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Iron-containing intermetallic phases in Al-Si based casting alloys

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Abstract

Iron is the most common impurity in aluminium and its alloys. It is not easily removed and it can cause adverse effects to ductility and castability, particularly in the popular Al-Si based casting alloys. The choice of whether to use alloys based on primary aluminium (low Fe levels, high cost) or secondary aluminium (moderate/high Fe levels, cheaper) for a cast product is often a commercial decision. However, a compromise may be necessary between the desire for reduced metal cost and the need to maximise casting productivity via reduced defect formation and to minimise the deleterious effect of iron on mechanical properties. This paper discusses the various sources of iron, how it enters aluminium alloys, the way that iron leads to the formation of complex intermetallic phases during solidification and how these phases can adversely affect mechanical properties (especially ductility) and lead to the formation of excessive shrinkage defects. The formation of the iron-containing β phase will be highlighted using the latest in situ solidification study using synchrotron X-radiation. The paper offers guidelines to the practical levels of iron that can be tolerated and how to minimise the negative effects of iron.

Keywords: Al-Si alloys, intermetallics, castability, mechanical properties

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1. Introduction

Iron is a common impurity in aluminium alloys that arises from a number of possible sources and which, at least for Al-Si based casting alloys, is usually considered detrimental in one or more ways. These will be discussed later in this paper. It should be noted however that iron does not always exert a negative influence: in certain wrought aluminium alloys (that is, alloys used in forged, extruded or rolled forms), iron can be a deliberate alloying addition that is made to improve the processability of the alloy and/or the strength of the final wrought product. These wrought alloys are not of specific interest to the foundry industry, which instead works with the casting alloys, particularly those based on the Al-Si family.

Iron is a natural impurity that arises during the manufacture of primary aluminium via the Bayer Process that converts bauxite (the ore) into alumina (the feedstock) and the subsequent Hall-Héroult electrolytic reduction process that converts alumina into molten aluminium (> 950ºC). Depending on the quality of the incoming ore and the control of the various processing parameters and other raw materials, molten primary aluminium metal typically contains between 0.02 – 0.15 wt.% iron, with ~ 0.07 – 0.10 % being average.

There is no known way to economically/commercially remove iron from aluminium so these primary Fe values are the typical baseline and all further melt activities only serve to potentially increase the iron level. Iron can enter the melt during further downstream melt activity through two basic mechanisms:

- Liquid aluminium is capable of dissolving iron from unprotected steel tools and/or furnace equipment. Equilibrium Fe levels can reach 2.5 wt% in the liquid phase at normal melt temperatures of ~700ºC and up to 5 wt% for a melt held at 800ºC, see Fig. 1 [Phillips, 1959].
- Iron can also enter an aluminium melt via the addition of low-purity alloying materials, e.g. silicon, or via the addition of scrap that contains higher background iron levels than the primary metal.

These mechanisms are the reason that Fe levels in Al alloys continue to increase with each remelt cycle, and why secondary alloys, particularly those Al-Si alloys destined for high pressure die casting (HPDC), can end up containing iron up to 1.5%. In the case of HPDC, this is not always a bad thing as high Fe content assists in minimising the costly problem of die soldering [Shabestari and Gruzleski, 1994]. However, typical secondary Al-Si alloys for non-HPDC casting operations usually contain much lower Fe levels ranging from ~ 0.25 to 0.8 wt%, with values around 0.4-0.7% being most common. The reason these moderate iron level alloys find such wide use arises from the necessary commercial balance between the benefits of reduced metal cost and the acceptable loss of some processing capability and/or mechanical properties. These detrimental effects of iron will be considered in later sections (Sections 4 and 5), after first considering what happens to the iron impurity during solidification (Section 2) and subsequent heat treatment (Section 3) of Al-Si alloys.

2. Formation of iron-containing intermetallics during solidification

Although iron is highly soluble in liquid aluminium and its alloys, it has very little solubility in the solid (max. 0.05 wt %, 0.025 atom %) [Phillips, 1959] and so it tends to combine with other elements to form intermetallic phase particles of various types [Mondolfo, 1976]. In the absence of Si, the dominant phases that form are Al_3Fe and Al_6Fe, but when Si is present, as in the most common foundry alloys, the dominant phases are the hexagonal α-Al_8Fe_2Si phase and the monoclinic/orthorhombic β-Al_5FeSi phase (also reported as $Al_{4.5}FeSi$ stoichiometry) [Kral, 2005]. If Mg is present with Si, an alternative phase can form, π-$Al_8FeMg_3Si_6$ (also reported as $Al_9FeMg_3Si_5$ stoichiometry). Another phase that forms when Mn is present with Si is the cubic $Al_{15}(Fe,Mn)_3Si_2$, also confusingly called α-phase. This phase tends to form in preference to the hexagonal α-phase whenever Mn is present. There are also less common phases which form when other elements are present, e.g. Ni, Co, Cr, Be, but these are beyond the scope of this paper. More detailed information on iron-bearing intermetallic phases can be found in several experimental studies and review papers published over the years [Phillips and Varley, 1943; Phragmén, 1950; Couture, 1981; Crepeau, 1995; Taylor, 1995; Mbuya et al., 2003].

