The Effects of Manganese Modification and Calcium Refinement on the Structure and Mechanical Properties of Aluminium-Silicon Alloy

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Abstract—This paper investigates the effect of manganese as modifier and calcium as refiner in Al-12%Si alloy. Modification with manganese was within the range 0.5%, 1.0%, 1.5%, 2.5% and 5.0% while refinement with calcium was effected with 0.01%, 0.02%, 0.05% and 0.10%. The representative mechanical properties studied were tensile strength, percentage elongation and impact strength while microstructural analysis was also undertaken. Standard (ASM) methods were employed in the investigations. Tensile strength and percentage elongation were determined using TUE-C-100 universal testing machine, chemical analysis was done using XRF analyzer while microstructural examination was conducted with the aid of microscopy using Neo Photo 2. The results obtained showed that the investigated modifier and refiner improved the mechanical properties studied and this was due to structural modification of the silicon plates and consequent refinement and recompaction of the fine particles.

Keywords—modification, refinement, silicon platelets, recompaction of fine particles.

I. INTRODUCTION

Aluminium enjoys a wide range of commercial applications due to the unique combination of good corrosion resistance, light weight, good mechanical properties, ease of fabrication and affordable cost (ASM, 1990). It is a non-combustible, non-absorbent and non-toxic material. Structural components made from aluminium and its alloys are vital to the aerospace industry and are important in other areas like transportation and structural applications. Aluminium is mostly demanded in automobile industry because the thrust of materials research is directed at the design of smaller and/or lighter components which can reduce fuel consumption and running costs though not at the expense of quality and environment (Chapman, 1994). Aluminium based alloys are fast replacing steel in automobile and aerospace industries because of their superior strength to weight ratio, high energy impact absorption properties and corrosion resistance. Alloys for military applications are known to have been produced by injecting copper, zinc, magnesium, tin, lead, nickel, bismuth, germanium, titanium and others into Al-Si alloy (Nnuka, 1985). The inoculation of aluminium with silicon incurs only a mild reduction in corrosion resistance of aluminium making the behaviour under atmospheric exposure self-stifling and improving the properties. The addition of silicon imparts high liquid fluidity on aluminium and low shrinkage to Al-Si alloy system resulting to good cast-ability and weld-ability (Nnuka, 1984). The high fluidity conferred on Al-Si alloy system accounts for its preference by foundry men (Hellawell, 1970). The Al-Si alloy system possesses high shock and corrosion resistance, thereby finding application in the ship building, aerospace, military equipment, automobile, spare parts and tractor industry. The low expansion coefficient is exploited in the production of pistons, engine blocks and the hardness of silicon particles for wear resistance (Mondolf, 1976). The use of cast aluminium alloys is still limited in comparison with wrought alloys, even though casting would be a more economical production method. Apart from the emerging economical processing techniques that combine quality and ease of operations, researchers are, at the same time, turning attention to modifying aluminum-silicon matrix and isotropic properties, especially in the applications not requiring extreme loading or thermal conditions, for example automobile components (Chawla, 1996). Silicon forms brittle needle-like particles which reduce impact strength in cast structures. The finger-like structure formed acts as stress raisers that initiates and propagates cracks thereby reducing the mechanical strength of the alloy. Again, there are many naturally occurring impurities in commercial aluminium which can only be removed at great cost. Iron is the most important
detrimental impurity in cast aluminium and its alloy as it degrades mechanical properties such as fracture toughness. Therefore, the need to produce high quality Al-Si alloys that can suit and enhance the technology of the time is of necessity. The modification of the Si morphology from flake-like structure to fibrous form was believed to greatly improve the mechanical properties as was discovered by Pacz in 1920. Jeffries 1922 reported that addition of fluxes to Al–Si alloys affects the morphology and dispersion of the silicon phase in the eutectic, so that silicon morphology changes from needle-like morphology that is characterized by unmodified eutectic to a finer and more or less globular shape and observably shifts the eutectic composition towards higher silicon content (Jeffries, 1922). In addition to shifting the eutectic composition to a higher silicon level, chemical modification lowered the eutectic freezing temperature from 577°C to 564°C (Archer, 1926).

