Original Article

Influence of plastic deformation and Cu/Mg ratio on the strengthening mechanisms and precipitation behavior of AA2024 aluminum alloys

J.L. García-Hernández a, C.G. Garay-Reyes a, I.K. Gómez-Barraza b, M.A. Ruiz-Esparrza-Rodríguez a, E.J. Gutiérrez-Castañeda c,d, I. Estrada-Guel a, M.C. Maldonado-Orozco b, R. Martínez-Sánchez a,*

a Centro de Investigación en Materiales Avanzados (CIMAV), Laboratorio Nacional de Nanotecnología, Miguel de Cervantes No. 120, Chihuahua, Chih., 31136, Mexico
b Universidad Autónoma de Chihuahua (UACH), Facultad de Ingeniería, Circuito No. 1, Nuevo Campus Universitario, Chihuahua, Chih., CP 31125, Mexico
c Instituto de Metalurgia, Universidad Autónoma de San Luis Potosí, Av. Sierra Leona 550, Lomas 2da Sección, 78210, San Luis Potosí, S.L.P Mexico
d Cátedra CONACYT, Consejo Nacional de Ciencia y Tecnología, Crédito Constructor, Del. Benito Juárez, 03940, Mexico

ARTICLE INFO

Article history:
Received 10 April 2018
Accepted 5 September 2019
Available online 20 September 2019

Keywords:
Aluminum alloy
Plastic deformation
Aging precipitation
Vickers microhardness

ABSTRACT

The strengthening mechanisms and precipitation behavior in AA2024 alloys with different Cu/Mg ratios (3.18 and 2.48) and different levels of plastic deformation (5 and 15%) were studied by X-ray diffraction, transmission electron microscopy and Vickers microhardness measurements. Results demonstrate that hardening depends significantly on the interaction of different strengthening mechanisms such as solid-solution, strain hardening and precipitation. Hardness is mostly influenced by precipitation, which in turn is modified by plastic deformation and the Cu/Mg ratio. Modification of Cu and Mg content as well as plastic deformation affect the precipitation behavior of the Al2CuMg (S) phase, since these lead to significant changes in size and numeric density of the S precipitates. A higher number density and a smaller size of S precipitates are obtained in the alloy with lower Cu/Mg ratio and 15% of thickness reduction.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

AA2024 aluminum alloys are extensively used as structural materials in commercial airplanes for their attractive combination of properties such as high specific strength, sufficient damage tolerance, formability and corrosion resistance [1,2]. For instance, aircraft wing and fuselage structures are made of AA2024 alloy sheets in the T3 and T4 conditions, respectively [1,2].
It is well known that the excellent strength in these aluminum alloys depends on the precipitation of coherent phases generated during aging heat treatment. These coherent precipitates contained in Al–Cu alloys were firstly observed by Guinier and Preston and are well known as Guinier–Preston zones (GP zones). In the early 1950s, Bagaryatsky proposed a four-stage precipitation sequence for the aging process of Al–Cu–Mg alloys, and for this reason they are also known as Guinier–Preston–Bagaryatsky (GBP zones) [3–5].

The precipitation behavior of coherent precipitates may be influenced by alloying elements additions and plastic deformation. At present, there are a lot of reports regarding the precipitation sequences of S and θ phases and the influence of Mg content on the precipitation behavior of Al–Cu–Mg alloys. For instance, it has been reported that the Cu/Mg ratio affects such behavior, for ratios greater than 8, the Al–Cu–Mg alloys are strengthened by precipitation of θ (Al₃Cu) phase. However, for ratios between 4 and 8, θ and S (Al₂CuMg) constituted the main strengthening phases. In Al–Cu–Mg systems with a low ratio (1.5–4), S is the most effective strengthening phase [6,7]. The effect of the deformation rate on the precipitation behavior of Al–Cu–Mg alloys, have been mainly investigated to improve the strength–ductility combination. Huang et al. [8] reported that the combination of a solution heat treatment followed by rolling at room temperature (~40% e) and aging at 175 °C for 7 h, leads to high strength values due to a high density of both nano-sized S’-phase precipitates and dislocations.

Although the effects of the Cu/Mg ratio and the plastic deformation on the precipitation behavior of Al–Cu-Mg alloys have been studied extensively on an individual basis, it has only recently been reported [9] that growth of a precipitate is strongly enhanced when it coincides with a dislocation. However, the combined effect of those variables has not been properly discussed. Therefore, the present investigation offers a better understanding of the combined effects of the Cu/Mg ratio and the plastic deformation on the strengthening mechanisms and precipitation behavior of Al–Cu-Mg alloys.

