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# Effect of Al content on the corrosion behavior of Mg–Al alloys in aqueous solutions of different pH

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## ABSTRACT

The effect of systematic increase of Al content on the electrochemical behavior of the Mg–Al alloys in aqueous solutions of different pH was investigated. Different electrochemical methods such as open-circuit potential measurements, polarization techniques and electrochemical impedance spectroscopy, EIS, were used to investigate the electrochemical behavior of the alloys in aqueous solutions. The results have shown that Mg–5Al is easily corroded due to the microgalvanic effect between $\alpha$-phase and $\beta$-phase, its corrosion rate is even higher than that of Mg itself. The increase of Al content increases the corrosion resistance of the alloy due to the formation of the $\beta$-phase ($Mg_{17}Al_{12}$) together with the Mg $\alpha$-phase. The ranking of the corrosion rate of these alloys was Mg–5Al > Mg > Mg–10Al $\cong$ Mg–15Al. The corrosion rates of the alloys in acidic solutions are pronouncedly high compared to those measured in neutral or basic solutions. The impedance measurements are in consistence with the polarization techniques and the impedance data were fitted to theoretical data obtained according to an equivalent circuit model describing the electrode/electrolyte interface.

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## 1. Introduction

Due to their low density, high strength/weight ratio and excellent dimensional stability, magnesium alloys are always used in different applications such as aerospace, automotive, cellular phones, recreational equipments and computer industries, where weight reduction is important [1–3]. The activity and poor corrosion resistance of magnesium and its alloys restrict their wide applications. In the last decades, many research works had concentrated on the effects of microstructure and environmental factors on the corrosion behavior of magnesium and its alloys [4–15]. Magnesium can quickly develop an oxide film on the surface in air, but this oxide, MgO, with the Pilling–Bedworth ratio of 0.81 can only provide limited protection [9]. In wet air and aqueous solutions, oxide and hydroxide layers of Mg, $MgO/Mg(OH)_2$, can form spontaneously on the surface. $Mg(OH)_2$ has the Pilling–Bedworth ratio of 1.77, and cannot provide enough corrosion protection to the metallic surface [13]. The morphology and structure of the film formed on pure magnesium after 1 h immersion in water were investigated by transmission electron microscopy, TEM, and was found to consist of three layers [6]. An inner cellular layer of 0.4–0.6 nm

thickness followed by a middle dense layer of 20–40 nm composed mainly of MgO, then an outer platelet-like layer of $Mg(OH)_2$. Both pure magnesium and its alloys have poor pitting resistance in aqueous solutions containing aggressive anions, especially chloride ions. The oxide and hydroxide films tend to breakdown chemically in solutions containing chloride, sulfate or bromide. The protective nature of the oxide films depends on the formation parameters, the chemical compositions of the metal or the alloy and the corrosive medium [16,17]. The high reactivity of Mg has a detrimental effect on coating qualities including adhesion, pore density and uniformity. It is therefore important to get more information about the electrochemical behavior of the metal and its alloys. Such information is necessary to understand the corrosion mechanism of these materials in aqueous solutions. In this paper, we are reporting on the effect of Al as an important alloying element with Mg on the electrochemical behavior of the metal and the formed alloys. The corrosion parameters were calculated and the mechanism of the corrosion process was discussed.

## 2. Experimental

The working electrodes were made from commercial grade Mg and Mg–Al rodes, mounted into glass tubes by two-component epoxy resin leaving a surface area of $0.385\,cm^2$ to contact the solution. The mass-spectrometric analysis of the electrodes used is presented in Table 1. The electrochemical cell was a three-

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**Table 1**
Mass-spectrometric analysis of the investigated materials (mass%).

| Alloys | Mg | Al | Cu | Ni | Fe |
|---|---|---|---|---|---|
| Mg | 99.9 | – | 0.03 | 0.03 | 0.04 |
| Mg–5Al | 94.9 | 5.0 | 0.03 | 0.03 | 0.04 |
| Mg–10Al | 89.9 | 10.0 | 0.03 | 0.03 | 0.04 |
| Mg–15Al | 84.9 | 15.0 | 0.03 | 0.03 | 0.04 |

electrode all-glass cell, with a platinum counter electrode and saturated calomel, SCE, reference electrode. Before each experiment, the working electrode was polished mechanically using successive grades emery papers up to 2000 grit. The electrode was washed thoroughly with triple distilled water, and transferred quickly to the electrolytic cell. The electrochemical measurements were carried out in stagnant, naturally aerated aqueous solutions of pH 2 (62.5 mL 0.2 mol L$^{-1}$ boric acid + 62.5 mL 0.05 mol L$^{-1}$ borax + 62.5 mL 0.4 mol L$^{-1}$ H$_3$PO$_4$ and 52.5 mL H$_2$O), pH 7 (127.8 mL 0.1 mol L$^{-1}$ COOKC$_6$H$_4$COOH + 122.2 mL 0.1 mol L$^{-1}$ HCl) and pH 12 (100 mL 0.2 mol L$^{-1}$ KH$_2$PO$_4$ + 163.7 mL 0.2 mol L$^{-1}$ NaOH). Before each measurement, the pH of the test electrolyte was controlled by a standard pH-meter.

The polarization experiments and electrochemical impedance spectroscopic investigations, EIS, were performed using a Volta-lab PGZ 100 "All-in-one" potentiostate/galvanostate system. The potentials were referred to the standard potential of the SCE (0.245 V vs. nhe). All the polarization experiments were carried out using a scan rate of 10 mV s$^{-1}$. The impedance, Z, and phase shift, $\theta$, were measured in the frequency domain 0.1–10$^5$ Hz. The superimposed AC-signal was 10 mV peak to peak amplitude. To achieve reproducibility, each experiment was carried out at least twice. Details of experimental procedures are as described elsewhere [18,19].

