

# Thermochemistry oxidation of trimetallic alloy modified by thermal procedure

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**ABSTRACT:** In the present paper, the evolution of an oxidation process has been associated to the collective atomic arrangement, the microstructure one. This microstructural analysis encompasses a metallographic examination and a relation of electricity to chemical changes in salt-water solution. The electrochemical experimental techniques used include corrosion potential measurements. To seek a deeper understanding of microstructure evolution throughout secondary manufacturing process, a natural and artificial ageing at 5, 24, 100 and 200 h has been used. The objective of this paper is expressed on correlated the dependence of the oxidative surface degradation with the microstructure development by the thermal aged condition. The performance of the expected optimum conditions was estimated considering the microstructural inspection and analytical studies using scanning electron microscopy and EDX. The thermochemistry oxidative degradation has a different behavior in each condition electrochemical test, that has been related with the microstructure, mostly occurring related to namely primary solid solution aluminium rich ( $\alpha$ -Al), eutectic ( $\alpha+\tau$ ), and precipitates. Eutectic phase showed influence on oxidative degradation behavior more significantly in artificial ageing thermal treatment. Alloys artificially aged with small eutectic size and fine precipitates offered marginally lower corrosion rate and better passivation compared with the higher time ageing condition. The EDX spectrum in interdendritic region before and after corrosion test revealed the removal of eutectic from alloy during corrosion. The corrosion behavior of the AlMg alloy modified with zinc is influenced by the microstructure, phase type and quantity of phases.

**KEYWORDS:** Eutectic phase, internal structure evolution, trimetallic alloy, potentiodynamic polarization, thermal aging procedure.

## I. INTRODUCTION

The chemical reaction associated with the degree of loss of electrons has been well established as oxidation state. The oxidation chemical specie could be an atom in a chemical compound. Meanwhile, when the material as trimetallic alloys combines with oxygen any chemical reaction could be developed with the alloyed elements.

As can be seen in the figure (1), a balanced chemical equation and state the reaction type the three molecular oxygen reacts with four aluminium atoms by chemical action and an inorganic coating can be produced [1,2].

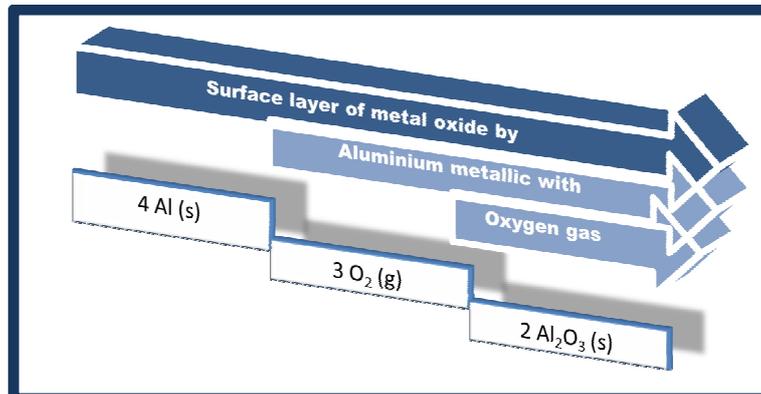


Figure 1. Metallic materials have been oxidized in environments containing oxygen by a chemical oxidation-reduction reaction between metal and oxygen from the second law of thermodynamics. For the aluminium and their alloys, the spontaneous reaction occurs when 4 mols of aluminium reacts with 3 mols of molecular oxygen gas to form 2 moles of Aluminium oxide, under conditions that both temperature and pressure are constant.

The oxide formation expressed in figure 1 is a natural oxide film for aluminium and aluminium alloys in solid solution. Likewise, the protective film of Al<sub>2</sub>O<sub>3</sub> could be altered by adding alloying elements [3]. It is necessary to study the properties that they confer on microstructure transformations. With all this in mind, the present study is focused on describes the development of microstructures after ageing thermal treatment. In addition, the paper correlated the dependence of the oxidative surface degradation with the microstructure. This microstructural analysis comprehends a metallographic examination and electrochemical tests in salt-water solution.

