

Solidification processing of scrap Al-alloys containing high levels of Fe

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Abstract. The accumulation of iron in molten aluminium is one of the main concerns for the recycling and casting industries because it leads to the formation of undesirable Fe-rich intermetallic compounds which are detrimental to mechanical properties. Many methods have been developed in the past to reduce the iron accumulated in molten aluminium scrap, but they all suffer from poor efficiency. Hence, a more efficient method is urgently needed to mitigate the negative effect of high iron levels in the melt, thereby avoiding downgrading secondary aluminium to low quality products or the dilution with expensive primary aluminium. This contribution provides a study of the Fe-rich intermetallic compounds developed in aluminium casting alloys with high levels of Fe as a function of melt processing conditions. Results show that the formation of the Fe-compounds is not only dependent on the cooling rate and holding time before solidification, but more on the initial melt treatment as it enhances the nucleation and growth of the Fe-phases. Elemental addition of Mn leads to the formation of large and compact intermetallic particles, but at slow rate. Physical melt treatment by intensive high shearing produces a much faster nucleation and results in a fine dispersion of smaller iron containing intermetallic particles. The latter could be used either to increase the tolerance to iron contamination or to facilitate the iron removal process, providing huge benefits for the recyclability of scrap aluminium alloys as it would allow the transformation of low-grade feedstock into a low cost and small carbon footprint material for high quality castings.

1. Introduction

Aluminium alloys are being widely used in various industrial sectors, especially in aerospace and automotive applications, for the purpose of weight saving and high performance [1]. Manufacturing components using primary aluminium requires 20 times more energy and produces 4 times more CO₂ emissions than directly using secondary aluminium scrap [2]. However, one of the main problems of repeated aluminium scrap recycling is the gradual accumulation of impurities in the molten scrap, mainly iron, due to the presence of high iron containing components (rivets, screws, nuts...) which cannot be fully separated prior melting or from the steel tools used during the casting processes [3].

Because Fe has low solubility in solid aluminium, it can lead to the formation of intermetallic compounds (IMCs) during solidification, which are detrimental to the mechanical properties [4]. First approach used in industry is to downgrade the contaminated material to low quality casting applications or to dilute with expensive primary aluminum, but this is non-sustainable short term solution. Molten refining processes include electrolysis, electroslag fluxing, fractional solidification and the precipitation of primary Fe-rich phases form when the melt is partially solidified [5].



Regarding the latter, many methods have been developed in the past (gravity, filtration, centrifuging and electromagnetic separation), all of them being very effective but also suffering from poor efficiency mainly because the long processing times required to first form and then separate the intermetallic compounds [5]. This limits their use to laboratory research and makes them unpractical for large scale processing in industry at an affordable cost and highlights that a better understanding of the intermetallic formation process is needed.

Among the primary Fe-rich compounds that can be formed in Al-Si based alloys widely used in automotive components, the most common are the needle-shape β -Al₅FeSi and the star-like α -Al₁₅(Fe,Mn)₃Si₂ in the presence of Mn [4-7]. Previous research has shown that these intermetallics tend to nucleate and grow on the wetted side of the natural occurring oxide bi-films [6, 8-11]. However, these oxides are normally agglomerated and not well distributed within the melt, something that hinders the nucleation and delays the growth of the Fe-rich intermetallics, making it difficult their separation from the low-Fe melt.

This work aims to present a more detailed study on the formation of primary Fe-rich intermetallic phases in an aluminium alloy (A380) containing increasing levels of Fe and Mn, by using both thermodynamic calculations and experimental evaluation. The influence of the solidification conditions and the use of melt treatment on the nucleation, growth and final type, size and morphology of the Fe-rich intermetallic phases has been also analyzed and discussed.

2. Experimental procedure

The alloy used in this study was a commercial Al-Si die casting alloy (A380) with a composition (wt.%) of Al-8.3Si-3.5Cu-0.15Mg-1.9Zn-1Fe-0.2Mn. Different additions were made to the base alloy using Al-80Fe and Al-60Mn master alloys, simulating typical compositions that can be found in recycled aluminum scrap [5] by adding Fe and to examine the formation of α -Al₁₅(Fe,Mn)₃Si₂ when adding Mn.

The alloys were prepared in SiC crucibles inside an electric resistance furnace and held at 700 °C for 1h before taking sample for analysis by optical emission spectroscopy (OES), using for casting the samples a steel mould cup (d30mmx40mm) preheated at 250 °C.

