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Chapter 4

Effects of Modification Techniques on Mechanical Properties of Al-Si Cast Alloys

Williams S. Ebhota and Tien-Chien Jen

Additional information is available at the end of the chapter

Abstract

Mechanical, physical and chemical properties of a part depend on the size, morphology and dispersion of the constituents of the microstructure of the part’s material. Therefore, this chapter discusses the different processes of altering the microstructure of Al-Si–based alloys to desired functional properties. These processes, commonly called modification methods, were broadly categorised into three: chemical, thermal and mechanical methods. Chemical method, which involves the addition of some elements, in trace levels, to alloys to be modified, is the best modification option. The elements for modifying are called modifiers. The three commonly used modifiers (sodium, Na, strontium, Sr and antimony, Sb) are discussed. The chapter, however, notes that for optimal alloy’s mechanical attributes, thermal treatment is usually combined with both chemical and mechanical modification processes. The thermal method involves rapid cooling of alloy for modification, while the mechanical method depends on force to break up large α-Al dendrites and plate-like Si phases.

Keywords: aluminium, Al-Si alloys, refinement, chemical modification, mechanical modification, thermal modification, mechanical properties, grain, eutectic silicon, microstructure, heat treatment

1. Introduction

Quite often, the functional requirements of a component are conflicting. For the engineer, this occurrence makes most materials in their natural form deficient. For instance, a part may require both hardness and ductility to function properly in a given working environment. It is more or less impossible to find such material existing naturally. This type of situation has led engineers to explore different production techniques that produce the desired conflicting properties [1]. At times, two different materials may be combined, with each having one of the required properties. The combined materials could be metal and metal, metal and non-metal.
or non-metal and non-metal, and during merging, they may be in the same state or otherwise. The new material reflects the properties of the different materials that are combined. Several techniques have been established and used to improve the properties of aluminium and its alloys. The concept behind these methods is modification of the material’s microstructure, which ultimately alters the properties of the material [2].

The light weight and high corrosion resistance of aluminium make it significant in its applications; however, there are restrictions on aluminium applications, due to its soft and brittle nature [3]. Thus, to optimally exploit its natural attributes in automotive, aerospace and defence sectors requires a high strength-to-weight ratio. Processes have been developed to strengthen and harden this metal. The primary method of strengthening aluminium is alloying, which is the addition of a calculated amount of selected elements to aluminium. Aluminium alloy is a metallic substance and consists of approximately 90–96% aluminium and another or more elements, most commonly silicon (Si), copper (Cu), magnesium (Mg), zinc (Zn) and manganese (Mn) [4]. However, commercially available aluminium alloys have about 0.1–0.4% iron (Fe) by mass, which gives the alloys special qualities. While the iron content could be seen as an unwanted impurity, it depends on the fed raw materials and the electrolytic reduction process. There are other alloy elements that provide special properties, and are usually applied in smaller amount (less than 0.1% by mass), and include elements such as bismuth (Bi), chromium (Cr), boron (B), lead (Pb), zirconium (Zr), nickel (Ni) and titanium (Ti) [5]. The most important and commonly used alloying element of aluminium is Si. Silicon addition to aluminium improves the fluidity of the Al-Si alloy, feeding, hot tear resistance, tensile strength and hardness.

However, alloying has not completely satisfied material engineers’ quest to meet the trends of Al-Si alloys functional requirements, due to as-cast mechanical properties limitations. Cast alloys of Al-Si produced by conventional processes of melting, pouring and solidification, without post-process is called as-cast alloys. Studies have shown that the microstructure of as-cast alloys under the conventional solidification conditions consists of coarse flakes of Si that promote brittleness within these alloys [6, 7]. The primary Si in the form of a plate in Al-17%Si is shown is Figure 1. Consequently, material engineers and scientists have developed several

![Figure 1. Primary Si in the form of a plate in Al-20%Si [8].](image-url)
processes to enhance Al-Si alloys mechanical and physical properties. The properties of a material are defined by the characteristics of its microstructure. In the case of Al-Si alloys, microstructures can be modified either chemically or mechanically. In a chemical modification, certain elements are added in trace levels to the matrix depending on the needed property. This chapter, therefore, discusses Al-Si alloys modification concept, Al-Si modification methods and their applications.

