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Semiconducting behavior of the anodically passive films formed on AZ31B alloy

A. Fattah-alhosseini*, M. Sabaghi Joni

Faculty of Engineering, Bu-Ali Sina University, Hamedan 65178-38695, Iran

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Abstract

This work includes determination of the semiconductor character and estimation of the dopant levels in the passive film formed on AZ31B alloy in 0.01 M NaOH, as well as the estimation of the passive film thickness as a function of the film formation potential. Mott–Schottky analysis revealed that the passive films displayed n-type semiconductive characteristics, where the oxygen vacancies and interstitials preponderated. Based on the Mott–Schottky analysis, it was shown that the calculated donor density increases linearly with increasing the formation potential. Also, the electrochemical impedance spectroscopy (EIS) results indicated that the thickness of the passive film was decreased linearly with increasing the formation potential. The results showed that decreasing the formation potential offer better conditions for forming the passive films with higher protection behavior, due to the growth of a much thicker and less defective films.

Keywords: AZ31B alloy; Mott–Schottky; Formation potential; Donor density

1. Introduction

Magnesium alloys have wide applications in many industries due to their high strength/weight ratio, low density (= 1.7 g/cm^3: about one-fourth the density of iron and one-third that of aluminum), high stiffness/weight ratio, and ease of machinability. Generally, the low density of magnesium alloys makes them useful wherever low weight is very important [1–5].

According to the potential– pH diagram for magnesium and water, this metal corrodes over a wide range of potential and pH. Indeed, the principal drawback of magnesium alloys is the low corrosion resistance, which is generally; much lower when compared to many other competing materials, like steels or Al alloys [6,7]. Nevertheless, at high pH (values over 11), in the region identified as passive, the surface film is protective [8].

In the last decade, many studies investigated the passive behavior of magnesium alloys in alkaline solutions. Mott–-Schottky analysis indicated that the passive film formed on magnesium alloys, exhibits semiconducting properties, because of its non-stoichiometric nature [6,9–11].

Despite the extensive works published on the passivity of the magnesium alloys, little information about the effect of the formation potential on the semiconductive behavior of the passive film formed on these alloys was available. In this work, EIS and Mott–Schottky analysis of AZ31B alloy in alkaline solution (0.01 M NaOH) have been performed to determine the semiconductor character and estimate the dopant levels in the passive film, as well as to estimate the film thickness as a function of the formation potential.

* Corresponding author. Fax: +98 811 8257400.
E-mail address: a.fattah@basu.ac.ir (A. Fattah-alhosseini).
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2. Experimental procedures

The specimens were fabricated from a thick plate of AZ31B alloy with the chemical composition (%, wt.): Al 2.3, Zn 0.89, Mn 0.43, Sn 0.002, and balance Mg. All samples were ground to 2500 grit and cleaned by deionized water prior to tests.

All the electrochemical measurements were performed in a conventional three-electrode flat cell under aerated conditions by using an Autolab potentiostat/galvanostat system. The counter electrode was a Pt plate, while the reference electrode was Ag/AgCl saturated in KCl. Also, the alkaline solution (0.01 M NaOH) was used as the test solution at 25 ± 1 °C.

The potentiodynamic polarization curves were measured potentiodynamically at a scan rate of 1 m*V*/s starting from −0.25 $V_{Ag/AgCl}$ (vs. E_{corr}) to 1.0 $V_{Ag/AgCl}$. Five formation potentials (−0.2, 0.0, 0.2, 0.4 and 0.6 $V_{Ag/AgCl}$) within the passive region were chosen for EIS and Mott–Schottky measurements. Films were grown at each potential for 1 h to ensure that the system was in steady-state. After each passive film growth period, EIS and Mott–Schottky measurements were performed. The impedance spectra were measured in a frequency range of 100 kHz–100 mHz at an AC amplitude of 10 mV (rms) [5,6]. For the EIS data modeling and curve-fitting method, the NOVA impedance software was used. Mott–-Schottky analyses were done by measuring the frequency response at 1 kHz during a 25 mV/s negative potential scan from each selected potential to −1.4 $V_{Ag/AgCl}$.

3. Results and discussion

3.1. Polarization measurement

Fig. 1 shows the potentiodynamic polarization curve of AZ31B alloy in 0.01 M NaOH. According to this figure, the current density was found to increase slowly with potential during the early stage of passivation and no obvious current peak was observed. Also, it is seen that the passive potential range extending from the corrosion potential. This alloy in alkaline solutions exhibits the same curve shapes [6], where the current changes smoothly and linearly around the rest potential manifesting cathodic and anodic Tafel behavior.

