Effect of Copper to Magnesium Ratio on Precipitation Induced Anisotropy during Ageing of Recrystallized Al-Zn-Mg-Cu Alloy

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Declared that except where specified by reference to other works, the experimental studies embodied in thesis is the result of investigation carried out by the author. Neither the thesis nor any part has been submitted to or is being submitted elsewhere for any other purposes.

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ABSTRACT

High strength Al–Zn–Mg–Cu alloys (7xxx series aluminium alloys) have been widely used in military and aerospace industries due to high strength, easy formability and low density. Other important properties that must be considered for these applications are strength, ductility, modulus, corrosion and damage tolerance (e.g. fracture toughness and fatigue resistance). Most of these properties can be controlled through appropriate alloying, processing or a combination of these. Age-hardenable 7xxx series aluminium alloys for high-performance structural applications are typically processed in the form of plates, extrusions or forgings. For thick plate products, a typical processing schedule involves casting, homogenising, hot rolling, solution treating, quenching and age hardening.

In this work, the effects of variation of Mg and Cu contents in some predefined ratios on the microstructures and mechanical properties of a 7xxx alloy both in longitudinal and transverse directions were studied. Initial cast and homogenised microstructure revealed dendritic structure which was lost completely during hot rolling. After hot rolling, solution treatment and ageing responses were observed at different temperature and time combustions. Interestingly, it was found that under same ageing condition, hardness and strength of the alloys were predominantly controlled by magnesium content, attributed to η-phase. Albeit similar behaviour was shown by copper content, the response was not as effective as that obtained with higher amount of magnesium. From microstructural analysis in optical microscopy and scanning electron microscopy, it can be asserted that higher magnesium to copper ratio yielded higher amount of second phase particles, which was validated by thermodynamic modelling of microstructural phases. In both longitudinal & transverse directions, better mechanical properties (ultimate tensile strength and hardness) were found for the alloy having Cu/Mg ratio of 1.32, owing to S-phase. Along longitudinal direction, fracture surfaces were heavily dimpled, and intergranular features were found that yielded better ductility with high UTS value for alloy of 1.32 Cu/Mg ratio. Along transverse direction, microstructure investigation revealed transgranular and cleave features, attributed to stable S-phases.

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INTRODUCTION

Lightweight and mechanically strong materials are of highly importance in modern automotive and especially the aerospace industry, where even a small reduction of craft weight can give rise to a considerable drop in the operation costs. Nowadays the materials used in this area are mostly based on aluminum, which is a reasonable compromise between the weight, cost and mechanical characteristics [1]**.** Aluminum (Al) the third most abundant metallic element on our earth planet, after oxygen and silicon. Today, the most widely used nonferrous metal is aluminum. In world production of nonferrous metals, Al moved into first place ahead of copper during the 1960s. From the cooking materials to medicine, transport vehicles and aircraft industry, aluminum and its alloys extensively used through the worldwide. Still now no health hazard effect is found for aluminum. There are many Al alloys used in industry today–over 400 wrought alloys and over 200 casting alloys are currently registered with the Aluminum Association (AA).

Aluminum is a light weight material with a density of 2.7 grams per cubic centimeter. Pure aluminum and its alloys have the face centered cubic (FCC) structure, which is stable up to its melting point at 657^0C [2]. Al does not undergo any polymorphic transformation as like Ti or Fe. The high strength to weight ratio make the Al and its alloys most attractive material for many engineering applications such as automobile and space ship industries, military equipment where weight reduction plays in important role.

The main drawbacks of Al and its alloys, are inferior tensile strength and hardness. To overcome these limitations (strength and hardness properties) pure Al is cast with alloying elements into a form that will be mechanically worked and develop the useful metallurgical properties and the shape for many engineering applications. These alloying elements form intermetallic compound with aluminum to improve its drawbacks.

Al 7xxx series alloys, among all Al alloys, possess better mechanical strength. The tensile strength of pure aluminum is around 90 MPa where it can be increased (for Al 7xxx alloys) four times or more than pure. Al is alloyed with zinc (Zn) as the major alloying element named Al 7xxx alloys. As a major alloying element Zn substantially increases strength and permits precipitation hardening. Aluminum-zinc alloys containing other elements offer the highest combination of tensile properties in wrought aluminum alloys. If Zn combines with some other elements, primarily magnesium (Mg) and/or copper (Cu) produces heat treatable Al alloys of the highest strength. This hardening is achieved through the precipitation of $\theta(Al_2Cu)$ or $S(Al_2CuMg)$ intermetallic phases during ageing which leads to strengthen.

Increasing Zn and Mg content can improve mechanical properties, keeping Cu content fixed. On the other hand, alone Zn can extensively increase strength. On the contrary, addition of Cu can improve strength and modify fracture behavior to more dimple containing ductile fracture. Recently, both Cu and Mg content together were observed to enhance precipitate volume fraction [3]. However, there is still no effective relationship and understanding about the effects of Cu and Mg ratio (varying amount) on ageing response to increase strength, size distribution of precipitates and fracture behavior.

The investigation of this work is to find out the effects of Cu and Mg ratio on ageing response to increase mechanical strength, size distribution of hardening particles, microstructure feature-grain size and fracture behavior. To demonstrate these findings, the journey is started from Foundry Lab (FL) through casting. Then step by step the whole work as accomplished as predetermined prescription. The findings of this work will optimize amounts of Cu and Mg required in AA7xxx series Al alloys for strengthening. Such development will lead to better understanding of fundamental characteristics of composition in this series. Processing route via suitable heat treatment cycle will also be established, which is beneficial for industries.

The remaining episodes are, as chapter two for literature review, chapter three about experimental procedure, chapter four for results and discussions, chapter five summarizes the predominant conclusion from the results of this work and finally chapter six stands for references.

Chapter 02

LITERATURE REVIEW

This chapter is concerned with a review on the literature related to the aluminum and its alloys, effects of various alloying elements on aluminum, designation system for aluminum alloys, effect of alloying elements, heat treatment process, solid solution, and ageing response to Al 7xxx series alloys.

2.1 Aluminum (Al)

Aluminum, symbol (Al), is a silvery white non-sparking metal, cataloged in Group 13 (IIIA group) of the periodic table with a melting point of 660^0C and a density of 2.7 grams per cubic centimeter. It is the third most abundant metallic element in the planet. In nature, it occurs chemically combined with oxygen and other elements. Aluminum is concentrated in the outer 16 km of the Earth's crust, of which it constitutes about 8 percent by weight; it is exceeded in amount only by oxygen and silicon.

Aluminum has face centered cubic (FCC) crystal structure, and does not undergo any polymorphic transformation as like Fe or Ti. Pure aluminum is soft and ductile, but it can be alloyed with many other elements to increase strength and provide a number of useful properties. Alloys of aluminum are light, strong, and formable by almost all known metalworking processes. They can be cast, joined by many techniques, and machined easily, and they accept a wide variety of finishes [4].

Since aluminum has FCC crystal structure, its ductility is retained even at very low temperatures. The main limitation of aluminum is its low melting temperature, which restricts the maximum temperature at which it can be used. The mechanical strength of aluminum may be enhanced by alloying and cold work; however, both processes tend to diminish resistance to corrosion. Due to the high chemical reactivity of Al, in contact with air, aluminum rapidly covers with a tough, transparent layer of aluminum oxide (Al_2O_3) that resists to further corrosive action. For this reason, materials made of Al do not tarnish or rust. Table 2.1 shows the basic properties of aluminum.

Table 2. 1 Basic properties for aluminum [5]

Attributes	Values
Atomic Number	13
Atomic Weight (g/mol)	26.98
Valence	3
Crystal Structure	FCC
Melting Point (°C)	660.2
Boiling Point (°C)	2520
Density (g/cm)	2.6898
Electron Configuration	2-8-3 or $1s^22s^22p^63s^23p^1$
Chemical Nature	Strongly electropositive & extremely reactive

2.2 Aluminum Alloys

Today, the most widely used nonferrous metal is aluminum. During the 1960s aluminum moved into first place, ahead of copper, in world production of nonferrous metals. There are many aluminum alloys used in industry today–over 400 wrought alloys and over 200 casting alloys are currently registered with the Aluminum Association. The two common classes of Al alloys are wrought and cast alloys. Wrought Al alloys offer some excellent properties those make it a more desired material for many engineering purposes. Aluminum alloy possesses high strength to weight ratio, gives them more eligibility for many engineering applications such as automobile and spaceship industries, military equipment where weight reduction plays in important role.

Normally, wrought aluminum alloys are free of the internal and external defects such as shrink and porosity that are common problems in castings. Aluminum alloys have excellent ductility, malleability and formability properties, but are inferior to tensile strength and hardness. To improve the inferior tensile strength and hardness properties, wrought Al alloys are cast with alloying elements into a form that will be mechanically worked and develop the useful metallurgical properties and the shape for many engineering applications. In general, the alloying elements form intermetallic compounds with aluminum to improve its drawbacks. For example, Al 7xxx series alloys are alloyed with zinc as the major alloying element, and can be precipitation hardened to the highest strength of any aluminum alloys. When it is combined with a smaller amount of magnesium, the result is a heat-treatable alloy which offers very high strength. The corrosion resistance of the alloy is reduced due to the inclusion of zinc and magnesium, so copper is often introduced into the alloy to improve corrosion resistance.

2.3 Properties of Al

Pure aluminum (99.996 percent) is quite soft and weak; commercial aluminum (99.0 to 99.6 percent pure) with small amounts of silicon and iron, is hard and strong. Ductile and highly malleable, aluminum can be drawn into wire or rolled into thin foil. The metal is only about one-third as dense as iron or copper. Though chemically active, aluminum is nevertheless highly corrosion-resistant because in air a hard, tough oxide film forms on its surface.

Aluminum is an excellent conductor of heat and electricity. Its thermal conductivity is about one-half that of copper; its electrical conductivity about two-thirds. It crystallizes in the face-centered cubic structure, have no allotropic form. All natural aluminum is the stable isotope aluminum-27. Metallic aluminum and its oxide and hydroxide are nontoxic. Aluminum is slowly attacked by most dilute acids and rapidly dissolves in concentrated hydrochloric acid. Concentrated nitric acid, however, can be shipped in aluminum tank cars because it renders the metal passive. Even very pure aluminum is vigorously attacked by alkalies such as sodium and potassium hydroxide to yield hydrogen and the aluminate ion [6].

2.3.1 Physical Properties

Physical appearance depends on surface roughness. Because of this, smooth surface ensures the regular reflection of visible light. The appearance of aluminum ranges from slivery white to dull gray. It’s depend on surface roughness.

Density: Aluminum has a density around one third that of steel, (2,700 kgm^{-3}) making it one of the lightest commercially available metals. The low density of aluminum accounts for it being lightweight, but this does not affect its strength. The resultant high strength-to-weight ratio makes it an important structural material [7].

Non-magnetic material: Aluminum is a non-magnetic, actually paramagnetic, material. To avoid interference of magnetic fields, aluminum is often used in magnet X-ray devices.

Reflectivity of aluminum: From ultraviolet (UV) to infrared, aluminum is an excellent reflector of radiant energy. Visible light reflectivity of around 80% means it is widely used in light fixtures.

Thermal conductivity: The thermal conductivity of aluminum is about three times greater than that of steel. This makes aluminum an important material for both cooling and heating applications such as heat exchangers. Combined with it being nontoxic (zero toxicity level), this property means aluminum is used extensively in cooking utensils and kitchenware.

Electrical conductivity: Along with copper, aluminum has an electrical conductivity high enough for use as an electrical conductor. Although the conductivity of the commonly used conducting alloy (1350) is only around 62 % of annealed copper, it is only one third the weight and can therefore conduct twice as much electricity when compared with copper of the same weight.

2.3.2 Chemical Properties

Aluminum is insoluble in water and alcohol. When exposed to air, aluminum reacts with the oxygen in the air, a layer of aluminum oxide forms almost instantaneously on the surface of aluminum, and effectively preventing further oxidation. This layer is dense and provides excellent corrosion protection-passivation phenomenon. The layer is self-repairing if damaged. The thickness of the oxide layer can be increased by anodizing, and thus improves the strength of the natural corrosion protection. Aluminum is extremely durable in neutral and slightly acid environments. In environments characterized by high acidity or high basicity, corrosion is rapid.

2.3.3 Mechanical Properties

Aluminum can be severely deformed without failure. This allows aluminum to be formed by rolling, extruding, drawing, machining and other mechanical processes. It can also be cast to a high tolerance. Alloying, cold working and heat treating can all be utilized to tailor the properties of aluminum. The tensile strength of pure aluminum is around 90 MPa, but this can be increased to over 690 MPa for some heat treatable alloys.

Pure aluminum doesn’t have a high tensile strength. Addition of alloying elements, like manganese, silicon, copper and magnesium can increase the strength properties of aluminum and produces an alloy with properties tailored to particular applications. Aluminum alloys commonly have tensile strengths of between 70 and 700 MPa. Aluminum is well suited to cold environments. It has the advantage over steel in that its tensile strength increases with decreasing temperature while retaining its toughness. On the other hand, steel becomes brittle at low temperatures [8].

2.4 Application of Al and Its Alloys

Aluminum alloys have been used in many applications, where structural lightness & corrosion resistance are important. They are also extremely good conductors of electricity (third best after silver and copper, respectively), but have a high coefficient of thermal expansion that makes them unsuitable for high temperature applications (e.g., outer skin of high-speed aircraft, some engine components).

When the pure aluminum is selected for a structural application, they are most often chosen for their superior corrosion resistance, or their high electrical conductivity. The most common applications for the 1xxx series alloys are aluminum foil, electrical buss bars, metallizing wire and chemical tanks and piping systems.

A given volume of aluminum weight less than one-third as much as the same volume of steel. The only lighter metals are lithium, beryllium, and magnesium. Its high strength-to-weight ratio makes aluminum useful in the construction of aircraft, railroad cars, and automobiles, and for other applications in which mobility and energy conservation are important [9]. Because of its high heat conductivity, aluminum is used in cooking utensils and the pistons of internal combustion engines. Aluminum has only 63 percent of the electrical conductance of copper for wire of a given size, but it weighs less than half as much. An aluminum wire of comparable conductance to a copper wire is thicker but still lighter than the copper. Weight is particularly important in long-distance, high-voltage power transmission, and aluminum conductors are now used to transmit electricity at 700000V or more.

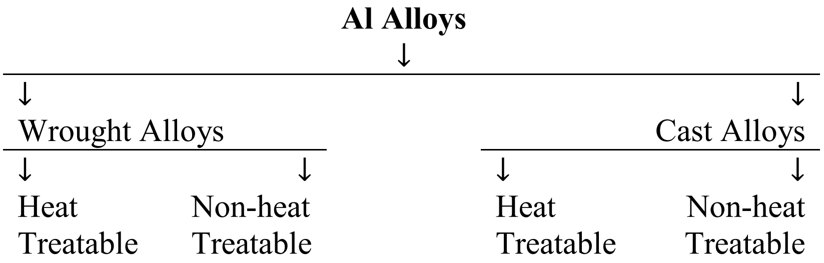
This metal is becoming increasingly important architecturally for both structural and ornamental purposes. Aluminum sidings, storm windows, and foil make excellent insulators. The metal is also used as a material in low-temperature nuclear reactors because it absorbs relatively few neutrons. Aluminum becomes stronger and retains its toughness as it gets colder and is therefore used at cryogenic temperatures. Aluminum foil, 0.018 cm thickness, is now a common household convenience, protects food and other perishable items from spoilage. Because of its light weight, ease of forming, and compatibility with foods and beverages, aluminum is widely used for containers, flexible packages, and easy-to-open bottles and cans. The recycling of such containers is an increasingly important energy conservation measure.

Aluminum's resistance to corrosion in salt water also makes it useful in boat hulls and various aquatic devices. A wide variety of coating alloys and wrought alloys can be prepared that give the metal greater strength, castability, or resistance to corrosion or high temperatures. Some new alloys can be used as armor plate for tanks, personnel carriers, and other military vehicles.

2.5 Classification of Al Alloys

In general, wrought means the alloys contain low percentages of elements; that is, alloying elements total less than about 4 percent. It is shaped by cold working-hammering, welding and rolling at room temperature. Cast means the metal is heated to its melting point, and then poured into a mold, which may or may not require post casting matching.

Two principal classes of Al alloys, namely cast alloys and wrought alloys, both of which are further subdivided into the categories heat treatable and non-heat treatable. Wrought alloys contain low percentages of elements; that is, alloying elements total less than about 4 percent. Casting alloys contain the same elements as wrought, but in greater amounts; for example, the silicon content in cast alloys can range up to 22 percent. Alloys whose strength as well as mechanical properties are achieved by heat treatment followed by cooling and natural or artificial ageing, called heat treatable alloys. Temper denoted by letter T.



Alloys whose strength, and mechanical properties are achieved by cold working (rolling, extruding, etc.) defined as non-heat treatable alloys. Sometimes called work harden alloys, and is denoted by letter H. Wrought alloys have both non-heat treatable and heat treatable alloys. Non-heat treatable alloys cannot be strengthened by precipitation hardening, but hardened primarily by cold working. The wrought non-heat treatable alloys include the commercially pure aluminum series (1xxx), the aluminum-manganese series (3xxx), the aluminum-silicon series (4xxx), and the Al-Mg series (5xxx). While some of the 4xxx alloys can be hardened by heat treatment, others can only be hardened by cold working.

On the other hand, wrought heat treatable alloys can be precipitation hardened to develop quite high strength levels. These alloys include the 2xxx series (Al-Cu and Al-Cu-Mg), the 6xxx series (Al-Mg-Si), the 7xxx series (Al-Zn-Mg and Al-Zn-Mg-Cu), and the aluminum-lithium alloys of the 8xxx alloy series. The 2xxx and 7xxx alloys, which develop the highest strength levels, are the main alloys used for metallic aircraft structure. Casting alloys include both non-heat-treatable and heat treatable alloys. The 2xx.x, 3xx.x, 7xx.x, and 8xx.x alloys can be strengthened by precipitation hardening, heat treatable alloys. Without these the rest are non-heat treatable.

2.5.1 Heat Treatable Alloys

Heat treatable alloys are strengthened by solution heat treating and then quenching, or rapid cooling. Heat treating takes the solid, alloyed metal and heats it to a specific point. The alloying elements, called solute, are homogeneously distributed with the aluminum putting them in a solid solution. The metal is subsequently quenched, or rapidly cooled, which freezes the solute atoms in place. The solute atoms consequently combine into a finely distributed precipitate. This occurs at room temperature which is called natural aging or in a low temperature furnace operation which is called artificial aging.

Natural ageing (T1, T2, T3, and T4) is the process which occurs spontaneously at ordinary temperature until the metal reaches a stable condition. This hardens the metal after solution heat treatment. The process, artificial ageing (T5, T6, T9), of heating for a prescribed period (2-30 hours) at a prescribed low temperature (100-200ºC) until the metal reaches a stable condition. This hardens or increases strength after solution heat treating quicker than natural ageing and to a greater level.

2.5.2 Non-Heat Treatable Alloys

Non-heat treated alloys are strengthened through cold-working. Cold working occurs during rolling or forging methods and is the action of “working” the metal to make it stronger. For example–when rolling aluminum down to thinner gauges, it gets stronger. This is because cold working builds up dislocations and vacancies in the structure, which then inhibits the movement of atoms relative to each other. This increases the strength of the metal. Alloying elements like Mg intensify this effect, resulting in even higher strength.

2.6 Designation System

Aluminum Association (AA), an US based organization, has adopted a nomenclature to specify the aluminum alloys. British standard and German institute for standardization, Deutsches Institut für Normung (DIN) have different designation systems. In this work, aluminum alloys are designated following the AA nomenclature.

2.6.1 Wrought Alloys Designation

According to AA, seven designated aluminum alloy series are available, used for immediately identifying the main alloying elements of the wrought as well as the cast aluminum alloys. The international alloy designation system is the most widely accepted naming scheme for wrought alloys, as given Table 2.2.

- The first digit (**X**xxx) indicates the principal alloying element, which has been added to the aluminum alloy and is often used to describe the aluminum alloy series, i.e., 1000 series, 2000 series, 3000 series, up to 8000 series.

- The second digit, if different from 0-indicates a variation of the alloy, and the third and fourth digits identify the specific alloy in the series. For example, in alloy 3105, the number 3 indicates the alloy is in the manganese series, 1 indicates the first modification of alloy 3005, and finally 05 identifies it in the 3000 series.

Table 2. 2 Designation of wrought alloys [4]

Alloy Series	Principal Alloying Element
1xxx	Unalloyed Aluminum, pure Al
2xxx	Copper
3xxx	Manganese
4xxx	Silicon
5xxx	Magnesium
6xxx	Magnesium and Silicon
7xxx	Zinc
8xxx	Other Elements

The second single digit (xXxx), if different from 0, indicates a modification of the specific alloy, and the third and fourth digits (xxXX) are arbitrary numbers given to identify a specific alloy in the series. For example, in alloy 5183, the number 5 indicates that it is of the magnesium alloy series, the 1 indicates that it is the 1st modification to the original alloy 5083, and the 83 identifies it in the 5xxx series.

The only exception to this alloy numbering system is with the 1xxx series aluminum alloys (pure aluminum) in which case, the last two digits in the 1xxx group correspond with the two digits after the decimal which indicate the minimum aluminum content. For example– the aluminum content of 1060 is 99.60% minimum, 1100 is 99.00% minimum, and 1350 is 99.50% minimum, and so on. The last two digits of the other groups are sequential numbers issued by the AA to ensure each alloy is uniquely identified. The second digit in all groups indicates a minor modification of the basic alloy. For instance, 5252 is the second modification of 5052 alloy.

2.6.2 Casting Alloys Designation

Alloys registered within the Aluminum Association (AA) Standard are identified by the prefix "AA" (e.g. AA 5754). The cast alloy designation system is based on a 3 digit-plus decimal designation xxx.x (i.e. 700.0). The first digit (Xxx.x) indicates the principal alloying element, which has been added to the aluminum alloy, and used to describe the aluminum alloy series. The second two digits reveal the minimum percentage of aluminum, e.g. 150.x correspond to a minimum of 99.50% aluminum. The digit after the decimal point takes a value of 0 or 1, denoting casting and ingot respectively. The main alloying elements in the AA system are given in Table 2.3.

Table 2. 3 Designation of cast Al alloys [4]

Alloy Series	Principal Alloying Element
1xx.x	99.000% minimum Aluminum
2xx.x	Copper
3xx.x	Silicon Plus Copper and/or Magnesium
4xx.x	Silicon
5xx.x	Magnesium
6xx.x	Unused Series
7xx.x	Zinc
8xx.x	Tin
9xx.x	Other Elements

The second and third digits (xXX.x) are arbitrary numbers given to identify a specific alloy in the series. The number following the decimal point indicates whether the alloy is a casting (.0) or an ingot (.1 or .2). A capital letter prefix indicates a modification to a specific alloy. For example, Alloy A356.0 the capital A (Axxx.x) indicates a modification of alloy 356.0. The number 3 (A3xx.x) indicates that it is of the silicon plus copper and/or magnesium series. The 56 (Ax56.0) identifies the alloy within the 3xx.x series, and the .0 (Axxx.0) indicates that it is a final shape casting and not an ingot.

2.6.3 Temper Designations

If different series of Al alloys are considered, it's clear that there are considerable differences in the first point to recognize. After understanding the identification system, there are two distinctly different types of Al within the series mentioned above. These are the heat treatable (those which can gain strength through the addition of heat) and the non-heat treatable aluminum alloys [10]. This distinction is particularly important when considering the effects of arc welding on these two types of materials.

- The 1xxx, 3xxx, and 5xxx series wrought aluminum alloys are non-heat treatable and are strain hardenable only. The 2xxx, 6xxx, and 7xxx series wrought aluminum alloys are heat treatable and the 4xxx series consist of both heat treatable and non-heat treatable alloys.

