Improvement of micro-hardness and electrochemical properties of Al-4%Cu-0.5%Mg alloy by Ag addition

Mejoramiento de la micro-dureza y de las propiedades electroquímicas de la aleación Al-4%Cu-0.5%Mg mediante la adición de Ag

Reinaldo Correa¹, Héctor Sánchez¹, Jorge A. Calderón²*


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Abstract

The base system of alloys Al-4% Cu-0.5% Mg, known as the designation of duralumin 201, are very appreciated by the aerospace, partly automotive and industrial in general, for its great strength, high temperature and corrosion resistant. These kinds of alloys have excellent response to precipitation hardening. This study evaluates the effect of silver content in the microstructure, mechanical properties and corrosion resistance of the alloy. It was found that the addition of silver in the alloys led to a delay time of homogenization and accelerates the aging time, causing the precipitation of Guinier Preston zones and the consequent increase in hardness and improvement of the mechanical properties of alloys. Moreover, the addition of Ag to alloys Al-4% Cu-0.5% Mg gives a better resistance to corrosion, giving noble features and reducing the corrosion current in chloride aqueous media. The global control of the dissolution of the alloys Al-4% Cu-0.5% Mg-Ag will be given by the diffusion of oxygen from the bulk of the solution to the metal surface. The corrosion potential of alloys Al-4% Cu-0.5% Mg-Ag coincide with the pitting potential of the material (-0.62V), this makes the material not generate a passive layer and its dissolution is controlled purely by activation of the surface and the reaction rate of the cathodic reduction of oxygen.
Introduction

The aluminum alloys designated as 201 (ANSI) are reported as the greatest and toughest in the families of the aluminum-based alloys, making them very special and appreciated by the aerospace, vehicular and hydropower industry. The additions of curing alloy elements such as copper, magnesium and silver increases the strength of the alloy, by heat treatment in adequate conditions corresponding to a T6. By increasing the homogenization temperature or prolonging the holding time, the residual phases are dissolved into the matrix gradually, grain boundaries become sparse and all elements become more homogenized [1]. The solubilization of copper at elevated temperatures and subsequent precipitation in the form submicroscopic, explain the improvement of mechanical properties obtained by heat treatment of these alloys [2]. Magnesium profoundly affects the properties of aluminum alloys, so it is very important to add small amounts of this element (about 0.5%) because it plays an important role in the precipitation hardening [2].

The content of the silver in these alloys provide high strength after heat treatment and increases tensile strength. In addition, these kinds of alloys respond well to the treatment of aging, which is why these alloys are recommended when high tensile strength, yield strength,
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moderate elongation, impact resistance and high temperatures are required [3 - 16]. The corrosion resistance becomes important when alloys work in a very aggressive media, as is in the case of internal combustion engines, turbines, etc. [4 - 7]. The corrosion mechanism and the alloy dissolution are related with the precipitation of noble intermetallic particles in the grain boundary, where micro galvanic cells are established.

The addition of silver in the base alloys Al-Cu-Mg can alter the kinetics of phase formation and delay the degradation of the material at high temperatures. [7] This behavior has been attributed to the formation of a fine uniform dispersion of precipitates of a phase, known as Ω, which presents plate forms and precipitates on the aluminum matrix α {111} hexagonal planes. The Ω phase is thermodynamically more stable that the incoherent and equilibrium phase θ in the system Al-Cu [9 - 16]. In the alloys Al-Cu-Mg-Ag precipitation of the phase Ω replaces partially or completely the phase θ, which is a characteristic of the system Al-Cu. The phase θ precipitates in alloys zones known as Guinier-Preston zones (GP) [17].

