EVALUATION OF CORROSION RESISTANCE OF AM60 MAGNESIUM ALLOY

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Abstract: The technological development and great concern with the sustainability have become the magnesium alloys used increasingly in industry, since the projects require elements that are both lightweight and sturdy. In this case, these alloys fall into this category because they have a lower density compared with common alloys used in the fabrication of structural elements, up to 75% lighter than steel. Moreover, it is important to consider that certain magnesium alloys can have mechanical resistance close to some low-carbon steels. However, there is great concern about the corrosive process that these alloys may suffer in certain environments. Since the magnesium alloys have high susceptibility to corrosion in media containing chlorides. The corrosion of magnesium alloy arises due to many factors such as environment (humidity and temperature), the composition of the alloy, the microstructure (presence of β phase) and the properties of the medium in which the alloy is exposed (sea water, for example). Therefore, this study aims to evaluate the corrosion resistance of AM60 magnesium alloy in medium with chloride. For such an investigation was necessary to conduct tests such as weigh loss, potential over time, potentiostatic polarization curves. All these tests were performed in the presence of solutions like artificial sea water and in a 3.5% (vol.) NaCl solution.

Keywords: Magnesium alloys, die casting, Corrosion tests in magnesium alloys.

1. INTRODUCTION

Magnesium is the lightest structural metals. Recently, Cheng et al. (2008), stated that the magnesium alloys compared with steel, aluminum alloys and plastics used in engineering, have excellent properties such as low density, high thermal conductivity and electromagnetic, and mechanical resistance. These properties make the appropriate magnesium alloys for aerospace and automotive applications, where lightweight metals are required in order to reduce weight and emission of gases that cause global warming, according to Pardo et al. (2007). But so far, its application is still limited due to its low resistance to corrosion.

However, since there are studies that report the low resistance to corrosion of magnesium alloys as a result of its chemical elements and the content of impurities. The Mg-Al alloys belong to the most common type of magnesium alloys, and exit several versions regarding the influence of aluminum on the corrosion resistance of magnesium alloy. Lunder et al. (1989), found that when the aluminum content reaches 8% (mass fraction), the corrosion resistance of magnesium alloy can be greatly improved. However, the study by Warner et al. (1992) indicated that 5% Al magnesium alloy was useful for corrosion resistance.

The aim of this study is to characterize the behavior of AM60 alloy from two different suppliers, and the number 1 is the Brazilian alloy and the number 2 is the Spanish alloy. They were tested in the presence of solutions such as artificial sea water and in a 3.5 % (vol.) NaCl solution. For that were made metallographic analysis, testing of weigh loss, potentiostatic polarization curves and analysis of potential over time.

2. BIBLIOGRAFIC REVIEW

Recently, Correa (2008) showed in their studies that the Magnesium is the eighth most abundant element on Earth, reaching approximately 1.93% by mass of 0.13 Earth's crust and oceans. Magnesium has a high strength-weight ratio with a density that is only 2 / 3 of the aluminum and 1/4 of the iron. This metal has several characteristics such as high thermal conductivity, good electromagnetic shielding characteristics, high damping characteristics and it is easily recyclable. However, one of the major limitations for more widespread use of magnesium industrially is its susceptibility to corrosion.

According Blawert (2004), the magnesium alloys have two disadvantages for automotive applications because of their low resistance at high temperatures and a relatively weak protection against corrosion. The main step to improve the corrosion resistance is the production of high purity alloys. Some alloys can improve resistance to corrosion, but can't avoid the problems of galvanic corrosion, because of contact with other metal magnesium alloy or an electrolyte. This problem can be solved using coating as a protection system.

According to Pardo et al. (2007), the corrosion resistance of Mg alloys depends of many factors:
- Environment;

- The alloy composition and microstructure;
- The properties of the medium in which the alloy is exposed;

With respect to corrosion due to environment, Zeng et al. (2006) claim that the corrosion of magnesium alloys increases with increasing relative humidity. In 9.5% of relative humidity neither pure magnesium nor any other alloy elements presents on the surface corrosion after 18 months. At 30% humidity, a little corrosion can occur. With 80% humidity, the surface may shows a considerable corrosion. In the marine atmosphere, magnesium alloys require protection to have a prolonged survival. The stress corrosion cracking is affected by environmental factors such as high temperatures and humidity.

