Behavior of AlxMgFeZn-alloy through microhardness, microstructure, thermal treatment and electrodissolution

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Microstructural changes induced by aged treatment shown a connection between differences of microhardness and electrodissolution. AlxMgFeZn alloys were prepared by metal mold casting method in order to diminish the process cost generating an alloy with homogenous microstructure and less casting porosity. In addition, was correlated the influence of chemical composition with the thermal treatment on the electrochemical dissolution or electrodissolution. With all this in mind, the AlxMgFeZn alloy has been studied by means of microhardness, X-ray diffraction, scanning electron microscopy, and short-term electrochemical test.

The formation of Mg3Zn3Al2 precipitate phase was identified for two conditions, the first one is when the chemical composition of magnesium is upper to 5.49% in as-cast condition and the second one is influenced by the thermal treatment of aging. In addition, the microhardness and electrochemical dissolution has been influenced by the presence and quantity of the Mg3Zn3Al2 phase. The chemical composition of magnesium alloying modifies the microstructure, increases the content of Mg3Zn3Al2 phase and provides a localized dissolution on the AlxMgFeZn alloy surface.

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1. Introduction

Most metallic materials have now moved beyond microstructure to nanostructure. However, research priorities are still non-understanding for technological applications and potential new power devices. With all these in mind, this article describes some of the most common and widely used materials, the binary AlZn and AlMg alloys. Furthermore, the Al-based alloys are used in packaging, construction, aerospace, and automobile [1].

Remarkable advances in environmental concerns, fuel economy, energy conservation, and safety has been positioned to aluminum alloys as transportation materials. While Zn-based alloys are candidates for the ultra-high temperature solder, applies for mold material used in automobile engine mounts, drive trains, agriculture equipment [2], and practical application [3]. Although Mg-based alloys promising in hydrogen storage, as lightweight of metallic structure materials, as armor materials in military and secondary or non-structural materials in aerospace area [4]. The variety of these industrial applications revives our interest as an excellent combination for an advantage alloy.

Combined with total life-cycle cost the alloy produced from Al, Mg, Zn, metallic elements basically are considered an effective substitute for a number of ferrous and nonferrous alloys [1]. These kinds of alloys could be considered lightweight and cost-effective materials. The AlMgZn alloys combine their ductility and formability with low density, excellent castability, high specific strength and high hardness [5]. The characteristic of AlMgZn alloys and almost all aluminum alloys is the recyclable after serving for their original purpose.

Alloying elements are present in solid solution or as segregated phase [6] and with the precipitation of intermetallic phases formed after heat treatment [7]. With a special thermal treatment [8] has been also improved the strong age-hardening given to the system their unique combination of lightweight and high mechanical properties [9]. That combination has been studied for some years because it gives raise to precipitation hardening.

The investigation of precipitation process in Al-base alloys indicates that several transformation sequences may occur in these materials during aging [10]. For the case in this work, heat treatment based on the fine precipitation of Mg3Zn3Al2 and MgZn2 phases. The formation of solute-rich precipitates begins from the supersaturated solid solution (SSS) α-aluminum matrix. The stable hardening phases strains the crystallographic planes of the aluminum matrix. Hardness is one of the mechanical properties, which have been highlighted with the microstructure on metallic alloys [11]. However, the link between hardness and electrochemical dissolution are critically dependent on both the chemical composition
and the internal structure. Microstructure is developed during casting, thermomechanical processing, and heat treatment [10]. It is well known that the microstructure is essential for the properties of alloys. For the case of corrosion or electrochemical dissolution particularly the influence of dendrite arm spacing has become related with mechanical properties. Dendrite arm spacing is principal change by cooling rate during solidification process. Even though the relationship between microstructure plus electrochemical dissolution and microhardness of AlxMgFeZn alloys has been few studied [12,13]. With all this in mind, the present study will deal without the microstructural evolution. Microstructure will be modified by different atomic combination of magnesium alloying in as-cast condition firstly. Aging thermal treatment was done as the second condition to transform the microstructure.

