The effect of alloying additions on the structure and properties of Al-Mg-Zn-Si-Mn alloy: A review

[1]Hemant Panchal, [2]Saloni Singh, [3]Rahul Sharma, [4]Krishna Solanki, [5]Sunil Kahar

[1,5]Assistant Professor, [2,3,4]Student
Department of Metallurgical and Materials Engineering,
The Maharaja Sayajirao University of Baroda, Vadodara, India

Abstract— **In recent years, aluminium and aluminium alloys are widely used in aerospace and automotive industries. Its high strength to weight ratio is responsible for its vast usage in structural applications. In the present study, aluminium alloys have been discussed in detail. The ensuing chapters discuss about the alloy series, their designation, heat treatment methods and followed by the effects of alloying additions. It is well known that; the principle aim of alloying is to enhance and amplify the properties of aluminium alloys. Hence, elements are added in calculated amounts for the optimization of properties. Aluminium alloys are finding increased applications in space, marine, brazing and transportation industries because of modified properties such as – excellent ductility, malleability, formability, corrosion & oxidation resistance, high electrical & thermal conductivity and increased strength, hardness, machinability & workability. Metallographers and metallurgists can learn a great deal from the phase diagrams, which are the starting point for our understanding of alloy systems. By analyzing these binary and ternary phase diagrams with the help of microstructures, one can study the physical, mechanical and tribological properties of aluminium alloys.**

Index Terms— **Aluminium, alloying, alloy series, properties, phase diagram, microstructure**

1. INTRODUCTION

Aluminium alloys evidently rank first in nonferrous materials from the viewpoints of both production and consumption. Al is a soft and light metal, but it was soon discovered that alloying it with other metals could remarkably improve its properties. This discovery resulted in increase in its usage (and invention of new Al-alloys) in the 19th and 20th centuries [1]. Al alloys are gaining huge industrial significance because of their exceptional properties such as lightweight, corrosion & oxidation resistance, high strength, hardness, machinability & workability, excellent ductility, malleability and formability, etc. Its lightweight property is the main reason for its vast usage in aerospace and automobile industries. A reduction in weight of these alloys is favorable because it improves its fuel efficiency & carbon footprint, alleviates power consumption and is economical. [2]

Adding a variety of elements to Al is the primary method used to produce a plethora of materials that can be utilized in various structural applications [3]. Different alloying elements influence the base alloy in different ways. Elements can be classified as Major (Cu, Si, Mg, Mg and Si, Zn), minor elements (Ni, Sn), modifiers (Ti and B, Sr, Na, Ca, Bi, P, S, Sb; Mn and Cr), impurity elements (Fe, Be), rare earth elements, etc. [2].

Alloying leads to formation of different phases. Each phase has its specific microstructure. An alloy's internal microstructure determines and varies the fundamental nature and the characteristics of the alloy and its operational uses. Al alloys are heat treated to improve strength and hardness of precipitation hardenable cast Al alloy. They are categorized as heat treatable and non-heat treatable Al alloys. In this paper, the influence of various alloying elements on Al- based casting alloy is studied. Its microstructure, phase diagrams and properties are analyzed for different alloy series.

2. Designation of Al-alloys

Wrought and Cast Aluminium alloys use different identification systems. The AAA (Aluminium Association of America) has bifurcated cast Al-alloys in accordance with a 3 digit-plus decimal system as shown in Table 1. Similarly, wrought Al-alloys are designated a four-digit system as shown in Table 2. The classification is done on the basis of alloying element in Al [5].

Table 1. Cast Al-alloy designation system

Series	Primary Alloying Element
1xx.x	Aluminium – 99.00% or greater
2xx.x	Copper
3xx.x	Silicon plus Copper and/or Magnesium
4xx.x	Silicon
5xx.x	Magnesium
6xx.x	Unused
7xx.x	Zinc
8xx.x	Tin
9xx.x	Other Elements

Table 2. Wrought Al-alloy designation system

Series	Primary Alloying Element
1xxx	Aluminium – 99.00% or greater
2xxx	Copper
3xxx	Manganese
4xxx	Silicon
5xxx	Magnesium
6xxx	Magnesium and Silicon
7xxx	Zinc
8xxx	Lithium

3. Heat treatment of Al-alloys

The main objective of heat treatment of Al-alloys is to elevate strength and hardness. Commonly used heat treatment processes for Al-alloys are:

- Annealing
- Homogenization
- Solution heat treatment
- Natural aging
- Artificial aging (precipitation hardening)

Wrought Al-alloys can be classified into two groups: heat treatable and non-heat treatable (NHT) alloys. 2xxx, 6xxx and 7xxx series alloy are heat-treatable. They are strengthened by solution heat treatment along with precipitation hardening. NHT alloys include 1xxx, 3xxx, 4xxx and 5xxx series. These alloys undergo solid solution strengthening followed by strain hardening or aging [7].

4. Effect of alloying elements

4.1 Pure Aluminium (1xxx series)

Aluminium of 99.00% or higher purity is designated as 1xxx series. These are non-heat treatable alloys with an ultimate tensile strength of 13-24 ksi. It would be very unusual to use pure Al for structural fabrication because of its moderate strength characteristic [3] and poor mechanical properties. However, these alloys have superior corrosion resistance, excellent thermal & electrical conductivity. Applications of 1xxx series are: [4]

- Power grid
- Electrical buss bars
- Food packaging trays
- Piping systems
- Chemical tanks
- Metallizing bars, etc.

4.2 Copper (2xxx series)

Copper being the major alloying element in the 2xxx series alters the mechanical properties significantly. In Al-Cu alloys, proportion of copper varies in between 2-10% [4]. Maximum solubility of Cu in Al is 2.5wt%, at the eutectic temperature of 548.2°C. There are several phases of intermetallic compounds (i.e. ζ, θ, α, θ, ϒ, η, ε, δ) present as shown in the Fig. 1. The micrograph of Al-20wt%Cu alloy is shown in Fig. 2. The light/white region in the microstructure represents α-phase, whereas the dark/black region represents theta phase. When the Cu content is increased to 33% (eutectic phase), lamellar structure starts forming, as shown in Fig. 3. [8] Hence, it can be concluded that on increasing Cu content α-Al crystals gradually change to columnar dendrites, equiaxed dendrites and finally into lamellar structure. A morphological discrepancy based on concentration of Al and Cu is observed in microstructure of θ phase as depicted in Fig. 4. [9]

