Potential Difference of Cyclic Polarization Curve of an Aircraft Al Alloy: $\Delta E (E_{\text{sec,corr}} - E_{\text{corr}})$

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ABSTRACT

This paper presents a hypothesis and its experimental validation that $\Delta E (E_{\text{sec,corr}} - E_{\text{corr}})$ of cyclic polarization curve of an Al-Zn-Mg-Cu alloy decreases firstly and then increases with the increasing of corrosion rate or corroded fraction F_{corr} of alloy surface. The minimum value of ΔE is obtained when $F_{\text{corr}} \approx 50\%$. In addition, a proportional relationship between ΔE and $|50\% - F_{\text{corr}}|$ was found. This non-monotonic relation between ΔE and extent of localized corrosion indicates that additional attention should be paid on using ΔE to assess localized corrosion behaviour of Al-Zn-Mg-Cu alloys.

Keywords : 7150 Al Alloy, Cyclic Polarization, Potential Difference, Localized Corrosion

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1. Introduction

Localized corrosion of Al and Al alloys in chloride-containing environments has been intensively investigated [1-5]. Various electrochemical methods such as cyclic polarization, EIS (Electrochemical Impedance Spectroscopy), SECM (Scanning Electrochemical Microscopy) and SKP (Scanning Kelvin Probe) were used in the last several decades [6-12], among which cyclic polarization (or pitting scans) has become one of the most important methods for the characterization of localized corrosion. This method can provide lots of quantitative data such as corrosion potential E_{corr} , pitting potential E_{pit} , pitting transition potential E_{ptp} , corrosion current density j_{corr} and corrosion potential $E_{\text{sec,corr}}$ of reverse scan as well as qualitative interpretation of localized corrosion of Al alloy. A typical cyclic polarization curve for 7150-T77 Al alloy is shown in Fig. 1. The potential is first increased in the anodic or noble direction (forward

scan). The potential scan direction is reversed at some chosen current or potential (the reverse is at the potential of $E_{\text{rev}} = -0.2 V_{\text{SCE}}$ in Fig. 1) and progresses in the cathodic or active direction (backward or reverse scan).

Potential differences such as $E_{\text{pit}} - E_{\text{sec,corr}}$, $E_{\text{pit}} - E_{\text{corr}}$ and $E_{\text{sec,corr}} - E_{\text{corr}}$ as criteria have been used for several decades to predict localized corrosion susceptibility of alloys [13-24]. For instance, after conducting experiments on AA 1050, AA 6082, AA 5754, AA 5083 and AA 2014 in chloride-containing solutions with and without additional cathodic reactants, M. Trueba and S.P. Trasatti [20] proposed that the trend of $E_{\text{pit}} - E_{\text{sec,corr}}$ is useful to predict the propensity towards pitting in some specific environments.

Another important potential difference is $\Delta E (E_{\text{sec,corr}} - E_{\text{corr}})$. In the early 1990s, Silverman [18,25] proposed that, for a given experimental procedure, the higher the value of ΔE is, the harder certain metals can repassivate. His work has been introduced into the famous book of *Uhlig Corrosion Handbook* as a whole chapter which cited by many following researchers [19,22,26,27]. However, the physical meaning of ΔE is still unclear and ΔE has not been theoretically derived so that it is empirical in nature.

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Fig. 1. Schematic representation of the characteristic parameters of cyclic polarization curves: E_{corr} – corrosion potential; E_{pit} – pitting potential; E_{rev} and j_{rev} – potential limit of the forward scan and the corresponding current density; E_{ptp} – pit transition potential; $E_{\text{sec,corr}}$ – second corrosion potential. The curve corresponds to experimental cyclic polarization of polished 7150-T77 Al alloy in naturally aerated 0.1 mol/L Na_2SO_4 + 20 mmol/L NaCl solution with $E_{\text{rev}} = -0.2 \text{ V}_{\text{SCE}}$.

For example, $E_{\text{sec,corr}}$ can change with experimental variables such as point-of-scan reversal and scan rate [14, 23,24,28,29] and the value of ΔE can be greatly influenced by the amount of prior damage done to the passive surface [18,21,23,24]. The farther the polarization scan is generated in the anodic direction, the greater corrosion degree of surface region will be. These results may lead to an erroneous prediction of corrosion behavior especially when the pitting potential is exceeded or some other electrochemical transformation is participated [18,21,23,24]. However, the reason that using ΔE criterion to evaluate corrosion behavior of alloys may lead to an erroneous prediction remains unknown. The scan rate also can alter the scan and cause a misinterpretation of features. Generally the scan rate should be slow enough so that double-layer capacitance remains fully charged and the current collected reflects only the interfacial corrosion process at every potential [28,29].