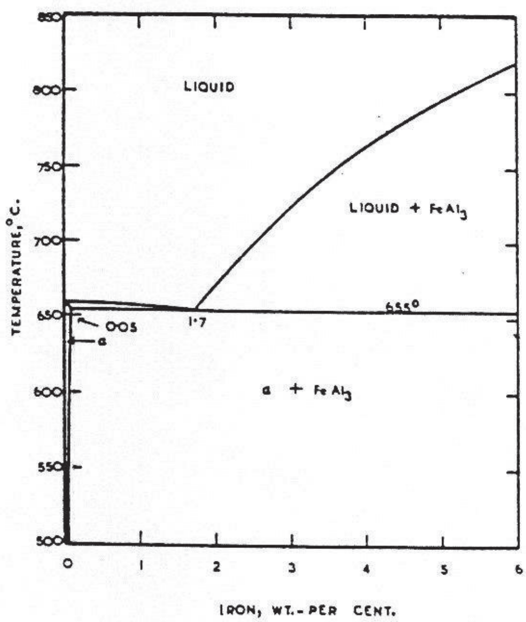


Fig. 1. Binary Al-Fe equilibrium phase diagram [Phillips, 1959].

The iron-containing intermetallic phases listed above are quite obvious within the microstructures of Al-Si alloys, and can usually be distinguished under the microscope by their dominant shape (morphology) and colour (unetched and etched). Both of the so-called α-phases form with a Chinese script morphology (see Fig. 2b) but the $Al_{15}(Fe,Mn)_3Si_2$ version is also found as a more compact blocky form, and sometimes as polyhedral crystals. The π-phase also forms with the a script-like morphology (Fig. 2d) and is often, but not always, closely connected via a peritectic reaction to the β-phase (Fig. 2c) which in turn forms with a distinctive platelet morphology (Figs. 2a, 2c). Note that although β-phase has a platelet form in three-dimensions, when observed in a two-dimensional image, the platelets appear to be "needles", and are often misleadingly described this way. The differing morphologies of these iron intermetallics are in part responsible for the impact of iron on castability and mechanical properties.

A critical issue for the impact of iron-containing intermetallics is the time or temperature at which the different phases form during solidification. This is influenced by both the concentration of the elements involved and cooling rates. Fig. 3 shows a typical cooling curve of an Al-Si-Cu-Mg-Fe alloy with the location(s) of intermetallic phase formation indicated. Intermetallic particles that form prior to the solidification of the aluminium dendritic grain network (i.e. that grow freely within the liquid phase) or that form independently at the same time as the dendritic network tend to grow relatively large. Particles that form much later, i.e. during or after the period of Al-Si eutectic solidification, are comparatively smaller because there is less liquid space available for growth to occur during later stages. Generally speaking, the larger the particle, the more detrimental its effects on properties and processability are likely to be.

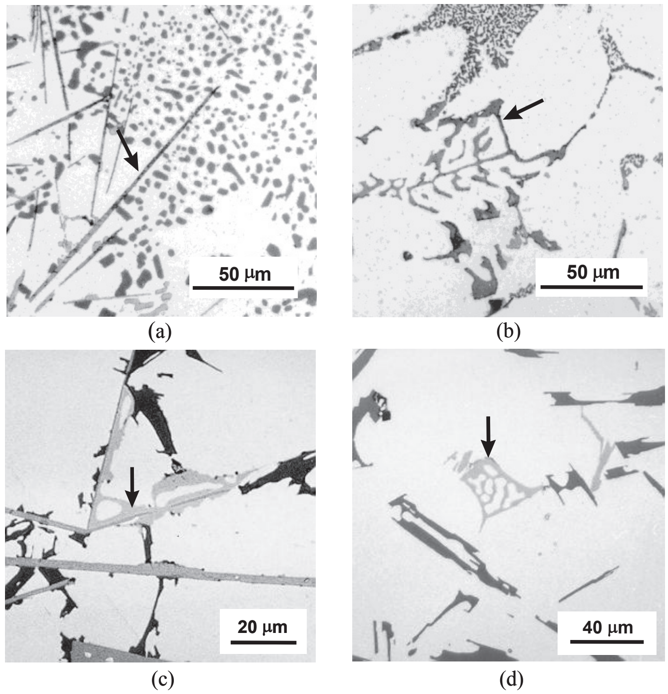


Fig. 2. Micrographs of various common iron-containing intermetallics showing their typical morphologies in an Al-5Si-1Cu-0.5Mg-(Fe) alloys: (a) β-Al_5FeSi platelets; (b) script-like α-Al_8Fe_2Si; (c) π-$Al_8FeMg_3Si_6$ phase growing from β; (d) script-like π-phase.

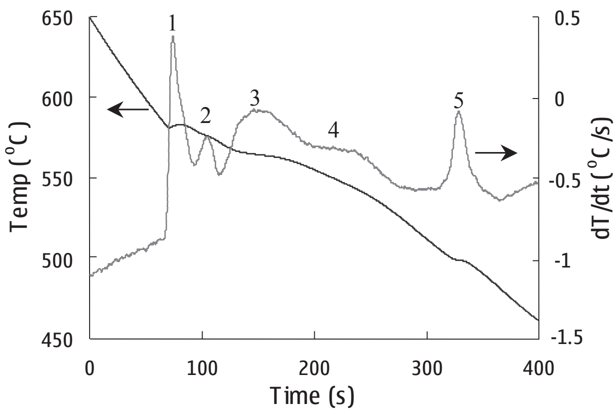


Fig. 3. Typical cooling curve (T vs. t) and cooling rate curve (dT/dt vs. t) for an Al-9Si-3Cu-0.5Mg-1.0Fe alloy. The labelled peaks represent the following reactions: (1) primary Al dendrites; (2) β-Al_5FeSi; (3) Al-Si eutectic; (4) complex Mg_2Si eutectic; (5) complex Al_2Cu eutectic [Dinnis et al., 2004].

