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Influence of Grain Size and Film Formation Potential on the Diffusivity of Point Defects in the Passive Film of Pure Aluminum in NaCl Solution

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Abstract: The influence of grain size on the corrosion behavior of pure aluminum and the defect density and diffusion coefficient of surface passive films were investigated using electron backscatter diffraction (EBSD) and electrochemical testing techniques, based on the point defect model (PDM). Samples with three different grain sizes (23 ± 11, 134 ± 52, and 462 ± 203 µm) were obtained by annealing at different temperatures and times. The polarization curves and electrochemical impedance spectroscopy results for the pure aluminum in the 3.5% NaCl solution showed that with decreasing grain size, the corrosion current (i_corr) decreased monotonously, giving rise to a noble corrosion potential and a large polarization resistance. The Motte–Schottky results showed that the passive films that formed on pure aluminum with fine grains of 23 ± 11 µm had a low density (3.82 × 10^{20} \text{ cm}^{-3}) of point defects, such as oxygen vacancies and/or metal interstitials, and a small diffusion coefficient (1.94 × 10^{-17} \text{ cm}^2/\text{s}). The influence of grain size on corrosion resistance was discussed. This work demonstrated that grain refinement could be an effective approach to achieving high corrosion resistance of passive metals.

Keywords: pure aluminum; passive film; grain size; formation potential; diffusion coefficient

1. Introduction

The high corrosion resistance of aluminum and its alloys was attributed to the formation of a uniform and dense passive film on the surface, which acted as a protective barrier between the solution and the substrate [1]. In recent years, the corrosion behavior and electronic properties of passive films on aluminum alloy surfaces have drawn significant attention. The studies suggested that the growth and dissolution of passive films were due to the mutual transfer of point defects between the substrate/films/solution [2–5]. The point defect model (PDM) describes the kinetics of growth and dissolution of passive films on metal or alloy surfaces [2,3]. The passive films exhibited semiconducting properties, allowing the diffusion of ions and electrons. Due to the close dependence of corrosion processes on these charged species, various electrochemical techniques are employed to characterize passive films. Among them, passive films were prepared under various film-forming potentials using the potentiostatic polarization method. Mott–Schottky (M-S) capacitance testing [6–10] is usually employed to study the properties of passive films on alloy surfaces, and the point defect density in passive films has been used to evaluate the corrosion resistance of materials. Therefore, the corrosion resistance was related to the semiconducting properties of the passive films [11,12].

The defect density has also been used to evaluate the properties of passive films in many studies. Generally, the higher the defect density in the passive films, the more likely the films are to be damaged by aggressive ions in the solution [11,13–16]. Passive films...
of the 1050 aluminum alloy surface had n-type doping via accumulative roll bonding (ARB) in the 0.5 M H$_3$BO$_3$ + 0.1 M NaOH solution, and the defect density of the nine-cycle ARBed sample increased from $2.19 \times 10^{-19}$ cm$^{-3}$ to $2.41 \times 10^{-20}$ cm$^{-3}$ [17]. The 2099 Al-Li alloy with refined grains, obtained via several plastic deformation processes, showed a lower defect density in passive films and higher corrosion resistance [18]. However, for the 2024 aluminum alloy, when the mean grain size decreased and the donor density of the passive layers increased with an increase in the amount of ARB, the corrosion resistance was reduced [19]. In the literature, the effects of grain refinement on the corrosion resistance of materials reported by different research groups are inconsistent and even contradictory. This discrepancy may be caused by the different alloys that contained different compositions and dislocation densities. Therefore, high-purity aluminum with a low defect density should be selected to study the effect of grain size on corrosion behavior.

The diffusion coefficient ($D_0$) of point defects in passive films is usually used to describe the transport properties of point defects and the kinetics of film growth [20,21]. There are many reports on the $D_0$ of passive films on various metals, including niobium in different temperature and pH conditions [22], titanium with different grain sizes [23,24], the Ni16Cr13Co4Mo alloy [25], iron [26], tungsten [27], etc., based on PDM using M-S testing and the Nernst–Planck equation. However, there have been no reports on the $D_0$ of point defects in passive films on aluminum alloys.

In this paper, we present our study on the corrosion behavior of pure aluminum and its dependence on grain size and defect density. The defect density and $D_0$ value of surface passive films have been determined using completely recrystallized samples with different grain sizes, which were obtained by rolling and annealing the as-cast high-purity aluminum metals.