2. Modification of Al-Si alloy techniques’ classification

Generally, modification and refinement processes are used for improving mechanical properties of alloys by altering the alloy’s Si morphology and distribution. There are several modification and refinement techniques that can be used and these techniques can be categorised into three:

i. Chemical modification and refinement processes; addition of a calculated amount of nucleation agents

ii. Mechanical modification and refinement processes; ultrasonic, squeeze, stirring, centrifugal and vibration methods

iii. Thermal modification process; superheating, quench and cooling

2.1. Chemical modification and refinement processes

The addition of trace levels of certain additive (modifier) to a molten Al-Si to alter its structure is called modification. Modification reduces the size of eutectic Si particles to enhance the cast’s mechanical properties such as ductility and strength. The addition of a modifier such as Sr transforms the Al-Si cast to fine and globular/fibrous morphology. Chemically stimulated modification produces a fine flake-like or fibrous structure. Many elements have been discovered to produce a fibrous eutectic Si structure such as Na, Sr, K, Ce and Ca. These following elements, Sb, As, and Se have been found also to produce a refined flake-like structure. These three elements Sr, Na, and Sb are the most effective modifiers in trace levels of additions and widely used in the foundry industry. The strongest modifiers known are Na and Sr. Other modifying elements are K, Rb, Ba, La, Yb, As and Cd, as presented in Table 1.

2.1.1. Sodium: Na-modification

The first commercially modifier applied to Al-Si alloys was Na. It is required in trace levels, usually <0.007%Na, to make the full modification. Advantages of Na-modification include: its effective use for many years; small amount required for modification; short residence time (the time it takes to remove inclusions); minimal surface agitation; and reduced offensive fumes. However, there are several drawbacks: it has about 10–50% volatility recoveries; limitation due to the danger in handling caused by its rapid reaction with moisture; formation of thick oxide skin that hinders fluidity, which may cause entraining in casting; it makes surface appearance of casting scaling; Na attacks mould coatings; and over modification challenges.
Modification of Al-Si microstructure is performed by the addition of a minute quantity of ternary element such as Na to Al-Si. The use of addition of a trace level alkaline earth metals or alkali metals to Al-Si alloys to alter their structures began several years ago. This alteration enhances the mechanical properties; raise the ultimate tensile strength (UTS) and increases the ductility. The influence of Na on tensile strength and elongation is shown in Figure 2.

Describing this morphological alteration, conventionally, there are two versions of explaining the principle of Na-modification [12, 13]: (i) based on Na influence on Si growth and; (ii) based on Na influence nucleation of the Si phase. However, Day and Hellawell identified three various modes of eutectic nucleation and growth in Al-Si alloys that are composition and solidification conditions depended. These modes are [13]:

i. Nucleation at or near to the wall and front growth facing the thermal gradient

ii. Nucleation of eutectic on primary dendrites

iii. Heterogeneous nucleation of eutectic on nucleant particles in the interdendritic liquid

The growth model seems to have the widest acceptance, due to the appearance of Si interconnectivity in both unmodified and modified structures. Consequently, the continuous

