

# Degradation analysis of Aluminum cellular alloy in saline ionic electrolyte

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**ABSTRACT:** As-cast pure metals exhibit a different microstructure than as-cast alloys, influenced by solute content, soluble solutes several factors. In this work, the as-cast and melting, in an alumine crucible, was considered for the AlZnMg alloy manufacture. The molten alloy was poured into steel containers with sodium chloride crystals, in order to produce the cellular-type material. After solidification and cooling process the salt crystals was removed using hot water. The electrochemical degradation of the material was characterized by potentiodynamic polarization and electrochemical impedance spectroscopy. The dissolution process was studied when the alloy was exposed to saline solution at room temperature in order to estimate the degradation resistance. The adding of the chemical elements changed the phase atomic arrangement, and induced a resistance of degradation oxidative.

**KEYWORDS:** Electrochemical degradation, cellular-type alloy, saline solution, chemical elements, sodium chloride.

## I. INTRODUCTION

The complex interactions involving mechanical properties like ductility, and conformability with low density, excellent castability, and high specific strength can give rise to the mechanical-light material performance [1]. The characteristic properties of mechanical behaviour in combination with light-weight has been reaching out the usage of Al-base alloys. The synthetic aluminium-base alloys have been used for automotive applications, due to the great interest to decrease the oil consume. This consideration tended to result in the use of 5XXX and 6XXX aluminium alloys which are added with silicon, magnesium and microalloying elements most frequently used in car body panels [2].

An additional advantage of aluminium material, for all knows is the capability of forming a passive oxide film on its surface when it is exposed to aqueous environment. This oxide protective coat provides to aluminium their characteristic resistance of electrochemical degradation.

Besides, the electrochemical degradation reaction is associated with the chemical alloying elements. In addition, the atomic impurity presence exhibits an essential function on particular phase degradation. Thus, the chemical composition of elements added to aluminium base alloy influenced the attack morphology, repassivation of metastable pits, and including the dissolution kinetics [3]. Furthermore, the microstructural electronic defects in combination with a 4.0-8.5 pH range, has been correlated with the pitting corrosion in aluminium alloys.

The most comprehensive and successful model in electrochemical degradation including the absorption and localized penetration of chemical anions. The negative charge of anion nature give an electrochemical activity in defective sites highly conductive of aluminium layer, which conduced to their breakdown [4].

Similarly, aluminium alloys with appropriate porous design have been proposed as functional material by mean of recycling and environmental affinity [5]. Previous work on porous materials has been studied in grapheme, in order to make full utilization of the high intrinsic surface area. Which has been attracted research interest, owing to heir exceptional porous structure with advantage in high surface area, and high pore volume [6].

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Overall, in the case of metallic material, improved alloys take advantage of potential applications in packing, automobile, aerospace, and construction industries [7]. The properties as strength, sound absorption, sound isolation, heat shield, interception of electric wave and impact, vibration absorption [8] demonstrated their general uses.

These materials have received a lot of attention over the last few years, and it has been improved understanding of their physical, chemical, and mechanical properties [9,10] however the electrochemical properties have been poorly studied. A previous work [11], reported the corrosion loss rate and corrosion potential by immersing in simulated seawater of cellular aluminium, Al– 5 wt.% Cu and Al–2 wt.% Mg–Re fabricated by using the melt foaming method.

Many measurements, analysis, and modelling techniques have been assumed for this framework bases on cellular-type alloys based in aluminium chemical element.

However, in this work, the cellular-type AlZnMg was studied by the characterization of the electrochemical degradation using electrochemical techniques as alternative representations of cellular base aluminium alloys. Direct Current basis techniques helped to estimate the corrosion rate and the anodic dissolution trend due to the different chemical alloying elements, while Alternating Current basis technique, such as electrochemical impedance spectroscopy helped to elucidate the interfacial evolution when exposed to electrolytic environment. The electrochemical characterization described the differences between the chemical composition alloys.