Increasing the concentration of Fe (and/or Mn) in the alloy also results in the earlier formation of the dominant intermetallic phase and hence more unconstrained growth of particles is able to occur. A slower cooling rate also increases the risk of forming large particles because the time available for unconstrained growth is increased. Iron-bearing intermetallics (especially β-Al_5FeSi platelets and α-$Al_{15}(Fe,Mn)_3Si_2$ script) can grow up to several millimetres in size in slowly-cooled Al-Si alloy castings with high Fe and/or Mn levels. However, under normal casting conditions and with moderate Fe levels, these intermetallics grow more typically in the size range of 50 – 500 μm. In castings with very high cooling rates (e.g. HPDC) and/or when using low Fe levels (e.g. primary alloy ingot), the intermetallic particles are typically of the order of 10 - 50 μm. The effects of Fe level and cooling rate (as indicated by secondary dendrite arm spacing, SDAS) can be seen in Fig. 4 [Vorren et al., 1985].

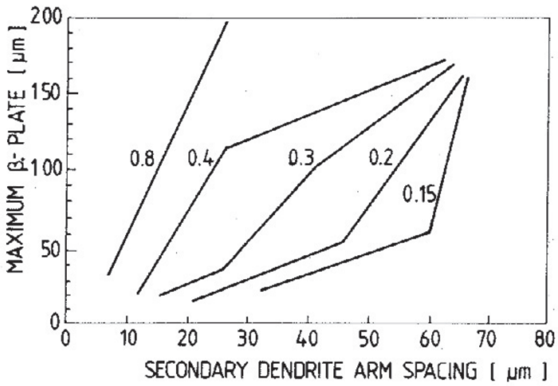


Fig. 4. Graph showing trends of maximum observed length of β phase platelets versus secondary dendrite arm spacing for an AlSi7Mg0.3 alloy containing various amounts of iron [Vorren et al., 1985].

There have only been a few attempts made to study the 3-dimensional structure of the iron-containing intermetallic phases in Al-Si alloys. Apart from deep etching techniques [Simensen et al., 1984; Gupta et al., 1996] used to directly reveal intermetallic particles denuded of surrounding matrix (successfully applied in wrought Al alloy studies [Chen, 1998]), the only other common technique that can be applied is serial sectioning of polished metallographic samples. Dinnis *et al.* [Dinnis et al., 2005] carried out such serial sectioning of both α- and β-phase particles in an Al-Si-Fe-(Mn) alloy and then reconstructed those sections to reveal the 3-D morphology of these key phases (Fig. 5).

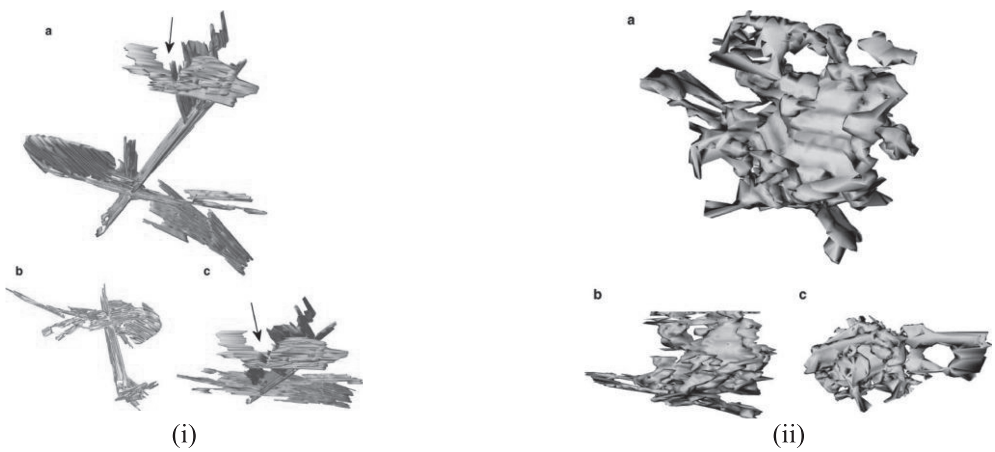
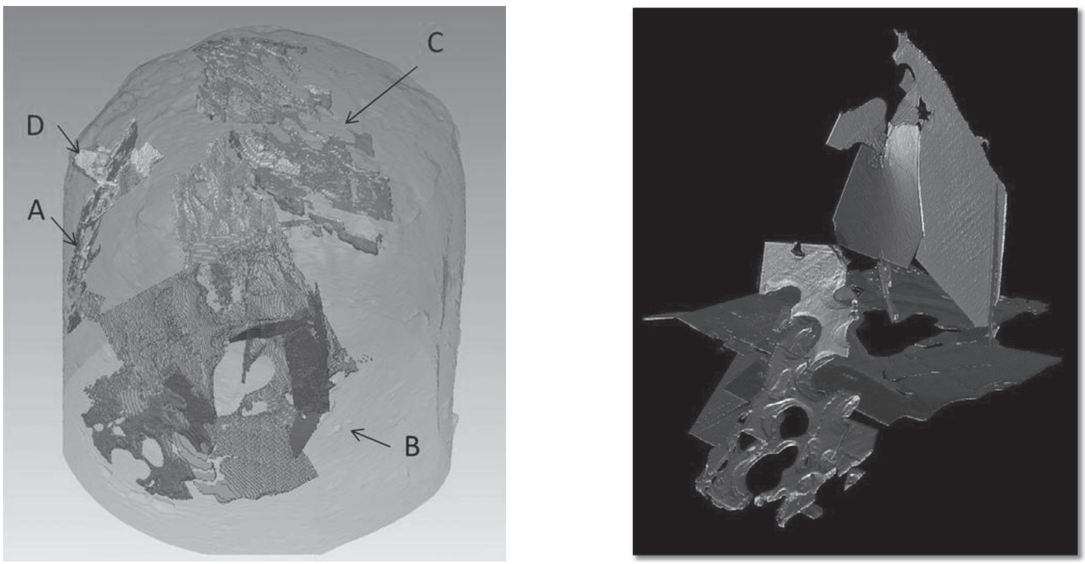


Fig. 5. 3-D reconstructions of (i) interconnected β-Al_5FeSi platelets and (ii) script-like α-$Al_{15}(Fe,Mn)_3Si_2$ phases, following serial sectioning of polished metallographic samples [Dinnis et al., 2005].