The present investigation is concentrating on studying the effects of magnesium addition on the microstructure in as-cast and after aging treatment. Likewise, we correlated it with microhardness and electrochemical dissolution (electro dissolution). The purpose of the present study was to understand better the role played by magnesium on the \( \text{Mg}_5\text{Zn}_2\text{Al}_2 \) particles distribution and the microhardness for the \( \text{AlxMgFeZn} \) alloy. This includes microstructural examination, electrochemical dissolution, and microvickers hardness tests. Microstructure was studied using Scanning Electron Microscopy with an Energy-Dispersive X-ray spectroscopy analysis, and X-ray diffraction. In order to know the electrochemical dissolution capacity of \( \text{AlxMgFeZn} \) alloys the short term electrochemical test was studied by open-circuit potential measurements. We found that the effective temperature of thermal treatment and high chemical composition of magnesium are the principal factors for microstructure changes, microhardness results, and also for the electrochemical dissolution of the \( \text{AlxMgFeZn} \) alloy. The susceptibility of \( \text{AlxMgFeZn} \) alloy was influenced basically by the presence and quantity of the \( \text{Mg}_5\text{Zn}_2\text{Al}_2 \) phase.

## Table 1

<table>
<thead>
<tr>
<th>Alloy type</th>
<th>Mg</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.96</td>
<td>5.36</td>
<td>Bal.</td>
</tr>
<tr>
<td>2</td>
<td>4.89</td>
<td>5.35</td>
<td>Bal.</td>
</tr>
<tr>
<td>3</td>
<td>5.49</td>
<td>5.32</td>
<td>Bal.</td>
</tr>
<tr>
<td>4</td>
<td>6.55</td>
<td>5.32</td>
<td>Bal.</td>
</tr>
<tr>
<td>5</td>
<td>7.33</td>
<td>5.30</td>
<td>Bal.</td>
</tr>
<tr>
<td>6</td>
<td>8.65</td>
<td>5.29</td>
<td>Bal.</td>
</tr>
<tr>
<td>7</td>
<td>9.58</td>
<td>5.29</td>
<td>Bal.</td>
</tr>
<tr>
<td>8</td>
<td>11.53</td>
<td>5.31</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Microsoft Windows environment. These results are the average of five analyses in different regions of the specimens.

With the purpose of investigate the effect of magnesium and heat treatment on the microstructure of the eight \( \text{AlxMgFeZn} \) alloys, samples of 100 g, were cut from the cast ingot. These samples were thermally treated at 450 °C for 5 h, allowing that all solute atoms from each solute phase enrich the solid solution until the quenched. The quenched was carried out in water at room temperature to development of supersaturation. The homogenized samples were then artificially aged at 400 °C for 1 h, with the goal of starting the precipitation process, characterized by increasing solubility with increasing temperature. This is sensitive to the selected trace elements and microalloying elements, which can change the process and/or kinetics of precipitation in many hardenable alloys by aging [14]. Frequently the aging heat treatment involves the formation of finely dispersed precipitates from the supersaturated solid solutions in order to increase the hardening/strengthening in the alloy system.

### 2.2. Metallographic analysis

The as-cast and aged samples were sectioned longitudinally at mid-width using a band saw. Just one side has been prepared for microstructural characterization by the standard technique. It begun through the grinding with metallographic paper of SiC up to # 1000, and mechanical polishing with 0.5 and 0.05 μm alumina powder. Based on the chemical etching it is controlled by the electrolytic action between surface areas at different potentials, the surface alloys etching in Keller's reagent [15]. The Keller reagent contained 5 ml of HNO₃, 3 ml of HCl, 2 ml of HF, and 190 ml of H₂O; the etch was done at room temperature for 15 s.