## II. EXPERIMENTAL MATERIALS AND PROCEDURE

### 1.-Synthesis of cellular type-AlMgZn alloys

Knowledge of manufacturing metallic alloys characteristics opens the path to the discovery and understanding the route of casting cellular alloys. In some cases, the understanding approaches to the engineering and management basic process, like our case.

The matrix alloy was processed by stoichiometrically mixing pieces of commercially available elemental aluminum and zinc ingots with 99.8% commercial purity. An interesting and basic reactions occur during the alloy melting which start when aluminium and zinc ingot pieces were put inside of a steel crucible, kept in a resistance electrical furnace, at 700°C.

The formulation of a flux mixture of salts has been utilized to avoid the elements oxidation in contact with the environment atmosphere. Although many basic processing find a partial solution with a atmosphere control, we used a excess to the required amount of these constituents, in order to compensate some oxidation losses, 3wt% Al and 10wt% Zn were taken. By taking advantage of the heterogeneity of the alloying atomic elements has proposed four different compositions of magnesium added to the aluminium with zinc melt alloy.

The magnesium pieces was preheated at 300°C and incorporated at the melt AlZn matrix alloy via refractory feeder tip directly into the alumina crucible, and then was stirring 5 minutes for a better homogenization. The AlZnMg molten alloy was poured into a cast iron mould, in order to evaluate the electrochemical properties. Stringent conditions, such as high pressures, high vacuum, well-controlled atmospheres, or long fabrication times were not required.

### 2.-Processing of cellular-type AlMgZn alloy

All economic casting process has been demonstrated their efficient and statically regularities in final ingot properties. With all this in mind, a predetermined quantity of AlMgZn melt was poured into a cylindrical steel mould. Previously, sodium chloride crystals were put inside the mould in order to produce the cellular-type material.

Cylindrical mould dimensions are 50 mm inner diameter, 80 mm in height, and 2 mm wall thickness. After solidification process the sodium chloride was removed by their dissolution in hot water at 45°C.

The nominal chemical composition of cellular-type AlMgZn obtained by Inductively Coupled Plasma is given in Table 1, with a positive metal identification that allows the elemental analysis.

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Cellular-type alloy	Chemical Elements					
	Si	Fe	Mn	Zn	Mg	Al
Cell-base	0.1519	0.4531	0.3189	5.36	3.96	Bal.
Cell-X	0.1444	0.3946	0.3125	5.35	4.89	Bal.
Cell-Y	0.1930	0.3634	0.2320	5.32	6.55	Bal.
Cell Z	0.1488	0.4534	0.2851	5.29	9.58	Bal.

Table 1. This chemical composition for trace elements, solute, and solvent element was obtained from matrix of Al-Zn-Mg cellular-type. The chemical composition shows the concentration variations correlate with the principal solute, the magnesium element.

### 3.-Metallographic analysis

With a basic technique, the cellular-type samples surfaces were prepared by the standard grinding with SiC up to # 1000 emery paper, and mechanical polishing with Al<sub>2</sub>O<sub>3</sub> suspension solution, followed by etching in Keller’s reagent. To prepare the reagent solution 5ml of HNO<sub>3</sub>, was mixed with 3ml of HCl, and 2ml of HF, and 190ml of distilled water, the etched was done at room temperature for 20 secs. After that, the samples were observed by Scanning electron microscope (SEM) STEREOSCAN-440 using backscattered electron imaging operated at an accelerating voltage of 20 kV equipped with an energy dispersive X-ray spectroscopy (OXFORD Isis 300).

### 4.-Electrochemical testing

To predict the behavior of electrochemical degradation it has been considered necessary to start with a real-work data based on three-electrode electrochemical cell.

This description form the basis of faraday laws, in which the working electrode was the sample aluminum alloy, the reference electrode was the calomel saturated electrode and the counter electrode was a platinum mesh.

The ionic electrolyte was 3.5% NaCl solution prepared with distilled water and sodium chloride in reagent grade. The most successful sequence of electrochemical testing initiated with open circuit potential during 2000hr that combined with the steady state impedance measurements was performed.

To expect the conduct of that aluminum samples, the amplitude signal of the AC impedance was 5mV rms; the frequency range was 10<sup>4</sup> to 10<sup>-2</sup> Hz using an electrochemical unit Solartron 1280B.

