MECHANICAL PROPERTIES AND PRECIPITATION BEHAVIOR AS A FUNCTION OF HEAT TREATMENT OF Al–4.4Cu–1.5Mg-0.6Mn-0.25Si (WT %) ALLOY

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ABSTRACT

The aim of the present paper is to investigate the mechanical properties and precipitation behavior of the Al–4.4Cu–1.5Mg-0.6Mn-0.25Si (wt%) alloy as a function of heat treatment. The X-Ray diffraction analysis (XRD), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Microhardness Vickers test (HV) have been used to examine the effects of microalloying and the origins of hardening precipitates during heat treatment. The combined application of these techniques is particularly important in the study of nanoscale precipitation processes. The solute clusters precede the formation of GP zones or precipitation and have a defining role on the nature and kinetics of the subsequent precipitation processes. The lower values of the activation energy of the precipitate particles indicate that, the driving force of the clustering process is low and the Cu addition to this kind of alloys enhances the clustering process.

KEYWORDS: Electron Microscopy, Microhardness Measurement, X-Ray Diffraction, Aluminum Alloys, Age Hardening, Precipitation

INTRODUCTION

Aluminum alloys are used in a wide range of applications in transport, packaging, building and many engineering sectors. In recent decades, there is a trend in the automobile industry to use aluminum alloys as car body panels to reduce weight and thus improve fuel economy and emissions [1]. Both Al–Mg alloys, which are mostly non-heat-treatable and heat-treatable Al–Cu, Al–Mg–Si–Cu and Al–Mg–Si alloys are used. Although the Al–Mg–Mn alloys have good formability, they have a relatively low strength with a tendency of Lüders band formation [2, 3], which restricts their use to interior structural applications. Hence, for automotive applications, there is a growing trend to exploit new alloys [4, 5]. The alloys AA5182 and AA5052 with composition around Al–3Mg–0.3Mn–0.1Cu–0.2Si with small Cu additions are very promising candidates for these applications because of their excellent formability, good strength and the benefits of precipitation hardening during paint-baking due to Cu additions [6]. However, precipitation hardening induced by Cu additions make the interactions between work hardening, recovery and precipitation more complicated during processing. Precipitation strengthening is applied to some aluminum alloys. Precipitation strengthening is one of the most important hardening methods used to increase strength in aluminum alloys.

The hardness and strength values increase as a result of precipitation of a new precipitate due to period and heat from supersaturated solid solution [7, 8]. The 2024 Alloy is an aluminum alloy containing copper, magnesium, manganese and some minor alloying elements. It is fabricated mainly by hot extrusion and hot rolling. It has the highest hardness value between aluminum alloys. The values of elasticity modulus and strength of 2024 aluminum wrought alloy are high. It is used in engineering applications such as aero plane constructions, orthopedic soles, rivet and pulling wheels. One of the most important property of the 2024 aluminum alloy is that, the treatment of solid solution is not so critical [9, 10]. This alloy can be aged naturally or artificially. The 2024 Aluminum wrought alloy has Mg, so its production is made by special methods. The formability of this alloy is very good and its corrosion resistance is higher than other aluminum alloys. The physical and mechanical properties of 2024 aluminum wrought alloy are very good [11-16]. The high mechanical property
levels of 2024 alloy make it ideal for the applications which require high strength. Typical applications include aircraft fittings and structures, computer parts, gears, shafts, hinge pins, valve blocks and valve parts, bolts, nuts, fasteners, truck parts and brake components. In Al–4.4Cu–1.5Mg-0.6 Mn-0.25 Si alloy that is used in this study, the element provides precipitate is copper. The principal precipitation-hardening reactions however, are those of the ternary aluminum–copper–magnesium system [17, 18]. The commercially important alloys contain copper as major addition and the phase reactions which occur are those between an aluminum solid solution and the intermetallic phases CuAl₂ and CuMgAl₂. Precipitation hardening at high ratios of copper to magnesium is achieved in the sequence GP zones through a coherent phase (θ') to CuAl₂ (θ). Precipitation hardening at lower ratios of copper to magnesium is achieved in the sequence GP zones through a coherent phase to S (CuMgAl₂). These intermetallic precipitates are incoherent with main structure and affect on mechanical and physical properties of the material [19–21]. The main purpose of this study is to investigate in details the effect of aging temperature and time on the strength and microstructure of the Al–4.4Cu–1.5Mg-0.6 Mn-0.25 Si alloy. The activation energies which control the developed precipitates could be determined.