Fig. 1. Phase Diagram of Al-Cu Alloy

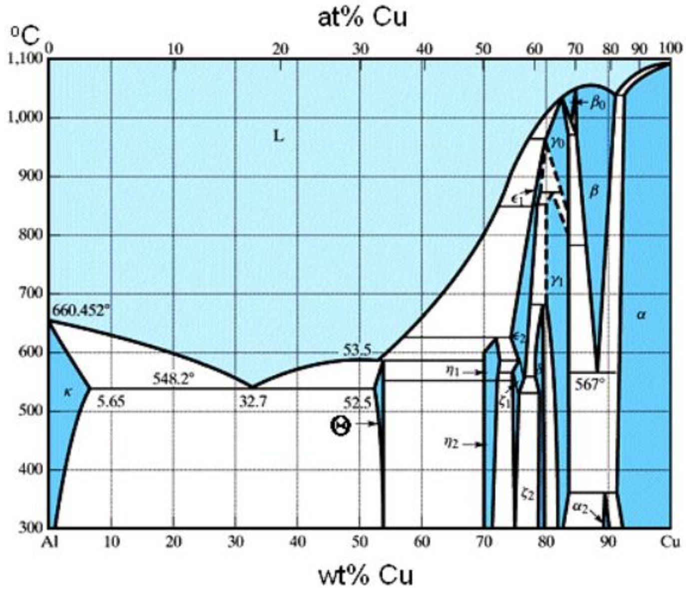


Fig. 2. Micrograph of Al-20wt%Cu alloy, etched in dil. 10% HNO3

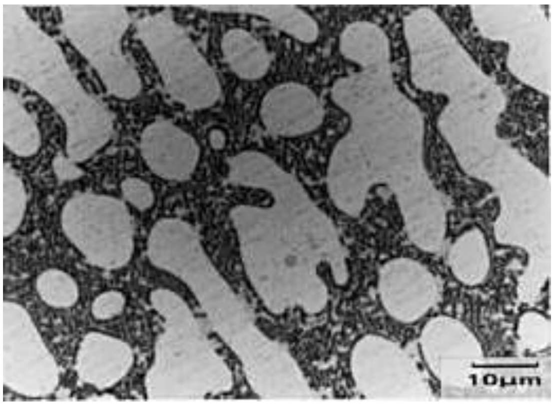
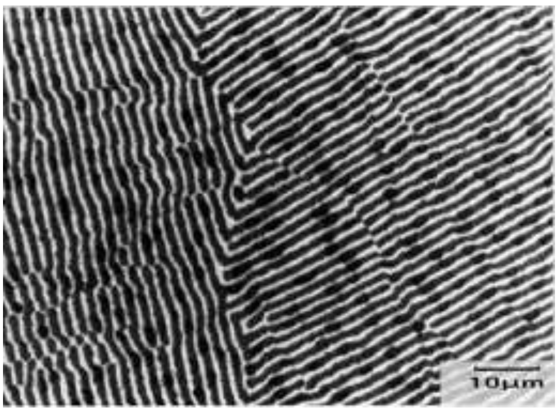
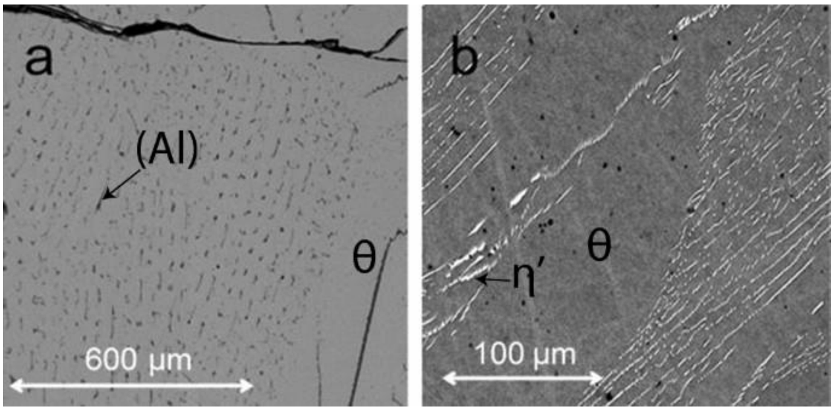


Fig. 3. Micrograph of Al-33wt%Cu alloy (eutectic phase), etched in dil. 10% HNO3



By understanding these various phases one can predict as well as refine the characteristics of the hence developed alloys. Being heat treatable in nature, this alloy series allows increase in strength by precipitation hardening. Here the precipitated phases mainly comprise of Al_2Cu and Al_2CuMg both being Cu-bearing strengthening phases [10]. In case of industrially used Al-Si-Mg-Cu alloy ($Al_9Si_{0.5}Mg_xCu$), addition of copper enhances yield strength and hardness. Here, with increase in Cu content β-Mg_2Si intermetallic phase decreases and eventually disappears at 0.85 wt.% Cu [11]. Another benefit of Cu addition is increased elongation (Al-3Mg-0.5Mn) which can be attributed to the combined effect of crystal grain refinement on addition of 0.2wt% Cu and the presence of Al_2CuMg intermetallic, as it pins dislocations and reduces plasticity [12]. However, Cu containing alloys in the series tend to show poor resistance towards corrosion as Cu precipitates at grain boundaries creating a potential difference and rendering the metal high vulnerability to pitting, intergranular corrosion and stress corrosion. Presence of Cu compromises alloy's hot tear resistance and thus decreases castability [13]. Cu also adversely affects anodizing. On dissolving with the anode electrolyte, Cu precipitates create holes in the oxide layer [10]. These alloys have a wide operational utility in aerospace, rocket fins and military vehicles.

Fig. 4. (a) Al rich θ-phase (b) Cu rich θ-phase



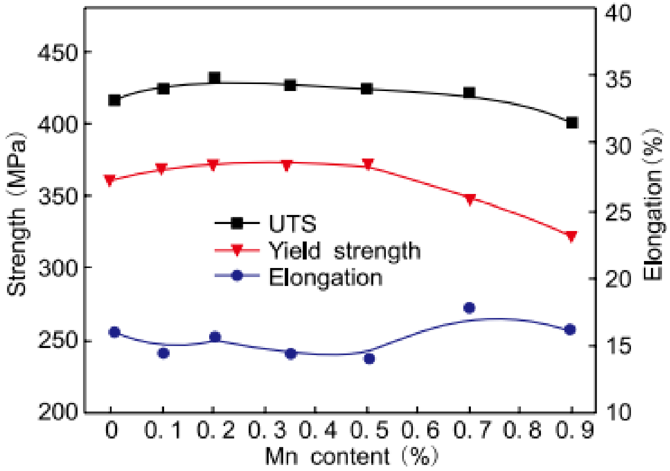
4.3 Manganese (3xxx series)

This group includes Manganese as the major alloying element. Mn addition results in strain hardening along with strengthening effect, without compromising the alloy's ductility or corrosion resistance property [3]. Adding Mn to Al-alloys enhances the tensile strength as well as significantly improves low-cycle fatigue resistance [14]. Mn alloys form NHT alloys, which can be strengthened by cold working. Mn forms intermetallics with Al, Si, Cr and enhances the microstructure and properties of the base alloy.

Zhao Zhihao [15] investigated the effect of Mn addition on the mechanical properties and microstructure of Al-Mg-Si-Cu-Cr-V alloy. He mentioned that manganese is an effective element which influences the recrystallization of this alloy. The results showed that 0.2wt% Mn (optimum content) can refine the as-cast microstructure of the alloy, as well as strengthen the +T6 state alloy without damaging the plasticity [15]. Mn content of more than 0.7wt% coarsens the as-cast grains which eventually affects the mechanical properties. Hence, its addition is usually kept under 0.6wt%. The relation between the variations in the mechanical properties of Al-Mg-Si-Cu-Cr-V alloy with changing Mn content after extrusion+T6 treatment can be clearly understood from Fig. 5.