2. Materials and methods

A commercial AA2024 alloy and magnesium master alloy (Mg-5Al-0.35 Mn) were used as the raw materials. The AA2024 alloy was melted in a LINDBERG BLUE electric furnace at 740 °C, and modified by magnesium additions. The chemical composition of alloys obtained with different Cu/Mg ratios (3.18 and 2.48, respectively) was determined by plasma emission spectroscopy (Table 1). Degassing of molten aluminum was achieved by an argon gas flow for 5 min using a graphite propeller with a rotation speed of 490 rpm, followed by additions of 0.33 g (0.055 wt.%) of Al-5Ti-1B as grain refiner. The molten was casted into preheated steel molds (260 °C) to obtain specimens of approximately 100 mm long × 12 mm wide × 10 mm thick. Ingots were machined to obtain samples of about 95 mm long × 10 mm wide × 8 mm thick, which were subjected to a solution heat treatment (SHT). The conditions of the SHT were 495 °C for 300 min followed by quenching in water at 60 °C. Quenched specimens were subjected to cold rolling (CR) to obtain thickness reductions of 5 and 15%. Cold-rolled specimens were sectioned to obtain samples of around 20 mm in length for further aging heat treatments (AHT). The conditions of this later were, 195 °C for 30, 60, 300, 600, 3000 and 6000 min, followed by quenching in water at room temperature. Fig. 1 illustrates the thermal treatments and processing variables used in the present work. The microstructural evolution was followed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Analyses by XRD were performed in a Panalytical X’Pert PRO diffractometer operated at 40 kV and 35 mA using Cu Kα radiation (λ = 0.15406 nm). Characterization by TEM was carried out using a PHILIPS CM-200 microscope (operated at 200 kV) and a JEOL™ JEM2200F + CS microscope (operated at 200 kV) equipped with spherical aberration corrector. Samples for TEM observations were prepared by electropolishing in a Struers™ TenuPol-5 equipment using a mixture of MeOH:HNO₃ 80:20 (in volume) at −50 °C. Vickers microhardness (HV0.3) was measured in a LEJO LM300AT hardness tester with 300 g load and 10 s of dwell time; the reported value for each sample was the average obtained from 20 indentations.

Table 1 – Chemical composition and Cu/Mg ratio of the experimental AA2024 aluminum alloys (wt.%).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Al</th>
<th>Mo</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Si</th>
<th>Ti</th>
<th>Zn</th>
<th>Cu/Mg Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Balance</td>
<td>0.026</td>
<td>3.286</td>
<td>0.152</td>
<td>1.032</td>
<td>0.338</td>
<td>0.049</td>
<td>0.622</td>
<td>0.034</td>
<td>3.18</td>
</tr>
<tr>
<td>2</td>
<td>Balance</td>
<td>0.034</td>
<td>3.088</td>
<td>0.142</td>
<td>1.242</td>
<td>0.330</td>
<td>0.023</td>
<td>0.538</td>
<td>0.031</td>
<td>2.48</td>
</tr>
</tbody>
</table>

Fig. 1 – Experimental parameters used for the alloys processing.
3. Results and discussion

3.1. Strengthening mechanisms

Fig. 2 shows the age-hardening curves of alloys as a function of the Cu/Mg ratio and the plastic deformation (5 and 15%). According to these results, the following strengthening mechanisms may be suggested: i) solid-solution strengthening (SSS), ii) strain hardening (SH), and iii) precipitation hardening (PH).

The SSS mechanism may be assumed by comparing the alloys 1 and 2 in the non-deformed condition. The smaller Cu/Mg ratio causes strengthening of the aluminum matrix, which is evidenced by an increase of the hardness value. The increase of this property relates to the higher dissolution of magnesium into the aluminum matrix during the SHT, which causes a lattice distortion due to the atomic ratio mismatch and makes the dislocations movement very difficult.