EXPERIMENTAL PROCEDURES

Materials participating in the alloy subjected to the present study and their percentage sharing (in wt. %) are given in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Mg</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Zn</th>
<th>Cr</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual</td>
<td>0.25</td>
<td>1.5</td>
<td>0.25</td>
<td>4.4</td>
<td>0.6</td>
<td>0.12</td>
<td>0.05</td>
<td>Balance</td>
</tr>
<tr>
<td>Nominal</td>
<td>0.5</td>
<td>0.5</td>
<td>3.8-4.9</td>
<td>0.3-0.9</td>
<td>0.25</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

X-ray diffraction analysis was performed using a powder diffractometer (Philips Type PW 1710) equipped with graphite monochromator and automatic diversion slit. Sheet samples with 18×14 mm² area and thickness of 1mm were used in this study. The measurements were swapped from 2θ =5º to 90º with a scanning speed of 0.06/sec, operating potential of 40 kV and 30 mA current. The target used is Cu and the incident wavelength is 0.154187 nm. A computer program and an automatic unit attached to the X-ray diffractometer gives directly the data of 2θ, D spacing and the intensity of each reflection plane. The contribution of the Kα₂ radiation can be subtracted from the total profiles; the result obtained then corresponds to the Kα₁ component of the Kα doublet. All the x-ray diffraction investigations are performed at room temperature. The differential scanning calorimetry (DSC) technique was used to follow the precipitation processes which take place in the studied alloy during continuous heating with constant rates of quenched specimens from the solid solution state. Disc-shaped samples of 5 mm diameter and 0.5 mm thickness of average weight of ~24 mg are machined from the alloy ingot.

The specimens were solution heat treated for 1 h at 803 K in a standard convection furnace and then quenched into a mixture of ice and water at equilibrium (~273 K). An annealed pure aluminum disc of similar shape and mass was used as a reference. Non-isothermal scans for the as-quenched specimens using a DSC thermal analyzer (DSC-DO 8T-12TG01 type Shemadzu) at different heating rates 5, 10, 15, 20, 30, 40 and 50 K min⁻¹ were carried out. The DSC measurements were performed between room temperature and 773K in purified nitrogen flow at a rate of 30 ml min⁻¹. The output signal is in mW and the net heat flow to the reference material was recorded with temperature. The peak temperature of the reaction processes was identified with an uncertainty of (± 0.1 K) using the microprocessor of the thermal analyzer.
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For SEM observations, disc shaped specimens of 10 mm diameter and 1 mm thickness were prepared and polished. The specimens were solution heat treated at 803 K for 1 h and then quenched into water maintained at ~273 K. Before microscopic examinations, the surfaces of the specimens were gently polished by 0.25 μm diamond paste to remove the surface reactions that may occur during heat treatment. Then, the specimens were etched using a solution of 1%HF+2.5%HNO₃ (by volume) in H₂O. The SEM examinations were performed after aging for 30 mins at the temperature of the developed precipitate using a scanning electron microscope (SEM, JEOL JSM-5400LV, Japan). For Transmission Electron Microscopy (TEM) examinations, thin foils were prepared from the quenched and aged specimens. Thin discs of 3 mm diameter were punched from the foils and then electropolished by the twin-jet technique using a solution of 25% nitric acid and 75% methanol cooled to 263 K. The electropolishing was performed using a DC current source operating at ~20V. The TEM examinations were performed after aging the sample for 30 min at temperature of the developed precipitate using a transmission electron microscopy (TEM, JEOL JEM-100 CXII). It was operated at 100 kV to avoid sample damage by the electron beam. All images were taken by a charge-coupled device (CCD) camera XR41.

For isochronal microhardness (HV) measurements, disc shaped specimens of about 15 mm diameter and 2 mm thicknesses were used. The surfaces of the specimens were mechanically polished. The final polishing was achieved using (Struers) diamond paste of ≤0.25 μm grain size and a piece of cloth. Prior to every HV measurement, the specimen surfaces were gently polished by the 0.25 μm diamond paste to remove the surface reactions that may occur during the heat treatment. The microhardness measurements were performed using Vickers method. The probable error in HV is due to the diagonal of impression measurement, which leads to an overall error in HV of about 3%.

RESULTS AND DISCUSSIONS

Structure Properties

In order to determine the crystalline phases that precipitated in the annealed sample the X-ray diffraction pattern of the studied alloy was analyzed. Figs. 1(a and b) show XRD patterns of the as-prepared and annealed samples of the studied alloy.