One of the main reasons for adding Mn to Al-based casting alloy is to enhance the morphology of the Fe-bearing phases. It has been reported that combination of Mn and Cr changes the microstructure of a typical platelet of Al_5FeSi phase into a more cubic form - $Al_{13}(Fe,Cr)_4Si_4$, which results in the improvement in ductility & corrosion resistance [14]. Al-Mn alloys are used in cooking utensils, beverage cans, radiators and evaporators, heat exchangers, piping systems, AC condensers, furniture, highway signs, roofing, siding and other architectural applications.

Fig. 5. Changes of mechanical properties of extrusion+T6 alloy *v/s* Mn content [15]



4.4 Silicon (4xxx series)

Aluminium-Silicon cast alloy is designated as the 4xxx series, where Al is the parent metal and Si is the major alloying element (ranging from 0.6 to 21.5%). Adding silicon alone in aluminium results in a NHT alloy; whereas in combination with Mg or Cu it produces a precipitation hardenable heat treatable alloy. Consequently, 4xxx is the only series having both heat treatable and NHT alloys [3]. Silicon addition in Al-based alloy reduces its melting point and enhances fluidity (Hence, widely used for manufacturing of castings). For this reason, Al-Si alloys are used in brazing and welding applications for joining aluminium, where a lower melting range is required than that of the base metal [16]. Added Si is primarily responsible for good castability and low shrinkage. As Si is a very hard phase, it contributes significantly to the alloy's wear resistance property.

Fig. 6. Schematic binary phase diagram of Al-Si alloy

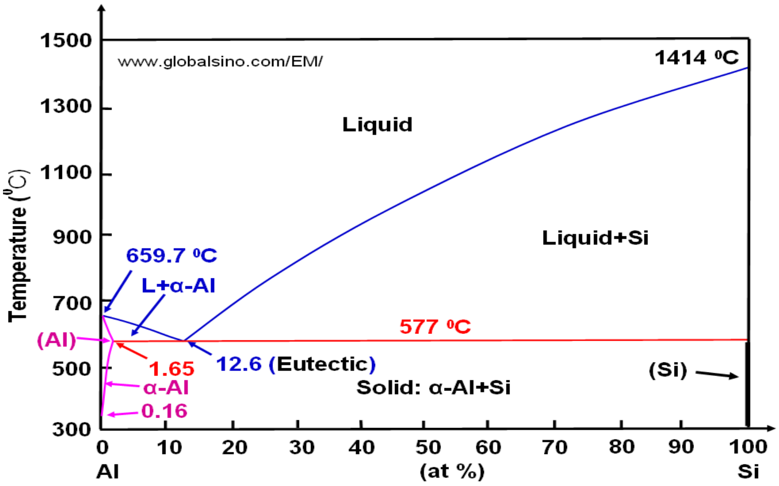


Fig. 6 represents the binary phase diagram of Al-Si alloy with a eutectic point. Al-Si alloys are classified into three groups depending on the Si concentration in weight % namely: - (a) Hypoeutectic (<12 wt. % Si), (b) Eutectic (12-13 wt. % Si) and (c) Hypereutectic (14-25 wt. % Si) [14]. The eutectic point is at 12.6 wt. % Si and the eutectic temperature is 577^{0}C. Al dissolves a maximum of 1.6 wt. % of Si while the solubility of Al in Si is almost zero [17]. The solubility percent is quite low because of the vast difference in melting points of Al & Si and in their nature of bonding.

The mechanical properties can be governed by the understanding of size, morphology and distribution of microstructural features. The microstructures of this alloy series consist of α-aluminium phase, eutectic Si particles and several intermetallic phases such as Al_2Cu, Mg_2Si and Fe bearing phases, etc. As Si % is increased, 3-dimensional eutectic networks of interconnected Si-platelets embedded in the ductile Al matrix, are formed upon solidification (i.e. Dendrite formation) [17]. These Si plates are hard & have sharp ends which give rise to high stress concentration points (Fig. 7), which eventually results in poor mechanical properties. This flake like structure can be modified by adding certain elements (example - strontium) or by rapid cooling [17]. Modification changes the morphology of eutectic Si from fibrous structure to Si-globules, as shown in Fig. 8. Besides porosity and oxides, Fe is the most common and detrimental impurity in Al-Si cast alloy, which can be controlled by Mn additions. Al-Si alloy have poor machinability. By adding optimum Si content in Al-alloy, properties such as – good castability, wear resistance & corrosion resistance, moderate strength & ductility, increased hardness, yield strength & ultimate tensile strength can be obtained. This alloy is used in pump casings, thin wall castings, cookware, filler wires, automotive & aerospace industries as well as architectural applications.

Fig. 7. A typical Al-Si microstructure at 13wt% Si

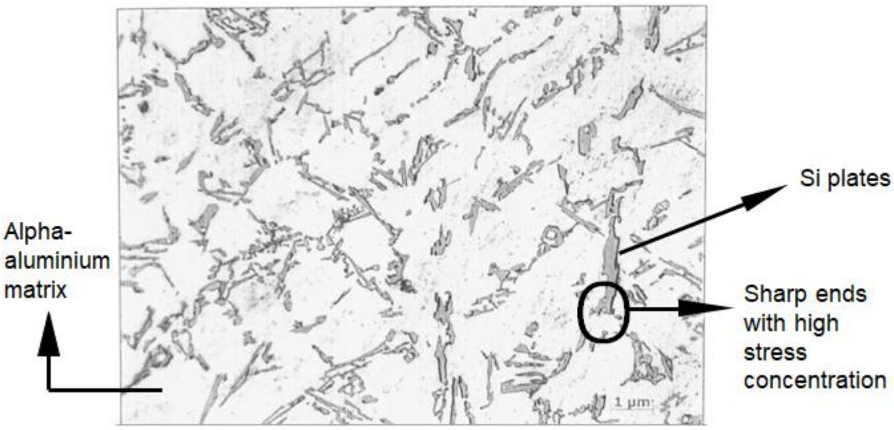
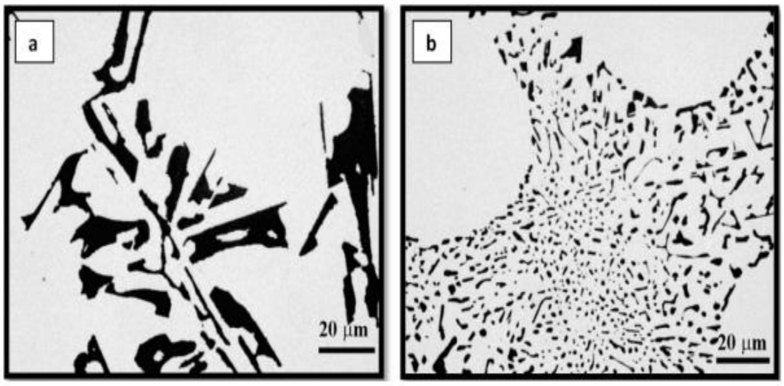


