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CURRENT TECHNOLOGIES FOR THE REMOVAL OF IRON FROM ALUMINUM ALLOYS

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Abstract

In the current paper, the Fe-rich phases in and their detrimental effect on aluminum alloys are summarized. The existence of brittle platelet β-Fe-rich phases lowers the mechanical properties of aluminum alloys. The methods to neutralize the detrimental effect of iron are discussed. The use of high cooling rate, solution heat treatment and addition of elements such as Mn, Cr, Be, Co, Mo, Ni, V, W, Cu, Sr, or the rare earth elements Y, Nd, La and Ce are reported to modify the platelet Fe-rich phases in aluminum alloys. The mechanism of the modification is briefly described. Technologies to remove iron from aluminum are extensively reviewed. The precipitation and removal of Fe-rich phases (sludge) are discussed. The dense phases can be removed by methods such as gravitational separation, electromagnetic separation, and centrifuge. Other methods include electrolysis, electro-slag refining, fractional solidification, and fluxing refining. The expensive three-layer cell electrolysis process is the most successful technique to remove iron from aluminum so far.

Introduction

During refining and recycling of aluminum alloy scraps, iron gradually accumulates [1] and is of more difficult to be removed with decreasing Fe content [2]. Most aluminum alloy production requires tight composition controls on iron. For example, iron content level above 0.15 wt% is unacceptable in premium aerospace alloys such as 7050. Iron is the most pervasive impurity element in aluminum alloys, which stems from the bauxite and steel tools used during both primary and secondary production. Iron usually forms second phases in the aluminum alloys owing to its low equilibrium solid solubility in the aluminum (max. 0.05%), such as Al_3Fe, α-AlFeSi and β-AlFeSi [3]. Since the solid solubility of iron in aluminum is less than 0.05 % at equilibrium, almost all iron forms second phases in aluminum [4]. The binary Al-Fe and ternary Al-Fe-Si phases are the main Fe-rich phases in aluminum alloys [3]. Three dimensional morphology of the Fe-rich intermetallic compounds observed by current authors (Figure 1 [5]) suggests that Fe-rich intermetallic phases have much more complex morphologies, with fragile and brittle appearance than what is shown in two dimensional observation. These morphologies imply why they are detrimental to the mechanical properties of aluminum.

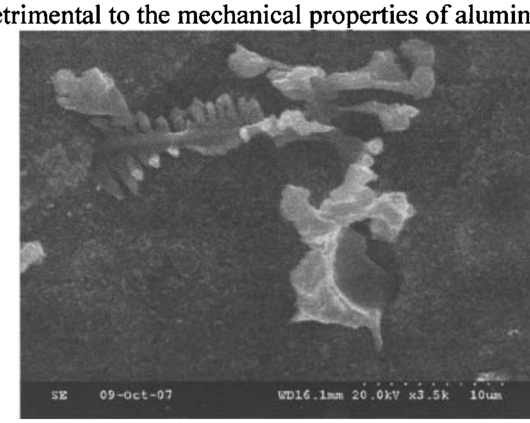

Figure 1. 3-D morphologies of Fe-rich intermetallic phases of β-$Al(FeMn)_3Si$ [5].

A number of Fe-rich phases in Al-Fe-Si ternary system have been identified as shown in Table 1. Al_3Fe (also reported as θ-Al_3Fe or θ-$Al_{13}Fe_4$ [4, 6]), a common equilibrium phase, forms a eutectic with aluminum at about 655 °C [3]. The most important Fe-rich phases in aluminum alloys containing silicon are β-phase and α-phase. Among all the Fe-rich phases, β-AlFeSi is thought to be the most deleterious, and most efforts have been devoted on how to avoid the formation of β-AlFeSi, which is brittle and generally assumed to act as stress raisers and points of weak coherence.

There are no effective practical methods to directly remove iron from aluminum alloys by conventional refining. The techniques or theories on direct iron removal from aluminum have made no satisfactory progress so far.

