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Intermetallics Formation and Their Effect on Mechanical Properties of Al-Si-X Alloys

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Abstract

This study focuses on primary impurities, called intermetallics, in the microstructure of Al-Si-X alloys, their formation, effects and treatments to eliminate or ameliorate their deleterious effects. Intermetallic compounds are usually formed when alloying elements, such as Fe, Cu, Mn, Mg and Sr. are added to Al-Si based alloys. These elements are depicted by X in the alloys formation expression. The chapter noted that the most common intermetallics are iron (Fe) based, and several of these Fe-phases, including the most harmful Fe-phase, β -Al₅SiFe, are listed and discussed. Fe-phase intermetallics are deleterious to the mechanical properties of Al-alloys; however, addition of <0.7% Fe helps prevent soldering in die casting mould. The effects of Fe-phase and other intermetallics formed by Cu, Mg and Mn were examined. Further, some techniques of eliminating or mitigating the negative influences of intermetallics were discussed.

Keywords: Al-Si alloys, Fe intermetallics, aluminium alloys intermetallics, impurities in aluminium alloys, alloying elements

1. Introduction

Eutectic and near-eutectic alloys of Al-Si-X (ternary systems) have many areas of applications, particularly in the automotive, airspace and marine industries, due to their exceptional properties. X in Al-Si-X formation represents one or more alloying elements, such as copper (Cu), magnesium (Mg), nickel (Ni), iron (Fe), etc. Large quantities of aluminium (Al) alloys (Al-Si-X) are required in engineering applications, especially in automotive and airspace industries [1–4]. The mean aluminium consumption in automobiles in Europe is shown in **Figure 1**. The increasing demand and studies on these alloys seem to be proportionate, as several studies have been reported on Al-Si-X alloys' microstructure, mechanical properties and

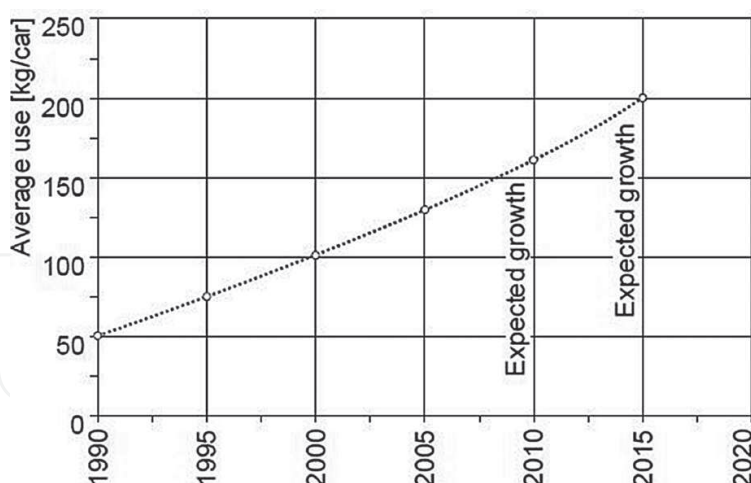


Figure 1. The mean aluminium consumption in automobiles in Europe [15].

their modifications [5–11]. The high demand is due to the excellent high strength-to-weight ratio, abrasion and corrosion resistance and low coefficient of thermal expansion possess by aluminium alloys. Besides these properties, aluminium alloys application is limited by certain mechanical property drawbacks, such as partially inherited as-cast microstructure, existence of unavoidable metastable intermetallics and intra-dendritic zones of microstructure [12, 13]. Eutectic and near-eutectic Al–Si–X alloys depend on chemical composition, morphology of dendritic α -Al, and intermetallics that are present in the microstructure for mechanical properties. Coupled with the size and morphology of eutectic Si and the precipitation hardening phases during heat treatment, describing the myriad variables responsible for mechanical properties is quite complex.

These alloys are usually produced from secondary alloys and recycling processes. Many of their based alloys contain impurities, while the levels of impurities in the recycled ones are multiplied during recycling process. Alloying elements, such as Mg, Cu and silicon (Si) are deliberately added to Al alloys to enhance their mechanical properties. Apart from the intentionally added elements, impurities such as Fe, Cu, Cr, Manganese (Mn), and transition metals are usually present [14]. Although these impurities are at trace levels in the alloys, they form new phase components called intermetallics that significantly influence the properties of the microstructures. Quite often, these impurities are strong sites for crack initiation that serve as weak points for decohesion failure. However, intermetallics of Al or Si show resistance to corrosion and oxidation due to their adherent surface oxides; intermetallics of light elements are applied in light weight areas due to their attractive low density, which gives rise to highly specific properties.

The total amount of intermetallics in as-cast alloys is below 5% volume. Despite a few intermetallics in the cast microstructure, the detrimental effects on the ductility and service performance of alloys are huge. Controlling and manipulating the development of the metastable intermetallics during non-equilibrium solidification are of technological interests. This chapter, therefore, centres on the understanding of intermetallics in Al–Si–X alloys, their formation, nature, their effects on mechanical properties and methods of mitigating their adverse influences. There are several published studies on the type of intermetallics in Al–Si–X alloys and their effects as presented in **Table 1**.

Ref	Al-Alloy	Intermetallics	Effects on mechanical properties
[16, 17]	Al-Fe-Fe is highly soluble in molten Al but low in solid Al (max 0.05 wt.%, 0.025 atm.%)	Al_3Fe	It cracks and reduces formability and fatigue resistance but Improves wear resistance
		Al_6Fe	The effect of Al_6Fe fibres on fatigue properties of Al-Fe alloys is not very clear yet, though is said to be finely dispersed.
[18–22]	Fe combines with other elements to form intermetallic phase particles of various types		
	Al-Si-Fe	$\beta\text{-Al}_5\text{FeSi}$;	Deleterious; stress raiser
		$\alpha\text{-Al}_8\text{Fe}_2\text{Si}$	Less harmful
		$\delta\text{-Al}_4\text{FeSi}$	Metastable
	Al-Si-Mg-Fe	$\pi\text{-Al}_8\text{Mg}_3\text{FeSi}_6$	It has negative impact on ductile properties; lower strength and ductility
		$\text{Al}_9\text{FeMg}_3\text{Si}_5$	improved significantly after the T6 heat treatment
[23]	Al-Mn-Fe	$\text{Al}_6(\text{Fe,Mn})$	Detrimental to the alloys' ductility
	Al-Si-Mn-Fe (Excess Mn + Al_5FeSi)	$\alpha\text{-Al}_{15}(\text{FeMn})_3\text{Si}_2$ (China script)	Significantly deteriorate the mechanical properties of alloy
			Not very harmful but reduces the machinability
[24, 25]	Al-Cu (Cu 1–4%)	$\theta\text{-Al}_2\text{Cu}$	Improve mechanical properties-they decrease the grain size and increase the fatigue life
	Al-Si-Cu-Mg (Cu 1–4%)	(Q) $\text{Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$	

Table 1. Studies on the types of intermetallics in al-Si-X alloys and their effects on mechanical properties.

2. Formation processes of intermetallic compounds and their identification

The equilibrium and non-equilibrium reactions that occur during the casting of Al alloy account for intermetallic phases. Coarse intermetallic particles are formed in the interdendritic regions during solidification or at a relatively high temperature in the solid state during solution treatment, homogenisation, or recrystallization [14]. Most metals, except for Mg and Cu, exhibit a low solid solubility in Al. When the amount of solute element exceeds the limit of solid solubility, an intermediate phase, also called second phase, is developed. The composition of the intermediate phase is in between two pure metals (primary components) and has a varied crystal structure from the primary components. The intermediate phase, with unchanging composition, is called an intermetallic compound. Therefore, intermetallics are products of incomplete solid solubility by alloy systems. Intermetallic compounds identification in Al alloys is critical to complex structure examination. Microstructural examination is one of the primary ways of evaluating the evolution of phases in materials. This evaluation promotes the understanding of the effects of composition, production technique, heat treatments and deformation process on

alloys’ mechanical behaviours. Also, it is used to investigate the influences of new fabrication processes and to analyse failure mechanisms and causes.