## II. RELATED WORK

Aluminium alloys could be considered as an Engineering Materials due to their good ductility, high mechanical properties after heat-treating by the strong age hardening. Besides, aluminum and its alloys possess one third of steel density, this advantage has been used for the need of weight reduction. Their uses as light alloys have extensive projections applications in the aerospace and automobile fields, the transport industry [4]. The importance of aluminium becomes stronger through small additions of alloy elements in first place. Moreover, a key role is assigned for the manufacturing process as the metalworking procedure called heat treatment [5,6]. In light of the aluminum applications, with no explicit reference, we consider that thermal treatment relies on the transformation of microstructure. The microstructure that is developed during casting involves formation of a solid solution, which is a primary aluminum phase. Secondary phases and microsegregation of the alloying element has been involved in the microstructure [7,8]. However, the effects of the thermal treatment in casting microstructure include several sequences. For the case of aging thermal treatment, the presence of fine particles, in the last thermal stage, strains the crystallographic planes of aluminum matrix [9]. With the increase of strength, ductility and hardness appear to be the most important mechanical properties critically dependent of heat treatment [10]. Nevertheless, if microstructure and mechanical properties are modified, the formation of protective Al-rich oxide it may be related with the microstructure evolution [11].

The kinetics of oxide formation and surface degradation has been associated with the corrosion behavior, in our case, of Aluminum alloys. For the case of formation and local breakdown of passive films, the processing as casting and thermal treatment influences the oxidative degradation events of these metal materials [12]. Furthermore, in processing and manufacture, the additions of alloying elements contribute to the electrochemical characteristic. Which are also related considerably with the environment to which metallic material is exposed. In fact, there are so many aspects and chemical elements answerable for oxidative degradation [13]. Although, the effect of microstructure on the oxidative performance, and electrochemical degradation of aged Al-alloys under simulated condition of marine atmosphere should be systematic studied.

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In our work, the multiphase of microstructure was examined using optical microscopy, segregation and chemical details was observed by scanning electron microscopy and EDX. One of the problems facing in the field of electrochemistry is the oxidative degradation, in our case, it was monitoring by open-circuit potential (OCP) measurements. Through this paper, it is has been broadly referenced the relationship found between the microstructure and heat treatment as secondary manufactured process, and their influence with the oxidative degradation. For the microstructure study, it has been considered the grain size morphology and the phases on the alloy.

The present contribution indicate the microstructural observations together with heat treatment, the results displays a mean grain size was much lower for samples with 200 h heat treatment. Current preoccupation between maximum losses weighted with thermal feature can be attributed to the initial evidence to the increase of eutectic phase amount for 100 and 200 h heat treatment. These result provided that the time of heat treatment as the principal factor for the weight loss 3.5% NaCl electrolyte. The oxidation and reduction processes reveal the susceptibility of AlMg alloy with the heat thermal conditions plus the eutectic microstructure formed. More recent investigations examined the influence of microstructure on the properties of variety kind of alloys processed by emergent manufacturing process.

## III. EXPERIMENTAL MATERIALS AND PROCEDURE

### 3.1 Foundry and casting process

Magnesium and zinc have been used as alloying elements in Al alloys simultaneously to make them display their own advantages associated with low density and mechanical properties. These chemical elements were commercially available with purities of 99.98 % for atomic level of mixing from casting manufacturing through metal molding method. Molding performs include the select of metal material for the mold itself and the gating design that causes a better ingot quality characteristics.

For a given uniform atomic distribution in the liquid composition, it was stirred with argon for 10 minutes. The molten metal alloy was poured into a copper mold with geometry of 2.0x5.0x7.0 cm, which creates a successful casting design. Successful AlMg castings were obtained from the tilted bonded copper molds when poured with a superheat above 120°C. Because of the importance of multi-microalloying in modifying the microstructure, the nominal composition of the alloy is expressed in Table 1, which shows the average of three chemical analyses obtained by inductive coupled plasma-atomic emission spectroscopy (ICP-AES).