Therefore, it is paramount of importance to promote industrial consumption of aluminium-silicon alloy without compromising quality and aesthetics of products. In view of these, a strict microstructural control is needed to remove the deleterious effects of impurity elements which impair the overall mechanical properties of aluminium-silicon based alloys. By applying adaptable alloying and process technology, the mechanical properties such as ductility will therefore be radically enhanced, leading to expanded application fields of complex cast aluminium components (Nnuka, 1985).

A very effective way of enhancing the stability of aluminium-silicon alloy utilization in the industry is to improve the mechanical properties, thereby ensuring structurally sound and dimensionally accurate Al-Si castings and fabricated products at reduced cost. The key to achieving the improvement of properties is to understand the structure-property-application relationship of the aluminium-silicon alloy additives. Also, better quantitative understanding of the microstructure-property relationships in cast Al alloys coupled with improved foundry practice will allow wider application of reliable castings in low mass structures. The essence of adding additives to Al-Si alloys is to improve strength, enhance mechanical properties and disperse porosity and shrinkage as they modify the eutectic structure (Nnuka, 2004). The modified alloy displays a finer, less needle-like microstructure which is necessary in the production of structurally sound and dimensionally accurate Al-Si castings and fabricated products. Among the various methods available to neutralize the deleterious effects of iron is by adding trace elements such as Co, NaCl, NaF, Mn, Ca, Mo and Cu (Nnuka, 2007).

II. MATERIALS AND METHODS

Materials and equipment used for this research are: high purity aluminium, silicon, manganese, calcium, electronic weighing balance, beakers, bailout heating furnace and microscope. Ten different compositions of alloys were produced with amounts of Mn varied from 0.5% to 5% and Ca from 0.01% to 0.1% at 12% of Si present in the alloy. Before casting, the control sample was chemically analyzed to ascertain the composition and after the casting, the samples were also analyzed chemically to ascertain the end composition provided in Table 1. The aluminium was charged into an alumina crucible and then loaded into a bailout crucible furnace. The aluminium was melted at a temperature of 750 °C, the silicon was then added and then dissolved by stirring with a spatula. The melt Al-Si was then removed from the furnace, the Ca was added into the crucible with further stirring. The alloy was the cast into the moulds, allowed to solidify and then extracted from the moulds. The castings were then prepared for the property tests. They were machined according to ASM standard tests for tensile strength, percentage elongation and impact strength. Samples for structural analysis were also prepared.

**Tensile Strength Test**

Tensile strength and relative elongation tests: tensile and relative elongation of the samples were determined using the TUE-C-100 testing machine. The test pieces which were machined to a standards shape were mounted and loaded to fracture. Tensile test were conducted according to standard method and relative elongation was calculated using the equation,

\[
\text{% Elongation} = \frac{\text{Extension}}{100} \times \frac{\text{Gauge length}}{\text{Extension}}
\]

**Impact Test**

Impact strength was obtained using the Izod test technique. The standard specimen was clamped in a horizontal position with the centre of the notch in the line with the upper face of the jaws. A waited pendulum was released from the rest
position and allowed to strike the notched specimen held in the vice. The energy absorbed to fracture the specimen was read and recorded.

**Micrography**

Micrography was conducted using standard test techniques. The table size metallography microscope was used to study the specimens. The images of the micrographs were captured at magnification of 300 times. The test pieces were then ground roughly, finely and finally polished and then etched. Fine grinding was done using abrasives of 320, 400, and 600 grits with the corresponding particle sizes of the silicon carbide of 33, 23, and 17 microns respectively (1 micron = 10^-6 cm) rough polishing was done using powdered diamond dust abrasives of 6 micron size, which was poured on emerald cloth covering the surface of the rotating polishing wheel. Final polishing was done using alumina (Al2O3) powder (gamma form) of particle size of 0.05 microns. It was poured and emerald covered wheel and distilled water served as lubricant. Etching was done using natal (25% solution of nitric acid in alcohol and one drop of hydrofluoric acid). The etching period for each specimen was 30 seconds.