In this work, we conducted cyclic polarization tests of 7150 Al alloy under four groups of corrosive environments. The suitability and limitations of using ΔE for 7150 Al alloy corrosion evaluation are discussed. The relation between ΔE and corrosion rate/corrosion degree is established as well.

Table 1. Four groups of experimental condition used for cyclic polarization test

Group	Solution	Temperature
A	0.1 mol/L Na_2SO_4 + $x^\#$ mmol/L NaCl	303 K
B	0.1 mol/L Na_2SO_4 + $x^\#$ mmol/L NaCl	353 K
C	0.1 mol/L HCl + 1 mol/L NaCl	298, 308, 318, 333 K
D	0.1 mol/L Na_2SO_4 + 20 mmol/L NaCl	298, 308, 318, 333 K

$^\# x = 1, 5, 10, 50, 100, 500, 1000$

2. Experimental

2.1. Alloy and heat treatment

The investigated material is a rolled 7150 Al alloy plate received from Aluminum Corporation of China. The chemical composition (mass fraction) of the plate is Al-6.5Zn-2.4Mg-2.2Cu-0.15Zr-0.08Fe-0.061Si. The samples, cut into 15×15×3 mm plates, were solution heat treated for 30 min at 480°C, followed by cold water quenching and RRA/T77 ageing process (120°C * 24h + 180°C * 0.5h (water cooling) + 120°C * 24h). The optical microstructure of alloy after heat treatment has been shown elsewhere [30].

2.2. Cyclic polarization curve

For electrochemical characterization, 7150 Al alloy samples were wet ground through successive grades of silicon carbide abrasive papers from P240 to P1500, followed by diamond finishing to 0.1 μm . A CHI 660C electrochemical workstation (Shanghai Chenhua, China) connected to a three-electrode cell was used for the electrochemical measurements. The working electrode was the test material with an immersed area of 0.5 cm^2 and platinum plate and saturated calomel (SCE) electrodes were used as the counter and reference electrodes, respectively. Cyclic polarization curves were performed under different solutions and different temperatures. As listed in Table 1, four groups of experimental corrosion environments were selected. Cyclic polarization curves were obtained after 1 h of immersion, at a scanning rate of 1 mV/s. For group A, B and D, the scanning potential ranges from -1.2 V_{SCE} to -0.2 V_{SCE} and for group C -1.2 V_{SCE} to -0.4 V_{SCE} . All the electrochemical tests were performed in a Faraday cage.

2.3. Surface corrosion fraction calculation after cyclic polarization

The corrosion morphologies of 7150 Al alloy after the cyclic polarization tests were characterized by optical microscopy (LEICA NEOPHOT-21). The surface corrosion fraction (F_{corr}) of sample after polarization test was calculated by ImageJ2x software, using at least 5 images for each experimental point. Fig. S1 (a) shows the corrosion morphology of alloy after cyclic polarization in 0.1 mol/L HCl + 1 mol/L NaCl at the temperature of 318 K. As can be seen, the corroded surface corresponds to the dark area in Fig. S1 (a). And corrosion fraction F_{corr} equals to the ratio of the dark area and the whole area. The corrosion fraction is 64.3% from the analysis of binary image using ImageJ2x software, as shown in Fig. S1 (b).

3. Results

3.1 Cyclic polarization curve

Fig. 2 shows the anodic section of cyclic polarization curves of 7150 Al alloy obtained for group A, B,

C and D. For group A and B, pitting potentials E_{pit} occurs at solutions with lower chloride concentrations. Corrosion current density j_{corr} and current density at reverse potential j_{rev} of group A and B are shown in Fig. 3a. Clearly, both j_{corr} and j_{rev} increased with higher chloride concentrations. Compared with group C, obvious E_{pit} can be found in group D and the value of E_{pit} shifts to the negative direction with increasing temperature. From j_{corr} and j_{rev} values of group C and D shown in Fig. 3b, it can be easily concluded that, for both group C and group D, the corrosion rate of 7150 Al alloy is accelerated by higher temperature.

3.2 Corrosion morphology

Representative corrosion morphologies of 7150 Al alloy after cyclic polarization are shown in Fig. 4. The mean corrosion fraction F_{corr} of alloy surface after polarization test is obtained from at least five images with different magnifications for each experimental point. In the case of 303 K (group A), the corrosion fraction of alloy surface after cyclic

Fig. 2. Cyclic polarization of 7150 Al alloy for different experimental conditions: (a) group A; (b) group B; (c) group C; (d) group D. The details of different groups are listed in Table 1.