2. Materials and Methods

An aluminum metal with a purity of 99.99% was re-melted at 770°C and cast into an ingot with a size of 200 × 150 × 30 mm$^3$. The ingot was cold-rolled at 90% into a 3 mm thick sheet and then annealed at different temperatures. The grain size and recrystallization fraction in the rolling plane were determined using the EBSD technique. Samples for EBSD were electropolished using an electrolyte of 10 % HClO$_4$ and 90 % ethanol at 30 V DC for 30 s. The AFM measurements were made on a Nanoscope Multimode 8 atomic force microscope from Digital Instruments (Bruker, Berlin, Germany). The tests were carried out in air at room temperature and an ambient relative humidity of approximately 40%.

The electrochemical measurements were conducted in the PAR2273 (3000A DX, Berwyn, PA, USA) electrochemical workstation using a conventional three-electrode system in 3.5 wt% NaCl solution at room temperature. The saturated calomel electrode (SCE) and Pt sheet serve as the reference electrode and the counter electrode, respectively. The test area of the working electrode is 10 × 10 mm$^2$. Samples were prepared by mechanical polishing using 2000 grit SiC paper and then ultrasonic cleaning with alcohol and distilled water. Prior to measurements, 60 min immersion was applied to ensure a steady state. The polarization was initiated at −100 mV versus open circuit potential and was scanned at a rate of 1mV/s. Within the passive region, we selected three potentials to study for potentiostatic film growth, which are −1000, −900, and −800 mV$_{SCE}$, respectively.

Before anodic polarization, the working electrode was cathodically polarized. The working electrode is polarized under the cathode for 5 min to remove the oxide film formed in the air. Anodic polarization was performed for 3 h at different film formation potentials to generate steady-state passive films. The electrochemical impedance spectroscopy (EIS) was measured using a 10 mV amplitude sinusoidal signal and a frequency range of 100 kHz–100 mHz. Mott-Schottky (M-S) measurements were performed from −1.1 to −0.7 V$_{SCE}$ with a fixed frequency of 1 kHz and a perturbation voltage of 10 mV, with a scan rate of 20 mV/step. All experiments were repeated at least 5 times under the same conditions with reasonable reproducibility.
3. Results and Discussion

3.1. Microstructure

To obtain recrystallized grains with different grain sizes, the samples were annealed at different temperatures. The grain size was counted using channel 5 software (Oxford instruments, Abingdon, UK). Figure 1(a1–c1) shows the surface morphology after mechanical polishing. The results show that the surface of the sample was flat and without defects. Figure 1(a2–c2) shows the SEM images of the samples after annealing at different temperatures after electrolytic polishing. The micrograph of the annealed aluminum in Figure 1(a2–c2) shows a homogenous equiaxed microstructure. When annealed at 275 °C for 4 h, the average grain size was 23 ± 11 µm. As the annealing temperature increased to 500 °C for 1 h, the grain size increased to 462 ± 203 µm.

Figure 1. SEM images of the sample annealed at (a) 275 °C for 4 h, (b) 375 °C for 1 h, (c) and 500 °C for 1 h, respectively. (a1–c1) The secondary images after mechanical polishing; (a2–c2) SEM images after electrolytic polishing.

Figure 2 shows the AFM topographic morphology of the samples with different grain sizes. Prior to the AFM measurements, the samples underwent potentiostatic polarization for 3 h in a 3.5 wt% NaCl solution and were then cleaned with deionized water and dried. It can be seen that the oxide film on the surface of all samples exhibited cellular granular structures. The surface roughness (Ra) of the samples was approximately 50.7 nm for 275 °C/4 h, 16.8 nm for 375 °C/1 h, and 13.4 nm for 500 °C/1 h, respectively. It was evident that the surface roughness of the sample increased with a decrease in grain size. This variation arises from the accelerated growth of the passivated oxide layer following 4 h treatment at 275 °C. Owing to the fact that grain boundaries have higher energy than the interior of the grain, they are more chemically reactive. Consequently, a high density of grain boundaries enhances the surface reactivity by promoting electron activity and diffusion, which leads to faster formation of the oxide layer and results in a thicker oxide layer with high roughness [28].
Figure 2. AFM images of the pure aluminum with different grain sizes after 3 h of potentiostatic polarization in a 3.5 wt% NaCl solution, (a) 275 °C for 4 h, (b) 375 °C for 1 h, (c) 500 °C for 1 h.

Anodic polarization was performed for 3 h at −800 mV film formation potentials to generate steady-state passive films. Then the sample was sectioned using a focused ion beam (FIB). Figure 3 shows the cross-section of the sample annealed at 275 °C for 4 h. The surface of the sample is uneven at the top of the red line, which is an oxide layer. The bottom of the red line represents the matrix metal, which presents a smooth surface. Figure 3 displays that a uniform oxide layer with a thickness of approximately 4 µm formed on the surface of the sample after 3 h of potentiostatic polarization in a 3.5 wt% NaCl solution.