Fig. 8. The morphology of eutectic Si; (a) Unmodified (b) Modified structure [17]



4.5 Magnesium (5xxx series)

The main alloying element in 5xxx series is Magnesium. Al-Mg alloy is a non-heat treatable alloy being used for various structural applications. Mg addition enhances the alloy's strength by solid solution strengthening and also improves its strain hardening ability [3]. The Al-Mg binary phase diagram shows Al crystalline in FCC form which melts at 660.25^{0}C and Mg crystalline in HCP form which melts at 649^{0}C. The diagram gives information about alloy properties and its microstructure on varying Mg content and temperature. Formation of different phases by changing Mg content can be clearly understood from Fig. 9. The maximum solubility of Mg in Al solid solution is 18.9% at 723 K, whereas the maximum solubilty of Al in Mg solid solution is 11.8% at 705 K. For using Al-Mg as casting alloy, 5-13 wt.% Mg is added.

The microstructure of Al-Mg system in the Fig. 10 shows that it has 2 main phases namely α-Al and β-Al_3Mg_2. The α-Al phase contains the solute Mg atoms whereas the secondary phase (black spots) is the constituents that cannot be dissolved by the primary α-Al phase which tends to form the β phase [18]. Al-Mg alloy has the tendency of aging naturally which increases its strength and hardness. However, due to the precipitation of β-Al_3Mg_2 phase along the grain boundary, ductility decreases and causes embrittlement. This difficulty can be avoided by reducing the Mg content to 8% along with 1.5% Zn addition [6]. For brazing purpose, Mg level is kept around 0.3wt% because higher amounts (1~2 % or more) result in increased oxidation layer which is difficult to avoid by flux. [2]

Table 3. Different phases and composition of Mg

Phase	Composition wt.% Mg
Al	0 – 17.1
β(Al3Mg2)	36.1 – 37.8
R	39
γ(Al12Mg17)	42 – 58
Mg	87.1 – 100

Fig. 9. Binary phase diagram of Al-Mg alloy

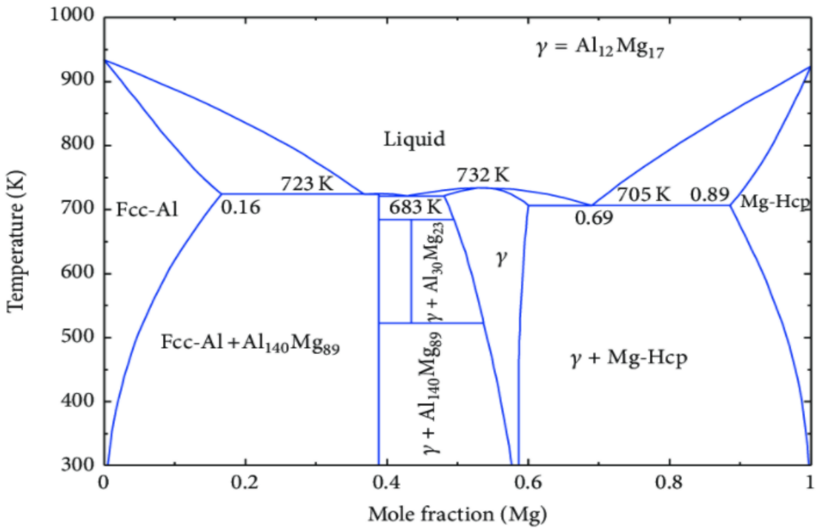
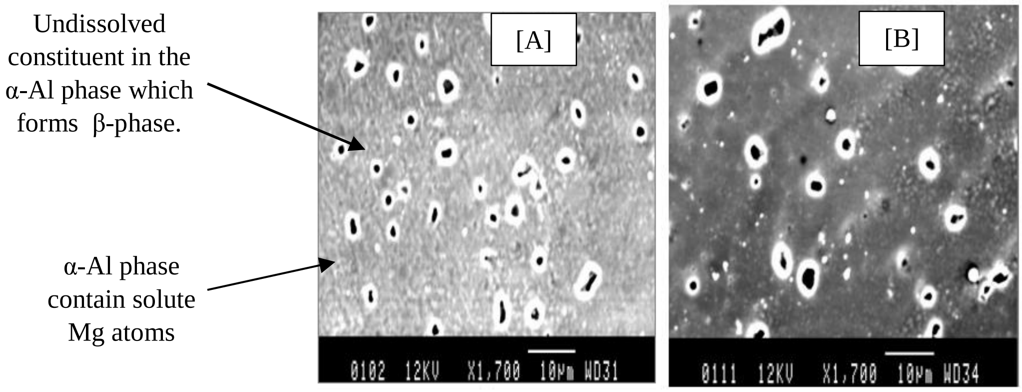
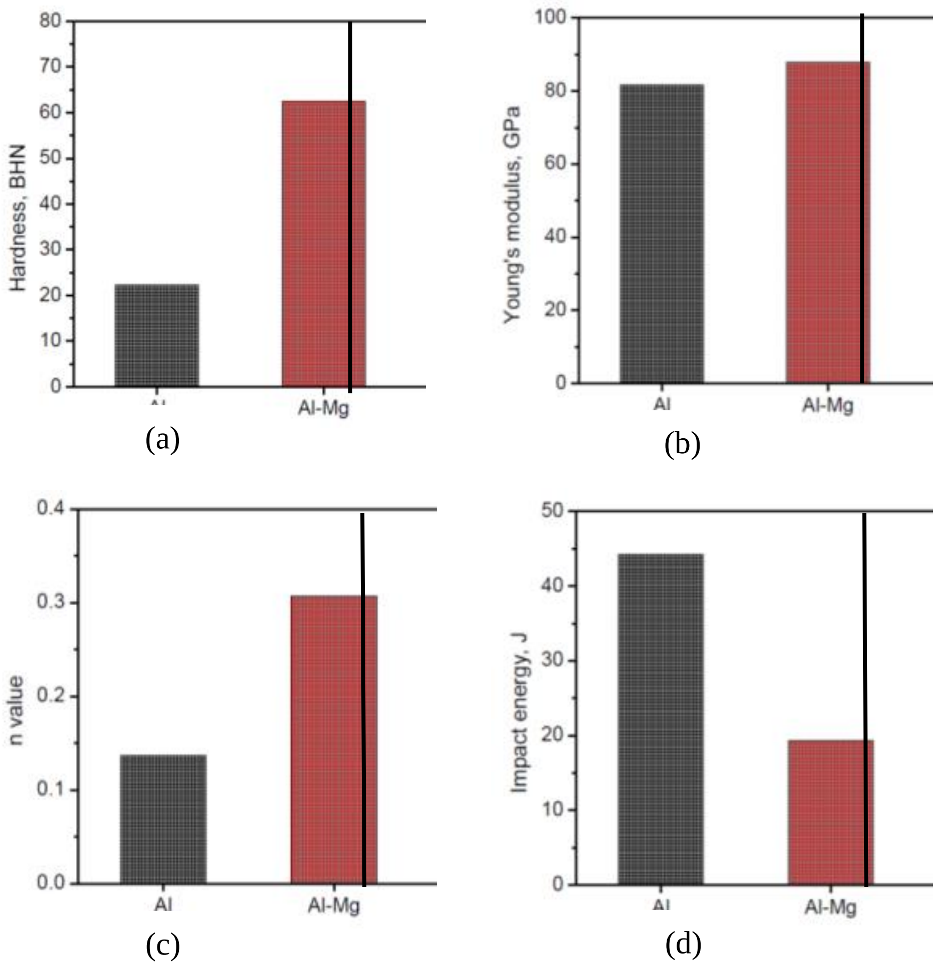