<table>
<thead>
<tr>
<th>Elements</th>
<th>Morphology of eutectic Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>No addition</td>
<td>—</td>
</tr>
<tr>
<td>Sodium, Na</td>
<td>Fibrous</td>
</tr>
<tr>
<td>Calcium, Ca</td>
<td>Fibrous</td>
</tr>
<tr>
<td>Strontium, Sr</td>
<td>Fibrous</td>
</tr>
<tr>
<td>Potassium, K</td>
<td>Fibrous</td>
</tr>
<tr>
<td>Barium, Ba</td>
<td>Fibrous</td>
</tr>
<tr>
<td>Cerium, Ce</td>
<td>Fibrous</td>
</tr>
<tr>
<td>Rubidium, Rb</td>
<td>Fibrous</td>
</tr>
<tr>
<td>Europium, Eu</td>
<td>Fibrous</td>
</tr>
<tr>
<td>Antimony, Sb</td>
<td>Lamellar (or a fine version of acicular)</td>
</tr>
<tr>
<td>Ytterbium, Yb</td>
<td>Lamellar (or a fine version of acicular)</td>
</tr>
<tr>
<td>Arsenic, As</td>
<td>Lamellar (or a fine version of acicular)</td>
</tr>
<tr>
<td>Selenium, Se</td>
<td>Lamellar (or a fine version of acicular)</td>
</tr>
<tr>
<td>Cadmium, Cd</td>
<td>Lamellar (or a fine version of acicular)</td>
</tr>
<tr>
<td>All rare earth metals and misch metals except Eu including Laa, Cea, Pra, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tb, Yba and Lu</td>
<td>Lamellar (or a fine version of acicular)</td>
</tr>
</tbody>
</table>

Table 1. Modifier elements and their effects on eutectic Si [9–11].
nucleation of Si has been contested. However, two limitations were observed in the growth model. In a Na-modified casting, a significant change of the microstructure was noted, while little spacing changed and fibrous Si form are produced in the directionally grown specimens. Again, it was noted that Na addition has little influence on the equilibrium liquidus temperature, but there is a huge change in the plateau temperature produced during the thermal investigation of a cast alloy [13]. Enhancement of capacity of Si to branch by Na, in the growth models, has been advocated and this reduces spacing and total undercooling, at a specified growth velocity.

Conversely, Flood and Hunt concluded in their work that nucleation and Si growth are both affected by the addition of Na to Al-Si cast alloys. In the Na-modified casting, two effects were reported that [15]:

i. Sodium presence transforms the Si growth morphology from the plate-like form to the fibrous form.

ii. If the temperature rise in the liquid is small, Na stops nucleation from happening ahead of the eutectic growth front. The lack of nucleation primarily accounts for the finer structure and larger undercooling of modified castings or ingots.

Trace of phosphorous is often found in Al-Si alloys, which causes the formation of a granular structure and aluminium phosphite (AlPO₃). Aluminium phosphite accelerates primary Si crystallisation that appears in the microstructure in the form of polyhedral platelets. In Na-modification, Na reacts with phosphorus to form sodium phosphite (Na₃O₃P). The solid solution phase in the form of dendrites crystallises out first before the Si phase.
Significant change is observed in Si morphology and particle spacing when 0.01 wt.% Na was added. This process transforms solidifying alloy into highly refined Al-Si eutectic and also, reduces temperatures and moves the eutectic point to a higher Si content. The broken line in Figure 3 shows the modified Al-Si alloy phase diagram.

Addition of Na modifies the eutectic Si growth to an irregular fibrous form instead of the usual coarse flakes. The composition of Al-Si alloy at the new eutectic point due to the Na-modification is hypoeutectic instead of hypereutectic, which results in the formation of primary $\alpha$-Al instead of Si. Figure 4 shows micrograph of Al-13%wtSi and Al-13%wtSi-0.01%Na respectively. Addition of small of the quantity of 0.01% Na as an impurity to Al-Si alloy modifies its microstructure and improves its properties.

Wessén, Andersson and Granath investigated Na-modification effect on the mechanical properties of a secondary alloy, Al-6%Si-2.5%Cu, produced from rheocasting, applied to thick wall components production [17]. The study revealed noteworthy alterations in the microstructure of the Na-modified; individual Si lamellar could not be identified, while the average size of Si lamellar of the unmodified alloy was 100 μm. The reduction of the quantity of Na from $4.3 \times 10^{-5}$ wt.% to $3 \times 10^{-5}$ wt.% did not show a significant change in the structure and shows that a trace level of Na can substantially transform eutectic. The energy disperse X-ray spectroscopy (EDX) analysis shows intermetallic phases Al$_2$Cu and Al$_{15}(Fe, Mn)_3Si_2$ and these are shown in the SEM image in Figure 5.

Figure 3. Modified Al-Si alloy phase diagram [16].