IV. RESULTS AND DISCUSSIONS

The results of the effects of manganese and calcium additions on the structure and mechanical properties of Al-12%Si alloy are presented in Table 1 and 2, Figures 1-6 and in Plates 1-10. Table 2 shows the mechanical results, Figures 1-6 presents the analysis and Plates 1-10 presents the micrographs of the studied alloys.

**Table 1 chemical composition of the studied alloys**

<table>
<thead>
<tr>
<th>Samples</th>
<th>% Si</th>
<th>% Mn</th>
<th>% Ca</th>
<th>% Fe</th>
<th>% Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-12%Si</td>
<td>11.57</td>
<td>-</td>
<td>0.93</td>
<td>Bal</td>
<td></td>
</tr>
<tr>
<td>Al-12%Si+0.5%Mn</td>
<td>11.53</td>
<td>0.44</td>
<td>0.84</td>
<td>Bal</td>
<td></td>
</tr>
<tr>
<td>Al-12%Si+1.0%Mn</td>
<td>11.54</td>
<td>0.90</td>
<td>0.76</td>
<td>Bal</td>
<td></td>
</tr>
<tr>
<td>Al-12%Si+1.5%Mn</td>
<td>11.55</td>
<td>1.50</td>
<td>0.65</td>
<td>Bal</td>
<td></td>
</tr>
<tr>
<td>Al-12%Si+2.5%Mn</td>
<td>11.54</td>
<td>2.31</td>
<td>0.55</td>
<td>Bal</td>
<td></td>
</tr>
<tr>
<td>Al-12%Si+5.0%Mn</td>
<td>11.54</td>
<td>4.60</td>
<td>0.66</td>
<td>Bal</td>
<td></td>
</tr>
<tr>
<td>Al-12%Si+0.5%Mn+0.01%Ca</td>
<td>11.55</td>
<td>0.90</td>
<td>0.01</td>
<td>0.72</td>
<td>Bal</td>
</tr>
<tr>
<td>Al-12%Si+0.5%Mn+0.02%Ca</td>
<td>11.55</td>
<td>1.00</td>
<td>0.03</td>
<td>0.60</td>
<td>Bal</td>
</tr>
<tr>
<td>Al-12%Si+0.5%Mn+0.05%Ca</td>
<td>11.58</td>
<td>1.02</td>
<td>0.06</td>
<td>0.55</td>
<td>Bal</td>
</tr>
<tr>
<td>Al-12%Si+0.5%Mn+0.10%Ca</td>
<td>11.56</td>
<td>1.00</td>
<td>0.11</td>
<td>0.47</td>
<td>Bal</td>
</tr>
</tbody>
</table>

**Table 2 Results of the Mechanical Test on the Alloys**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (N/mm²)</th>
<th>% elongation (%)</th>
<th>Impact strength (J/M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-12%Si</td>
<td>99.70</td>
<td>1.40</td>
<td>1.10</td>
</tr>
<tr>
<td>Al-12%Si+0.5%Mn</td>
<td>112.30</td>
<td>9.20</td>
<td>2.20</td>
</tr>
<tr>
<td>Al-12%Si+1.0%Mn</td>
<td>121.90</td>
<td>10.90</td>
<td>2.60</td>
</tr>
<tr>
<td>Al-12%Si+1.5%Mn</td>
<td>126.40</td>
<td>11.10</td>
<td>3.50</td>
</tr>
<tr>
<td>Al-12%Si+2.5%Mn</td>
<td>131.10</td>
<td>12.70</td>
<td>4.30</td>
</tr>
<tr>
<td>Al-12%Si+5.0%Mn</td>
<td>123.20</td>
<td>7.20</td>
<td>4.60</td>
</tr>
<tr>
<td>Al-12%Si+0.5%Mn+0.01%Ca</td>
<td>126.60</td>
<td>11.90</td>
<td>4.60</td>
</tr>
<tr>
<td>Al-12%Si+0.5%Mn+0.02%Ca</td>
<td>129.20</td>
<td>14.00</td>
<td>6.60</td>
</tr>
<tr>
<td>Al-12%Si+0.5%Mn+0.05%Ca</td>
<td>134.40</td>
<td>15.50</td>
<td>7.00</td>
</tr>
<tr>
<td>Al-12%Si+0.5%Mn+0.10%Ca</td>
<td>132.00</td>
<td>12.40</td>
<td>6.30</td>
</tr>
</tbody>
</table>