2.1. Identification of intermetallics

2.1.1. Fe-Intermetallics

The known intermetallic compounds in aluminium and its alloys are categorised into two systems: binary (Al-Fe and Fe-Si) and ternary systems. The following phases have been reported to exist in Al-Fe binary systems: Al_5Fe_2 , Al_3Fe , Al_2Fe , $\text{Al}_{13}\text{Fe}_4$ and Al_8Fe_5 [26–28]. In the case of a Fe-Si system, the following stable compounds were found: FeSi , Fe_2Si , FeSi_2 , and Fe_5Si_3 [29, 30]. Phase equilibria of the binary systems are generally well known. The ternary system is characterised by a large number phases, both metastable and stable. Several review papers on Al-Fe-Si ternary phases have been published [23–25]. Gosh appraised over 150 research papers on ternary phases that covered unto 1986 [30, 31]. More updates have been provided by other authors [30] and in 2008, Du et al. presented about 24 Al-Si-Fe ternary compounds [32]. A summary of all the significant phases of both binary and ternary systems are presented in **Table 2**.

In a study, the effects of Cu, Fe, Mg, Mn, and Sr. additions on the type of intermetallic compounds formed in Al-Si eutectic alloys were investigated and reported [33]. Many eutectic alloys (SP0, SP1 SP2, SP3, SP4, and SP5) were developed by adding elements Cu, Fe, Mn, Mg and Sr. to A413.1. The chemical compositions of the various alloys produced for the experiment are presented in **Table 3**.

Microstructural examination shows the presence of α -Fe Chinese script phases in alloys SP0, SP4 and SP5, with a reasonable amount of Mn, as shown in **Figure 2**. The morphology of Chinese script of the α -Fe phase arises during solidification of eutectic alongside α -Al. The appearance of α -Fe phase could be polyhedrons if it solidifies before the eutectic reaction occurs [34].

Binary systems			Denary systems (Al-Si-Fe)	
Al-Fe	Al-Si	Fe-Si	$\text{Al}_2\text{Fe}_3\text{Si}_3$	$\text{Al}_{4.5}\text{FeSi}$
$\text{AlFe} (\alpha_2)$	$\text{HT-FeSi}_2 (\text{Fe}_2\text{Si}_5)$	FeSi	Al_3FeSi	$\text{Al}_3\text{Fe}_2\text{Si}_3$
$\text{AlFe}_3 (\alpha_1)$	LT-FeSi_2	FeSi_2	$\text{Al}_{21.5-45}\text{Fe}_{36.5-37.5}\text{Si}_{8.5-41.5}^a$	$\text{Al}_{64.5-67.5}\text{Fe}_{15.5-16.5}\text{Si}_{17-19}^a$
Al_2Fe	Fe_2Si	Fe_2Si	Al_2FeSi	$\text{Al}_{12}\text{Fe}_3\text{Si}_4$
Al_5Fe_2	Fe_5Si_3	Fe_5Si_3	$\text{Al}_{53.9-65.3}\text{Fe}_{19.5-20.5}\text{Si}_{15.2-25.6}^a$	$\text{Al}_{39.2-48.7}\text{Fe}_{23.5-24.5}\text{Si}_{27.8-36.3}^a$
$\text{Al}_{13}\text{Fe}_4$	FeSi		Al_3FeSi_2	$\text{Al}_{24.1-28.6}\text{Fe}_{31.9-32.9}\text{Si}_{39.5-43}^a$
$\text{Al}_8\text{Fe}_5 (\text{e})$			$\text{Al}_{53-56}\text{Fe}_{23.5-24.5}\text{Si}_{20.5-22.5}^a$	$\text{Al}_{57-59}\text{Fe}_{24-25}\text{Si}_{17-18}^a$
			$\text{Al}_{7.4}\text{Fe}_2\text{Si}$	$\text{Al}_4\text{Fe}_{1.7}\text{Si}$
			$\text{Al}_{45.5-54}\text{Fe}_{15.5-16.5}\text{Si}_{30.5-38}^a$	$\text{Al}_{64-66.5}\text{Fe}_{24-25}\text{Si}_{9.5-11}^a$
			$\text{Al}_{68-72}\text{Fe}_{18-19.5}\text{Si}_{10-12.5}^a$	

Table 2. A summary of both binary and ternary systems.

Phase type	Alloy code	Al	Si	Cu	Fe	Cr	Mn	Mg	Sr/ ppm*	Suggested composition
α -Fe	Sp0	60.30	9.93	0.48	18.43	1.83	8.99		120	$Al_{12.7}(Fe,Mn,Cr,Cu)_3Si_2$
	Sp0	60.32	9.93	0.49	19.17	1.67	8.41		00	$Al_{12.7}(Fe,Mn,Cr,Cu)_3Si_2$
	Sp0	59.81	9.58	0.98	21.10	0.96	7.57		00	$Al_{13.6}(Fe,Mn,Cr,Cu)_{3.3}Si_2$
	Sp0	66.36	9.90	0.88	14.72	1.42	6.71		00	$Al_{14}(Fe,Mn,Cr,Cu)_{2.3}Si_2$
	Sp0	65.14	9.52	0.58	16.07	1.48	7.19		180	$Al_{12.6}(Fe,Mn,Cr,Cu)_3Si_2$
	Sp0	61.09	10.10	0.39	19.05	1.87	9.11		42	$Al_{12.1}(Fe,Mn,Cr,Cu)_{2.9}Si_2$
	Sp0	60.10	10.13	0.40	18.28	1.90	8.78		110	$Al_{12.3}(Fe,Mn,Cr,Cu)_{2.8}Si_2$
	Sp4	59.9	10.5	1.29	14.7	1.79	12.8	0.01	132	$Al_{11.7}(Fe,Mn,Cr,Cu)_{2.9}Si_2$
	Sp5	60.59	10.4	0.79	17.0	2.32	10.3	000	109	$Al_{12.2}(Fe,Mn,Cr,Cu)_3Si_2$
	Sp5	70.51	8.92	1.44	12.88	0.63	4.94	0.08	000	$Al_{16.5}(Fe,Mn,Cr,Cu)_{2.2}Si_2$
	Sp5	61.83	9.63	0.67	20.10	1.29	8.79	000	452	$Al_{13.4}(Fe,Mn,Cr,Cu)_{3.3}Si_2$
	Sp5	61.8	9.43	0.60	20.62	1.26	8.30	000	000	$Al_{13.7}(Fe,Mn,Cr,Cu)_{3.3}Si_2$
	Sp5	61.09	10.4	0.90	19.04	1.58	8.77	000	000	$Al_{12.3}(Fe,Mn,Cr,Cu)_{2.9}Si_2$
	Sp5	61.46	10.1	1.10	20.77	1.02	8.03	0.01	236	$Al_{12.7}(Fe,Mn,Cr,Cu)_{3.1}Si_2$
	Range	59.8– 70.6	8.9– 10.5	0.4– 1.44	14.7– 21.1	0.63–2.3	4.9– 12.8			$Al_{11.7-16.5}(Fe,Mn,Cr,Cu)_{2.2-3.3}Si_2$
	Average	62.2	9.9	0.79	18.0	1.5	8.5			$Al_{13}(Fe,Mn,Cr,Cu)_{2.9}Si_2$
β -Fe	Sp1	66.25	18	0.21	14.1	0.11	4.68		00	$Al_{7.1}(Fe,Mn,Cr,Cu)Si_{1.8}$
	Sp1	71.2	9.66	0.33	13.56	0.11	4.23		241	$Al_{8.0}(Fe,Mn,Cr,Cu)Si$
	Sp1	56.7	17.68	0.05	22.8	0.03	3.8		00	$Al_{4.4}(Fe,Mn,Cr,Cu)Si_{1.3}$
	Sp1	68.5	17.3	0.25	16.5	0.05	3.55		00	$Al_{7.0}(Fe,Mn,Cr,Cu)Si_{1.7}$
	Sp2	72.3	14.8	0.13	10.7	0.07	2.72		352	$Al_{10.7}(Fe,Mn,Cr,Cu)Si_{2.1}$
	Sp2	60.9	17.9	0.05	20.0	0.05	4.5		00	$Al_{5.0}(Fe,Mn,Cr,Cu)Si_{1.4}$
	Sp4	55.7	17.9	0.10	22.2	0.05	3.88	0.11	129	$Al_{4.39}(Fe,Mn,Cr,Cu)Si_{1.36}$
	Sp4	54.7	18.4	0.15	21.3	0.06	3.72	1.69	000	$Al_{4.47}(Fe,Mn,Cr,Cu)Si_{1.59}$
	Sp4	55.6	17.9	0.10	22.1	0.03	3.61	0.44	000	$Al_{4.43}(Fe,Mn,Cr,Cu)Si_{1.41}$
	Sp4	56.4	18.1	0.06	23.0	0.03	3.79	0.02	000	$Al_{4.33}(Fe,Mn,Cr,Cu)Si_{1.34}$
	Range	54.4– 72.3	9.6– 18.4	0.05– 0.33	10.7– 23	0.03– 0.11	2.72– 4.68			$Al_{4.3-10.7}(Fe,Mn,Cr,Cu)Si_{1-2.21}$
	Average	61.8	16.7	0.14	18.6	0.06	3.8			$Al_6(Fe,Mn,Cr,Cu)Si_{1.5}$