Figure 4. Micrograph of [16] (a) Al-13%Si; (b) Al-13%Si-0.01%Na, where 1 = $\alpha$-Al dendrite; 2 = primary Si; 3 = Eutectic Si; 4 = $\alpha$-Al; and 5 = fibrous eutectic Si.
2.1.2. Strontium: Sr-modification

Modification by Sr and Na has the similar result of fibrous eutectic Si structure. However, Na is much more volatile than Sr, as is often considered as a semi-permanent modifier. This property and its easy application, coupled with other metallurgical advantages have increased the use of Sr as a modifier in recent years. Other advantages are [18–29]: about 80–90% recovery rate; addition melt easily; wide effective concentration range; last long in the melt during holding times; less delicate to over-modification; produces smooth appearance castings; found in suitable master alloy form; and it does not react with refractories; it has no environmental challenges. In a well Sr-modified hypoeutectic casting microstructure, the estimated average area of the fibrous eutectic Si particle is $3.8 \pm 0.6 \mu m^2$ and the aspect ratio is about $1.58 \pm 0.29$. The impact of Sr concentration on strengths is shown in Figure 6.

![SEM image showing main intermetallic phases in microstructure](image)

**Figure 5.** SEM image showing main intermetallic phases in microstructure [17].

**Figure 6.** Impact of Sr concentration on strengths of: (a) AA601 cast alloy; and (b) AA401 alloys [20].
There are challenges that are associated with Sr-modification such as the promotion of gas levels in the melt and the cost is comparatively high. Nevertheless, these challenges can be overcome by easier melt treatment practice and other casting quality enhancement processes. Over modification causes the mechanical properties of the alloy to revert to that of a typical unmodified alloy, Figure 7 shows the microstructures of, unmodified, modified and over modified alloys.

The transformation of eutectic Si morphology in Al-Si casting alloys from coarse plate-like to fine fibrous networks can be achieved by trace addition of Sr to the alloy. To further explain the process of Sr-modification, Timpel et al investigated the distribution of Sr in two ways: in nanometre resolution by transmission electron microscopy (TEM) and in atomic resolution by atom probe tomography (APT). The two methods showed that within the eutectic Si phase, there is Sr co-segregation with Al and Si. Two kinds of segregations, type I and type II, were identified:

i. Type I segregation is a nanometre-thin rod-like, accountable for the formation of numerous twins in a Si crystal and facilitate its development in various crystallographic directions.

ii. Type II segregations are more stretched structures that impede the growth of a Si crystal and regulate its branching.

This study agrees with earlier studies of modification mechanisms, which hinged the modification on growth restriction of eutectic Si phase and impurity induced twinning [11, 25]. Figure 8 shows the optical micrographs of Al–10%Si–0.1Fe alloy for unmodified alloy and 200 ppm Sr-modified alloy.

Atom probe tomography analysis and TEM images of Al and Si interface are presented in Figures 9 and 10 respectively. The ATP data set does not contain crystallographic information. Therefore, TEM is used to obtain such information with a spotlight on the structural and compositional characteristics of the eutectic Si phase.

**Figure 7.** Eutectic microstructures of fully solidified Al-Si alloys: (a) unmodified commercial purity; (b) unmodified high purity; (c) Sr modified commercial purity; (d) Sr modified high purity [21]; over Sr-modification of AA601 alloy: (e) >0.03%Sr formation of Al4SrSi2 phase; (f) >0.09%Sr formation of coarse of the eutectic Si [22]; SEM images of etched microstructures of the Al-Si eutectic [23], (g) unmodified Al-Si alloy; (h) Sr-modified Al-Si alloy.
Figure 8. Optical micrographs of Al–10%Si–0.1Fe alloy [24]: (a) and (b) unmodified alloy; (c) and (d) alloy modified by 200 ppm Sr.

