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Chapter 5

OVERVIEW OF BETA-AL_5FESI PHASE IN AL-SI ALLOYS

M. Mahta[1], M. Emamy[1], X. Cao[2, 3] and J. Campbell[3]
[1] School of Metallurgy and Materials, University of Tehran, Tehran, Iran
[2] Aerospace Manufacturing Technology Center, Institute for Aerospace Research,
National Research Council Canada, 5145 Decelles Avenue, Montreal, Quebec,
Canada, H3T 2B2
[3] Department of Metallurgy and Materials, University of Birmingham, B15 2TT, UK

Abstract

In aluminum alloys one of the most pervasive and important impurity elements is iron, stemming from the impurities in bauxite ores and the contamination of ferrous metals such as melting tools. Since iron has a very low solid solubility in aluminum (max. 0.05%), almost all iron in aluminum alloys is present in the form of second intermetallic phases. One of the most common Fe-rich intermetallics that form in cast and wrought aluminum alloys upon solidification is the β-Al_5FeSi phase. This phase has long been thought to be brittle and responsible for the inferior mechanical properties (in particular ductility) of aluminum cast alloys. The commonly accepted method to ameliorate the harmful influence of iron is the addition of one or more corrective elements. Such additions generally convert the β-Fe platelets into α-Fe dendrites. Various studies have been carried out by researchers on the modification of β-Al_5FeSi intermetallics in aluminum alloys using Mn, Cr, Co, Mg, Sr, Li and Be. The relative effectiveness of these elements is collected and compared in the present review. The mechanisms for the action of the chemical modifiers are critically reviewed particularly in the light of the modern theory of their nucleation on oxide films present in aluminum melts, probably in large populations. The new insights into the Fe-rich phase in aluminum alloys will aid in better understanding the role of iron in aluminum alloys.

Introduction

Aluminum alloy castings are extensively used to manufacture a large number of components for automotive and aerospace industries. However, the mechanical properties and casting quality of these materials are strongly determined by the microstructures of the alloys. It is common to add a number of different alloying elements to improve mechanical properties and simultaneously suppress the impact of some unwanted impurities, particularly iron because of its serious effect on mechanical properties.

The presence of Fe, even in small amounts, degrades the mechanical properties of aluminum alloys such as strength, fatigue, fracture toughness, and especially the ductility, since it forms β-Al_5FeSi intermetallic phase in a plate-like morphology (needle-like in 2D cross-section). Figure 1 exhibits some β-Fe intermetallics in A413 alloy with high concentration of Fe and without any modifiers. Because of its importance, the phenomenon has been reviewed many times before [1-10].

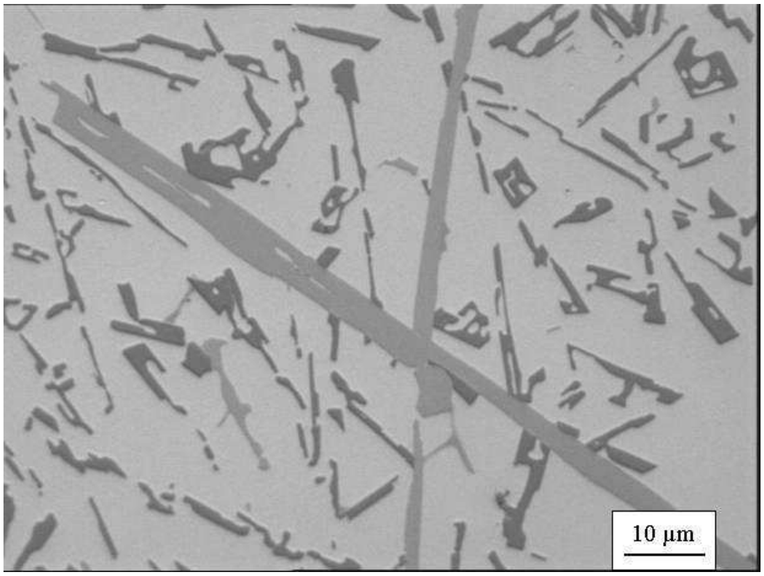


Figure 1. Microstructure of A413 alloy with 1.1 wt% Fe showing β-Fe platelets surrounded by unmodified eutectic silicon particles.

The liquid solubility limits for Fe in aluminum alloys is 1.87 wt% at 655 °C but its solid solubility is only 0.052 wt% at 655°C and is less than 0.01 wt% at 427°C [11,12]. Therefore, during solidification and cooling, there is a strong driving force for the formation of Fe-rich intermetallic compounds containing Al and other alloying elements. Typical morphologies of Fe-rich intermetallics include plate-like β-Al_5FeSi (β-Fe), and dendritic α-Al_8Fe_2Si, i.e. α-Fe, often reported as α-$Al_{12}Fe_3Si_2$ with a probable range of existence of 30-35% Fe and 6-12% Si [13]. In the presence of Mn, the α-Fe phase will precipitate as α-$Al_{15}(FeMn)_3Si_2$. Recently Kral et al. [14,15] has revealed that the Chinese script α-Fe phase is probably cubic $Al_{19}(FeMn)_5Si_2$. The crystal lattice of β-Fe is generally taken to be monoclinic [13,16,17], or $Al_3(FeMn)Si_2$ tetragonal [14,15] (or pseudo-tetragonal) [18,19], or perhaps a multi-layer composite including an orthorhombic phase [20]. Its growth is limited mainly to two dimensions, forming large plates. In contrast, the crystal structure of the α-Fe is cubic (bcc) [13-15,21]. Thus its more uniform surface energy and structure allows it to grow more freely in three dimensions, forming a variety of morphologies.

The work by Kral et al. [14] showed that the α-Fe and β-Fe phases may not clearly exhibit the dendritic (Chinese script) or plate shapes, respectively, and therefore cannot always be identified by their morphologies. Mondolfo [13] reported that Al_5FeSi phase may appear in either Chinese script or platelet form. Even so, acknowledging these reservations, intermetallic phases are generally identified based upon their morphology and/or energy dispersive X-ray spectra (EDS) [14,15,19-21], and there seems little doubt that this usually leads to correct identification. Crystallization of various morphologies of Fe-rich intermetallics is shown in Figure 2. The β-Fe has a well-defined stoichiometry and compared with the α-Fe phase, it dissolves smaller amounts of other corrective elements such as Mn, Cr and Co [22]. In addition, the final morphology of intermetallics in aluminum foundry alloys is greatly affected by casting conditions, particularly the solidification and cooling rates, and alloy chemistry.