Phase type	Alloy code	Al	Si	Cu	Fe	Cr	Mn	Mg	Sr/ppm*	Suggested composition
Mg ₂ S Pi phase	Sp3	0.33	37.3					62.4	00	Mg _{1.9} Si
	Sp3	49.3	26.5	0.13	8.16	0.10	1.66	14.76	00	Al _{10.3} (Fe,Mn,Cr,Cu)Si _{5.3} Mg _{3.4}
	Sp3	52.3	25.8	0.19	7.89	0.05	1.23	13.27	00	Al _{11.8} (Fe,Mn,Cr,Cu)Si _{5.6} Mg _{3.3}
	Sp3	48.6	26.1	0.08	9.19	0.01	0.96	15.03	00	Al _{9.9} (Fe,Mn,Cr,Cu)Si _{5.1} Mg _{3.4}
	Sp2	51.0	25.4	0.11	8.11	0.08	1.44	13.87	00	Al _{11.0} (Fe,Mn,Cr,Cu)Si _{5.3} Mg _{3.3}
	Sp2	49.6	26.5	0.20	8.77	00	0.63	14.22	00	Al _{10.9} (Fe,Mn,Cr,Cu)Si _{5.6} Mg _{3.5}
	Sp2	48.0	26.8	0.12	9.30	00	0.79	14.97	127	Al _{9.9} (Fe,Mn,Cr,Cu)Si _{5.3} Mg _{3.4}
	Sp4	46.7	27.4	0.18	7.91	0.04	1.91	15.9	000	Al _{9.6} (Fe,Mn,Cr,Cu)Si _{5.4} Mg _{3.6}
	Sp4	47.5	27.4	0.27	8.50	0.02	1.26	15.9	000	Al _{9.9} (Fe,Mn,Cr,Cu)Si _{5.5} Mg _{3.7}
	Sp4	48.4	26.7	0.46	9.58	0.13	2.44	15.1	000	Al _{8.1} (Fe,Mn,Cr,Cu)Si _{4.3} Mg _{2.8}
	Sp4	46.9	27.4	0.15	8.15	0.03	1.98	15.9	000	Al _{9.4} (Fe,Mn,Cr,Cu)Si _{5.2} Mg _{3.5}
	Range	46.7– 52.3	25.4– 27.4	0.08– 0.46	7.9–9.6	0–0.13	0.6– 2.44	13.3– 15.9		Al _{8.1–11.8} (Fe,Mn,Cr,Cu)Si _{4.3– 5.6} Mg _{2.8–3.7}
	Average	48.9	26.6	0.19	8.6	0.04	1.43	14.9		Al ₉ (Fe,Mn,Cr,Cu)Si _{5.3} Mg _{3.4}
	Sp3	16.56	31.6	19.23	0.10	0.01	0.01	34.67	000	Al ₄ Mg _{9.4} Cu ₂ Si _{7.4}
Q phases	Sp3	17.56	31.6	20.36	0.04	000	000	36.51	117	Al ₁₄ Mg _{9.4} Cu ₂ Si ₇
	Sp3	18.62	31.4	19.51	0.12	000	0.01	36.29	000	Al _{4.5} Mg _{9.7} Cu ₂ Si _{7.3}
	Sp3	20.88	26.6	17.25	0.02	00	00	38.01	000	Al _{4.4} Mg _{8.4} Cu ₂ Si ₇
	Sp4	22.51	28.5	18.9	0.14	0.01	0.01	39.28	000	Al _{4.6} Mg ₈ Cu ₂ Si _{6.8}
	Sp4	21.7	30.2	18.4	0.10	0.02	000	37.89		Al _{4.1} Mg _{7.8} Cu ₂ Si _{7.7}
	Range	16.6– 22.5	26.6– 31.6	17.2– 20.3	0.02– 0.14			28–36.5		Al _{4–4.4} Mg _{7.8–9.7} Cu ₂ Si _{6.8–7.7}
	Average	23.6	30	18.9	0.8			32.8		Al ₄ Mg _{8.8} Cu ₂ Si _{7.2}

Table 3. Analysis of chemical composition of intermetallic phases [33].

2.1.2. α - and β -Fe phases

The platelet β -AlFeSi particles are found in the Sp1, Sp2 and Sp4 alloys. The β phase is known to be a primary phase, with a three-dimensional form of a platelet that looks like needles in a two-dimensional optical micrograph, as shown in **Figure 3**. The β -Fe phase chemical composition observed vary within Al₉Fe₂Si₂, Al₉FeSi, Al_{13.6}Fe₃Si_{3.05}, Al_{13.3}Fe₃Si_{3.3} and Al_{13.6}Fe₃Si_{3.4} [35]. The phases are generally represented by the chemical formula Al₅FeSi, despite the non-inclusion of alloying elements such as Cu, Mn, etc. The α -phase is the second type of the script-like; it has a lower amount of Fe which is between 23.88 and 26.79 wt.%, with Si in the range of 6.87 and 8.38 wt.%. The chemical formula of the phase is Al_{10.42–11.67}Fe₂Si_{1.08–1.25}. The second type of