![Figure 1: The X-ray Diffraction Patterns of the Studied Alloy (a) As Quenched, Aged at 580 K, 615 K and 738 K, and (b) is a Representative Pattern of the Studied Alloy Aged at 738 K](image)

The crystallites size (D) were calculated from the Scherer’s formula from the full-width at half-maximum (FWHM) of the peaks expressed in radians [22].
\[ D = \frac{\text{d}_{\text{exp}}}{\text{d}_{\text{stand}}} \]  

(1)

Where \( D \) is the average particle size, \( \text{d}_{\text{exp}} \) is the X-ray wavelength used, \( \text{d}_{\text{stand}} \) is the FWHM calculated from the (111) plane and \( \theta \) is the Bragg angle. The strain value \( \varepsilon \) is calculated from the slope of \( \frac{\text{d}_{\text{exp}}}{\text{d}_{\text{stand}}} \) versus \( \sin \theta \) plot using the relation [22].

\[ \varepsilon = \frac{\lambda}{D_{\text{exp}}} - \text{d}_{\text{stand}} \]  

(2)

The dislocation density \( (\rho) \), is defined as the length of dislocation lines per unit volume of the crystal and is given by \( \rho = \frac{1}{D^2} \) [23]. The values of particle size, strain and dislocation density for the studied alloy at different aging temperatures are listed in table 2.

**Table 2: Structure Parameters of the Studied Alloy at Different Aging Temperatures**

<table>
<thead>
<tr>
<th>Aging Temp.(K)</th>
<th>( d_{\text{exp}} )</th>
<th>( d_{\text{stand}} )</th>
<th>( h ) ( k ) ( l )</th>
<th>Kind of phase</th>
<th>Grain size D (nm)</th>
<th>Strain values (( \text{ln}^2 \cdot \text{m}^{-2} ))</th>
<th>Dislocation density ( \rho \times 10^{10} ) (lines/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>580</td>
<td>3.884</td>
<td>3.883</td>
<td>1 1 0</td>
<td>Al-CuMg</td>
<td>13.67</td>
<td>0.0534</td>
<td>0.535</td>
</tr>
<tr>
<td></td>
<td>2.289</td>
<td>2.299</td>
<td>1 1 1</td>
<td>Al</td>
<td>29.59</td>
<td>0.00344</td>
<td>0.114</td>
</tr>
<tr>
<td>615</td>
<td>3.879</td>
<td>3.883</td>
<td>1 1 0</td>
<td>Al-CuMg</td>
<td>7.56</td>
<td>0.01037</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>2.289</td>
<td>2.299</td>
<td>1 1 1</td>
<td>Al</td>
<td>31.60</td>
<td>0.00614</td>
<td>0.100</td>
</tr>
<tr>
<td></td>
<td>1.201</td>
<td>1.203</td>
<td>1 3 7</td>
<td>MgCuAl</td>
<td>45.17</td>
<td>0.00072</td>
<td>0.049</td>
</tr>
<tr>
<td></td>
<td>1.338</td>
<td>1.337</td>
<td>2 2 8</td>
<td>MgAl₂</td>
<td>37.42</td>
<td>0.00053</td>
<td>0.071</td>
</tr>
<tr>
<td>738</td>
<td>3.884</td>
<td>3.883</td>
<td>1 1 0</td>
<td>Al-CuMg</td>
<td>19.55</td>
<td>0.00398</td>
<td>0.261</td>
</tr>
<tr>
<td></td>
<td>2.292</td>
<td>2.299</td>
<td>1 1 1</td>
<td>Al</td>
<td>33.09</td>
<td>0.00608</td>
<td>0.091</td>
</tr>
<tr>
<td></td>
<td>1.879</td>
<td>1.888</td>
<td>6 0 3</td>
<td>CuAl</td>
<td>36.84</td>
<td>0.00102</td>
<td>0.073</td>
</tr>
<tr>
<td></td>
<td>1.296</td>
<td>1.295</td>
<td>3 0 7</td>
<td>MgAl₂</td>
<td>16.40</td>
<td>0.00157</td>
<td>0.371</td>
</tr>
<tr>
<td></td>
<td>1.201</td>
<td>1.203</td>
<td>1 3 7</td>
<td>MgCuAl</td>
<td>46.12</td>
<td>0.000524</td>
<td>0.047</td>
</tr>
</tbody>
</table>

It is found that, the strain and dislocation density decrease with increasing the aging temperature which indicates the improvement, coarsening and stability in the precipitated particle which increases the hardness of the investigated sample. Fig. 1 shows that the number of precipitated phases in the lower aging temperature 580 K is lower than that of the higher aging one whereas the increase of the aging temperature increases the dissolution of pre-precipitated phases in the lower temperature. These pre-precipitated phases in the higher aging temperatures become the nucleated sites of the more stable phases as S (Al₂CuMg) phase.