Figure 9. APT analysis of eutectic Al–Si interface of Al–10%Si–0.1%Fe alloy of 200 ppm Sr-modified; (a) iso-density surface; (b) representation of 0.17 Sr atoms/nm$^3$ in both co-segregations; (c) concentrations of Al, Si and Sr in proxigram, which depend on the distance to the Si/Sr–Al–Si co-segregation interface in (a) and (b) [24].
In another study, hypoeutectic Al-Si alloys containing two levels of Fe (0.5 and 1.1 wt.%) and modifier (Sr) in the range of 30–500 ppm, were investigated. Significant reduction in the number of eutectic grains and the formation of polygonal-shaped Al$_2$Si$_2$Sr intermetallic were observed in excess addition (100 ppm) of Sr. TEM examination showed that the Al$_2$Si$_2$Sr phase is bounded by the P-rich particles, and this infers poisoning or deactivation of nuclei for the Al-Si eutectic. The poisoning is due to the formation of Al$_2$Si$_2$Sr phase about the particles. Further reduction in the number of eutectic Al-Si nucleation actions was recorded at 1.1 wt.% Fe due to the formation of pre-eutectic, β-Al$_5$Fe$_3$Si platelets.

There is the difference in the nucleation temperatures between unmodified and Sr-modified Al-10%Si alloys. In the Sr-modified alloy, the eutectic-nucleation temperature is depressed with minimum occurrence before recalescence and growth temperature. Figure 11 shows unmodified and Sr-modified Al-10%Si alloys of low Fe (0.5 wt.%) and high Fe (1.1 wt.%) cooling curves recorded during solidification, respectively. Considering the curves, $T_a$ is α-Al nucleation temperature; $T_b$ is β-Al$_5$Fe$_3$Si nucleation temperature; and $T_N$ is Al-Si eutectic nucleation temperature.

2.1.3. Antimony: Sb-modification

Addition of Sb produces a refined flake-like eutectic structure, unlike Sr or Na-modified alloys, which result in a fibrous structure. Sb remains a permanent constituent of the alloy, unlike
Sr and Na, which fade away with time. Because of this, the supplier adds it to the foundry ingot. The ultimate tensile strength of unheated treated alloy, AlSi$_6$Cu$_4$, was improved from 5 to 10% by increasing the addition of Sb from 1000 to 2500 ppm to the alloy respectively [26]. The Sb-modification decreases the size of grain but increases the number. The maximum size of unmodified Al-Si alloy grain is about 220 μm. The size of the eutectic grain is reduced from 156 μm (0 ppm Sb) to 84 μm (1000 ppm Sb) by Sb-modification. Antimony, Sb, is widely used in Japan and Europe and commonly called permanent modifier. Its addition to molten Al-Si alloy is straightforward, as it does not require any special set up, and once it is added, it becomes a permanent part of the alloy. The use of Sb as a modifier has merits such as insensitive to re-gassing; it does not fade; and is appropriate for components that are susceptible to porosity formation. However, Sb-modification has the following drawbacks: Sb reacts and reduces the effectiveness of Sr and Na; Sb may react with hydrogen dissolved in the metal and forms a stabile gas, a toxic material; may cause the slower solidifying regions of casting poor mechanical properties; and Sb is least effective, as lowest level of transformation is achieved compared to Sr and Na [20, 27].

2.2. Effect of modification on casting quality

Despite many years of application, Na and Sr modification and its influence on the gas content of Al-Si alloy melts are still being contested by researchers. Several studies declare that Sr-modification has no effect on the alloy’s hydrogen content [28, 29]. The measured hydrogen content in a melt after 0.03% Sr addition, using Al-90% Sr master alloy, to a non-degassed A356 melt at 710°C, is shown in Figure 12. Others claim that Sr-modification levels addition above 0.10–0.12% causes gas porosity [30–32]. Porosity formation in alloys during solidification is a major challenge for casting industry due to its negative effect on total elongation and fatigue performance. Jahromi et al. reported that 0.013% Sr and 0.1% Sb were found to be the optimum additions to modified A356 alloy to fibrous structure in a sand casting. More porosity developed in Sr-modified than Sb-modified [29]. Denton and Spittle reported that hydrogen content of Al-Si alloys increased significantly in the addition of Sr to Al-Si melts, at elevated temperatures [33].
3. Rapid cooling (quenching) and mechanical modification

Coarse columnar grain structures are developed by Al-Si cast alloys under normal casting conditions. But these structures can be transformed into fine grain structures and uniform distribution in the alloy by mechanical modification and through rapid cooling. Rapid cooling results in a fine dendritic structure in the alloy [34, 35]. Large dendritic structure is due to undercooling during solidification. Rate of cooling affects the size of critical nuclei, and subsequently, the effective number of nuclei that will ultimately produce fine-grained structures.