Concerning the alloy composition and microstructure, Cheng et al. (2008) says that the corrosion property of magnesium alloy is closely related to its chemical activity and its high content of impurities. Mg-Al alloy is the most common category of magnesium alloy and there are many different versions about the influence of aluminum on the corrosion resistance of magnesium alloy.

According to Pardo et al. (2007), Magnesium metal is a little resistant to corrosion, with great weakness in the presence of aggressive ions like chloride, for example, could limit its applications. This happens because usually in Mg-Al alloys, the aluminum is the solid solution and partially precipitated in the form of $Mg_{17}Al_{12}$ along the grain boundaries as a continuous phase and a lamellar structure. It is known that the $Mg_{17}Al_{12}$ presents a passive behavior when exposed to a higher pH than other components of aluminum and magnesium, it appears that the distribution of phase $Mg_{17}Al_{12}$ determines the corrosion resistance of Mg-Al alloys. Suggesting that the β phase mainly serves as a galvanic cathode and accelerates the corrosion of the matrix.

Cheng et al. (2008) say that the corrosion resistance of different magnesium alloys, is directly related to the concentration of alloying elements and microstructure. The ratio of β phase in AZ91 is higher than the AZ31 and the β phase can form micro-galvanic cells with the alloy's matrix, hence the corrosion resistance of the AZ31 is higher than AZ91. In the magnesium alloy AM60, the Mn can form the second phase particle AlMnFe, which can reduce the Fe content in the matrix of magnesium alloy, which leads to the purification of the alloy's microstructure. As a result, the corrosion resistance of AM60 is improved.

Lu et al. (2007), argue that the magnesium alloys can corrode easily when small amount of aggressive ions such as chloride anions are present in the middle. Moreover, with increasing oxidation temperature change occurs in the film of magnesium oxide in the porous structure and the alloy loses its protective property for oxidation.

3.EXPERIMENTAL

The magnesium alloy investigated in the trials was the AM60, which has the following chemical composition presented in Table 1. The sample 1 refers to the Brazilian material and the sample 2 refers to the Spanish material. The specification is according to ASTM B93/B93M-00. There were two different tests on each sample. For this, we used two different instruments, the Optical Emission Spectrometer (EO), where the analysis was performed using standard traceable A91-M-00 (HYDRO). The other was the equipping Plasma Spectrometer (ICP), and analysis was performed using traceable standard GMI-14 (SUS).

Chemical Composition - Magnesium Alloy AM60										
Identification		Equipment	%Al	%Zn	%Mn	%Cu	%Si	%Fe	%Ni	%Be
Alloy	Test	-	5.6-6.4	0.20Max.	0.26-0.50	0.008Max.	0.08Max.	0.004Max.	0.001Max.	0.0005-0.0030
AM60-1	1st test	E.O	4.7	0.13	0.31	0.008	0.035	0.0032	0.001	0.0001
AM60-2	2nd test	E.O	5.0	0.15	0.33	0.008	0.026	0.0034	0.001	0.0002
AM60-1	1st test	E.O	6.3	0.10	0.30	0.001	0.017	0.0035	0.001	0.0007
AM60-2	2nd test	E.O	6.0	0.11	0.26	0.002	0.016	0.0030	0.001	0.0006
AM60-1	1st test	ICP	4.8	0.12	0.28	0.009	0.032	0.0035	0.001	0.0002
AM60-2	2nd test	ICP	5.1	0.13	0.30	0.008	0.025	0.0037	0.001	0.0001
AM60-1	1st test	ICP	6.2	0.12	0.28	0.002	0.018	0.0034	0.001	0.0008
AM60-2	2nd test	ICP	6.1	0.10	0.27	0.002	0.016	0.0024	0.001	0.0008