The strengthening mechanism by SH can be observed by comparing the non-deformed and deformed alloys after SHT, it is clear that hardness of the cold-rolled alloy is higher than the one observed in non-deformed alloy. In addition, samples with lower Cu/Mg ratio present higher hardness after cold-rolling, which could indicate that SSS is more significant when plastic deformation is applied. SH mechanism affects the precipitation kinetics; as observed in Fig. 2, the time needed to achieve the maximum peak during aging is shorter for samples in the cold-rolled condition. It is well known that, an increase in the dislocation density can increase the nucleation sites for precipitation; therefore, it is expected that higher amounts of plastic deformation prior to AHT lead to a faster precipitation process [10–13]. Samples with lower Cu/Mg ratio present higher hardness during the aging process (Fig. 2), the maximum hardness value in non-deformed and deformed alloys is reached for aging times of 300 and 60 min, respectively, confirming the assumption that precipitation is faster in deformed alloys.

Fig. 3 – XRD patterns corresponding to peak-aged condition of alloys 1 and 2, including those of alloy 2 in the cold-rolled condition (5 and 15% CR).

Regarding the PH mechanism, the highest hardness value is 169 HV\textsubscript{0.3} (alloy 2 with 15% of thickness reduction). The first stage of strengthening is characterized by an initial rapid increase of the hardness values, this increment can be attributed to the formation of Cu-Mg clusters or GPB zones and S\textsuperscript{+} phase or GPB2. It has been reported in a recent work that the later phase, which is a semi-coherent phase with orthogonal structure, is formed before the maximum peak of age-hardening is reached [14–19], since S\textsuperscript{+} and S phases are responsible for the maximum hardness peak. The S\textsuperscript{+} phase has been generally considered as semi-coherent with the matrix having the same structure than the S phase, but with very small variations in its lattice parameters [14–19]; for this reason recent publications make no distinction between the S\textsuperscript{+} and S phases. The decrease in hardness is attributed to coarsening of S phase [14–19].

As can be seen in Fig. 2, all of the curves present a single peak aging; the maximum hardness values for alloys 1 and 2 in the non-deformed condition are 133 and 144 HV\textsubscript{0.3}, respectively, and increase to 163 and 169 HV\textsubscript{0.3} after 15% of thickness reduction. The times for reaching the peak aging hardness in both alloys in the non-deformed and deformed conditions are 300 and 60 min, respectively (Fig. 2). Different hardness values have been reported in AA2024 and Al-Cu-Mg alloys. Li et al. [20], reported a hardness peak of 152 HV\textsubscript{0.5} after 360 min of AHT in samples without deformation (non-deformed condition). Increasing the plastic deformation level to 10%, results in two peaks aging with maximum hardness values of 158 and 160 HV\textsubscript{0.5} after 300 and 590 min, respectively. At higher deformation levels (20%) were obtained higher hardness values 170 and 170 HV\textsubscript{0.5} after 250 and 590 min, respectively. Nevertheless, it is important to mention that Li [20] used a Cu/Mg ratio of 3.2 (4.8 Cu–1.5 Mg), a temperature/time of SHT of 500 °C/3 h, and an aging temperature of 180 °C. Ghosh et al. [21], obtained hardness value of 135 HV\textsubscript{10} after 600 min of AHT (peak aging) in a non-deformed alloy. In this case, Cu/Mg ratio, temperature/time of SHT and aging temperature were 2.93 (4.4 Cu–1.5 Mg), 490 °C/0.5 h and 190 °C, respectively. Zhao et al. [22] also obtained a double peak aging with maximum hardness of 162 and 171 HV\textsubscript{0.1} after 20 and 720 min of AHT in samples with 20% of plastic deformation. However, they
used a Cu/Mg ratio of 2.93 (4.4 Cu–1.5 Mg), temperature/time of SHT of 505 °C/6 h, and an aging temperature of 180 °C. The following important aspects related to strengthening mechanisms, specifically those related to precipitation hardening (PH), can be determined from the information described above. The Cu/Mg ratio in ternary phase diagram affects the type of phases present in the system; nevertheless, it has not direct relationship to hardness. Hardness is associated to the transformed fraction of the S phase in the (α + S) region, as a matter of fact, hardening occurs in systems with a Cu/Mg ratio close to the solvus line in the ternary phase diagram due to the fact that it generates a high transformed fraction of precipitates. The accepted precipitation sequence of AA2024 aluminum alloys is SSS → GPB zone → S″ → S′, which is evident in the formation of a double peak ageing in a system with a Cu content greater than 4 Cu wt.% independently of the Cu/Mg ratio (α + S region). However, for Cu/Mg ratios with low Cu contents (∼3 wt. %) the second peak ageing is not evident which relates to the faster kinetics of the S″ to S′ phase transformation.