### 2.3. Characterization

Structural investigations were carried out with a Siemens D5000 X-ray diffractometer (XRD) with a power of 40 kV accelerating voltage × 30 mA current, using Cu tube of Kx line radiation: \( x = 0.15406 \) nm and a diffracting beam graphic monochrometer. The XRD patterns were recorded in the 2Ө range of 30–90° (step size 0.02°, time per step 0.6 s) and the evaluation of the diffractograms was made by DIFRACT/AC software.

The \( \text{AlxMgFeZn} \) microstructures were studied using a Stereo-scan 440 scanning electron microscope (SEM) using backscattered electron imaging (SEM) operated at 20 kV. SEM combined with energy dispersive X-ray spectroscopy (EDS) OXFORD Isis 300 was used to analyze microstructural modifications as well as to identify the elemental composition of the phases formed.

In order to observe the \( \text{AlxMgFeZn} \) alloy’s ability to resist plastic deformation hardness was measured. The measurement was done with a hardness tester INSTRON model 210013. Values were obtained on the cross-sections of the samples using a load of 2 N for 10 s and at least 10 impressions were recorded of each sample. The resulting hardness reading depends on the load and the area...
of the permanent pyramid impression. Hardness values were averaging excluding the maximum and the minimum values and the experimental error was estimated.

2.4. Performance dissolution

In order to know how many ampere–hours of protective current will be available for each unit-weight of AlxMgFeZn alloys, the capacity current performances were evaluated by a short-term electrochemical test [16]. The working electrodes, also called anodes, in an oxidation reaction with 10 mm² width × 50 mm length, were prepared from AlxMgFeZn ingots of as-cast and aged condition. All the specimens were polished with 1200 emery paper, then degreased in acetone and washed thoroughly in double distilled water.

The working electrode used for each test was mounted in a specially designed electrochemical cell using the three-electrode system and was connected electrochemically to a galvanostat DC current source. A saturated calomel electrode (SCE, E = +0.242 V saturated) was the reference electrode, which was used as half-cell. The reference electrode controls the working electrode potential and is a reference from the potentials measured. An auxiliary electrode, from electrochemically inert platinum wire, was used as counter electrode. It functions as cathode (in a half cell) and passes all the current needed to balance the reaction at the working electrode. A sheet of carbon steel served as the cathode.

The electrolytic test solution was synthetic sea water. This solution was prepared with sodium chloride analytical grade reagent and distilled water with an initial pH of 8.3 according to ASTM D1141 [17].

The test anode and cathode were both galvanically coupled together at different current density levels (0.4, 1.5, 4.0) and immersed in the electrolytic solution for 3 days. The anodic current density, mA/cm² was applied during a 24-h period. The samples were taken out and were cleaned by ASTM G 31 standard practice. The samples were then rinsed with distilled water, dried by blow-drying hot air and weighed in order to obtain their weight loss. The weight of the AlxMgFeZn was measured before and after the immersion. From the actual weight loss measured, the capacity and theoretical current charge to be produced by the alloy could be calculated by:

\[ CC = \frac{Am}{TAm} \]

where CC is current capacity, Am is Actual ampere hours delivered by AlxMgFeZn alloy and TAm is theoretical ampere hours calculated from weight loss of AlxMgFeZn alloy.

3. Results and discussion

With the AlxMgFeZn alloys encompasses a materials processing and materials characterization with the properties alloy and appropriate application. With all this, we can show in Fig. 1 the interaction between the X-ray and polycrystalline AlxMgFeZn phases. The qualitative analysis of diffraction pattern belongs to the alloy probably due to the formation of a supersaturated solid solution enriched by solute atoms like magnesium and zinc. These two phases appears when the Mg content is 1.38 times more than the atomic percentage of zinc, which one is nearly constant for all the alloys.

X-ray diffraction follows the structural changes of AlxMgFeZn alloys produced by casting process and alloys with an aging thermal treatment. The X-ray diffractograms for samples in as-cast and aged conditions show that Mg3Zn3Al2 phase precipitates are formed in our alloys with high Mg addition. But there are few reflections of the Mg3Zn3Al2 phase precipitates for samples with low Mg as can be shown in Fig. 1. These observations demonstrate that the formation of the Mg3Zn3Al2 phase particles was promoted through the high Mg addition plus the aging treatment condition. Previously, it has been assumed the fact that 7000 series aluminum alloys has a strong trend for preferential precipitation during the subsequent aging process [11].