First set of samples (fast cooling) involved the ones taken for composition analysis. A second set of samples (slow cooling) was collected by pouring the melt into a SiC crucible (d50mmx60mm) preheated at 700 °C and placed on an insulated base and allowed to naturally cool down. In both cases the temperature during cooling was recorded by placing a K-type thermocouple in the middle of the sample and data was acquired at 100Hz using a data logger connected to a PC.

To evaluate the effect of time on the formation of the intermetallics, on a second set of experiments the melt was cooled controlled by pouring into launder that ended into a cylindrical steel mould (d50mmx250mm) externally heated controlled at 600 °C (above the temperature of α -Al formation) where it was held for different times before allowing the melt to fully solidify.

Physical melt treatment was performed on selected alloys by means of high shear melt conditioning technology (HSMC) developed at BCAST [12]. The system comprises a rotor-stator unit, attached to an electrical motor with speed control that was immersed into the melt and set at 3000rpm for 2min, being the melt later processed in the same way as described above.

Solidified samples were cut, mechanically polished and then examined using a combination of optical microscopy and EDX analysis to identify type and size of the intermetallic compounds.

Pandat software was used to calculate the phase diagrams of the alloys under consideration in order to know the expected primary Fe-phases and the concentration of Fe in the liquid phase as the precipitation of the IMCs occurs during the solidification [13, 14]. This was useful information about the thermodynamic limit for iron removal and a reference to compared with the experimental evaluation.

3. Results and discussion

3.1. Effect of Fe addition

The presence of iron in the aluminium alloy leads to the formation of a variety of Fe-rich intermetallic compounds as it is shown by the calculated phase diagram in figure 1a. With the increase of iron content some primary intermetallic phases quickly appear above the temperature of formation of α -Al (595 °C). Figure 1b shows the typical microstructure of the alloy with 1% Fe when directly solidified in the composition mould. The material exhibits a small amount of compact or star like primary intermetallics, identified as α -Al₁₅(FeMn)₃Si₂.

With higher Fe content (figure 1c), the amount of α -Al₁₅(FeMn)₃Si₂ particles increases and become more compact, but their size remains the same, while the most significant effect is the appearance of high amount of large and needle shape intermetallics, identified as β -Al₅FeSi. Elongated porosity (cracks) is also appreciated in the microstructure, something consistent with the idea of nucleation of the intermetallics on the oxide bi-films present in the melt [8-11]. It is important to observe that in both cases the amount and size of α -Al₁₅(FeMn)₃Si₂ particles is small, suggesting that the formation of this primary phase is difficult [15].

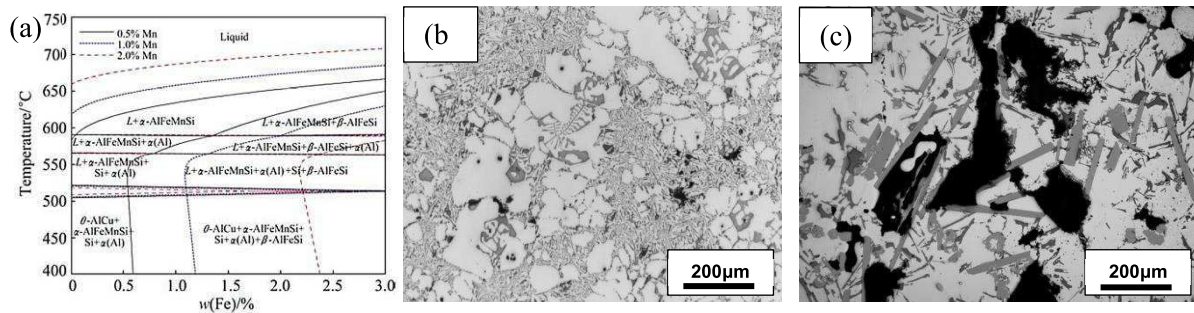


Figure 1. (a) Phase diagram for A380 alloy with different Fe and Mn contents [14]. (b) Fe-rich intermetallics formed in A380-0.2Mn with 1%Fe and with (c) 2%Fe.

3.2. Effect of Mn addition

Increasing the Mn content in the alloy promotes the formation of α -Al₁₅(FeMn)₃Si₂, in detriment of the β -Al₅FeSi phase [14]. The microstructure for the A380 alloy with 0.5 and 1% Mn content (figure 2), reveals the presence of only one type of primary compound, with compact shape and increased size. The average particle size is 83 μ m for 0.5 %Mn (figure 2a) and 137 μ m for 1%Mn (figure 2b), in comparison with the base alloy with only 0.2%Mn (28 μ m, figure1b). Despite the increase in size is in agreement with previous findings, the area fraction of particles in the whole sample is below expected for these Fe and Mn contents [16,17], once again highlighting that the formation of the particles is a slow process and might not be fully completed under high cooling rates.