Fig. 10. The SEM of Al-7wt% Mg and Al-10wt% Mg samples from top (A) to bottom (B) respectively [18]



Samiul Kaiser [19], in his paper investigated effect of Mg addition on commercially pure Al. He mentioned that due to the formation of L1$_2$ (Al_3Mg) and β (Al_3Mg_2) intermetallic during solidification, hardness of Al-Mg alloy increases. Primary α-Al, Al_3Fe, Mg_2Si precipitates also play a role in improving hardness level. Mg addition enhances the mechanical properties, work hardening, corrosion resistance, weldability, reduces ductility and renders super castability [19]. Fig. 11 shows the variation in properties by comparing commercially pure Al and Al-Mg alloy. Major applications of this alloy include truck and train bodies, cryogenic tanks, buildings, pressure vessels, armoured vehicles, chemical tankers, ships and boats. [4]

Fig. 11. Comparing properties of commercially pure Al and Al-Mg
(a) Hardness, BHN (b) Young's modulus (c) Strain hardening exponent (d) Impact energy



4.6 Magnesium and Silicon (6xxxseries)

The 6xxx Aluminium alloy series consists of Magnesium and Silicon as the major alloying elements. These alloys have ultimate tensile strength in the range of 18-80 ksi [22]. Owing to their ability of absorbing large amounts of energy during collisions, they are used in automotive industry on a large scale. Magnesium silicide (Mg_2Si) is formed on adding Mg & Si in aluminium. This phase allows the alloy to be solution heat treated so as to achieve high strength. Alloys containing 1.0wt% of Mg and Si, are widely utilized in welding fabrications and are also incorporated in many structural compounds [22]. As these alloys are naturally sensitive about solidification crack, they should not be arc welded without any filler material. On adding silicon in Al-Mg phase diagram; we get a ternary phase diagram of AlMgSi alloy. The intermetallic and grain boundary phases as a result of thermal treatment are identified [23]. The intermetallic compound obtained is composed of Fe-IMCs and Mg_2Si precipitates. Fig. 12 shows a schematic phase diagram of Al-Mg-Si 6xxx series alloy.

Fig. 13 shows the microstructure of a hypoeutectic Al-Si-Mg alloy. The light grey region represents the primary Al grains which are highly spherical and globular in shape. The shape of grains with a lower spherical shape factor but with larger aspect ratio mainly depends on their actual position in the magnetic field during stirring [24]. The rest of the dark grey region is the fraction of eutectic mixture. The microstructure shown in fig.17 has a very large fraction of primary Al grains which are spherical and relatively big in size. The dark grey rosettes indicate a small number of nuclei formed at the start of solidification process. Fe based intermetallic and Mg_2Si are present in the inter-globular region [24]. Mg and Si are primarily responsible for precipitation strengthening, whereas Fe intermetallics are harmful for the ductility of alloy.

Fig. 12. Al-Mg-Si Phase Diagram

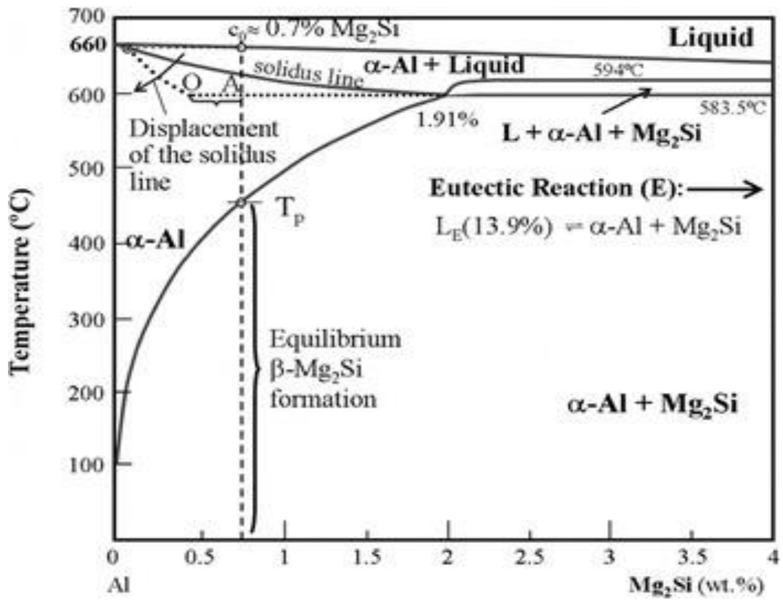
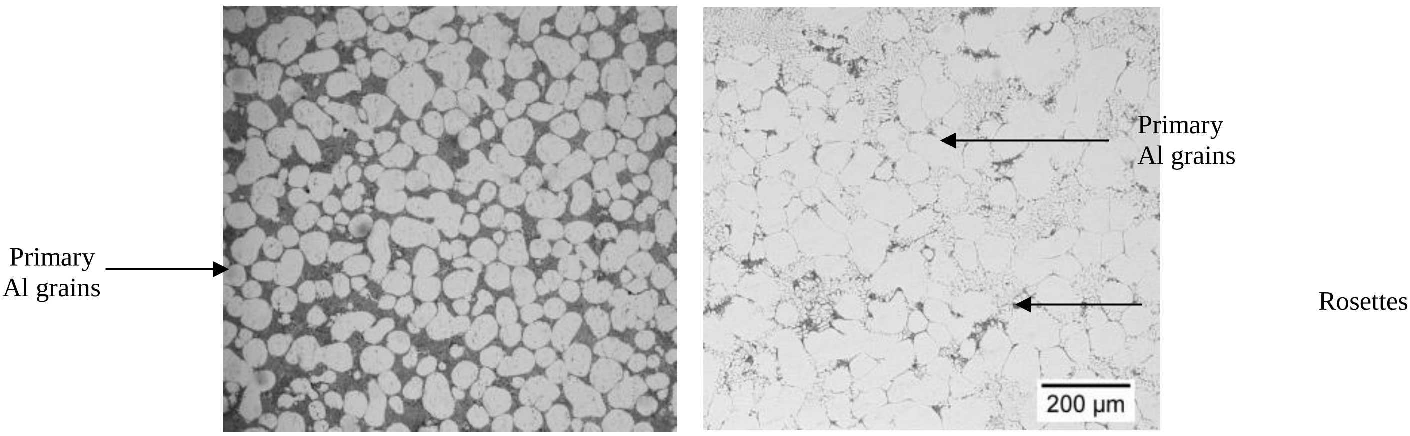


Fig. 13. As-cast microstructure of a CSIR R-HPDC (a) Al-Si-Mg alloy A356 (b) Al-Mg-Si alloy AA6082 [24]



The Al-Mg-Si alloy has a high tensile strength of the order 220-390 MPa, while tensile strain remains in between 17-12%. Tensile strain decreases with an increase in strength [2]. The Mg/Si ratio = 1.74 is responsible for Mg_2Si formation and optimum behavior of alloy. This ratio is difficult to achieve and most of these alloys have excess Mg or Si [2]. Alloys with excess amount of Mg are rendered undesirable for the purposes of joint formation as it leads to a significant decrease in strength and formability of the alloy.

