# A Study of the Corrosion Behavior of Magnesium and its Alloys in Aggressive Environment

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## Abstract

Magnesium presents indeed a low corrosion resistance [1, 2, 3, 4]. Moreover the behavior of this metal and its alloys is still poorly known in many corrosive environments which limit its applications. Magnesium is particularly sensitive to galvanic corrosion. The presence of impurities (Fe, Ni, Cu, Cr ...) in its matrix with potential higher than that of Magnesium promotes the reduction reactions, especially that of hydrogen and thus generates the galvanic corrosion of magnesium [1, 5]. From its purity depends its resistance to corrosion. The use of alloying elements can improve the corrosion resistance of magnesium (and also the mechanical properties). A beneficial effect of aluminum and manganese on the corrosion resistance of magnesium has been demonstrated [4]. The objective of this work was to evaluate the corrosion of Mg and its alloys by electrochemical method (potentiodynamic) in an aqueous solution of 0.5 M Na2SO4.

**Keywords:** Corrosion, magnesium, protection, passivation, alloying elements.

## 1. Introduction

At the dawn of XXI century, ultra-light materials have greatly developed. Among these, magnesium in which resources are considered inexhaustible is extremely promoter for many applications, they are in the field of automotive, aerospace, industrial electronics and armament. The desire to decrease by 30% the weight of vehicles in the coming years have significantly increased number of application of these alloys. Its low density (1.7) place it before aluminum (2.7), titanium (4.7) or steel (8). Magnesium alloys appear very interesting, even if they are still little used, compared to aluminum alloys for industrial applications, mainly because of their sensitivity to corrosion.

## 2. Experimental Procedure

The materials used in this study are: pure Mg, AZ91 alloys (Al 9%, Zn1%), AM50 (5% Al, 0.13% Mn) and AM60 (6% Al, 0.13% Mn). Samples of useful surface 0.2 cm2, the active surface of samples is polished with sandpaper and cleaned with compressed and dry air.

The electrochemical tests were carried out in an aqueous solution of sodium sulfate Na2SO4 (monapur for analysis MW = 142.02) with concentration of 0.5 M at ambient temperature and at atmospheric pressure.

The assembly used is a conventional electrochemical assembly with three electrodes: The electrode of reference with saturated mercurous sulfate (E = 640 mV / SHE) in contact with the solution through an electrolyte bridge (Hg2/Hg2SO4), the platinum auxiliary electrode and a working electrode. In order to stabilize the free potential of magnesium, an immersion of 25 minutes of working electrodes in the solution of Na2SO4 is performed.

All curves log I = f (E) were drawn from the potential -2.45 V to -1.50 V / E.N.H. The potential sweep rate is 0.5 mV/s. This speed was taken by considering that the evolution of the potential is low (less than 20 mV) in the path of a curve I = f (E).

The apparatus used was a potentiostat-galvanostat EGG273A controlled by a computer DELL using M352 corrosion software.

## 3 Results and Discussion

The curves of cathodic and anodic polarization of pure magnesium and its alloys AZ91, AM50 and AM60 (in aqueous 0.5 M Na2SO4 not deaerated), drawn from the potential-2.5V to -1.950V are given on the Figure I. We notice an increase in pH of the solution Na2SO4 when drawing curves from the value of 6.4 to 9.5 and the observation of a gassing probably of dihydrogen.

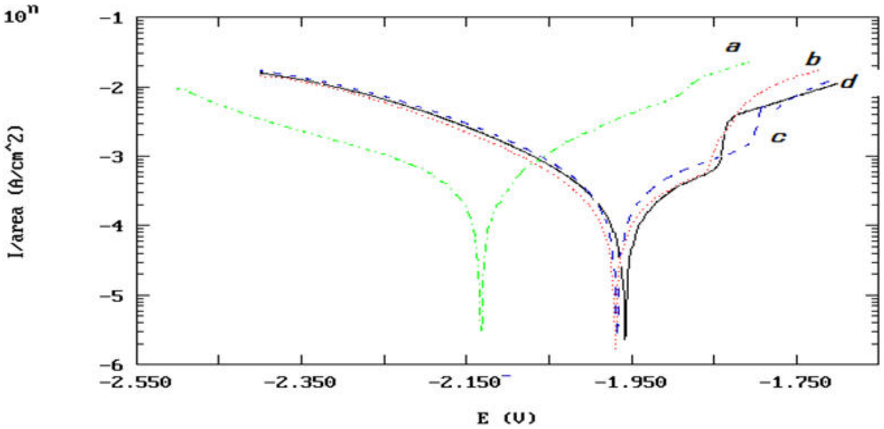

Figure 1 : Anodic and cathodic polarization curves of pure Mg and its alloys. Environment: Na2SO4 0.5 M Na2SO4, not deaerated.