- The 2xx.x, 3xx.x, 4xx.x and 7xx.x series cast alloys are heat treatable. Strain hardening is not generally applied to castings.

The heat treatable alloys acquire their optimum mechanical properties through a process of thermal treatment, the most common thermal treatments being solution heat treatment and artificial aging. Solution heat treatment is the process of heating the alloy to an elevated temperature (around $532^0\mathrm{C}$) in order to put the alloying elements or compounds into solution. This is followed by quenching, usually in water, to produce a supersaturated solution at room temperature.

Solution heat treatment is usually followed by aging. Aging is the precipitation of a portion of the elements or compounds from a supersaturated solution in order to yield desirable properties. The aging process is divided into two types: aging at room temperature, which is termed natural aging, and aging at elevated temperatures termed artificial aging. Artificial aging temperatures are typically about $160^0\mathrm{C}$. Many heat treatable aluminum alloys are used for welding fabrication in their solution heat treated and artificially aged conditions.

The non-heat treatable alloys acquire their optimum mechanical properties through strain hardening. Strain hardening is the method of increasing strength through the application of cold working. The temper designation system addresses the material conditions called tempers. The temper designation system is an extension of the alloy numbering system and consists of a series of letters and numbers which follow the alloy designation number, and are connected by a hyphen. For examples, 6061-T6, 6063-T4, 5052-H32, 5083-H112.

2.6.3.1 Basic Temper Designations

A letter with possibly a one to three-digit number, temper designation, which indicates the mechanical and/or heat treatment to which the alloy has been subjected. The temper designation follows the alloy code and is separated by a hyphen.

For example, illustrated in Table 2.4, F, H, and O represent the as-fabricated, strain hardened, and annealed states respectively. T3 means that the alloy was solution heat treated, cold worked, and then naturally aged (age hardened). A solution heat treatment followed by artificial aging is indicated by T6.

Table 2. 4 Abbreviation and illustration of letter symbol used [10]

Letter	Meaning
F	Fabricated – Applies to products of rolling or forming where there is no special control over the thermal or work-hardening conditions. Since mechanical properties may vary widely, no limits have been assigned. This temper usually applies to sheet products which are at intermediate stages of production.
O	Annealed – Applies to wrought products which have been heated above the recrystallization temperature to produce the lowest tensile strength condition to improve ductility and dimensional stability of the alloy.
H	Strain Hardened – Applies to wrought products which are strengthened by cold-rolling or cold-working. The strain hardening may be followed by supplementary thermal treatment, which produces some reduction in strength. The “H” is always followed by two or more digits.
W	Solution Heat Treated – An unstable temper applicable only to alloys which age spontaneously at room temperature after solution heat-treatment.
T	Thermally Treated – To produce stable tempers other than F, O, or H. Applies to product which has been heat-treated, sometimes with supplementary strain-hardening, to produce a stable temper. The “T” is always followed by one or more digits.

2.6.3.2 H-Temper Subdivision

The wrought alloys can be strengthen by cold working. H-temper, H for strain hardening, can be further classified as following.

The First Digit

There are four different methods used to achieve the final temper of strain hardened material.

H1−Strain Hardened Only: This applies to products which are strain hardened to obtain the desired strength level without any subsequent thermal treatment.

H2−Strain Hardened and Partially Annealed: This applies to products that are strain hardened to a higher strength level than desired, followed by a partial anneal (or “back anneal”) which reduces the strength to the desired level.

H3−Strain Hardened and Stabilized: This designation only applies to magnesium-containing alloys which gradually age- soften at room temperature after strain hardening. A low temperature anneal is applied which stabilizes the properties.

H4−Strain Hardened and Lacquered or Painted.

The Second Digit

The amount (degree) of strain hardening, and hence the strength level, is indicated by a second digit. The second digit after the H indicates the degree of strain hardening.

2 = 1/4 Hard	H×2–Quarter hard
4 = 1/2 Hard	H×4–Half hard
6 = 3/4 Hard	H×6–Three quarter
8 = Full Hard	H×8–Full hard
9 = Extra Hard	H×9 Extra hard

Hx5 and Hx7 tempers are intermediate between those defined above. The mechanical property limits that correspond to each temper designation can be found by referring to an appropriate aluminum standard such as the Aluminum Association Standards and Data or ASTM B 209. Here, it is mentioned that a third digit is sometimes used to indicate a variation of the basic two-digit temper.

2.6.3.3 T-Temper Subdivisions

Alloys in the 2xxx, 6xxx and 7xxx groups can be strengthened by a heat treatment process. The aluminum is heat treated by carrying out a solution treatment process, in which the metal is heated to an elevated temperature followed by rapid cooling, then a precipitation hardening process (or aging process). The tempers are designated by T followed by a digit. Some common T−tempers are given in Table 2.5.

Table 2. 5 Explanation of T-temper designation [10]

T-Temper	Explanation
T1	Naturally aged after cooling from an elevated temperature shaping process, such as extruding.
T2	Cold worked after cooling from an elevated temperature shaping process and then naturally aged.
T3	Solution heat-treated, cold worked, and naturally aged: Applies to products that are cold-worked to improve strength after solution heat treatment, or which the effect of flattening or straightening is recognized in mechanical property limits.
T4	Solution heat-treated and naturally aged: Applies to product that are allowed to age harden at room temperature following a solution treatment.
T5	Artificially aged after cooling from an elevated temperature shaping process.
T6	Solution heat-treated and artificially aged: Applies to products that are reheated to a low temperature following a solution treatment. This allows the metal to achieve its highest heat-treated strength level.
T7	Solution heat treated and stabilized (overaged).
T8	Solution heat treated, cold worked and artificially aged.
T9	Solution heat treated, artificially aged and cold worked.
T10	Cold worked after cooling from an elevated temperature shaping process and then artificially aged.

2.6.3.4 Additional Digits for T-Tempers

Additional digits have been assigned for stress-relieved tempers of Al alloys for special cases.

- **Txx51-Stress Relieved by Stretching:** applies to the following products when stretched the indicated amounts after solution heat treatment or cooling from an elevated temperature shaping process.

- **Txx52-Stress Relieved by Compressing:** applies to products which are stress relieved by compressing after solution heat treatment, or cooling from an elevated temperature shaping process to produce a permanent set of 1 to 5 percent.

2.7 Effects of Alloying Element

To overcome the limitations of pure aluminum-e.g. inferior tensile strength and hardness, selected elements called alloying elements are added to aluminum during casting or proper heat treatment procedure is applied to enhance the mechanical properties. The strength and hardness get enhanced as a result of restriction on the dislocation movement.

The mechanical, physical and chemical properties of aluminum alloys depend on composition and microstructure. The addition of selected elements to pure aluminum greatly enhances its properties. The major alloying additions used with Al are Cu, Mg, Si, Mg and Zn; other elements are also added in the smaller amounts for grain refinement and to develop special properties. The total amount of these elements up to 10 wt. % of the alloy composition. Impurity elements are also present, but their percent is usually less than 0.15 wt. % in Al alloys. That is, the alloying elements added to aluminum, are classified following categories–

1. Major alloying elements
2. Minor alloying elements and
3. Micro-structure modifying elements

2.7.1 Major Alloying Elements

Major alloying elements, also called principal alloying elements are added as selected to base metal to server as desired. Depending on the principal alloying elements, aluminum alloying are classified into different sort of series, as discussed in the previous section. The effects of principal alloying elements is described as following.

2.7.1.1 Copper (Cu)

The Al– Cu alloys typically contain between 2 to 10% copper. The copper provides substantial increases in strength and facilitates precipitation hardening, improves the machinability of alloys by increasing matrix hardness. Cu also have greatest impact of all alloying elements on the hardness of Al casting alloys, both heat treatable and non-heatreatable at both ambient and elevated service temperatures.

On the downside, the introduction of copper to aluminum can also reduce ductility and corrosion resistance. The susceptibility to solidification cracking of Al-Cu alloys is increased; consequently, some of these alloys can be the most challenging aluminum alloys to weld. These alloys include some of the highest strength heat treatable aluminum alloys. Both cast and wrought Al-Cu alloys respond to solution heat treatment and subsequent aging with an increase in strength and hardness and a decrease in elongation. The strengthening is maximum between 4 and 6% Cu, depending upon the influence of other constituents present [11]. The intermetallic compound Al_2Cu at 53% Cu is called the θ phase, given in Figure 2.1. The microstructure of Cu containing phase $\theta(Al_2Cu)$ is shown Figure 2.2.

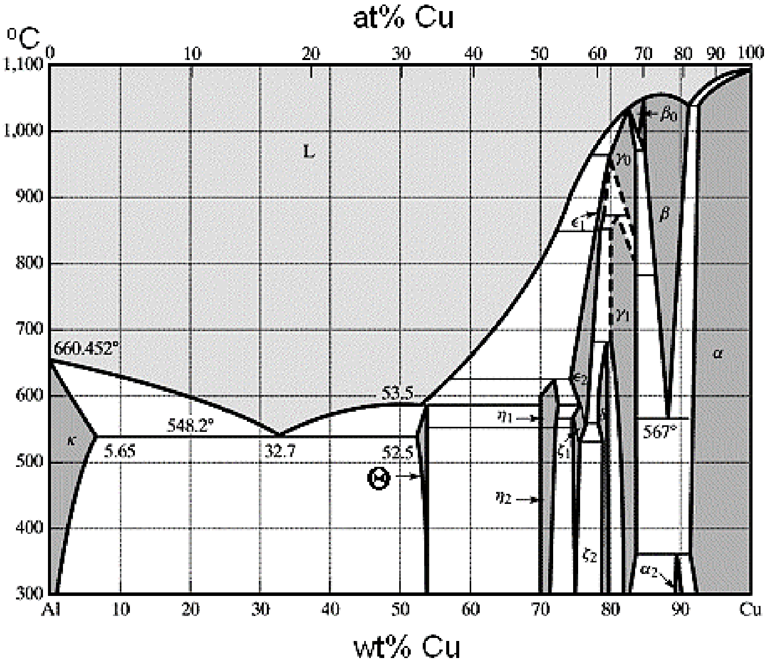


Figure 2. 1 Equilibrium phase diagram of the binary Al-Cu system [12]

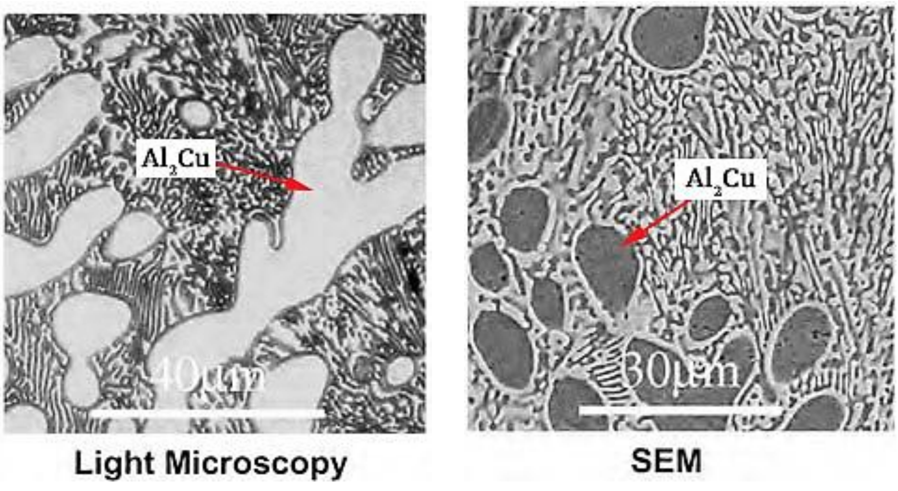


Figure 2. 2 Microstructure of $\theta(Al_2Cu)$ phase [13]

2.7.1.2 Manganese (Mn)

The addition of manganese to aluminum increases strength somewhat through solution strengthening and improves strain hardening while not appreciably reducing ductility or corrosion resistance. The most common applications for the 3xxx series alloys are cooking utensils, radiators, air conditioning condensers, evaporators, heat exchangers and associated piping systems.

Mn as well as Cr-alone or in combination, Mn and Cr change the $\mathrm{Al_5FeSi}$ phase from its typical platelet or acicular form to a more cubic $\mathrm{Al_{15}(MnFe)_3Si_2}$ form that is less harmful to ductility. While Mn and/or Cr cause a beneficial change to the morphology of Fe phases, the change in combination with large concentration of iron, the rule is if iron exceeds 0.45%, Mn content shall not be less than one-half the iron content. Combine manganese and chromium that lead to "sludge" in traditional secondary die casting alloys. Mn has proven to be a suitable substitute for iron to minimize soldering of the cast melt to steel tooling during die casting.

2.7.1.3 Silicon (Si)

Silicon, after iron, is the highest impurity level commercial aluminum. The addition of silicon to aluminum reduces melting temperature and improves fluidity. Si alone in aluminum produces a non-heat treatable alloy; however, in combination with magnesium, it produces a precipitation hardening heat treatable alloy. Consequently, there are both heat treatable and non-heat treatable alloys within the 4xxx series. Silicon additions improve casting characteristics by improving fluidity, form a eutectic with Al at 11.7% Si at $577^0\mathrm{C}$.

The Si rich phase is hard, so the hardness of the alloys is increase with Si content but ductility and machinability are reduced. The lower silicon alloys are used where higher strength is needed [14]. Si alone contributes very little to the strength of Al casting alloys. It combines with other elements to improve the alloy strength and make alloys heat treatable.

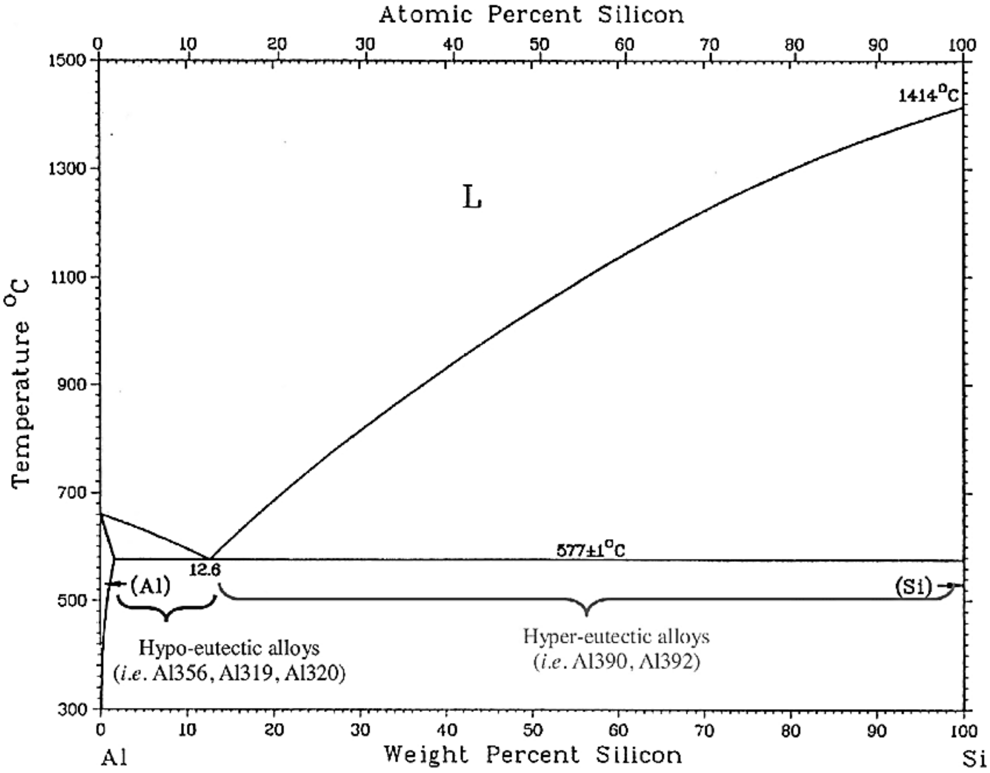


Figure 2. 3 Al-Si phase diagram showing hypo-and hyper-eutectic alloys [15]

When Si combine with Mg to form Mg_2Si provides a very effective strengthening mechanism in Al casting. Mg_2Si solubility limit about 0.7% Mg, provides the precipitation strengthing basis for an entire family of heat treatable alloys. Si in Al form hard phase, contributes significantly to an alloy's wear resistance. Wear resistance property, Al-Si casting, makes the alloys more attractive substitutes for gray iron in automotive applications. Figure 2.3 shows the Al-Si phase diagram with hypo and hyper-eutectic alloys. The hyper-eutectectic Al-Si alloys are used extensively in premium Al bare bore engine blocks, for example, as well as in numerous pumps, compressor, pistons and automatic transmission components.

The addition of silicon to aluminum reduces melting temperature and improves fluidity. Silicon alone in aluminum produces a non-heat treatable alloy; however, in combination with magnesium, it produces a precipitation hardening heat-treatable alloy. Consequently, there are both heat treatable and non-heat treatable alloys within the 4xxx series.

2.7.1.4 Magnesium (Mg)

Magnesium is the major alloying element in the 5xxx series of alloys. Its maximum solid solubility in aluminum is 17.4%, but the magnesium content in current wrought alloys does not exceed 5.5%. The addition of magnesium markedly increases the strength of aluminum through solid solution strengthening without unduly decreasing the ductility. Corrosion resistance and weldability are good. These alloys are the highest strength non-heat treatable aluminum alloys are therefore, used extensively for structural applications.

Mg take great influence on strength except the 5xxx alloy series but rather when it is combined with silicon in 3xxx alloys to form $\mathrm{Mg_2Si}$ and/or with copper in 3xxx or 2xxx alloys, forming the precipitation hardening phase $\mathrm{S(Al_2CuMg)}$.

2.7.1.5 Zinc (Zn)

The major alloying element in the 7xxx series of alloys is zinc. The zinc substantially increases strength and permits precipitation hardening, but hot cracking of the casting alloys and the susceptibility to stress corrosion cracking of the wrought alloys curtailed their use. Zinc is quite neutral, neither enhance nor detracts from an alloy’s properties but facilitate hardening [16]. Since, Zn is relative dense, heave element and as such it increases an alloy’s mass density.

Al-Zn alloys containing other elements offer the highest combination of tensile properties in wrought aluminum alloys. The addition of zinc to aluminum (in conjunction with some other elements, primarily magnesium and/or copper) produces heat treatable aluminum alloys of the highest strength. Some of these alloys can be susceptible to stress corrosion cracking, and for this reason, are not usually fusion welded. Other alloys within this series are often fusion welded with excellent results. Some of the common applications of the 7xxx series alloys are aerospace, armored vehicles, baseball bats and bicycle frames.

2.7.2 Alloying Element Optimization

To extract the best useful properties from the alloys two or more alloying elements are optimized. From this point of view, the following combinations are simultaneously applied during concerned aluminum casting. Table 2.6 shows the main strengthening phase in different Al base alloy systems.

2.7.2.1 Magnesium-Silicon

The addition of magnesium and silicon to aluminum produces the compound magnesium silicide (Mg_2Si). The formation of this compound provides the 6xxx series their heat-treatability. The 6xxx series alloys are easily and economically extruded and for this reason are most often found in an extensive selection of extruded shapes. The common applications for the 6xxx series alloys are handrails, drive shafts, automotive frame sections, bicycle frames, tubular lawn furniture, scaffolding, stiffeners and braces used on trucks, boats and many other structural fabrications.

Magnesium-Silicon, each of magnesium and silicon in the approximate ratio to form Mg_2Si, that is 1.73:1. Precipitation upon age hardening occurs by formation of Guinier-Preston zones and a very fine precipitate. Both confer an increase in strength to these alloys, though not as great as in the case of the 2xxx, or the 7xxx alloys.

2.7.2.2 Zinc-Magnesium

The addition of magnesium to the aluminum-zinc alloys develops the strength potential of this alloy system, especially in the range of 3 to 7.5 wt. % Zn. Magnesium and zinc form $\eta(MgZn_2)$, which produces a far greater response to heat treatment than occurs in the binary Al-Zn system. The strength of the Al-Zn alloys also is substantially improved by the addition of magnesium. Increasing the $MgZn_2$, concentration from 0.5 to 12% in cold-water quenched 1.6 mm sheet continuously increases the tensile and yield strengths. The addition of magnesium in excess (100 and 200%) of that required to form $MgZn_2$ further increases tensile strength.

2.7.2.3 Copper-Magnesium

The main benefit of adding magnesium to Al-Cu alloys is the increased strength possible following solution heat treatment and quenching. In wrought material of certain alloys of this type, an increase in strength accompanied by high ductility occurs on aging at room temperature. On artificial aging, a further increase in strength, especially in yield strength can be obtained, but at a substantial sacrifice in tensile elongation.

2.7.2.4 Copper-Magnesium plus Other Elements

The cast Al-Cu-Mg alloys containing iron are characterized by dimensional stability and improved bearing characteristics, as well as by high strength and hardness at elevated temperatures. Iron in concentrations as low as 0.5% lowers the tensile properties in the heat treated condition, if the silicon content is less than that required to tie up the iron as the FeSi constituent.

Table 2. 6 Precipitates of Al based different Alloy systems

Alloy Systems	Alloy Strengthening from
Al-Cu	Al_2Cu
Al-Cu-Mg	Mg intensifies precipitation
Al-Mg-Si	Mg_2Si
Al-Zn-Mg	$MgZn_2$
Al-Zn-Mg-Cu	Al_2CuMg

2.7.2.5 Copper-Magnesium-Zinc

The addition of copper to the Al-Zn-Mg system, together with small but important amounts of chromium and manganese, results in the highest-strength aluminum-base alloys commercially available. In this alloy system, Zn and Mg control the aging process. The effect of copper is to increase the aging rate by increasing the degree of super saturation perhaps through nucleation of the Cu-Mg-Al phase. Copper also increases quench sensitivity upon heat treatment.

In general, copper reduces the resistance to general corrosion of Al-Zn-Mg alloys, but increases the resistance to stress corrosion. The minor alloy additions, such as chromium and zirconium, have a marked effect on mechanical properties and corrosion resistance. When Zn combined with copper and magnesium, heat treatment and natural aging characteristics are improved. The fluidity is increased but shrinkage problems may occur.

2.7.3 Microstructure Modifying Elements

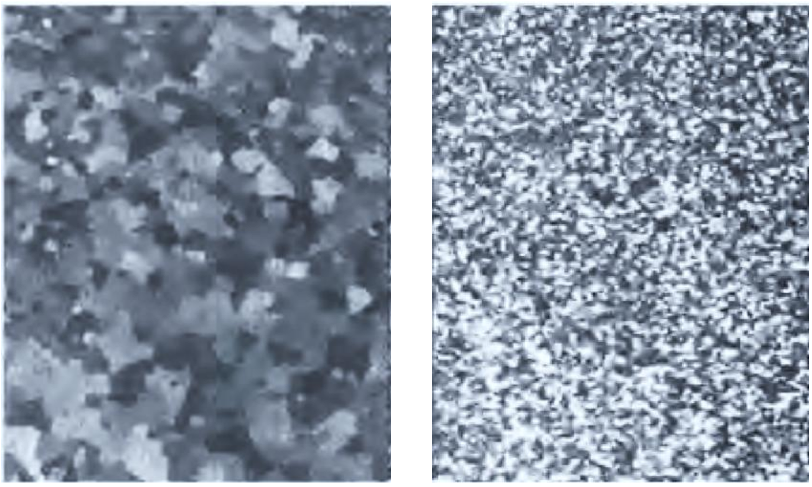
Besides alloying elements, either alone or combined some other elements are selected to modify the micro-structure of the concerning alloys. Boron and titanium are two elements that are commonly used as micro-structure modifier to aluminum alloys.