## 3. Results and discussion

### 3.1. Open-circuit potential measurements

The open-circuit potential of Mg and Mg–Al alloys with different Al contents was traced over 180 min in stagnant, naturally aerated aqueous solutions of different pH covering the acidic, neutral and basic media. The electrode potential for all alloys was found to shift towards less negative values and the steady state was reached in less than 20 min from electrode immersion in neutral solutions. In acidic and basic electrolytes it needs more than 100 min from electrode immersion in the electrolyte to be achieved as presented in Fig. 1(a–c). This means that the electrode surface is subjected to more corrosion and passivation processes in acidic and basic solutions and stabilizes readily in neutral solution as will be confirmed by the potentiodynamic and impedance measurements.

### 3.2. Potentiodynamic measurements

Fig. 2 presents the potentiodynamic polarization behavior of Mg, and the three different Mg–Al alloys in the acidic solutions of pH 2 (Fig. 2a), neutral solutions of pH 7 (Fig. 2b) and basic solutions of pH 12 (Fig. 2c). The corrosion parameters i.e. corrosion potential, $E_{corr}$, corrosion current density, $i_{corr}$, and corrosion resistance, $R_{corr}$, were calculated from polarization data and presented in Table 2. The results show that the presence of small amounts of Al ($\leq$5%) in the Mg matrix did not improve the corrosion resistance of the material. In the contrary the corrosion rate of Mg–5Al is higher than that of Mg itself (cf. Fig. 3 and Table 2). The increase of the Al content leads to an increase in the corrosion resistance of the alloy. The Mg–10Al alloy has shown the lowest corrosion rate, especially in neutral and basic solutions. This observation can be explained
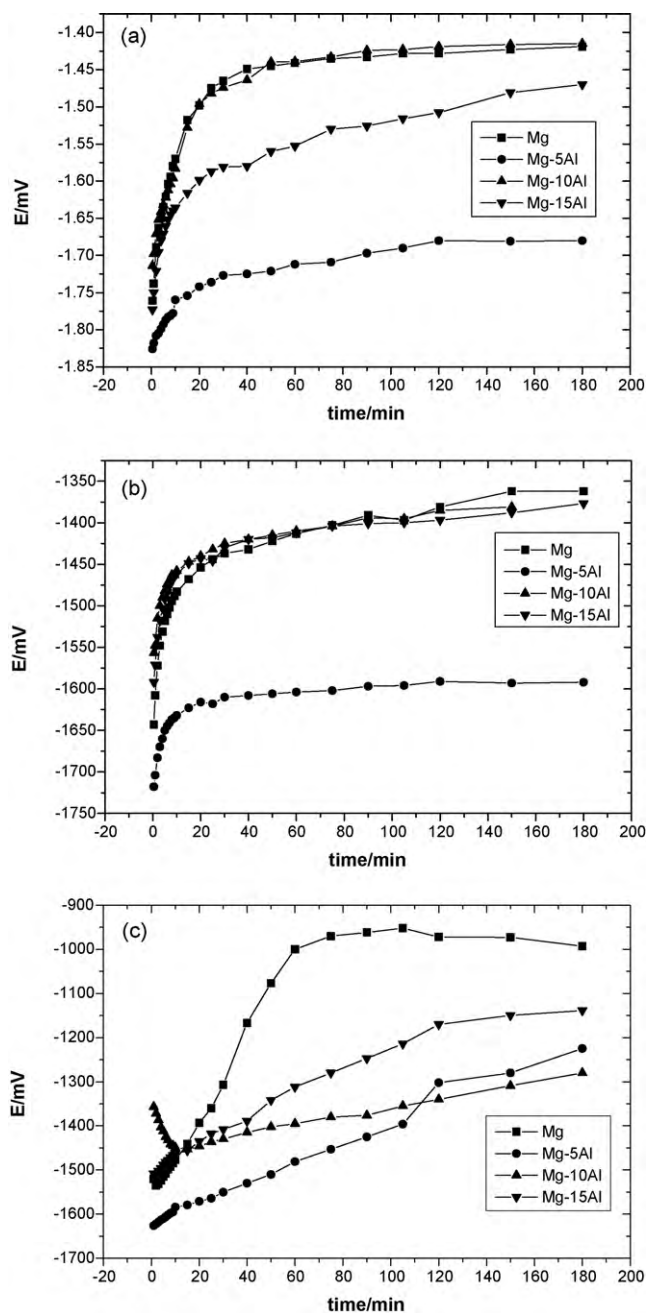


**Fig. 1.** Variation of the open-circuit potential of Mg electrode and the Mg–Al alloys with time in stagnant naturally aerated aqueous solutions at 25 °C. (a) pH = 2, (b) pH = 7 and (c) pH = 12.

on the basis that, the addition of Al to Mg produces a secondary intermetallic phase, β-Mg$_{17}$Al$_{12}$, together with the single α-phase matrix of pure Mg. As the Al content increases up to 8%, the matrix becomes anodically active and the rate of corrosion increases due to microgalvanic effects [20]. Above this ratio the corrosion resistance increases due to the increased amount of the β-phase, which decreases the microgalvanic effect occurring between α- and β-phases [8,21,22].

As can be seen from Fig. 3 and the data in Table 2, the investigated materials can be ranked according to their rates of corrosion in neutral and basic solutions in the following order Mg–5Al > Mg > Mg–10Al ≅ Mg–15Al. The presence of microgalvanic effect between the α-phase and the β-phase that formed due to the presence of the small amount of Al is responsible for the rel-