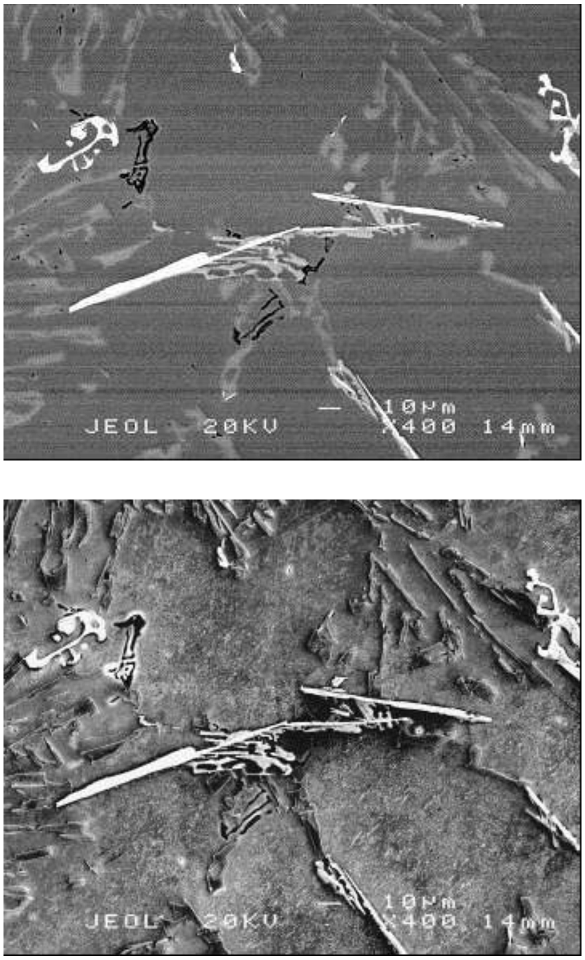


Figure 2. Typical α-Fe, β-Fe and π-Fe phases in Al-11.5Si-0.4Mg cast alloy containing Fe and Mn

In the present review work, the damage and modification mechanisms of β-Fe phase are critically reviewed, and the effectiveness of the various chemical elements as modifiers is compared.

Damage Mechanism

The powerful deleterious effect of the presence of β-Al_5FeSi has generally been attributed to its stress raising potential as a result of its plate-like morphology, and its apparently brittle nature. In addition, Iwahori and coworkers [23] reported that the presence of the plate-like intermetallics considerably increases cracking tendencies and shrinkage cavities during solidification, because of the blockage of the interdendritic channels, thus hindering the flow of liquid metal to feed solidification shrinkage at a late stage of solidification [24,25]. The presence of interdendritic shrinkage cavities adjacent to β-Fe particles has all the appearance of compelling evidence for this mechanism. Even so, there are some authors [26-28] who claim that the presence of porosity and shrinkage defects are not directly related to β-Fe intermetallic particles, but propose that the phenomenon may be due to the effect of β-Fe platelets on the nucleation and growth of eutectic silicon. A further mechanism is proposed here that harmonizes the observations on which both of these approaches are based, introducing the concept of the growth of β-Fe on double oxide film (bifilm) substrates as will be discussed below.

Recent researches have shown that doubled-over oxide films (bifilms) form substrates for the nucleation and growth of iron-rich particles [29-34]. Oxide films become incorporated into melts by an entrainment process [35-39]. This is an enfolding mechanism whereby the oxide skin of the melt becomes incorporated into the bulk liquid. Folded oxide films in melts have two sides: the dry unbonded inner surfaces and their wetted exterior surfaces. The wetted outer interfaces of oxide films appear to act as preferred substrates for the nucleation and growth of some Fe-rich phases. It is expected that there will be good atomic contact between the wetted side of the film and Fe-rich phases or aluminum matrix [29]. However, the gaps between the dry sides constitute the cracks that are commonly observed in association with β-Fe particles. Such cracks are particularly straight for β-Fe (Figure 3), but more irregular for α-Fe (Figure 4). Both α-Fe and β-Fe phases can grow either on the one side or on both sides of the doubled-over film. Thus the cracks automatically form along either the side or the centre of the precipitate. Figure 5 shows a longitudinal crack associated with a β-Fe particle showing an apparent decohesion of the matrix along its upper part (formation of the precipitate only on one side) and along a more central axis in the lower part (formation of the precipitate on both sides of the doubled-over film).

When the melt is first poured, the internal turbulence is sufficiently strong to ensure that the entrained bifilm is repeatedly folded into a small volume, in which form, as a highly convoluted and compact, if somewhat untidy, defect, it is relatively harmless. However, the growth of the monoclinic β-Fe crystal forces a progressive straightening-out action on its substrate, causing the substrate (the bifilm) to become a significant planar crack, thus degrading the properties of the alloy [40]. The reported brittleness of the β-Fe particles is a natural, but perhaps erroneous conclusion drawn from their necessarily cracked appearance as a result of the presence of bifilms. The bifilm is not always observable as a crack in the β-Fe particles; the bifilm will only open to reveal its presence if gas or shrinkage problems operate; otherwise, it will remain closed and practically invisible. Its behavior as a crack, however, is not expected to be significantly impaired. The straightening of the bifilm from relatively harmless compact features into extensive planar cracks by the growth of β-Fe appears to be the mechanism whereby Fe reduces the ductility of Al-Si alloys [35]. In contrast, the α-Fe phase also nucleates and grows on convoluted and compact bifilms, but the bifilm is not straightened; its form remains compact and so relatively harmless because the higher crystal symmetry of the α-Fe phase does not strongly influence its growth morphology, allowing the crystal to be more influenced by the irregular shape of its substrate.