2.7.3.1 Boron (B)

Boron is used in aluminum and its alloys as a grain refiner and to improve conductivity by precipitating vanadium, titanium, chromium, and molybdenum. Boron can be used alone (at levels of 0.005 to 0.1%) as a grain refiner during solidification, but becomes more effective when used with an excess of titanium. Commercial grain refiners commonly contain titanium and boron in a 5-to-1 ratio.

2.7.3.2 Titanium (Ti)

Titanium is added to aluminum primarily as a grain refiner. The grain refining effect of titanium is enhanced if boron is present in the melt or if it is added as a master alloy containing boron largely combined as TiB_2. Titanium is a common addition to aluminum weld filler wire as it refines the weld structure and helps to prevent weld cracking, as shown in Figure 2.4.



$> 3000\mu\mathrm{m}$, unrefined $< 300\mu\mathrm{m}$, unrefined

Figure 2. 4 Illustration of grain-refined aluminum by Titanium and Boron [17]

Titanium alone, added to as a titanium aluminum master alloy, forms $TiAl_3$ which serves to nucleate primary Al dendrites. More frequent nucleation of dendrites means a larger amount of smaller grains. Grain refining efficiency is better when titanium and boron are used in combination. Master alloys of aluminum with 5% titanium and 1% boron are commonly used for this purpose. Both form TiB and $TiAl_3$, which together are more effective grain refiners than alone Ti. The most efficient grain refiner for Al-Si alloy has a Ti: B ratio closer to 1.5: 1.

2.7.4 Minor Alloying Elements

Besides major alloying elements some other elements called minor alloying elements, trace in quantity, are added to desired alloys. The effects of minor alloying elements for aluminum alloys are illustrated as following.

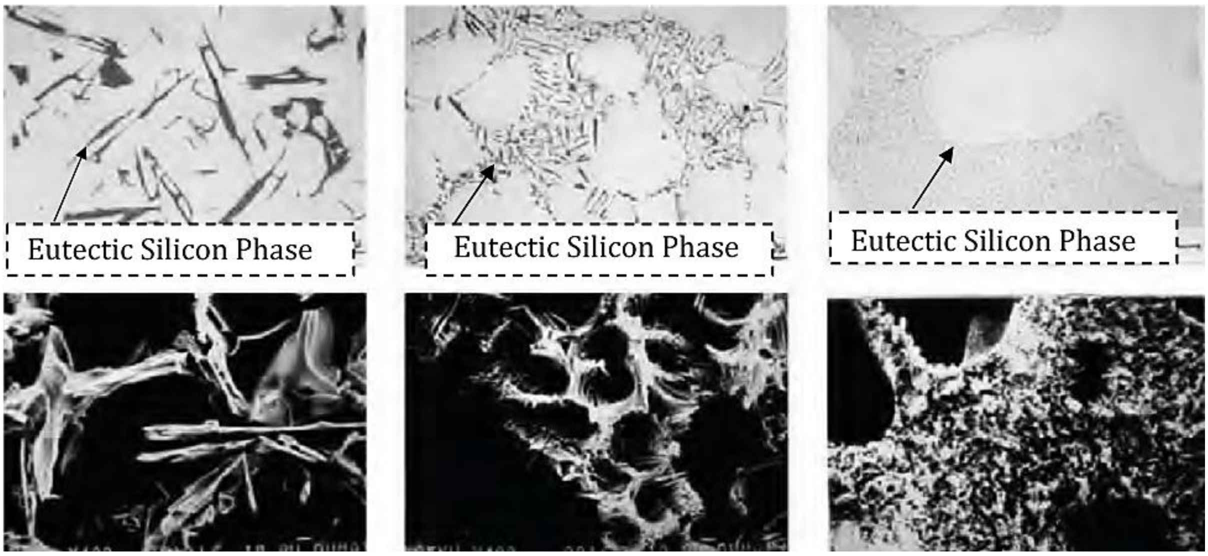
2.7.4.1 Iron (Fe)

Iron is the most common impurity found in aluminum and is intentionally added to some pure (1xxx series) alloys to provide a slight increase in strength. It has a high solubility in molten aluminum and is therefore easily dissolved at all molten stages of production. The solubility of iron in the solid state is very low (0.04 %), and therefore, most of the iron present in aluminum over this amount appears as an intermetallic second phase in combination with aluminum and often other elements. Iron concentration of 0.8% or more greatly reduces the tendency of an alloy to solder and die casting tooling. The Al-Fe-Si ternary eutectic composition occurs at about 0.8 % Fe [18].

Iron combines with Al, Si and other elements to form a variety of hard, complex insoluble phases. The beta Al_5FeSi phase forms as very thin plates, which appear acicular or needle like in a polished cross section. Such morphologies provide stress risers that significantly reduce, destroy the ductility of an alloy. Castability is decreased by Fe due to the formation of sludge phases with Mn and Cr, etc. For this reason, alloys for processes other than pressure die casting are limited to less than 0.8% Fe.

2.7.4.2 Tin (Sn)

Although tin (Sn), a major alloying elements of cast Al 6xxx series alloys; Sn, Na, Ca and antimony, alone not in combination, are added to eutectic or hypoeutectic Al-Si casting alloys to morphology of the eutectic silicon phase. Without the benefits of a modifying treatment, eutectic silicon solidifies in a relatively coarse continuous network of thin plates, shown in Figures 2.5 a-b. This morphology provides abundant stress riser, and thus limits the attainment of maximum strength and ductility. Modification with one of the above elements changes the eutectic silicon into a fine or lamellar structure (Figures 2.5 b-c).



(a) Unmodified silicon (b) Modified silicon (c) Super modified phase

Figure 2. 5 Morphology of the eutectic Si phases in Al-Si casting alloy [18]

2.7.4.3 Chromium (Cr)

Chromium is a common addition to many alloys of the Al-Mg, Al-Mg-Si, and Al-Mg-Zn groups, in which it is added in amounts generally not exceeding 0.35%. In excess of these limits, it tends to form very coarse constituents with other impurities or additions such as manganese, iron, and titanium. Chromium is added to aluminum to control grain structure, to prevent grain growth in Al-Mg alloys, and to prevent recrystallization in Al-Mg-Si or Al-Mg-Zn alloys during heat treatment. Chromium will also reduce stress corrosion susceptibility and improves toughness. Alone or in combination with manganese (Mn) change the morphology of the iron rich Al_5FeSi phase (Figure 2.6) from its typical platelet/acicular form to a more cubic $Al_{15}(Mn\text{-}Fe)_3Si_2$ form (Figure 2.7) that is less harmful to ductility.

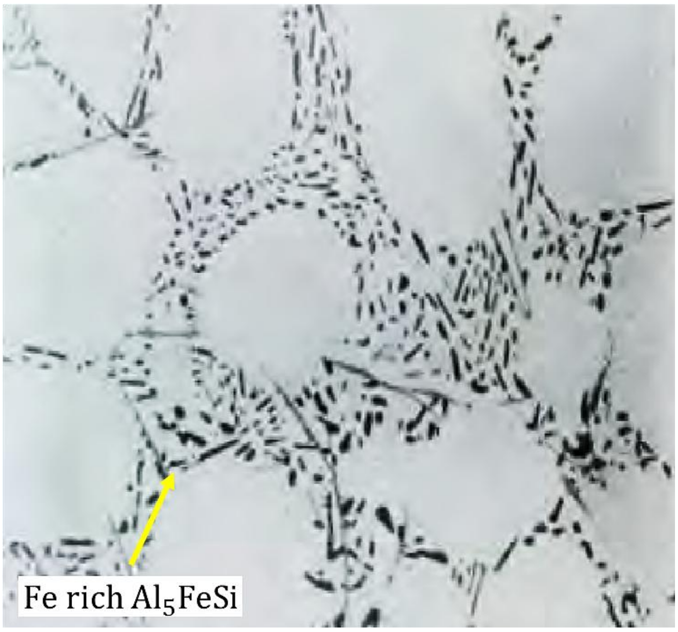


Figure 2. 6 Morphology of Fe-rich Al_5FeSi [18]

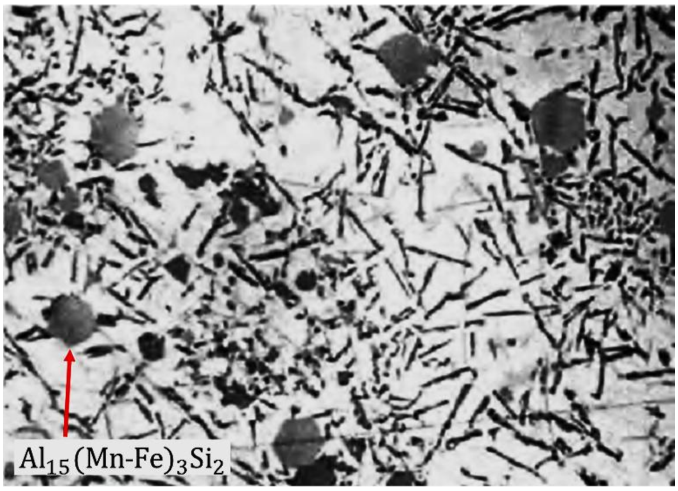


Figure 2. 7 Cubic $Al_{15}(Mn\text{-}Fe)_3Si_2$ phase in the platelet form [18]

2.7.4.4 Nickel (Ni)

Nickel (up to 2%) increases the strength of high-purity aluminum but reduces ductility. Binary Al-Ni alloys are no longer in use but nickel is added to Al-Cu and to Al-Si alloys to improve hardness and strength at elevated temperatures and to reduce the coefficient of expansion.

2.7.4.5 Zirconium (Zr)

Zirconium additions in the range 0.1 to 0.3 % are used to form a fine intermetallic precipitate that inhibits recrystallization and recovery. An increasing number of alloys, particularly in the Al-Zn-Mg family, use zirconium additions to increase the recrystallization temperature and to control the grain structure in wrought products.

2.7.4.6 Lithium (Li)

Lithium is the lighter element, with atomic number 3 in the periodic table. The main advantage of Li addition reduction of weight of the alloy system. The addition of lithium to aluminum can substantially increase strength and Young's modulus, and provides precipitation hardening, in addition to decrease density. Li has harmful effect on casting properties by reducing the effectiveness of Na or Sr (both are eutectic modifier) at level 0.5%. At even lower levels, above 0.01%, porosity are experienced. Therefore, it is recommended that Li levels below 0.003% are used for casting.

2.7.4.7 Hydrogen (H)

Hydrogen has a higher solubility in the liquid state at the melting point than in the solid at the same temperature. Because of this, gas porosity can form during solidification. Hydrogen is produced by the reduction of water vapor in the atmosphere by aluminum and by the decomposition of hydrocarbons. In addition to causing primary porosity in casting, hydrogen causes secondary porosity, blistering, and high temperature deterioration (advanced internal gas precipitation) during heat treating. It probably plays a role in grain boundary decohesion during stress corrosion cracking. Its level in melts is controlled by fluxing with hydrogen-free gases or by vacuum degassing.

2.8 Heat Treatment Process

A thermal process, where a metal is heated according to a predetermine time and temperature cycle, then cooling to ambient temperature to extract the desired hardness, tensile strength is outcome by alternate heating and cooling. Depending on the alloy and its conditions, heat treating can harden or soften a metal. The primary purpose of the heat-treating process is to control the amount, size, shape and distribution of the hardening particles.

The heat treatment processes, applied to aluminum alloys may be classified into four categories–homogenizing or preheating, annealing, solution hardening and ageing. Homogenizing reduces chemical segregation of cast structure and improve the workability of casting. Annealing for stresses relieve and stabilize properties and dimensions of stain-hardened (work-hardened) or heat treated alloy structure.

Hardening treatments take a policy, heating the alloy to a sufficiently high temperature to dissolve solute-rich precipitates. The alloy is then rapidly cooled to avoid reprecipitation; most often it is done by quenching in water or oil. The concentration of solute dissolved in the metal is now much greater than the equilibrium concentration. This procedure is known as solid-solution hardening, but the alloy can usually be hardened appreciably more by aging to allow a very fine precipitate to form. Aging is done at an elevated temperature that is still well below the temperature at which the precipitate will dissolve.

If the alloy is further heated still, the precipitate will coarsen; that is, the finest particles will dissolve so that the average particle size will increase. This will reduce the hardness somewhat but increase the ductility. Precipitation hardening is used to produce most high strength alloys. In products made of soft, ductile metals such as aluminum or copper, the age-hardened alloy is put into service with the finest precipitate (that is, the highest strength) possible [19].

That is, heat-treatable alloys are strengthened by solution heat-treating and then quenching, or rapid cooling. Heat treating takes the solid or alloyed metal and heats it to a specific point. The alloying elements (solute) are homogeneously distributed through the aluminum (solvent) putting them in a solid solution. The metal is subsequently quenched, or rapidly cooled, which freezes the solute atoms in place. The solute atoms consequently combine into a finely distributed precipitate. This occurs at room temperature, which is called natural aging, or in a low temperature furnace operation, which is called artificial aging.

Natural ageing (T1, T2, T3, and T4) is the process which occurs spontaneously at ordinary temperature until the metal reaches a stable condition. This hardens the metal after solution heat treatment. The process, artificial ageing (T5, T6, & T9) of heating for a prescribed period (2-30 hours) at a prescribed low temperature (100-200^0C) until the metal reaches a stable condition. This hardens/increases strength after solution heat treating quicker than natural ageing and to a greater level [20].

2.9 Ageing Response of Al 7xxx Series Alloys

As mentioned before, the Al 7xxx alloys are always solution heat treated and quenched. Heat treatment to increase strength of aluminum alloys is a three steps process–(1) solution treatment-dissolution of soluble phases; (3) quenching-development of super saturation; and (3) age hardening-precipitation of solute atoms either at room temperature (natural aging) or elevated temperature (artificial aging or precipitation heat treatment).

Solution treatment involves the heating of an alloy to a suitable temperature, holding at that temperature for sufficient time to induce one or more of the constituents to enter into solid solution that ensures maximum practical amounts of the soluble hardening elements in the alloy. This time delay is called "aging". Solution treatment and aging is sometimes abbreviated as "STA". The process consists of soaking the alloy at a temperature sufficiently high and for a time long enough to achieve a nearly homogeneous solid solution. Afterwards the solution is cooled rapidly enough to hold these constituents in solution. This process is called Quenching. After solution treatment and quenching, hardening is achieved either at room temperature (natural aging) or with a precipitation heat treatment (artificial aging) [21].

Artificial aging, also called precipitation hardening, is the process in which one or more constituents precipitate from the solid solution to induce an appreciable increase in hardness. Precipitation hardening increases the yield strength of malleable materials. Precipitation hardening relies on changes in solid solubility with temperature to produce fine particles of an impurity phase, which impede the movement of dislocations, or defects in a crystal's lattice. Since dislocations are the dominant carriers of plasticity, this serves to harden the material.
Precipitation heat treatment for Al 7xxx series followed solution heat treatment and quenching produces T6-type tempers. Alloys in T6-type tempers generally have the highest strengths practical without sacrifice of the minimum levels of other properties and characteristics, found by experience to be satisfactory and useful for engineering applications. For the alloys that are used in these tempers, the relatively high super saturation of atoms and vacancies retained by

rapid quenching cause rapid formation of GP zones. Precipitation heat treatments or aging for Al alloys are low-temperature, long-term processes. Temperatures may range from 115 to 190°C; times may vary from 5 to 48 h. Choice of time-temperature cycles for precipitation heat treatment should be carefully. Because, larger particles of precipitate result from the longer times and higher temperatures; however, the larger particles must be fewer in number with greater distances between them.

The objective is to select the time-temperature cycle that produces optimum precipitate size and distribution pattern. Unfortunately, the cycle required to maximize one property, such as tensile strength, is usually different from that required to maximize others, such as yield strength and corrosion resistance. Consequently, the time-temperature cycles used represent compromises that provide the best combinations of properties.

2.10 Thermodynamic Modeling

Solidification of alloys depends on the cooling rate, temperature gradient and growth rate. In most practical cases, solidification is too fast to allow equilibrium to be maintained between the solid and liquid phases, and thus a model is needed that is capable of dealing with non-equilibrium solidification. At first it is necessary to introduce the term “partition coefficient”, k. It is expressed as

$$k = \frac{X_S}{X_L} \qquad \text{[Equation 2-1]}$$

Where, X_S and X_L are the mole fraction of solute in the solid and in the liquid at a temperature T. If the alloy has C_0 composition then the first solid formed will have the composition kC_0. Under equilibrium condition, diffusion will occur extensively and composition of the solid and liquid will be homogeneous and so, the fraction of solid can be determined by the lever rule and the alloy will have same C_0 composition along its length. For a binary alloy, the composition of solid can be expressed as [22].

$$C_S = \frac{kC_0}{f_S(k-1)+1} \qquad \text{[Equation 2-2]}$$

Where, f_S is the fraction of solid. The fraction of solid can be expressed as a function of temperature as

$$f_S = \left(\frac{1}{1-k}\right)\left(\frac{T_L - T}{T_S - T}\right)$$ [Equation 2-3]

Where, T_L and T_S are the liquidus and solidus temperatures respectively. However, in practice, solidification rarely occurs under these equilibrium conditions because there is insufficient time for the necessary diffusion. Gibbs free energy should be minimized to achieve an equilibrium state under constant pressure, temperature and composition. Gibbs free energy for pure element and stoichiometric compound phases (e.g., Cu_2FeAl_7) can be expressed in terms of temperature as [23].

$$G_{m[T]} - H_m^{SER} = a + bT + cT\ln(T) + \sum_2^n d_n T^n$$ [Equation 2-4]

Where, left hand side represents the Gibbs free energy relative to a standard element reference state (SER), H_m is the enthalpy of the element under SER at 298.15 K, a, b, c and d_n are experimentally determined coefficients, n is a set of integers with value 2, 3 & -1 and T is the absolute temperature.

Other thermodynamic variables such as enthalpy (H) and entropy (S) are also possible to define using equation 1-4 in the form

$$S = -b - c - c\ln(T) - \sum n d_n T^{n-1}$$ [Equation 2-5]

$$H = a - cT - \sum (n-1) d_n T^n$$ [Equation 2-6]

Where, the terms are as defined earlier. In ferromagnetic and anti-ferromagnetic materials, a magnetic contribution to the Gibbs free energy should be considered. Magnetic ordering can make a significant change in the structure of the material. For a pure metal, this term is expressed as

$$G^{mag} = RT\ln(1+\beta_0)g(\tau)$$ [Equation 2-7]

Where, R is the gas constant, T defined earlier, β_0 is the average magnetic moment per atom (it is the saturation magnetism β at 0 K) and $\tau = T/T^*$, T^* is the critical temperature T_C (curie temperature for ferromagnetic materials) or T_N (Neel temperature for anti-ferromagnetic materials). The difference between these two temperatures is the different forms of polarisation of electron spins [23]. If parallel electron spin configuration is preferred between nearest neighbours of atoms, the critical ordering temperature is known as the Curie temperature and if anti-parallel electron spin is favoured between nearest neighbours of only one species of atoms, the critical temperature is known as the Neel temperature. Now, for multi-component systems, Gibbs free energy can be made minimum according to the following expression [24]

$$G = \sum_{i=1}^{p} x_i G_i^{\varphi} = \text{minimum} \qquad \text{[Equation 2-8]}$$

Where, p is the number of phases, x_i is mole fraction of component i and G_i^{φ} is the Gibbs free energy of the phase φ. Gibbs free energy is elaborately expressed in terms of pressure, temperature and composition. For a phase φ

$$G^{\varphi} = G_T^{\varphi}(T,x) + G_P^{\varphi}(p,T,x) + G_m^{\varphi}(T_C \beta_0, T, x) \qquad \text{[Equation 2-9]}$$

Where, the 1st term shows the dependency on temperature (T) and composition (x), the 2nd term shows pressure dependency and the 3rd term is the magnetic contribution. T_C and β_0 are defined earlier. The 1st term can be expressed as the power series in terms of temperature according to equation 1-4. The contribution from 2nd term is ignored for low or moderate pressure. A complicated expression is required for determination of dependency of high pressure. The 3rd term can be expressed by equation 1-9.

Alloys include solution phases, such as random substitutional and sublattice phases, require different considerations [25]. A random substitutional model is required where the atoms can mix on any available site (e.g. fcc phase Al). In a sublattice phase, atoms show preferential mixing on similar types of site. Sublattice models are used, for example, to describe intermetallic phases (e.g., Ni_3Al, $ZrAl_3$, Fe-C, etc.). A regular solution model can be found elsewhere [26]. For a solution phase φ, molar Gibbs energy can be expressed as [27]

$$G^{\varphi} = G^{\varphi,ref} + G^{\varphi,ideal} + G^{\varphi,xs} \qquad \text{[Equation 2-10]}$$

Where, the terms refer to reference, ideal mixing and excess contributions. The 1st term corresponds to a mechanical mixture of the Gibbs free energy of constituents of the phase, i.e., weighted sum of the data for pure elements (equation 1-8). The 2nd term corresponds to entropy of mixing for an ideal solution as

$$G^{\varphi,ideal} = RT \sum_{i=1}^{n} x_i \ln(x_i) \qquad \text{[Equation 2-11]}$$

Where, all the terms are as defined earlier. The 3rd term considers the deviation from ideal mixing due to interactions between constituents of the phase (Gibbs excess energy of mixing). It is expressed as

$$G^{\varphi,xs} = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j L^{\varphi}_{i,j} \qquad \text{[Equation 2-12]}$$

Where, $L^{\varphi}{}_{i,j}$ is the interaction parameter. For an ideal solution $G^{\varphi,\ xs}$ is zero. As an example, the following complex expression can be considered according to the above discussion. This expression is for liquid and solid solution phases. Considering a substitutional solution, Gibbs free energy for two constituents (1 & 2) can be expressed by the following equation.

$$G = x_1\ G^0{}_1 + x_2\ G^0{}_2 + RT\left(x_1 \ln x_1 + x_2 \ln x_2\right) + x_1 x_2 \sum_{i=0}^{1} L_i \left(x_1 - x_2\right)^i \qquad \text{[Equation 2-13]}$$

Where, $G^0{}_1$ and $G^0{}_2$ are reference states of elements 1 & 2, x_1 & x_2 are mole fractions. 1st two terms refer to $G^{\varphi,\ ref}$, 3rd term refers to $G^{\varphi,\ ideal}$ and L_i of the 4th term is defined earlier (coefficient $G^{\varphi,\ xs}$ of equation 1-11). For ordered intermetallic phases like $Al_{12}Mg_{17}$, it has been found that Gibbs free energy is a function of one independent variable only [28]. So, calculations can be made efficiently in this case.

Thermodynamic information for lower order systems, such as binary or ternary systems, is obtained experimentally. This information then can be extrapolated for higher order (multi-component) systems to calculate the phase formation [29]. Compensation for interactions in multi-component systems can be introduced if deviation from the experimental values is obtained.

2.11 Why Cu/Mg Ratio Selected

Copper (Cu) and magnesium (Mg) are primary alloying element. The addition Cu to aluminum reduces ductility and corrosion resistance. The Cu provides substantial increases in strength and facilitates precipitation hardening, improves the machinability of alloys by increasing matrix hardness. Cu also have greatest impact of all alloying elements on the hardness of Al casting alloys, both heat treatable and non-heatreatable at both ambient and elevated service temperatures. These alloys respond to solution heat treatment and subsequent aging with an increase in strength and hardness and a decrease in elongation. The strengthening is maximum between 4 and 6% Cu, depending upon the influence of other constituents present [11].

The addition of Mg markedly increases the strength of aluminum through solid solution strengthening without unduly decreasing the ductility. Good corrosion resistance and weldability and have the highest strength, that is why, used extensively for structural applications. The main benefit of Mg to alloys is the increased strength possible following solution heat treatment and quenching. On artificial aging, a further increase in (yield) strength can be obtained at a substantial sacrifice in tensile elongation. Mg take great influence on strength. When it is combined with Cu forming the precipitation hardening phase $S(Al_2CuMg)$.

