

# Galvanostatic response of AA2024 aluminium alloy in 3.5% NaCl solution

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**Abstract.** Galvanostatic responses of AA2024T3 alloy in de-aerated and naturally aerated 3.5% NaCl solution have been investigated. In the de-aerated condition, two distinct stages of polarization were revealed. From the first stage, the relationships between the pitting incubation time, pitting potential and applied current density for AA2024T3 alloy in the de-aerated condition were established. The curves in the aerated condition showed no particular incubation time-applied current density relationship.

**Keywords.** Galvanostatic polarization; AA2024T3; pitting potential; pitting initiation potential; pitting incubation time.

## 1. Introduction

The quest for finding lasting solutions to pitting corrosion, which occurs in structural alloys that form passive films appears to be perennial. As such, developments that will further the understanding of this attack, pitting, in a bid to finding lasting solutions are generally being embraced.

Janik-Czachor *et al* [1], in their review on the assessment of processes leading to pit nucleation, mentioned that the presence of aggressive anions (such as chlorides, bromides and iodides) must be beyond critical values, the electrochemical potential must be higher than the pit nucleation potential and the pitting induction time must be surpassed before pitting can nucleate on a passive alloy surface.

Appreciably, the galvanostatic polarization technique has long been established as a means of determining pitting potential [2]. Also, general relationships between incubation time (induction time), pitting potential and applied current densities for some alloys have been found [2–5]. However, it is understood that different alloys respond differently to galvanostatic polarization [2,4,5]. Thus, given the simple and reproducible nature of the galvanostatic technique (compared with potentiostatic and potentiodynamic polarization techniques) [2,4,6], individual alloys have their own characteristic curve patterns and features that require their own definitions.

In this study, the distinct galvanostatic polarization response of the AA2024-T3 alloy has been studied. To our knowledge, little or no information exists in the literature on the galvanostatic response of this alloy, particularly as it concerns the pitting incubation time, potential, and applied current density relationships. Such information may provide

useful insight into approaches that could lead to finding an improved solution for pitting corrosion in aluminium alloys.

## 2. Experimental

AA2024T3 alloy samples (with nominal composition in wt.% of Cu 3.8–4.9, Mg 1.2–1.8, Mn 0.3–0.9, Fe 0.50, Si 0.50, Zn 0.25, others 0.4 and Al balance) were degreased in acetone for 10 min in an ultrasonic bath. The samples were then etched in 10% NaOH at 60°C for 30 s followed by rinsing in deionized water. The etched samples were desmutted in 30% HNO<sub>3</sub> for 30 s at ambient temperature and rinsed in deionized water. The samples were dried in a cool air stream and masked with beeswax to expose a surface of 1 cm<sup>2</sup> before being polarized in 3.5% NaCl solution using a Solatron Analytical Modulab Potentiostat.

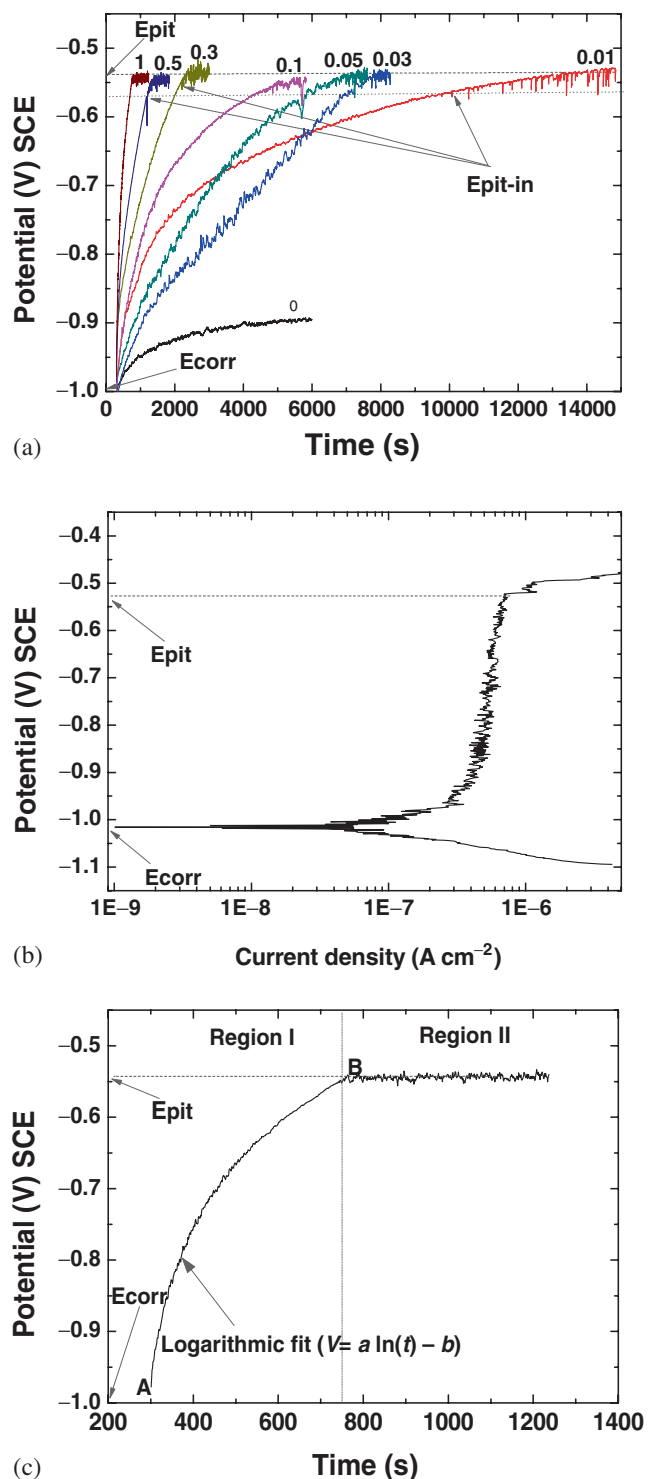
Galvanostatic and potentiodynamic polarization tests were conducted in both aerated and de-aerated conditions using a 3-electrode cell. A scan rate of 1 mV s<sup>-1</sup> was used and recordings were made with reference to a saturated calomel electrode, and a platinum electrode was used as the counter electrode. The galvanostatic polarization measurements were conducted at varying impressed current values, from 0 to 3 μA cm<sup>-2</sup>.