With the X-ray diffraction measurement, we found the atomic-structure differences between the two phases in AlxMgFeZn alloys. But it is apparent also from inspection of Fig. 1 that the relative intensities for the (1 1 1) reflection of the α-Al (which is a rich-aluminum solid solution with crystalline structure fcc) is much higher than the other peaks. This higher relative intensity indicates the presence of a texture which, was developed during the casting operation. It should be mentioned that the XRD intensities are influenced also by the phase content, the crystallite size, lattice strain and, degree of crystallinity [20]. During the heat treatment an atomic reordering of the aluminum matrix exists towards a preferential direction of the planes (2 2 0) and (3 1 1) as it can be observed in Fig. 1.

The variations in intensity and small displacements of the diffraction angle have their origins from the variations in composition of the alloy probably due to the formation of a supersaturated solid solution enriched by solute atoms like magnesium and zinc. These are the primary elements of alloy, also called second elements associated with a metal to form an alloy.

Properties of casting alloys have continually improved due to their greatly influence by microstructural features such as grain size and orientation and dendrite-arm spacing. This trend was controlled during the foundry process with the melting and casting temperature and also minor additions of manganese.

The first results showed that the Mg3Zn3Al2 phases are formed by two routes, a first one route as product of the solidification process when the Mg addition is up 5.49% Mg. And the second route by the aging precipitation process in the composition range of
7.33–11.53 at.% Mg. The other phase in the Al-alloys under study was the α-Al, which is formed through the solidification route mainly. All the alloys contain α-Al with a dendritic structure developed by the combination of thermal and constitutional undercooling. It is well-known, that a solidification structure depends strongly on the solidification conditions.

The representative microstructure (Fig. 2a) from as-cast condition reveals the presence of equiaxed morphological structure. In four of the AlMgFeZn alloys with a composition from 7.33 to 11.53 at.% Mg, the primary solidification for the α-Al solid solution is followed by the eutectic solidification of α+τ-Mg₃Zn₃Al₂ phase.

It has been reported [2] that the lamellar eutectic structure is derived from the decomposition of the α phase by the following cellular reaction at 762 K, α → α-AlFe + Mg₃Zn₃Al₂ or τ-Mg₄₉Zn₄₉Al₃₂.

The stable phase Mg₃Zn₃Al₂ was observed homogeneously dispersed on the Al-matrix with geometry of rods. These precipitates (Fig. 2b) were observed in aged samples firstly. The heat treatment and high content in Mg addition caused an increase of volume fraction of Mg₃Zn₃Al₂ precipitates.

The microstructure of AlₓMgFeZn alloys observed in as-cast condition was modified with heat treatment. It can be observed from the Fig. 3a that dendritic structure is broken down and show a quasibinary eutectic mixture. This apparent eutectic structure is formed by Al and Mg₃Zn₃Al₂. This was always observed along the grain boundaries of the primary α-Al matrix in aging condition alloys. In the eutectic region the light contrast corresponds to the phase Mg₃Zn₃Al₂. While dark contrast corresponds to the α-Al phase (Fig. 3b), Al-matrix or solid solution rich in aluminum, for each name is also the same FCC crystalline structure of aluminum.

The literature on alloys [12,13] of the type studied in this work, point out that the solidification equilibrium involves the existence of two phases. One of them is an aluminum based α-solid solution and another phase, the τ-Mg₃Zn₃Al₂. The last one phase, having a variable composition around the Mg₄₉Zn₄₉Al₃₂ formula, which is considered a non-stoichiometrically intermetallic phase. These intermetallic particles are the second phase that dominate the feature of AlₓMgFeZn microstructures.