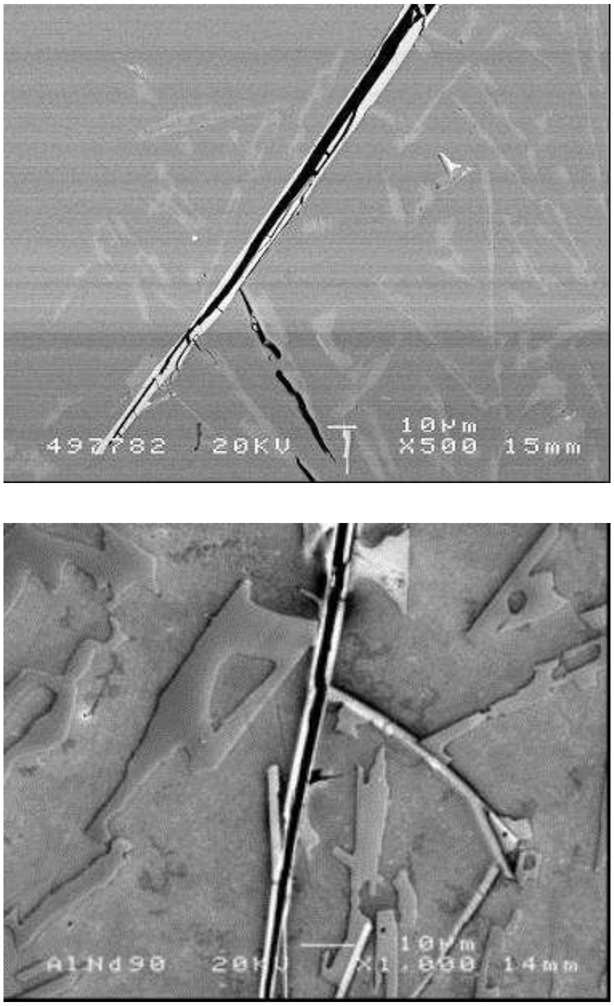


Figure 3. β-Fe platelet and its longitudinal crack in Al-11.5Si-0.4Mg cast alloy containing Fe and Mn

The second type of damage to the properties of castings linked with the presence of β-Fe particles is the apparent association of the particles with porosity, as though the particles have nucleated pores, or obstructed feeding. It is proposed here that the association with the pore occurs if the β-Fe particle happens to have formed on only one side of the bifilm as shown in Figure 6. The remaining oxide film on the opposite side of the bifilm is diaphanously thin, and therefore easily pulled away from its unbonded opposite half, and sucked deep into the dendrite mesh. By this mechanism a shrinkage pore or a gas pore is created, depending on conditions of either poor feeding reducing the external pressure, or high gas content in solution in the melt increasing the internal pressure in the bifilm [34-41].

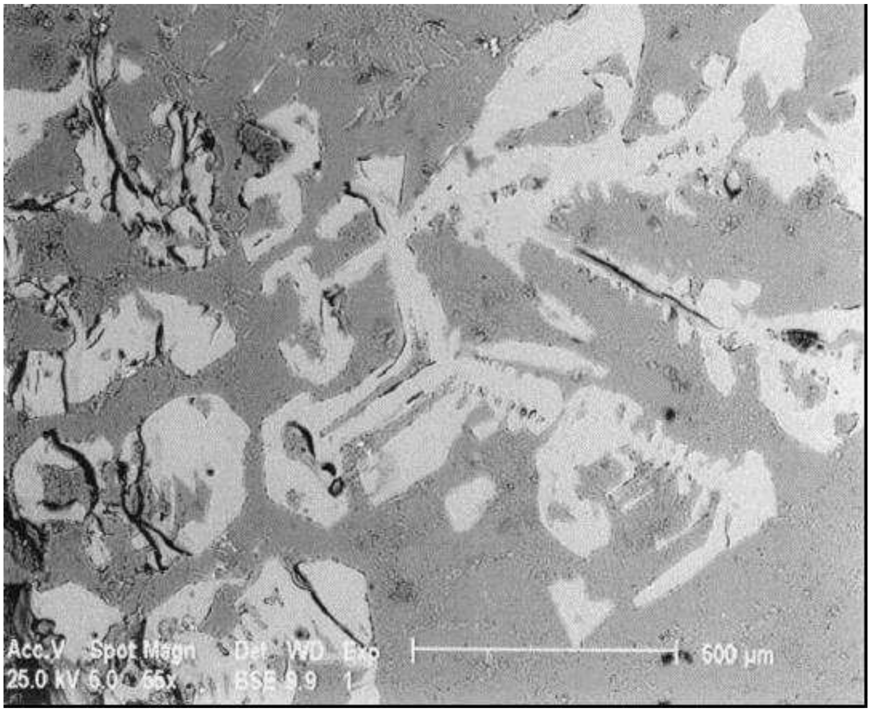


Figure 4. SEM secondary electron image of α–Fe crystals showing a mixture of irregular cracks leading to the formation of irregular particles and more regular dendrites associated with planar central cracks [41].

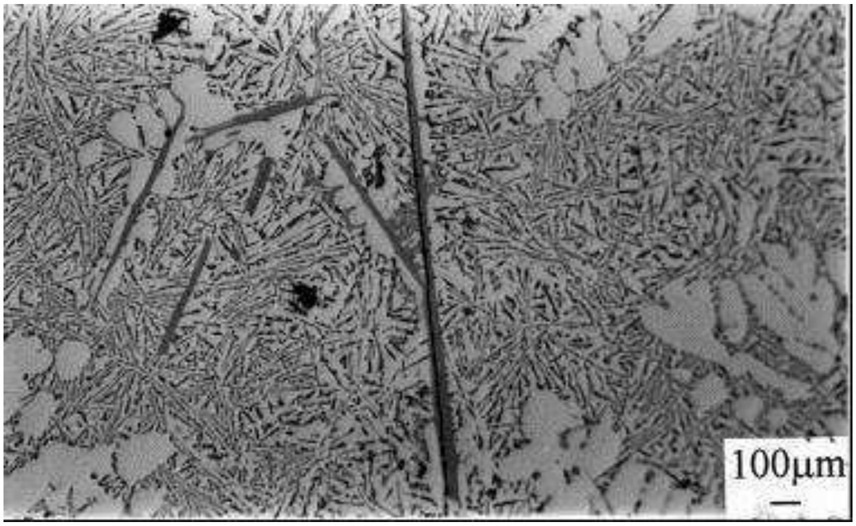


Figure 5. β-Fe platelet and its longitudinal crack in Al-11.5Si-0.4Mg cast alloy containing Fe and Mn