It is reported in several publications that addition of Ag in amount of about 0.5% in Al-Cu-Mg alloys affects its composition and crystallographic orientation, enhancing the precipitation of the phases during artificial aging [6, 11, 12]. This is the cause of the changes observed in the final mechanical properties in the alloy. During the artificial aging of these alloys, the maximum resistance is given by the precipitation of the phases, S", S ' and T stage (Al6CuMg4). In the Al6CuMg4 alloy with addition of Ag, the Ω phase is stable and has a similar structure to the θ phase but Ω phase forms thin platelets along α {100} planes, forming a surface layer of magnesium and silver atoms [6, 11 - 13]. It has been postulated that the appearance of fine silver particles gives more stability to the Ω phase and is the reason that alloy achieves high resistance and good strength properties at high temperatures [6]. Phase precipitation is also observed in the Al-Cu-Mg alloys with no Ag, forming in areas of GP zones [14], but with less significant effects.

Although Al-Cu alloys, Al-Cu-Mg and Al-Cu-Mg-Ag have been studied in great detail, especially in issues related with the precipitation of phases and their close relation to the improvement of mechanical properties, few studies have aimed to know the effect of addition of noble metals like Ag, in the electrochemical behavior of the alloys [18]. The formation of fine precipitates with higher concentrations of Cu and Ag can generate galvanic micro-cells which would affect the chemical and electrochemical stability of the metal, promoting rapid dissolution. This study is aimed to contribute to the knowledge of the potential effect of the addition of silver on the electrochemical and corrosion properties in the Al-Cu-Mg alloys. Additionally, it is looking for adequate heat treatment of these alloys in order to improvement mechanical properties without compromising the chemical stability of the alloys.

**Experimental**

**Alloys preparation, thermal treatments and hardness tests**

The cast alloys are made from recycled material, aluminum from electrical cable power line. Previous to the melting operation, furnace and crucible were preheated at a temperature of 770 °C during 10 minutes in order to remove remnant moisture. Once this temperature was reached, temperature was diminished to 750 °C to load the aluminum and other metallic elements. Subsequently the alloy was gassed with argon during 3 to 5 minutes to lower the partial pressure of hydrogen [19 - 20] and avoid excessive porosity and micro-contractions in the final product of the respective alloy. Three types of Al-Cu-Mg alloys were fabricated, one without Ag and the other two with 1.5 Ag, 2.5% Ag. Once obtained, the alloys were prepared for analysis of chemical composition by arc spectrometry. The results are shown in Table 1. According to the chemical composition shown in Table 1, it is confirmed that the alloys are type Al-4% Cu-0.5%Mg.
Table 1 Chemical composition of alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mg</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-4%Cu-0.5%Mg-1.5% Ag</td>
<td>94.03</td>
<td>0.307</td>
<td>0.155</td>
<td>4.855</td>
<td>0.627</td>
<td>1.52</td>
</tr>
<tr>
<td>Al-4%Cu-0.5%Mg-2.5% Ag</td>
<td>94.14</td>
<td>0.061</td>
<td>0.141</td>
<td>4.985</td>
<td>0.634</td>
<td>2.48</td>
</tr>
<tr>
<td>Al-4%Cu-0.5%Mg</td>
<td>94.41</td>
<td>0.000</td>
<td>0.141</td>
<td>4.929</td>
<td>0.489</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Samples of 10x10x5 mm of each alloy were prepared. Sample homogenization was made in a muffle furnace at 520 °C for 8, 32, 40, 100 and 170 hours. Then samples were quenching in water at room temperature and finally aged at 180, 200 and 220 °C for different times. Subsequently these samples were prepared metallographically by grinding with sandpaper and gradually polished to mirror shape for micro-structure observation. Microhardness measurements were made on a micro hardness tester “Vickers” from Wilson brand instruments, (MUD 401 model). The hardness test was done with a diamond pyramid identity 136 and a load of 100gf. For microstructure observation, samples were attacked with Keller acid solution and then observed at the optical microscope (Nikon Epiphot 200).