Table 1. Identified Fe-rich phases in aluminum alloys

Fe-rich intermetallics	Crystal structure	Reference
Al_mFe	Bct	[3, 7]
Al_6Fe	Orthorhombic C-centred orthorhombic	[3-4] [7]
Al_xFe		[3, 8]
Al_pFe	Bcc	[7]
θ-Al_3Fe or θ-$Al_{13}Fe_4$	Monoclinic C-centred monoclinic	[3-4, 9] [7]
α-Al_8Fe_2Si or α-$Al_{12}Fe_3Si_2$ α-$Al_{15}Fe_3Si_2$	Hexagonal Bcc	[2-4, 6, 9] [10-12]
β- Al_5FeSi $Al_9Fe_2Si_2$	Monoclinic B-face centered orthorhombic Orthorhombic Tetragonal	[2-4, 6, 9, 13] [14] [15] [12]
δ- Al_4FeSi_2 δ- Al_3FeSi_2	tetragonal	[2-4, 16]
q_1-AlFeSi	C-centred orthorhombic	[3, 7]
q_2-AlFeSi	monoclinic	[7]
γ-Al_8FeSi	C-centred monoclinic	[4, 6]
p-$Al_8Mg_3FeSi_6$ π-$Al_8Mg_3FeSi_6$		[2] [17]

Precipitation of High Fe-Rich Phases

The method is mainly applied to purify Al-Si cast alloys. Iron is removed by the formation of primary Fe-rich intermetallics, generally primary α-$Al_{15}(Fe, Mn)_3Si_2$ or α-$Al_{15}(Fe, Mn, Cr)_3Si_2$ (called "sludge").

Manganese

Although Mn is harmful to the mechanical properties of aluminum alloys, it is widely used to neutralize Fe in Al-Si cast alloys. Mn has an atomic radius and crystal structure close to Fe [4, 18]. Yoo reported that the crystal structure of precipitated α-$Al_{15}(FeMn)_3Si_2$ depended on the Mn/Fe ratio. The crystallization of the sludge has proved to be an effective method to remove Fe from Al-Si alloys, as shown in Figure 2 [19]. After the formation of the sludge, further steps including gravity separation, filtration, electromagnetic separation or centrifuge separation are conducted to remove the sludge phase from the molten aluminum. The iron concentration generally decreases from 1 – 2 wt% to at most 0.4 wt% after the treatment [20-21].

Cobalt

Fe, Cr and Co have similar atomic radii and Cr also has the same Bravais lattice with Fe. Thus Cr and Co can also be used to precipitate Fe-rich phases. Mathta [18] reported that the optimum ratio of Co/Fe was ~1.0 for A413 Al-11Si alloys and the Co-Fe phases were identified approximately as $Al_{15}(Fe,Co)_4Si_2$, while Murali [22] stated the Co-Fe phase was $Al_{14}Co_2(Fe,Si)$.

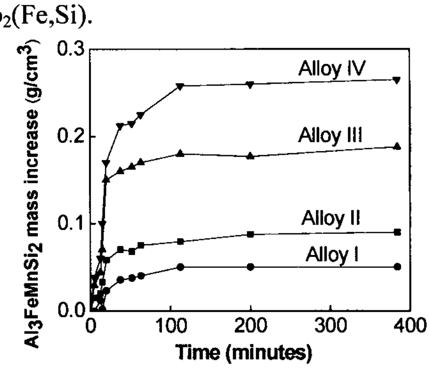

Figure 2. Effect of holding time and initial Fe, Mn content on the formation of sludge at 605°C [19]

Chromium

Mondolfo [4] claimed that Cr was a possible additive to neutralize Fe phases in aluminum. Cr was believed more effective than Co, and a ratio of Cr/Fe= 0.33 can prevent the formation of β-AlFeSi [18]. The function of Cr is similar to that of Co. The calculated isothermal section of Al-Fe-Cr at 700°C was shown in Figure 3. [23] The formation of $Al_{11}Cr_2$ and $Al_{13}Cr_2$ at high Cr content (~10 at%) above the liquidus surface may remove iron from the Al melt. However, the iron solubility of $Al_{11}Cr_2$ and $Al_{13}Cr_2$ is too small to effectively remove iron, and a lot of Cr should be added into the Al melt, which is impossible for the real industrial practice.

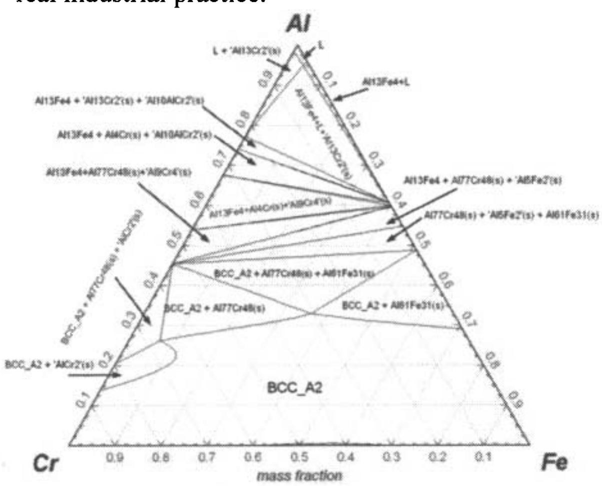

Figure 3. Al-Fe-Cr phase diagram (700°C and 1 atm) [23]

Beryllium

Murali considered beryllium was a more effective neutralization element than Mn, Co and Cr [24]. Crepeau reported that the addition of Be > 0.4 wt% was required [2], while other references showed that the trace addition of Be 0.06-0.27 wt% was enough [24-27].

