Effect of Magnesium and Manganese on the Secondary Phase and Mechanical Properties of Aluminium-4% Copper Alloy

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Abstract - The effect of magnesium and manganese on the secondary phase and mechanical properties of aluminium-4% copper alloy was studied using standard techniques. The dopants were added in concentration of 0.25%, 0.5%, 0.75%, and 1% by weight by mixing with stirrer and cast by gravity die casting. Subsequently the specimens were subjected to machining. The Mechanical properties such as ultimate tensile strength, hardness and impact strength were determined for each specimen. The microstructure of the samples was also studied using metallurgical microscope with image analysis software for measuring grain size and dendrite arm spacing and the photographs taken. The results obtained from the study showed that the ultimate tensile strength and hardness value of the alloy increased with increase in the concentration of magnesium. Manganese reduced all the mechanical properties in the order of its increasing concentration. The micro-structural analysis result showed that magnesium refines the grain size and dendrite structure, and manganese retarded the precipitation of the strengthening or secondary phase in the alloy in the order of its increasing concentration. Results obtained showed a striking dependence of the mechanical properties on the atomic sub-structure of the dopants such as atomic size and valence electrons concentration.

Keywords: secondary phase, dopants, grain size, dendrite, valence electrons, concentration, atomic size.

INTRODUCTION

Aluminium alloys have highly heterogeneous microstructures compared to many other metal alloys (Birbilis et al; 2005). This heterogeneity originates from alloy additions and impurities which combine to produce the desired microstructure as well as undesired large particles, called constituent particles and residual impurity particles which have a range of compositions (Chester et al; 1983). Strengthening in non-heat-treatable alloys occurs from solid solution formation, second phase microstructure constituents and dispersed precipitates etc. For those elements that form solid solutions, the strengthening effect when the element in is solution tends to increase with increasing difference in the atomic size of the solvent (Al) and solute atoms (alloying element) (Dieter, 1988). Recently, aluminium-base alloys have been actively replacing various ferrous components in automobiles to reduce the weight and improve the performance. Strengthening in aluminium alloys can be achieved by the difference in atomic diameter between the alloy metals. Since no two elements have the same atomic diameter, solute atoms will be either smaller or larger in size than the solvent atoms. Due to the difference in size, lattice distortion is produced when one element is added to the other (Kojima, 1974). The solute atom with smaller atomic radius will occupy the empty spaces (interstices) in the solvent, but solute atom with bigger atomic radius will occupy the position normally occupied by the solvent atoms in a solution (Wang et al 2004). The interstitial atom produces a local tensile stress field and the substitution atom produces a local compressive field in the solvent matrix (Gable et al; 2004). In both cases, the stress field of a moving dislocation interacts with the stress field of the solute atom which increases the stress required to move the dislocation through the crystal (Grushko et al; 2004). Atomic size difference has a great effect on the hardness and tensile strength of a material. With the increase in the atomic size difference between the solute and the solvent, the intensity of stress field around solute atoms increases (Nnuka, 1991). This increase in stress field leads to increase in resistance to the dislocation movement, thereby increasing the tensile strength and hardness of the alloy (Suarez et al; 2011). The tensile strength and hardness of aluminium alloy can also be determined by the amount or number of solute atoms in the matrix. An increase in the amount of solute or the number of solute atom causes...
greater local distortion in the lattice which leads to increase in resistance to the dislocation motion (Eixeira et al; 2008).