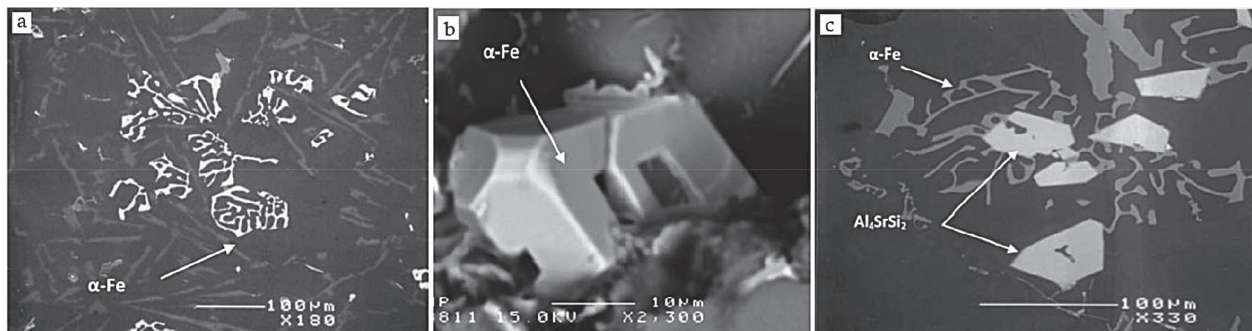


Figure 2. Refs. [33, 34] shows (a) non-modified PS0 alloy; (b) shows compact SEM image of phase; (c) structure of over modified PS4 alloy –note the presences of Al₄SrSi₂ particles on top of a-Fe morphology.

the script-like a phase has a lower iron content, between 23.88 and 26.79 wt.%, a silicon content lying between 6.87 and 8.38 wt.%, and a chemical formula of $\text{Al}_{10.42-11.67}\text{FeSi}_{1.08-1.25}$.

2.1.3. δ - and π -phase α - and β -Fe phases

Apart from α - and β -AlFeSi phases commonly found in Fe intermetallic compounds, there are other phases that are occasionally found [33]. These phases include δ -Al₄FeSi₂ and π -Al₈Mg₃FeSi₆ compounds, shown in the micrographs in **Figure 4**. The formation of the δ -Al₄FeSi₂ phase is favoured by high amount of Si in Al-Si eutectic alloys. This phase is considered to be the richest in Si of the Al-Fe-Si phases, and looks like platelet morphology and shows grey level under optical microscope like β -phase [21, 36]. The disparity in the Fe/Si atomic ratio in the examined β -phase particles is most likely the outcome of the partial conversion of the δ -phase to the β -phase via the peritectic decomposition as in the expression [37]:

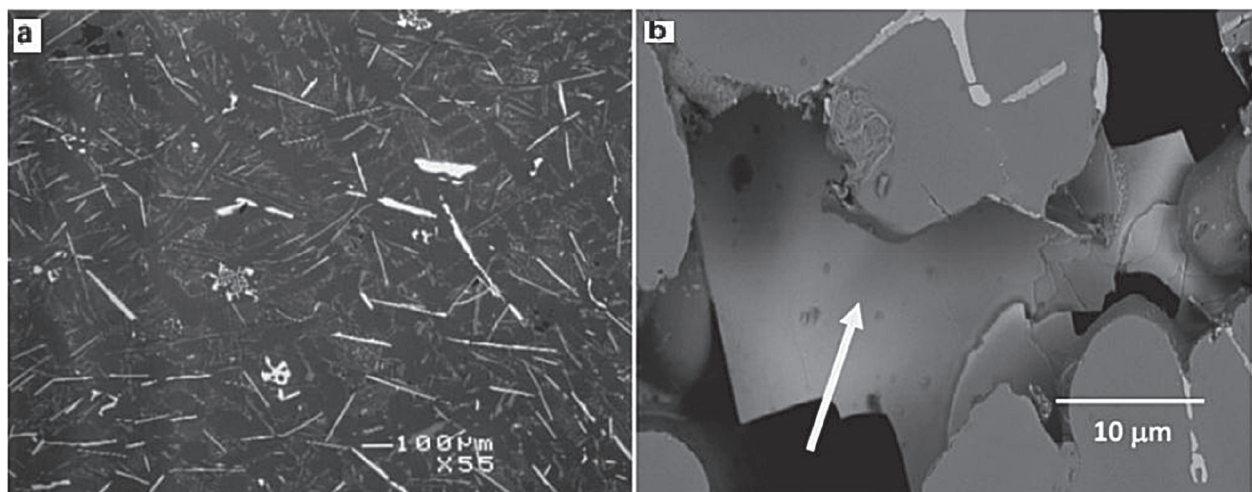
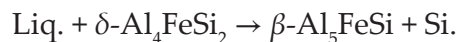


Figure 3. Optical micrograph of (a) β -Fe phase (needles) in alloy Sp1 and (b) SEM image showing 3-D platelet morphology of β -Fe phase [33].

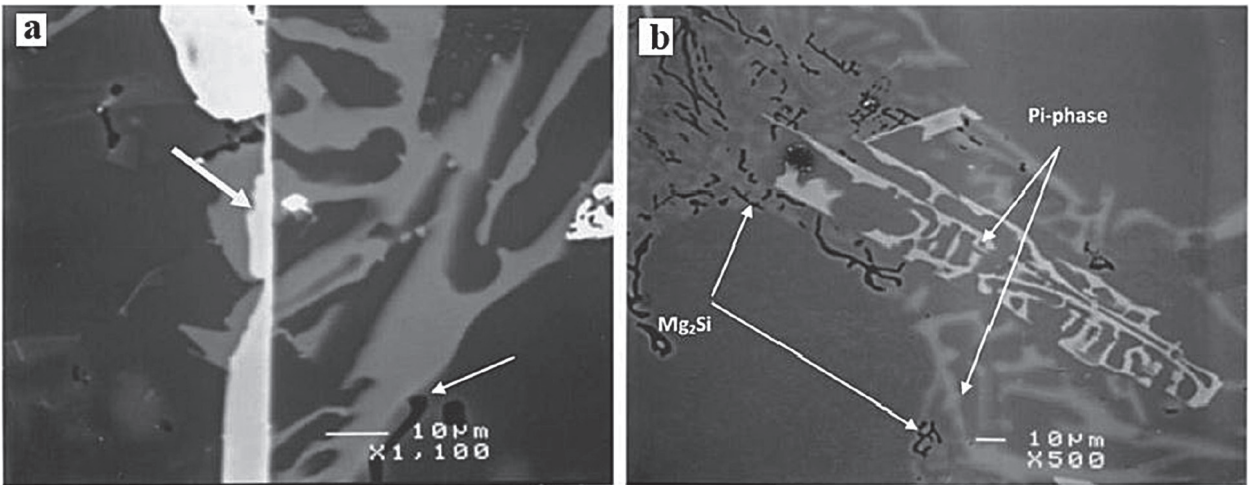


Figure 4. (a) β - Al_5FeSi transforming into pi-phase in Sp4 alloy; (b) presence of pi-phase and phases of Mg_2Si Chinese script in SP3 alloy [33].

The $\text{pi-Al}_8\text{Mg}_3\text{FeSi}_6$ phase is usually present in the precipitates of an alloy containing relatively high Mg, such as Sp3 and Sp4 in **Table 3**.

2.2. Mg_2Si phase

The precipitate, Mg_2Si , is usually observed to in all Al–Si–Mg alloys, at the edge of pi phase particles. It appears in the form of black Chinese script particles, as shown in **Figure 4**. The precipitate can also be found at the edge of primary Si and the average chemical analysis of the Mg_2Si provided in **Table 3**.