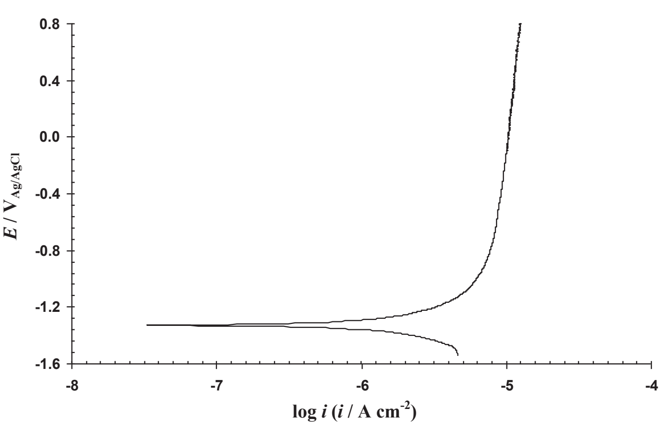

Fig. 1. Polarization curve of AZ31B in 0.01 M NaOH in the anodic direction at 1 mV/s.

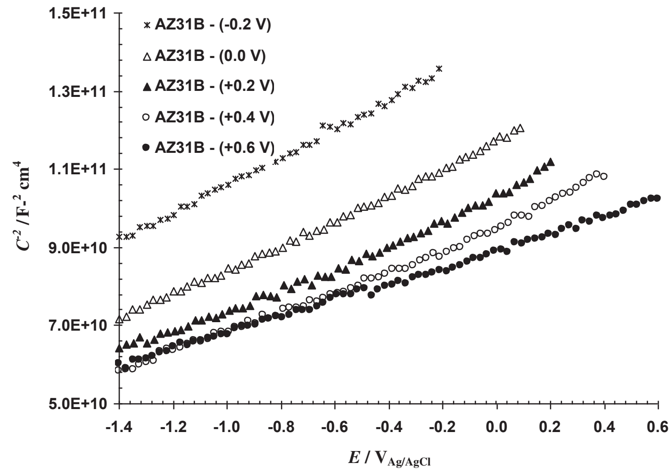

Fig. 2. Mott–Schottky plots of passive film formed at different formation potential on AZ31B in 0.01 M NaOH.

3.2. Mott–Schottky analysis

Based on the Mott–Schottky analysis, the charge distribution at the semiconductor/solution is usually determined by measuring electrode capacitance C_{SC}, as a function of electrode potential (E) [6,12]:

$$\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon\varepsilon_0 e N_D}\left(E - E_{FB} - \frac{k_B T}{q}\right) \text{ for n} - \text{type semiconductor} \quad (1)$$

where ε is the electron charge, N_D is the donor density (cm^{-3}), ε is the dielectric constant of the passive film ($\varepsilon = 9.6$ [6,12]), K_B is the Boltzmann constant, T is the absolute temperature and E_{FB} is the flat band potential. Fig. 2 shows the Mott–-Schottky plots of AZ31B in 0.01 M NaOH at selected formation potentials. As can be seen, C^{-2} clearly decrease with increasing the formation potential. In this Figure, the positive slopes are attributed to n-type behavior.

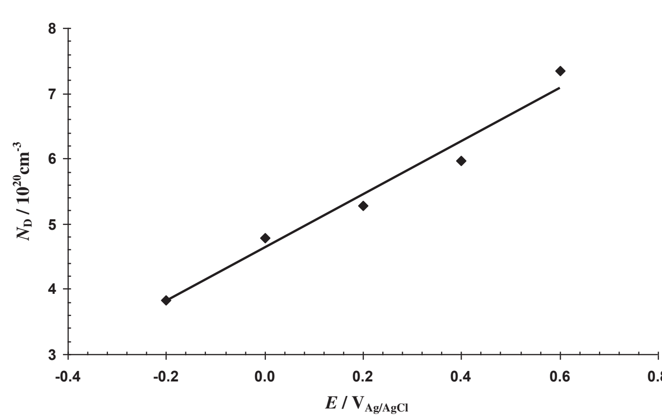

Fig. 3. Donor densities of the passive films formed on AZ31B in 0.01 M NaOH as a function of film formation potential.

Fig. 3 shows the calculated donor density of the passive film formed on AZ31B in 0.01 M NaOH at selected formation potentials. The orders of magnitude are around 10^{20} cm^{-3} and increases linearly with the formation potential. The values are comparable to the calculated donor density of the passive film formed on AZ31B in NaOH solutions at open circuit potential [6]. According to the point defect model (PDM) [13–16], the flux of oxygen vacancy and cation interstitials through the passive film is essential to the film growth process. In this concept (n-type behavior), the dominant point defects in the passive film are considered to be oxygen vacancies and/or cation interstitials acting as electron donors.

3.3. EIS measurements

The EIS response of AZ31B in 0.01 M NaOH at selected formation potentials are presented as Bode plots in Fig. 4. In this figure, the Bode plots show a resistive behavior at high frequencies, but in the middle to low frequency range there was a marked capacitive response. The Bode-phase curves show one time constant. The phase angles values (remained very close to 80°) revealed the formation and growth of a passive film. Similar plots for the EIS response of AZ31B in NaOH solutions at open circuit potential are observed [6].