**Electrochemical evaluation**

The evaluation of the electrochemical properties of the samples under study was carried out by potentiodynamic polarization curves in NaCl 3.0% and natural aeration solution. These measures were performed in a classical 3-electrode cell, using as working electrode discs of 0.2 cm² of surface area, mounted as a rotating disk electrode (RDE). The lateral side of the electrodes was insulated with epoxy resin, taking care of avoid crevice in the interface metal-resin. The samples used for the fabrication of electrodes were thermal treated by homogenization at a temperature of 520 °C for 12 hours, quenched in water at room temperature and aged at 180 °C for 3 hours. A platinum grid of large area was used as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. All potentials shown in this study are referred to the potential of saturated calomel electrode (V_sce). Potentiodynamic polarization curves were performed by duplicate at a scan rate of 20 mV / min, starting from a cathodic overpotential of -0.6 V up to anodic overpotential of 0.8 V. Polarization curves were made in a Zahner potentiostat IM6e. To evaluate the effect of mass transport in the anodic and cathodic reactions, the polarization curves were made at various RDE rotation speeds. Before performing the polarization curves the working electrodes were cleaned with 600 grit sandpaper, cleaned and degreased in a mixture 50% acetone - 50% distilled water under ultrasound action by 3 minutes. Before starting the polarization test, the system remained idle for a time of 20 minutes to reach its steady state at open circuit potential (E_{ocp}). From the polarization curves were determined the variables that characterize the susceptibility to corrosion of materials, such as corrosion potential (E_{corr}) and the corrosion current (I_{corr}).

**Results and analysis**

**Analysis of the microstructure to different thermal treatments**

Figure 1(a) shows the micrograph of the alloy Al-4% Cu-0, 5% Mg-1.5% Ag “as cast”. From this micrograph it is possible observe copper precipitates in the grain boundaries in the form of dendrites and aluminum-rich light regions. Figure 1(b) shows the micrograph of the Al-4% Cu-0.5% Mg-1.5% Ag homogenized at 520 °C for 32 hours and aged at 220 °C for 27 hours. In this micrograph there are some thinner copper
precipitates in the grain boundaries even without dissolving in the matrix. Figure 1 (c) shows the sample of the alloy Al-4% Cu-0.5% Mg-1.5% Ag homogenized at 520 °C for 100 hours and aged at 220 °C for 1 hour, it can seen the difference respect to figure 1 (b), where grain boundaries are so thin as threads without precipitates, which form the binary phase α - θ. In Figure 1 (d) shows the sample of the alloy Al-4% Cu-0.5% Mg-1.5% Ag homogenized at 520 °C for 170 hours and aged at 220 °C for 1 hour. This micrograph lets to observe fully dispersed precipitates in the matrix without the presence of grain boundaries clearly defined. This result clearly indicates that the heat treatment conditions followed in this sample facilitate the diffusion of copper from the grain boundaries into the matrix, thus improving the homogeneity of the composition of the phases in the alloy. This type of microstructure can be classified as ideal for maximum strength, since the precipitates are very finely divided and homogeneously dispersed in the matrix, which ensure the minimization of stress concentration points and fewer pockets of initiation of micro-cracks when the alloy is subjected to mechanical stress.

Figure 2 shows the results of metallographic analysis made at the Al-4% Cu-0.5% Mg-2.5% Ag alloy with different heat treatments. Figure 2 (a) shows the “as cast” alloy with heat treatment of homogenization of 520 °C for 32 hours, quenched in water at room temperature and aged at 220 °C for 5.5 hours. Similar to it was observed for the alloy with 1.5% Ag, this micrograph lets to observe copper precipitates in grain boundaries in the form of dendrites and aluminum-rich light regions. A progressive decrease of the grain boundaries is observed in figures 2 (b) (c) and (d). This is consequence of the increasing in homogenization time and the decreasing of the aging time. In these micrographs it is possible to observe the phase changes that occur when homogenization times are increased. The phase changes are similar to those already explained in the alloy containing 1.5% silver in figure 1. Despite the changes in microstructure are similar in both 1.5% Ag and 2.5% Ag alloys, there was a slight delay in the disappearance of grain boundaries in the alloy with 2.5% Ag. Apparently higher silver content in the alloy contributes to more slowly diffusion of alloying elements from the grain boundaries into the alloy matrix.