2.3. Al_2Cu and Q-phases

Copper concentration increases with the solid fraction and segregates to the liquid during solidification. $\text{Al-Al}_2\text{Cu}$ is formed to the end of solidification. A study has suggested that addition of alloying elements, such as Mg and Sr phase, does not alter the stability of the Al_2Cu [33]. During final solidification, the Q-phase, $\text{Q-Al}_5\text{Mg}_8\text{Si}_6\text{Cu}_2$, grows out from Al_2Cu

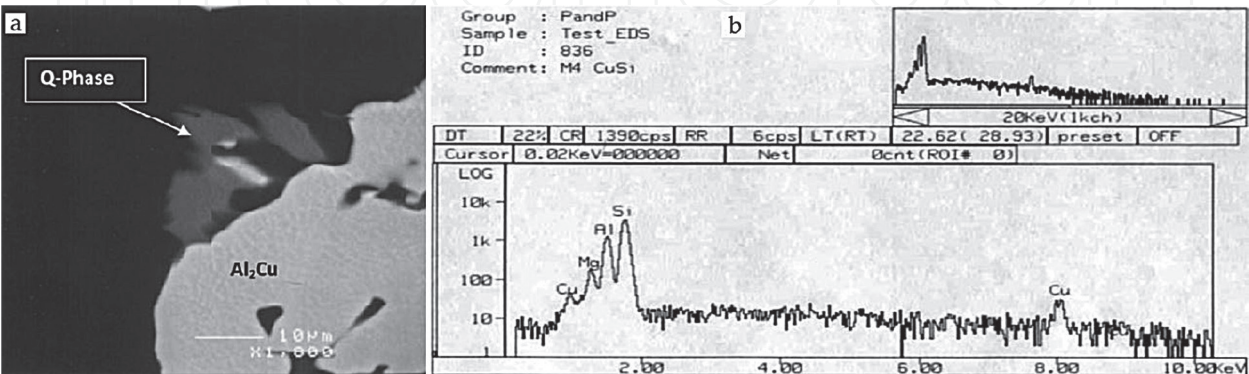


Figure 5. (a) Q-phase growing out of Al_2Cu phase; (b) energy dispersive spectroscopy corresponding to Q phase in (a) [33].

particles. The EDX spectrum in **Figure 5**, shown that Q-phase has a reflection of elements, such as Al, Cu, Si and Mg, in the alloy.

Secondary alloys were prepared from recycling of cast Al alloys scrap of AlSi9Cu3, AlSi12Cu1Fe and AlSi8Zn10Mg were investigated for intermetallic compounds [38]. The chemical compositions of the recycled alloys are presented in **Table 4**.

The intermetallics found in recycled cast alloys, AlSi12Cu1Fe, AlSi8Zn10Mg and AlSi9Cu3, are presented **Figures 6 and 7**.

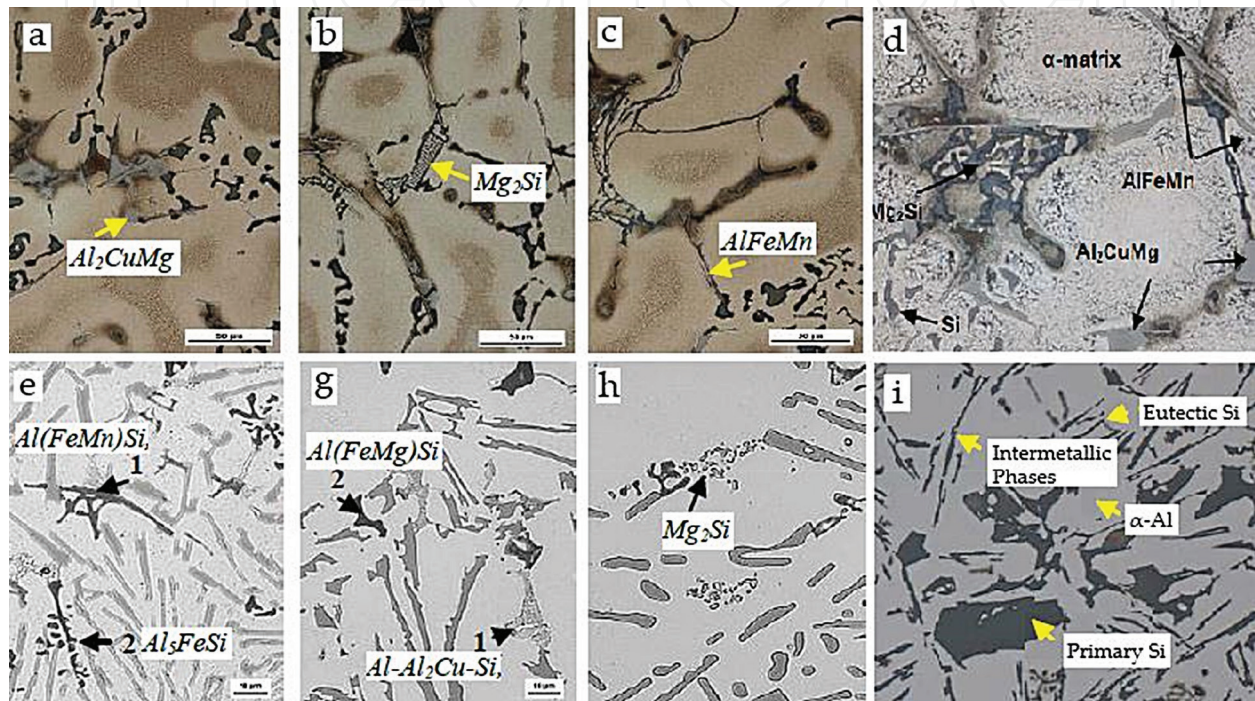


Figure 6. Intermetallic phases in the microstructures of recycled al-Si-X cast alloys [38] (a–c) intermetallics in AlSi8Zn10Mg cast alloy; (e–h) intermetallics in AlSi12Cu1Fe cast alloy; (d & i) microstructures of secondary AlSi8Zn10Mg and AlSi12Cu1Fe alloys respectively.

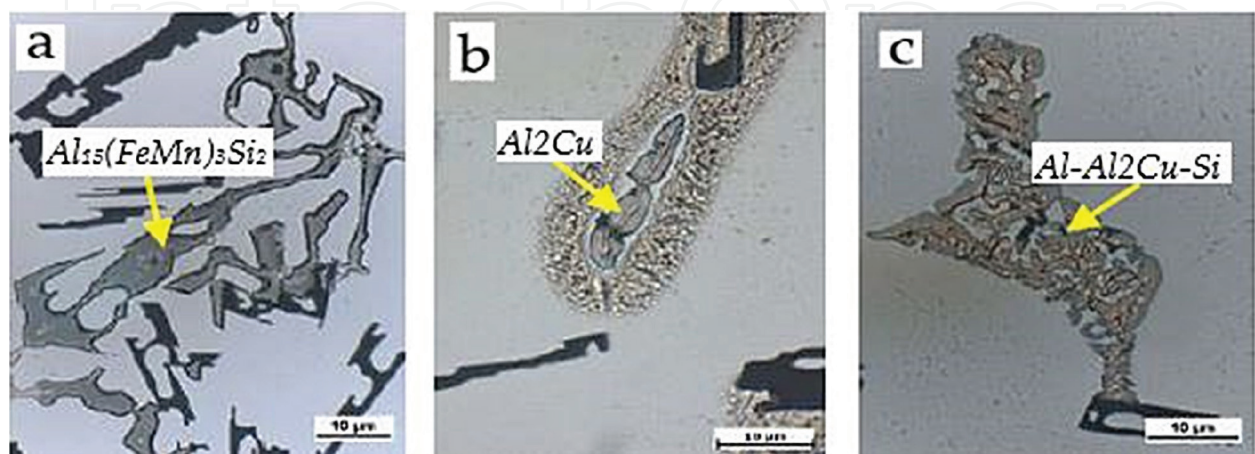


Figure 7. Intermetallic compounds in recycled AlSi9Cu3 cast alloy.