Fig. 3. Corrosion current density j_{corr} and current density at reverse potential j_{rev} of different groups: (a) group A and B; (b) group C and D.

Fig. 4. Representative corrosion morphologies after cyclic polarization: a₁, a₂, a₃ and a₄ is for x = 1, 10, 100 and 1000 under the temperature of 303K, respectively (group A); b₁, b₂, b₃ and b₄ is for x = 1, 10, 100 and 1000 under the temperature of 353K, respectively (group B). c₁, c₂, c₃ and c₄ for 298 K, 308 K, 318 K and 333 K in 0.1 mol/L HCl + 1 mol/L NaCl, respectively (group C); d₁, d₂, d₃ and d₄ for 298 K, 308 K, 318 K and 333 K in 0.1 mol/L Na₂SO₄ + 20 mmol/L NaCl, respectively (group D).

Fig. 5. E_{corr} , $E_{sec,corr}$ and ΔE ($E_{sec,corr} - E_{corr}$) of 7150 Al alloy for different groups: (a) group A and B; (b) group C and D.

polarization is 13.5%, 20.9%, 29.1%, 42.1%, 48.5%, 53.5% and 57.6% as x equals to 1, 5, 10, 50, 100, 500 and 1000, respectively; In the case of 353 K (group B), the corrosion fraction is 25.4%, 33.3%, 40.4%, 43.8%, 52.8%, 62.6% and 68.3%, for x equals to 1, 5, 10, 50, 100, 500 and 1000, respectively. In the case of 0.1 mol/L HCl + 1 mol/L NaCl (group C), the mean F_{corr} value of Al alloys after cyclic polarization under 298 K, 308 K, 318 K and 333 K is 38.5%, 50.1%, 68.1% and 100%, respectively. In the case of 0.1 mol/L Na₂SO₄ + 20 mmol/L NaCl (group D), the mean F_{corr} of Al alloys under 298 K, 308 K, 318 K and 333 K is 14.2%, 28.5%, 38.6% and 68.4%, respectively. As implied by Fig. 5, the corrosion degree of alloy surface increased with higher chloride concentration and higher temperature.

3.3 Potential difference

As shown in Fig. 5, for group A and B, ΔE ($E_{sec,corr} - E_{corr}$) decreases firstly and then increases with the increasing of chloride concentration. The turning point of group A and group B is the same as 100 mmol/L chloride. For group C and D, similar trend between ΔE and also does not decrease linearly with increasing temperature. The turning temperature of ΔE values for group C is 308 K, while it is 318 K

for group D. Furthermore, ΔE ($E_{sec,corr} - E_{corr}$) as a function of corrosion current density j_{corr} for group A, B, C and D are shown in Fig. 6. As can be easily seen, for all groups, ΔE exhibits non-mono tonic trend with j_{corr} . The critical value of j_{corr} at turning point varies for different groups.

The link between ΔE ($E_{sec,corr} - E_{corr}$) and corrosion fraction F_{corr} after cyclic polarization test is exhibited in Fig. 7. As expected, ΔE value does not decrease linearly with the propagation of corrosion. For all groups, it has a minimum turning point at which the corrosion fraction equals to approximately 50%. Therefore we can conclude that at the first stage of localized corrosion, ΔE decreases with promoted corrosion. On this stage, higher values of ΔE means less susceptible to localized corrosion of the metal. When it moves into next stage where more than half of the surface area corroded, inversely, ΔE increases with further corrosion propagation.

4. Discussion

Wilde and Williams [13] proposed that $E_{sec,corr}$ varies with the amount of pitting propagation that has taken place. Pitting propagation varies not only with the specific electrolyte and temperature, but also with

Fig. 6. $\Delta E (E_{\text{sec,corr}} - E_{\text{corr}})$ as a function of corrosion current density j_{corr} for group A, B, C and D, respectively.