Cooling rate can be expressed by this relation:

\[ d = C v^n \]  

(1)

where \( d \) — secondary dendrite arms spacing, SDAS, (μm); \( C \) and \( n \) — are constants; and \( v \) — cooling rate (°K/s).

The local solidification times \( (t_f) \) can be calculated in terms of SDAS measurements through the following expression [36]:

\[ SDAS = 5.5 \left[ \frac{\Gamma_a D_l \ln \left( \frac{C_e}{C_0} \right)}{m(1-k)(C_{eut}-C_0) t_f} \right]^{\frac{1}{3}} \]  

(2)

where \( \Gamma_a \) — Gibbs-Thomson coefficient; \( D_l \) — diffusion coefficient in liquid; \( m \) — liquidus curve slope; \( k \) — coefficient of partition; \( C_{eut} \) and \( C_0 \) — are the eutectic composition and the initial alloy concentration respectively.
The removal of superheat and latent heat from a liquid at a cooling rate of $10^2$–$10^6$ K/s to form a solid is called rapid solidification. To accomplish this, there are certain conditions that must be satisfied [37]. There should be impressive:

i. High undercooling before solidification occurs  
ii. High solidification front speed during continuous solidification  
iii. Rapid cooling during solidification

Duwez and his team at the California Institute of Technology developed an innovative method in 1960 to increase solid solubility and to yield metastable crystalline in some simple binary eutectic alloy structures [38]. A similar process was performed earlier by a Russian researcher, Salli, in 1958 [7]. In their modification technique, a gun was applied to deposit a small droplet of molten metal, at high velocity, on a freezing surface. This resulted in the formation of an irregular solidified splat of metal. The estimated cooling rate range of the process reported was $10^5$ to $10^6$ K/s as against the conventional cooling rate of $10^2$ K/s or less. Other metal rapid quenching systems, with varied solidification effects, have been introduced since the development of fast cooling by Duwez. However, the common principal aims of these systems are to: increase solid solubility limits; decrease grain size; create metastable crystalline phases; form metallic glasses; and increase chemical homogeneity. Recent studies have shown that rapid cooling systems such as atomisation, melt spinning and splat quenching are effective in the modification of Si phase in Al-Si alloys. In an investigative study, the microstructure and mechanical properties of A356 alloy prepared from a copper mould cooled by a phase-transition medium [34]. The study reported that a cooling rate of $10^2$ K/s was obtained using this method and this method was described as a fast-cooling technology. The study indicated that:

i. Variation in the quantity of cooling medium controlled the cooling rate to a certain extent.  
ii. The primary and SDAS were better refined by this technology compared to the use of conventional casting technique  
iii. Increase in cooling rate decreases SDAS while strength and microhardness increase correspondingly.

The studies essentially focused on: characterisation of rapidly solidified Al-Si alloys microstructure; and the determination of retained-Si amount in $\alpha$-Al by X-ray diffraction methods, which depends on lattice parameter.

3.1. Al-Si alloy quenching media

There are several quenching fluids (quenchants) used in the quenching of high strength Al-Si alloys. There is no an ideal all-purpose quenchant, their applications depend on some factors such as composition, cast thickness, etc. Quenchants that are commonly used for different
aluminium alloys are water spray, cold water immersion, hot water immersion, air blast, still air, glycols/polymers, fast quenching oil, liquid nitrogen and brine solutions [39]. Water is the most common quenchant, with the advantages of being cheap, readily available and providing the fast cooling rate needed to produce the required properties. Furthermore, the temperature of water can be altered to produce a wide range of quenching characteristics. Boiling water is used in many aluminium alloys quenching operations due to sufficient cooling rate. Colder water or polymers may be used in the case of premium property requirements, such as in A357 and A201 castings alloys [40].

