicated that the mechanism for Mg effects on the morphology of Al_6(Fe,Mn) is by modifying the phase rather than changing the internal crystal structure.

The TEM examination results showed that the Al_6(Fe,Mn) particles remains {1 1 0} faceted in Al-1.4Fe-0.7Mn-*x*Mg alloys. It is also presented that the Mg discontinuously displayed at the surface of the BE-Al_6(Fe,Mn) particles. The Mg segregation on the surface especially on the {1 1 0} planes of Al_6(Fe,Mn) modified the interface, Fig.5b. It shows that some part of the Al_6(Fe,Mn) even at the {1 1 0} planes is non-faceted due to the Mg segregation. It is known that the terminated planes of the crystals indicate the different growth rates along different directions. The planes with slowest growth rates will be finally terminated. The as-cast results in this study showed that the morphology of BE-Al_6(Fe,Mn) changed from need-like to plate-like and then Chinese script, which indicated that the growth rates along different growth directions are possibly changed by the Mg segregation at the surface. In the Mg containing Al-Fe-Mn alloys, Mg segregated at the surface of the Al_6(Fe,Mn) during the growth. The more Mg content in the melts, the more Mg will be segregated on the surface of the Al_6(Fe,Mn) during the growth of the Al_6(Fe,Mn). Therefore, with 0.5wt.% Mg addition, the Al_6(Fe,Mn) grows into 2-directions and shows as plate-like morphology, Fig.2b. The Al_6(Fe,Mn) was modified and grown into 3D Chinese script morphology in the Al alloys with 3wt.% Mg addition, Fig.2c.

The effects of Mg addition on the compositions, Table 3, and lattice parameters, Table 4, of Al_6(Fe,Mn) in Al-1.4Fe-0.7Mn alloys were investigated. As shown in Table 3, the total concentration of Fe and Mn increased slightly with the increase in Mg addition. The Fe/Mn ratio decreased slightly with the increase in Mg addition. The previous reports [6-8, 25-26] showed that the composition of Al_6(Fe,Mn) can be different in different alloys and different Fe/Mn ratios. Their reported lattice parameters [27-28] were listed in Table 4. The difference of the compositions and lattice parameters between this work and the reported is mainly due to the differences in Al alloys compositions and the casting conditions. As reported [9], there are 3 Al sites and 1 Mn site for Al_6Mn. In the Al_6(Fe,Mn) phase, the Fe and Mn share the Mn sites. Due to the different atomic radii of Fe and Mn, different Fe/Mn ratio in the Al_6(Fe,Mn) phase changes the lattice parameters correspondingly. Therefore, as shown in Table 4, the lattice parameters of Al_6(Fe,Mn) changed slightly with the changes in composition in this study.

5. Conclusions

Summarising the major findings from this study, the morphology of eutectic $Al_6(Fe,Mn)$ intermetallic phase changed from needle-like to plate-like, and Chinese script with increasing Mg concentration in Al-1.4Fe-0.7Mn alloys. No Mg was detected in the $Al_6(Fe,Mn)$ particles in this study. The segregation of Mg was observed on the surface of $Al_6(Fe,Mn)$ particles. Mg has very little effect on the composition and lattice parameters of the $Al_6(Fe,Mn)$ intermetallic compound. However, the composition and lattice parameters of $Al_6(Fe,Mn)$ can be affected by the Fe/Mn ratio in different alloys and casting conditions. The α-Al grain size of the Al-Fe-Mn alloys decreases with the increasing Mg content. The major in-situ oxides changed from Al_2O_3 to $MgAl_2O_4$ after Mg addition in Al-Fe-Mn alloys. The $MgAl_2O_4$ particles do nucleate α-Al with a well-defined orientation relationship between the oxide and α-Al: $(\bar{1}\,1\,\bar{1})$ α-Al // $(\bar{1}\,1\,\bar{1})MgAl_2O_4$ and [1 1 0]α-Al // [1 1 0] $MgAl_2O_4$.

Acknowledgement

The EPSRC is gratefully acknowledged for providing financial support under Grant EP/N007638/1.

References

[1] G.S. Cole, A.M. Sherman, Light weight materials for automotive applications, Materials Characterization 35(1) (1995) 3-9.

[2] G.B. Burger, A.K. Gupta, P.W. Jeffrey, D.J. Lloyd, Microstructural control of aluminum sheet used in automotive applications, Materials Characterization 35(1), (1995) 23-39.

[3] M. Jinta, Y. Sakai, M. Oyagi, S. Yoshizawa, K. Matsui, K. Noda, Press forming analysis of aluminium auto body panel: wrinkle behavior in 5000 and 6000 series aluminium alloy sheet forming, JSAE Rev. 21 (2000) 407–409.

[4] S. Toros, F. Ozturk, I. Kacar, Review of warm forming of aluminum–magnesium alloys, Journal of materials processing technology 207 (2008) 1–12.

[5] D. J. Lloyd, S. A. Court, Influence of grain size on tensile properties of Al-Mg alloys, Materials Science and Technology, 19(10) (2003) 1349-1354.

[6] S.L. Lee, S.T. Wu, Influence of soaking treatments on hot ductility of Al-4.85 pct Mg alloys containing Mn, Metallurgical Transactions A 17(1986) 833–841.

[7] K. J. Gardner, R. Grimes, Recrystallization during hot deformation of aluminium alloys, Metal Science, 13(3-4) (1979) 216-222.