The solubility of copper in aluminium matrix increased with increasing temperature and the maximum solubility of copper in aluminium matrix is at the eutectic temperature (540°C) with maximum concentration of 5.7%. The widely use of aluminium-4% copper alloy in automotive components, such as space frames, engine blocks, wheel frames, and housings, aircraft, aerospace, ships and boat making, armored vehicles, baseball bats and bicycle frames, screws, bolts, fittings, and machinery components, industrial and architectural components makes it necessary for them to possess both high strength-to-weight ratio and hardness (Castillo et al; 2000). The high strength, and hardness or reliability of aluminium-4%-wt copper alloy is dependent on the percentage of copper in solution (α-solid solution of copper in aluminium matrix) and on the form, size, number, and the distribution pattern of the intermetallic compound. The increase in strength is proportional to $C^{1/2}$, where C is the solute concentration. For atomic solutions, there is a linear relationship between the concentration of the solute and increase in strength of the material (Castillo et al; 2000). As the concentration of the alloying element increases, there will be an increase in local distortion in the lattice, thereby causing more hindrance to the dislocation movement in an alloy (Chester et al; 1983). The nature of distortion created in a lattice has a greater effect on the mechanical properties of an alloy. Substitutional solute atoms create spherical distortion which creates less hindrance to the dislocation motion than non-spherical distortion produced by interstitial solute atoms (Polmear, 1995). The increase in hardness and tensile strength is due to the interaction of the stress field around the particles with the stress field of a moving distortion and also due to physical obstruction by the hard particles to the moving dislocation (Nnuka, 2000). The extent to which strengthening is produced depends upon the amount of second phase particles, the characteristics and properties of second phase, and the particles size, shape and distribution (Nnuka, 1991).

One method to achieve required mechanical properties is the addition of alloying elements that dissolve in solid solution at elevated temperatures and precipitate out at lower temperature (Kanibolotsky et al; 2004). The increased yield strength in these alloys is due to a very high density of precipitates of Al-Cu intermediate phases. The density of such precipitates is determined by the processes of nucleation, growth and coarsening. A high precipitate nucleation rate is essential to produce a dense array of precipitates that enhance hardness (Kojima, 1974).

2.1 Materials and method

2.2 Materials sourcing and preparations.

Aluminium wire (99.9% pure) and copper powder were used as the base materials in this study, while magnesium and manganese were used as the dopants in various compositions. The mass by weight of the materials were calculated using weight percent calculation and the mass of each material was measured using the weighing balance.

2.3 Method

Aluminium (99.9% pure) was melted in the furnace and copper powder was dissolved in the aluminium melt. The dopants were added in concentration of 0.25%, 0.5%, 0.75%, and 1% by weight in interval of 0.25% mixing with stirrer and cast by gravity die casting. Subsequently the specimens were machined to the required dimensions for the various mechanical tests. The specimens for microstructure examination were grinded using different grades of emery paper (230, 240, 400 and 600 grits respectively), polished using gamma alumina (aluminium oxide: Al$_2$O$_3$) and etched in Keller’s reagent.

3.1 Result and discussion

3.2 Micrographs and quantitative microstructure analysis of studied specimens

Plates: 1–9 represent the micrographs of aluminium-4% copper alloy doped with different alloying elements. This was done using metallurgical microscope.

Plate 1: Micrograph of Al-4%Cu (x400)
A- intermetallic compound; B – α-solid solution; C – grain boundary

The micrograph of the control specimen (Al-4%wtCu) presented in Plate 1; showed that the microstructure of the control specimen comprise of the eutectic α-solid solution (the region where copper formed a solid solution with the aluminium matrix) and the intermetallic compound (Al₂Cu) precipitates. Plate 1 also shows that the intermetallic compound existed in form of coarse needle-like precipitates separated from the α-solid solution by the grain boundary.

Plate 2: Micrograph of Al-4%Cu-0.25%wtMg (x400)

Plate 3: Micrograph of Al-4%Cu-0.5%wtMg (x400)

Plate 4: Micrograph of Al-4%Cu-0.75%wtMg (x400)
A- intermetallic compound and B – α-solid solution

Plates 2-5 show the micrographs of aluminium-4% copper alloy doped with 0.25%wt, 0.5%wt, 0.75%wt and 1%wtMg respectively. The micrographs show dendrites of aluminium solid solution as the primary phase, with a eutectic mixture filling the interdendritic spaces. The eutectic is of the divorced type-particles of a second phase in a solid solution. The second phase can be intermetallic compounds that contain aluminium and one or more alloying elements (Al₂Cu and Al₃CuMg). These soluble phases: Al₂Cu or Al₃CuMg appeared in various amounts and at various locations in the microstructure, depending on the concentration of magnesium. The addition of magnesium allows the formation of more intermetallic compounds. Magnesium gives rise to the formation of copious amounts of non-coplanar, lenticular shaped precipitates. Plate 2-5 also show that the size of the precipitates formed reduced, increased in number and dispersed evenly as the concentration of magnesium increased in the alloy matrix.
Plate 7: Micrograph of Al-4%Cu-0.5%wtMn (x400)