The quantities of three major precipitated phases (η, S, T) and phase diagrams of Al-Zn-Mg-Cu alloys with various Cu contents have been calculated based on materials models. S-phase starts to form when there is a small percentage of Cu as little as about 1.0 wt. % and large amount of S-phase precipitates as Cu content increases. As the Cu to Mg content ratio 1.32, S-phase is predominant as-rolled condition, even as-aged condition. The amount of the main hardening η ($MgZn_2$) phase increases with an increase in Cu content. On the contrary, T-phase reduces significantly as the Cu content increases, and the presence of T-phase in the alloy largely depends on the Cu: Mg ratio. Al-Cu-Mg alloy system occurs and the $\theta(Al_2Cu)$ phase precipitates as a result of excessive Cu in the alloy. Therefore, the Cu variation of Al-Zn-Mg-Cu alloys must be well controlled within a reasonable range so as to obtain optimum properties for this type of alloys.

2.12 Scope of This Work

The findings of this work involves study of effects of varying composition on mechanical properties of a 7xxx series aluminum alloy. Recently, a good amount of research papers available on aluminum alloys. There is still no effective relationship and understanding about the effects of copper, magnesium and zinc ratios (varying amount) on ageing response to increase strength, size distribution of precipitates and fracture behavior in different direction of rolling.

As known, physical, chemical and mechanical properties depend on the composition of alloying element and microstructure features of the concerning alloy. From this research it will be possible to develop aluminum alloys using different alloying elements. These might provide important information regarding the influence of alloying elements on microstructure and mechanical properties. Such development will lead to better understanding of fundamental characteristics of composition in this series. Processing route via better heat treatment cycle will also be established, which is beneficial for industries.

Chapter 03

EXPERIMENTAL PROCEDURE

3. 1 Materials Collection

Aluminum, the base material for the investigating alloys, bought from local market as ingot, manufacture by a Canadian Company. Chemical composition of this ingot was ensured by optical emission spectroscopy (OES), found 99.75% purity. The main alloying elements-copper, magnesium and zinc were collected with 99% purity. Total three alloys of different composition with balanced Al, wt. % composition is demonstrated in Table 3.1 prepared for casting.

Table 3. 1 Estimated composition (wt. %) of as-cast

Primary Alloying Element	Zinc 6 wt.%
Other Alloying Element	Mg 1-2 wt.% Cu 1-4 wt.%
Base Metal	Balanced Al

3. 2 Alloy Preparation

First of all, as prescribed schedule of the investigated alloy, base metal Al and alloying elements Cu, Mg and Zn were accumulated for casting. The furnace was heated above melting point of all elements (800^0C). Using a stirrer, the mixture is stirred uniformly. Except Mg all metal was melted, the predetermined Mg added that created silver lightening. To remove the gaseous product as well as porosity of the cast, ammonium chloride (NH_4Cl) used as degasser as per 0.2% for 1kg raw materials. The melt, then, was poured into a mold of dimensions 215 mm length, 63 mm width and 50 mm thickness. After casting the melt was cooled to room temperature.

3. 3 Chemical Composition Determination of Casting Alloys

Chemical analysis of casting samples performed by Optical Emission Spectroscopy (OES). The polished samples, at least four sparks were made in different location of the cast samples through Shimadzu PDA-7000 to determine average composition. Weight chemical analysis also carried out to measure actual percentage of Cu in the as-cast alloys.

3. 4 Homogenization Treatment

As the casting samples was experience to homogenization treatment through Protherm Furnace. The furnace with samples heated to 400^0 C for 3 hours. After holding the samples, as given in following Figure 3.1, the samples were quenched into water.

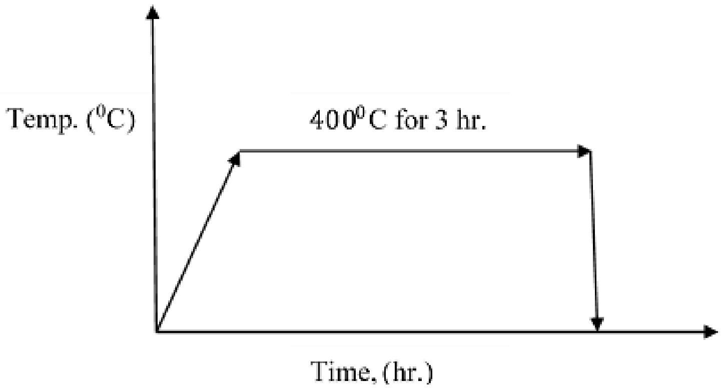


Figure 3. 1 Heat treatment cycle for homogenization

3. 5 Hot Rolling

The samples, after homogenization, were prepared for hot rolling treatment. The thickness of these sample were about 12mm. The furnace, named as Protherm Furnace, with samples was heated to 500^0C for 1hr. In the mean time, the manually handled rolling machine is switched on. Through 10 minutes intervals, the samples was hot rolled from 12 mm to 2.9 mm thickness. As-rolled conditions samples were made for Metallography, the rolled samples were polished and then etched by Keller reagent (2 ml HF (48%) + 3 ml HCl + 5 ml $HN0_3$ + 190 ml H_2O) to reveal grain structure.

3. 6 Tensile Test

Dog bone like shaped specimens were prepared from hot rolled samples to preform tensile test. The dimensions of these samples were given in Figure 3.2. The tensile tests were carried out with an Instron-3369 Universal Testing Machine (5 mm/min) at room temperature. At least three samples of each composition were tested to get an average value. The fractured samples were preserved in a desiccator to investigate under Scanning Electron Microscope (SEM) to assess the fracture mode.

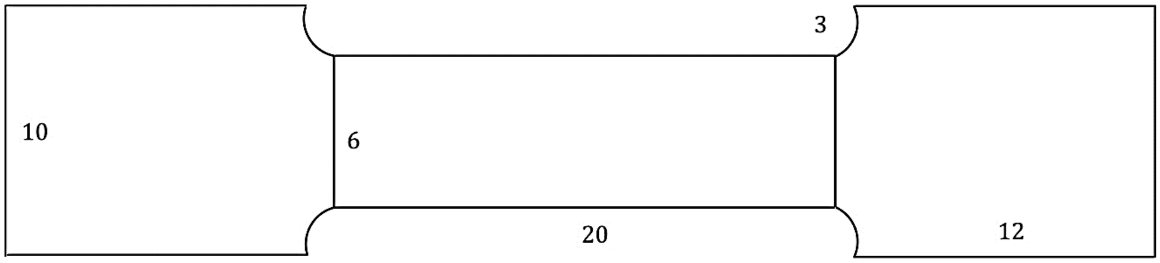


Figure 3. 2 Tensile test sample diagram (millimeter in units) for investigate alloy Al 7xxx

3.7 Optical Microscopy

To examine the microstructure of the cast samples, specimens were prepared through standard procedure available for findings dendritic structures. As-cast and as-rolled conditions, the specimens were made to reveal the microstructural changes. This job was performed at Metallography Lab, by following standard procedure. Almost 50 images were captured.

To reveal the microstructural feature of as-cast and as-rolled conditions, optical microscopy performed. First, the sample surface polished through different sorts of abrasive and emery paper, until mirror like and scratch free smooth surface were exposed. Then the surface was etched by Keller reagent. The reagent preferentially attack the grain boundaries that is why, under Light Microscope (LM) observation this regions demonstrate dark. Whereas the crystallized regions appears as white.

After etching, the prepared specimens were observed at by optical microscope, as named Olympus BH2 microscope. Digital greyscale images captured using the camera attached to it using the software Leica DC View at a resolution of 1798×1438.

3.8 Scanning Electron Micrographs (SEM)

Scanning electron microscopy was carried out with energy dispersive X-ray analysis system. The operating voltage was 25 kV. Images were acquired both in secondary and backscattered mode because in backscattered mode some phases gave better contrast. Presence of phases and particles in the alloys due alloying elements, i.e., copper and magnesium, was determined by Scanning Electron Microscope, Energy Dispersive X-Ray and Image analysis software.

3. 9 Energy Dispersive X-Ray (EDX)

For EDX, the measuring time was 100 seconds in all cases. Quantax QX2 1.6 and EDAX software packages were used for EDX analysis. To identify the images optically, at first, some spots were marked on the specimen surface using a pen and then in SEM those spots were identified and a nearby area was analyzed by EDX.

3.10 X-Ray Diffraction (XRD) Analysis

X-ray Diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material. Primarily, it is used for phase identification of a crystalline material**.** The XRD arrangement was furnished with one-dimensional compound silicon strip detector for high quality diffraction data. It is executed by X-ray diffractometer using Cu-Kα radiation of wavelength 1.54 Å. The samples were placed on a non-diffracting sample holder positioned in the Bragg-Brentano diffractometer setup. The XRD pattern was analyzed by using software.

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3.11 Thermodynamic Modelling

JMatPro v4.0 was used to predict phase fractions of all the alloys. The temperature range used was 700-100 ^{0}C for both equilibrium and Scheil conditions. A 5^{0}C step temperature was used for the equilibrium condition and 4^{0}C was used for the Scheil condition. Simulations were saved in graphical and tabular form to interpret the results in different format. Stability information of all the phases during cooling was observed. Also, variations in composition of a particular phase were extracted. The most important information taken from the simulations was phase fractions at a pre-defined temperature (200^{0}C). Al-data database (v 5.0) was used in JMatPro. This database is able to run simulation with the following elements: Al, B, C, Ca, Cr, Cu, Fe, H, La, Mg, Mn, Ni, Sc, Si, Sr, Ti, V, Zn and Zr. It includes all the elements present in the alloys considered in current work. The phases this database can predict are as below (Sente 2005).

Al (fcc)
Al$_7$Cr
Al$_3$Ni
Mg$_2$Si
Al$_{20}$CU$_2$Mn$_3$
Al(Fe,Mn,…)Si _Alpha
Liquid
Al$_2$Cu
Al$_3$(Ni,Cu)$_2$
Al$_{18}$(Cr,Mn)$_2$Mg$_3$
Al$_7$Cu$_4$Ni
Si
Al$_3$(Fe,Mn,Ni…)
Al$_{13}$Cr$_4$Si$_4$
Al$_9$(Fe,Ni)$_2$
Al$_5$Cu$_2$Mg$_8$Si$_6$
Al$_3$Mg$_2$
Al$_3$M_DO22
Al$_7$Cu$_2$Fe
AlFeSi_Alpha
Al$_8$FeMg$_3$Si$_6$
Al$_6$(Mn,Fe,CU,…)
Al$_3$M_DO23
Al$_2$CuMg
AlFeSi_Beta

The step temperature method was applied for modelling. The step size was kept very low−only 5^0C for equilibrium calculation. Low step size should able to prevent any abrupt change in phase fraction during calculation. A high step sizes like 20 K, which were found to be used in the literature [30], sometimes lead to incomplete liquid reaction. A 5^0C step was tried but for most of the alloys it returned a calculation error. A solidification cut-off of 0.10% was used to prevent liquid being retained to unrealistically low temperatures, which can occur in the Scheil model since diffusion is ignored.

3.12 Solution Treatment & Ageing Cycles

The hot rolled sheets were solution treated for 4hr at approximately 490^0C, followed by water quenching prior to artificial ageing, called precipitation hardening. Ageing process involves the elevating the temperature of an alloy to change its properties. When the aging process occurs at room temperature, the properties of investigate alloys transform and settle very slowly. Artificial aging accelerates the process of changing and settling, includes the decomposition at elevated temperature, normally in the range of 100-200^0C, for times between 2 to 48 hr. The artificial aging treatment is designed to produce optimum size, size distribution, constitution and morphology of precipitates and amount of solute in solid solution. Three sets of temperature-time cycles, e.g. 120^0C/24hr, 150^0C/24hr, and 180^0C/24hr, are selected for alloys,

3.13 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a thermo-analytic technique, investigate and inert reference is made to undergo identical thermal cycles, while recording any temperature between them. Any change in the sample (either exothermic or endothermic) can be detected with respect to the inert reference. In this work, the heating rate was maintained 30^0C per minute, test temperature range 30^0C to 600^0C.

3.14 Hardness Measurement

The samples (2.9 mm thickness approximately) for hardness tests were taken from mid thickness of the sheets. Vickers hardness was measured (with 3 kg load, duel-time 10 sec.) through hardness tester, model FV-800, to study the ageing kinetics at 180^0C.

RESULTS AND DISCUSSION

4.1 Composition of Alloys

The chemical compositions, after casting, were estimated by chemical analysis procedures. Limitation was appeared, due to Mg presence, either lower or higher limit % wt. Mg in OES alloy groups, wt. % Cu may not be exactly appeared. To overcome this limitation, manual wet analysis procedures were followed. The procedures ensured exact percentage of copper (wt. % Cu), as given in Table 4.1.

Table 4. 1 Composition (wt.%) of as-cast

As-cast	Alloying Element			Sum	Ratio	
	Cu	Mg	Zn	$\mathrm{Cu}+\mathrm{Mg}+\mathrm{Zn}$	Cu/Mg	Zn/Mg
1	1.09	1.8	3.67	6.56	0.61	2.04
2	1.33	1.01	4.24	6.58	1.32	4.20
3	4.32	0.98	4.36	9.66	4.41	4.45

(Other elements: $\mathrm{Fe} < 0.8, \mathrm{Si} < 0.95, \mathrm{Mn} < 0.05, \mathrm{Ti} < 0.015$, bal. Al)

4.2 As-Cast Microstructure

The crystallization process occurs, in case of the cast metal alloys, after casting of the liquid metal into the mold. Multibranched shapes often grow in many crystalline materials. These branches form a geometrical arrays that are directly related to the structure of the crystal. The branching in crystal leads to a tree-like appearance, defined as dendrites. The shape, size and orientation of the dendrites have profound effects on the properties of as-cast alloys. About all cast metal products that are used in industries are composed of thousands to millions of tiny dendrites, which can be observed under the microscope on a specially polished surface [22].

The presence of secondary phases at the inter-dendritic regions is an evident in the micrographs. For all alloys, optical microscopy revealed a typical cored dendritic microstructure of primary (α-Al) solid solution surrounded by inter-dendritic secondary phases, shown in Figures 4.1-4.3.

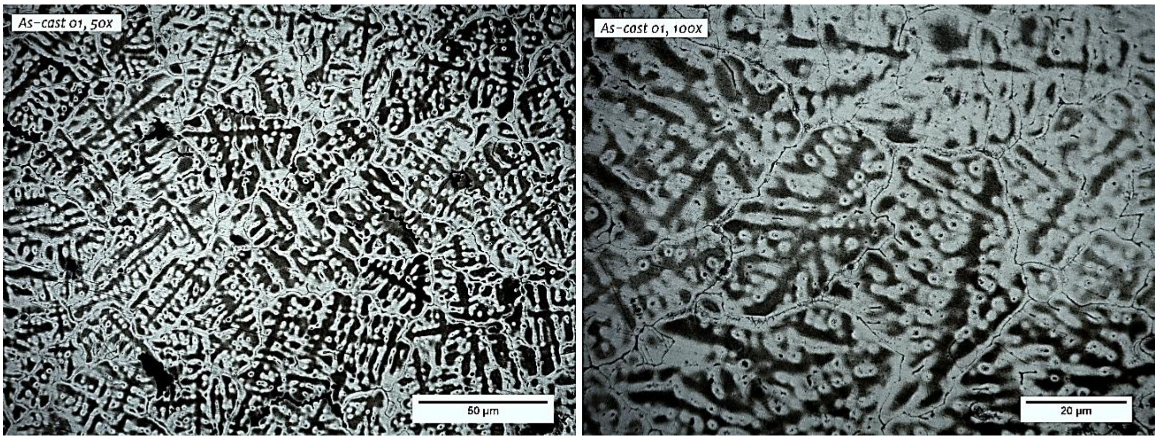


Figure 4. 1 As-cast micro-structure of alloys 01 (1.09% Cu, 1.8% Mg)

The predominant eutectic structure of the alloys is understood to be consisting of a 'quasi-binary reaction' products, evolving from parallel solidification of three quasi-binary eutectic reactions viz. α-Al/η($MgZn_2$), αAl/T($Al_2Mg_3Zn_3$) and α-Al/ S(Al_2CuMg) [23].

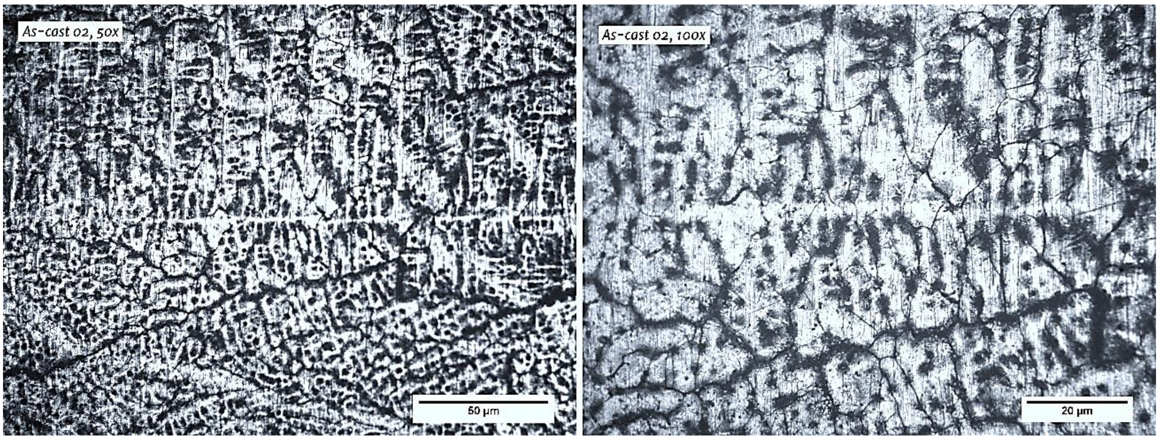


Figure 4. 2 As-cast micro-structure of alloy 02 (1.33% Cu, 1.01% Mg)

Figures 4.1-4.3 represent the optical micrographs of grain structure developed in the cast alloys. The microstructures of all samples consist of primary Al grains (the light areas) and the eutectic precipitates (grey). The preferential morphology of α-Al is a globular-rosette morphology and Al grains are surrounded by eutectic colonies. As-cast microstructure made up of coarse primary α-Al dendrites and acicular-shaped eutectic phase, which lowers the mechanical properties and limits its industry applications. Heat treatment and aging are important to homogenize α-Al dendrites in aluminum alloys to achieve better mechanical properties. The mechanical properties can determine by controlling the microstructures of the alloys. Heat treatment and aging are important processes to homogenize α-Al dendrites in aluminum alloys.

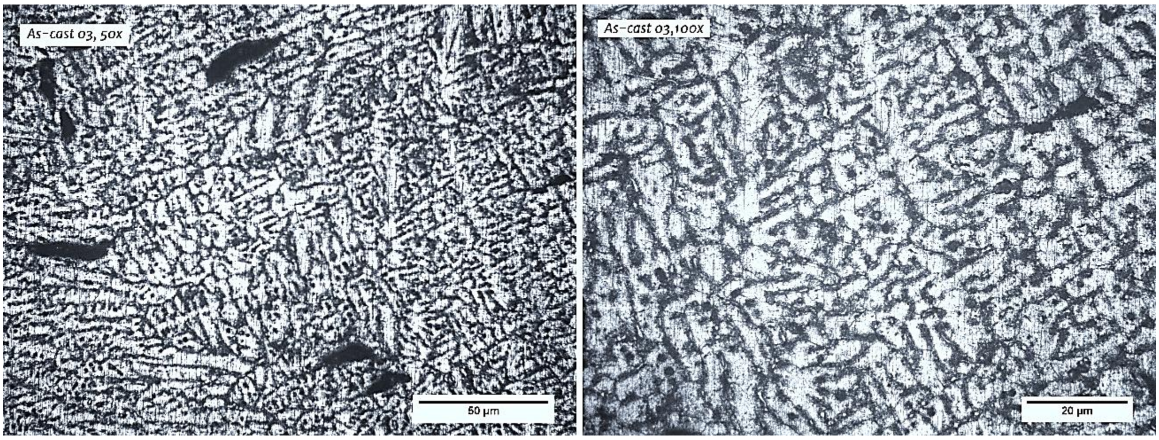


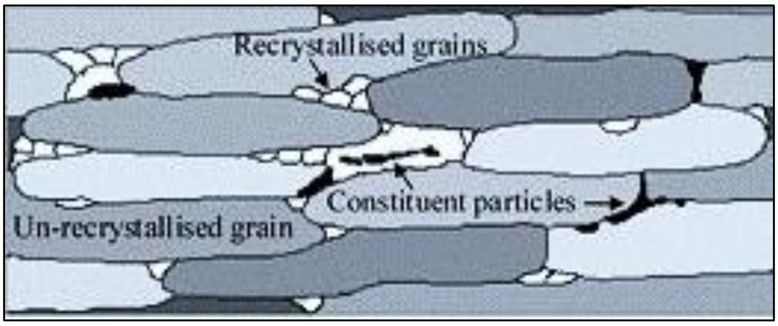
Figure 4. 3 As-cast micro-structure of alloy 03

4.3 Effects of Homogenization

Homogenization, the samples were heated to 400^0C and hold for 3hr, and then quenched into water. It may cause a microstructural changes. This treatment causes the dissolution of some phases into the Al matrix. Since, the samples were heated up to 400^0C, some low melting point phases merged into Al matrix.

4.4 Effects of Rolling

During hot rolling, the thickness of as-cast sheets reduced from 12 mm to approximately 2.9 mm in thickness through multiple passes at 500^0C. The grain structure, an elongated pancake type morphology develops as a result of the rolling. Constituent particles are broken up and dispersed in the direction of rolling (stringers). On hot rolling, a significant dynamic recovery usually occurs, whereby dislocations rearrange themselves to form subgrains or cells with low-angle boundaries characterized by $< 15^0$ misorientation [24].

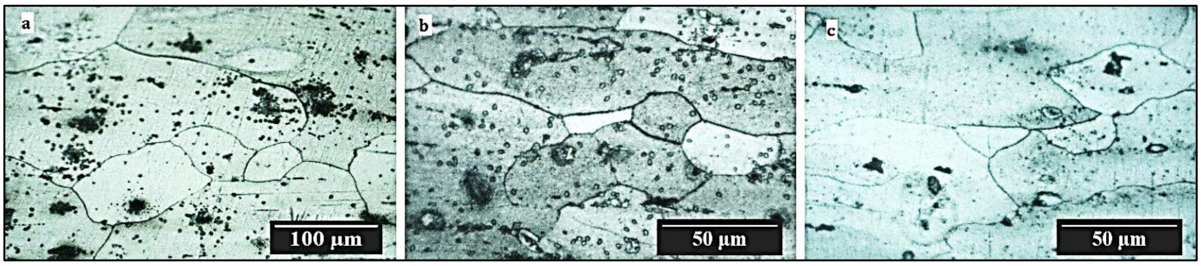


Rolling direction ⟶

Figure 4. 4 Schematic illustrations of a typical grain structure after hot rolling [24]

Recrystallization concerned with the nucleation and growth of relatively defect free grains within deformed grains, where growth occurring through the movement of high-angle grain-boundaries ($> 15^0$misorientation). The high angle grain boundaries are concentrated with higher internal energy and lower activation energy for mobility than low-angle boundaries during recrystallization. Full recrystallization only occurs in the most highly strained regions.

Since dispersoid particles make a barrier or pin the movement of both dislocation cell boundaries (low-angle) and grain boundaries (high-angle). Therefore, hot rolled material will not completely recrystallize under normal solution treatment conditions, because of this, there is no enough stored internal energy to overcome the pinning effects of the dispersoids. Hot rolled alloys typically comprise a partially recrystallized grain structure with constituent particles, whereas average grain size is about 15-25μm (Figure 4.5). The recrystallized grains are distributed along the grain boundaries of unrecrystallized grains, as shown in schematic in Figure 4.4.