In Al-Mg-Si alloy the excess amount of Si provides higher strength and does not affect its formability and brazing ability, but it induces a tendency of corrosion failure [2]. Therefore, Mg content should be wisely decided taking into consideration its joint properties before being used in practical applications. Due to ease of application and low cost, these alloys are extensively used for extrusion of numerous shapes and structures [22]. Some common applications for the 6xxx series alloys are automotive frame sections, scaffolding, handrails, bicycle frames, drive shafts, tubular lawn furniture, stiffeners and braces used on trucks, boats and many other structural fabrications [3].

4.7 Zinc (7xxx series)

Zinc being the major alloying element of 7xxx series is quite neutral in nature. It neither improves nor deteriorates any particular properties appreciably [14]. However, it has been observed in several alloys that Zn does influence the microstructure as well as other mechanical properties [14]. In this series of alloys, highest ultimate tensile strength has been reported in case of alloy with 1.5wt%Zn. When 1-2 wt% Zn is added in Al-Mg alloys, stable Al-Mg-Zn phase is formed which significantly improves the SCC resistance property [14]. 7xxx series alloys are heat treatable and thus their strength can be increased by precipitation hardening. In case of 3003 Al alloy, high density rod-like precipitates were observed while zinc content being 1.8% [14]. Sometimes Fe is also present in the composition of these precipitates which leads to the ellipsoid or spheroid precipitate shape [25] as depicted in Fig. 14(a) and Fig. 18(b). [26]

Fig. 14(a) SEM Micrograph of as solidified Al-30 wt% Zn showing spheroid and nut shape like precipitates [27]

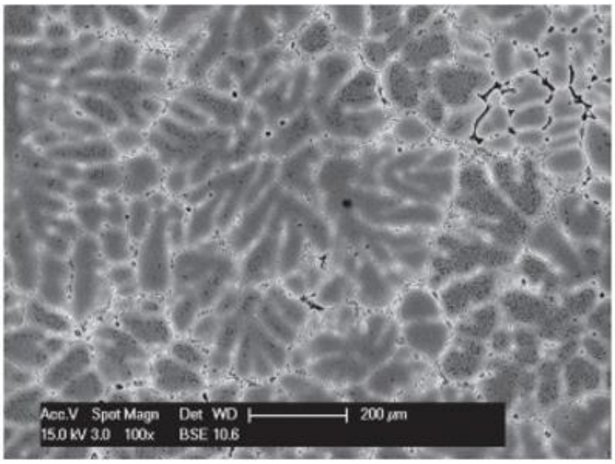


Fig. 14(b) SEM Micrograph of as solidified Al-10 wt% Zn showing spheroid and nut shape like precipitates [27]

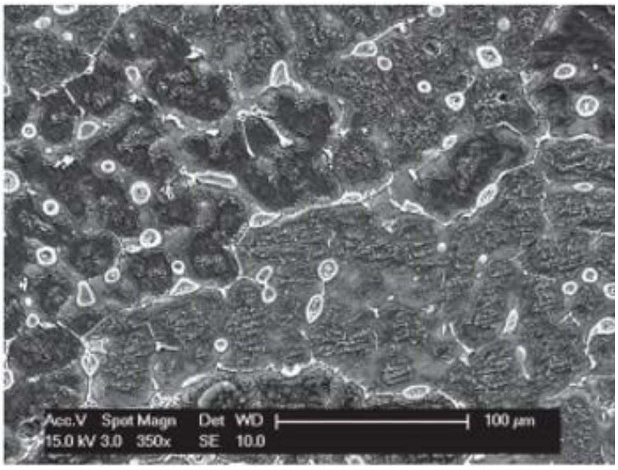
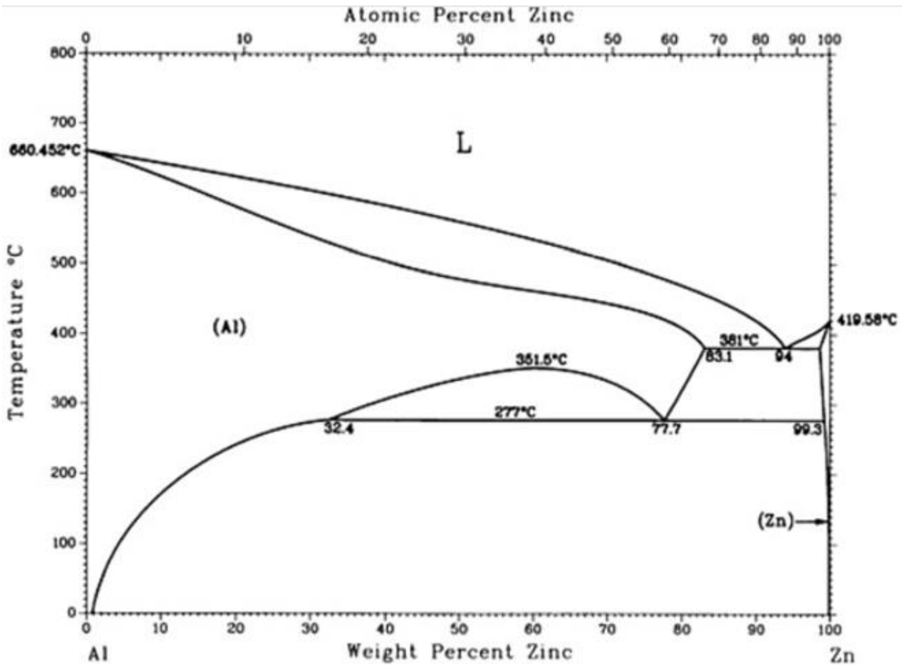


Fig. 15. Phase Diagram of Al-Zn Alloys [28]



The phase diagram of Al-Zn alloys has been shown in Fig. 15. There are two major phases in the phase diagram namely - alpha and beta. Alpha is the solid solution on Zn in Al. Its maximum solubility is 83.1% at 381°C. Whereas beta phase is the solid solution of Al in Zn having negligible solubility at the same temperature. Addition of Zn boosts the hardness level of Al-based alloy, due to the formation of precipitates which act as obstacle to dislocation motion. Solid solution hardening and grain size refinement are the two major factors responsible for increased hardness [25]. It has been observed that zinc addition can reduce the ability to resist against corrosion. Moreover, D. Lamrous mentioned in his paper that Zn is not favorable in case of brazing due to its higher vapor pressure as it results in porosity and cracks in joints [2]. 7xxx series alloys have a wide spectrum of operational applications ranging from aerospace and armored vehicles to baseball bats and bicycle frames.