More recently, Lee *et al.* [Lee et al., 2009] carried out 3-D reconstruction of β phase particles in an solidified Al-Si-Cu-Fe alloy using synchrotron X-ray tomography. They identified a number of independent platelets within the microstructure. They also carried out 2-D in situ observations of the same alloy during solidification and identified and measured the growth rates of several β phase platelets. They observed very rapid longitudinal growth initially, followed by a period of slower diffusion limited growth.

The most recently reported work by Terzi *et al.* [Terzi et al., 2010] carried out an in-situ solidification study of an Al-8Si-4Cu-0.8Fe alloy using a synchrotron X-radiation beam line at ESRF in Grenoble. In this work, they were able to observe in real time the 3-D formation of β phase intermetallic particles. Subsequently, the gathered image data were processed and reconstructed to visualise the nucleation and growth sequence of several β phase particles (Fig. 6) in the context of the α-Al/β-Al_5FeSi irregular eutectic reaction. It was noted that nucleation of β particles occurred at or near the surface oxide of the sample, but that the growth of the β component of the eutectic grew largely independent of the Al eutectic phase. Interaction with primary Al dendrites or with other β platelets was the trigger to promote the branching of platelets commonly observed. Note: the nucleation of β phase on γ-Al_2O_3 seems to have been first proposed by Narayanan *et al.* [Anantha Narayanan et al., 1994].



(a) (b)

Fig. 6. Reconstructed β phase platelets from a solidifying Al-8Si-4Cu-0.8Fe alloy imaged by synchrotron X-ray [Terzi et al., 2010]: (a) the entire sample at 573°C showing four independent nucleation/growth events at low resolution; (b) high resolution reconstruction of one complex β event after solidification was complete.

3. Heat treatment of iron-containing intermetallic phases

The iron-containing intermetallic phases in Al-Si based alloys are generally largely unaffected by typical T4 or T6 heat treatments, with one notable exception (see below). This means that the α and β phases, apart from undergoing some degree of fragmentation, spheroidisation and Ostwald ripening with increasing soak time, show little sign of undergoing any phase transformations at typical solutionising temperatures of ~540°C max. However, it is a little different in the wrought aluminium alloys, particularly the 6xxx extrusion alloys, where homogenisation treatments are commonly applied to convert the harmful β phase to α phase (known as the β → α transformation) so that extrusion performance and properties are improved. This transformational treatment occurs at slightly higher temperatures, ~580-620°C.

The exception (noted above) occurs in Al-Si-Mg based casting alloys such as A356 and A357. During solution treatment, three key actions occur: (i) the eutectic Si phase is broken up and spheroidised; (ii) the Mg_2Si particles dissolve releasing Mg solute for subsequent precipitation hardening; and, (iii) the solute levels become homogenised across the aluminium grains [Apelian et al., 1990]. However, another transformation also occurs during the solution treatment stage that is often missed or ignored. This is the π to β phase transformation (which releases further Mg for precipitation hardening) [Taylor et al., 2000a; Taylor et al., 2001a; Taylor et al., 2001b]. The transformation occurs to various degrees, but is particularly noticeable when the Mg content lies in the mid-range of 0.35-0.55 wt%. This additional release of Mg leads to slightly improved mechanical properties following the full T6 treatment, but the property gain also occurs because some of the large script-like π-phase particles are dissolved and replaced by re-precipitated fine-scale β needles/platelets (Fig. 7).

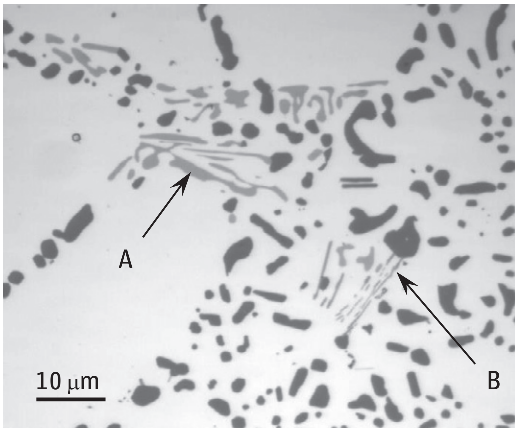


Fig. 7. Micrograph showing the formation of fine "needles" of β phase (arrow B) as the script-like π phase (arrow A) dissolves during solution treatment of an Al-7Si-0.4Mg-0.12Fe alloy at 540°C.

4. Effect of iron-containing intermetallics on mechanical properties

The effect of iron on the mechanical properties of aluminium alloys has been reviewed extensively by several authors [Couture, 1981; Crepeau, 1995; Mbuya et al., 2003]. It is consistently reported that as Fe levels increase, the ductility of Al-Si based alloys decreases. This is usually accompanied by a decrease in tensile strength; however in general, the yield strength remains largely unaffected by iron, unless ductility is reduced to such an extent that brittle fracture occurs prior to yield.