Materials elements	AlSi9Cu3	AlSi12Cu1Fe	AlSi8Zn10Mg
Si	9.4	12.5	8.64
Cu	2.4	0.85	0.005
Mn	0.24	0.245	0.181
Mg	0.28	0.347	0.452
Zn	1	0.42	9.6
Ni	0.05	0.039	0.0022
Fe	0.9	0.692	0.1143
Pb	0.09	0.055	—
Ti	0.04	0.026	0.0622
Cr	0.04	0.023	0.0014
Sn	0.03	0.01	—
Hg	—	—	0.0006
Ca	—	0.001	0.0002
Cd	—	—	0.0001
Bi	—	—	0.0003
P	—	—	0.0001
Sb	—	—	0.0007
Al	Remainder	Remainder	Remainder

Table 4. Chemical composition of the recycled of cast al alloys scrap (wt.%).

3. Effect of intermetallic on mechanical and physical properties of al-Si alloys

The presence of intermetallic compounds in Al alloys is of a great concern to materials engineers due to their harmful effects on mechanical properties. Mechanical properties of Al-Si-X alloys are greatly affected by the structures of the intermetallic. Intermetallics compounds appear more in recycled Al-Si based alloys, however, cycling which is a secondary production process of Al and its alloys is cheaper than primary production process. Therefore, producing Al alloys devoid of deleterious intermetallic phases will positively affect Al and its alloys recycle market and decrease the use of primary method that requires high fabrication power consumption.

The β -phase platelets are usually potential sites for crack initiation, where eventual breakup failure occurs. Iron-based intermetallics dominate Al-Si-X alloys' intermetallics studies. Commercially available alloys contain Fe impurities in the form of Al and Si and other elements phases. In conductive liquids, the presence of certain Fe-phases, Al_3Fe and

α -AlFeSi, on the surface stimulates pitting attacks on the surface because α -AlFeSi is cathodic in the Al matrix. The greatest disadvantage of intermetallics is their low ductility, especially at low and transitional temperatures. This has been attributed to several factors, such as [39]:

- i. A restricted number of simple deformation modes to suit the von Mises criterion,
- ii. Dislocations operation with large slip vectors
- iii. Restricted cross-slip
- iv. Transmitting slip across grain boundaries complexity
- v. Inherent grain boundary weakness
- vi. Isolation of harmful solutes to grain boundaries
- vii. High Peierls-Nabarro stress and covalent bonding
- viii. Environmental vulnerability.

3.1. Fe intermetallics

The presence of the dispersed brittle intermetallic β -Al₅FeSi phase in the structure is one of the primary barriers that impede the bendability of Al-Si based alloy sheet and consequently, poor mechanical formability. During sheet bending and forming processes, these particles create damage and premature failure. Intermetallic, β -Al₅FeSi, forms thin brittle platelets that cause weak bond strengths within the matrix of α -Al, thus initiating crack sites around the structure. This deleterious behaviour is especially severe in sheets produced by strip casting, a cost-effective fabrication method, which should be economically suitable for automotive Al alloys production [40]. In Al-Si based casting, Fe is the most common deleterious impurity element and forms the intermetallic compound β -Al₅FeSi when levels of Fe in an alloy exceed critical percentage. Solid solubility of Fe in Al is very low and consequently combines with other impurities or alloying elements to form intermetallic compounds. The type of compound formed depends on the other available impurities. An optical micrograph of the Al-Si-1.8Fe-0.8Mn microstructure is shown in **Figure 8**.

However, Fe is required in pressure die casting to prevent liquid metal from soldering to the die [42, 43]. For optimal thermal performance, Fe is desirable for Al-Si alloys to maintain stable mechanical properties at high temperatures. The Al alloys formed by Cu and Mg addition, are known for high strength due to precipitation hardening. These alloys, however, lose their strength at elevated temperatures because of unstable precipitates formed by Cu and Mg. Addition of Fe to alloys makes them stable at high temperatures compared to alloys with Cu and Mg addition. Transition elements such as Fe, upon addition to Al alloys, yield thermally stable intermetallics. The composition of eutectic Al-Si-Fe alloy is about 0.8 wt.% Fe. The liquid metal does not show affinity of dissolution with the steel mould, once the iron content is at approximately this level. The desirable Fe content in alloys in most Al pressure die casters is in the range of 0.8–1.1 wt.% Fe.



Figure 8. Optical micrograph of al-Si-1.8Fe-0.8Mn microstructure [41].

The class of wrought Al alloys, 6xxx series, is known for good corrosion resistance and high strength to density ratio. These alloys are good substitutes for steel in the manufacturing of automobile body panels. Apart from their principal compositional elements, Al, Mg, and Si, 6xxx alloys also possess Fe, Cu, Mn, and Cr, which sometimes are not deliberately added. The presence of these elements, especially Fe, promotes the development of different brittle iron-containing intermetallic compounds [44]. These Fe intermetallics cause poor formability and consequently, stimulate premature failure and damage during bending and forming operations. This drawback limits the application of 6xxx alloys in both automotive and aerospace industries [40, 45, 46].

3.2. Other Fe-phases

Other phases that have a detrimental influence on the alloy properties are Al_3Fe and $\alpha\text{-AlFeSi}$, which is cathodic to the $\alpha\text{-Al}$ matrix. Their presence on the surface accelerates pitting attacks in conductive liquids. Subsequently, these affect the mechanical property of the alloy by decreasing its ductility and resulting in de-cohesion failure. Equally, the platelets and needles of β -phase intermetallic, may adversely affect the alloy's castability, fluidity, and dendrites channel feeding, which results in cast defects. The different intermetallic phases in Al-Si eutectic alloys depend on the composition of the alloys. However, the phases in the microstructure with Cu and Mg, $\beta\text{-Al-Fe-Si-X}$ and Sr, which are usually called Chinese script phases, are most studied. Virtually in all the alloys microstructures, $\alpha\text{-AlFeSiCuMg}$ phases

with the Chinese script morphology are the dominant Fe intermetallic phases [47]. The composition of the alloy affects the morphology and location of intermetallic phases in α -Al or in the interdendritic regions.

3.3. Manganese, Mn

Often, Mn is found in secondary metal made from recycled wrought product and is usually not deliberately added to virgin cast alloys. Manganese can transform iron-rich (Al_5FeSi) phases morphology of Al-Si-X alloy from platelets to a more cubic or globules ($\text{Al}_{15}(\text{MnFe})_3\text{Si}_2$) and this improves the alloy's ductility and tensile strength. **Figure 9** shows micrographs of Al-Si-X structure with (a) iron-rich $\text{Al}_{15}\text{FeSi}$ phase; and (b) Cubic $\text{Al}_{15}(\text{MnFe})_3\text{Si}_2$ form.

It is recommended that Mn should be over 50% of Fe when the amount of Fe exceeds 0.45 wt.%. Manganese (Mn) is more influential in causing gravity segregation than Fe. Application of Mn concentration that exceeds 0.6 wt.% causes segregation whether the Fe content is 0.8 or 2.3 wt.% [48]. Further, Mondolfo [21] reported that Mn marginally improves strength at the expense of ductility, while Kashyap et al. [49] indicate that presence of Mn weakens the strength of Al-7Si-Mg alloy.

Several literatures have indicated that Mn enhances yield strength and ultimate tensile strength of wrought Al-Si alloys [50, 51]. Formation of fine dispersoids of about 0.03–0.3 μm by the addition of Zr, Cr and Mn to commercial aluminium alloys was reported in these studies. Dispersoids significantly affect alloy's fracture toughness, strength, grain structures and recrystallization characteristics. Investigation has revealed that commercial 6000, 7000 and 8000 series aluminium alloys are improved by the addition of manganese with it ductility retained [52].