## 3. Results and discussion

### 3.1 Galvanostatic response of AA2024T3 in de-aerated condition

Figure 1a displays the anodic polarization curves of AA2024T3 alloy in de-aerated 3.5% NaCl solution for constant applied current density values of 0, 0.01, 0.03, 0.05, 0.1, 0.3, 0.5 and 1.0 μA cm<sup>-2</sup>. The individual curves (except

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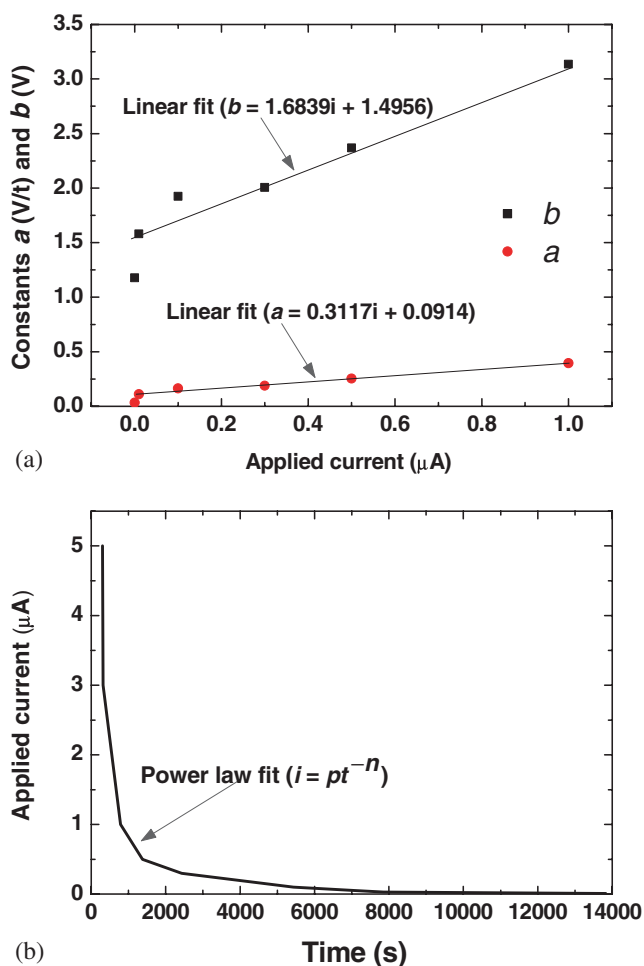
**Figure 1.** (a) Galvanostatic polarization curves of AA2024T3 alloy in de-aerated 3.5% NaCl solution at applied current density values of 0, 0.01, 0.03, 0.05, 0.1, 0.3, 0.5 and  $1 \mu\text{A cm}^{-2}$ . (b) Potentiodynamic polarization curve of AA2024-T3 alloy in de-aerated 3.5% NaCl solution. (c) Isolated galvanostatic polarization curve for an applied current density value of  $1 \mu\text{A cm}^{-2}$  displaying the two regions of polarization when AA2024T3 alloying is galvanostatically polarized in de-aerated 3.5% NaCl solution, and logarithmic relationship between the potential and the pitting incubation time.