**Figure 1** Optical micrographs of Al-4% Cu-0.5% Mg-1.5% Ag. (a) “as cast”. (b) homogenized at 520 °C for 32 hours, aged at 220 °C for 27 hours. (c) homogenized at 520 °C for 100 hours, aged at 220 °C for 1 hour. (d) homogenized at 520 °C for 170 hours and aged at 220 °C for 1 hour

**Figure 2** Optical micrographs of Al-4% Cu-0.5% Mg-2.5% Ag. a) “as cast”. b) homogenized at 520 °C for 32 hours, aged at 220 °C for 5.5 hours. c) homogenized at 520 °C for 70 hours, aged at 220 °C for 7 hours. d) homogenized at 520 °C for 100 hours, aged at 220 °C for 3 h
Figure 3 shows the micrographs of the alloys Al-4% Cu-0.5% Mg without Ag. Figure 3(a) shows the specimen “as cast”, where there are copper precipitates in grain boundaries and aluminum-rich light regions. Figure 3(b) shows the micrograph of the specimen with heat treatment of homogenization at 520 °C for 8 hours and rapidly quenching in water at room temperature. In this micrograph can be seen that the chains formed by the grain boundaries are breached, leaving the grain boundaries like loose links in short and thin sections dissolved in the matrix. The breaking of the grain boundaries and its dissolution in the matrix of the alloy without Ag are given at lower homogenization times that those observed in the alloys with Ag, suggesting that the effect of silver in the alloy is increase the homogenization time and accelerate the aging time. This could facilitate the precipitation of Guinier Preston zones (GP) and consequently increase the mechanical properties of the alloy [17], although the GP zones are not show in this work.

**Evaluation of the micro-hardness at different aging times**

The results obtained by Vickers micro-hardness tests on samples of non-silver alloys (0.0% Ag) “as cast” was 87.5 Vickers and for the alloy with homogenization at temperature of 520 °C for 8 hours, quenched in water at room temperature and aged at 180 °C for 3 hours, was 135 Vickers. Figure 4 shows the micro-hardness with respect to different aging times for various samples of alloys Al-4% Cu-0, 5% Mg with 1.5 and 2.5% Ag, homogenized at 520 °C for 8 hours, quenched in water at room temperature and aged at 180 °C for different times. The micro-hardness of the non-silver alloy is also showed. It can be seen that samples with 2.5% Ag reach greater hardness than samples with 1.5% Ag, in a relatively short time of 3 hours. Additionally, 2.5% Ag alloy exhibits more stable hardness after reaching its maximum value about 170 Vickers. It was observed that after 3 hours of aging a fall of hardness occurs, as a consequence of the over-aging treatment in the alloys. Thus it is evident that the maximum hardness of the alloys is achieved at 3 hours of aging, being not suitable to expose the alloy to longer times. Additionally, it is clear that the alloy with 2.5% Ag, is more properly aged than alloy with 1.5% Ag.