### 3.2 Thermal Treatment

In the possibility to analyze the phase and precipitates we have been made aluminum-magnesium cubes of 2.0x1.0x1.0 cm, which were heated in a muffle furnace at 430°C during 21h. Then, the cubes were cooled in liquid nitrogen in order to get a homogenization treatment. After that, the samples were natural aging during 97 h. In view of that, the aging effect has long been recognized as a critical stage of synthesis four test samples were prepared using different artificial heat treatments aging. The main assumption in our treatment is that aging influence a subsequent microstructural evolution, to reach all goal the samples were artificially aged at 230°C for 5, 24, 100, and 200 h, to further examine the aging effects of the alloy on the resulting phase an air cooled was carried out after aged time.

### 3.3 Metallographic preparation.

Ingots were sectioned longitudinally to the plane normal. Their samples surfaces were mounted in bakelite and were prepared by the standard technique. Metallographic preparation of encapsulated specimens was performed by grinding the specimens from 100 to 2000-grit paper and polished with 1 μm Al<sub>2</sub>O<sub>3</sub> suspension solution. After that the top surface of samples alloys were etched in Keller's reagent [14], which contained 5ml of HNO<sub>3</sub>, 3 ml of HCl, 2ml of HF, and 190 ml of H<sub>2</sub>O; the etch was done at room temperature for 20 s in order to reveal the microstructure.

### 3.4 Microstructural analysis.

In order to determine crystal structure and phases identification the as-cast and corroded specimen surfaces were examined by optical microscopy, and scanning electron microscopy with an accelerating voltage of 25 keV. Chemical

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microanalysis was carried out with an energy dispersive X-ray analyzer (EDX) attached to the SEM (shown in Table 1).

Table 1. Nominal chemical composition of the experimental trimetallic alloy, given in wt.%. This atomic composition suggests to the type and ratio of major alloying elements and trace atoms. Is very important to determine the Chemical composition due to high impact of alloying elements in the structure, properties and performance of trimetallic aluminium alloys.

### 3.5 Electrochemical test.

An analysis of electrochemical test has been carried out by suspending a square sample (1 cm<sup>2</sup>) in a still NaCl solution. Exposed areas of 1.0 cm<sup>2</sup> were essay in each thermal procedure under static conditions, without stirring the electrolytic solution. The electrical contact was made by welding an 80 wt. % Cr–20 Ni wires to the alloys samples.

The test electrolytic solution was prepared using A.R grade NaCl in distilled water and was aerated substitute ocean water with an initial 8.3 pH according to ASTM D1141 [15]. Before the immersing in NaCl solution, square samples were ground, polished and then cleaned with deionized water followed by rinsing with ethanol, dried and weighted. The square samples were exposed to the NaCl solution for twenty-eight days. At the end of the test, the samples were removed, cleaned, and weighed to obtain weight loss date.

The electrochemical corrosion test results were evaluated by weight loss measurements, performed following the ASTM G31-12a recommended practice [16]. The accelerated electrochemical test was carried out to determine electrochemical working potential. All potentials were measured relative to a saturated calomel reference electrode. Samples were held galvanostatically at different current density levels. Each level was applied during a 24-hour period with 96 total test hours. The alloys samples were prepared in the same way as that for weight loss evaluation. To reveal any tendencies to passivation, the electrochemical working potential was measured at the beginning and at the end of each current density level period.