In 2014, Abdulazeez et al. observed that microhardness of Al-Si-Mg alloys is affected by quenchants differently [41]. Water quenching was said to give higher microhardness compared to polymers. This was attributed to faster cooling rate, restraining elements from solid solution (α-Al) diffusion and grain boundary precipitation by water. The generally acceptable water quenching temperatures ranges for various aluminium alloys are presented in Table 2.

<table>
<thead>
<tr>
<th>Type</th>
<th>Alloy/temper</th>
<th>Water temperature (°C)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>21–32</td>
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<tr>
<td>Casting</td>
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</tr>
<tr>
<td></td>
<td>A356</td>
<td>✓</td>
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<td></td>
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<td></td>
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<td>✓</td>
</tr>
<tr>
<td></td>
<td>AA201</td>
<td>✓</td>
</tr>
</tbody>
</table>

Table 2. Normal water quenching temperatures for some aluminium casting alloys.

In the heat treatment sequence, quenching is the next vital process, and its purposes are as follows: to suppress precipitation; to preserve the maximum amount of hardening elements precipitates in solution to develop a supersaturated solid solution at low temperatures; and to confine several vacancies [42]. Quench rate limit is 4°C/s, above this, the yield strength increases slowly. To maximise vacancy confinement concentration and minimise part deformation after quenching, optimal quenching rate is required. A slow quenching rate reduces residual distortion and stresses in parts, but it causes harmful effects such as precipitation during quenching; reduction in grain boundaries; increase tendencies for corrosion; localised over-ageing and leads to a response to ageing treatment reduction. Optimal cooling rate should be established, and the optimum combination of ductility and strength depends on rapid cooling.

4. Mechanical modification techniques

Modification of Al-Si alloy can as well be achieved through the use of mechanical techniques, such as centrifuge, sonic and ultrasonic vibration, squeezing, etc. These mechanical means have
been identified to cause grain refinement, density increase, shrinkage, degassing, change size, shape and distribution of the second phase [43, 44]. Refinement is produced through some mechanical means of breaking up newly developed dendrites, as in case of semisolid-metal (SSM) casting technique. The size, distribution and morphology of α-Al particles govern die filling, and subsequently, control the ability to produce thin wall castings.

4.1. Vibration energy

Refinement of primary austenite structure was achieved by Chernov in 1868 by applying vibration during solidification [45]. Since then, several other researchers have investigated and applied the beneficial effects of vibration energy to treat many alloys of aluminium, zinc, brass, etc. during solidification [46, 47]. Vibration influences the structure of a solidifying alloy by suppressing the growth of columnar and the formation of equiaxed grains. The effect of vibration on unmodified and Na-modified alloy has been reported. A schematic of a mould mounted on the vibrator or shaker is shown in Figure 13.

These beneficial effects include nucleation promotion, which reduces as-cast grain size; decreases shrinkage porosities; and stimulates the formation of a more homogeneous metal structure with cracking susceptibility decrease. Therefore, due to vibration, alterations occur to the morphologies and dispersion of eutectic and dendritic phases in the microstructure. Pillar’s study revealed that eutectic Si of unmodified Al-Si alloys was modified by vibration at a frequency of 12 Hz and amplitude of 10 mm [48]. Contrarily, it was found that vibration coarsened the eutectic Si in Na-modified Al-Si alloys and this was attributed to fine eutectic Si agglomeration. Abu-Dheir et al. observed that at constant frequency of 100 Hz and varying amplitude resulted in different degree of breakup of the dendrites and eutectic Si phase [49]. Micrographs of Al-12.5% Si castings of without vibration and with vibration at 100 Hz are shown in Figure 14.