The detrimental effect of iron begins at quite low primary Fe levels but becomes much more serious once a critical Fe level (dependent on alloy composition) is exceeded. Note: The concept of a silicon dependent critical iron content for Al-Si based alloys was introduced by Taylor *et al.* [Taylor et al., 1999a; Taylor et al., 1999b; Taylor et al., 1999c] in the context of castability, not properties, but mechanical behaviour can be similarly described. The detrimental effect of iron on ductility is due to two main reasons:

- the size and number density of iron-containing intermetallics (particularly the deleterious β-phase) increases with iron content, and therefore since these participate directly in the fracture mechanism, the more intermetallics there are, the lower the ductility;

- as iron level increases, porosity also increases (see Section 5), and this type of casting defect also has a significant impact on ductility

The critical iron level is directly related to the silicon concentration of the alloy. Fig. 8 shows a section of the liquidus projection of the Al-rich corner of the Al-Si-Fe ternary phase diagram (with additional construct lines) that highlights the existence of a critical iron content. As the silicon content of the alloy increases, the amount of iron that can be tolerated before the β-phase starts to form prior to the Al-Si eutectic increases. At 5% silicon, the critical iron content is ~0.35%, at 7%Si it rises to ~0.5, at 9% it is ~0.6 and by 11% it reaches ~0.75%. Also for a given Fe content, the temperature (and therefore time) at which β can form prior to Al-Si eutectic decreases with increasing Si content. The line AB between the β phase field and the Al phase field is the period during which the larger and more detrimental intermetallic particles form.

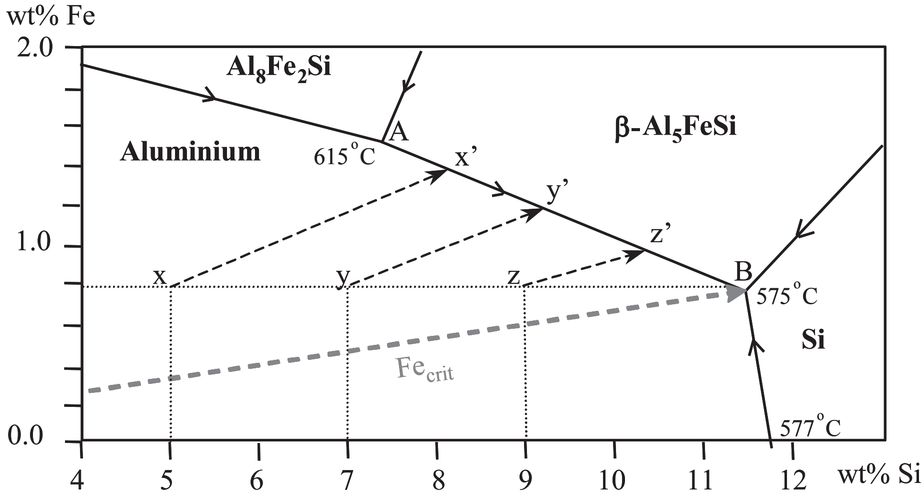
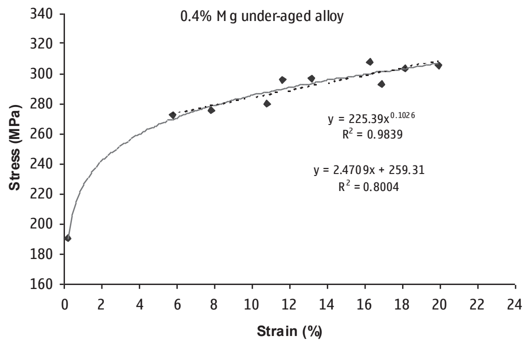
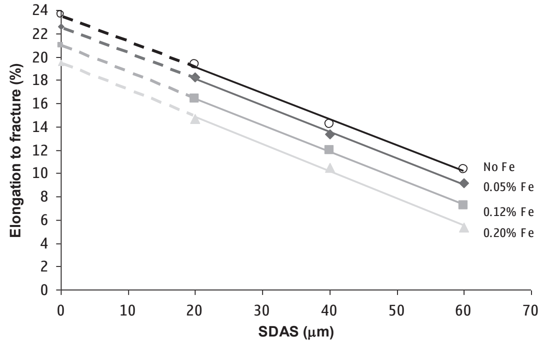


Fig. 8. Simplified liquidus projection of the ternary Al-Si-Fe system, showing primary Al solidification paths (using Scheil assumptions) for alloys with Fe_{crit} iron levels (red dashed line), and for 5%Si (x-x'), 7%Si (y-y')and 9%Si (z-z') alloys with 0.8%Fe. The points of intersection with line AB is where the formation of large β phase platelets starts to occur prior to formation of ternary eutectic at B.

When a given cast aluminium alloy (at a given heat treatment, if any) is subjected to tensile testing and elongated to the point of failure, and the fracture points (fracture stress, fracture strain) of each test are plotted, they are seen to fall along a line of the form shown in Fig. 9a [Taylor et al., 2000b]. They fall along a common line because they share a common yield point and work hardening rate exponent. The different points of fracture occur because of the combined effects of several variables including casting defects (e.g. oxides and porosity), cooling rate (secondary dendrite arm spacing, SDAS) and Fe content. As an alloy contains fewer defects, has higher cooling rate (reduced SDAS) and/or lower Fe content, the fracture points of the tensile specimens move to higher levels of both ductility and tensile strength. If only the best fracture points of samples are taken for each SDAS and Fe content (thus effectively eliminating the role of defects) and plotted against elongation to fracture, as in Fig. 9b, the effect of Fe content on ductility can be clearly seen. In the example shown, an Al-7%Si-0.4%Mg alloy made from low-iron primary aluminium given a particular under-aged T6 treatment demonstrates a strong influence of even small amounts of iron, even when cooling rates are high (i.e. at low SDAS). Unfortunately, as noted previously, iron intermetallic particles are not substantially altered during subsequent heat treatment.