Rolling Direction⟶

Figure 4. 5 Microstructure of (a) alloy 01, (b) alloy 02, and (c) alloy 03 as-rolled condition

The grain structure of investigated alloys, after casting, is dendritic structure (Figures 4.1-4.3). The dendritic structure is dissolved by hot rolling, forms mostly coarse grain microstructure, shown in Figure 4.5. During the preheating temperature before rolling high Cu content promotes the formation of coarse particles, which act as nucleation sites for particle stimulated nucleation of recrystallization.

Following hot rolling, Al 7xxx alloy plates were solution treated at $490^0\mathrm{C}$ for up to several hours to dissolve particles that remain from previous processing steps. Dispersoids and iron (Fe) containing particles remain insoluble during solution treatment. Recovery or recrystallization can occur during solution treatment, depending on the degree of stored strain energy from prior deformation and the effectiveness of the dispersoids in pinning grain boundaries.

4.4.1 Rolling Effects of Microstructure on Tensile Properties

Mechanical properties were improved with grain refinement. Since the mechanical properties are mainly dependent on their microstructure, a lot of efforts have been done for refining microstructure of casting to improve the mechanical properties of aluminum alloy AA7xxx.

As-cast alloys, Figures 4.1-4.3 shows Al 7xxx alloys are made up of coarse primary α-Al dendrites with precipitate colonies, which lowers the mechanical properties and limits its industry application. Heat treatment and aging are important to homogenize α-Al dendrites in aluminum alloys to achieve better mechanical properties. Heat treatment and aging processes are the most important processes determining casting microstructure and mechanical properties.

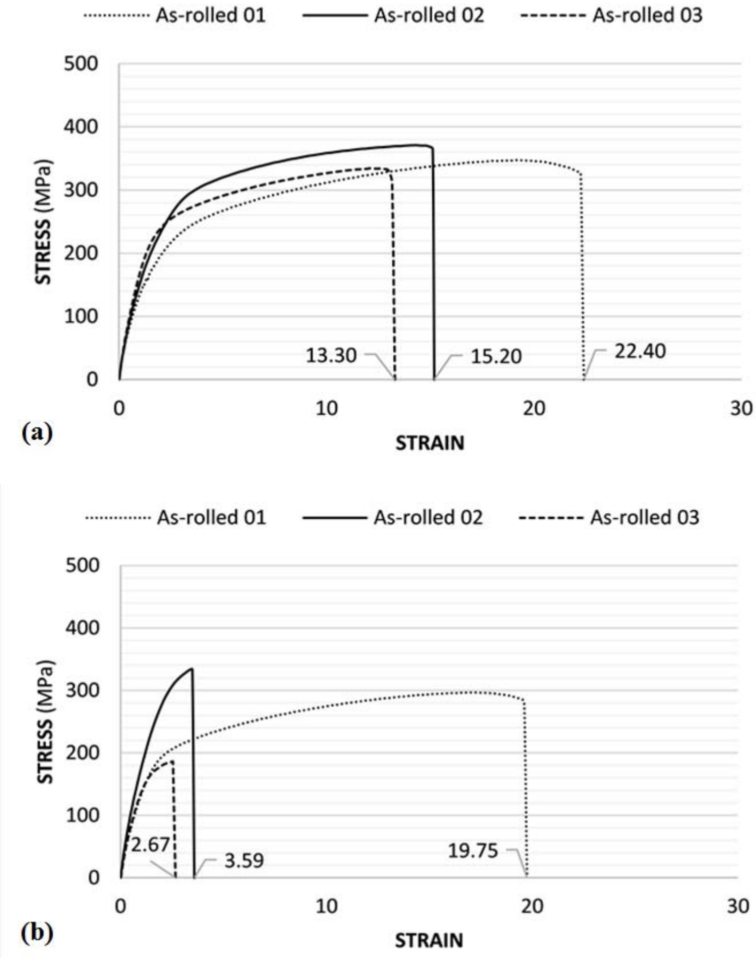


Figure 4. 6 Stress-strain curve for alloys 01, 02 & 03 as rolled condition along (a) longitudinal and (b) transverse directions

Hereby, in order to investigate the effect of heat treatment and aging processes on microstructure, the mechanical properties-tensile strength along both longitudinal and transverse directions were analyzed as-rolled condition, and after heat treatment and aging process.

Figure 4.6 shows the comparison of stress-strain curve as rolled condition both in longitudinal and transverse directions. In as-rolled condition, Figure 4.7 shows the strain to fracture values 22, 15, 13 (%) along longitudinal direction and values 20, 4, 3 (%) along transverse direction for alloys 01, 02 & 03 respectively. These strain to fracture values both longitudinal and transverse direction are listed in Table 4.2.

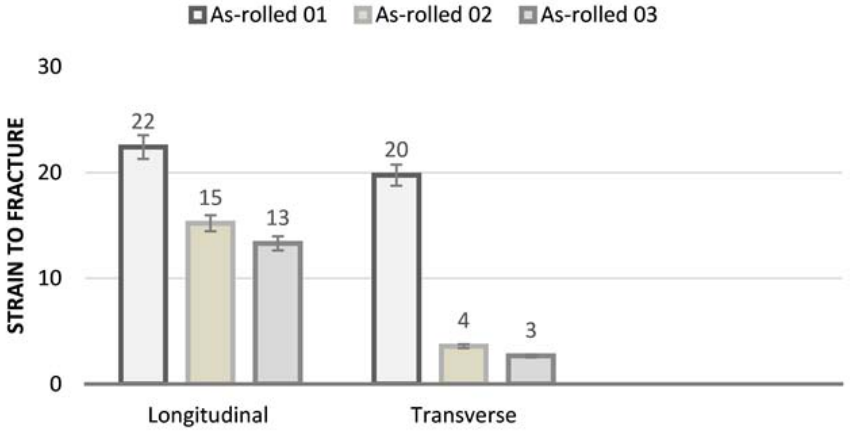


Figure 4. 7 Strain to fracture values along longitudinal, and transverse directions as-rolled condition

From Figure 4.8, as-rolled condition the Ultimate Tensile Strength (UTS) 348, 371, 335 MPa along longitudinal direction and 296, 334, 186 MPa along transverse direction for alloys 01, 02 & 03 respectively. These UTS values are listed in Table 4.3.

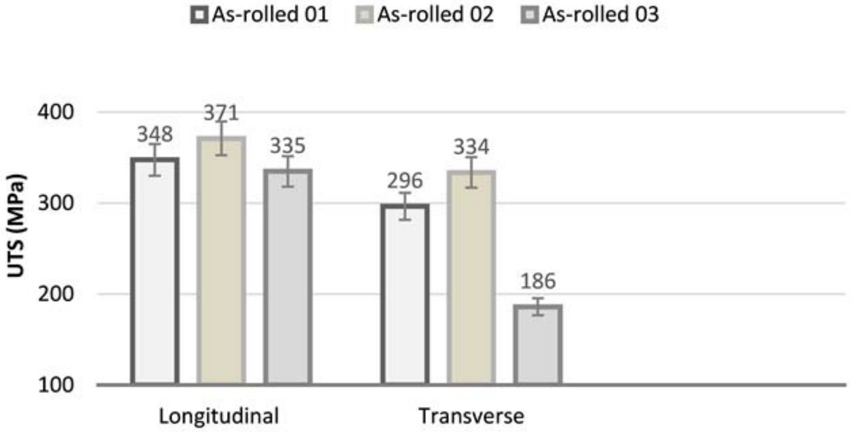


Figure 4. 8 UTS values for longitudinal, and transverse directions as-rolled conditions

Table 4. 2 Strain to fracture as-rolled condition both in longitudinal & transverse directions

Alloys (as-aged 120^0C, 24hr)	As-rolled (strain to fraction value)	
	Longitudinal Direction	Longitudinal Direction
01	22	20
02	15	4
03	13	3

Table 4. 3 UTS values as-rolled both along longitudinal and transverse directions

Alloys (as-aged 120^0C, 24hr)	As-rolled (UTS, MPa)	
	Longitudinal Direction	Longitudinal Direction
01	348	296
02	371	334
03	335	186

4.5 Solution Treatment

The samples, for solution treatment, were heated to 490^0C for 4hr, below the low melting of aluminum, and then quenched in water. The rest of secondary phases, then, merged into Al matrix. This treatment causes to microstructural and mechanical properties.

Change in microstructure, during the samples were heated to 490^0C and hold for 4hr. Al-Cu-Mg secondary phases dissolved into the Al matrix. This treatment resulted the decrease the secondary phases, thus solution treatment reduces the hardness of Al alloys. It is due to the complete dissolution of the rest of Mg_2Si and Al_7Cu_2M (M = metal).

4.6 Thermodynamic Modelling of Phases

Below solidus line the main hardening precipitation sequences involve the precipitation of $\eta(MgZn_2)$ phase, $S(Al_2CuMg)$ phase, and $T(Al_2Mg_3Zn_3)$ phase. The precipitation of η phase is thought to dominate hardening in most Al 7xxx alloys.

At the equilibrium state, η phase and S phase are the major phases, whilst T phase only occurs when temperature relative lower temperature (300^0C), as illustrated in Figure 4.9a.

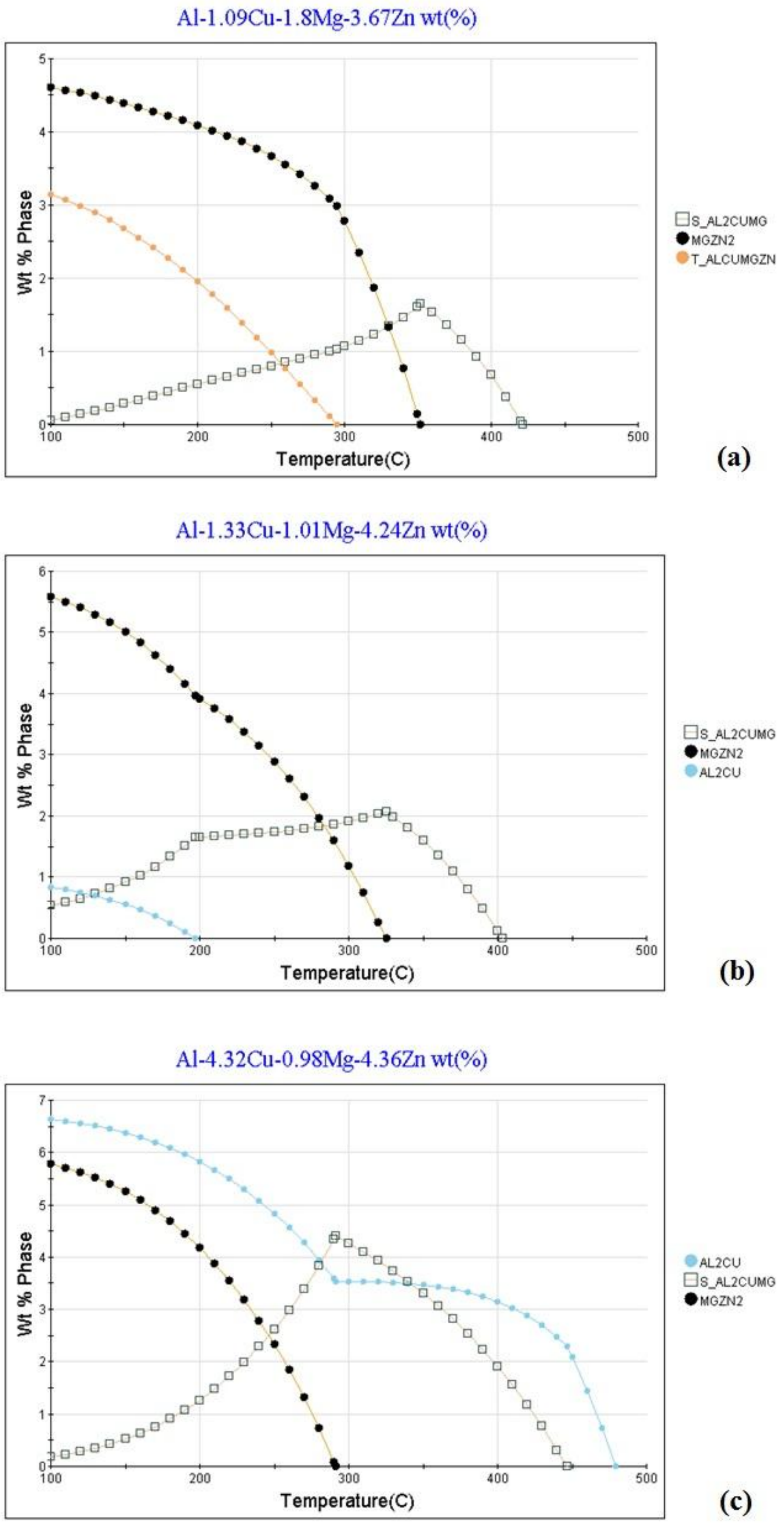


Figure 4. 9 Thermodynamic modelling for (a) alloy 01 (b) alloy 02 (c) alloy 03

Other phases, such as Al_2Si, Al_6Mn, Al_7Cu_2Fe, Al_3Fe, and Al_3Zr also form in the precipitation processes. It is due to additions of minor alloying elements into the alloys or irremovable impurities, but have relatively small percentages and therefore only take minor effects on the properties of the alloys. The major alloying elements, i.e., Zn, Mg, and Cu, have dominant effects on the formation of the main phases which determine the overall properties of the alloys [26]. On other hand, S phase starts to form when there is a small percentage of Cu as little as about 1.0 wt. % and large amount of S-phase precipitates as Cu content increases. As the Cu to Mg content ratio 1.32, S-phase is predominant as-rolled condition, even as-aged condition.

The quantities of three major precipitated phases (η, S, T) and phase diagrams of Al-Zn-Mg-Cu alloys with various Cu contents have been calculated based on materials models. From Figure 4.9c, it is found that, the amount of the main hardening η ($\mathrm{MgZn_2}$) phase increases with an increase in Cu content. On the contrary, T-phase reduces significantly as the Cu content increases, and the presence of T-phase in the alloy largely depends on the Cu: Mg ratio. The addition of Zn has no effects on the formation of S or T phase. However, Zn with Mg as the major alloying elements have significant effects on the precipitated phases η($\mathrm{MgZn_2}$), precipitation hardening and resultant properties as much as Cu.

Al-Cu-Mg alloy system occurs and the $\theta(\mathrm{Al_2Cu})$ phase precipitates as a result of excessive Cu in the alloy. Therefore, the Cu variation of Al-Zn-Mg-Cu alloys must be well controlled within a reasonable range so as to obtain optimum properties for this type of alloys.

4.7 Verify Modelling

4.7.1 DSC Analysis

The DSC technique used in many investigations to characterize the solid state reactions accompanying the dissolution of precipitates, as well as the formation of addition precipitates. Four possible precipitation sequences: (1) supersaturated α ⟶ GP zones (spherical ⟶ η′ (plate) ⟶ η ($\mathrm{MgZn_2}$); (2) α ⟶ T (nominally $\mathrm{Al_2Mg_3Zn_3}$); (3) α → Cu/Mg nanoclusters → GPB zones (S′) → S′ → S ($\mathrm{Al_2CuMg}$); and (4) α →GP→θ″→θ′→θ, ($\mathrm{Al_2Cu}$) [24].

The α-θ (GP) phases are Guinier-Preston zones, and α-S (GPB) are Guinier-Preston-Bagaryatsky zones. The Super Saturated Solid Solution (SSS) in the Al (α) matrix and Cu/Mg nanoclusters are considered as precursors of the GPB zones. Fine precipitation of GPB zones as well as the S′-phase is considered to cause the second stage of hardening in Al-Zn-Mg alloys. Generally, the peak temperature of a specific thermal event in DSC thermogram, for age-hardenable Al alloys, is a measure of the temperature at which a precipitation or dissolution reaction is occurred at its maximum rate. The area under the peak is a measure of the related reaction heat, which is proportional to the volume fraction of the precipitates that are formed/dissolved.

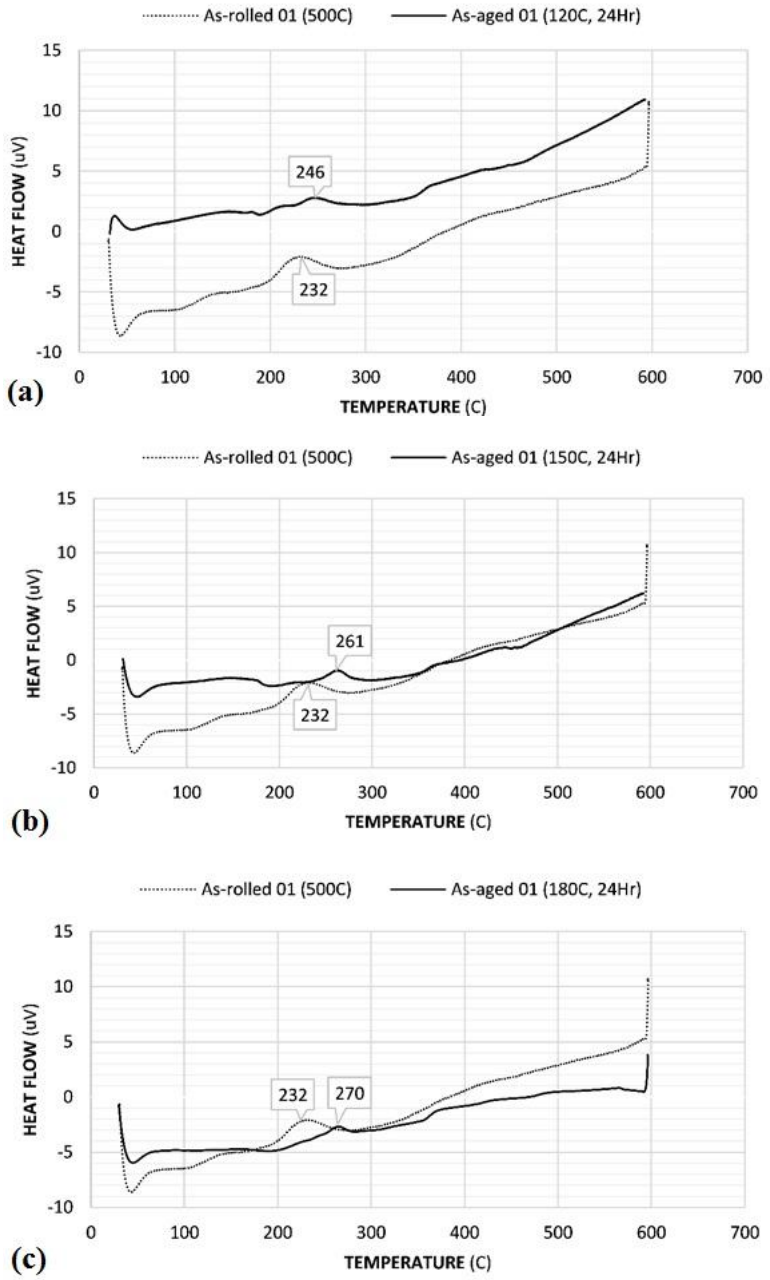


Figure 4. 10 DSC thermogram of alloy 01 at (a) 120^{0}C/24hr, (b) 150^{0}C/24hr, and (c) 180^{0}C/24hr

Typical DSC thermograms were obtained after aging treatment and compared with the thermograms of the alloy in as-rolled condition. Figure 4.10 shows the comparison of DSC thermogram of alloys 01 both as-rolled and as-aged conditions. As-aged condition, it is found that the exothermic peak of eutectic phases around 232^0C shifts downwards compared with smaller height, which suggests that the dissolution of phases took place here.

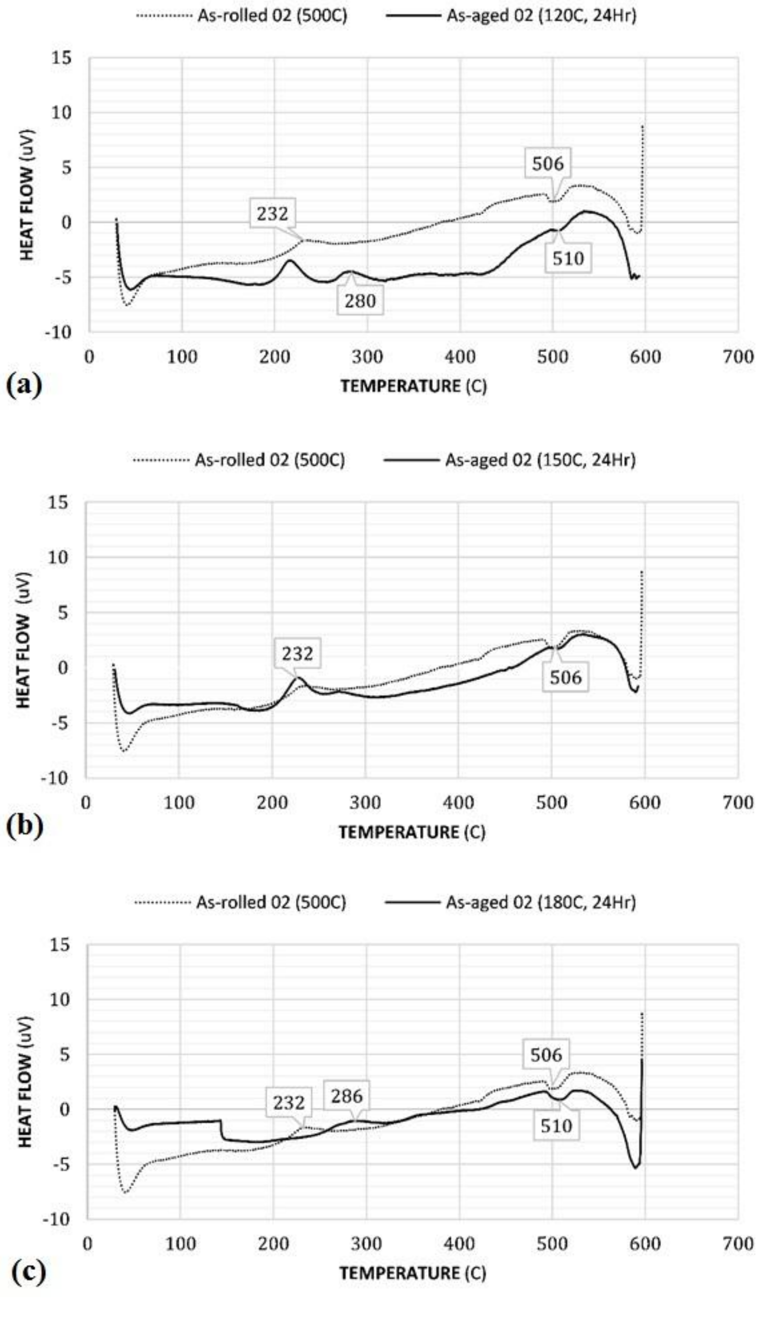


Figure 4. 11 DSC thermogram of alloy 02 at (a) 120^0C/24hr, (b) 150^0C/24hr, and (c) 180^0C/24hr

Figure 4.11 presents the DSC thermogram relationship of alloys 02 both as-rolled and as-aged conditions. In as-cast 02, the DSC result reports that two precipitation reactions occur in as-rolled condition, found as exothermic pick at 232^{0}C and endothermic pick at 506^{0}C, as-rolled. It is strong evident from Figure 4.11a-b-c, after solution treating and aged (temperature-time cycle, 180^{0}C for 24hr), S phase stands without any dissolution. That is, the dominating phase in as-rolled condition and even as-aged condition is S-phase.