Table 1 - Chemical composition of the AM60-1 and AM60-2

The data has an error around ± 1 unit. For the experiments we used specimens of AM60 alloy, designated as 1 and 2, both die castings and two kinds of solutions: artificial sea water and in a 3.5 %(vol.) NaCl solution. The compositions of these solutions are shown in Table 2:

Artificial sea water	3.5%(vol.) NaCl solution
- distilled water; - 15g / L NaCl; - 1.2 g / L CaCl$_2$; - 15g / L of MgCl$_2$; - 3g / L of MgSO$_4$;	- 965mL of distilled water; - 35 g NaCl;

Table 2 - Chemical composition of the solutions.

To perform the evaluation metallographic, the samples were ground to number 1500 sandpaper and polished with alumina 0.3 µm. The etching was carried out with glycol with immersion time between 15 and 20 s.

For the testing of weigh loss, the specimens were machined in the shape of cubes, weighed in a precision electronics scale and separated into two beakers, one with a solution of artificial sea water and other with a 3.5 %(vol.) NaCl solution. Every seven days, the solutions were exchanged and the samples removed from the solution, washed and weighed. The test lasted about 60 days.

The laundering was done with distilled water and sponge steel, which was carefully passed over the specimens for the removal of oxide, so that it would not affect the measure. Soon after thorough washing, the samples were immersed in ethanol for several seconds and dried with the aid of a conventional dryer. The weighing was performed on an electronic scale whose accuracy has reached the fourth decimal place.

For the determination of the polarization curves, were fabricated two specimens, one of the AM60-1 alloy and another one AM60-2 alloy. The samples were welded to a wire and they were isolated with resin and enamel, to ensure that the contact would not occur between the wire and tested solution.

Polarization curves were determined for each sample, with their respective triplicates for each of the solutions, AM60 1 and AM60 2 in artificial sea water and in a 3.5%(vol.) NaCl solution. The tests were made using the method of cyclic voltammetry in conventional electrochemical cell with three electrodes, WE (work), RE (reference) and CE (counter) electrodes are AM60-1 and AM60-2 alloy samples, saturated calomel (SCE) and wire (or plate-like) platinum, respectively. These electrodes were engaged in a AUTOLAB PGSTAT101 potentiostat at a scan speed of 0.005 V / s and the tests started at the open circuit potential.

To test the potential over time we used three specimens of each alloy. The samples were immersed in artificial sea water and in a 3.5%(vol.) NaCl solution. The alloy's potential were monitored three times daily for 13 days until stabilization occurs. For the realization of each measure were used as reference electrode a saturated calomel and a multimeter.

4. RESULTS AND DISCUSSION

4.1. Metallographic analysis

The Figure 1 shows the metallography of the alloys AM60-1 and AM60-2.

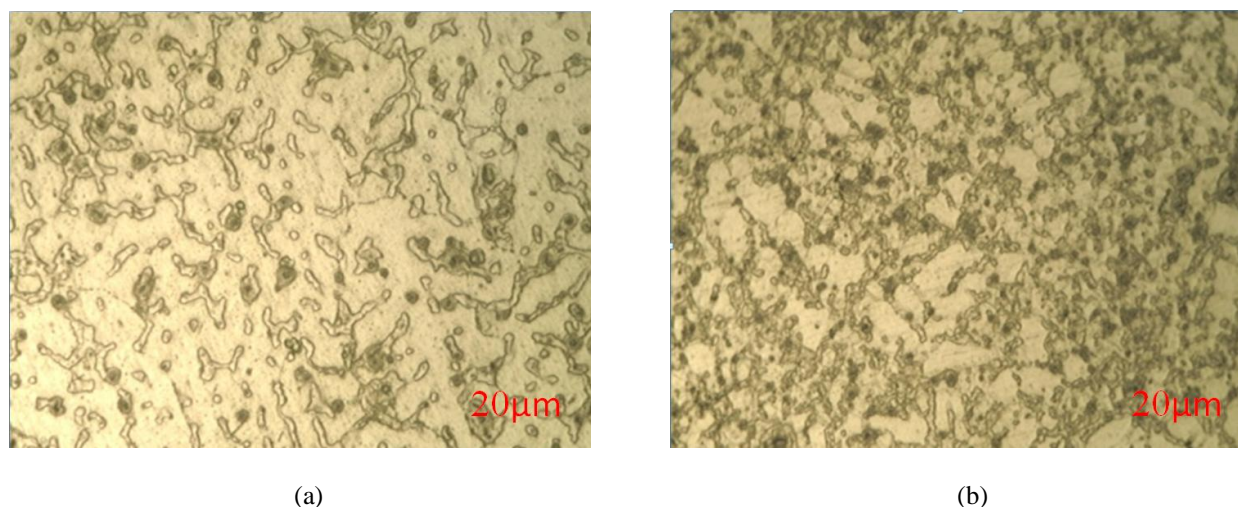(a)   (b)