Most electrochemical degradation research is represented via the corrosion rate. To represent our cellular type samples in this way, we must be able to consider the corrosion rate, which was estimated by the polarization resistance measurements from -0.015V to 0.015V vs. SCE with 0.1mV/sec scan rate.

Each corrosion rate of this samples set, were commonly estimated by using the Rp fit. On the other hand, a new set of samples was represented by measurement of potentiodynamic test from -1.5V to 1.5V vs ref at scan rate 1mV/sec.

## III. RESULTS AND DISCUSSION

Different structural properties have been indicated in porous or cellular materials. In cellular-type metallic alloy, one of the most important parameter is the porosity degree, and their distribution in relationship with the pore or cell morphology, and pore dimensions. The parameters like bulk porosity (Prb); Plane porosity, (Prp) and Real-time porosity, (Pr): has been previously studied in metallic cellular alloys. In the relationship under the study it has been reported the bulk porosity, by following the multiple common expression [10]:

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$$Pr_b = \left( \frac{\sum V_i}{V} \right) \times 100\% = \frac{V_s - (W/\rho)}{V_s} \times 100\% \quad \text{eq.1}$$

Where W is weight of cellular-type AlMgZn alloy; and Vs, is the volume, so the bulk porosity refers to the volume fraction of all the pores in an ingot of the cellular-type AlMgZn alloy.

The Prb for cellular-type AlMgZn is  $60\% \pm 0.79$ . We may avoid the assumption of chemical variations between aluminum and magnesium chemical elements. For any given pair of such components, the porous relationship is uniquely associated with sodium chloride content into the mold.

In order to predict this interactions, between porous and morphology, an image of the solid atomic arrangement evolve in figure 1, in where we can observe the formed the  $\alpha$ -Al homogeneous solid solution, in gray dark color, with dendritic morphology. This one is the most frequent solid morphology of an alloy solidified from a melt.

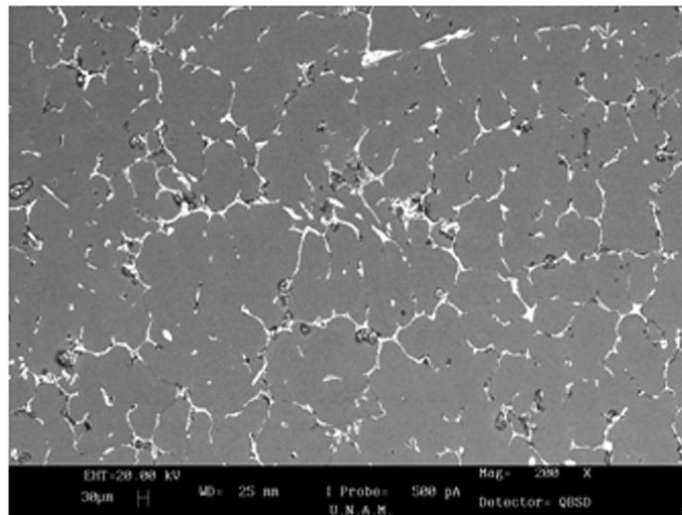


Figure 1. Typical morphology observed for the cellular-type AlMgZn alloy. The microstructure observed show white sections that provides the grain boundary regions.

The dendritic microstructure is an array of primary and secondary arms, where the voids between the dendrite branches were filled by eutectic-type phase. It has been reported [12] that the side branches are formed by the amplification of fluctuations induced on the tip of the primary branches.

The table 2 shows the different containment of the chemical elements Aluminium, magnesium, and zinc in the grain boundary regions and also the diffusion solutes into the matrix alloy. Such information is vital for development and verification of improved solidification process, for example.

In fact, based on modern metallurgical understanding, the chemical composition influences the morphology of a solidification reaction that took place under cooling of a solid transformation.