for the  $0 \mu\text{A cm}^{-2}$  curve) show a rise to a stable potential that can be termed the pitting potential (Epit), as will be explained later. Before the Epit, the first sharp transients are observed at a potential value of about  $-0.568 \text{ V}$ , which can be termed the pitting initiation potential (Epit-in). The curves also reveal a corrosion potential (Ecorr) of  $-1.0 \text{ V}$  under this condition. Figure 1b shows the potentiodynamic polarization curve of AA2024T3 alloy in de-aerated 3.5% NaCl solution. The curve displays Epit and Ecorr values that agree with the values in figure 1a. In figure 1c, two distinct regions, region I and region II, that are characteristic of the individual curves in figure 1a are displayed. This curve also shows (after fitting) that in the first region (region I), the potential (V) has a logarithmic relationship with the incubation time (i.e., the time required to polarize the alloy to the pitting potential).

From figure 1a, it can be seen that regardless of the magnitude of the applied current density (except for  $0 \mu\text{A cm}^{-2}$ ), the AA2024T3 alloy is polarized up to a potential value of about  $-0.535 \text{ V}$ , where the alloy no longer polarizes with time. This potential value is the Epit of the alloy, which is validated by the Epit value in the potentiodynamic polarization curve in figure 1b. Just before the Epit, the first significantly conspicuous drop in potential (for current density values below  $1 \mu\text{A cm}^{-2}$ ), as shown in the curve, was usually observed at an average value of about  $-0.568 \text{ V}$ . This gives a strong indication that the pit initiation potential (Epit-in) may be this value. The applied current density of  $0 \mu\text{A cm}^{-2}$  did not show a rise to the pitting potential over time. However, it does show a slight increase in potential values over time from the Ecorr value (approximately  $-1.0 \text{ V}$ ) to values in the range of  $-0.9 \text{ V}$ . This increase in potential values is as a result of the passivation of the alloy in this open circuit condition [7].

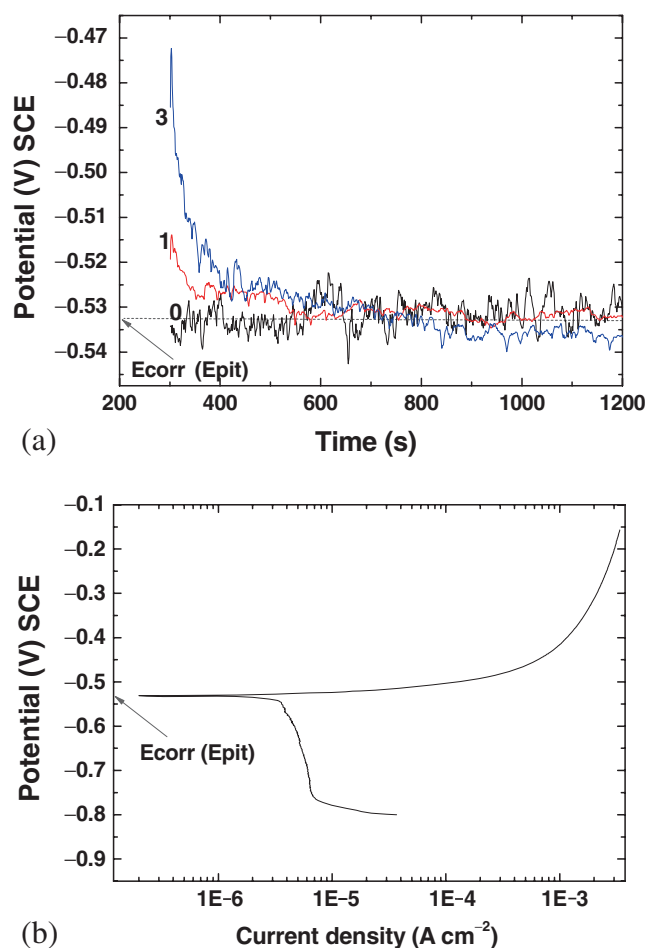
Understanding that a passive film of optimum thickness must be formed on the surface of the alloy before pitting [4], the two distinct regions of the curves, as shown in figure 1c, can be termed the passivation region/pit initiation region (region I) and the pitting or stable pitting region (region II). Similar phenomena, on zinc, have been reported in the past [2]. The interesting part, however, is the logarithmic trend of each curve in figure 1a, designated as curves A and B in figure 1c. Fitting of the curve gives a relationship of potential  $(V) = a \ln(t) - b$ , where  $a$  and  $b$  are constants directly dependent on the applied current density value (this is shown in figure 2a) and  $t$  the pitting incubation time (i.e., the time required for the alloy to be polarized to the pitting initiation/stable pitting potential). This relationship indicates that for every applied current density, there is a pitting incubation time.