Figure 1 – Optical Microscopy analyzes - Sample AM60 alloy with an increase of 400 times - (a) AM60-1 (b) AM60-2.

After performing the etching in the samples, it was possible to obtain metallographic images. In these images, may be noted the differences existing between the two samples. Based on the metallographic analysis of alloy phase appears dark Mg17Al12 in greater quantity in the alloy AM60-2. On the other hand, it is possible to observe on the images that the Mg17Al12 phase is white and elongate (Fig 1-a). On Fig 1-b the Mg17Al12 phase appears thin and better distributed. The dark aspect of Fig 1-b results of a very thin precipitation of this phase (similar to pearlite in steels, the finer the pearlite is, the darker it appears).

4.2. Open circuit potentials

The Figure 2 presents an evaluation of the open circuit potential versus time of both alloys AM60 1 and AM60 2 in artificial sea water and in a 3.5% (vol.) NaCl solution. The table 3 shows the values of corrosion potentials after 300 hours of immersion.
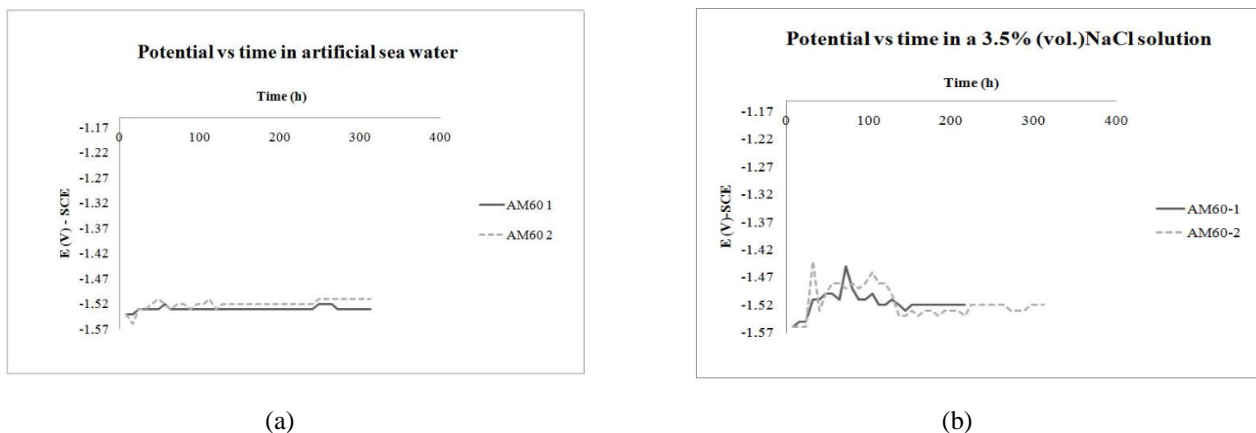

| (a) | (b) |

Figure 2 - Variation of corrosion potentials of the alloys AM60-1 and AM60-2 immersed in (a) artificial sea water; (b) 3.5% (vol.) NaCl solution;

Alloys	Open circuit potential V (saturated calomel electrode)	
	Artificial sea water	3.5%(vol.) NaCl solution
AM60-1	-1.51	-1.52
AM60-2	-1.53	-1.52

Table 3: Potential open circuit VS. Time.