![Fig. 1 Effect of Mn on Tensile Strength of Al-12%Si alloy](image)

![Fig. 2 Effect of Mn on % Elongation of Al-12%Si alloy](image)
In Figures 1-3, it was observed that the tensile strength, % elongation and impact strength increased insignificantly as the concentration of Mn increased. Better mechanical properties were achieved when the alloy were refined with calcium as observed in Figures 4-6. This was because at this level the silicon particles were greatly reduced and distributed homogenously at the grain boundaries (Nnuka, 1994). The results showed that the mechanical properties improved in comparison with the reference sample of the alloy and these confirmed the report that a small amount of Ca is effective in improving the fracture toughness even in alloys having relatively high iron content (Kobayashi et al, 1979). The dramatic decrease in the properties beyond 0.05%Ca addition could be as a result of overmodification of eutectic Si leading to the formation of porous Al-Ca-Si intermetallics in the sample as observed by Kobayashi in 1993 that Ca-containing intermetallics form at high levels of Ca addition (Al-Ca-Si) which leads to higher porosity in the casting (Kobayashi et al, 1993). These observations confirm the result of a research work on the mechanical properties of aluminium alloy where it was reported that the effects of alloying elements on the mechanical properties are generally an increase of hardness, tensile strength and a decrease in plasticity (Mbuya, 2003).
Micro-structural examination

Plate 1. Al-12%Si alloy  x300

Plate 2. Al-12%Si-0.5%Mn  x300

Plate 3. Al-12%Si-1.0%Mn  x300

Plate 4. Al-12%Si-1.5%Mn  x300

Plate 5. Al-12%Si-2.5%Mn  x300

Plate 6. Al-12%Si-5.0%Mn  x300

Plate 7. Al-12%Si-0.5%Mn+0.01%Ca  x300

Plate 8. Al-12%Si-0.5%Mn+0.02%Ca  x300
The photomicrographs Plates 1-10 are the results of eutectic alloys corrected for iron content. Plate 1 consists of finger-like spikes of the brittle Fe intermetallic platelets and coarse primary eutectic Si and aluminium. Plates 2-6 show the eutectic composition of the alloy modified with manganese. Here, the distributions of silicon finger-like spikes are not uniform over entire sample and the sizes of silicon needles are not refined. There has been presence of primary nucleated silicon phase that clustered together confirming its lead at the growth interface. Plates 7-10 show micrographs of the Al-12%Si alloy modified with Mn and doped with different percentages of calcium. Plates 7 and 8 showed a remarkable reduction in the sizes of the platelets and eutectic Si by changing its morphology from acicular to fine fibrous form. In Plate 9, it was observed that the spheroidised silicon crystals are interspaced with aluminium and distributed uniformly between grain blocks and this improved the mechanical properties of these alloys. There has been significant reduction in the size of the platelet of Fe intermetallic to very fine form as observed in Plate 10 hence, the precipitation of Al-Si-Ca intermetallic.

VI. CONCLUSION
The results from this research work have clearly explained the following facts; that a low level of calcium addition reduces porosity in the alloy by refining the eutectic Si morphology from acicular to fine fibrous form with improved mechanical properties. It was also established that fine distribution of silicon particles in the alloys improved the structural and mechanical properties of the Al-Si alloys and finally, this paper has x-rayed the mechanism of structural modification and refinement of eutectic alloys with calcium.

REFERENCES