Therefore, material requirements included the distribution of chemical compositions. Throughout the atomic content in each region of microstructure, the material provides the chemical influence on degradation properties. In order to do that, the EDX analysis was done, which reveals that the grey dark zone corresponds to  $\alpha$ -Al solid solution with atomic magnesium and zinc dissolved on it. The solutes, magnesium and zinc, distributions are related with the experimental alloy composition and the limit of solubility denoted by the corresponding AlMg phase diagram.

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Cellular-type	Matrix		Interdendritic region	
	Zn	Mg	Zn	Mg
base	3.84 ± 1.70	2.44 ± 1.22	4.76 ± 0.44	2.85 ± 0.63
x	5.30 ± 0.83	4.48 ± 1.19	12.75 ± 3.33	14.38 ± 1.59
y	1.46 ± 0.20	3.80 ± 0.66	15.66 ± 2.39	13.67 ± 1.88
z	4.05 ± 0.20	10.34 ± 0.65	19.73 ± 3.12	26.85 ± 3.12

Table 2. This table shows the EDX results from principal phases of AlMgZn. The precise spatial composition makes the material with chemical variations that affect the electrochemical response.

Additionally, from the EDX results, was observed a phase into the interdendritic regions with high chemical composition of zinc, and magnesium content in contrast with the matrix  $\alpha$ -phase rich in aluminium.

The amount of aluminum added to zinc-based alloy varies over a wide range in addition while the equilibrium solid solubility of Zn in Al lattice at room temperature is less than 1 wt%. However the zinc (hcp) content in cellular-type AlMgZn alloys are present in the matrix until 4.05 % due to the presence of magnesium, a hexagonal close-packed (hcp) element, and also the table 2 shows that the amount of Zn and Mg atoms is higher in the bright phase which corresponds with the interdendritic region.

The figure 2 shows the microstructure representative to the cellular-type AlMgZn with maximum presence of interdendritic phase for the cellular-type AlMgZn z-sample). Previous work [12], has been reported the presence of a third phase, identified as FeMn precipitates with morphology like Chinese symbol distributed close to dendritic regions as consequence of Fe-containing Al alloys, however, we can observed it in figure 2B.

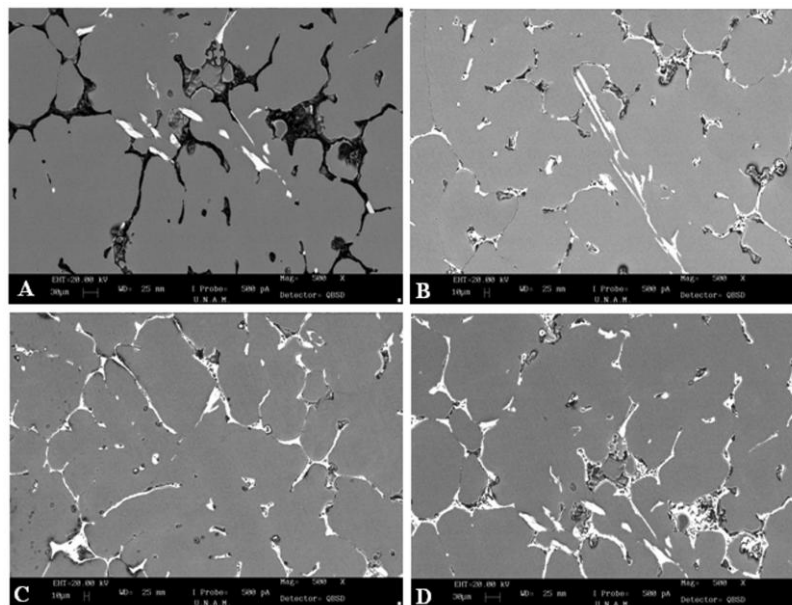


Figure 2. SEM microstructure from cellular-type AlMgZn alloys. This photomicrograph shows the principal phases, such as matrix, grain boundary and interdendritic regions.



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Selected microstructure features within a SEM field of view show an equiaxed dendritic morphology. The microstructure observed, evidential the absence of segregation or impurities, and even more SEM photomicrograph in figure 2 did not shows internal fissuring, associated with abnormal microsegregation.