4.8 Lithium (8xxx series)

Lithium is the major alloying element in 8xxx series. Solubility of Li in Al varies from 4.3 wt.% at 602°C to 0.4 wt.% at 200°C; at eutectic temperature it is 4.2 wt.% [29]. Alloying with Li leads to decrease in density. For every 1% Li added by mass, density of Al decreases by 3% and stiffness increases by 5%. It also leads to solid solution strengthening and precipitation hardening of the alloy. It has been observed that in as-cast condition, Brinell hardness and microhardness of Al-6.5Mg-2.8Si-0.62Mn+Li alloy (HB = 98 and HV0.05 = 98.6 kgf/mm2) is higher than the base alloy. However, it has also been observed that with increase in Li content, fluidity of the Al-Mg-Si-Mn alloy decreases [30].

4.9 Iron (Fe)

Iron is the most common impurity and is added for the sole purpose of slightly increasing strength of 1xxx Al-alloy. Iron in aluminium forms complex intermetallic phases, which adversely affect the mechanical properties of the alloy. Particularly in Al-Si alloy, increase in iron content results in formation of β-$FeSi_5Al$ -IMC. The thin plate like structure of this IMC has weak bonding with the aluminium matrix and is thus, responsible for the brittle nature, decrease in ductility & castability. Ashutosh Sharma, [2] in his paper mentioned that low concentration of Fe may act as a promoter for grain refinement, although the effect diminishes shortly. Considering the deleterious actions of Fe, its reduction or control is always suggested. Usage of Mn and Be are quite effective measures for neutralizing the effects of iron.

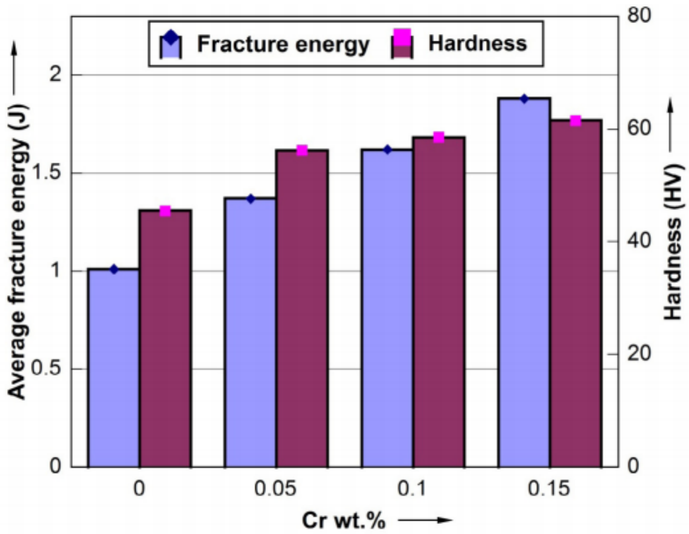
4.10 Chromium (Cr)

Chromium is added in Al-alloys to control the grain structure, to protect grain growth in Al-Mg alloys, and to prevent recrystallization in Al-Mg-Si or Al-Mg-Zn alloys during heat treatment [4]. R Ahmad [31] investigated the effect of Cr on microstructure and properties of LM6 cast Al-alloy. He mentioned that Cr in Al-Si alloy, forms intermetallics with β-AlFeSi and changes the morphology of sharp needle-shaped iron platelets into harmless polyhedral, star-like IMC. This results in improved toughness, ductility & stress corrosion resistance. Usually Cr content is kept under 0.1wt%. The impact of Cr addition on the fracture energy and hardness of base alloy can be understood from Fig. 16.

4.11 Nickel (Ni)

Nickel is added to Al-Si and Al-Cu alloys to enhance strength & hardness at elevated temperatures and alleviate the coefficient of expansion [3]. When Ni is alloyed with 2xxx series, formation of Cu-Ni aluminides occur and these IMCs are responsible for providing additional strengthening effect to the base alloy. On the other hand, addition of Ni in 4xxx series (particularly for 10-16 wt. % Si) results in improved hot hardness (up to 600F). An upsurge in Ni content increases the amount of intermetallic Al_3Ni, which improves hardness, compression and bending resistances but significantly reduces ductility. [2,14]

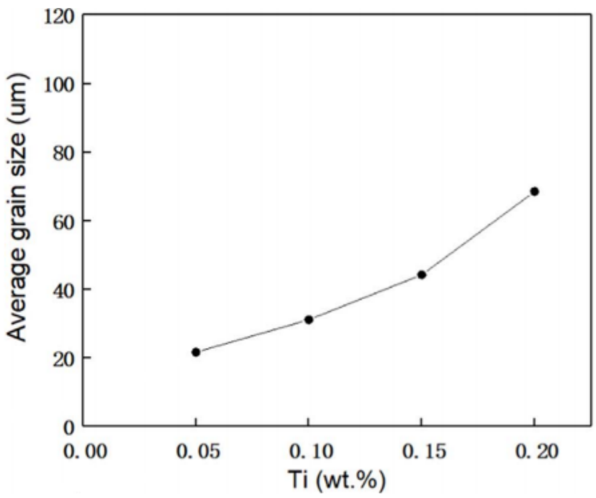
Fig. 16. Energy observed of fracture and hardness for base alloy and treated with different Cr concentration at room temperature [31]



4.12 Titanium (Ti) &Boron (B)

Ti is added to Al-alloy to serve as a grain refiner. It forms Al_3Ti intermetallic phase which act as a nucleating agent for α-Al crystal during solidification process. [32] Yu Zhang in his paper- effect of Ti addition on the microstructure and properties of Al-Mg-Zn-Si alloy mentioned that 0.10 wt. % Ti can significantly increase the mechanical properties of this alloy especially after T6 heat treatment. Fig. 17 shows the relation between the average grain sizes of Al_3Ti with increasing Ti content. It was proved that with 0.1wt% Ti addition, best mechanical properties were achieved for the alloy. [32] Higher Ti content results in larger Al_3Ti IMC, which eventually degrades the mechanical properties. It was also reported that combined action of Ti and B resulted in even better grain refinement. Commercially, the mother alloys of Al-5wt%Ti-1wt%B are manufactured to serve as a regular grain refiner in the Al 4XXX alloys [2].