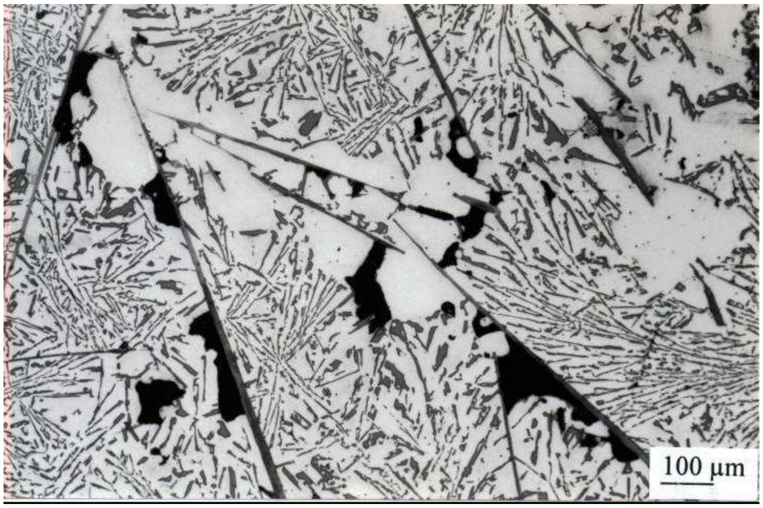


Figure 6. Porosities associated with β-Fe platelets in Al-11.5Si-0.4Mg cast alloy

Modification Mechanism

Following the bifilm hypothesis, in the presence of any modifying action, the formation of α-Fe particles is thought to be the consequence of its nucleation and growth on bifilms [29], but as a result of its high crystal symmetry, it can take up practically any growth form without undue difficulty. Thus chemical modification of β-Fe to α-Fe is advantageous because of the fixing of bifilms in their convoluted state.

Another point that is useful to clarify, is the concept of "fragmentation". This term has been used to describe the appearance of the conversion of β-Fe plates into smaller α-Fe particles. It seems that there has been an unstated assumption that the production of smaller α-Fe particles arises by some kind of mechanical fracturing process, implied by the apparently brittle nature of iron-rich phases. It seems more likely that the apparent fragmentation of plate-like β-Fe to α-Fe occurs because of (i) the dendritic form of the α-Fe appears in cross sections as separated particles, and (ii) the presence of the bifilm cracks in the particles [41,42]. (The bifilm cracks only become clearly visible if the alloy has a high gas content, or suffers some reduction of pressure due to shrinkage, that expands the residual air layer in the centre of the bifilms as shown in Figure 4).

The crystal structure of α-alumina (corundum) is hexagonal. The γ-alumina, spinel and magnesia all have cubic structures [29]. The calculation of the disregistry between the α-Fe phase with some typical oxides such as γ-alumina, α-alumina, spinel and magnesia showed that such oxides may be good substrates for the nucleation and growth of α-Fe phase [29]. To explain the effect of superheat temperature on Fe-intermetallics in Al-Si alloys, however, it has been reported that at low melt superheat temperature, the γ aluminum oxide is stabilized and acts as nucleation substrates to β-Fe platelets. Transformation of γ-alumna to α-alumina with increasing superheat temperature decreases the potential to nucleate β-Fe platelets but provides effective nuclei for the α-Fe phase [43,44].

The addition of chemical neutralizers may stabilise the α-Fe compared to the β-Fe. This effect results from the thermodynamics, i.e. the relative free energies of the phases, as would be apparent on an equilibrium phase diagram. Such considerations have been foremost in the arguments put forward by some authors and are undoubtedly a factor of major importance [45-50]. Even so, the use of equilibrium reactions to explain the changes from β-Fe to α-Fe requires some caution. Most work on the establishment of the currently accepted equilibrium diagrams (for instance the Al-Si-Fe-Mn systems) has been carried out on material that was, unwittingly, of unknown and variable bifilm content. Thus the kinetics of the reactions may have interfered with the accuracy of these early results. Thus, before placing too much faith in classical sources, for instance [13], some of the phase diagrams may require review.

As a further detail considering the equilibrium phase diagram approach, during work on the common industrial alloy A413 containing appreciable amounts of Fe and with the presence of sufficient quantity of a modifier such as Cr, α-script particles were formed probably via a peritectic reaction (L + α-Fe dendrite → α-Al + α-Fe script) [42]. Even so, following the logic presented in this work, this reaction would have taken place on the wetted outer surface of the bifilms in suspension in the melt.

A serious effect of reliance on the use of the equilibrium diagram is that non-equilibrium conditions are normally dominant in solidification. For instance, it seems possible to envisage that Fe-rich intermetallics would not precipitate at all in the absence of suitable substrates such as oxide bifilms [40]. Therefore, if the liquid metal were very clean, it is predicted that the iron would remain in supersaturated solid solution. In this form it is expected that it could be of significant benefit to the alloy, aiding solid solution strengthening, or possibly being manipulated to act as a precipitation-hardening constituent. If this is true, the role of the bifilm in aiding the approach to equilibrium is seen to be central, and its meticulous control leading to its absence can be envisaged to lead to a new generation of metallurgical alloys of low cost but high performance.

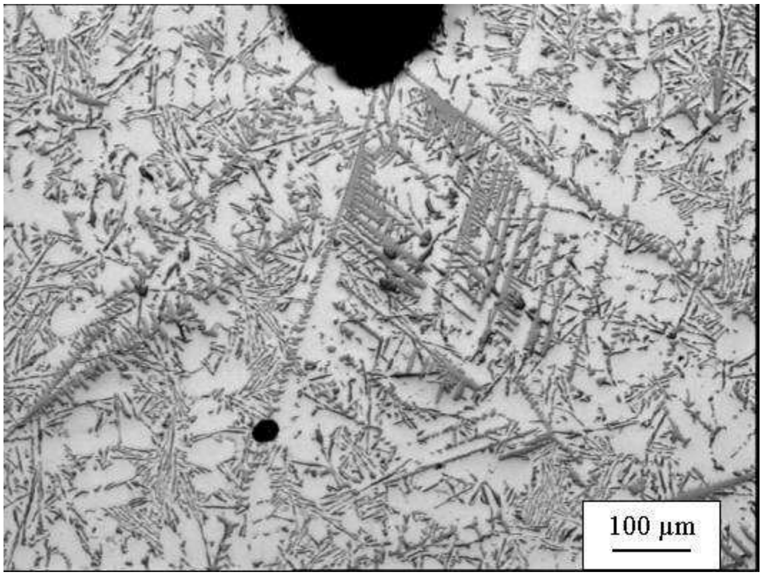


Figure 7. α-Fe dendrites associated with porosity, sedimented near the bottom of the mould in A413 alloy modified with Cr.