(a)

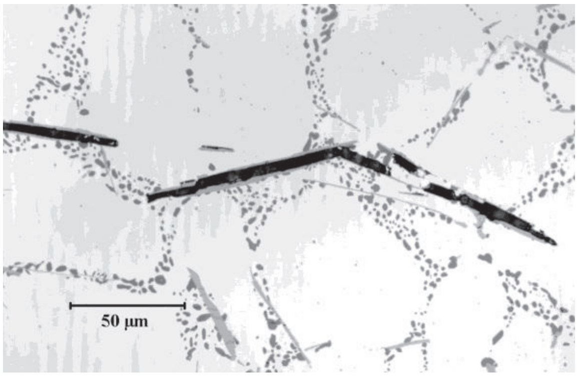


(b)

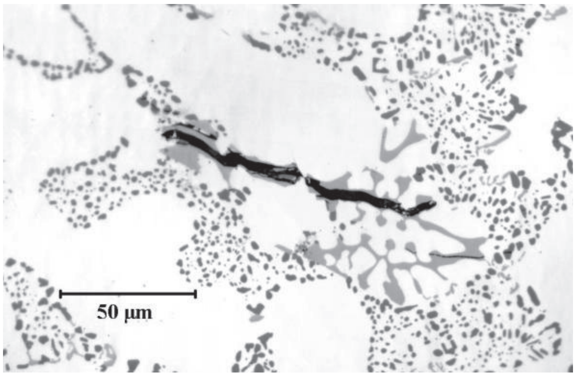
Fig. 9. Graphs showing (a) the best average fracture points for under-aged Al-7%Si-0.4% Mg alloy (with varying Fe levels and SDAS values) and the lines of best fit; and (b) maximum ductility (i.e. best elongation to fracture) as a function of SDAS for various Fe contents (including hypothetical zero iron) for tensile specimens of the same alloy [Taylor et al., 2000b].

In many instances however, the effect of iron on an alloy's ductility is not so clearly demarcated because as the Fe level increases above Fe_{crit} , the cooling becomes slow and/or the number and size of casting defects increases, the ductility tends to drop to extremely low levels, < 1%, and sometimes tensile specimens fail before yielding (i.e., < 0.2% elongation).

The reason that Fe-containing intermetallic particles are detrimental to an alloy's mechanical properties is that they are much more easily fractured under tensile load than the aluminium matrix or the small silicon particles (if they have been refined through Na- or Sr-modification) [Cáceres et al., 2003; Cáceres and Taylor, 2006]. Micro-cracks tend to initiate at these particles and they provide easy pathways for macro-cracks to propagate through. Fig. 10 shows samples of both β-Al_5FeSi platelets and α-$Al_{15}(Fe, Mn)_3Si_2$ script-like particles that have fractured under tensile loading. It should be noted that the β platelets tend to be much more prone to fracture and crack linkage than the α script particles; the latter tending to be more isolated, while the former are often connected together as "strings" along grain boundaries.



(a)



(b)

Fig. 10. Micrographs of fractured (a) β-Al_5FeSi platelets, and (b) an α-$Al_{15}(Fe, Mn)_3Si_2$ script particle in tested tensile bars of Al-5%Si-1%Cu based alloys [Cáceres and Taylor, 2006].

This observation helps to explain the commonly accepted practice of adding Mn to Fe-containing Al-Si alloys to promote the formation of the α phase instead of the more detrimental β phase. This process has been called iron neutralisation, or iron correction [Couture, 1981; Murali et al., 1994]. The Mn is typically added at a Mn:Fe ratio of at least 0.5, however detailed microstructural observations of a range of Al-Si-Cu-Mg alloys has shown that even when Mn is added to these levels it is not always possible to completely eliminate the β phase platelets [Dinnis and Taylor, 2007]. Furthermore, the addition of Mn actually results in a higher volume fraction of iron intermetallic particles that can counter some of the ductility gains to be made. It can also lead to machining difficulties, especially when the hard α phase forms in very large, colonies within the alloy [Mondolfo, 1976].

Other iron neutralising/correcting elements have been identified and proposed, e.g. Co, Mo, Cr, Ni and Be [Mondolfo, 1976; Couture, 1981; Gustafsson et al., 1986; Murali et al., 1994], all of which change the iron intermetallic phase that forms, but none of these find any widespread use, partly because of cost but also because of health and safety issues. Strontium, a common eutectic Si modifying element has also been shown to exert a slight refining influence on β phase size [Liu et al., 2009].

In recent years, Cáceres *et al.* [Cáceres et al., 2003; Cáceres and Taylor, 2006] have observed that increasing silicon content provides a refining and dispersing influence on the key intermetallic phases (α, β, and Al_2Cu) in various Al-Si-Cu-Mg-(Fe,Mn) alloys. This translates to comparable Quality Index (QI) values in low Si, low Fe alloys and high Si, high Fe alloys, with the low Si, high Fe alloy variants being significantly inferior. However, it has been noted that the refining influence of Si only operates in alloys containing Cu [Taylor et al., 2008]. The mechanism remains unclear.

5. The effect of iron content on castability

The effect of iron on castability of Al-Si based alloys has been reviewed by Taylor [Taylor, 1995] and more recently by Mbuya *et al.* [Mbuya et al., 2003]. It is generally agreed that iron has the potential to seriously degrade castability, in particular through an increased tendency to form porosity at high iron levels, but no particular mechanism enjoys universal agreement. There are two popular theories. First, high Fe levels result in more β particles which then act as nucleation sites for porosity [Roy et al., 1996]. This mechanism does not stand up to scrutiny and observations of some pores in close association with β platelets are merely coincidental, not cause and effect. The second idea is that large β platelets impede the flow of interdendritic liquid during feeding and thus shrinkage porosity forms more readily [Mascré, 1955]. This seems to be partly correct, although some other mechanism is also clearly at work.