**Electrochemical behavior of alloys Al-4% Cu-0.5% Mg**

As the silver is the more noble metal among the other metal alloying elements in the alloy Al-4% Cu-0.5% Mg, it might assume that the silver-rich
phases in the microstructure behave as cathode respect to those poor-silver phases. If this happen it is likely that galvanic corrosion occurs between the phases, wherein the silver-rich phase polarizes anodically the silver-poor phase, accelerating the dissolution of this phase. Thus, it becomes important to characterize the electrochemical behavior of alloys Al-4% Cu-0.5% Mg with and without Ag in a corrosive media and evaluate the effect of addition of silver on the potential and current corrosion of the alloy. Figure 5 shows the potentiodynamic polarization curves of alloys with 0.0%, 1.5% and 2.5% of Ag, conducted at two different rotation rates of the electrode, 225 and 625 rpm. The global behavior of the anodic branch (E> E_{OCP}) in the polarization curves of alloys with and without Ag is very similar. In the range of anodic polarization is not observed any tendency to passivation of the alloys; this probably due to the presence of chloride ion which inhibits the formation of a stable passive layer on the metal. Additionally, no evident influence of the rotation rate in the anodic behavior of the metal is observed, since the anodic branch of the polarization curves performed at 225 rpm and 625 overlap. This indicates that there is not influence of mass transport of the dissolution products, generated during the anodic polarization, on the corrosion kinetic. A different situation is observed in the cathodic branch of the polarization curves. In the cathodic branch (E <E_{OCP}) is clearly seen that there is a diffusion-controlled cathodic reaction, exhibiting a current plateau at cathodic polarizations higher than -50 mV in all evaluated alloys. The apparent small slopes observed in the cathodic branch of polarization curves of Ag alloys are due to the polarization scan, which avoid to achieve complete stationary currents. In despite of that, cathodic limit-current (I_{LC}) can be read in the cathodic regions of the polarization curves. Being the electrolyte a chlorides solution with natural aeration, it is expected that the cathodic reaction is the oxygen reduction [21] and therefore the overall control of the metal dissolution is given by the diffusion of oxygen from bulk solution onto the metal surface. As consequence, at higher electrode rotation rates greater cathodic limit-currents are observed. In this way the cathodic limit-currents (I_{LC}) define the corrosion current and the corrosion rates of the alloys.

Figure 5 Potentiodynamic polarization curves of alloys Al-4% Cu-0.5% Mg in 3.0% NaCl solution at different electrode rotation rates. (a) without Ag, (b) 1.5% Ag, (c) 2.5% Ag
Table 2 shows the values of the potential and corrosion currents of the alloys tested in 3.0% NaCl solution for two electrode-rotation conditions, 225 and 625 rpm. It is noted that the rotation of the electrode, i.e. the hydrodynamic and mass transport, has no influence on the corrosion potential, but it does in the kinetics of metal dissolution. Increasing the mass transport by forced convection, due to the increased rotational rate, the reactive oxygen increase on the metal-dissolution interface; this causes an increase in the rate of cathodic reaction of oxygen reduction and hence anodic reaction rate of metal dissolution.

Additionally, in relation to the influence of the Ag content on the electrochemical behavior of the alloys, it is observed that the corrosion potential (E_{corr}) of alloys with Ag are slightly more positive than those (E_{corr}) the alloy without Ag. This means that the addition of silver gives a nobler characteristic to the alloy. This can be seen more clearly in figure 6, which shows potentiodynamic polarization curves of alloys Al-4% Cu-0.5% Mg with different contents of Ag. Corrosion current of the alloys were calculated by Tafel extrapolation from polarization curves and using the Tafel expressions:

\[ \varepsilon_c = b_c \log \left( \frac{I_c}{I_{corr}} \right) \quad \text{and} \quad \varepsilon_a = b_a \log \left( \frac{I_a}{I_{corr}} \right) \]

Were \( \varepsilon_c \) and \( \varepsilon_a \) are the cathodic and anodic overpotentials, \( b_c \) and \( b_a \) are the cathodic and anodic Tafel constants, and \( I_c \) and \( I_a \) are the cathodic and anodic currents. Lower current corrosion for the equal rotation rates of the electrode were observed in alloys with 1.5% and 2.5% Ag, being the alloy with 2.5% Ag the one with lower value, see table 2 and figure 6. These results show that addition of Ag in Al-Cu-Mg alloys gives lower susceptibility to metal corrosion. Indirectly it could be argued that due to the heat treatment performed, silver is uniformly distributed in the alloy matrix, because otherwise, if any phase or grain boundaries rich in Ag is formed these phases would increase the current corrosion as Ag content increases, which was not observed experimentally.