Fig. 17. Average grain size of Al_3Ti phase with different Ti additions [32]



4.13 Zirconium (Zr)

The properties of Al based alloys can be altered by addition of transitional elements such as Zr in trace amounts. Upon cooling, the added zirconium firstly reacts with α-Al and forms Al_3Zr phase which is very stable against particle coarsening. This phase significantly refines the alloy grain and inhibits recrystallization. Hence, it helps in strengthening the matrix of the Al based alloys. When alloyed with $Al_5Cu_{0.4}Mn$, in combination with other transitional elements such as Y and Er, it has been observed that it enhances the alloy's fluidity, improves layer by layer solidification and also reduces the temperature interval for liquid solid transition [33]. On the contrary, the Al_3Zr precipitates responsible for grain refinement also act as early nucleation sites for micro voids and eventually decrease the alloy's fracture resistance [19]. Al-Zr alloys have a special application in the electrical industry where these materials are drawn into wires and used in special high temperature conductors of HTLS (High Temperature Low Slag) type. This material permits the operation temperature to rise from 80°C to 210°C thereby increasing the efficiency of energy transmission [34].

4.14 Strontium (Sr)

Sr is usually alloyed with Al-Si based alloys in order to amend the morphological and microstructural aspects of the alloy. Si solidifies as coarse continuous network of thin plates which hinders the alloy to reach its maximum strength and ductility [14]. Sr aids in modifying silicon's morphology from needle-like, blocky and irregular shape to round or spheroidal one. In order to successfully use Sr as a modifier, its addition should be restricted in the range of 0.01 to 0.015%. Higher percentage addition can lead to coarsening of Si particles and formation of Al-Si-Sr intermetallic phase [2]. It has also been observed that 0.03% of Sr addition can result in a modest increment in ultimate tensile strength, yield strength and percentage elongation.

4.15 Lead (Pb) & Bismuth (Bi)

Lead and Bismuth are usually added to Al based alloys to improve their machinability by promoting chip formation [3,4]. Moreover, Pb has extremely low solubility in Al, i.e. 0.025 wt. % at 659°C. On alloying with Pb, the resulting phase melts at a lower temperature than Al. So at higher temperature these phases melt and reduce friction. However, it also acts as an impurity which is why its content should be controlled. It reduces toughness, ductility, thermal conductivity and promotes intergranular corrosion. Bismuth also adversely affects the oxidation resistance of Al-Si alloys and reduces their castability [35]. Moreover, alloys with Pb and Bi are not weldable as they form low melting segments and can lead to poor mechanical properties and/or high crack sensitivity on solidification.

4.16 Beryllium (Be)

Beryllium is used in aluminium alloy casting because of its unique physicochemical characteristics. Even in minute quantities such as 5 to 100 ppm, the presence of Be dramatically reduces oxidation and provides a considerable gain in metal yield, a cleaner metal as well as an improved and more consistent metallurgical quality [36]. Foundry industry refrain from processing the aluminium alloys without minute addition of Be because Be provides substantial improvement to the alloy. In the alloying process, Beryllium improves the yield strength of the alloy and decreases the use of flux. Moreover, it also enhances mechanical properties, provides more consistency during processing, minimizes scrap and leads to overall customer satisfaction with the product [36].

4.17 Tin (Sn)

Tin is a soft metal, used in Al-alloy casting. It is used to reduce the friction in bearing and bushing applications [14]. It acts as a lubricant between the rubbing surfaces and facilitates elongation as a result of softening. This property is exploited in brazing application [2]. In brazing applications, tin improves the additional braze ability by increasing the fluidity of the braze alloy [2]. Moreover, Tin addition also retards the anodic dissolution of oxide film. The corrosion resistance of the alloy could be increased by various heat treatments [37]. However, a high content of Sn in the Al-Si alloy may weaken the brazed joints and increase vulnerability towards corrosion [2]. In case of Al 2xxx, by adding Sn in trace amounts (0.05%), age hardening is facilitated which in turn enhances the strength of the brazed joint [2].

4.18 Sodium (Na), Calcium (Ca), Potassium (K), Sulphur (S) & Antimony (Sb)

In alloys with eutectic silicon, sodium and calcium are used as modifiers in the form of flux and salts. It has been observed that sodium-modified alloys have more regular silicon morphology than Sr, which is responsible for improved mechanical properties of the alloy. Sr and Ca when simultaneously added can accelerate the modifying effect. To improve the mechanical property in hypoeutectic Al-Si alloys, phosphorus is used in amount of 0.001-0.02 %. Antimony in kept on the level of < 0.05 % to improve the strength as well as corrosion resistance. It has been observed that when 0.2% Sb is present in Al-Si alloys, it reduces the inter-flake spacing of the eutectic Si rather than flake refinement. Like others sulphur also affects modification of the Si particles in Al-Si alloy. Sharpness of Si particles is decreased with increase in sulphur content. However, sodium or strontium modified alloy produces more refined eutectic morphology and enhanced mechanical property [2].

4.19 Rare earth metals

Previous studies show that rare earth metals modify the microstructure and properties like mechanical, electrical conductivity, optical quality, and corrosion resistance. Rare earth metals like Er, Ce, La, Gd, Nd, Y and Sc are used for alloying. Among all of them, Er is the most effective alloying element in case of high purity aluminium [38]. In pure Al alloy and Al- Mg alloy, with an increase in the content of Er, the hardness and strength are increased as well. In Al-Zn-Mg alloy, as Er addition increases, tensile properties and yield strength are enhanced with a slight decrease in elongation [38]. It has been observed that with the addition of Yttrium and scandium, recrystallization temperature of the aluminium alloy increases. Scandium is an effective grain refiner component as it prevents recrystallization owing to the presence of Al_3Sc-phase particles in an aluminium matrix [2]. It was reported that Ce addition to Al-Cu-Mg-Ag alloy improved the thermal stability of the Ω phase and resulted in increased service temperature of the alloy [14]. The addition of La (0.05-0.1 wt. %) in the Al-Si-Cu-Mg alloy reduces the mutual poisoning effect of the B and Sr by forming the LaB_6 rather than SrB_6 [2]. It has also been demonstrated that addition of Nd elevates the strength of the Al-Cu alloy due to the uniform distribution of AlCuNd at high temperature [2]. In few recent reports, Ytterbium (Yb) has been added in Al-alloy which improves the mechanical properties of the Al-Zn-Mg-Cu-Zr alloy & Al-Cu-Mg-Ag alloy [2].

5. Conclusions

In order to subdue the modern-day challenges while taking economic and ecological sustainability into consideration, Al alloys are being widely utilized in every sector of applications from domestic and automobile to even aerospace industries. Alloying is carried out in accordance with the requirement of physical and chemical necessities.

- Alloying with Cu enhances the mechanical properties along with degrading resistance to corrosion
- Mn improves tensile strength along with remarkably enhancing low cycle fatigue resistance
- Si and Zr improve fluidity of the base alloy whereas Li reduces it
- Si when added with Mg enhances strength
- Zn significantly improves resistance to SCC and results in high UTS
- Mg addition results in highest strength NHT alloy
- Ni enhances hardness while Sn improves elongation of the base alloy
- Ti and B in trace amounts carry out grain refinement and Be leads to an increased yield strength
- Cr and Sr are majorly used as modifiers
- Fe, Pb and Bi are responsible for poor physical characteristics and are to be tolerated only as impurities

Rear earth elements such as Er, Yb, Ce, Nd, etc. can improve thermal stability and increase recrystallization temperature

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