Finally, one of the approaches to remove suspended oxide crack defects has suggested the use of the precipitation and sedimentation of primary intermetallic compounds from the liquid metal [30-34]. For this purpose, the molten metal must be cooled to a temperature as low as possible (below the effective liquidus for the precipitation of the primary intermetallic compound, but, of course, above the general liquidus temperature for the precipitation of the α-Al dendrites). In these conditions the primary intermetallics precipitate on the oxide films and mutually sink under their combined weight to the bottom of the holding furnace or crucible [30-34]. Figure 7 illustrates this effect, showing the sedimentation of α-Fe dendrite intermetallic ($Al_{15}(FeCr)_{3.3}Si_{2.2}$) in the bottom of a vertical cylinder casting.

Modifying Elements

Manganese

Mn addition to aluminum alloys is the most commonly used modifying treatment. The effect is probably governed by equilibrium diagram type of considerations [46-49].

Its use in industrial grade 319 aluminum alloy containing 1 wt% Fe with a Fe:Mn ratio of 1.5 causes the crystallization of α-Fe phase, at low and high cooling rates (0.1 and 10 K/s). At 10 K/s cooling rate, α-$Al_{15}(FeMn)_3Si_2$ is formed in interdendritic regions but at even higher solidification rates (20 K/s) almost 50% of the Fe-rich intermetallics crystallizes in the plate-like morphology (β-Fe phase), so, optimum Fe:Mn ratio for the formation of α-Fe phase is greatly related to cooling rate [43]. Another report of work using a relatively high cooling rate of 10 K/s [51] indicated that the optimum Mn concentration is estimated to be 0.5 wt% for 319 alloy with 1.0 wt% Fe and 0.3 wt% for 413 alloy with 1.2 wt% Fe + 0.1 wt% Cr respectively [51]. There is also a report claiming that addition of more than 0.9 wt% Mn to A413 alloy with 2.5 wt% Fe (below the normally accepted Fe:Mn ratio of 2 [4, 52]) leads to the precipitation of "numerous and compacted" α-Fe phase instead of β-Fe plates [41]. Additional investigation reported that for at least partial neutralization of Fe, the ratio Fe:Mn must be less than 2.0, but even higher Mn additions (lower ratios) may not be sufficient [4]. Thus although there is a consensus that Mn is helpful in substituting α-Fe for β-Fe, it seems that the definition of an 'optimum' or 'safe' ratio for Mn in relation to Fe remains unclear at this time.

Chromium

The main benefit of adding Cr to Al-Mg, Al-Mg-Si and Al-Mg-Zn group alloys is the formation of fine dispersed phases (dispersoids) that prevent grain growth and recrystallization during hot working or heat treatment.

As a common addition to neutralize the effects of Fe, the action of Cr is likely to be analogous to that of Mn, in that the equilibrium distribution of phases is probably altered to promote the formation of α-Fe [42]. The addition of Cr causes the formation of very coarse complex compounds with other impurities such as Fe in those alloys commonly used in the pressure-die-casting industry [11,24,53,54]. The formation, growth and sedimentation of these multicomponent particles can lead to a depletion of Fe concentration, generally accepted to be beneficial to casting quality [5]. Gustafsson et al. [55] claimed that additions of Cr to 356 aluminum alloy have a strong effect on the morphology of Fe-rich intermetallic compounds and can cause the precipitation of α-$Al_{13}(Fe,Cr)_4Si_4$ Chinese-script.

Figure 8 shows various types of α-Fe and β-Fe phases in A413 alloys in the presence of Cr. The recent work by some of the present authors shows that in A413 alloy with an Fe:Cr ratio of 3.0 is required to obtain the crystallization of Fe intermetallics mainly as α-Fe Chinese-script form or branched phases with chemical composition of $Al_{15}(FeCr)_{3.7}Si_{2.3}$ [42]. The combined addition of Mn and Cr (1.0 wt% Mn + 0.1 wt% Cr to counter 1.5 wt% Fe) was found very effective to enhance the tensile properties of 319 automobile alloy [56]. In that study, Fe-rich intermetallics are precipitated completely in a star-like form [56] but higher concentration of Cr is not recommended because of the formation of branched phases and their impact on fluidity and castability [25]. Unfortunately, it was found [42] that presence of Cr also appeared to promote the precipitation of primary silicon (Figure 9).