3.2. Precipitation behavior

Fig. 3 shows some XRD patterns corresponding to peak-aged condition of alloys 1 and 2. The effect of plastic deformation in alloy 2 is also shown in this figure. Some reflections corresponding to the Al phase and Cu-containing intermetallic compounds generated during the alloy melting (AlCu, Al2Cu, and Al2CuMg) are observed. It can be noticed that all of the alloys show the characteristic peaks of Al2Cu (α) phase (tetragonal, 14/mcm, a = 0.6066 nm, c = 0.4878 nm [14]) and Al2CuMg (S) phase (orthorhombic, Cmcm, a = 0.400 nm, b = 0.923 nm, c = 0.580 nm [14,22–26]). The intensity of the characteristic peaks of S phase is higher in alloy 2 due to the lower Cu/Mg ratio. On the other hand, a high intensity of the characteristic peaks of the AlCu phase (monoclinic, C2/m, a = 0.9889 nm, b = 0.4105 nm, c = 0.6913 nm) is observed in all of the XRD patterns. This intensity does not show a significant variation with plastic deformation or with the Cu/Mg ratio, indicating that it is not altered by the above mentioned variables.

Fig. 4a–c shows representative views of precipitates at peak aging. Fig. 4a shows TEM micrographs with the incident beam along the [001]α zone axis and the corresponding selected area electron diffraction pattern (SAED) for alloy 1. It can be observed that Sprecipitates are oriented along the [010] and [001] directions. The orientation spatial of these precipitates is in accordance with typical studies of as-aged Al-Cu-Mg alloys [16–18,27–29]. The [001]α SAED pattern (square inset in Fig. 4a) reveals faint reflections which correspond to precipitates. These faint reflections observed in SAED of Fig. 1a, are in agreement with those reported elsewhere [16]. Fig. 4b and c shows the precipitates present in alloy 2 after being subjected to 5% and 15% of thickness reduction, respectively. These figures show STEM micrographs, which evidence that S precipitates are oriented along [100]5, [010]5 and [001]5 directions [30–33]. Number density and size of precipitates in alloy 2, differ from those in alloy 1. The apparent number density of S precipitates in alloy 2 with 15% of thickness reduction, is higher than the one in alloy 1, or that in alloy 2 with 5% of thickness reduction. The size of S precipitates in alloy 2 with 15% of thickness reduction is smaller compared to alloy 2 with 5% of thickness reduction or alloy 1.

The microstructural changes previously described for lower Cu/Mg ratio can be related to a precipitation mechanism induced by plastic deformation. The high number density, small size and homogenous spatial distribution of S precipitates provide effective sites for trapping and accumulation of dislocations, which favors hardening. In addition to above mentioned characteristics, the SAED in Fig. 4c (square inset) present different reflections respect to Fig. 4a derived from the deformation process. Recently, Liu et al. [9] reported that the growth of a precipitate is strongly enhanced when it coincides with a dislocation. Therefore, it is expected that dislocations generated by plastic deformation will modify the nucleation and growth sequence of precipitates during the aging process.

4. Conclusions

Hardness of the experimental AA2024 aluminum alloys is influenced by the contribution of different strengthening mechanisms: i) solid-solution, ii) strain hardening and iii) precipitation. Precipitation induced by plastic deformation for lower Cu/Mg ratio represents the main hardening mechanism of the studied alloy. The precipitation behavior is affected by both the Cu/Mg ratio and the plastic deformation, since they promote higher volume fractions as well as changes in size and numeric density of S phase. The apparent number density of S precipitates in alloy 2 with 15% of thickness reduction is higher than the one of alloy 1 in the non-deformed condition or alloy 2 with 5% of thickness reduction. The size of S precipitates in alloy 2 with 15% of thickness reduction is smaller.
than that of alloy 2 with 5% of thickness reduction or the one of alloy 1 in the non-deformed condition.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

Project Supported by the Sectorial Research Fund for Education, CONACYT, A1-S-32226. The authors gratefully thank C. Ornelas-Gutierrez, R. A. Ochoa-Gamboa, J. E. Ledezma-Sillas and E. Guerrero Lestarjette for their valuable technical support throughout the study. E. Gutiérrez duly recognizes the CONACYT for the Cátedra assigned at The Institute of Metallurgy of The Autonomous University of San Luis Potosí (UASLP). This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

REFERENCES