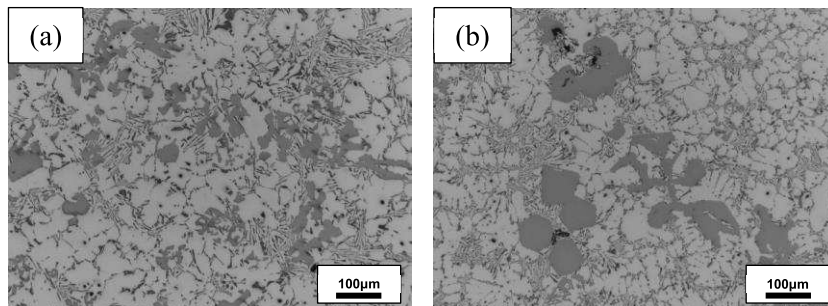


Figure 2. Fe-rich particles formed in A380-1Fe with increasing Mn, (a) 0.5Mn, (b) 1Mn.

3.3. Effect of physical melt treatment by HSMC

The application of intensive melt shearing to the molten alloy breaks up the oxide films present in the liquid and disperses them into very fine particles, thus increasing significantly the amount of nuclei for the intermetallic compounds. This not only increases the possibilities of forming more primary Fe-rich particles, but at the same time they are expected to be much finer [12]. Figure 3 shows the microstructure of the alloy with 0.2%Mn (figure 3a) and 1%Mn (figure 3b), similarly to figure 1b and figure 2b, but in this case when intensive melt shearing has been applied before solidification. In both cases the number of particles increases significantly and they become more rounded and compact.

Regarding the average size, it varies from 28 to 51 μm for low Mn content alloy (figure 1b vs. figure 3a). This can be explained considering that an early nucleation gives the particles more time to grow during the solidification. On the other hand, with increasing Mn content, by itself already promoting the formation of the particles, the average size decreases from 137 to 102 μm (figure 2b vs. figure 3b) when the melt has been intensively sheared.

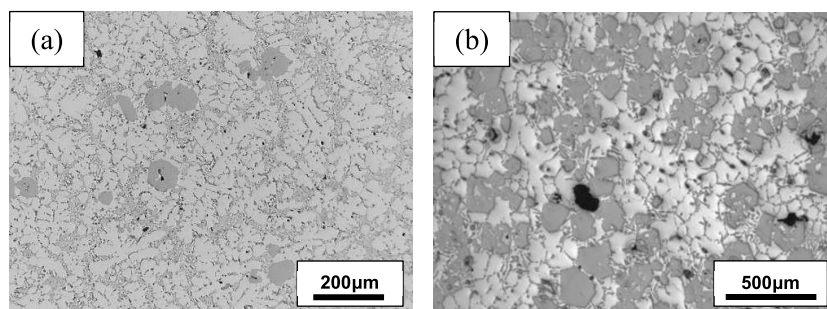


Figure 3. Fe-rich particles formed after intensive melt shearing on A380-1Fe (a) 0.2Mn, (b) 1Mn.

3.4. Effect of cooling rate on solidification process

In order to understand better the results from previous sections, it is important to evaluate the temperature evolution during the solidification process. Figure 4 presents the cooling curves for the A380 alloy with 1%Fe and 1%Mn (with and without HSMC) as function of the cooling rate, estimated as $-3.2\text{ }^{\circ}\text{C/s}$ and $-0.3\text{ }^{\circ}\text{C/s}$ for the fast and slow cooling respectively. It can be seen that all curves present an inflexion point between 600 and 650 $^{\circ}\text{C}$, different in each case, which corresponds to the precipitation of the primary $\alpha\text{-Al}_{15}(\text{FeMn})_3\text{Si}_2$ [17]. Under natural conditions, the undercooling increases with the cooling rate from -30 to $-50\text{ }^{\circ}\text{C}$, supporting the idea that nucleation of primary phases requires long time and that can be easily suppressed if the cooling rate is high enough [15]. On the other hand, the application of high shear to the melt reduces the undercooling to -10°C for slow cooling and to -28°C for fast cooling, much smaller in both cases than the reference material.