AlMgZn cellular-type	OCP (V. vs SCE) @ 1hr	Corrosion rate (mpy)
base	-1.0	19.0
x	-1.06	76.2
y	-1.1	105.8
z	-1.09	99

Table 3. This table shows a summary table of data of the Electrochemical Testing results of the Open Circuit Potential, and the Corrosion rate for the cellular-type AlMgZn alloy.

Table 3 displays the magnitudes of the corrosion rate; the base alloy shows the lowest rate in NaCl solution (3.5% wt) and the sample label as Y alloy show the highest magnitude. In this cellular-type sample, was detected the lowest Mg + Zn solute elements dissolved into the  $\alpha$ -Al matrix (table 2).

The alloy elements define the interfacial characteristics, the magnesium allow represents good agreement with the dissolution rate. Is well known that the corrosion rate of cast aluminium alloys is strong influenced on microstructure it related with morphologies and chemical phases.

Figure 3 shows the potentiodynamic tests for different cellular-type AlMgZn alloy, the corrosion rates are reported following the Tafel slopes using non-linear least square fitting process by anodic and cathodic branch.

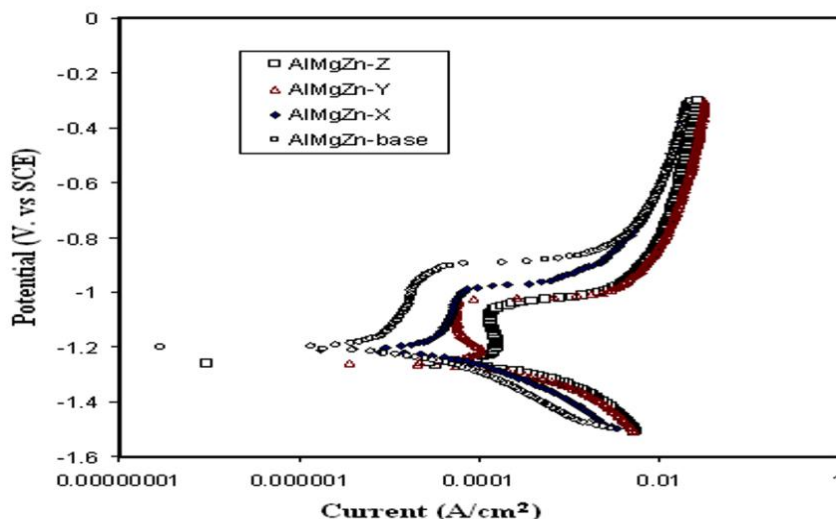


Figure 3. An Electrochemical testing by the polarization potentiodynamic, show the plots for cellular-type AlMgZn samples exposed to NaCl at 1mV/sec scan rate

The importance of polarization potentiodynamic is widely understood in the corrosion process. A considerable amount of research has been frequently involved with the polarization potentiodynamic and their principal parameters the potential and current.

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Figures 4 show the impedance characteristics of each cellular-type AlMgZn alloy with time, the plots were tested in a sequence of experiments; four plots represent 300 min of total exposure. Figure 4 represents the alloy samples in NaCl solution.

Two loops with different amplitudes are displayed. The first loop at high frequencies is related to the corrosion layer formed at the surface by the initial dissolution process. The characteristics of the layer are considered constant by assuming a capacitive response and pore resistance of the layer associated with the first loop.

The second loop displayed at medium to low frequencies increases the amplitude with respect to time. The second capacitive response can be attributed to the charge transfer reaction occurred at the interface between the substrate cellular type alloy with the electrolyte. The complex representation is typical of a coating type behavior previously reported by several authors [10]. Previously Aluminum-Magnesium alloys in NaCl solutions have corroborated the second loop as the indication of the dissolution precipitation process [11].

