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Advancement in High Strength Aluminium Alloys: Formation of Nanoprecipitates through Microalloying

Bondan T. Sofyan
Department of Metallurgy and Materials, Faculty of Engineering, University of Indonesia, Kampus UI Depok 16424, Phone: + 62-21-786 3510, Fax: + 62-21-787 2350, Email: bondan@metal.ui.ac.id

Abstract
Some aluminium alloys can be strengthened through ageing process. Ageing will result in the formation of precipitates which directly increase the mechanical properties of the alloys. Strengthening will be greatly enhanced by adding a minor amount of alloying elements, which is known as minor alloying. The alloying elements will stimulate the formation of nanoprecipitates that finely and uniformly distributed. This paper discusses the formation of nanoprecipitates in Al-Cu alloys by microalloying with Cd and Mg. Observation on the nanostructure of the materials was conducted by using advanced equipment, such as TEM (transmission electron microscope), STEM (scanning TEM) and 3DAPFIM (three-dimensional atom probe field ion microscopy), that have excellent capabilities in nano-scale analysis.

Research results show that the trace addition of Cd and Mg increased the peak hardness of the alloys. This is due to simultaneous formation of $\eta$ (Al$_2$Cu, 14 mcn, $a=0.404$ nm and $c=0.580$ nm), $\alpha$ (Al$_2$Cu$_3$Mg$_2$, Pm3m, $a=0.831$ nm) and $\Omega$ (Al$_2$Cu, Fmmm, $a=0.496$ nm, $b=0.859$ nm and $c=0.848$ nm) nanoprecipitates in a dense and uniform distribution. These precipitates form through a mechanism called as cluster-assisted precipitate nucleation, which is closely related to the interaction between the alloying elements and vacancies within the structure of materials.

Keywords: aluminium alloys, nanoprecipitates, TEM (transmission electron microscope), 3DAPFIM (three-dimensional atom probe field ion microscopy), microalloying

1. Introduction
Aluminium alloys have been developed since early 1900’s and now are used for various engineering application, mostly due to their lightweight, corrosion resistance and fatigue endurance. However, there is limitation in terms of strength of the materials. New advancement to significantly increase the strength of aluminium alloys is through enhancement of nanoprecipitates formation within the alloys. This can be accomplished by addition of minor amount of alloying element (microalloying), followed by heat treatment processes. For example, Al-Cu alloys microalloyed with Cd, Sn and In are known to have a fine dispersion of $\theta$ (Al$_2$Cu) and exhibit an increased hardening response [1-4]. Although various mechanisms have been proposed to account for this effect, one-dimensional atom probe (1DAP) experiments on an Al-1.7Cu-0.01Sn (at. %) alloy have shown that $\theta$' nucleation is preceded by clustering of Sn atoms and the precipitation of $\beta$-Sn. The fine and uniform dispersion of $\theta$' which follows occurs such that the incoherent rim of the precipitates is associated with Sn atoms [5]. Furthermore, Kanno et al [6] have observed in particles in Al-Cu-In alloys and Nie et al [7] have recently discussed the enhanced precipitation of $\theta$' in Al-Cu-Sn/In alloys in terms of cluster-assisted nucleation.

Minor additions of Mg to Al-Cu alloys are known to promote $\{120\}_h$ types of precipitates, such as S (Al$_2$CuMg) [8], and using 1DAP, it was shown that Mg-Cu co-clusters predominate during the early stages
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Bondan T. Sofyan

Department of Metallurgy and Materials, Faculty of Engineering, University of Indonesia, Kampus UI Depok 16424.
Phone: + 62 – 21 – 786 3510, Fax: + 62 – 21 – 787 2350
Email: bondan@metal.ui.ac.id

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Some aluminium alloys can be strengthened through ageing process. Ageing will result in the formation of precipitates which directly increase the mechanical properties of the alloys. Strengthening will be greatly enhanced by adding a minor amount of alloying elements, which is known as minor alloying. The alloying elements will stimulate the formation of nanoprecipitates that finely and uniformly distributed. This paper discusses the formation of nanoprecipitates in Al-Cu alloys by microalloying with Cd and Mg. Observation on the nanostructure of the materials was conducted by using advanced equipments, such as TEM (transmission electron microscope), STEM (scanning TEM) and 3DAPFIM (three-dimensional atom probe field ion microscope), that have excellent capabilities in nano-scale analysis.