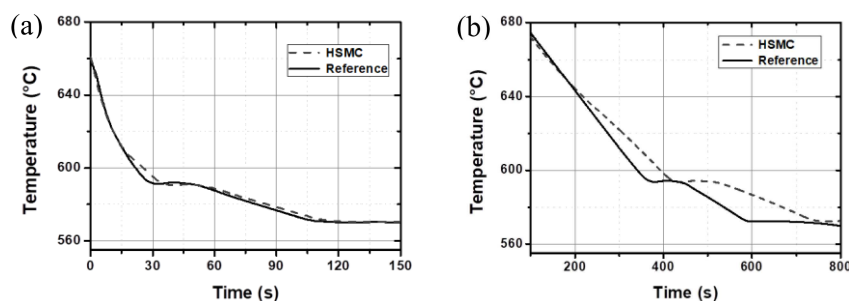


Figure 4. Cooling curves for A380-1Fe-1Mn under (a) fast and (b) slow cooling.

3.5. Effect of holding time

The density of $\alpha\text{-Al}_{15}(\text{Fe,Mn})_3\text{Si}_2$ particles is about 3.2 g/cm^3 [14], higher than the density of molten aluminium (2.3 g/cm^3). As a consequence, they naturally tend to settle in the melt, leaving the top part with a lower Fe level. Without any treatment (figure 5a) the direct solidification produces a very small gradient from top (0.95%) to bottom (1.1%), because the intermetallic do not have enough time to

grow, in case they have nucleated on the agglomerated oxides, and then settle. It is only when the melt is held at 600 °C that the particles can grow and a increasing with time gradient is observed. Complete sedimentation of the intermetallic phase requires in this case between 10 to 15 min.

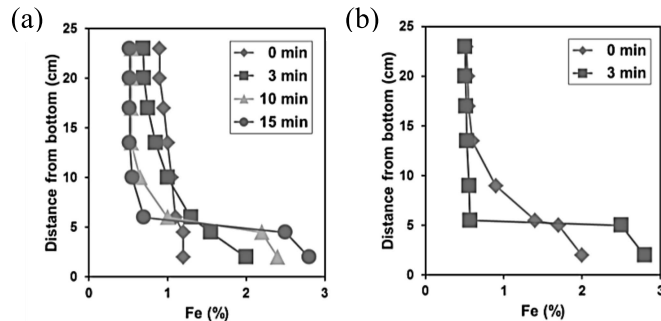


Figure 5. Fe concentration along the vertical section of samples after keeping the melt at 600 °C for different times before solidification. (a) without and (b) with physical melt treatment by HSMC.

On the other hand, when high shear melt treatment is applied, the sedimentation is much faster (figure 5b). Even for a direct cooling the sedimentation has taken place in most of the casting, leaving the top half with Fe levels close to the thermodynamic limit for this alloy (0.5% [14]). Full sedimentation takes place in less than 3 minutes in this case, therefore 3 to 5 times faster, evidencing the earlier formation and growth of the primary Fe-rich compounds during the cooling stage.

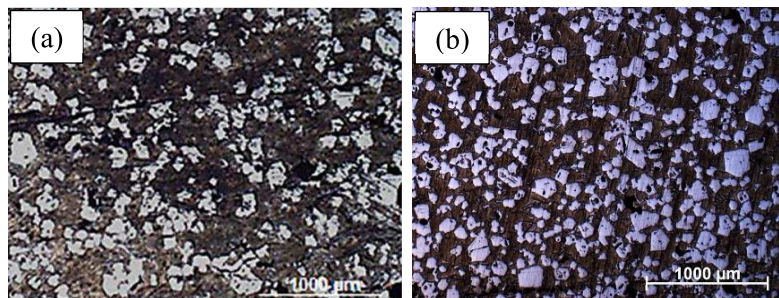


Figure 6. Microstructure of the bottom of the samples after complete sedimentation of the intermetallic particles by holding at 600°C (a) without and (b) with physical melt treatment by HSMC.

The sludge in the reference material consists of irregular particles of 180 μm with poor distribution as it is shown in figure 6a. For the treated material (figure 6b) it consists of smaller intermetallics of 119 μm, with more rounded shape and higher density. This result supports the idea that a low nucleation rate (progressive) promotes higher growth and branched shape, while a high nucleation rate (explosive) results on low growth but compact particles [18].

4. Conclusions

Due to the natural agglomeration of the oxides in molten aluminium, the formation and growth of primary Fe-rich intermetallic compounds on top of them is a slow process and tends to produce more needle shape β -Al₅FeSi than compact α -Al₁₅(Fe,Mn)₃Si₂ particles at high levels of Fe. The addition of Mn promotes the formation of α -Al₁₅(Fe,Mn)₃Si₂ in detriment of β -Al₅FeSi, for Mn/Fe ratio over 0.5, resulting in compact and bigger particles. However under natural cooling conditions the fraction of these intermetallics is below expected, suggesting the process is still slow even with chemical melt treatment. The nucleation and growth is favored by a slow cooling rate and/or long holding times, but this solution is far from efficient.