Cobalt

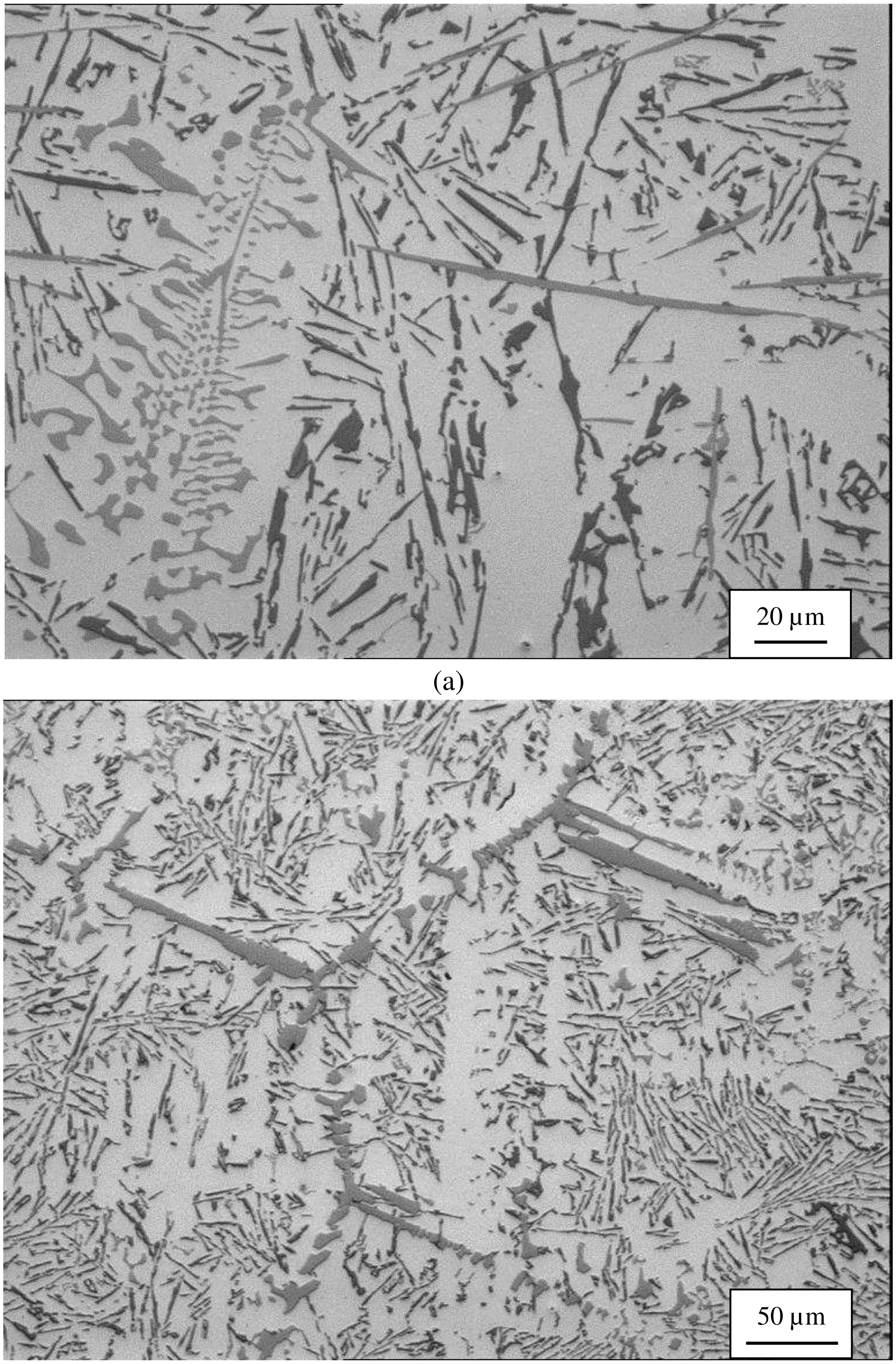
Co is not a common addition to aluminum alloys [11]. It has an effect similar to Mn and Cr in the neutralization of iron, but a higher concentration of Co is needed to suppress the formation of β-Fe [4,42]. It was reported by the present authors that an optimum Fe:Co ratio of approximately 1.0 is required in commercial A413 alloy to cause the precipitation of Fe-rich intermetallics mainly as α-Fe dendrites with the composition of $Al_{15}(Fe,Co)_4Si_{2.2}$ instead of β-Fe platelets [42]. Analogously to the action of Cr, a potentially unwelcome consequence of the Co addition was the appearance of primary Si particles [42].

Magnesium

Mg is commonly used for strengthening purposes and hardness development in heat-treated Al-Si alloys [11] by the formation of the extremely fine theta phase [50,57]. In Al-Si based alloys, Mg is also known to have a minor effect on refining the silicon eutectic [58].

According to Samuel et al [58], addition of Mg, in amounts up to 0.5 wt% to the 310 alloy at very slow cooling rates (close to equilibrium) leads to the precipitation of rounded black Mg_2Si particles along the sides of the eutectic Si particles. A large proportion of the pervasive β-Al_5FeSi phase was modified into Chinese-script phase with a composition of $Al_8Mg_3FeSi_6$. It was also reported by the same authors that at higher concentrations of Mg (> 1.0 wt%) β-plates are very rarely found, but modification of eutectic Si does not occur due to the consumption of Mg in the precipitation of Mg_2Si and $Al_8Mg_3FeSi_6$ phases. Addition of Mg to A319.1 and A319.2 alloys (with 750°C pouring temperature in graphite moulds) transforms a large number of β-Al_5FeSi plates into the compacted Chinese-script phase [22]. The interesting result of the last reference is the equivalency in the effect of a 1.2 wt% Mg addition and a combination of 0.5 wt% Mg with 0.03 wt% Sr in reducing the volume fraction of β-Fe platelets in 319 alloy [22]. Addition of Mg to the 1000-series wrought alloys promotes the formation of α-Al_8Fe_2Si phase in dendritic form [22]. However, some confusion remains because of the contradictory results of Awano and Shimizu [3]. These authors found that the shape of Fe-rich compounds could not easily be altered from plate-like to Chinese-script morphology with the addition of Mg.

The conflicting findings for the effect of Mg seem likely to be the result of the effect of Mg on bifilms in suspension in the melt. For instance it is known that the iron-rich phases



(a)

(b)

Figure 8. Various types of α-Fe phase in A413 alloy in the presence of Cr showing: (a) α-Fe Chinese-script (together with some β–Fe platelets) and (b) α-Fe dendrites.

precipitate on oxide films [29]. In addition, there is strong evidence that Si may also precipitate on oxide films [29,31], but that these favoured substrates are deactivated by modifiers such as Na and Sr [59]. By reasonable extrapolation, therefore, it seems probable that Mg, being an alkaline earth metal like Sr, will also deactivate oxide films as substrates for both Si and Fe-rich precipitates. However, being somewhat less effective than Sr will require higher concentration to give an effect equivalent to that of Sr. In addition, the variable nature of experimental results would be expected, since populations of oxide substrates will be highly variable from melt to melt; an effect so far overlooked by investigators, and in any case not easily controlled or measured [60].\

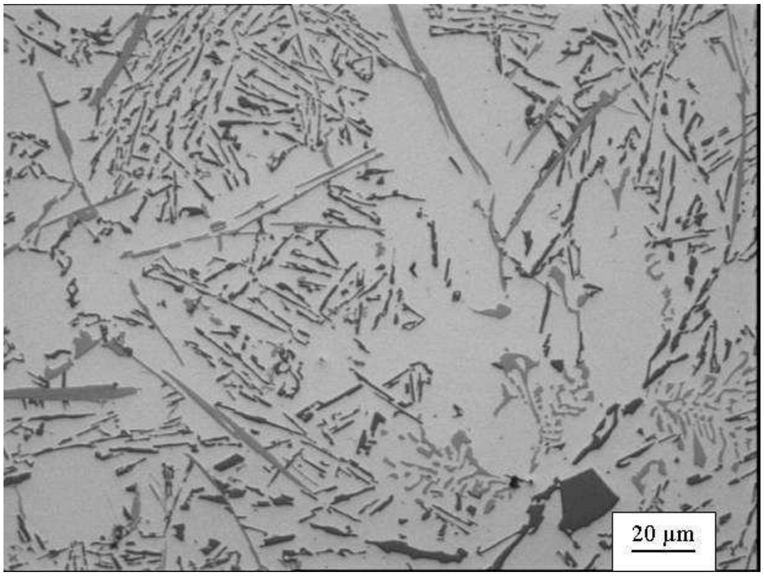


Figure 9. Numerous β-Fe plates in a partial modified Al-Si eutectic, containing both Chinese-script α-Fe particles and primary Si crystal (black) in A413 alloy modified with Cr.