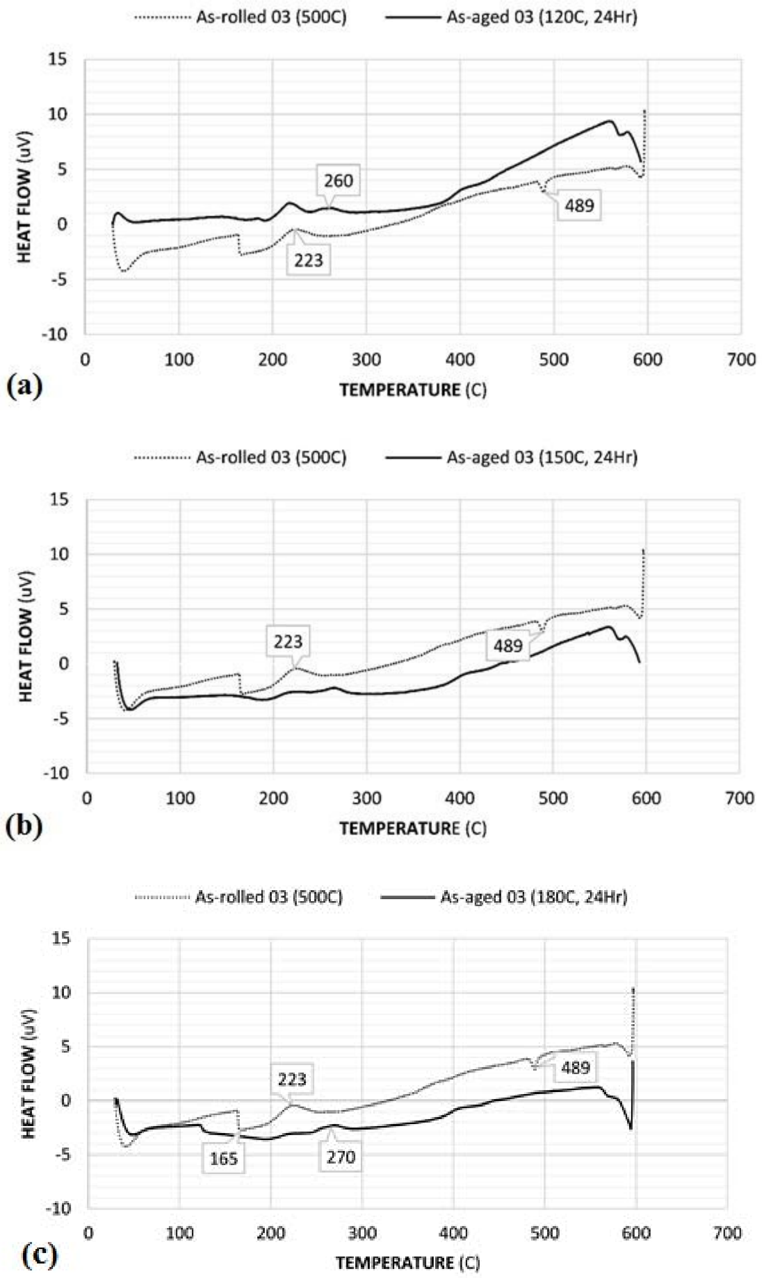


Figure 4. 12 DSC thermogram of alloy 03 at (a) 120^{0}C/24hr, (b) 150^{0}C/24hr, and (c) 180^{0}C/24hr

Figure 4.12 represents the DSC thermogram relationship of alloys 03 both as-rolled and as-aged conditions. As-rolled condition, it is found two endothermic picks at 165^0C, 489^0C and an exothermic pick at 223^0C.

The endothermic peak at 165^0C revealed the relevant reactions of the GP zones and η′ phases, which determines the strength of the alloy. These endothermic peaks associated with the melting of the η phases (489^0C). It is an evident, after solution treating and aged (at different temperature-time cycles 120^0C, 150^0C and 180^0C for 24hr respectively, no η-phase remains. The phases that are identified in these alloys 01, 02 & 03, analysis by DSC thermogram are given in Table 4.4.

Table 4. 4 Phase identification by DSC thermogram

Alloys	Phases
01	η′ phases (223^0C)
02	η′ phases , S-phase (506^0C)
03	η′ phases, η phases (481^0C)

4.7.2 Phase Confirmed by XRD

X-ray diffraction is mostly used for the identification of unknown crystalline materials, characterization of fine grained minerals that are difficult to determine optically [27]. Results from x-ray diffraction are presented as peak positions at 2θ and X-ray counts (intensity) in the form of a table or an x-y plot, as shown in Figures 4.13-4.15.

Both as-rolled and as-aged conditions, the UTS value−along longitudinal and transverse directions, and hardness values are better of alloy 02. These mechanical properties of all investigate alloys are enhanced by heat treatment and ageing process. The maximum UTS and hardness values are mostly raised for alloy 02. XRD results for alloy 02 are given in following Figures 4.13-4.15.

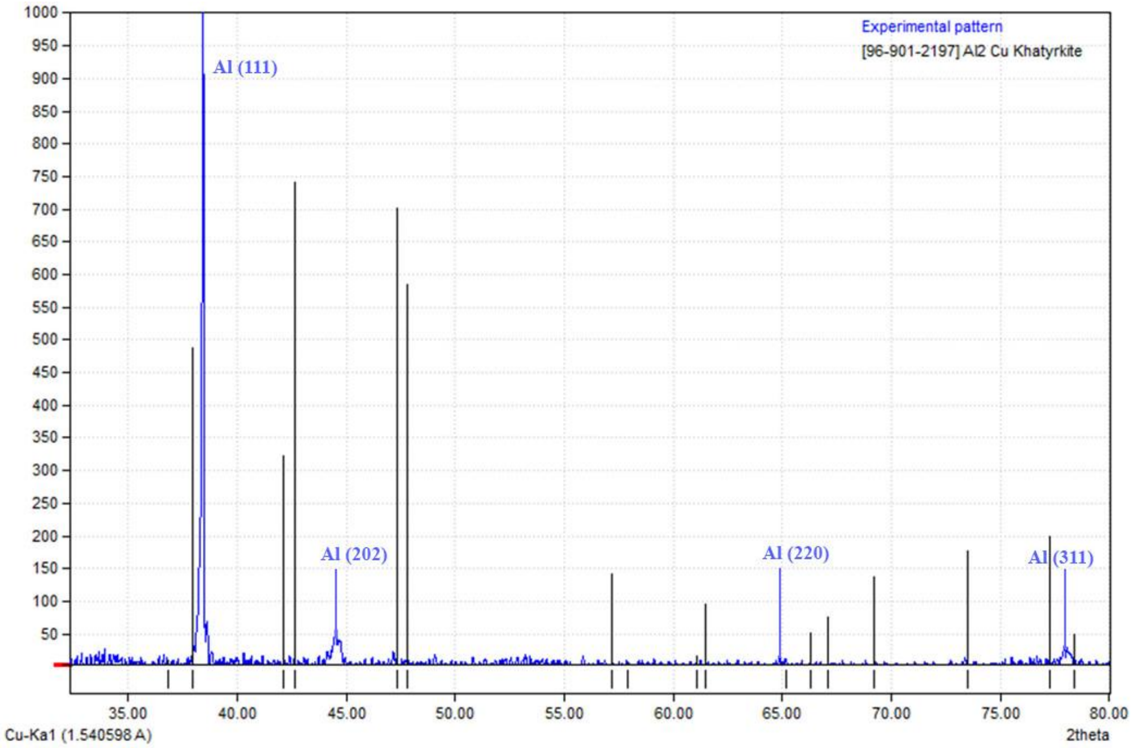


Figure 4. 13 XRD pattern of alloy 02, blue lines for experimental pattern and black lines indicate $\theta(Al_2Cu)$ phase

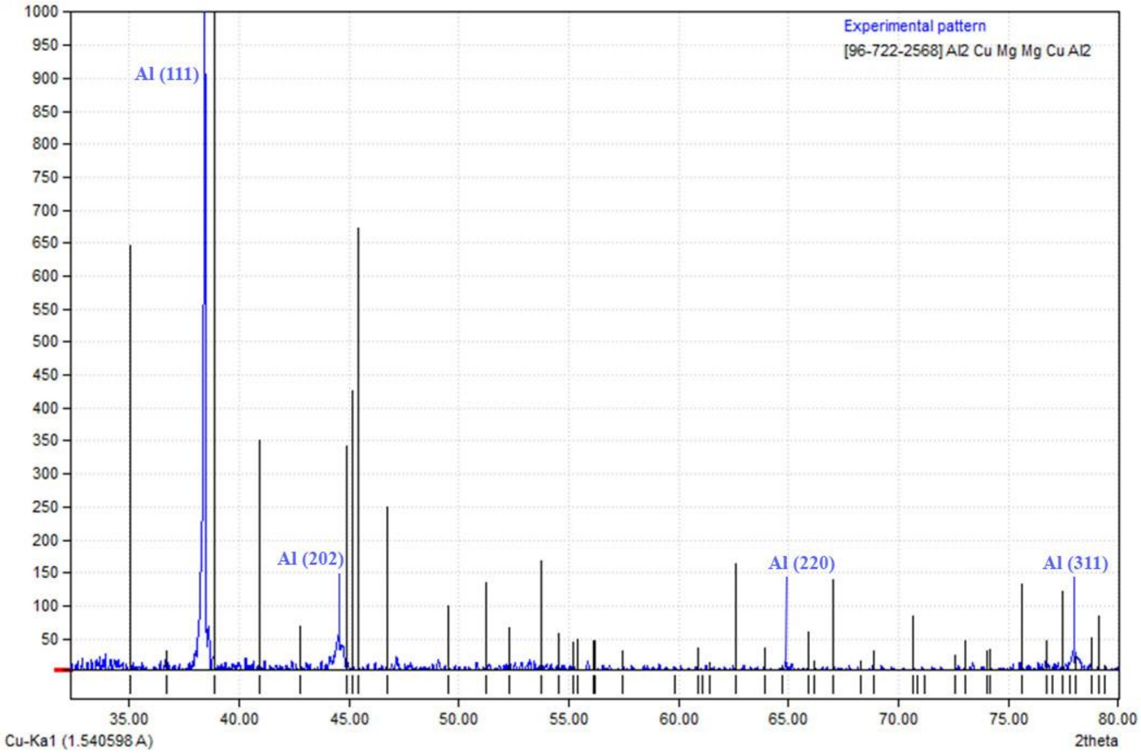


Figure 4. 14 XRD pattern of alloy 02 for $S(Al_2CuMg)$, blue lines for experimental pattern and black lines indicate S phase

Figure 4.13 shows that the presence of θ(Al_2Cu) phase was detected by XRD where Cu to Mg ratio is 1.32 (alloy 02). In any alloy, the dominant second phase is based on η ($MgZn_2$), pattern is shown Figure 4.15, present in the form of a eutectic structure.

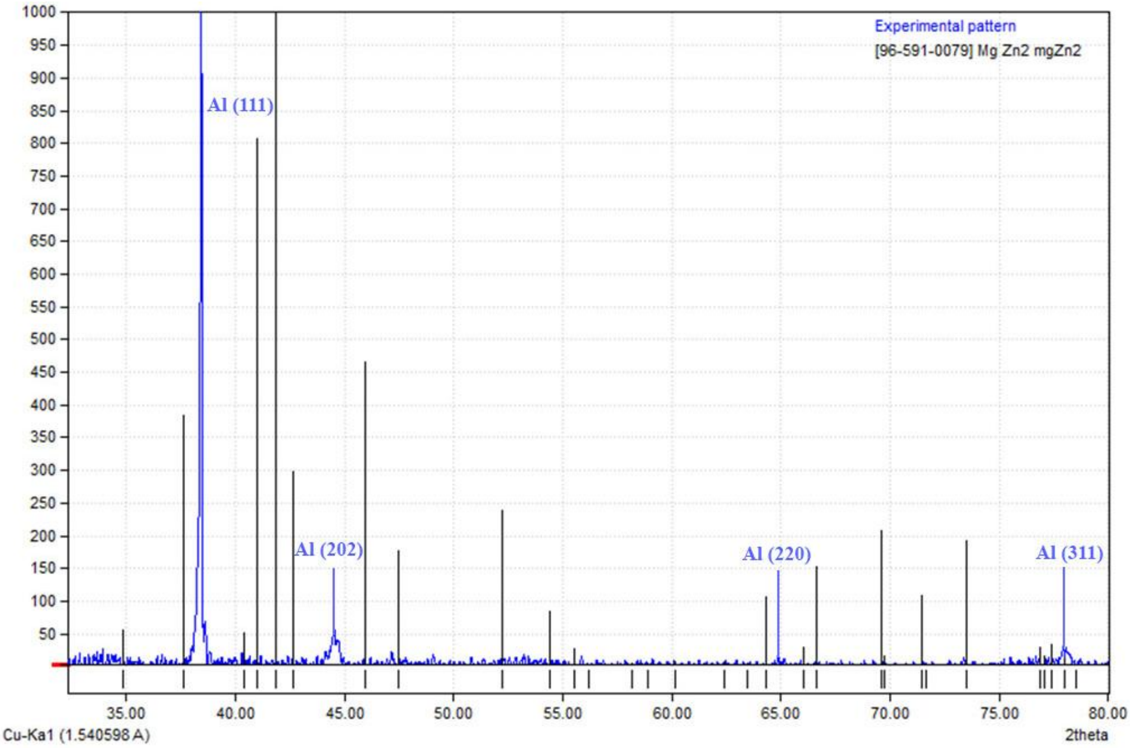


Figure 4. 15 XRD pattern of alloy 02 for η($MgZn_2$), blue lines present experimental pattern and black lines for η phase

Figure 4.14 presents the pattern for S(Al_2CuMg), it is found to be present mostly as part of the eutectic. Secondary phases that are confirmed by XRD pick is listed in Table 4.5. In this XRD analysis, the experimental pattern is present by blue line whereas the black line is for examine secondary phases.

Table 4. 5 Phases determination of alloy 02 by XRD analysis

Alloy	Phases
02	Al_2Cu, θ-phase
	Al_2CuMg, S-phase
	$MgZn_2$, η-phase

4.7.3 Phase Identification for EDX

Energy Dispersive X-ray Spectroscopy (EDS or EDX) is a chemical microanalysis technique used in conjunction with SEM. This technique detects x-rays emitted from the sample. The x-ray energy is characteristic of the element from which it was emitted [28].

The spectrum of x-ray energy, as determined from the voltage measurement, versus counts is evaluated to determine the elemental composition of the sampled volume, illustrated in Figures 4.16-4.18. From Figure 4.16, it is found by qualitative analysis of EDX image, island of secondary phase in matrix composed of Al, Cu and Mg both in longitudinal and transverse direction for 120^0C/24hr temp.-time cycle. The phase made by these elements is $\mathrm{S(Al_2CuMg)}$, confirmed DSC thermogram as well as XRD pattern.

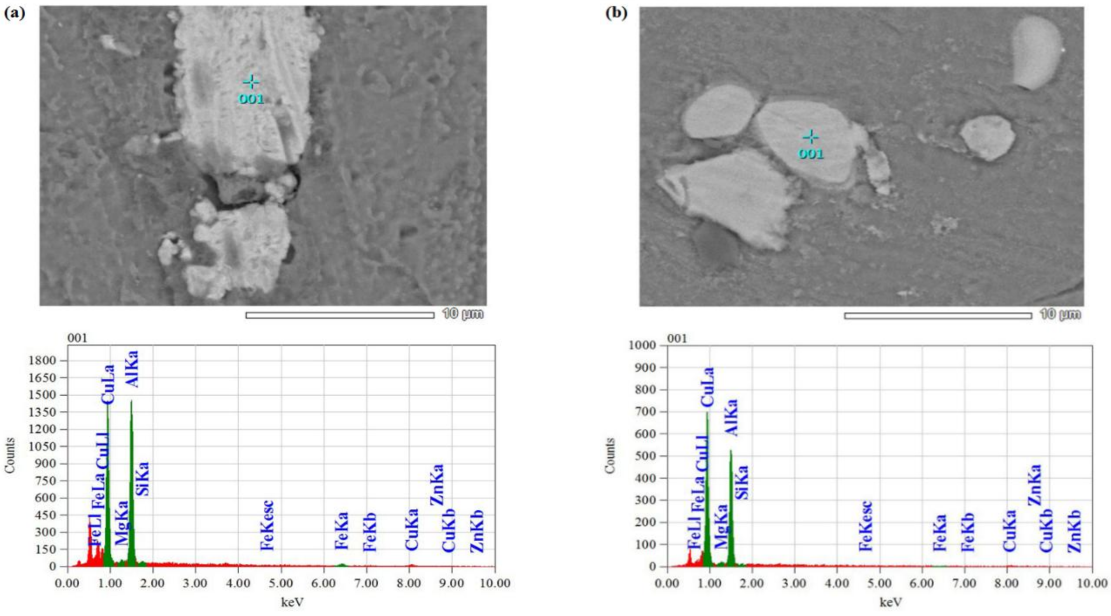


Figure 4. 16 EDX image of alloy 02 as aged 120^0C/24hr, phases represent for (a) longitudinal-$\mathrm{S(Al_2CuMg)}$, and (b) transverse-$\mathrm{S(Al_2CuMg)}$ directions

By analysis of EDX image for 150^0C/24hr cycle, Figure 4.17 shows the secondary phase island in matrix composed of Al, Cu, & Mg along longitudinal, but Al, Cu, Mg & Zn along transverse direction. The secondary phase made for these elements along longitudinal direction $\mathrm{S(Al_2CuMg)}$ phase and transverse direction T-phase.

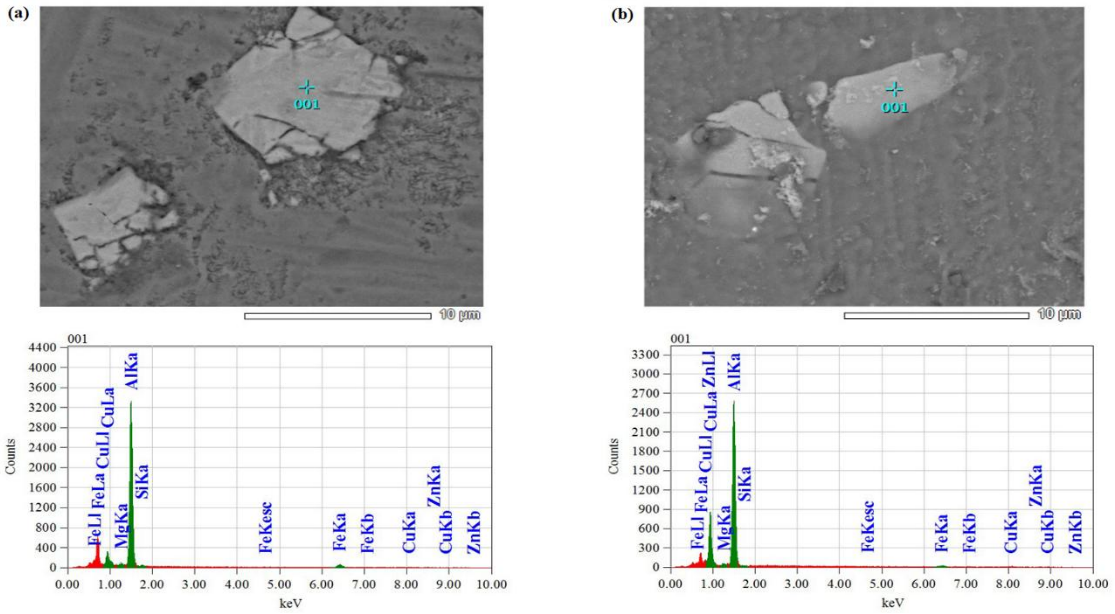


Figure 4. 17 EDX image as aged 150^0C/24hr, phases found along (a) longitudinal direction-$S(Al_2CuMg)$ for alloy 1, and (b) transverse direction-T phase for alloy 2

Figure 4.18 presents the EDX image for 180^0C/24hr temp.-time cycle. It is found by analysis of EDX image, phase island in matrix demonstrates Al, Cu, Mg & Zn along longitudinal, but Al, Cu & Mg along transverse direction. The phase in matrix made by these elements along longitudinal direction is T-phase and transverse direction $S(Al_2CuMg)$.

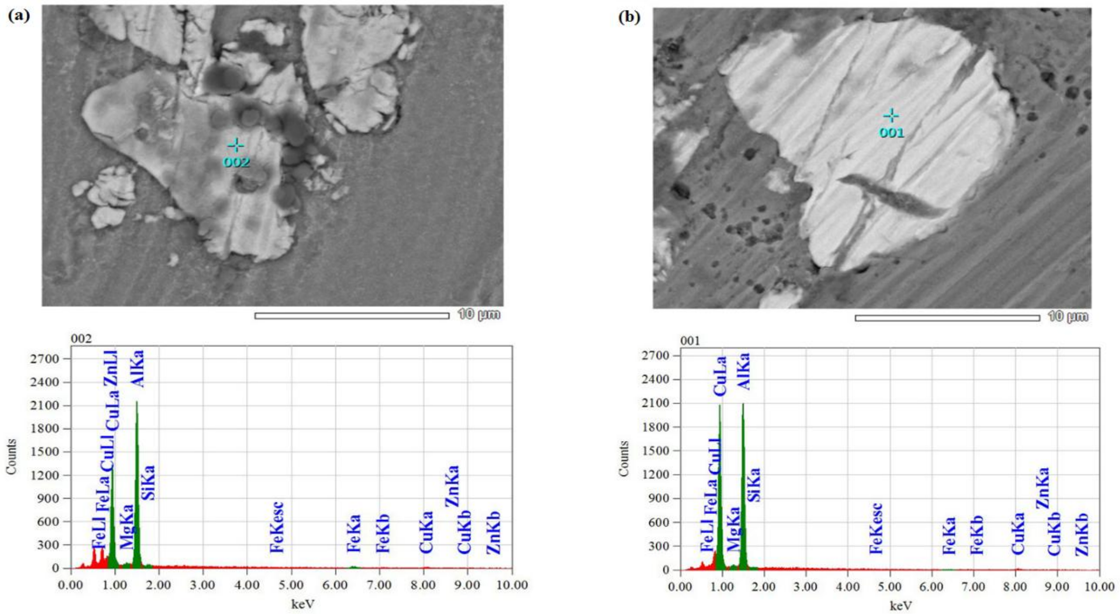


Figure 4. 18 EDX image of alloy 03 as aged 180^0C/24hr, phases identified for (a) longitudinal-T phase, and (b) transverse-$S(Al_2CuMg)$ directions

From EDX presentation (Figures 4.16-4.18), the presence of second phases (θ, S, T) in alloys in the form of island in matrix of Al indicates the incomplete diffusion of particles. Here, by EDX the center and the outer region of the second phase a remarkable concentration gradient of alloying elements, which demonstrated the process is diffusive or controlled diffusion. The secondary phases identified by EDX analysis are listed in following Table 4.6.

Table 4. 6 Phase confirmed by SEM EDX

Ageing temperature-time cycle	Longitudinal		Transverse	
	Phases	Alloys	Phases	Alloys
120^0C, 24Hr	$S(Al_2CuMg)$	02	$S(Al_2CuMg)$	02
150^0C, 24Hr	$S(Al_2CuMg)$	01	$T(Al_2Mg_3Zn_3)$	02
180^0C, 24Hr	$T(Al_2Mg_3Zn_3)$	02	$S(Al_2CuMg)$	02

4.8 Effects of Secondary Phases

Prediction from modeling, that addition of Cu and Mg result the formation of certain phases in the matrix. The main phases are Al_2Cu, Al_2CuMg, $Al_2Mg_3Zn_3$ and $MgZn_2$. Some phases dissolve into matrix, some remain in the matrix even heat treatment, 500^0C for 1hr, performed.