Strontium

In aluminum wrought alloys, Sr was also applied to transform the platelet Fe-rich phases to α-AlFeSi (Al_8Fe_2Si) [28-31]. It was reported that the 0.01-0.10 wt% addition of Sr to Al-Cu-Mg-Zn wrought alloys refined the intermetallic phases [32].

Gravity Sedimentation

Gravity sedimentation is a method to remove the heavier phase, like Fe-rich phase, from aluminum. Donk [33] found that sludge formed and segregated immediately during the cooling from 840 °C to 600 °C. Reported removal efficiency data was summarized in Table 2. Flores and Cao reported an Fe removal fraction over >70 % with Mn/Fe>1 and relative high Fe content [19, 21, 34]. Figure 4 [35] shows a microstructure of an aluminum alloy after gravity sedimentation. Most of the sludge settled to the bottom and thus the upper alloy was purified.

Filtration

Primary Fe-rich inter-metallic particles also can be removed by porous filters similar to the removal of nonmetallic inclusions by filtration. Figure 5 [20] shows the schematic steps of the filtration operation. After a short time (10-20min) holding at sludge formation temperature, the melt is decanted through a preheated filter. Small amount of sludge also precipitates at the bottom of the melt during the holding time. The holding time used for filtration is much shorter than holding time used for gravity separation and so filtration is suitable for the continuous treatment. Donk [33] concluded that finer-pore foam filters can remove small size sludge particles but actually only slightly increased the removal efficiency because the captured small particles easily blocked the filter pores. The efficiency increases with increasing Mn/Fe (>1) or initial Fe and Mn content (Table 2) [36-37].

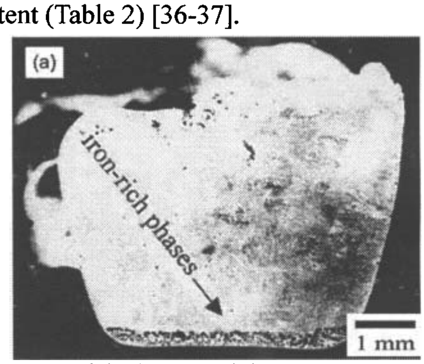

Figure 4. Fe-rich phase precipitation and subsequent gravity separation in an aluminum alloy [35]

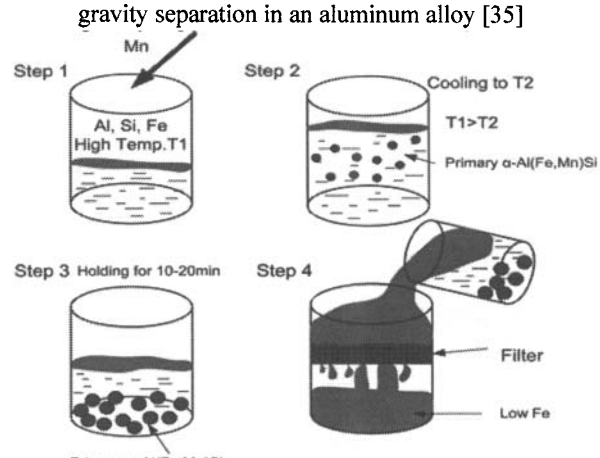

Figure 5. Schematic of the filtration process (T1: melting temperature, T2: holding temperature) [20]