An investigation carried out by Taylor *et al.* [Taylor et al., 1999a; Taylor et al., 1999b; Taylor et al., 1999c] noted the existence of a critical Fe content that depends on the silicon level of the alloy (Fig. 8). Iron levels above critical, resulted in a solidification sequence that saw the formation of β-phase platelets prior to the solidification of the Al-Si eutectic, and when this occurred there was an increased tendency to form extensive and damaging shrinkage porosity defects (Figs. 11 and 12a). Taylor proposed that the defect porosity occurred because Al-Si eutectic grains nucleated on these prior β platelets and it was this that led to the rapid breakdown in permeability and hence feeding. Taylor also observed that a minimum level of total porosity occurred at the critical Fe content (Fig. 12b) however later work by Otte *et al.* [Otte et al., 1999] and Dinnis *et al.* [Dinnis et al., 2004; Dinnis et al., 2006] showed that although the increase in shrinkage porosity is universal for Al-Si-(Cu)-(Mg) based alloys at super-critical Fe levels, the minimum in porosity level at the critical Fe content is in fact a special feature of only certain alloy compositions, particularly the low silicon alloys containing copper (e.g. 5% Si, c.f. 7-9%, with ≥ 1% Cu).

The detrimental effect of iron on porosity formation has been noted to be particularly prominent in regions of castings with marginal solidification conditions, i.e. poorly-fed hot spots. Nevertheless, increasing iron levels can also increase the level of background porosity, and hence the total porosity, throughout a casting even when the critical Fe content is not exceeded (Fig. 13).

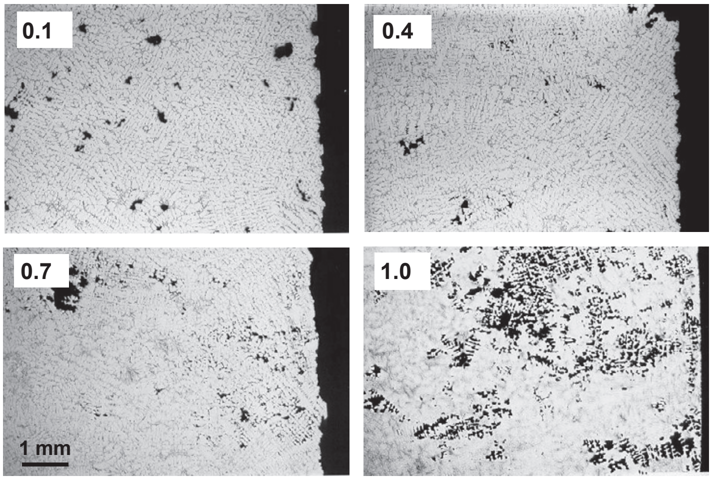


Fig. 11. Shrinkage porosity in the hot spot region of a cylindrical casting of Al-5Si-1Cu-0.5Mg alloy with varying iron levels (values shown). For this alloy, 0.4 is the critical Fe content [Taylor et al., 1999a].

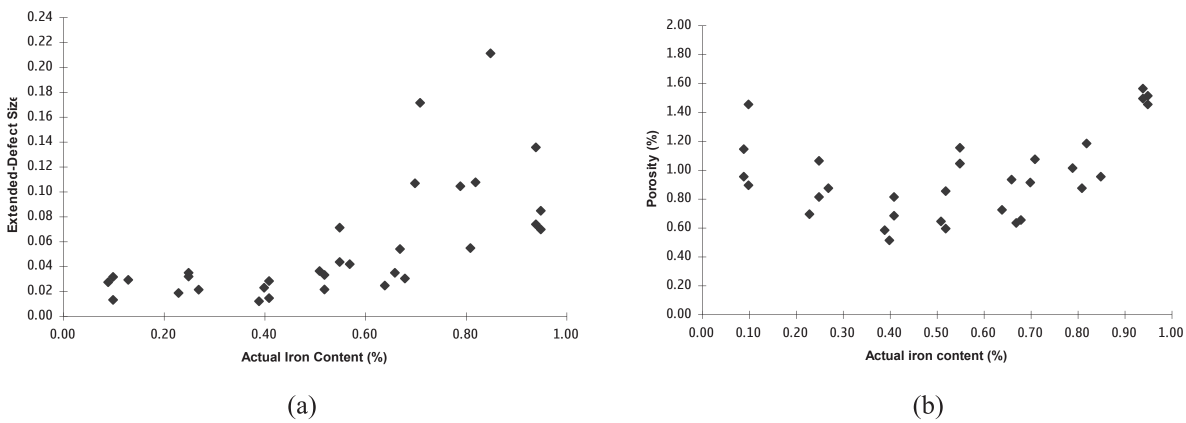


Fig. 12. Graphs of (a) hot spot (shrinkage defect) porosity in volume % vs. iron content showing a significant increase after the critical Fe content of 0.4%, and (b) total casting porosity in volume % vs. iron content showing a minimum at the critical Fe content, for cylinder castings made from Al-5Si-1Cu-0.5Mg alloy [Taylor et al., 1999a].

Dinnis *et al.* [Dinnis et al., 2004] studied how iron interacts with the developing grains of the Al-Si eutectic to degrade feeding and hence increase porosity. They observed that rather than the β-platelets acting as a strong nucleation sites for the eutectic (as proposed earlier by Taylor), an increased iron level actually results in a poisoning of nucleation sites (possibly in a similar way that Sr does) such that fewer, but much bigger Al-Si eutectic cells form (Fig. 14). It is these larger Al-Si eutectic cells, in conjunction with the large β-platelets that appear to reduce permeability and feeding, and hence increase shrinkage porosity.