**DSC Measurements**

Fig. 2(a) shows typical non-isothermal DSC traces of the supersaturated Al–4.4Cu–1.5Mg-0.6Mn-0.25Si alloy performed at different heating rates ranging from 5 to 50 K min⁻¹. The DSC scans are carried out from room temperature up to 773 K. Four exothermic reaction processes can be identified from the DSC traces indicated by I, II, III and IV as shown in Fig. 2(b) for representative heating rate of 30 K min⁻¹. It is found that, the thermal transition data are shifted to higher temperatures with increasing the heating rate. This confirms the thermally activated nature of these reactions. The first exothermic peak I is ascribed to the formation of Cu-Mg-Mn-vacancy clusters and GP zones, where this reaction takes place at a wide range of temperature ranging from 370 to 417 K depending on the heating rate. The second exothermic peak II, may be attributed to the precipitation of the coherent needle shaped precipitates \( \theta^0 \). The third exothermic peak III, may be due to the transformation from coherent \( \theta^0 \) to incoherent \( \theta \) (Al₂Cu) particles. The peak IV, can be explained by the precipitation of the equilibrium S (Al₂CuMg) phase precipitates.
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Figure 2: DSC Traces of the Al–4.4Cu–1.5Mg-0.6Mn-0.25Si Alloy at (a) Different Heating Rates Ranging from 5 to 50 K Min⁻¹, (b) Large Magnification of the DSC Curve at 30 K Min⁻¹

To confirm these results, the SEM examinations are carried out for specimens heated at a rate of 30 K min⁻¹ up to a temperature of 540 K, 620 K and 750 K and aged at this temperatures for 20 min. Scanning electron microscopy examination revealed needle shaped from θ' precipitates, rod shaped from θ (Al₂Cu) precipitates and equilibrium plat shaped from S (Al₂CuMg) as shown in Figs. 3(a, b and c) respectively. The SEM micrograph of the specimen aged at 750 K for 30 min Fig. 3(c) which indicates the existence of the equilibrium S (Al₂CuMg) phase precipitates confirms the result of X-ray diffraction pattern.

A confirmation of these phases existence were obtained from the TEM micrograph given in Fig. 4a and b for specimens heated at the same rate of 30 K min⁻¹ to the corresponding peak temperature 620 K and 750 K kept there for 30 min and then cooled to room temperature. Careful inspection of the TEM micrograph shows rod shaped precipitates characterizing the evolution of θ (Al₂Cu) fig. 4-a and plate shaped S (Al₂CuMg) phase precipitates Figure 4-b.
Figure 4: TEM Micrograph Shows the Nanoscale Precipitates in Al–4.4Cu–1.5Mg–0.6Mn–0.25Si Heated at 20 K Min⁻¹ Up To (a) 620 K and (b) 750 K and Aged for 30 Min

Phase Transformation Mechanism

The transformation processes (precipitation and dissolution of the precipitates) are always related to the concept of the activation energy. Also, the study of the precipitation processes is associated with nucleation and growth processes dominating in supersaturated alloys. In general, separate activation energies must be identified with individual nucleation and growth steps in a specific transformation, although they have usually been combined into an activation energy representative of the overall precipitation process [24]. From the results of the DSC traces, the dependence of a certain process peak temperature $T_p$ on the heating rate $\gamma$ can be used to evaluate the activation energy of that process by applying one of the non-isothermal thermo-analytical studies proposed by Kissinger and Starink [25] as shown in Table 3.

Table 3: Activation Energies of the Precipitated Particles in the Studied Alloy

<table>
<thead>
<tr>
<th>Process</th>
<th>Activation energies, kJ mol⁻¹</th>
<th>Kissinger</th>
<th>Starink</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP Zones</td>
<td>25.2 ± 0.6</td>
<td>25.4 ± 0.1</td>
<td>25.3 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>$\theta$ phase</td>
<td>111.8 ± 0.5</td>
<td>112.0 ± 0.5</td>
<td>111.9 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>$\theta$ phase</td>
<td>107.0 ± 0.4</td>
<td>106.0 ± 0.8</td>
<td>106.5 ± 0.6</td>
<td></td>
</tr>
</tbody>
</table>

These methods are based on the Avrami treatment of transformation kinetics and define an effective crystallization rate coefficient having Arrhenian temperature dependence. Several different ways of data mathematical treatment have been proposed. Most of them are based on an incorrect neglecting of the temperature dependence of the rate coefficient as shown in Figure 5.