Fig. 7. (a) $\Delta E (E_{\text{sec,corr}} - E_{\text{corr}})$ as a function of surface corrosion fraction F_{corr} after cyclic polarization test for group A, B, C and D, respectively. A minimum turning point can be seen when the corrosion fraction equals to approximately 50%.

cyclic polarization parameters such as scan rate and reversal potential. Point of reversal is such a factor that can influence the amount of pitting propagation. It is well-known that the farther the polarization scan

is generated in the anodic direction, the greater the corrosion degree of the surface region will be. As shown in Fig. 8, $E_{\text{sec,corr}}$ descends dramatically as E_{rev} changes from $-0.7 \text{ V}_{\text{SCE}}$ to $-0.6 \text{ V}_{\text{SCE}}$, followed by a slight fluctuation from $-0.6 \text{ V}_{\text{SCE}}$ to $-0.2 \text{ V}_{\text{SCE}}$ and an obvious upward from $-0.2 \text{ V}_{\text{SCE}}$ to 0 V_{SCE} . The value of $\Delta E (E_{\text{sec,corr}} - E_{\text{corr}})$ first decreases and then increases as E_{rev} shifts to the anodic direction. This is exactly the expected result on the basis of the non-monotonic relationship between ΔE and corrosion degree of alloy surface. Thus, Fig. 8 is a re-validation of this non-monotonic trend observed above. This non-monotonic trend between ΔE and F_{corr} , though empirical in nature, is of great importance for the interpretation of localized corrosion of 7000 series Al alloys using cyclic polarization method. One must very careful when using ΔE as a criterion to assess localized corrosion of 7000 series Al alloy, because it can be less rigorous and or even deceptive.

Furthermore, a linear relationship between $\Delta E (E_{\text{sec,corr}} - E_{\text{corr}})$ and $|50\% - F_{\text{corr}}|$ was found, as shown in Fig. 9. $|50\% - F_{\text{corr}}|$ is the absolute value of the difference between 50% and F_{corr} . The linear regression equation between $\Delta E (E_{\text{sec,corr}} - E_{\text{corr}})$ and $|50\% - F_{\text{corr}}|$

Fig. 8. E_{corr} , $E_{\text{sec,corr}}$ and ΔE ($E_{\text{sec,corr}} - E_{\text{corr}}$) of 7150 Al alloy as a function of E_{rev} . Cyclic polarization curves were performed in 3.5 wt% NaCl solution under room temperature, scan rate 1 mV/s.

Fig. 9. ΔE ($E_{\text{sec,corr}} - E_{\text{corr}}$) as a function of $|50\% - F_{\text{corr}}|$ for group A, B, C and D, respectively.

for the four groups are listed below:

$$\text{Group A: } y = 0.2072x - 0.1654 \quad R^2 = 0.5978$$

$$\text{Group B: } y = 0.4068x - 0.3265 \quad R^2 = 0.8622$$

$$\text{Group C: } y = 0.0779x - 0.0381 \quad R^2 = 0.9834$$

$$\text{Group D: } y = 0.3583x - 0.3098 \quad R^2 = 0.9576$$

Though a linear trend between ΔE and $|50\% - F_{\text{corr}}|$ existed (especially for Group C and D, R^2 values are quite high), the mechanism of which still is not well

understood. It probably due to that the difference in features between forward scan and reverse scan is a result of changes in surface state before and after anodic polarization. For example, in very aggressive environment (Group C, 333 K high temperature and 1 h prior immersion duration, see Fig. 2c), the forward scan and the reverse scan are completely overlapped, thus ΔE value is zero. In this case, anodic polarization altered slightly on alloy surface because the surface has been completely corroded by immersion before anodic polarization, as one can observe a totally black area on alloy surface caused by prior immersion using un-aided eye. The value 50% might be corresponds to the largest degree that can be altered by anodic polarization for these four groups of corrosive environments, especially for Group C and D. We emphasize that 50% is not a universal value, because corrosion is a complex phenomenon that can be influenced by various factors such as ion concentration, temperature and immersion duration, and more importantly, corrosion potential (no matter E_{corr} and $E_{\text{sec,corr}}$) is a mixed potential which altered by both anodic and cathodic reactions.

5. Conclusions

ΔE ($E_{\text{sec,corr}} - E_{\text{corr}}$) exhibits a non-monotonic trend with corrosion current density j_{corr} . It decreases firstly and then increases with the increasing of j_{corr} . For 7150 Al alloy, the link between ΔE value and corrosion fraction (F_{corr}) after cyclic polarization was determined. At the first corrosion stage where F_{corr} is less than one certain critical percentage ($\sim 50\%$), ΔE value decreases with higher corrosion degree. And then, by contrast, ΔE value increases with further corrosion propagation. We believe this non-monotonic relation between ΔE and corrosion degree is applicable at least for 7000 series Al alloys. Empirically, proportional relationship between ΔE and $|50\% - F_{\text{corr}}|$ was found for 7150 Al alloy in the four studied groups of corrosion environments.

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Supporting Information

Supporting Information is available at <https://doi.org/10.33961/jecst.2019.00507>

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