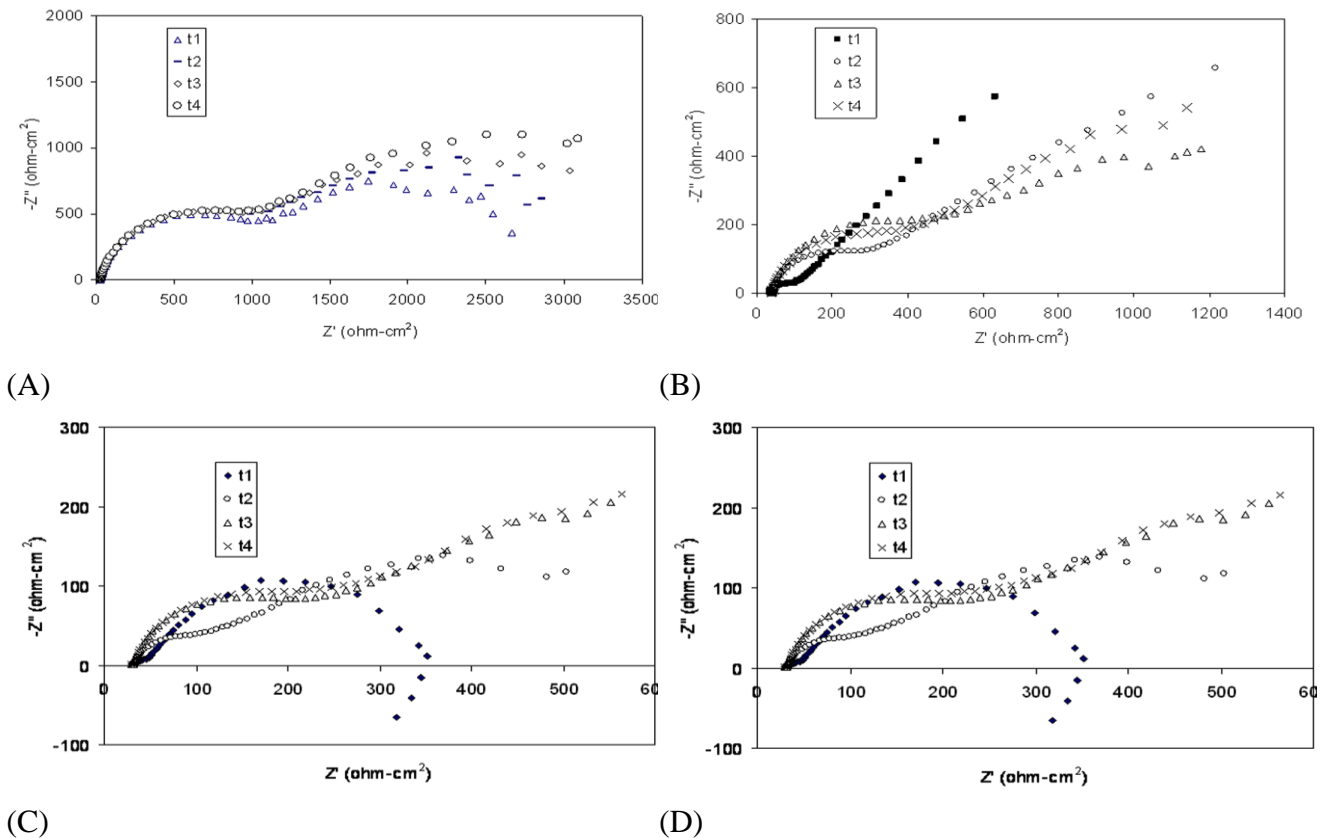


Figure 4 Show the complex representations of electrochemical impedance for cellular-type AlMgZn exposed to 3.5% NaCl solution, for the case of (A) w-sample, and (B) X-sample, (C) Y-sample, and (D) Z-sample.

The evolution of impedance when the alloy sample is modified is represented in figure 4(B) the nature of the impedance signal is different at low frequencies when the alloy contains less Mn and Si. Initially at low frequencies the response represents diffusion like behavior; this latter can be attributed to the mass transfer process of the chloride species within the porous of the layer formed with time. The film formed in this alloy X has pathways to the alloy substrate. The impedance evolution for cellular-type AlMgZn sample-X shows the shift response at low frequencies in Figure 4(B), this latter can be attributed to the modification of the corrosion product pores formed by the active dissolution process. The lineal response in low frequency represents mass transfer process characteristic of porous layer in electrochemical cells. The formation of the second loop is influenced by the denser layer or less pores density