Table 2 Potential and current corrosion of the alloys Al-4% Cu-0.5% Mg with and without Ag. Values obtained from potentiodynamic polarization curves, Figure 5

<table>
<thead>
<tr>
<th>Rotation rate (rpm)</th>
<th>AI-0.0%Ag</th>
<th>AI-1.5%Ag</th>
<th>AI-2.5%Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E_{corr} / (V)</td>
<td>I_{corr} / (A)</td>
<td>E_{corr} / (V)</td>
</tr>
<tr>
<td>225</td>
<td>-0.627</td>
<td>5.5x10^{-5}</td>
<td>-0.621</td>
</tr>
<tr>
<td>625</td>
<td>-0.627</td>
<td>8.9x10^{-5}</td>
<td>-0.621</td>
</tr>
</tbody>
</table>

As mentioned above, during the anodic polarization of alloys, there was no tendency to form passive layers on the metals; contrarily it was observed an activation region during anodic dissolution at high anodic potential values. It is well known that aluminum is an amphoteric metal, and in aqueous media tends to dissolve extremely rapidly at pH values below 4 and above 9. At intermediate pH values, aluminum passivates by forming a stable layer of hydrated alumina (Al_{2}O_{3}-3H_{2}O) [22]. In this case of study it was observed that the addition of Ag to Al-4% Cu-0.5% Mg alloys, does not give stability to the passive films that could possibly be formed on the metal surface.

Figure 7 shows the polarization curves performed on the alloy with 2.5% of Ag in chloride media and pH values of 11 and 6.9. In the polarization curve made at pH 11, it is clearly observed a region of passivation, however present a more active corrosion potential (more negative) and higher corrosion rate than at pH 6.9. These results are in agreement with those predicted by Pourbaix diagram for aluminum [22]. As can be seen in the polarization curve at pH 6.9, the corrosion potential of alloy in chloride solution
Improvement of micro-hardness and electrochemical properties of Al-4%Cu-0.5%Mg alloy by Ag ... at pH value of 6.9 is coincident with the pitting potential of the metal (-0.62V), remaining above of the potential region in which the passive layer could be stable. This makes that the material can not generate a passive layer and its dissolution is controlled purely by activation of the surface and by the reaction rate of the cathodic reduction of oxygen. The chloride ion solution in this process plays a key role by breaking the passive layers that eventually could be formed.

**Conclusions**

- Manufacture of Al-4% Cu-0.5% Mg-Ag alloys required long homogenization times, usually superior to 100 hours, because the dissolution of phase $\theta$ into phase $\alpha$ is a slow process. Taking long homogenization times an ideal structure is achieved; with this procedure it is possible to dissolve large precipitates, which are responsible for the formation of stress concentration points. The more it achieves dissolve precipitates in the matrix, less aging time needed to reach higher hardness in the alloy. The effect of the silver addition in Al-4% Cu-0.5% Mg alloys increase the homogenization time and accelerate the aging time, causing the precipitation of Guinier Preston zones and the consequent increase of hardness.

- Long times of aging causes drop in hardness. This occurs because the Guinier Preston zones are formed at the beginning of aging, approximately during the first 3 hours. If aging time is excessive (over-aging) GP zones tend to disappear. With lower temperatures and moderate times (close to 3 hours) greater hardness are achieved.

- The addition of Ag to Al-4%Mg-0.5%Cu alloys gives superior resistance to corrosion, giving noble features to the alloy and reducing the current-corrosion of the alloy when is exposed to aqueous media with chlorides.

- The global control of the Al-4% Cu-0.5% Mg-Ag alloys dissolution is given by the diffusion of oxygen from the bulk solution to the metal surface. It is observed that at higher electrode rotation rates greater cathodic limit-currents are observed. In this way, the cathodic limit-current establishes the current-corrosion and defines the corrosion rates of the alloys.

- The corrosion potential of Al-4% Cu-0.5% Mg-Ag alloys is coincident with the pitting potential of the alloys (-0.62V), remaining
above of the potential region in which the passive layer could be stable. This makes that the material can not generate a passive layer and its dissolution is controlled purely by activation of the surface and by the reaction rate of the cathodic reduction of oxygen.

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References