Table 2. Reported removal efficiency of iron from aluminum alloys

Authors and reference	Composition (wt.%, Al balance)	Mn/Fe	Holding		After Purification (wt.%)		Fe removal fraction (%)	Filter (ppi)	Sludge separation method
			Temp (°C)	Time (min)	Mn	Fe			
Kim [38]	6Si-1.64Fe-1.66Mn	1	690	20	NA	0.45	72.6	NA	EM separation
Li [35, 39-40]	12Si-1.13Fe-1.22Mn	1.1	640	30	0.26	0.41	63.7		
Jiao [41]	10Si-1Fe-1.1Mn	1.1	NA	NA	0.39	0.30	70		
Xu [42]	11.7Si-1.2Fe-1.8Mn	1.5	NA	NA	0.26	0.41	65.8		
Cao [21, 43]	12Si-1.23Fe-1.11Mn	0.9	600	240	0.36	0.52	57.7	NA	Gravitational separation
Cao[21]	12Si-1.11Fe-1.03Mn	0.9	600	240	0.29	0.57	48.6		
Cao [21]	12Si-1.22Fe-2.15Mn	1.8	600	240	0.30	0.35	71.3		
Flores [19]	9.5Si-1.6Fe-2.2Mn	1.4	605	380	0.5	0.37	77		
Flores [34]	9.2Si-1.5Fe-2.2Mn	1.5	640	180	NA	0.4	73		
Nijhof [36]	12Si-1.1Fe-1Mn	0.9	605	20	0.42	0.64	42	NA	Filtration
	8Si-1.22Fe-1.12Mn	0.9	630	20	0.67	0.82	32.8	NA	
	12Si-1.1Fe-1.8Mn	1.6	605	20	0.57	0.47	57.2	NA	
Van Der Donk [37]	8Si-1.22Fe-1.12Mn	0.9	640	30	0.63	0.79	35.2	30	
	11.5Si-1.12Fe-0.99Mn	0.9	605	15	0.42	0.64	42.9	10	
	11.4Si-1.09Fe-1.86Mn	1.7	605	15	0.58	0.47	56.9	10	
	11.2Si-1.58Fe-1.9Mn	1.2	605	15	0.50	0.61	61.4	10	
	12Si-2.07Fe-1.91Mn	0.9	605	15	0.53	0.85	58.9	10	
De Moraes[20]	12Si-1.32Fe-1Mn	0.75	605	30	NA	0.4	69.7	20	
	12Si-1.30Fe-1Mn	0.77	625	30	NA	0.48	63.1	20	
	9.5Si-1.34Fe-1.5Mn	1.1	605	30	NA	0.25	81.3	30	
	9.5Si-1.14Fe-1.5Mn	1.4	610	30	NA	0.41	64.0	20	
	9.5Si-0.98Fe-1.5Mn	1.5	605	30	NA	0.18	82	20	
Matsubara [44]	11Si-2.07Fe-2.03Mn	1	NA	NA	0.30	0.36	82.6	NA	Centrifuge
	11Si-2.07Fe-2.53Mn	1.22			0.20	0.23	88.9		
	11Si-2.07Fe-3.00Mn	1.45			0.12	0.15	92.8		
	11Si-2.07Fe-4.15Mn	2			0.1	0.13	93.7		

Centrifugal Separation

The centrifugal separation technique was applied to directly remove iron-rich phases from the partially solidified aluminum alloy melts without any other elements addition. Matsubara *et al* [44] studied the sludge removal from Al-11Si alloys by the centrifugal separation technique. The iron-rich phases moved to the edge side of the melt and the central part was purified, as shown in Figure 6 [44]. The rotational speed has a great influence on the purification efficiency [44].

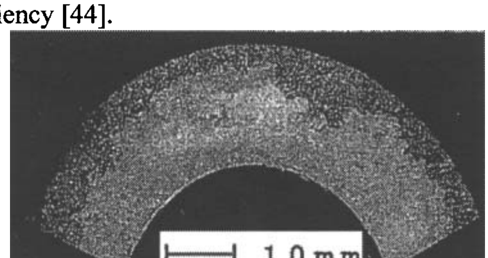

Figure 6. Microstructure of the transverse cross section of the centrifugal separated melt [44]

Electromagnetic Separation

The principle of Electromagnetic (EM) separation of particles from liquids was first proposed by Kolin in 1953 [45], and by Leenov and Kolin in 1954 [46]. When a uniform electromagnetic force is applied to a liquid metal, the metal is compressed by the electromagnetic force (Lorentz force) and a pressure gradient is generated in the metal. The non- or less-conductive particle suspended in the liquid metal receives only the pressure force because it does not experience the electromagnetic body force. As a result, the particle is forced to move in the opposite direction of electromagnetic force. The conductivity of Fe-rich phases is less than that of molten aluminum Researchers [35, 38-42, 47-51] have applied electromagnetic separation method to remove iron (in the form of sludge) from the melt. Kim *et al* [38] successfully purified Fe from 1.64 wt% to 0.45 wt% in Al-7Si scraps. Figure 7 [38] shows that the angular Fe-rich sludge settled on the side and bottom of the tube.