The cathodic curve of pure magnesium (a) has two portions. The first portion characterized by a Tafel slope of the order of 180 mV and a quasi-linear decrease of the cathodic current. The second portion begins to-2.188V shows a sharp decrease of cathodic current and the appearance of an anodic current.

The slope of the linear portion of the cathodic curve is frequently found for the reaction of reduction H + ions or molecules of H2O [6]. In fact, when drawing the cathodic curve, a release of gas is observed and an increase in pH that may correspond to the reduction of water and proton.

The film formation by interaction between the magnesium and ions from the water during the immersion period prior to measurement may be considered. This film may change during the cathodic polarization. Presumably during the cathodic polarization, hydrogen adsorbed on the surface, from the reduction of water is evacuated to the solution.

Locally, the OH-ions product generate an increase in pH, and probably the strengthening of the layer of magnesium hydroxide. On the anodic curve, we observe : a first portion which is characterized by an increase in the anodic current, a second portion starting at about-2.075V is manifested by a quasi-linear evolution, a third portion shows an increase in anodic current from the potential about-1.975V, we note that there is a lack of passivation of magnesium.

The increase in anodic current in the first portion reflects a destabilization of the surface layer with weak protective properties that is present on the surface of magnesium. This destabilization can be attributed to a competition between different types of surface compounds such as hydroxides and oxides. The sudden increase in the anodic current in the third portion may be associated with an important anodic dissolution leading to the formation of a non-protective discontinuous corrosion layer.

Moreover, the polarization curves (b, c and d) traced on the magnesium alloys AZ91, AM50 and AM60 shows the movement of corrosion potential of them towards more positive values. This must be associated on the one hand to the inhibition of the anodic dissolution of magnesium and on the other hand the movement of the reaction of cathodic reduction to more negative values. Improved corrosion behavior of AZ91 alloys (curve b) compared to pure magnesium can be explained by the formation of protective oxides on the surface of Mg-Al alloys [4]. It has been shown that the aluminum introduced into the magnesium alloy with 9% to 29% allows an increase in corrosion resistance [4,7]. Figure 1 also shows that AM50 alloys (curve c) and AM 60 (curve d) have better corrosion resistance than AZ91 alloy. In fact, there was a significant decrease in dissolution for samples

AM50 and AM60. This could be due to the formation of a protective surface layer, some authors argue the inhibition of anodic dissolution (pitting corrosion and galvanic corrosion) of magnesium: the participation of aprotic ions such as MnOx to the anodic reaction forming stable mixed oxides of magnesium and manganese on the surface [1,4,7,8]. In addition, the manganese is part of the transition metals, known as <<valve metal>>. These metals are able to develop on their surface a protective oxide layer vis-à-vis to corrosion.

On the other hand, it is known that iron traces or other transition metals such as copper, nickel and cobalt generate an increase in the corrosion rate of pure magnesium due to a low overvoltage of the hydrogen on these metals [9]. These sites of impurities cause the activation of the reduction cathodic reaction with release of hydrogen and promote the anodic reaction of magnesium corrosion. Manganese is an improvement of the corrosion resistance of Mg-Al alloys by lowering the difference of galvanic potential between the anode sites (the matrix) and cathodic sites (impurity) and by improving the passive state of the matrix [10]. In the presence of aluminum and manganese, the iron is trapped in the form of intermetallic AlMnFe [4,7, 11]. Most studies on the role of Mn on the impurity concentration have focused on the iron, the main impurity of Mg. A similar effect was shown for copper and Ni, whose concentrations are also strongly lowered in the presence of Mn. Encompassing the iron particles, copper or nickel that are found in trace amounts, the manganese reduces their harmful character.

## 4 Conclusion

In this work, we studied the corrosion of pure magnesium and its alloys in a solution of Na2SO4 in an area of slightly acidic pH to slightly alkaline by the potentiodynamic method.

The results show the temporal evolution of pH to alkaline values and a high sensitivity to corrosion of pure magnesium leading to the anodic dissolution and the formation of a discontinuous corrosion and not protective layer.

On the other hand we have highlighted the role of manganese and aluminum in improving the resistance to corrosion of magnesium. The results obtained are in agreement with numerous studies to clarify the influence of alloying elements on the corrosion of magnesium. However, manganese appears to be far more effective for improving the corrosion resistance. This is mainly due to the formation of complex oxides and hydroxides of this element with magnesium which are relatively insoluble in aggressive electrolytes and which modify the electrochemical reactivity of the surface of magnesium [9].

Moreover, in the presence of manganese and aluminum, the iron is trapped in the form of intermetallic AlMnFe [4,11]. The alloy thus formed has a better resistance to corrosion.

Given the encouraging results obtained with AM50 and AM60 alloys, these alloys can probably be improved by an optimized composition.

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