It was seen in the optical micrographs that degree of fragmentation is a function of the amplitude, which shows proportionality. However, the study indicated that there is a limit of

Figure 13. Schematic of mould assembly mounted on the vibrator.
amplitude above which the size of fragmented dendrites and eutectic Si start to form coarse flakes due to agglomeration. The microstructural characteristics of Al–12.5% Si casting without and with vibration at constant frequency (100 Hz) and varying amplitude are presented in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>Casting condition</th>
<th>Lamellar spacing (μm)</th>
<th>Si flake length (μm)</th>
<th>Notes</th>
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</thead>
<tbody>
<tr>
<td>No vibration</td>
<td>2.5</td>
<td>27</td>
<td>Si cuboids, large dendrites</td>
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<td>18 μm</td>
<td>2</td>
<td>15</td>
<td>Broken dendrites</td>
</tr>
<tr>
<td>49 μm</td>
<td>2.77</td>
<td>31</td>
<td>Refined broken dendrites</td>
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<tr>
<td>149 μm</td>
<td>N/A</td>
<td>N/A</td>
<td>Fibrous Si observed</td>
</tr>
<tr>
<td>199 μm</td>
<td>1.5</td>
<td>10.5</td>
<td>Coarse Si flakes</td>
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</tbody>
</table>

Figure 14. Micrographs of Al-12.5% Si castings (a) casting without vibration; (b) with vibration at 100 Hz and 18 μm; (c) with vibration at 100 Hz and 149 μm; (d) with vibration at 100 Hz and 199 μm [49].
There are different methods of applying vibration. Electromagnetic vibration is one of the non-contact methods used to generate vibration in the solidifying alloy. The vibration is produced by using an orthogonal static magnet and alternating electric fields [50]. It was observed that the collapse of the cavities created by this method was accountable for the refinement of the microstructure for Al–7% Si and Al–17% Si [51].

4.2. Centrifugal casting technique

Centrifugal casting technique (CCT) is a casting production process that involves rotation of a mould during pouring and solidification of the casting. The schematic in Figure 15 shows the forms and the major components of a centrifugal casting machine [52].

The attributes of material depend not only on the composition chemistry but also on the morphologies and distribution of the microstructural features present in the microstructure. These microstructural features include the primary and eutectic Si phases, α-Al dendritic and intermetallics. Low solidification rate results in large flakes of Si, large dendritic cells and large inter-dendrite arm spacing of α-aluminium dendrites. Centrifugal casting process increases cooling rate and consequently, produces small dendritic cells, small inter-dendrite arm spacing and small flakes of Si. Alloys of Al-Si by CCT are morphologically transformed from acicular to fibrous [52]. Micrographs of A390-5%Mg alloy as-cast fabricated by gravity casting and CCT are shown in Figure 16.

Speed of rotation is a parameter that controls the rate at which centrifugal casting process affects cooling. Some studies have reported that mould rotational speed range of 1200–1500 RPM as the optimum [53] and other relevant processing parameters are pre-heating and pouring temperatures [52]. The effect of CCT on casting can be classified into three: centrifugal pressure, inherent vibration of the process and fluid dynamics.

Figure 15. Classification of centrifugal casting methods [52]. (a) horizontal true centrifugal casting process; (b) horizontal inclined centrifugal casting process; (c) vertical true centrifugal casting process; (d) semi vertical centrifugal casting process; (e) vertical inclined centrifugal casting process.
5. Conclusion

Components made of materials in their natural forms often do not satisfactorily meet functional requirements, due to harsh and extreme working environments. Scientists and engineers have continuously modified these natural occurring materials, using different production processes, to suit their harsh working environments. Material’s mechanical, physical and chemical properties depend on the size, morphology and dispersion of the constituents of the microstructure of the material. Aluminium is one of such natural materials that have evolved into several alloys and composites. The mechanical properties of aluminium-based alloys and composites have further been improved by microstructural alteration processes, termed as modification processes. These modification techniques can be classified into three:

i. Chemical modification processes; addition of a calculated amount of nucleation agents

ii. Mechanical modification processes; ultrasonic, squeeze, stirring, centrifugal, and vibration methods

iii. Thermal modification process; superheating, quench and cooling

Chemical modification, which is the addition of trace levels of certain elements, such as Na, Sr and Sb, into aluminium alloys, is most effective. However, optimal modification occurs when thermal modification process is combined with chemical or mechanical process.

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