4.8.1 Cu Containing Phases

Although the most dominating phase for Al-Cu alloy system is $\theta(Al_2Cu)$, this phase is observed for alloys 02, and 03. This is due to the increase of Cu addition in Al-Zn-Cu-Mg alloy system.

With other additions, here Al alloys containing 1.09-4.32 wt. % Cu form important alloys respond to solution heat treatment and subsequent ageing, that results the increase in strength and hardness with decrease its elongation. In this investigation, Cu content increases $1.09 < 1.33 < 4.32$ wt. % Cu containing phases increase, thus results better mechanical properties.

4.8.2 Mg Containing Phases

With addition of Mg, the Mg containing phases formed. It increases the strength as possible following solution treatment and quenching. A further enhance in strength on artificial ageing, but substantial sacrifice in tensile elongation. Existing papers suggested that, copper have same crystallographic structure cubic close packed (CCP) as Al, and Mg take same structure as Zn hexagonal close packed (HCP) both increase the hardness and strength of Al alloys. Our investigation also have this same effect of Cu and Mg in Al-Zn alloy system.

As Mg content increase the second phases hold Mg continue increase as per modelling. This investigation demonstrated that, with the decrease of Mg content $1.8 > 1.01 > 0.98$, the better properties is for 1.01Mg containing alloys, as discussed above.

4.9 Effects of Ageing

Thermal treatment is performed over as-cast of Al alloys to improve their mechanical properties. It is found, over all the mechanical properties enhanced after ageing treatment done. As-rolled condition, along longitudinal direction the Ultimate Tensile Strength (UTS) is observed 348, 371 and 335 MPa for as-cast 01, 02, and 03 respectively. Here, it is found that as rolling condition UTS value (371 MPa) is maximum for as-cast 02, as shown in Table 4.2.

Along transverse direction the UTS value is found to be 296 MPa, 334 MPa, and 186 MPa for as-cast 01, 02, and 03 respectively. Here, it is also investigate that as rolling condition UTS value (334 MPa) is maximum for as-cast 02, as shown in Table 4.2. As heat treated and ageing for 120^0C, 150^0C & 180^0C for 24hr respectively, ultimate tensile strength and hardness values as heat treated and aged condition was enhanced by grain refinement, as compared to as-rolled condition.

4.9.1 Tensile Properties in As-Aged Condition

A total three sets of temp.-time cycles is preferred in this investigation. Stress-strain is plotted for longitudinal and transverse direction.

4.9.1.1 Ageing at 120^0C/24hr

Figure 4.19 shows the stress-strain curve both in longitudinal and transverse direction. As aged 120^0C/24hr, Figure 4.22a-b presents the UTS values for alloys 01, 02 and 03 is found to be 326, 421 & 371 MPa along longitudinal direction, for transverse direction 344, 371 & 288 MPa. The sequence of UTS values along longitudinal direction-alloy 02> alloy 03> alloys 01, and transverse direction- alloy 02> alloy 01> alloys 03. The better stress-strain curve is for alloy 02.

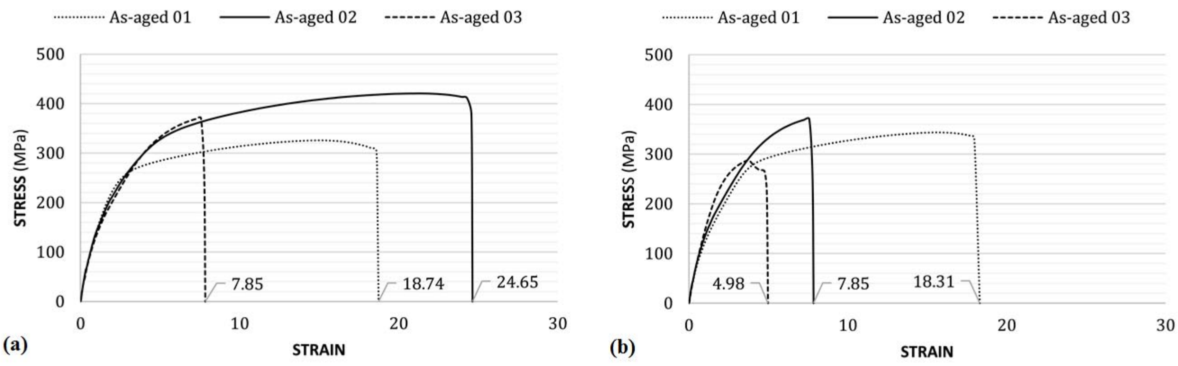


Figure 4. 19 Stress-strain curve along (a) longitudinal and (b) transverse directions for alloys 01, 02 & 03 as-aged 120^0C/24hr

Figure 4.23a-b shows the strain to fracture values for alloys 01, 02 and 03 along longitudinal direction 18.74, 24.65, 7.85 (%) and for transverse direction 18.31, 7.85, 4.98 (%) respectively. The sequence of strain to fracture values along longitudinal direction- alloy 02> alloy 01> alloys 03, and for transverse direction- alloy 01> alloy 02> alloys 03.

4.9.1.2 Ageing at 150^0C/24hr

For ageing 150^0C/24hr temp.-time cycle, the stress-strain curve is illustrated in Figure 4.20 both in longitudinal and transverse direction. Figure 4.22a-b shows the UTS values is found to be 377, 374 & 349 MPa along longitudinal direction, along transverse direction 370.86, 377 & 349 MPa for alloys 01, 02 and 03 respectively. The sequence of UTS values along longitudinal direction- alloy 01> alloy 02> alloys 03, and transverse direction- alloy 02> alloy 01> alloys 03.

Figure 4.23a-b presents the strain to fracture values for alloys 01, 02 and 03 along longitudinal direction are 17.79, 17.63, 13.06 (%) and along transverse direction 17.79, 12.70, 3.08 (%) respectively. The sequence of strain to fracture values along longitudinal direction-alloy 01> alloy 02> alloys 03, and for transverse direction-alloy 01> alloy 02> alloys 03.

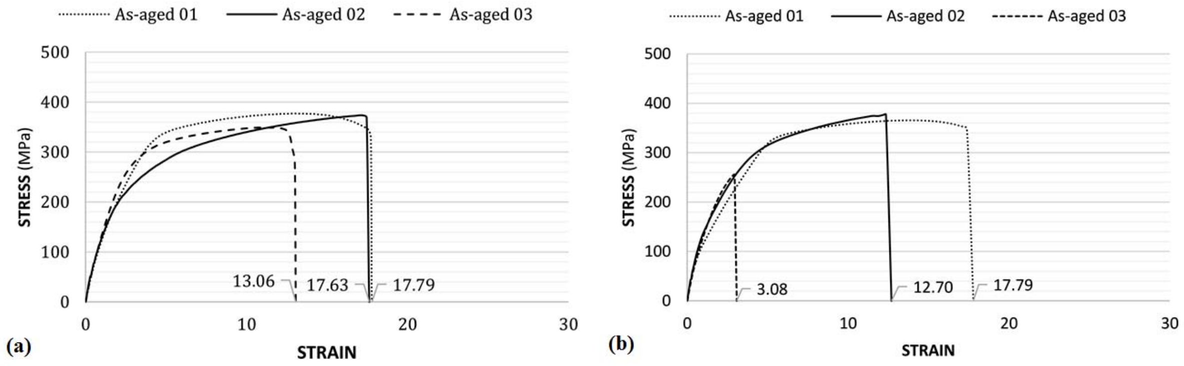


Figure 4. 20 Stress-strain curve along (a) longitudinal and (b) transverse directions for alloys 01, 02 & 03 as aged 150^0C/24hr

4.9.1.3 Ageing at 180^0C/ 24hr

When ageing 150^0C for 24hr, the stress-strain curve is illustrated in Figure 4.21 both in longitudinal and transverse direction. From Figure 4.22a-b the UTS values is found to be 317, 400 & 351 MPa along longitudinal, and along transverse direction 334.64, 359 & 331 MPa for alloys 01, 02 and 03 respectively as aged 180^0C/24hr. The sequence of UTS values along longitudinal direction- alloy 02> alloy 03> alloys 01, and transverse direction- alloy 02> alloy 01> alloys 03.

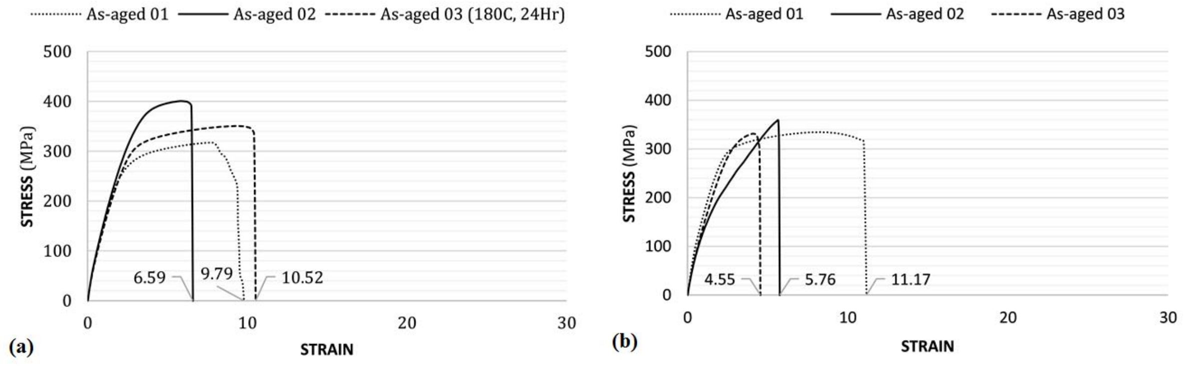


Figure 4. 21 Stress-strain curve along (a) longitudinal and (b) transverse directions for alloys 01, 02 & 03 as aged 180^0C/24hr

Figure 4.23a-b shows the strain to fracture values along longitudinal direction 9.79, 6.59, 10.52 (%) and along transverse direction 11.17, 5.76, 4.55 (%) for alloys 01, 02 & 03 respectively. The sequence of strain to fracture values along longitudinal direction- alloy 03> alloy 01> alloys 02, and for transverse direction- alloy 01> alloy 02> alloys 03.

4.9.2 Ultimate Tensile Strength (UTS) Values in As-Aged Condition

As-aged condition at different temperature and time cycles, Table 4.7 presents contents about UTS value for alloys 01, 02 and 03 both in longitudinal and transverse directions.

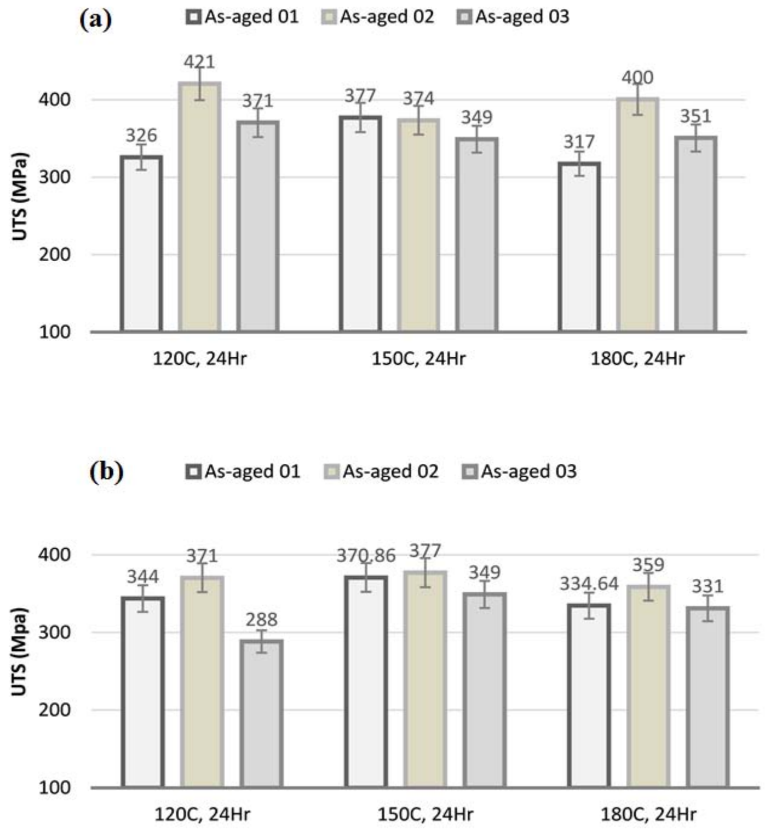


Figure 4. 22 UTS values for (a) longitudinal, and (b) transverse directions as-aged conditions at different temperature-time cycles

- For 120^0C/24hr temperature-time cycle, the max. UTS value 421 MPa along longitudinal direction, 371 MPa value for alloy 02 along transverse direction, shown in Figure 4.22.
- 150^0C/24hr, the max. UTS value 374 MPa along longitudinal direction for alloy 01, but 377 MPa along transverse direction for alloy 02 among them, given in Figure 4.22.
- Max. UTS 400 MPa for ageing temperature-time cycle 180^0C/24hr, along longitudinal direction for alloy 02, in transverse direction 359 MPa for alloy 02, illustrated in Figure 4.22.

Table 4. 7 UTS values at different temp.-time cycles both longitudinal & transverse directions

Alloy	120^0C/24hr.		150^0C/24hr.		180^0C/24hr.	
	Longitudinal	Transverse	Longitudinal	Transverse	Longitudinal	Transverse
01	326	344	377	371	317	335
02	421	371	374	377	400	359
03	371	288	349	349	351	331

4.9.3 Strain to Fracture in As-Aged Condition

As-aged for different temperature-time cycles, the obtained strain to fracture values is listed in following Table 4.8. Maximum strain to fracture for 120^0C/24hr temperature-time cycle is found for alloy 02 (24.65) along longitudinal direction, alloy 01 (18.31) for transverse direction.

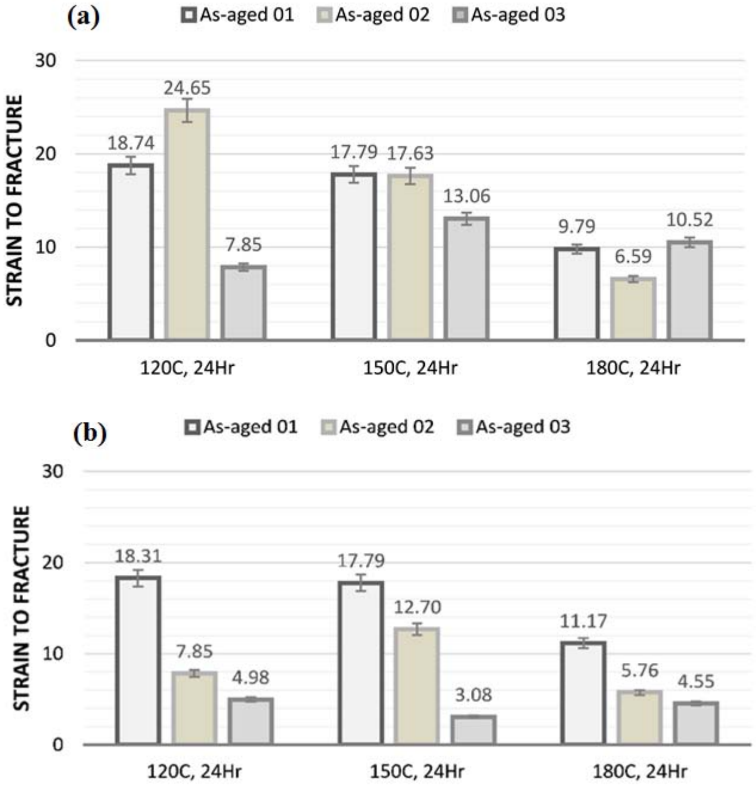


Figure 4. 23 Strain to fracture along (a) longitudinal, (b) transverse directions as-aged at (a) 120^0C/24hr, (b) 150^0C/24hr, and (c) 180^0C/24hr

For 150^0C/24hr cycle better value is found for alloy 01 (17.79) along longitudinal direction, and along transverse direction alloy 01 (17.79). At 180^0C/24hr cycle, higher stress to facture value among investigate alloys reached for alloy 03 (10.52) along longitudinal direction, and along transverse direction it is found to alloy 01 (11.17), shown in Figure 4.23.

Table 4. 8 Strain to fracture both longitudinal and transverse directions as-aged at (a) 120^{0}C/24hr, (b) 150^{0}C/24hr, and (c) 180^{0}C/24hr

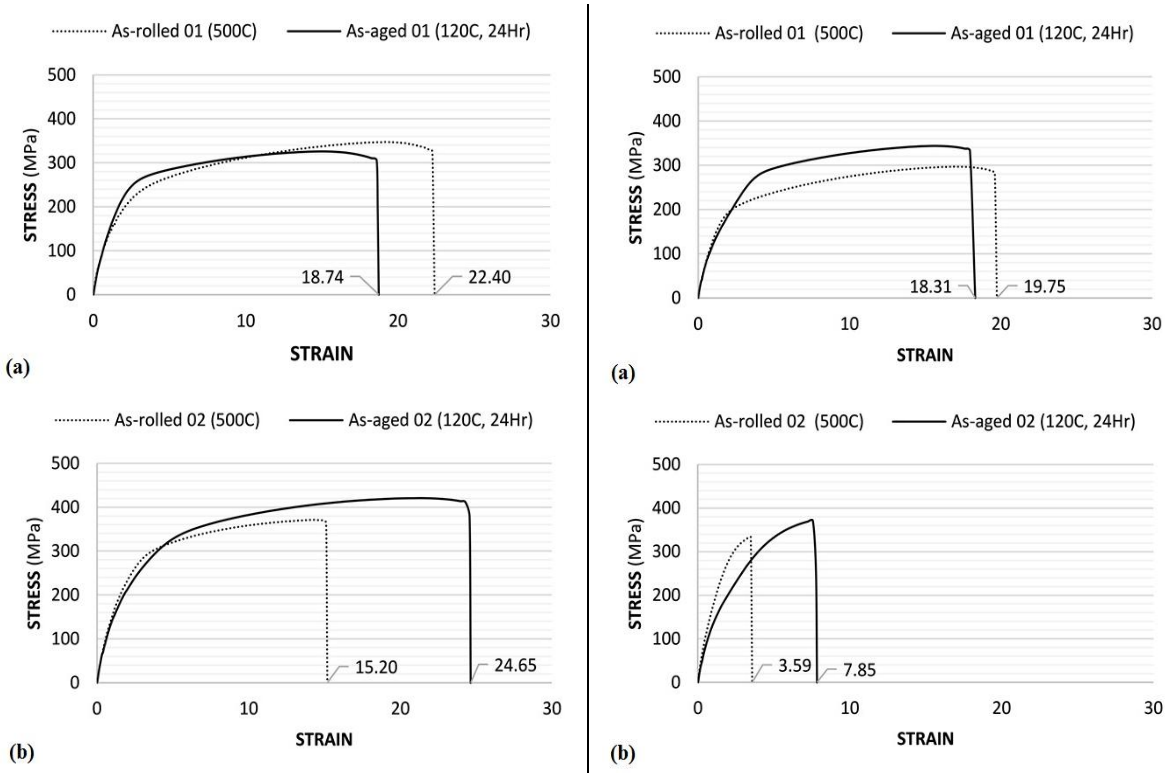
Alloy	120^{0}C, 24hr.		150^{0}C, 24hr.		180^{0}C, 24hr.	
	Longitudinal	Transverse	Longitudinal	Transverse	Longitudinal	Transverse
01	18.74	18.31	17.79	17.79	9.79	11.17
02	24.65	7.85	17.63	12.70	6.59	5.76
03	7.85	4.98	13.06	3.08	10.52	4.55

4.10 Comparison of Tensile Properties among As-Rolled and As-Aged Conditions

Mechanical properties (strength, hardness, strain to fracture etc.) improved by grain refinement, and the presence of second phase. Second phases make a barrier or pin the movement of the dislocation planes and grain boundaries. These properties improvement given illustrates in following Figures 4.24-4.26.

4.10.1 Comparison between As-Rolled and As-Aged (120^{0}C/24hr) Conditions

In Figure 4.24 the temperature-time cycle at 120^{0}C/24hr, mechanical strength is developed from rolling to aged condition.



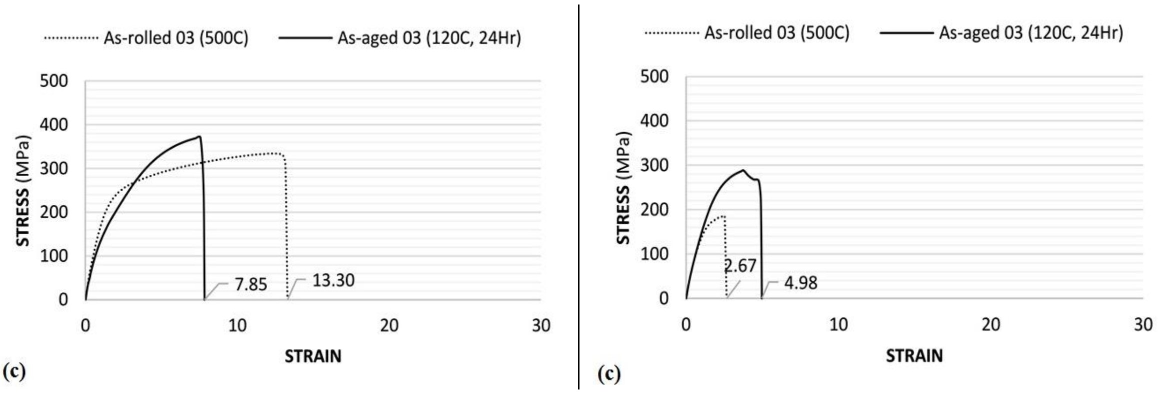


Figure 4. 24 Comparison of stress-strain curve for alloys 01, 02 & 03 at ageing 120^0C/24hr, along longitudinal (left) and transverse directions (right) as-rolled and as-aged condition

Table 4. 9 Comparison of UTS values as-aged at 120^0C/24hr

Alloys (as-aged 120^0C, 24hr)	Longitudinal (UTS, MPa)		Transverse (UTS, MPa)	
	As-rolled	As-aged	As-rolled	As-aged
01	348	326	296	344
02	371	421	334	371
03	335	371	186	288

As-aged condition at 120^0C/24hr, the UTS value experiences to maximum for alloy 02 along both longitudinal (421 MPa) and transverse direction (371 MPa), as illustrated in Table 4.9. After the ageing cycle is done, except alloy 02 (longitudinal) for the remaining alloys both longitudinal & transverse direction the strain to fracture value decreased (Table 4.10).

Table 4. 10 Comparison of strain to fracture values as-aged at 120^0C/24hr

Alloys (as-aged 120^0C, 24hr)	Longitudinal		Transverse	
	As-rolled	As-aged	As-rolled	As-aged
01	22	18.74	20	18.31
02	15	24.65	4	7.58
03	13	7.85	3	4.98

4.10.2 Comparison between As-Rolled and As-Aged (150^0C/24hr) Conditions

At 150^0C/24hr temp.-time cycle, with respect to rolling condition Figure 4.25 shows the better mechanical strength. The UTS value is being to maximum for alloy 01 along longitudinal (374 MPa), and transverse direction (377 MPa) for alloy 02, as given in Table 4.11.

As-aged condition, the strain to fracture value is found to be enhanced only for alloys 02 both in longitudinal and transverse directions, as shown Table 4.12.