[8] O. Engler, S. Miller-Jupp, Control of second-phase particles in the Al-Mg-Mn alloy AA 5083. Journal of Alloys and Compounds 689 (2016) 998-1010.

[9] X.Z. Zhu, P. Blake, K. Dou, S.X. Ji. Strengthening die-cast Al-Mg and Al-Mg-Mn alloys with Fe as a beneficial Element, Materials Science & Engineering A 732 (2018) 240–250.
[10] J.G. Barlock, L.F. Mondolfo, Structure of some aluminium-irion-magnesium-manganese-silicon alloys, Zeitschrift fuer Metallkunde 66(10) (1975) 605-611.
[11] Z. P. Que, Y. P. Zhou, Y. Wang, Z. Fan, Effect of MgO on Phase Selection in Al–Mg–Si–Fe–Mn Alloys, Trans Indian Inst Met 68(6) (2015) 1167–1172.
[12] S.G. Shabestari and M. Ghanbari, Effect of plastic deformation and semisolid forming on iron–manganese rich intermetallics in Al–8Si–3Cu–4Fe–2Mn alloy J. Alloys Compd. 508 (2010) 315–319.
[13] Y.B. Zhang, J.C. Jie, Y. Gao, Y.P. Lu, and T.J. Li, Effect of ultrasonic treatment on the formation of iron-containing intermetallic compounds in Al-12% Si-2% Fe alloys, Intermetallics, 42 (2013) 120–125.
[14] M. Wang, W. Xu, Q.Y. Han, Study of Refinement and Morphology Change of AlFeSi Phase in A380 Alloy due to Addition of Ca, Sr/ Ca, Mn and Mn, Sr, Materials Transactions, 57(9) (2016) 1509-1513.
[15] B. Suárez-Peña, J. Asensio-Lozano, Influence of Sr modification and Ti grain refinement on the morphology of Fe-rich precipitates in eutectic Al–Si die cast alloys, Scripta Materialia, 54(9) (2006) 1543-1548.
[16] A. M. Samuel, F. H. Samuel, Modification of iron intermetallics by magnesium and strontium in Al-Si alloys, International Journal of Cast Metals Research, 10(3) (1997) 147-157.
[17] T. Smith, K. O'Reilly, S. Kumar, I. Stone, Influence of Grain-Refiner Addition on the Morphology of Fe-Bearing Intermetallics in a Semi-Solid Processed Al-Mg-Si Alloy, Metallurgical and Materials Transactions A, 44A (2013) 4866-4871.
[18] A. Lui, P. S. Grant, I. C. Stone, K. A. Q. O'Reilly, The Role of Grain Refiner in the Nucleation of AlFeSi Intermetallic Phases During Solidification of a 6xxx Aluminum Alloy, Metallurgical and Materials Transactions A 50 (2019) 5242–5252
[19] A. Hassani, K. Ranjbar, S. Sami, Microstructural evolution and intermetallic formation in Al-8wt% Si-0.8wt% Fe alloy due to grain refiner and modifier additions, International Journal of Minerals, Metallurgy and Materials 19(8) 2012 739-746.
[20] Z. Fan, Y. Wang, Y. Zhang, T. Qin, X.R. Zhou, G.E. Thompson, T Pennycook and T. Hashimoto, Acta Materialia, 2015, 84, pp. 292–304.
[21] Z.P. Que, Y.P. Zhou, Y. Wang and Z. Fan: Composition templating for heterogeneous nucleation of intermetallic compounds, Solidification Processing (2017)158-161.
[22] Y. Birol. Effect of solute Mg on grain size of aluminium alloys. Materials science and technology. 28(8) (2012) 924-927.
[23] Y. Zuo, B. Jiang, P. Enright, G.M. Scamans, Z. Fan, Degassing of LM24 Al alloy by intensive melt shearing, Int. J. Cast Metal. Res. 24(5) (2011) 307-313.

[24] Standard Test Procedure for Aluminium Alloy Grain Refiners: TP-1, Aluminium Association, Washington DC, 1987.
[25] Y.J. Li, L. Arnberg. Solidification structures and phase selection of iron-bearing eutectic particles in a DC-cast AA5182 alloy, Acta Materialia 52(9) (2004) 2673-2681.
[26] W.W. Zhang, B. Lin, Z. Luo, Y.L. Zhao, Y.Y. Li, Formation of Fe-rich intermetallic compounds and their effect on the tensile properties of squeeze-cast Al–Cu alloys, J. Mater. Res. 30(16) (2015) 2474-2484.
[27] L.K. Walford, The structure of the intermetallic phase FeAl6, Acta Crystallographica 18 (1965) 287-291.
[28] A. Kontio, P. Coppens, New study of the structure of MnAl6. Acta Crystallographica, Section B: Structural Crystallography and Crystal Chemistry 37 (1981) 37 433-435.
[29] Z.P. Que, Y. Wang, Y.P. Zhou, L. Liu, Z. Fan, Effect of Al-5Ti-1B Grain Refiner Addition on the Formation of Intermetallic Compounds in Al-Mg-Si-Mn-Fe alloys, Materials Science Forum, 828-829 (2015) 53-57.
[30] S. Kumar, K.A.Q. O'Reilly, Influence of Al grain structure on Fe bearing intermetallics during DC casting of an Al-Mg-Si alloy, Materials Characterization, 120 (2016) 311-322.