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presented in the film. After 300min or t4 the formation of the layer stabilizes the impedance response by comparing the previous test time (t3) with the last measurement (t4). Figure 4(C) displays the impedance signal for cellular-type AlMgZn sample-Y had similar behavior as alloy sample X at 4 different times. The HF loop describes the capacitance and resistance characteristics of the corrosion product layer while LF represents the dissolution precipitation process. Figure 4(D) shows the evolution of cellular-type AlMgZn sample-Z following exposure in NaCl solution, the last time represents the stability of the interface following 300min of exposure. The transient state during the first time, t1, illustrates the active state of the alloy in NaCl solution, attributed to the behavior to the localized corrosion process occurring at the initial exposure time.

It should be mentioned the aluminum alloys capacity to form passive films. The alumina film is a protector layer formed by the diffusion of Al atoms through the grain boundaries to the surface of the alloy, and to form the protective passive layer that gives at the aluminum their corrosion resistance. When alloying elements are present into aluminum-base alloy it could be modified the cast aluminum corrosion response.

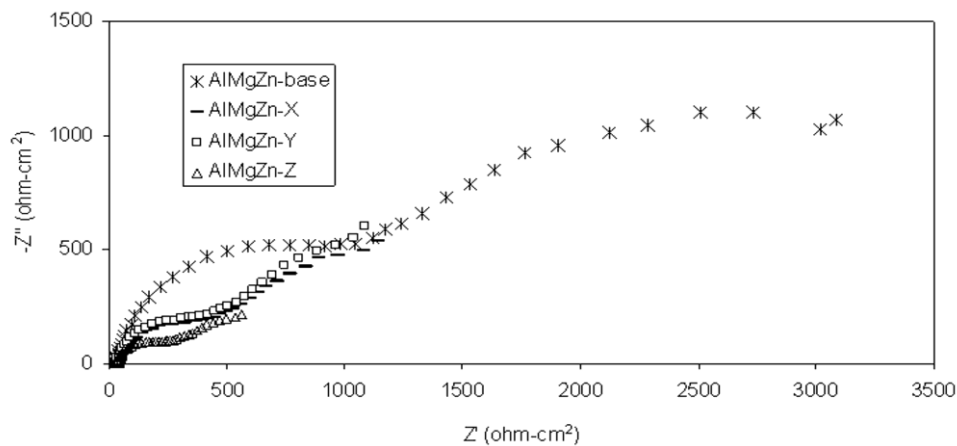


Figure 8 Impedance responses after 300 min by Nyquist representation for the cellular-type AlMgZn alloys exposed to NaCl solution by considering the last measurement with the variations of chemical composition.

In figure 8, it has been represented the behaviour of the impedance response after 300min for different cellular-type AlMgZn samples, which shows the interfacial modification due to the corrosion product/film behavior.

The corrosion rates magnitudes displayed in table 3 are in agreement with the impedance magnitude at low frequencies. The alloy-w (base) resulted in the lowest corrosion rate while the corrosion product formation shows a layer with higher impedance magnitude at low frequencies. The layer formed helped to control the dissolution rate associated with the dissolution precipitation process. The other alloys samples (x,y,z) show the formation of corrosion product layer due to same control process with lower impedance magnitudes at low frequencies. Table 3 shows the corrosion rate for alloy-x four times higher than the alloy w (base), and the impedance is higher in alloy-w than alloy-x. The highest corrosion rate is alloy-y. The Mg alloying element is in good agreement with the corrosion rate trend for each alloy.

#### IV. CONCLUSION

The experimental results presented the microstructure and corrosion behavior of cellular-type AlMgZn alloys in 3.5% NaCl solution. The results can be summarized as follows;

- The microstructure observed is composed by dendritic  $\alpha$ -Al matrix, with interdendritic regions rich in solute Mg + Zn alloying.
- Interdendritic phase increase with magnesium content and is a microstructural factor in the corrosion behavior.



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- The second parameter influencing corrosion is the microalloying distribution (Mn and Si) into the matrix plus interdendrite phase.

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