Plate 8: Micrograph of Al-4%Cu-0.75%wtMn (x400)

Plate 9: Micrograph of Al-4%Cu-1%wtMn (x400)
A- intermetallic compound and B – α-solid solution

Plates 6-9 represent the micrographs of aluminium-4% copper alloy doped with different concentration of manganese (0.25%wt, 0.5%wt, 0.75% and 1%wt Mn). The micrographs show that manganese increases the quantity of the eutectic in aluminium-4% copper alloys system, which exists in the form of a continuous mesh of precipitates at the grain boundaries, but no change in the distribution pattern. Manganese contributed to the formation of the stable dispersion strengthening phase, which is known to aid in grain size control with little removal of copper in the form of coarse intermetallic compound.

3.3 Mechanical properties

![Mechanical Properties Graph](image1)

Figure 1.1: Effect of magnesium concentration on ultimate tensile strength (UTS) and hardness of Al-4%Cu alloy

![Mechanical Properties Graph](image2)

Figure 1.2: Effect of magnesium concentration on impact strength (energy absorbed) and percentage elongation of Al-4%Cu alloy
Figures 1.1-1.4 represent the mechanical properties of aluminium-4% copper alloy doped with magnesium and manganese. An increase in ultimate tensile strength and hardness with corresponding decrease in ductility and impact strength were noted when the alloy is doped with magnesium. This could be as a result of the closer packed structure developed because of the formation of substitutional solid solution between the aluminium lattices and the magnesium atoms. Secondary, the valence electron of magnesium atoms were contributed to the electron cloud in accordance with the Summer-field electron theory, so enhancing a stronger metallic bond between the atoms. The
bond is non-specific and non-directional acting strongly in all directions and resulting to a highly coordinated close packed structure and hardening of the alloy. The tensile strength and hardness also increased as the composition of magnesium (positive nuclei) increased. With increase in the concentration of magnesium, more of its atoms also went into bonding in the substitutional solid solution with the aluminium lattice and resulted to strengthening of the alloy. It was also observed from the bar charts (Figure 1.2 and 1.3), that magnesium among the dopants produced the maximum ultimate tensile strength and hardness. Magnesium acts as a grain refiner and hence reduces the grain size as well as the dendritic arm spacing of the alloy and thereby created more grain boundaries in the alloy matrix which resulted to increased strength and hardness. Magnesium also promotes the formation of insoluble hard particles that hinders or impedes the dislocation motion. A decrease in mechanical properties was observed from the Figures 1.1 to 1.4 with the increased concentration of manganese in the alloy. Manganese-bearing phases such as Al₃CuMn caused the solid solution level of copper in the matrix to decrease. More importantly, increasing the manganese solution level retards the precipitation of the strengthening phases in the alloy. Figures 2 and 3 shows that manganese improved the ultimate tensile strength and hardness of Al-4%Cu alloy at a certain level of concentration, but decreases as the concentration increased. This could be as a result of the inability of manganese to form solid solubility in aluminium matrix as its concentration increases.

4.1 Conclusion and Recommendation

4.2 Conclusion
Mechanical properties such as hardness and ultimate tensile strength increased slowly with increase in concentration of magnesium with a corresponding decrease in ductility and impact strength. The increased ultimate tensile strength and hardness were due to simultaneous formation of both θ (AlₓCu) and S’ (AlₓCuMg) intermetallic compounds respectively and a decrease in grain size and dendritic structure as was shown in Plates 2-5, 10- 16. This was also as a result of the spherical structures developed as a result of the formation of substitutional solid solution formed between the aluminium lattices and the dopants atoms. From the Figures, it was also noted that all the mechanical properties decreased with increase in the concentration of manganese. Plates 6-9 showed that at levels beyond a maximum of 0.5%wt Mn, it has been shown to lead to the formation of large fractions of coarse and brittle constituents which act as crack initiators and reduce the mechanical properties of the material. Above all, the study found that:

1. The effect of the dopants on the mechanical properties depends on the concentration of the alloying elements. This was confirmed by the effects of the variation of the composition of the alloying elements.
2. The mechanical properties are dependent on the atomic size of the alloying element.