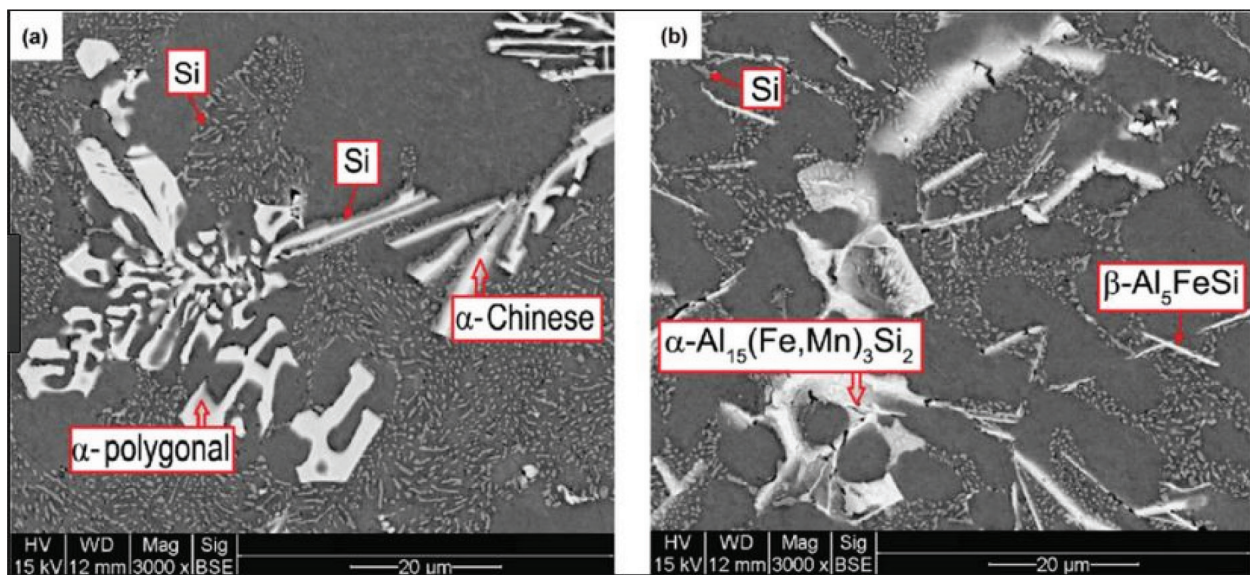


Figure 9. (a) Formation of a thick polyhedral $\alpha\text{-Al}_{15}(\text{Fe,Mn})_3\text{Si}_2$ phase in the microstructure of the Al9Si0.8Fe alloy containing 0.7 wt.% of Mn; (b) micrograph of the Al9Si0.8Fe alloy containing 0.7 wt.% of Mn showing the presence of the $\beta\text{-Al}_5\text{FeSi}$ particles [2].

4. Processes to eliminate or ameliorate intermetallic deleterious effects

Many studies have reported various approaches and techniques in improving the mechanical properties of Fe-bearing intermetallics by the application of modification principle. Rapid solidification process increases the solubility fields and alters the morphology and size of microstructural elements but does not eliminate intermetallics. Das et al. demonstrated the effect of rapid cooling on alloy by processing Rheocast A380 alloy, using cooling slope (CS) technique to generate semisolid slurry from the superheated alloy melt [53]. The study observed finer, near spherical grains within the cooling slope fabricated slurry and in the solidified castings. This structure is different from the dendritic grains bounded by large eutectic phase within the conventionally cast A380 alloy. However, the most harmful intermetallic phase, β -Al₅FeSi (monoclinic), was found to be present, accounting for the alloy's low ductility and consequent poor mechanical formability [54].

The Al-Si-Cu ternary system alloy, A380, has minute fractions of Fe, Mg, Mn, Ni and Zn. These impurity elements interact to form intermetallic compounds near the grain boundary and occasionally in the parent matrix. The expected intermetallics phases in A380 alloy are α -phase, β -phase (Al₅FeSi), and (Al₁₅(Fe,Mn)₃Si₂). β -phase morphology is platelet-like (needle-like) appearance and serves as a stress-raiser in the matrix, while α -Phase morphology is like polyhedral crystals and sometimes like Chinese script. The detrimental effects of intermetallic need to be removed or reduced; some of the techniques that are exploited include thermal treatment, chemical solutions and microstructural control by co-injecting inoculated intermetallic particles [54–56].

Thermal treatment—Heat treatment is a normal alternative to be considered. However, the dissolved phase possibly precipitated by thermal homogenisation process during artificial or natural ageing. This is not very effective because thermodynamically, stable phases are not influenced by heat treatment.

Chemical solutions—Conventional metallurgical chemical processes are used to eliminate the deleterious effects of Fe in Al alloys by limiting the amount of Fe to prevent the formation of Al-Fe-Si compounds.

Microstructural control—Co-injecting inoculated intermetallic particles is used to manipulate the microstructure. The particles, which vaporised during spray-forming, act as a substrate for heterogeneous nucleation, promoting nucleation and grow into the cubic. This principle involves the alteration of the type, size, morphology and the dispersion of the intermetallics in these alloys. Hosseinifar and Malakhov reported that the addition of 0.2% wt lanthanum (La) decreased the fraction of deleterious plate-like β -AlFeSi phase and increased the amount of a lesser harmful, α -AlFeSi phase [57]. It was explained that La covers the surface of the Chinese script particles (α -AlFeSi), a behaviour inferred to be like that of Strontium (Sr) addition. SEM images of Chinese script-shaped intermetallic compounds and the morphology of the β -AlFeSi phase are shown in **Figure 10**.

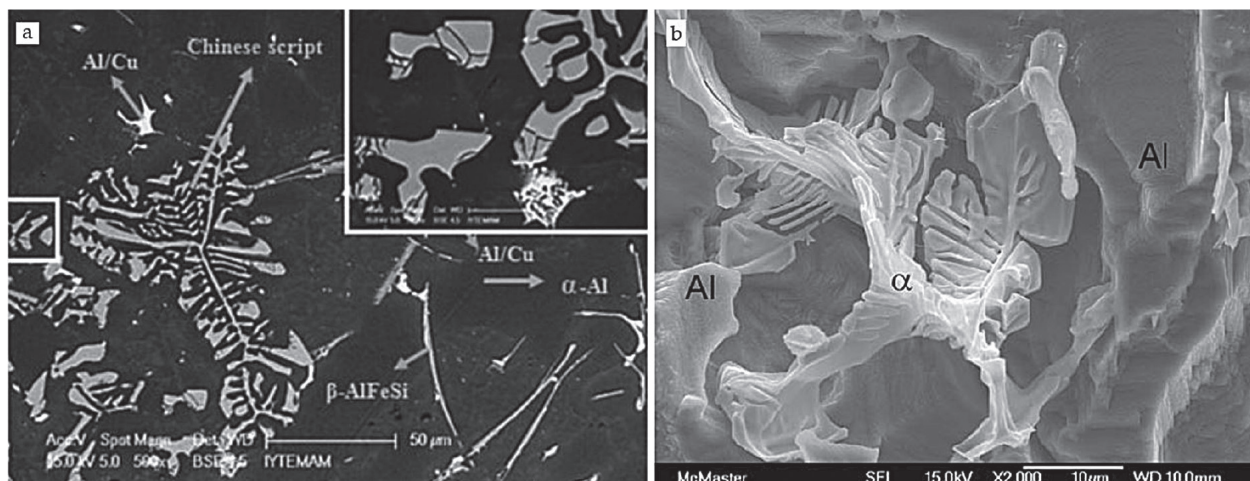


Figure 10. SEM images showing the (a) presence of the Chinese script-shaped intermetallic compounds [58]; (b) morphology of the b-AlFeSi phase [57].