Strontium

Modification of eutectic silicon is routinely carried out, using Sr, to transform the flake morphology into a fibrous form [61,62]. Mechanical properties such as ductility, UTS, hardness and machinability are generally increased appreciably only at low concentration of Sr (0.008-0.04 wt%) [11]. The effect seems to be associated, once again, with the deactivation of the oxide as a favored substrate for Si, so that Si no longer nucleates in the liquid ahead of the solidification front, thus giving a more planar front. The conversion of a ragged to a planar front has the effect of reducing the area of the front, but since the rate of extraction of heat from the casting remains unchanged, the rate of advance of the front is greatly increased, as though it were chilled, so that the eutectic is refined. This clever idea proposed in 1981 by Flood and Hunt [63] is given additional support more recently [35]. The reduced nucleation ahead of the front, and the increased rate of its advance is naturally associated with an observed increase in the undercooling at the front. The consequent reduction in Si spacing will also reduce the size of other second phases such as Fe-rich intermetallics. Most of the effect of Si (and by implication, also of Na and other Al-Si eutectic modifiers) is assumed to be explained by this mechanism. Thus to reduce the detrimental effect of Fe in both wrought and foundry aluminum alloys, Sr can be added as a powerful modifying element. The formation of β-Fe phase can be reduced and even suppressed with the use of Sr modification [64,65].

However, it is also well established that the addition of Sr increases the amount of hydrogen porosity in castings especially with slow cooling rates [11,35,66-70]. This is a complicating effect of Sr that to some extent counters its benefit with respect to the refinement of Si and Fe-rich phases. Those foundries that enjoy good melting and metal transfer technology generally experience relatively good freedom from oxide bifilms [59]. As a natural consequence they do not therefore receive any significant benefit of the suppression of the prior nucleation of Si and/or Fe phases, because there are few films on which nucleation can occur. Thus such foundries receive practically no benefit from Sr, but suffer the disadvantage of additional porosity, probably from the precipitation of the additional hydrogen on their population of old bifilms. Thus these few foundries have suffered a degradation of the mechanical properties of their alloys when attempting to modify with Sr, and such foundries have therefore abandoned the use of Sr modification [59].

There are, however, many reports of the beneficial effects of Sr in reducing the proportion of β-Fe plates and replacing these with α-Fe Chinese script. These reports are at least partly explained by the action of Sr to suppress the precipitation of β-Fe on bifilms, so that bifilms are not straightened by the subsequent growth of the β-Fe phase, and properties are not therefore impaired. The Chinese script form of α-Fe is clearly a dendritic growth form, requiring, in an extreme case, only a single nucleus (which might be an oxide) from which to start. Being relatively free of internal defects such precipitates are relatively strong, resisting failure by cracking or apparent decohesion. Some of the experimental findings are listed below.

The addition of 0.01 to 0.05 wt%Sr to 6069 wrought aluminum alloy has been reported to transform a large proportion of β-Fe plates, into the compact α-Fe Chinese-script [71]. Another report claimed the same effect of Sr in modification of 1XXX and 6XXX DC alloys [72]. It was also claimed that at approximately 0.05 wt% Sr, all of the intermetallic phases in Al-Cu-Mg-Zn wrought alloy are modified [73]. If the bifilm concept is also in operation in this instance, we may surmise that the Sr may also be deactivating the oxide bifilms, making them less favorable for precipitation of the AlCuMg-rich compounds. The Sr addition of 0.06 wt% changes the morphology of Fe-rich intermetallics from plate-like to Chinese-script form [74].

Pennors et al. [75] indicated that Sr is effective in causing the modification and control of the β-Al_5FeSi phase to a large extent in Al-6 wt%Si-3.5 wt% Cu (319) alloy, when the Fe content is 0.5 and 1.0 wt%. It was found that the optimum range of Sr in minimizing the β-plate lengths is approximately 400-600 ppm (irrespective of cooling rate) and higher levels of Sr cause an “overmodification” effect [75]. Effectiveness of Sr addition in the reduction of the total amount of intermetallics during solidification of an Al-12.2 wt% Si alloy has been demonstrated [76]. The maximum reduction in the size, number and vol% of β-Fe phase and alteration of morphology from plate-like to dendritic form was observed when adding Sr in a range of 0.04-0.06 wt% in A413 and 413P cast alloys in both sand and permanent mold castings [77]. These studies have been supported by observations carried out by Samuel et al. [73], where the authors have attributed the shortening of β-plates to the poisoning of nucleation sites by Sr, in agreement with the proposition that Sr deactivates the bifilm substrates for β-Fe. They found the effect was accelerated with increasing Sr content to approximately 300 ppm (the optimum level) in commercial 319 alloy end-chilled castings [78]. In another work by these authors [57,58], the optimum range of Sr was concluded between 0.02 and 0.04 wt% for the elimination of more than two thirds of the β-Fe plates and modification of the Mg_2Si particles in 319 alloy. The presence of Sr (300 ppm) leads to precipitation of a large part of the Fe-rich phases in the form of coarse pre-dendritic particles situated within the α-aluminum dendrites in A380.1 alloy with 1 wt% Fe [79]. Addition of Sr together with Mn was found to be effective in the conversion of β-Fe phase into α-Fe dendrites [41]. The precipitates of α-Fe are likely to be precipitated together with the bifilm substrate in the melting furnace prior to the melt being poured. Thus the poured melt is likely to be relatively free from both Fe-rich precipitates and bifilms, and so improved in properties.

The claimed optimum addition levels of Sr reported above at 300-600 ppm, contrast with other foundry operations that have found 50 ppm is ideal, and yet others that have found that 0 ppm is best. These conflicting results seem likely to be consistent with the varying bifilm contents of melts. As melts become cleaner, the increased rarity of substrates means that less area of oxide is required to be deactivated by Sr [59].