The Ecorr of both alloys began in negative values around -1.56 V (SCE) after 30 hours of the potentials of both alloys in both solutions were stabilized around -1.51 to -1.53 V (SCE). In this case, there was a slight trend toward anode.

According to the electrochemical equilibrium diagram for the system Mg/H2O at 25 ° C (Pourbaix, 1976), the potentials of both alloys in both solutions stabilized within the field of corrosion stability of the ions with Mg + + and below the equilibrium line H / H +. In this case, two thermodynamically spontaneous reactions occurred on the metal surface, the anodic dissolution of Mg to Mg + + and hydrogen reduction.

Liu and Wang (2009), reports that the change in Ecorr occurs due to formation of a passive film. However, the ions chlorides easily penetrate in this film and they can causing damage.

Thus, the anodic dissolution process occurs spontaneously without the occurrence of stable passivation process. This is due to chloride ions and cause overall deterioration of the alloys under these conditions.

4.3. Weigh loss

The Figure 3 and 4 show the curves of percentage weigh loss after about 8 weeks of weighing the specimens immersed in artificial sea water and in a 3.5%(vol.) NaCl solution.
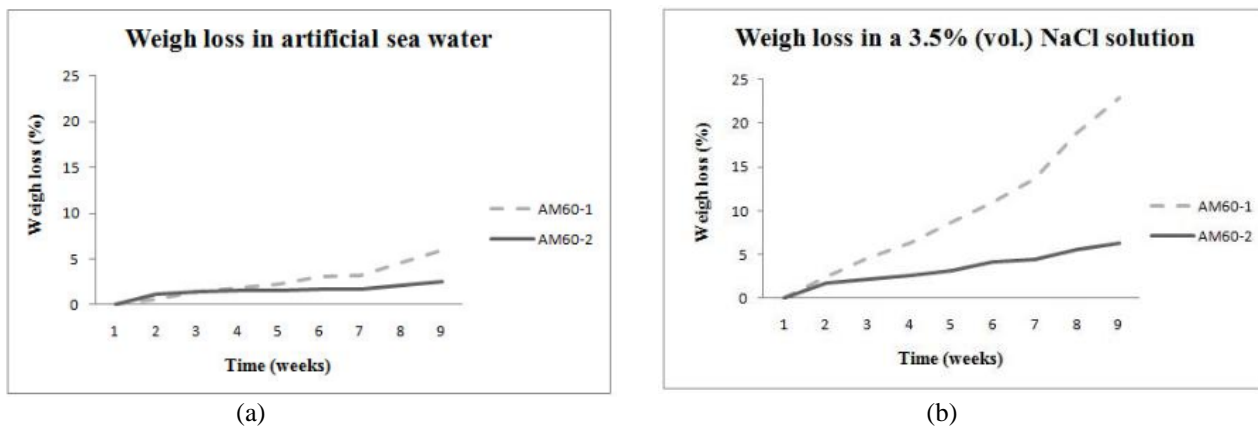
(a)

(b)