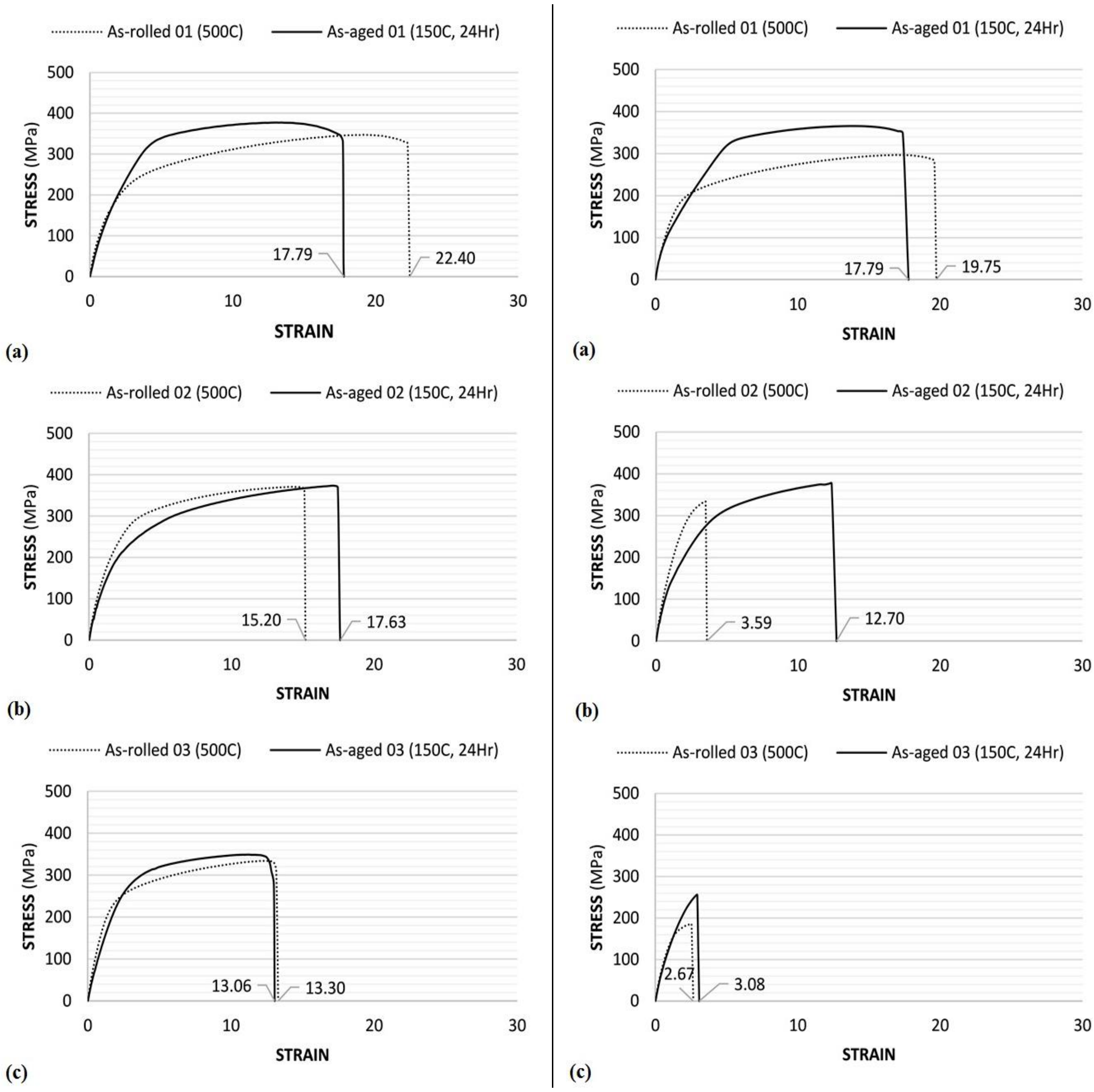


Figure 4. 25 Comparison of stress-strain curve for alloys 01, 02 & 03 as ageing 150^0C/24hr, along longitudinal (left) and transverse directions (right) both as-rolled & as-aged condition

Table 4. 11 Comparison of UTS values as-aged at 150^0C/24hr

Alloys (as-aged 150^0C, 24hr)	Longitudinal Direction (UTS, MPa)		Transverse Direction (UTS, MPa)	
	As-rolled	As-aged	As-rolled	As-aged
01	348	377	296	371
02	371	374	334	377
03	335	349	186	349

Table 4. 12 Comparison of strain to fracture values as-aged at 150^0C/24hr

Alloys (as-aged 150^0C, 24hr)	Longitudinal Direction		Transverse Direction	
	As-rolled	As-aged	As-rolled	As-aged
01	22	17.79	20	17.79
02	15	17.63	4	12.70
03	13	13.06	3	3.08

4.10.3 Comparison between As-Rolled and As-Aged (180^0C/24hr) Conditions

For 180^0C/24hr, it is observed the mechanical strength enhanced as compared to rolling condition, shown in Figure 4.26.

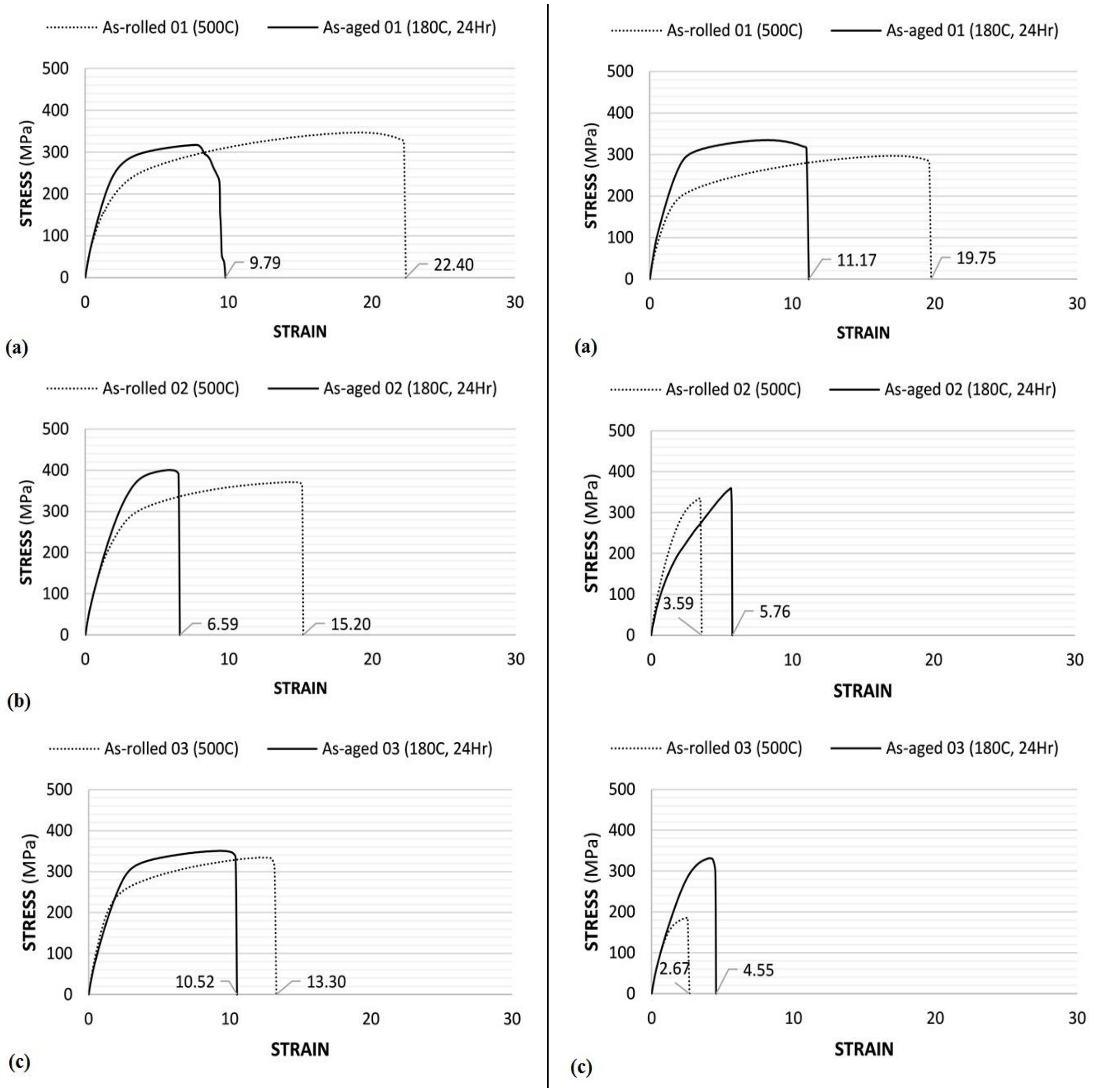


Figure 4. 26 Comparison of stress-strain curve for alloys 01, 02 & 03 at ageing 180^0C/24hr, along longitudinal (left) and transverse directions (right) as-rolled and as-aged conditions.

Table 4. 13 Comparison of UTS values as-aged at 180^0C/24hr

Alloys (as-aged 180^0C, 24hr)	Longitudinal Direction (UTS, MPa)		Transverse Direction (UTS, MPa)	
	As-rolled	As-aged	As-rolled	As-aged
01	348	317	296	335
02	371	400	334	359
03	335	351	186	331

The UTS value reaches maximum height for alloy 02 both in longitudinal (400 MPa) and transverse directions (359 MPa), as given Table 4.13. But the strain to fracture value except alloy 01, is found to be dimed both longitudinal and transverse directions after the ageing cycle done, as illustrated in Table 4.14.

Table 4. 14 Comparison of strain to fracture values as-aged at 180^0C/24hr

Alloys	Longitudinal Direction		Transverse Direction	
(as-aged 180^0C, 24hr)	As-rolled	As-aged	As-rolled	As-aged
01	22	9.79	20	11.17
02	15	6.59	4	5.76
03	13	10.52	3	4.55

4.11 Hardness Effects

Cast Al-Cu alloys as well as wrought, respond to solution and subsequent aging to increase the strength and hardness, decrease in elongation. This strengthening is maximum between 4 to 6% Cu depending upon the influence of other alloying elements presence.

The main benefits adding Mg to Al-Cu alloys, is to increase strength possible by solution treatment and quenching. On artificial aging, a further increase in strength, especially in yield strength can be demonstrated, but a substantial sacrifice in tensile elongation. From previous investigation, it was found that by the addition of Cu and Mg in Al alloys increase in hardness and strength of Al alloys [29].

On the other hand, as the Mg content increases Mg containing phases continues to increase, leads to change in microstructural change and property of Hardness, as shown in Figure 4.27 shows the Vickers hardness as-aged at different time-temperature cycle for alloys 01, 02 & 03. It is clear that, among alloys as-aged condition, temperature-time cycles at $120^0, 150^0$ & $180^0\mathrm{C}$ for $24\mathrm{hr}$, the height hardness value (165.2 HV) stands with alloys 02.

The reason behind this effect, Figure 4.11b illustrated even in as-aged condition the high temperature (HT) phase S-precipitates and low temperature (LT) precipitates are predominated.

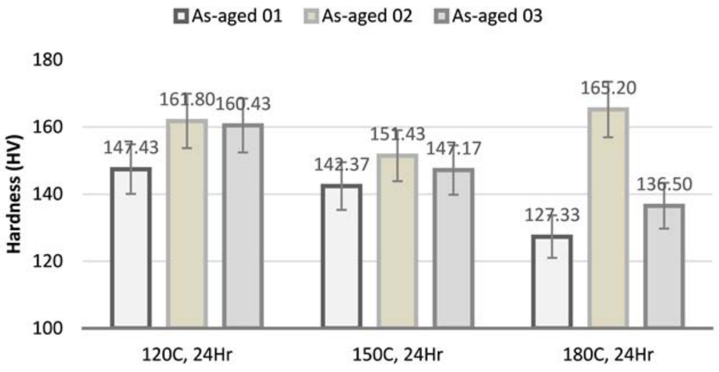


Figure 4. 27 Vickers hardness for alloys 01, 02 & 03 as-aged at (a) 120^0C/24hr, (b) 150^0C/24hr, and (c) 180^0C/24hr

4.12 Fractography Analysis

Failure analysis (FA) is a multidisciplinary scientific field. This episode summarizes the main types of overload fracture, which occurs instantly, once the intensity of the operating conditions exceeds the load-carrying capability of the components. Typically, the main overload fracture classes are categorized according to the accompanied plasticity (ductility) criterion, leading to two main groups– (1) Ductile fracture, and (2) Low or limited ductility fracture.

In this case, the term “brittle fracture” is intentionally avoided and it is included with the present fracture type. Brittle fracture is an extreme case of low/limited ductility fracture where the absorbed plastic strain energy is negligible [30].

4.12.1 Ductile Fracture

At the microscopic level, ductile fracture is characterized by a dimple structure (Figure 4.28a, 4.29a). The cavities arisen from inclusions or coarser precipitates are enlarged and during further yielding the material between them is necked and sheared. To a first approximation the depth of these dimples can be considered as a measure of the ductility. Ductile fracture is accompanied by an appreciable amount of permanent plastic deformation, which is manifested even macroscopically by shape-geometry or cross section distortion (necking).

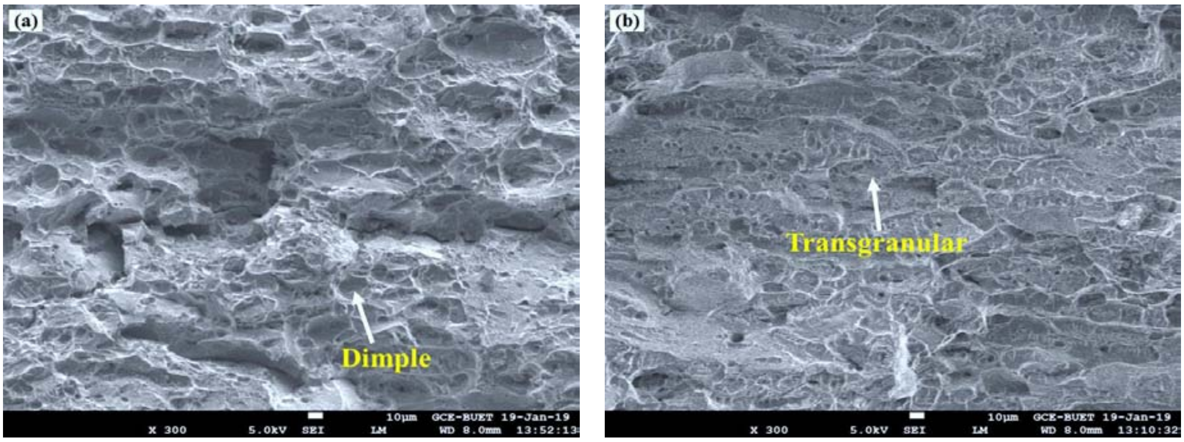
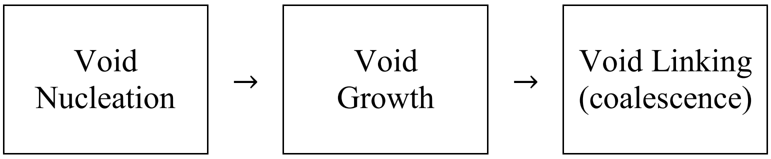


Figure 4. 28 SEM image of fracture surface along (a) longitudinal-alloy 02, and (b) transverse directions- alloy 02 as-aged at 120^0C/24hr

Microscopically, voids are generated around inclusions, inclusion/matrix interfaces, and at the center of the neck, where the hydrostatic stress is maximized and stress triaxiality dominates. The process of fracture development includes the following three steps– (1) void nucleation, (2) void growth, and (3) void linking (or coalescence).



The inclusion density affects the microvoid nucleation rate, leading to a higher number of nucleation sites and lower growth potential, resulting in a high void distribution density and lower size dimples, signifying lower overall plasticity. The microvoid coalescence gives rise to the evolution of ductile (plastic) fracture, which creates characteristic signatures and fracture surface patterns. The observation of fracture surface topography, using SEM reveals a specific anaglyph consisting of dimples of various size, shape, and distribution [31].

4.12.2 Low or Limited Ductility Fracture

In general, brittle fracture propagates through the grains (transgranular) along crystallographic plane. In the case of high strength, i.e. hardened and tempered metals, sometimes the crack follows the grain boundaries (intergranular fracture). In this class of fracture, there are two principal categories: (a) transgranular (cleavage) fracture, and (b) intergranular fracture

In cleavage, separation occurs along a well-defined crystallographic plane. The cleavage fracture proceeds on a planes directions showing minimum surface energy without any preferred crystallographic direction. Since dislocation processes accompany cleavage, it has been postulated that preferred cleavage planes and directions are those of the lowest plasticity around the crack. River-line patterns are characteristic features of transgranular (or cleavage) fracture. Very frequently, intergranular fractures are observed rather than cleavage, due to either the concentration of low melting-point impurity phases or the segregation of impurity elements at grain boundary areas.

The surface of tensile fracture in the samples both in longitudinal and transverse direction, was characterized using SEM to determine the type of fracture. The fracture surfaces of the tensile specimens distributed in various proportions depending on the alloy composition can be classified as (a) dimpled fracture, resulting from tensile overload of a ductile material, (b) transgranular cleavage fracture, caused by overload of a material with low ductility (c) intergranular fracture, occurred in a hardened, brittle specimen with microstructural precipitates that weakened the grain boundaries. Figures 4.28-4.30 shows the SEM fractography of Al 7xxx samples.

As aged for 120^0C/24hr cycle, the dimple density along longitudinal direction (strain to fracture, 24.65) demonstrate that the ductility is better than transverse direction (7.85), as shown Figure 4.28. That is, higher dimple density indicates the higher grain refinement. This higher density of dimples along longitudinal direction demonstrates the better strain to fracture than transverse direction.

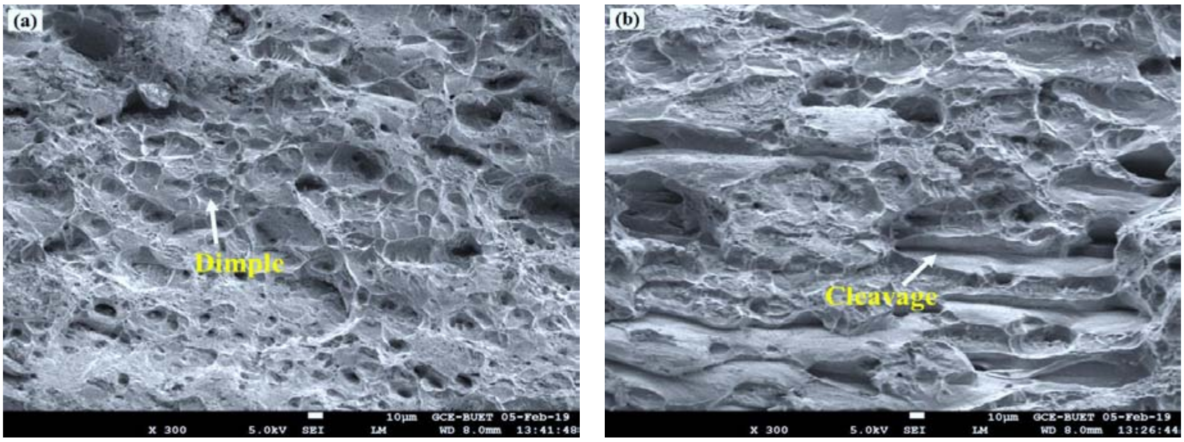


Figure 4. 29 SEM image of fracture surface along (a) longitudinal- alloy 01, and (b) transverse directions-alloy 02 as-aged at 150^0C/24hr

Figure 4.29 shows the SME image of alloy 01 along longitudinal direction, and transverse direction alloy 02, as aged for 150^0C/24hr. Dimple density is found to be better for alloy 01, stress to facture value along longitudinal direction is 17.79 (%). The cleavage pattern is observed for alloy 02 along transverse direction whereas strain to fracture value 12.70 (%). This cleavage microstructure illustrates its columnar grain structure of alloy 02 along transverse direction.

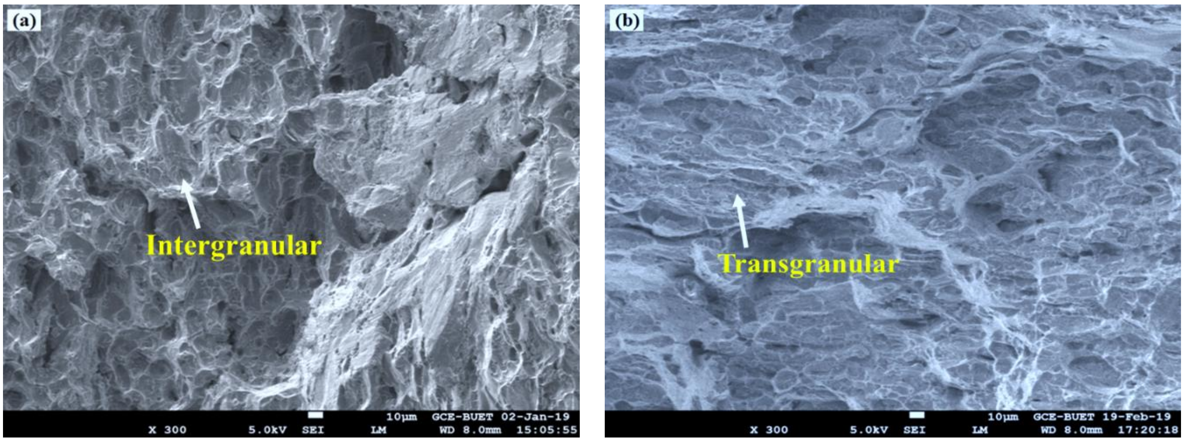


Figure 4. 30 SEM image of fracture surface along (a) longitudinal- alloy 02, and (b) transverse directions-alloy 02 as-aged at 180^0C/24hr

As aged for 180^0C/24hr, Figure 4.30 presents the SEM image of alloys 02 both longitudinal and transverse directions. The intergranular pattern is predominant along longitudinal, strain to fracture drop to 6.59 (%), whereas along transverse direction this strain to fracture is 5.76 (%). Intergranular feature offers coarse grain single structure that reduces the strain to fracture value. Other hand, the transgranular feature of microstructure of surface indicates its lower ductility.

Chapter 05

CONCLUSIONS

The main stream of the investigation is to find out the effects of alloying elements on the Al microstructure and the mechanical properties (tensile strength and hardness) both longitudinal and transverse direction, with varying amount of Cu and Mg.

Results outcome from this investigation can be stated as following,

01. Homogenization Treatment causes the dissolution of low melting point phases other segregations in the Al matrix.

02. Addition of Cu as alloying elements through manner, $1.09<1.33<4.32$ (wt.%) to the base metal Al enhances the Cu containing phases Al_2Cu and Al_2CuMg. This results the better mechanical strength.

03. Hot rolling and solution treatment can accomplish the dissolution of other phases into the base metal Al matrix.

04. In this investigation, Mg percentage is maintained a composition (wt.%) pattern $1.8>1.01>0.98$ for investigation alloys 01, 02 and 03 respectively . Mg containing phase $\eta(MgZn_2)$ increases the strength as possible following solution treatment and quenching.

05. Both longitudinal and transverse directions, the better mechanical properties (ultimate tensile strength, hardness) mostly for investigation alloys 02, whereas Cu/Mg ratio 1.32, the high temperature precipitate S-phase demonstrates responsible behind this effect, before and after the different ageing cycles of the alloys is accomplished.

06. The strain to fracture values decreases both longitudinal and transverse direction as the increase of temperature at temp.-time cycle.

07. From microstructure analysis, along longitudinal direction it is found to be dimpled and intergranular features that relates better ductility with high UTS value for alloy

02 at different temperature-time cycles. It also demonstrates that high temperature precipitate S-phase stands after ageing cycle complete of alloy 02.

08. Along transverse direction, microstructure investigation presents transgranular and cleave features. These microstructural features minimize the strain to fracture value with UTS value high temperature S-precipitates.

09. Among three investigate alloys, the better mechanical properties (strength, hardness etc.) is raised for alloy 02 both longitudinal and transverse directions, where base metal Al, primary alloying element Zn, 1.33 wt.% Cu and 1.01 wt.% Mg.

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