Intensive melt shearing efficiently disperses the oxide bi-films, resulting in the explosive nucleation of primary α -Al₁₅(Fe,Mn)₃Si₂, something that has two important consequences to improve the recyclability of the high-Fe alloys. First, increased iron tolerance, as the final particles tend to be smaller and better dispersed, improving the mechanical properties of castings. Second, faster iron removal from the melt, as the earlier formation speeds up the sedimentation of Fe-rich intermetallics.

Acknowledgments

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References

- [1] Lumley R N 2018 *Fundamentals of Aluminium Metallurgy: Recent Advances* Woodhead Publishing Series in Metals and Surface Engineering, Volume 2
- [2] Polmear I J 1995 *Light Alloys, Metallurgy of light alloys 3rd edition*
- [3] Green J 2007 *Aluminium Recycling and Processing for Energy Conservation and Sustainability* **274** 53
- [4] Mondolfo L F 1976 *Aluminium Alloys: Structure and Properties* Butterworths, London
- [5] Zhang L, Gao J, Damoah L N W and Robertson D G 2012 Removal of iron from aluminum: A review. *Mineral Processing and Extractive Metallurgy Review: An International Journal* **33** 99–157
- [6] Cao X and Campbell J 2000 Precipitation of primary intermetallic compounds in liquid Al-11.5Si-0.4Mg alloy *Int. J. Cast Metals Res.* **13** 175–184
- [7] Shabestari S G 2004 The effect of iron and manganese on the formation of intermetallic compounds in aluminium-silicon alloys *Mater. Sci. Eng. A* **383(2)** 289–98
- [8] Cao X and Campbell J 2003 The nucleation of Fe-rich phases on oxide films in Al-11.5Si-0.4Mg cast alloys *Metallurgical and Materials Transactions A* **34(7)** 1409-1420
- [9] Cao X and Campbell J 2004 The solidification characteristics of Fe-rich intermetallics in Al-11.5Si-0.4Mg cast alloys *Metallurgical and Materials Transactions A* **35(5)** 1425–1435
- [10] Khalifa W, Samuel F H, Gruzleski J E, Doty H W and Valtierra S 2005 Nucleation of Fe-Intermetallic Phases in the Al-Si-Fe alloys *Metallurgical and Materials Transactions A* **36(4)** 1017–1032
- [11] Orozco-González P *et al.* 2015 Nucleation of Fe-Rich Intermetallic Phases on α -Al₂O₃ Oxide Films in Al-Si Alloys *Journal of Minerals and Materials Characterization and Engineering* **3** 15–25
- [12] Fan Z, Zuo Y and Jiang B 2012 Apparatus and method for liquid metals treatment WO 2012035357 A1
- [13] Chen S L, Daniel S, Zhang F, Chang Y A, Yan X Y, Xie F Y, Schmid-Fetzer R and Oasted W A 2002 The PANDAT software package and its applications *Calphad* **26** 175–188
- [14] Yang W, Gao F and Ji S 2015 Formation and sedimentation of Fe-rich intermetallics in Al-Si-Cu-Fe alloy *Trans Nonferrous Met Soc China* **25** 1704–1714
- [15] Que Z, Wang Y and Fan Z 2018 Formation of the Fe-containing intermetallic compounds during solidification of Al-5Mg-2Si-0.7Mn-1.1Fe alloy *Materials and Metallurgical Transactions A* **49** 2173-2181
- [16] Ferraro S, Fabrizi A and Timelli G 2015 Evolution of sludge particles in secondary die-cast aluminium alloys as function of Fe, Mn and Cr contents *Materials Chemistry and Physics* **153** 168–179
- [17] Liu Y, Huang G, Sun Y, Zhang L, Huang Z, Wang J and Liu C 2016 Effect of Mn and Fe on the formation of Fe-rich intermetallics in Al-5Mg-Mn alloys solidified under rapid cooling *Materials* **9** 88
- [18] Bjunrenstedt A, Casari D, Seifeddine S, Mathiesen R H and Dahle A K 2017 In-situ study of morphology and growth of primary α -Al(FeMnCr)Si intermetallics in an Al-Si alloy *Acta Materialia* **130** 1–9