3. With increased amount of magnesium in the alloy, the average values of the dendrite arm spacing and grain size decreased.
4. The addition of magnesium in increasing concentration of 0.25, 0.5, 0.75, and 1% shows, in the same order, increase in ultimate tensile strength and hardness with a corresponding decrease of relative elongation and impact resistance.
5. Finest grain size and dendrite arm spacing were obtained when the concentration of magnesium was 1%wt Mg.
6. In the range of dopants additions tried, the sample containing 1%wt Mg seems to be most favorable alloy in terms of tensile strength and hardness.
7. Manganese reduced all the mechanical properties in the order of its increasing concentration.
8. The tensile strength and hardness of aluminium alloy can also be determined by the amount or number of solute atoms in the matrix. An increase in the amount of solute or the number of solute atom causes greater local distortion in the lattice which leads to increase in resistance to the dislocation motion.
9. Dopants do neither form any independent phase nor create any new phase with Al-4%Cu alloy system.

4.1 Recommendation
1. When the dopants are properly added to the alloy, a suitable structure hence improved properties are obtained. These properties necessitate the widely use of the alloy in aerospace and automobile industries.
2. When properly alloyed, the material could be used for automotive components, such as space frames, engine blocks, wheel frames, and housings etc. Cast Al-4%Cu-Mg and Al-4%Cu-Mn alloys are widely used in aircraft, aerospace, ships and boat making, industrial and architectural applications for their good mechanical properties of high strength-to-weight ratio.
3. It is advisable to understand the service condition of a particular alloyed material and try to combine the needed properties properly by addition of alloying elements in right proportion. When a material needs to combine many properties like high strength and hardness, low density, rigidity, corrosion resistance, and machinability etc, it is advisable to add the alloying elements in right proportion.
4. The concentration of manganese in the alloy (Al-4%Cu) should not be in excess (>1) to avoid formation of brittle structure, which could be detrimental to the service life of the material.
5. About 1%wt of magnesium should be added to Al-4%Cu alloy, in order to obtain a suitable structure with refined grains and reduced dendrite structures which will give the best mechanical properties.
REFERENCES

APPENDIX

Appendix 1: Mechanical properties of aluminium-4% copper alloy doped with magnesium and manganese.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Alloy composition</th>
<th>%E</th>
<th>UTS (MPa)</th>
<th>BHN</th>
<th>Energy absorbed (Joules)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Al-4%Cu</td>
<td>7.0</td>
<td>77</td>
<td>450</td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>Al-4%Cu-0.25%Mg</td>
<td>1.6</td>
<td>94</td>
<td>540</td>
<td>0.30</td>
</tr>
<tr>
<td>3</td>
<td>Al-4%Cu-0.5%Mg</td>
<td>1.3</td>
<td>102</td>
<td>635</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>Al-4%Cu-0.75%Mg</td>
<td>0.6</td>
<td>132</td>
<td>720</td>
<td>0.09</td>
</tr>
<tr>
<td>5</td>
<td>Al-4%Cu-1%Mg</td>
<td>0.3</td>
<td>150</td>
<td>729</td>
<td>0.04</td>
</tr>
<tr>
<td>6</td>
<td>Al-4%Cu-0.25%Mn</td>
<td>4.7</td>
<td>140</td>
<td>463</td>
<td>0.70</td>
</tr>
<tr>
<td>7</td>
<td>Al-4%Cu-0.5%Mn</td>
<td>4.5</td>
<td>103</td>
<td>454</td>
<td>0.64</td>
</tr>
<tr>
<td>8</td>
<td>Al-4%Cu-0.75%Mn</td>
<td>3.4</td>
<td>92</td>
<td>445</td>
<td>0.50</td>
</tr>
<tr>
<td>9</td>
<td>Al-4%Cu-1%Mn</td>
<td>1.5</td>
<td>84</td>
<td>405</td>
<td>0.20</td>
</tr>
</tbody>
</table>

NOTE: %E – Percentage elongation, MTL – Maximum tensile load (N), and UTS – Ultimate tensile strength (MPa).