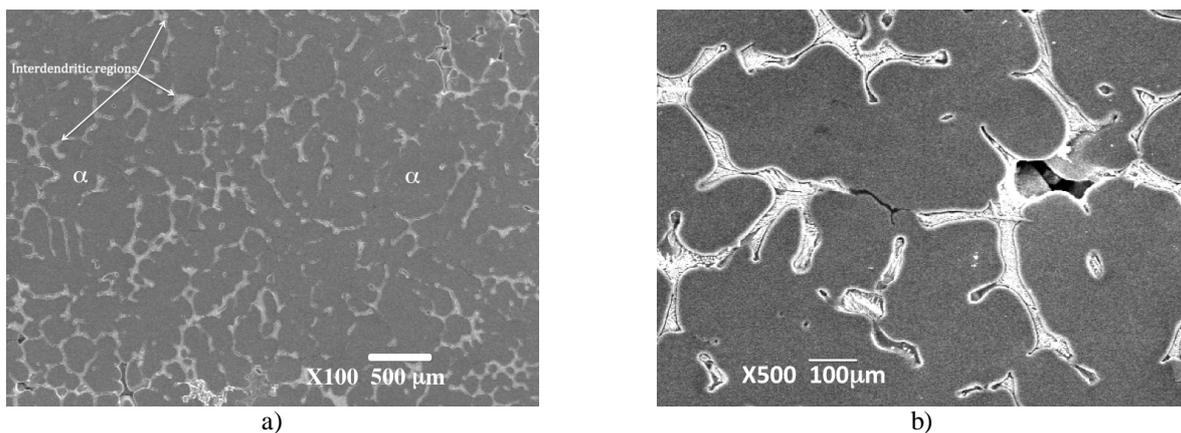


Figure 2. Scanning electron micrograph from the trimetallic aluminium-base alloy showing as-cast solidification morphology and type of phases. The electronic scanning microscope allow to understand structure and reactivity degradation because their images down to the atomic level. More advanced studies relates the atomistic calculation with the microscopic mean-field theory to calculate atomic structure and free energy.

IV. RESULTS AND DISCUSSION

In general, as the control of relationships between processing and performance of engineering materials conducted to provide a microstructure examination and its formation. Speaking of phases, morphology and arrangement atomic, the microstructure plays a pivotal role in metallurgy, corrosion and materials science. In attempt to do this characterization, our microstructural examination revealed the presence of three phases: A matrix  $\alpha$ -phase, and intergranular regions showed in Figure 2(a) with arrow, and finally phases as precipitates on the matrix. The first one is a  $\alpha$ -Al solid solution expressed as SS $\alpha$  and  $\alpha$ s $\alpha$ -phase, which is rich in aluminum and displays a dendritic structure, which can be seen in figure 2(b). Dendritic microstructure is the most frequent solid morphology when a metallic alloy is solidified [17,18]. Dendritic arrangement could be found in much commercial alloys with a columnar or equiaxed dendritic structure [19].

A renewed stimulus to understanding the mechanisms and factors involved of the evolution microstructure for AlMg alloys Zn added converges to show a figure 3. The figure 3 shows a detail of grain boundary precipitates observed from as-cast specimens. Which are commonly formed in Fe-containing Al alloys [20, 21] that have been determined the iron and aluminium presence in FeAl<sub>6</sub> stoichiometry composition by EDX microanalysis. Current preoccupation with microstructure predictive involves the backscattered electrons by SEM micrographs.

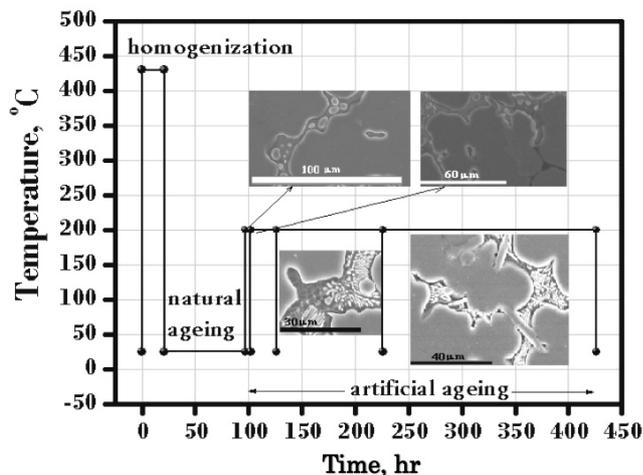


Figure 3. Scanning electron micrograph of an aged trimetallic aluminium-base alloy following the equiaxed dendritic microstructure evolution from initiated artificial ageing to maximum time of artificial ageing. The images presented show the morphology suitable for investigations concerning to the eutectic and precipitates phases formed. In addition, the equiaxed dendritic structure expressed to the primary, secondary and tertiary arms and the interdendritic regions has been related with the morphologic degradation by an oxidation reaction.