Figure 2b shows the relationship between the applied current density and the pitting incubation time for this alloy in de-aerated 3.5% NaCl solution. This curve was obtained by plotting the time required (for the different applied current density values) to polarize the alloy from points A to B (as indicated in figure 1c) against the applied current density values. Fitting the curve in figure 2b shows that the applied current density  $i$  has a power law relationship,  $i = pt^{-n}$ ,



**Figure 2.** (a) Curves showing the relation between the applied current and the constants in figure 1c. (b) Curve showing the power law relationship between the applied current density values and the pitting incubation time.

with the pitting incubation time  $t$ .  $p$  and  $n$  are constants, and with values of 20808 and 1.474, respectively, in this case (as obtained from the trend-line equation generated for the curve fitting). This implies that for an applied current density value the pitting incubation time can be determined. The expression ( $i = pt^{-n}$ ) also indicates that for a little increase in the magnitude of the applied current density from very low values (such as from 0.01 to 0.03  $\mu\text{A cm}^{-2}$ ), the pitting incubation time reduces significantly, and then reduces moderately with further increase in the applied current density up to a point where it becomes zero regardless of the magnitude of the applied current density. The drive for the rapid formation of an optimum passive film thickness on the surface of the alloy prior to pitting increases with the magnitude of the applied current density. This optimum passive film thickness is attained at a potential value of about  $-0.535$  V. Hence, the more rapid the formation of the optimum passive film the quicker the tendency of pitting. Thus, at certain magnitudes of the applied current density, the pitting incubation time approaches zero (e.g., at applied current density values



**Figure 3.** (a) Galvanostatic polarization curves of AA2024T3 alloy in natural 3.5% NaCl solution at applied current density values of 0, 1 and 3  $\mu\text{A cm}^{-2}$  displaying no pitting incubation time. (b) Potentiodynamic polarization curve of AA2024T3 alloy in naturally aerated 3.5% NaCl solution displaying no distinct difference between the Epit and  $E_{\text{corr}}$  values.

beyond 1  $\mu\text{A cm}^{-2}$ , in this case, as can be seen in figure 1a). It is sensible, therefore, to conclude that the relationship,  $i = pt^{-n}$ , only holds for applied current density values less than 1  $\mu\text{A cm}^{-2}$ .

### 3.2 Galvanostatic response of AA2024T3 in naturally aerated condition

Anodic polarization curves of AA2024T3 alloy in naturally aerated 3.5% NaCl solution for applied current density values of 0, 1 and 3  $\mu\text{A cm}^{-2}$  are displayed in figure 3a. The potentiodynamic polarization curve of the alloy under the same condition is shown in figure 3b.

Unlike the de-aerated condition, the features of the curves in the aerated condition are significantly different. The only similarity is the pitting potential (Epit) range, which is similar to that in the de-aerated condition (figure 1a-c).

In the aerated condition, there is no pitting incubation time. This is not unexpected as there is dissolved oxygen in the solution for more rapid cathodic reactions (oxygen

reduction), which lead to a corresponding rapid anodic dissolution (compared with the de-aerated condition where the major cathodic reaction is the reduction of hydrogen ions). Thus, even at the open circuit potential, dissolution had already begun on the surface of the alloy. Under this condition, the application of current will only lead to the initial superimposition of an equivalent overvoltage on the E<sub>pit</sub> (see the curves for applied current density values of 1 and 3  $\mu\text{A}$  in figure 3a), which returns back to the value of E<sub>corr</sub> over a short-time period. This is also revealing that pitting of the AA2024T3 alloy occurs just at or below the corrosion potential (E<sub>corr</sub>) in the aerated condition as evident in the potentiodynamic polarization curve of figure 3b. It is further clear that regardless of the value of the impressed anodic current, pitting will occur on AA2024T3 alloy in the aerated condition.

#### 4. Conclusions

This study has shown the galvanostatic responses of AA2024T3 alloy in naturally aerated and de-aerated 3.5% NaCl solutions. During galvanostatic polarization in the de-aerated condition, the drive for a well-formed passive film on AA2024T3 and the rate of attainment of the pitting potential are highly dependent on the value of the impressed current. The resulting potential has a logarithmic relationship with the time ( $t$ ) taken to initiate/attain pitting for the individual current values (in the form of: potential ( $V$ ) =  $a \ln(t) - b$ ),

where the constants  $a$  and  $b$  vary directly as the applied current density. Also, the applied current density obeys a power law relationship (of the form: applied current density ( $i$ ) =  $pt^{-n}$ , where  $p$  and  $n$  are constants) with the time ( $t$ ) taken to attain pitting potential (the pitting incubation time). The pitting potentials of the AA2024T3 alloy in aerated conditions are in good agreement with those in the de-aerated condition, except that there is no passive film formation region nor pitting incubation time in the galvanostatic curves in the aerated condition.

#### Acknowledgements

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