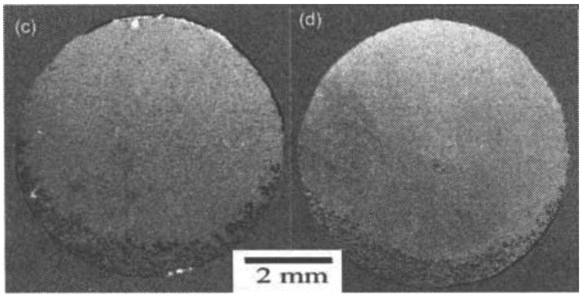

Figure 7. Distribution of sludge with induction (left) 30 A and (right) 40 A [38]

Table 2 shows reported iron removal efficiency by different sludge separation methods. Comparing with gravity and filtration, EM separation appears more efficient under similar experimental conditions. Furthermore, EM separation can also remove non-metallic inclusions, which has been proven by many researchers [52-55]. Gravitational separation can achieve a high iron removal but needs long settling time. The combination of gravitational separation and filtration gives impressive iron removal results but the disadvantages during gravitational separation step are still there, in addition to the problem of clogging of filter pores. Although the centrifuge has relatively high removal efficiency, it is also unpractical for the large scale processing due to challenges with temperature control. [56]

Electrolysis

The expensive process of three-layer-cell electrolysis is the most successful technique for the removal of iron and silicon from the molten aluminum so far [33]. Because the pure molten aluminum is the lightest, it will stay on the top of the three layers. Thus, the purified aluminum is obtained. However, the energy consumption for this process is relatively high, ~ 13-14 kWh per kg so far [57-60]. This technique is also applied to purify commercial aluminum with low level of initial impurities into high purity [61].

Fractional Solidification

The technique is based on the distribution coefficient (k) of impurities. For $k<1$, a much lower contents of impurities will result in the solidified than that in the residual liquid [62-63]. The distributions coefficient of iron is 0.03 therefore; it can be removed from aluminum by this method. However, the technique is not suitable for normal aluminum foundries owing to their low productivity, thus economically unfavorable. Large scale fractional solidification is used to produce extreme purity aluminum (99.999 wt% Al) [64-67] It is reported that iron content decreased from 747 ppm to 24 ppm after 2 hours processing in a fractional solidification apparatus [68].

Electroslag Refining

Electroslag refining process (ESR) is a secondary refining process in which the slag or flux is used both as a heating source and as a refining medium [69]. The process is already well established for ferrous metals but has not been used for aluminum refining. Mohanty's investigation reported 26% iron removal (from 0.22wt.% to 0.16wt.%) from commercial aluminum by ESR with a flux containing aluminum phosphide. [70]

Fluxing Refining

Few references have reported that significant iron removal can be achieved by using flux. The studies of the current author showed that the addition of $Na_2B_4O_7$ flux with NaCl and KCl significantly lowered the iron content from 0.33 wt% to 0.18 wt% in laboratory experiments, as shown in Figure 8. [71] However, industrial scale experiments showed little removal of iron. Nijhof *et al* reported iron removal with a mixed flux of NaCl, KCl, NaF, an iron removal from ~0.9 wt% to ~0.7 wt% was obtained. [36]

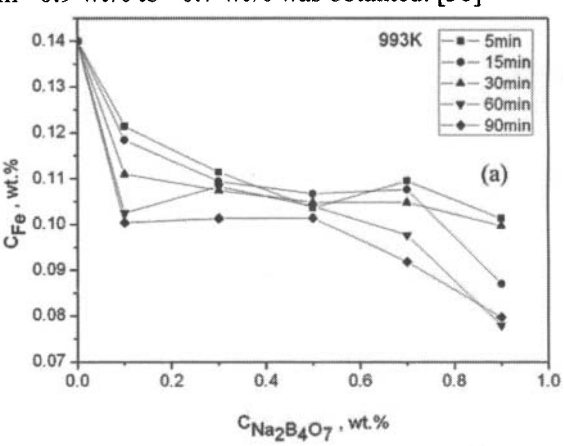

Figure 8. Relations between Fe concentration and $Na_2B_4O_7$ addition at different holding time [71]

Summary

Different technologies to remove iron from aluminum have been summarized in the current paper. Manganese is the most common element used for neutralization. So far, three-layer-cell electrolysis is the most successful technique to remove iron from the aluminum but it is expensive and only suitable for high purity aluminum production. The technology of EM separation can efficiently remove Fe-rich phases and could be a continuous process. EM separation is faster than gravitational separation, and avoids the problem of pore blockage during the filtration process.

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