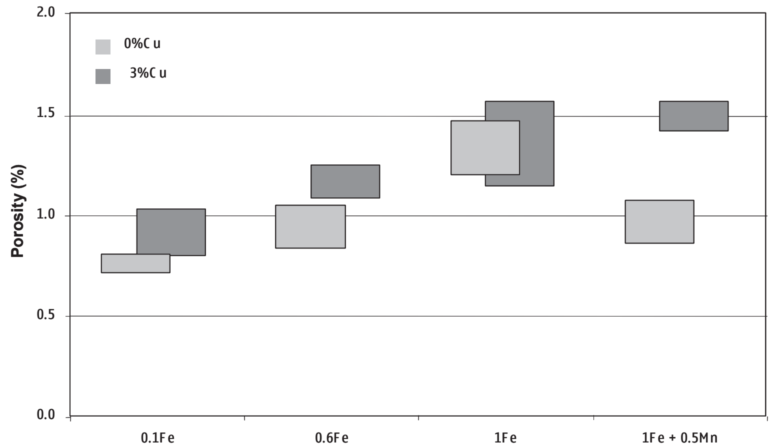


Fig. 13. Graph showing the continual increase in total casting porosity with increasing Fe content in both copper-free and copper-containing Al-9%Si alloy plate castings. The addition of Mn, an "iron-correcting" element reduces porosity in the copper-free alloy, but not in the Cu-containing alloy [Dinnis et al., 2004].

The use of iron correcting elements, particularly Mn and Be, for reducing casting porosity in Al-Si alloys with high Fe levels has been reported for many years [Iwahori et al., 1988]. Addition of Mn to achieve specific Mn:Fe ratios is a widespread practice in Al-Si based casting alloys to obtain improved mechanical properties (see §4), however it has also been observed to be beneficial in reducing porosity. It has been proposed that the α-phase does not restrict feeding in the same way that β-phase platelets do, or that the feeding temperature range is extended with manganese. However, the work of Dinnis *et al.* [Dinnis and Taylor, 2007] has shown that the presence of Mn in an alloy does not ensure improved porosity levels. Manganese alone in the absence of iron does not appear to do anything beneficial, even although the α-phase (Mn can fully substitute for Fe) is still dominant. Additionally, manganese appears to provide greater reductions in iron-related porosity in the absence of Cu (Fig. 13). It appears that the benefits provided by Mn additions probably relate to a reduction in the poisoning of Al-Si eutectic nucleation sites by Fe (Fig. 14). This results in the formation of a greater number of smaller Al-Si eutectic grains during solidification and this in turn results in improved permeability and feeding, and hence provides a reduction in overall porosity. It can also be seen in Fig. 13, that the addition of 0.5% Mn to a 1% Fe-containing Al-9%Si alloy is sufficient to reduce porosity levels to those obtained in the same alloy with 0.6% Fe (i.e. the critical iron content for that composition).

6. Practical guidelines for Al-Si casting alloys

- Wherever possible, iron levels in Al-Si alloys should be kept as low as practical in order to avoid the detrimental effects on mechanical properties, particularly ductility and fracture toughness. This means minimising iron contamination through careful selection of raw materials (i.e. ingots, silicon, etc.) and the maintenance of good coatings on all steel tools used to prepare melts.
- Iron levels above the critical level for the silicon content of the alloy should be avoided as these can cause serious loss of ductility in the final cast product and decreased casting productivity through increased rejects due to shrinkage porosity.
- The critical iron content (in wt%) for an alloy can be calculated using the following relationship:

$$Fe_{crit} \approx 0.075 \cdot [\text{wt\% Si}] - 0.05.$$

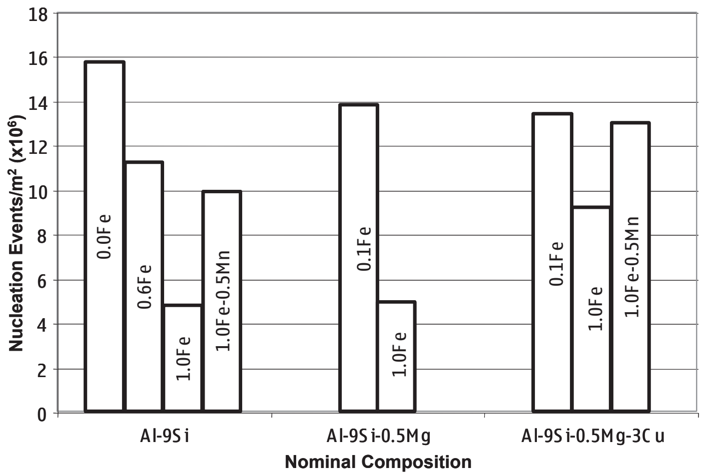


Fig. 14. The effect of iron and manganese additions on the Al-Si eutectic grain nucleation density for three different Al-9%Si alloys. Increasing the iron level reduces nucleation density, while Mn alleviates the poisoning effect of iron to some extent [Dinnis et al., 2004].

- If solidification/cooling rates are very high (as in high pressure die casting), super critical iron contents may not be detrimental, but as the cooling rate decreases (as in gravity die casting through to sand casting, etc.) the probability of super critical iron levels causing problems dramatically increases. Very slow cooling rates can lead to the formation of very large β platelets.
- Normal heat treatment regimes for Al-Si alloys, e.g. T6, do not generally alter the nature of the deleterious Fe-containing phases. As-cast intermetallics are retained and although the overall performance of an alloy may be improved by heat treatment, the properties can be improved further with low iron levels.
- Additions of Mn to neutralise the effects of iron are common, at Mn:Fe ratios of ~ 0.5, however, the benefits of this treatment are not always apparent. Excess Mn may reduce the amount of β-phase and promote α-phase formation and this may improve ductility, but it can lead to hard spots and difficulties in machining. Mn additions do not always improve castability or reduce porosity in high Fe alloys. The effect of Mn is sensitive to overall alloy composition.
- The addition of Mn to melts with high iron levels can also promote the formation of "sludge", if the sludge factor (as expressed by [%Fe] + 2[%Mn] + 3[%Cr]) exceeds a particular value for a given alloy and melt holding temperature. This in-liquid precipitation can pose a serious problem for die-casters who use low melt holding temperatures and high impurity secondary alloys.

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