Research results show that the trace addition of Cd and Mg increased the peak hardness of the alloys. This is due to simultaneous formation of \( \theta' \) (Al\(_2\)Cu, I\(_4/mcm\), \( a=0.404 \text{ nm} \) and \( c=0.580 \text{ nm} \)), \( \sigma \) (Al\(_2\)Cu\(_2\)Mg\(_3\), Pm\(_3\), \( a = 0.831 \text{ nm} \)) and \( \Omega \) (Al\(_2\)Cu, F\(_{mmm}\), \( a=0.496 \text{ nm}, b=0.859 \text{ nm} \) and \( c=0.848 \text{ nm} \)) nanoprecipitates in a dense and uniform distribution. These precipitates form through a mechanism called as cluster-assisted precipitate nucleation, which is closely related to the interaction between the alloying elements and vacancies within the structure of materials.

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1. Introduction

Aluminium alloys have been developed since early 1900's and now are used for various engineering application, mostly due to their lightweight, corrosion resistance and fatigue endurance. However, there is limitation in terms of strength of the materials. New advancement to significantly increase the strength of aluminium alloys is through enhancement of nanoprecipitates formation within the alloys. This can be accomplished by addition of minor amount of alloying element (microalloying), followed by heat treatment processes. For example, Al-Cu alloys microalloyed with Cd, Sn and In are known to have a finer dispersion of \( \theta' \) (Al\(_2\)Cu) and exhibit an increased hardening response [1-4]. Although various mechanisms have been proposed to account for this effect, one-dimensional atom probe (1DAP) experiments on an Al-1.7Cu-0.01Sn (at. %) alloy have shown that \( \theta' \) nucleation is preceded by clustering of Sn atoms and the precipitation of \( \beta\)-Sn. The fine and uniform dispersion of \( \theta' \) which follows occurs such that the incoherent rim of the precipitates is associated with Sn atoms [5]. Furthermore, Kanno et al. [6] have observed In particles in Al-Cu-In alloys and Nie et al. [7] have recently discussed the enhanced precipitation of \( \theta' \) in Al-Cu-Sn/In alloys in terms of cluster-assisted nucleation.

Minor additions of Mg to Al-Cu alloys are known to promote \{120\}_a types of precipitates, such as S (Al\(_2\)CuMg) [8], and using 1DAP, it was shown that Mg-Cu co-clusters predominate during the early stages
of ageing in ternary Al-Cu-Mg alloys [9]. Combined additions of Cd and Mg are known to promote a fine dispersion of \( \theta' \) which enhances hardening in Al-Cu-Mg-Cd alloys [10]. In this case, it seems that Cd atoms remain available to assist nucleation of \( \theta' \) since there are no known stable compounds formed between Cd and Mg [11].

This research investigates the effect of minor alloying of Cd and Mg on the mechanical properties of Al-Cu alloys and the mechanism by which the microalloying elements influence formation of nanoprecipitates within the microstructure and the hardness of the alloys during ageing. Observation on the nanostructure of the materials was conducted by using advanced equipments, such as TEM (transmission electron microscope), STEM (scanning TEM) and 3DAPFIM (three-dimensional atom probe field ion microscope), that have excellent capabilities in nano scale analysis.

2. Experimental Method

Three alloys were used in this study and their nominal compositions is presented in Table 1. Samples of each were cut into 10 x 10 mm blocks for hardness testing, 0.3 x 0.3 x 10 mm needles for 3DAPFIM, or were rolled to ~ 200 \( \mu \text{m} \) for TEM. After solution treatment at 525 °C for 1 h and cold water quenching, ageing was conducted at 200 °C. Hardening response was monitored by Vickers hardness measurements using a 5-kg load. The evolution of microstructure was followed by means of a Philips CM20 TEM operating at 200 kV. Energy dispersive x-ray spectroscopy (EDXS) was performed using a VG HB601 dedicated scanning TEM (STEM) which was aligned such that incident electron probe possessed a diameter \( \leq 1 \text{ nm} \). Samples for TEM were prepared in a twin jet polisher using a solution of 1:2 vol. % nitric acid : methanol at –25 °C. Samples for 3DAPFIM were prepared by electropolishing the needles, initially in nitric acid containing few drops of water, and then in a solution of 3 % perchloric acid in 2-butoxyethanol to sharpen the tips. Three dimensional atom probe analysis was carried out at 20K with a pulse fraction of 25 % in an ultra high vacuum of \( 1.3 \times 10^{-11} \text{ mbar} \).