The addition of a sufficient amount of Mn to Fe-rich intermetallics can defuse its brittleness and alter the platelet morphology to a less deleterious intermetallic compound [43, 59]. However, the addition of Mn to a melt containing Fe leads to another problem, as this increases the volume fraction of intermetallics and the mean diameter size of Fe solute. This development deteriorates the alloy's mechanical properties [60]. **Table 5** shows examples of intermetallics and their corresponding ductility improving alloying elements.

The thixoforming process has been described as an effective technique to modify the morphology of the primary phases. Gencalp and Saklakoglu used this method to improve the formability property of A390 alloy with excess levels of Fe and Mn [58]. The intermetallic compounds observed in A380 fabricated by thixoforming are $\alpha\text{-Al}_{15}\text{Si}_2(\text{Fe},\text{Mn})_3$ with polyhedral morphology, different from the Chinese script morphology observed in the traditional gravity casting. Also, in A380 alloy by thixoforming, the very harmful $\beta\text{-Al}_5\text{FeSi}$ particle morphology was small-plate and $\theta\text{-Al}_2\text{Cu}$ phase in the form of particle. These phases, Al_5FeSi and $\theta\text{-Al}_2\text{Cu}$ phase morphology are needle-like and thin plate respectively in gravity casting. SEM images of the varied intermetallics between thixoforming and gravity casting are shown in **Figure 11**. The A380 by thixoforming alloys had better mechanical properties compared to A380 by traditional gravity casting method.

The solidification paths of 6xxx series Al alloys with and without La were established using careful calorimetric and microstructural investigations. Studies have shown that the addition of Sr. to Al-Si-Fe alloys prevents the formation β -phase intermetallic but promotes the production of a

Intermetallic	$\beta\text{-AlFeSi}$	Ni_3Al	TiAl	Ti_3Al
Alloying element for ductility	Lanthanum (La)	Boron (B)	Manganese (Mn)	Niobium (Nb)

Table 5. Intermetallics with ductility improving alloying elements [39].

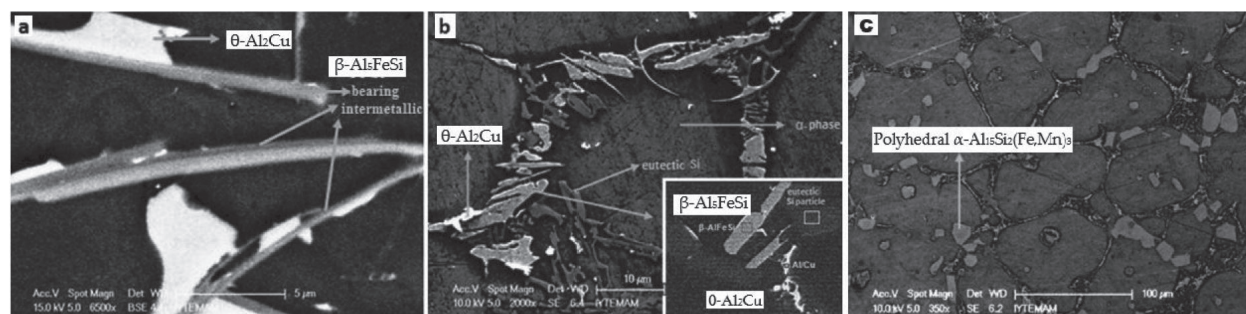


Figure 11. SEM images of (a) β -Al₅FeSi needle-like intermetallics present in the gravity casting (b) particle small plate intermetallics, β -Al₅FeSi found in thixoforming (c) α -Al₁₅Si₂(Fe,Mn)₃ with polyhedral morphology found in thixoforming [58].

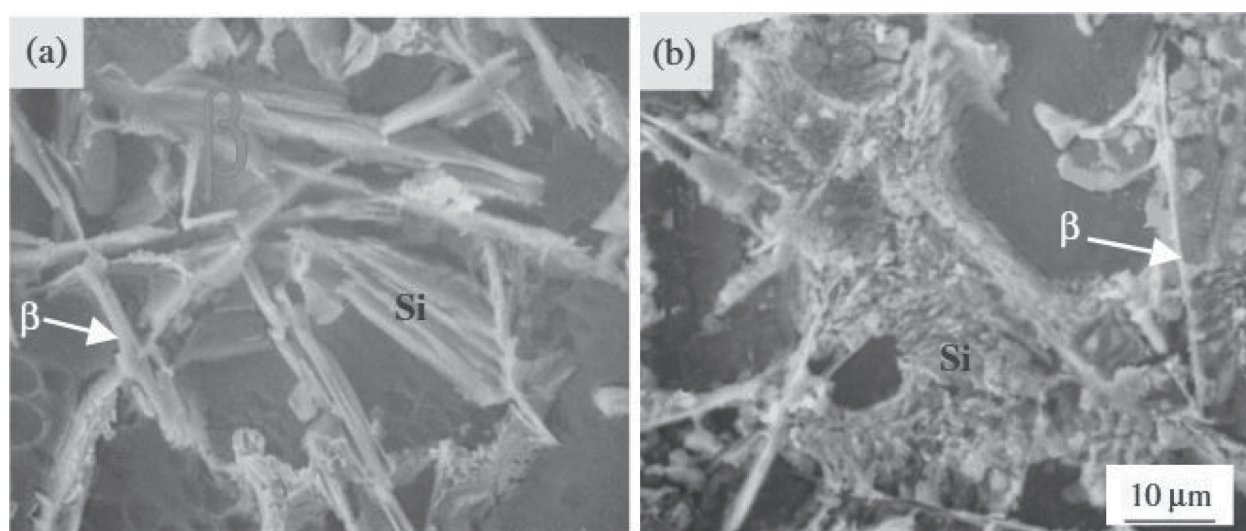


Figure 12. SEM images show the effect of adding Sr. on the microstructure of Al-6.5Si-3.5Cu-1.0Fe cast alloys (a) Sr. without; (b) with about 0.015% mass Sr [61].

less harmful phase, α -AlFeSi, in as-cast alloys [48, 61]. Adding Sr to Al alloys under a fast cooling is an effective way of altering the amount, size and morphology of needle-like of Al₅FeSi intermetallic compound. Chinese script or sludge are not formed in Al alloy without Mn. Addition of the combination of Fe and Mn at a high cooling rate was reported to be the most efficient technique of modifying intermetallic compounds [61]. SEM images in **Figure 12** show the Sr. unmodified and modified microstructure of Al-6.5Si-3.5Cu-1.0Fe (in mass %) alloy.

Apart from Sr., the less expensive rare-earth metal, lanthanum (La), was found to decrease the fraction of plate-like β -AlFeSi particles and increase the fraction of α -AlFeSi particles with Chinese script morphology.

5. Conclusion

The influences of ternary alloying elements (Fe, Cu, Mn, and Mg) additions to Al-Si alloys (binary alloys) were discussed in this paper. The chapter observed that:

- i. The equilibrium and non-equilibrium reactions that occur during the casting of Al alloy account for intermetallic phases.
- ii. Primary alloying elements are not completely soluble in the α -Al matrix and sometimes combine with impurities and matrix to form intermediate (intermetallics) phases.
- iii. Intermetallics are products of incomplete solid solubility by alloy systems.
- iv. Fe-based intermetallics are the most common. Fe-phases can be grouped into α - phase, β -phases, π -phase, and δ - phase, with α - and β -phases the most common. The most harmful intermetallics in Al-Si-Fe alloys is β -phase (β -Al₅SiFe).
- v. Iron is deliberately added to the alloy to prevent soldering in die casting mould.
- vi. Addition of Mn and Sr reduces the negative effect of β -phase of Fe intermetallics by improving the ductility. However, the addition of Mn weakens the strength of Al-7Si-Mg alloy.
- vii. Microstructural examination is one of the primary ways of evaluating the evolution of phases in materials.

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