Previous work [21] has been related the magnesium content with the hardness on an Al-alloy. Evidently the hardness property is directly connected with the semi-coherent and coherent precipitates rich in magnesium. The effect of coherency or semi-coherency of the second phase is effectively to impede the dislocation motion and get a hard material. In our case, the precipitate Mg₃Zn₃Al₂ and the solid solution of the matrix alloy has the bcc and fcc crystal structure respectively.

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**Fig. 1.** X-ray diffractograms of the AlₓMgFeZn alloy in as-cast condition showing the presence of the main lines of diffraction τ-Mg₃Zn₃Al₂ and α-Al peaks with eight different Mg content.

**Fig. 2.** (a) Shows the microstructure of AlₓMgFeZn alloys formed by α-Al equiaxed dendritic structure as-cast condition. (b) Mg₃Zn₃Al₂ precipitation in the matrix aged condition.
The precipitate has a different crystalline lattice spacing that the matrix material forming a connection between the hardness and crystallographic structure between these principal actors. Another effect related could be the atomic size of alloying elements. Due to the zinc and magnesium are smaller and larger, respectively than aluminum [4]. In addition, the presence of Mg3Zn3Al2 precipitates is also associated with the electrochemical dissolution. That is attributable to the difference in the electrical potential between precipitates and matrix.

Vickers hardness and current capacity curves, from as-cast and aging condition are shown in Fig. 4. The α-Al structure with aging treatment is 8% harder than the surrounding Al-matrix in as-cast alloys. Indeed, the average Vickers hardness measured inside the Al-matrix for as-cast structure is 83.65 HV, whereas the Al-matrix for aging is 91.81 HV. These values emphasize the influence of the Mg3Zn3Al2 particles inside the matrix. It can be seen from Fig. 4 the higher point from the alloy added with 5.49% Mg. This alloy has a significantly hardening and also a high current capacity. The high current capacity related to electrochemical dissolution for this alloy is developed at 1.0 vol.% Mg3Zn3Al2-phase particles. The peak in current capacity is achieved after 4.89% Mg addition. The current capacity curve for as-cast condition show the similar behavior: the high peak is reached when Mg3Zn3Al2-phase is equal to 1.0 vol.%. It is clear that aging treatment enhance the hardness and also the current capacity, when the Mg addition does not exceed 5.49%. It means that the phase Mg3Zn3Al2 increases due to the formation of quasibinary eutectic structure (α-Al + Mg3Zn3Al2). However, the α-matrix decreases and also its distribution of Mg3Zn3Al2 precipitate. These results emphasize that the precipitates on the matrix active the surface of the alloy. The activated surface influenced in electrochemical dissolution when it breakdown the oxide film. This passive oxide overlayer formed in air covered the surface of the α-AlMgFeZn alloy. The current capacity is greater when the initial attack is present for the intermetallic compounds distributed in the matrix. However, the intergranular eutectic phase begins to dissolve it and this intergranular corrosion is stronger than the Mg3Zn3Al2-phase.

4. Conclusions

According to the effects of magnesium addition as alloying element on the chemical composition of AlFeZn it has been related with the microstructure and the electrochemical dissolution of the alloys modified with magnesium, and the following conclusions are obtained:

- The precipitation of Mg3Zn3Al2 particles depends on the magnesium addition, aging condition and the quantity of the eutectic phase formation.
- The addition of Mg in just 5.49 at.% to the aging AlFeZn alloy clearly increases the peak of current capacity as electrochemical dissolution anode and generate the 1.0 vol.% of Mg3Zn3Al2 precipitates.
- For magnesium content upper than 5.49% with aging condition the eutectic phase increase more than Mg3Zn3Al2 precipitates and the dissolution of the alloy decrease while for low magnesium content the Mg3Zn3Al2 phase is poor such as current capacity.
- A current capacity as high as 81% has been achieved with magnesium plus aging treatment on AlxMgFeZn alloy that electrochemical dissolution process depends on the amount of Mg3Zn3Al2 particles deposited at the Al-matrix surface.

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