Table 1. Nominal composition (wt. %) of alloys used in this study

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Cu</th>
<th>Mg</th>
<th>Ag</th>
<th>Cd</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Cu-Mg</td>
<td>4</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>remaining</td>
</tr>
<tr>
<td>Al-Cu-Cd</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>remaining</td>
</tr>
<tr>
<td>Al-Cu-Mg-Cd</td>
<td>4</td>
<td>0.3</td>
<td>-</td>
<td>0.5</td>
<td>remaining</td>
</tr>
</tbody>
</table>

![Figure 1](image.png)

**Figure 1.** Age hardening curves during ageing at 200 °C.
3. Results and Discussion

3.1. Age Hardening Curves

The age hardening curves of the alloy following ageing at 200 °C are presented in Figure 1. The curves show single stage hardening which is the characteristic of many Al-Cu based alloys [4]. An incubation period of 15 – 60 min was observed in all alloys, which then followed by an increase to peak hardness. It is noted that the ternary Al-Cu-Cd alloy had higher peak hardness than the ternary Al-Cu-Mg alloy and a synergetic effect was obtained by combined additions of Cd and Mg. It confirms previous results that the addition of Cd increases the peak hardness and reduces the time to reach peak hardness [10, 12].

3.2. Microstructural Analysis

The as-quenched microstructures (not shown here) are relatively free from defects, with only some dislocation helices being present. The helices seem to be induced by cold rolling performed on the alloy strip when TEM samples were produced. No dislocation loops were observed, which is attributed to the high binding energy between Cd, Mg atoms and vacancies.

Bright field (BF) TEM images of the peak hardness microstructure for each alloy during ageing at 200 °C were recorded close to the <001> zone axis and examples are provided in Figure 2. The Al-Cu-Mg alloy microstructure is dominated by coarse plates, Figure 2 (a), and the corresponding SAED pattern shows reflections at \{110\}_a positions and sharp streaks emerging from those positions parallel to the <001>_a direction, which are consistent with \theta' phase. The S (Al$_2$CuMg, Cmcm, $a=0.404$ nm, $b=0.925$ nm and $c=0.718$ nm) and V precipitates were occasionally observed in this alloy.

Figure 2 (b) is the peak hardness microstructure of the Al-Cu-Cd alloy which consists of a denser and more uniform distribution of \theta' precipitates, together with a finer dispersion of much smaller, spherical particles. Some of these nanoscale particles formed independently in the \alpha matrix and some of them are attached to the \theta' phase. This microstructure is in excellent agreement with that reported previously [6]. The corresponding SAED pattern again shows reflections and streaks consistent with the diffraction effects of the \theta' nanoprecipitates.

![Figure 2](image)

**Figure 2.** Peak hardness microstructures and corresponding SAED patterns of (a) Al-Cu-Mg; (b) Al-Cu-Cd and (c) Al-Cu-Mg-Cd alloys. Electron beam was parallel to the <001>$_a$ direction.

The peak hardness microstructure of the quaternary Al-Cu-Mg-Cd alloy consists mainly of the \theta' and \sigma, Figure 2(c). In addition, occasional \Omega precipitates on \{111\}_a planes were also observed and these are inclined to the beam direction in this figure. Some S phase precipitates were also detected, as identified by the characteristic \{210\}_a trace. Careful inspection of the BF TEM images revealed that there were small
particles attached to both the $\theta'$ and $\sigma$ phases. These particles were usually located at the edges or corners of the precipitates. Similar to the Al-Cu-Cd alloy, a dispersion of spherical nanoparticles was also detected uniformly throughout the matrix.

Various TEM techniques were employed to identify the spherical nanoparticles, of ~4 nm in diameter, in the matrix. Figure 3(b) provides the EDXS spectra obtained from the VG STEM by analysing a series of points across the nanoparticles, as described in Figure 3(a). The data were acquired from near the $<111>_{\text{D}}$ orientation, which provided very clear contrast from the particles. Positions 2 and 3 were well inside the spherical nanoparticles and strong Cd peaks were detected on those positions. Little or no change was observed for the other elemental species indicating that the spherical nanoparticles are either Cd or a Cd-rich precipitate. Microbeam electron diffraction (MBED) patterns of these particles were recorded from the $<111>_{\text{D}}$ zone axis and results are presented in Figure 4(a). It is clear that the experimental pattern may be indexed as elemental Cd (hexagonal, mmc, $a = 0.298$ nm, $c = 0.562$ nm) as simulated in Figure 4(b). The Cd particles were observed to bear a simple orientation relationships with the matrix: $\{111\}_{\text{D}} // \{0001\}_{\text{Cd}}$; $<110>_{\text{D}} // <1\overline{1}2\overline{0}>_{\text{Cd}}$ [13]. These results confirm that the spherical nanoparticles distributed throughout the matrix are elemental Cd particles.