In Figure 3, the representative microstructures corresponded to the thermal treatment aged samples, especially for 100 and 200 h. It can be seen that the aged alloys contains spherical and long rod-like phase in intergranular regions. This microstructural behavior has provided dark contrast areas, which correspond to Al rich phase, while light contrast phase is rich in the microalloying elements zinc and magnesium. There are so many factors and elements responsible for corrosion, however studies have revealed that certain phase combination can lead to significant eutectic-type  $\alpha$ -Al +  $\tau$ -Mg<sub>3</sub>Zn<sub>3</sub>Al<sub>2</sub> phase [22,23]. The eutectic-type formation observed in interdendritic and intergranular regions was higher for both samples with 100 and 200 h aged than 5 and 24 h ageing time. In addition, could be observed in Figure 3 the heat treatment sequence and their relationship with the microstructure for each artificial ageing time. One can see that the microstructural evolution of the artificial ageing alloys towards to eutectic-type grows. Indeed, the eutectic-type measured in cast structure is 2.14 %, whereas the eutectic-type in 200h aged is 15.88 %. These values emphasize the influence of the time heat treatment eutectic-type grows.

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Various alloying elements, in terms of the properties they confer of variations on electrochemical performance [24]. In our case, the electrochemical tests results, as final weight loss of the samples with respect to ageing duration time is presents in table 2. For 100 and 200 h ageing, the oxidative corrosion progressed rapidly, by the way, could be mentioned that Lavoisier, who has been the first to use the term "oxidation" to mean reaction of a substance with oxygen [25]. The oxygen react with aluminium formed on surface a protective oxide film, which does not have an acceptable capability to protect the alloy derived from some alloying elements.

Initial evidence that alloying elements and thermal treatment affects the characteristics of the transformation during the oxidative degradation, our results suggest that at short duration aged times (5 h and 24 h) the samples exhibited lower weight loss. This is relationship with the increase of eutectic-type microstructure at high artificial ageing time, as occurs in the various binary equilibrium systems. The increase in oxidation state is due to the intergranular eutectic phase, which begins to dissolve it and this intergranular corrosion is stronger than the  $\alpha$ -Al phase. These observations are agreed with a similar event reported by Knight and Ming Zhao [26, 27]. Such reactions involve the formal transfer of electrons, a net gain in electrons being a reduction and a net loss of electrons being an oxidation.

Samples conditions					
	As-cast	Artificial ageing time, h			
		5	24	100	200
Loss weight, g/cm <sup>2</sup>	8.56 ± 0.1	17.57 ± 0.2	17.71 ± 0.1	17.01 ± 0.3	32.18 ± 0.3
Eutectic-phase, %	2.14 ± 0.001	8.41 ± 0.001	10.63 ± 0.003	13.69 ± 0.002	15.88 ± 0.004

Table 2. The final loss weight and the eutectic phase have been associated with two manufacturing conditions: the as-cast and the artificial ageing time for the trimetallic aluminium-base alloy. When the morphological evolution of solidifications microstructures have been modified by a heat thermal treatment, the microstructure absorb the energy during the modification of morphology, which tends to be the first one of the electrochemical degradation.

In the field of electrochemistry, involves the electrolyte media, which consider the acquisition or release of ionic charges. In addition, the table 3 shows the phases detected from an EDAX-spot between interdendritic and intergranular regions of the AlMg alloys before and after the electrochemical test corrosion. This result reveals the eutectic-type dissolution for 200 h ageing timesamples.