Figure 3 - Percentage of weigh loss over time (a) artificial sea water (b) in 3.5% (vol.) NaCl solution.
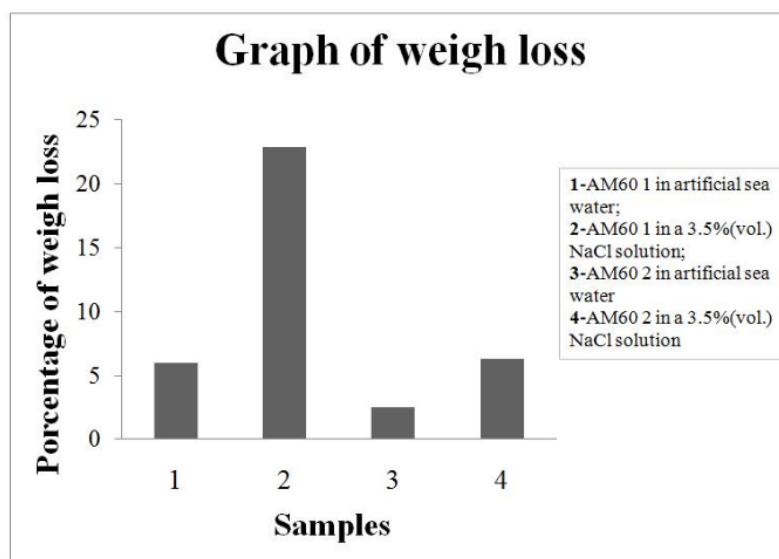

Figure 4 - Comparison of weigh loss.

The greatest weight loss occurred in sample AM60-1 in 3.5% (vol.) NaCl solution reaching approximately 23% of their initial mass. Since the sample AM60-2 in the same solution, showed a weigh loss of 6.3%. The smaller weigh loss observed throughout the trial was the sample AM60-2 in artificial sea water, and 2.5% of initial weigh.

The alloy AM60-1 showed greater weigh loss than the alloy AM60-2 in both solutions, and the process of anodic dissolution was much more aggressive in a 3.5% (vol.) NaCl solution than in artificial sea water. Once that 3.5%(vol.) NaCl solution is more aggressive than the artificial sea water.

The highest rate of weight loss from the alloy AM60-1 probably occurred because the chemical composition of this alloy is out of specification according to the standard (ASTM B93). According to Tab. 1, AM60-1 alloy showed concentrations of aluminum and beryllium below that specified by the standard. Pardo et al. (2007) reported that Mg-Al alloys tend to form a phase $Mg_{17}Al_{12}$ which improves resistance to corrosion. However, several authors (Song et. al., 1999 and Ambato et. al., 2000) report that the phase is cathodic $Mg_{17}Al_{12}$, and can have a dual role, depending on their volume fraction F: $Mg_{17}Al_{12}$ Phase / Stage Mg. In this case, if F is the small barrier, it acts as a cathode accelerating corrosion of the Mg matrix. If F is a high barrier, it acts as a corrosion inhibitor.

Based on these studies we can infer that because the concentration of Al in the alloy AM60-1 is below that specified by the standard, $Mg_{17}Al_{12}$ phase formation was impaired making low volume fraction F, which may have accelerated the corrosion process.