Figure 3. (a) $<111>_{\text{A}}$ Dark field (DF) STEM image of a spherical nanoparticles lie in the matrix in an Al-Cu-Mg-Cd alloy aged at 200°C for 200 h, with positions where EDXS analysis were performed. (b) EDXS spectra of points shown in (a).

Figure 4. (a) $<111>_{\text{A}}$ MBED pattern of the spherical nanoparticles in the matrix of Al-Cu-Mg-Cd aged at 200°C for 200 h, and (b) the corresponding simulation result based on the structure of Cd.
Although the microstructure of the peak hardness and overaged conditions successfully confirm that the addition of Cd stimulates the $\theta'$ precipitation in both the Al-Cu-Cd and Al-Cu-Mg-Cd alloys, and are in good agreement with previous observations [1-6, 10, 12], the early stages of precipitation remain unclear and need to be resolved. Therefore, 3DAPFIM experiments were conducted on the Al-Cu-Mg-Cd samples aged at 200 °C for 45 minutes. A three dimensional elemental map of the sample is presented in Figure 5. The Al atoms clearly reveal the stacking of (001)$_D$ planes and a Cu-rich precipitate is detected in the map. This precipitate would appear to be the $\theta'$ phase since it has a platelet morphology with habit planes parallel to the (001)$_D$ planes. It is noteworthy that a Cd-Mg –rich particle was detected at the rim of the $\theta'$ precipitate (arrowed). This is consistent with previous results [14] that found formation of Cd-Mg clusters during earlier stages of ageing. It is thought that the Cd-Mg clusters provide sites for nucleation of $\theta'$. The cluster then grow as Cd-Mg-rich particles that are associated with $\theta'$ precipitates.

![Figure 5. Three-dimensional elemental map of Al-Cu-Mg-Cd alloy aged at 200 °C for 45 min. A nano-scale particles (arrowed), rich in Cd and Mg, is detected attached to a Cu-rich precipitate ($\theta'$).](image)

Observation on the nanostructure of the alloys shows that microalloying Al-Cu alloys with Cd and Mg will result in the enhancement and refinement of various nanoprecipitates, such as $\theta'$, $\sigma$ and $\Omega$. The promotion of these nanoprecipitates seems to be determined mainly by the affinity of the alloying elements toward vacancy. Elements such as Cd and Mg, which have high binding energy with vacancy will form atomic clusters at earlier stages of ageing. These Cd-Mg-vacancy clusters facilitate formation of nanoprecipitates by accommodating shear strain occurred during nucleation. The higher the affinity of the elements towards vacancy, the greater the tendency of the elements to form atomic clusters and to stimulate particular nanoprecipitates. At the later stages of ageing, the atomic clusters may grow and form spherical nanoparticles, which are either independent in the matrix or attached to other nanoprecipitates. The mechanism of the enhancement of nanoprecipitate nucleation is termed as cluster-assisted precipitate nucleation. Design of aluminium alloys in nano scale may be made possible by adopting this proposed mechanism, that is by microalloying aluminium with elements which have high binding energy with vacancy. Design in nanostructure is also aimed to produce precipitates which are potential to significantly increase the strength of the aluminium alloys. These all will lead to the advancement of high-strength aluminium alloys.

### 4. Conclusions

1. Microalloying of Cd into Al-Cu alloys promotes nucleation of $\theta'$ (Al$_2$Cu) nanoprecipitates, so that increase the peak hardness.
2. Nanoscale particles of ~ 4 nm in diameter were observed in Al-Cu-Cd alloy, either independent in the matrix or attached to $\theta'$. These particles are identified as elemental Cd, with hexagonal structure, $a = 0.298$ nm and $c = 0.562$ nm.

3. The addition of Cd to the alloy Al-Cu-Mg increases the peak hardness by stimulating $\theta'$ (Al$_{2}$Cu), $\sigma$(Al$_{3}$Cu$_{3}$Mg$_{2}$), and $\Omega$ (Al$_{3}$Cu) nanoprecipitates simultaneously. Normally, the $\sigma$ phase is observed only occasionally in the ternary alloy.

4. Three-dimensional atom probe experiments revealed a new observation that Cd-Mg clusters form in the Al-Cu-Mg-Cd alloy during the very early stages of ageing. These clusters are rich with vacancies and are likely to assist nucleation of the $\theta'$, $\sigma$ and $\Omega$ phases by providing relief to the shear strain energy associated with nucleation. The clusters then evolve into Cd-Mg-rich particles, which are attached to these precipitates after prolonged ageing. This mechanism is termed as cluster-assisted precipitate nucleation, which can be used to design nanostructure of aluminium alloys in order to produce high strength aluminium alloys.

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