Fig. 5 shows a linear relationship between the passive film thickness (d) and the formation potential. This relationship

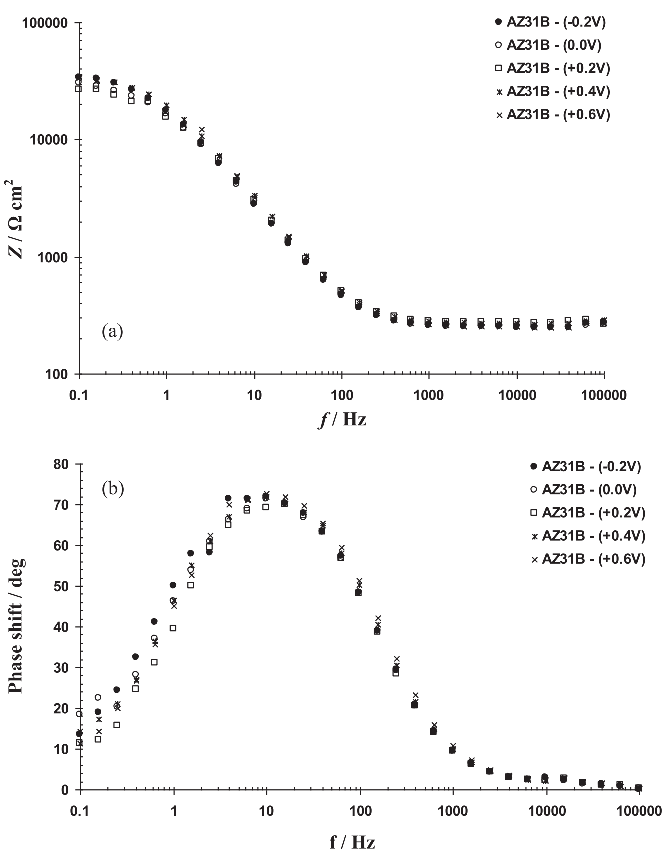

Fig. 4. (a) Bode and (b) Bode-phase plots of AZ31B in 0.01 M NaOH measured at different formation potential.

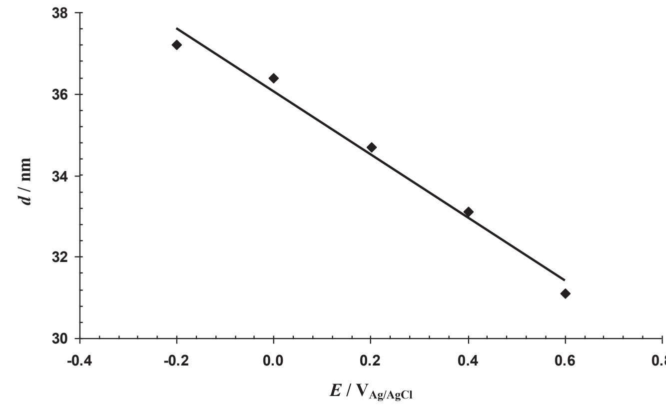

Fig. 5. Effect of the formation potential on the passive film thickness of AZ31B in 0.01 M NaOH.

between the passive film thickness and the formation potential has been reported by Macdonald [14]. The film thickness was calculated from the capacitance measured at 1 kHz after each 1 h constant potential growth. At this frequency, the impedance is largely capacitive in nature, with the measured capacitance being almost independent of frequency. The parallel plate expression was used for calculating the film thickness from the measured capacitance [6]:

$$d = \frac{\varepsilon\varepsilon_0 A}{C} \tag{2}$$

Also, C is calculated from Eq. (3) as follows [17]:

$$C = -\frac{1}{2\pi f Z_{img}} \tag{3}$$

where Z_{img} is the imaginary component of the impedance. The calculated thickness ranges from about 37.2 nm at −0.2 $V_{Ag/AgCl}$ to 31.1 nm at 0.6 $V_{Ag/AgCl}$. Therefore, it is clear that decreasing the formation potential give better conditions for forming the passive films with higher protection behavior, due to the growth of a much thicker and less defective films.

4. Conclusions

In this work, the passivity of AZ31B in 0.01 M NaOH has been explored using EIS, and Mott–Schottky analysis. Conclusions drawn from the study are as follows

1. Mott–Schottky analysis revealed that the passive films displayed n-type semiconductive characteristics, where the oxygen vacancies and interstitials preponderated.
2. Based on the Mott–Schottky analysis, it was shown that the calculated donor density increases linearly with increasing the formation potential.
3. The Bode plots show a resistive behavior at high frequencies, but in the middle to low frequency range there was a marked capacitive response.
4. Also, the EIS results indicated that the thickness of the passive film was decreased linearly with increasing the formation potential.

5. The results showed that decreasing the formation potential offer better conditions for forming the passive films with higher protection behavior, due to the growth of a much thicker and less defective films.

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