Finally, it should be noted that a quite different mechanism for the beneficial effects of Sr in reducing the numbers of β-Fe platelets has been proposed based on the assumption that Sr strengthens the oxide film on the melt [41]. This would have the effect, in some pouring operations, of holding back the oxide layer, reducing the area that enters the melt, and reducing the shredding of oxide film that does, by chance, enter the melt. It is clear that such a mechanism, if true, would be very much dependent on the detailed geometry of the pouring operation. There seems good circumstantial evidence that such an effect has been observed in the case of Be additions to Al melts [80].

Lithium

Presence of Li greatly increases the oxidation rate of molten aluminum [81,82] and changes the surface characteristics of wrought products [11]. Li increases the hydrogen solubility in aluminum melts [83] and is one of the effective modifiers of the eutectic Si phase in Al-Si alloys [84]. Thus, by analogy with the action of Sr, it is strongly suspected that Li may be expected to have a refining action on Fe-rich phases by the deactivation of favored oxide substrates and the consequential speeding up of the freezing front. This conclusion is given weight by the observation that Li addition increases the undercooling during the solidification of the eutectic [84].

The effect of adding Li to Al-6.5 wt%Si-3.5 wt%Cu-1 wt%Fe cast alloy cooled at 4.2 K/s has been reported by Ashtari et al. [84]. They indicated that the length of the β-plates decreased from 37.0 to 14.5 μm by the addition of 0.33 wt% Li. Shortening of the β-plates by Li is accompanied by the formation of AlLiSi phase, which is undesirable for mechanical properties [84], so only a low addition of Li is recommended. This understandable conclusion might be challenged if the AlLiSi phase only precipitates on bifilms in suspension in the liquid, as seems to be the case for many other intermetallics [35]. If so, we might predict that higher Li additions would create no problems if the melt were especially clean.

Beryllium

Be is used in aluminum alloys containing Mg to reduce oxidation losses from melts at elevated temperatures but only a few parts per million are required for this purpose.

Significantly higher levels of Be are required for alloying purposes. The addition of Be may be helpful in fluidity of automotive aluminum alloys [11]. According to Villeneuve et al. [56] Be additions in amounts of approximately 0.08 wt% to variants of Al-6 wt%Si-3.5 wt%Cu-0.1 wt%Mn (A319.2) with 1.4 wt% Fe caused a large proportion of β-Fe platelets to be replaced with α-Chinese-script phase identified as Al_8Fe_2SiBe. This phase was formed within the α-aluminum dendrites but a limited number of fine β-plates still remained in the microstructure. To enhance the effectiveness of Be an additional corrective element may be necessary. Exceptional improvement in ductility and strength was obtained by the addition of Be together with 200 ppm Sr, but the increase of Sr level beyond this limit led to precipitation of large β-Fe platelets [56]. Be up to 0.4 wt% can cause the formation of compact $Al_4Fe_2Be_5$ particles [3]. It was also noted that an approximately spheroidal form of Fe-rich intermetallics can be formed in aluminum containing 6 to 10 wt% Si by addition of 0.05 to 0.5 wt% Be [4]. The morphology of intermetallic compounds in Al-7 wt%Si-0.3 wt%Mg with 0.2-1.0 wt% Fe alloy in the presence of Be, transform from β-Fe plates into α-Fe Chinese-script form with the chemical formulae once again Al_8Fe_2SiBe [85,86]. The combined effect of 0.08wt%Be and 0.02wt%Sr in A380.1 alloy containing 1.4 wt% Fe is reported to be equivalent to the addition of 1 wt% Mn (Fe:Mn ratio of 1.4)[79].

The beneficial effect of Be in reducing the amount of β-Fe phase in Al melts may also be importantly influenced from a completely different mechanism. It is well known in semi-continuous DC casting of wrought alloys that attempts to eliminate Be from certain alloys has caused great problems with castability. It is thought that the Be greatly strengthens the oxide film on the surface of the liquid metal, to such an extent that the oxide formed in pouring and transfer operations 'hangs on' to the lip of the pouring vessel, and so does not find its way into the casting. Thus Be-containing castings are cleaner, containing fewer oxides entering the melt at the pouring stage of casting. Thus the precipitation of β-Fe is discouraged by reduced area of favorable substrate [80].

It must be mentioned that in practice the use of Be is currently limited, and will become more so, because of toxicity problems.

Counter-Modifying Elements

Recent work has found that Sr at low levels of addition (in contrast to its beneficial effects at higher levels [41]) used typically for the modification of the eutectic silicon in Al-Si alloys, is antagonistic towards the beneficial action of Mn in modifying β-Fe to α-Fe [41]. This negative action might also be expected to extend to other silicon modifiers such as Na, and possibly to other β-Fe modifiers such as Cr, Co, etc.

Some such effect is predictable if the action of Sr to modify the Si eutectic is a consequence of the deactivation of bifilms by Sr, making them unfavourable sites for the formation of Si [35]. Such deactivation might not unreasonably be expected to affect the effectiveness of the bifilms as sites for the formation of Fe-rich intermetallics as is observed [41].

Clearly, this effect very much complicates the overall action of Sr, since Sr has other beneficial and detrimental effects. A proper evaluation remains to be established. In particular, of course, the further complication of such an attempt at evaluation will be a challenge, because of the effects of bifilms will require to be controlled, and such control will not easily be attained.

Conclusions

1) The detrimental effect of Fe in Al alloys arises because β-Fe particles straighten bifilms, and thus convert relatively harmless convoluted cracks in suspension in the liquid to large straight cracks.
2) The prior cooling of the melt to cause the sedimentation of primary α-Fe intermetallics is beneficial to casting quality because (i) Fe remaining in the alloy is reduced, and (ii) oxide bifilms are simultaneously removed.
3) The reduction of the detrimental effect of Fe using the chemical modification of Mn, Cr, Sr or Be is found to be effective, and to be preferred to Co, Mg and Li.
4) There appear to be several different mechanisms for the different chemical modifiers.

    i) Mn and Cr appear to stabilise the α-Fe phase. Such action is in principle predictable from the equilibrium phase diagram.
    ii) Sr (and possibly other silicon eutectic modifiers) poisons the oxide film substrates for eutectic Si, deactivating and therefore effectively removing the favoured substrates, and simultaneously straightening and speeding the freezing front, giving β-Fe less time to grow.
    iii) Both Be and Sr may act by strengthening the oxide film so that it is held back during pouring, not entering the melt to provide substrates for the formation of β-Fe.

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