4.4. Potentiostatic polarization curves

After the electrochemical test, were obtained from the polarization curves, anodic and cathodic, of the alloys AM60-1 and AM60-2 in artificial sea water and in a 3.5% (vol.)NaCl solution. The result can be seen in figures 5 and 6.The tests were carried out in naturally aerated condition. The table 5 shows the corrosion potentials in each test condition and the current density on the applied anodic potential of -0.8 V (SCE) and pH of the solutions.
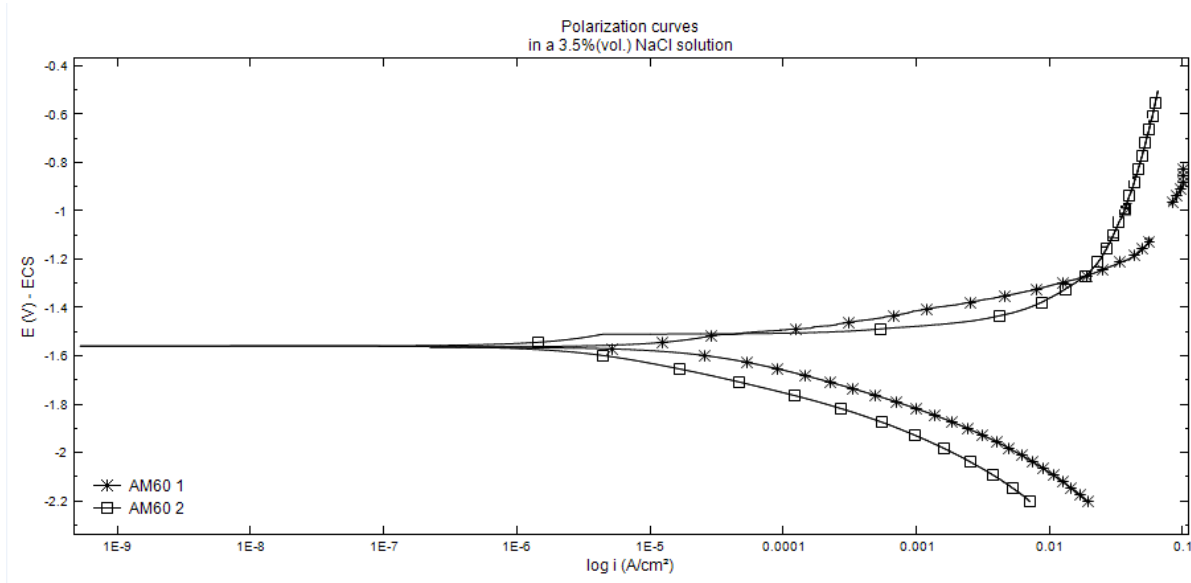
Figure 5: Polarization curves, anodic and cathodic, of the alloys AM60-1 and AM60-2 in a 3.5%(vol.) NaCl solution in naturally aerated condition.
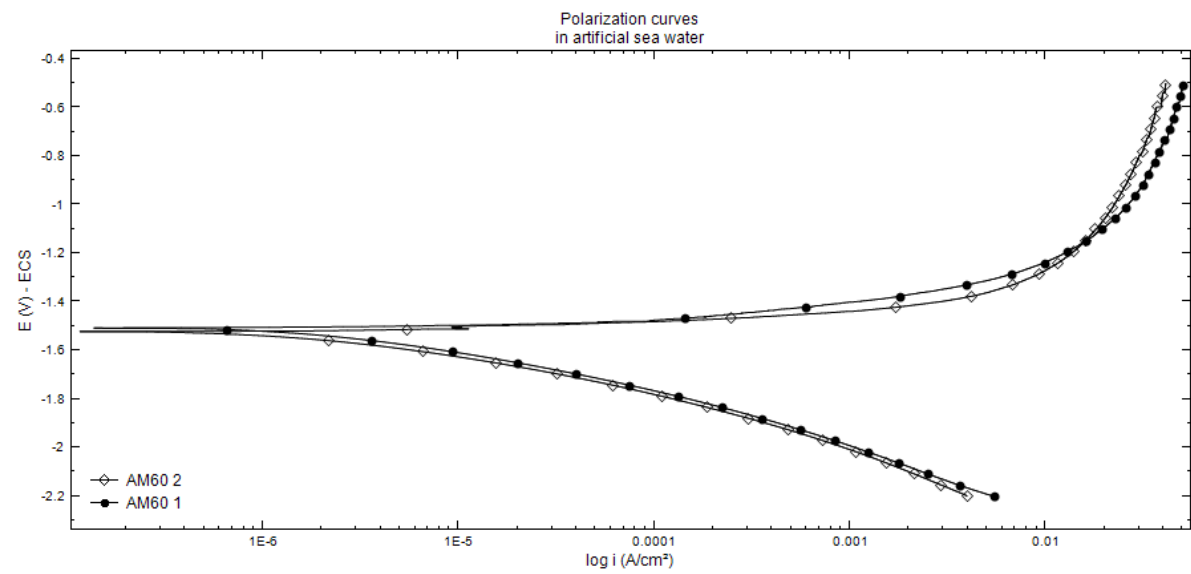

Figure 6: Polarization curves, anodic and cathodic, of the alloys AM60-1 and AM60-2 in artificial sea water in naturally aerated condition.