Figure 5: Plot of (a) $\ln(\Gamma)$ Vs $(1000/T_p)$ and (c) $\ln(\Gamma)$ Vs $(1000/T_p)$ for the Reaction Peaks; (i) Clustering Process and GP-Zones Precipitation, (ii) $\theta$ Phase Precipitation, (iii) $\theta$ Phase Precipitation for the Studied Alloy
The average activation energy associated with the GP-zones formation is 25.3±0.3 kJ mol$^{-1}$. Dutta and Allen [26] reported 33.1 kJ mol$^{-1}$ for the GP-zones formation of 6061 alloy, however Doan et al. [27] determined 79 kJ mol$^{-1}$ for the same process of the same alloy. In addition, while Gupta et al. [28] reported activation energy of 24.9 kJ mol$^{-1}$ for the same process of the Al–Mg–Si alloy. Moreover, Jena et al. [29] determined activation energy of 55.6 kJ mol$^{-1}$ for the first process of Al–Cu–Mg alloy. Therefore, our values for the activation energy for Cu–Mg–Mn vacancy clusters and GP zones process for the studied alloy are within the most acceptable values found in the literature. Therefore, the kinetics of the clustering process is probably contributed by coalescence of Cu-vacancy, Mg-vacancy and Mn-vacancy complexes to form Mg-Mn–Cu-vacancy clusters. This low activation energy indicates that, the driving force of the clustering process is low which implies that, the Cu addition to this alloy enhances the clustering process. The average activation energy associated with the precipitation of the $\theta^+$ phase is found 111.9±0.5 kJ mol$^{-1}$. The activation energy associated with the $\theta$ phase precipitation is found 106.5±0.6 kJ mol$^{-1}$. These values are found close to the diffusion energies of Mg, Cu and Al in Al which have the following values (131 kJ mol$^{-1}$), (135 kJ mol$^{-1}$) [30] and (144 kJ mol$^{-1}$) [31] respectively. Therefore, these precipitation processes can be controlled by the diffusion of Mg, Cu and Al in the Al matrix.

**Vickers Hardness Measurements During Isochronal Annealing**

The isochronal annealing regime of previously solution heat treated specimens of the studied alloy has been suggested to follow the decomposition behavior as a function of temperature. Normally the specimens are aged for 30 min at temperatures of 20 K intervals starting from room temperature up to 800 K and subsequently quenched into water maintained at ~273K. The microhardness measurements have been performed at room temperature after each quench without paying attention to the impression positions. Fig. 6 shows the variation of HV as a function of the aging temperature. It is clear that, the general behavior of the HV as a function of aging temperature is characterized by four successive reactions labeled as I, II, III and IV. The first precipitation peak (I), which appears at 345 K may be attributed to the formation of Cu–Mg–Mn vacancy clusters and GP-zones. As the temperature increases, the complex clustering between Cu–Mg–Mn and the precipitated GP-zones dissociate which indicated by the decrease in the microhardness of the sample. The second precipitation peak (II) which appears at 540 K may be attributed to the nucleation of the strengthening needle shaped $\theta^+$ (Al$_2$Cu) precipitates. This needle shaped precipitates are coherent to the Al-lattice and therefore, a strengthening of the alloy would take place.

![Figure 6: HV vs. Aging Temperature of the Studied Al Alloy](image)

The transformation from the coherent $\theta^+$ (Al$_2$Cu) to incoherent $\theta$ (Al$_2$Cu) phase takes place after the complete dissociation of the needle shaped $\theta^+$ precipitates at 610 K. The precipitation of incoherent $\theta$ (Al$_2$Cu) phase, the third hardening precipitated peak (III), which is measured above 675 K for the studied alloy has a limited contribution to the HV
(over-aging-case). After the completion of the \( \theta \) \((\text{Al}_2\text{Cu})\) phase, another shoulder increase peak (IV) which can be attributed to the formation of equilibrium plate-like \( S \) \((\text{Al}_2\text{CuMg})\) phase at 745 K. This equilibrium phase precipitate as a result of the abundant concentration of quenched in vacancies in this range of temperatures and the formation of vacancy clusters might explain it. This equilibrium phase has a limited contribution to the microhardness. This result implies that the material should be return to the as quenched state. The consistency in the behaviour of both results, HV and DSC of the studied alloy, is evident. Whereas the inconsistency of the precipitate temperatures in some cases can be explained by the lack of thermal equilibrium during the DSC scans.

**CONCLUSIONS**

The precipitation processes of all the precipitated phases can be controlled by the diffusion of Mg and Cu in the Al matrix. The driving force of the clustering process is low which implies that, the Cu addition to the studied alloy enhances the clustering process. The increase of the aging temperature increases the dissolution of pre-precipitated phases. These pre-precipitated phases become the nucleated sites of the more stable phases.

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