Phases detected in trimetallic alloy			
As-cast	200 h artificial ageing		Electrochemical degradation
$\alpha$ -Al	$\alpha + \tau$		Before
$\alpha$ -Al		$\alpha$ -Al	After

Table 3. Comparison of phases observed in trimetallic aluminium-base alloy under as-cast condition, and artificial ageing conditions, before and after test corrosion. The electrochemical degradation for the trimetallic aluminium-base alloy has been identified with preferential morphology for the quasi-eutectic-type phase  $\alpha + \tau$ . this kind of phase presents a dependence on both zinc and magnesium content. In another hand, the  $\alpha$ -Al phase is phase rich in aluminium atoms.

Eutectic-type was the phase detected by EDAX with the Zn, Mg presence close to stoichiometry composition of  $Mg_3Zn_3Al_2\tau$ -phase for samples 200 h ageing before the test corrosion, while the EDAX for interdendritic and

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intergranular regions at the same sample after the test corrosion shows a similar composition to the matrix alloy with a presence of oxygen, which evidence the eutectic oxidation.

The development of the complex as-casted microstructures during the as-cast and thermal treatment has been expressed previously thought out this work. The fundamental scientific principles on microstructure interactions has been reported elsewhere with the importance on microstructure-property relationships in as-cast solidification, precipitation-hardened and dispersion-strengthened aluminium alloys with specific reference to matrix microstructural features. In addition, several researchers have also highlighted the deleterious effects on surface oxides or films passive formation on mechanical behavior and electrochemical degradation for aluminum alloys. In order to evaluated the influence of electrochemical degradation we report in the table 4 the open-circuit potentials results with their artificial ageing time, which has been correlated with the eutectic-type presence. Efforts are being made to find out a correlation between heat treatment and microstructure because the corrosion potential values are eutectic-type dependent. It was noted that these values were more negative than  $-690$  mV, the value reported previously for high Al purity. This type of values could be related with the Mg and Zn microalloying elements.

	As-cast	Artificial ageing time, h			
		5	24	100	200
<b>Potential, V</b>	$-1.095 \pm 0.3$	$-1.067 \pm 0.1$	$-1.039 \pm 0.1$	$-1.028 \pm 0.2$	$-1.019 \pm 0.1$
<b>Eutectic-phase, %</b>	$2.14 \pm 0.001$	$8.41 \pm 0.001$	$10.63 \pm 0.003$	$13.69 \pm 0.002$	$15.88 \pm 0.004$

Table 4. The relationship between manufacturing conditions with the electrochemical potential results for the trimetallic aluminium-base alloy show a hard associated response with quasi-eutectic-type phase. The study relates the as-cast condition and different artificial ageing times with less electrochemical potential values when the quasi-eutectic type phase increases.

It is interesting to note in the table 4 that as-cast condition for 5 and 24 h artificial ageing sample, which contained less eutectic presence, was subjected to comparatively less corrosion attack. However, 200 h ageing sample show a severe corrosion represented by the potential values corresponding to eutectic-type dissolved phase.

## V. CONCLUSION

The experimental results presented have highlighted the oxidative degradation behavior of thermal treatment AlMg alloy Zn added in 3.5% NaCl solution. The results can be summarized as follows

- The analysis of microstructure displays a combination of dendritic  $\alpha$ -Al matrix, eutectic-type phase and an interdendritic  $\text{FeAl}_6$  precipitates. Eutectic phase increase with the heat treatment manufacturing process. This eutectic phase is the principal microstructural factor in the oxidative degradation behavior.
- The weight loss of the AlMg alloys Zn added in 3.5% NaCl solutions increase with accumulative thermal ageing time duration.
- The high loss weighted can be attributed to the high eutectic amount in the alloys for high time ageing.
- The electrochemical test reveals the susceptibility of AlMg alloy Zn added with the artificial ageing time and the  $\alpha + \tau$  phase formation.
- The corrosion potential results are sensitive to the thermal treatment time and the phases of microstructure.

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