Alloys	Solutions	Potential (V) Saturated calomel electrode	Current (µA)	Current in the anodic potential applied from -0.8 V (µA/cm²)	pH
AM60 1	Artificial Sea water	-1.507	0.13702	36856.0	6.9
AM60 1	3.5% (vol.) NaCl solution	-1.561	-0.22095	100000.0	6.82
AM60 2	Artificial Sea water	-1.5216	-0.11636	30106.0	6.9
AM60 2	3.5% (vol.) NaCl solution	-1.5564	-0.0005188	47437.0	6.82

Table 4 - Potential Corrosion of the alloys AM60-1 and AM60-2.

Both alloys, AM60-1 and AM60-2, showed active dissolution of all the solutions, were not observed in any field of passive range of 1000 mV polarization. It is observed that the corrosion potential did not vary from one alloy to another.

The cathode current density observed can be attributed to reactions of hydrogen reduction.

Based on the electrochemical equilibrium diagram for the system Mg/H_2O at 25 ° C. Both alloys in both solutions had the potential of corrosion in naturally aerated conditions, which were within the field of corrosion and below the equilibrium line H / H +. In this case, the reaction of anodic dissolution Mg/Mg2 + and hydrogen reduction was thermodynamically spontaneous. Thus, the alloys AM60-1 and AM60-2 underwent combined effect of active dissolution to be within the field of corrosion with solubility of Mg2 + ion concentrations of 10 ion g * L-1, and reduction of hydrogen in the alloy surface.

The table 5 presents the current densities measured in applied anodic potential of -0.8 V. Note that the alloy AM60-1 showed higher anodic current density in this potential than the alloy AM60-2. Accordingly, we can infer that the current density increased probably due to alloy AM60-1 is out of specification ASTM B93. That is, the protection carried out by phase $Mg_{17}Al_{12}$ was impaired due to low concentration of Al , as described above.

In a later article, will be investigated in detail the issues related to the Cu content and refinement of the microstructure. Furthermore, a closer study of the metallurgical part of AM60 magnesium alloy will be held.

5.CONCLUSIONS

1. The training phase $Mg_{17}Al_{12}$ was probably prejudiced because the Al concentration is below the specified by ASTM B93.

2. Based on the metallographic analysis of alloy phase appears dark Mg17Al12 in greater quantity in the alloy AM60-2. On the other hand, it is possible to observe on the images that the Mg17Al12 phase is white and elongate (Fig 1-a). On Fig 1-b the Mg17Al12 phase appears thin and better distributed. The dark aspect of Fig 1-b results of a very thin precipitation of this phase (similar to pearlite in steels, the finer the pearlite is, the darker it appears).

3. The highest rate of weigh loss from the alloy AM60-1 probably occurred because the chemical composition of this alloy is out of specification according to the standard (ASTM B93). The alloy AM60-1 showed concentrations of aluminum and beryllium below that specified by the standard. Based on the metallographic analysis of alloy phase appears dark $Mg_{17}Al_{12}$ in greater quantity in the alloy AM60-2. Thus, the phase formation Mg17Al12 was prejudiced because the concentration of Al in the alloy AM60-1 is below the value specified by the standard.

4. Both alloys, AM60-1 and AM60-2, showed active dissolution of all the solutions, ie, were not observed in any field of passive range of 1000 mV polarization.

5. Both alloys in both solutions had the potential of corrosion in naturally aerated conditions, which were within the field of corrosion and below the equilibrium line H / H +. Thus, the alloys AM60 and AM60-1-2 showed effect of active dissolution as they are within the field of corrosion with solubility of Mg2 + ion concentrations of 10 ion g * L-1, and reduction of hydrogen in the alloy surface.

6. The alloy AM60-1 showed the higher anodic current density than alloy AM60-2 on the applied potential of -0.8 V. Accordingly, we can infer that the current density increased probably due to alloy AM60-1 is out of specification ASTM B93. That is, the protection carried out by phase $Mg_{17}Al_{12}$ was impaired due to low concentration of Al As can be purchasable by metallographic analysis of alloys.

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