Figure 3. SEM image of the sample following cross-sectioning with a focused ion beam; the sample was previously potentiostatic polarization for 3 h in a 3.5 wt% NaCl solution.

3.2. Potentiodynamic Polarization Measurements

The potentiodynamic polarization curves of pure aluminum with different grain sizes in a 3.5 wt% NaCl solution are shown in Figure 4. The polarization curves in Figure 4 have good repeatability. It can be seen that the grain size has a significant influence on the electrochemical behavior of pure aluminum. The passive films spontaneously formed on the aluminum surface in the NaCl solution. The electrochemical parameters were determined by fitting the polarization curves, including corrosion potential (Ecorr), pitting potential (Epit), corrosion current density (icorr), and passive current density (ip). The ip was the average current density between −1050 mV and −750 mV, and the Epit was the potential at which the current density corresponding to the passive region started to increase.

The electrochemical parameters obtained by fitting the polarization curve are shown in Table 1. The results show that with decreasing grain size, the Ecorr becomes nobler and the icorr decreases monotonously (from 0.69 × 10−7 A/cm² to 0.38 × 10−7 A/cm²), which indicates that grain refinement enhances the overall corrosion resistance of pure aluminum.
in the solution. The \( i_p \) for the sample annealed at 500 °C for 1 h (13.22 \( \times \) 10\(^{-7} \) A/cm\(^2\)) is much higher than that at 275 °C for 4 h (3.4 \( \times \) 10\(^{-7} \) A/cm\(^2\)). This indicates that grain refinement enhances the stability and protective properties of the passive films formed on the surface of pure aluminum samples. Meanwhile, the \( E_{\text{pit}} \) remains almost unchanged, varying between −0.68 and −0.69 V.

![Figure 4](image)

**Figure 4.** The potentiodynamic polarization curve of samples with different grain sizes in 3.5% NaCl solution.

**Table 1.** Fitting electrochemical parameters for the pure aluminum with different grain sizes in 3.5 wt% NaCl solution. \( E_{\text{corr}} \) and \( E_{\text{pit}} \) are corrosion potential and pitting potential, respectively; \( i_{\text{corr}} \) and \( i_p \) are corrosion current density and passive current density, respectively.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( E_{\text{corr}} ) (V)</th>
<th>( i_{\text{corr}} ) (10(^{-7}) A/cm(^2))</th>
<th>( i_p ) (10(^{-7}) A/cm(^2))</th>
<th>( E_{\text{pit}} ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>275 °C/4 h</td>
<td>−1.12 ± 0.03</td>
<td>0.38 ± 0.09</td>
<td>3.41 ± 0.07</td>
<td>−0.68 ± 0.03</td>
</tr>
<tr>
<td>375 °C/1 h</td>
<td>−1.20 ± 0.08</td>
<td>0.48 ± 0.12</td>
<td>8.71 ± 0.21</td>
<td>−0.69 ± 0.02</td>
</tr>
<tr>
<td>500 °C/1 h</td>
<td>−1.23 ± 0.04</td>
<td>0.69 ± 0.11</td>
<td>13.2 ± 1.5</td>
<td>−0.69 ± 0.03</td>
</tr>
</tbody>
</table>

The corrosion morphologies of the specimens annealed at 275 °C for 4 h, 375 °C for 1 h, and 500 °C for 1 h after potentiodynamic polarization in the 3.5% wt% NaCl solution are shown in Figure 5. It was found that the number of corrosion pits on the surface of the sample increased after annealing at 500 °C for 1 h compared with the sample at 275 °C for 4 h. The results showed that the surface of the specimen was more susceptible to being attacked by chloride. Inclusions, contaminants, and grain boundaries were not observed around the pits.

![Figure 5](image)

**Figure 5.** The corrosion morphology of the pure aluminum with different grain sizes after potentiodynamic polarization test in 3.5% wt% NaCl solution, (a) 275 °C for 4 h, (b) 375 °C for 1 h, (c) 500 °C for 1 h.

### 3.3. Electrochemical Impedance Spectroscopy

Figure 6 shows the Nyquist (a–c) and Bode (d–f) plots of samples after potentiostatic polarization for 3 h in the 3.5 wt% NaCl solution. The Nyquist plots of the samples with
different grain sizes displayed similar characteristics, and a capacitive semicircle was observed. At the same film formation potential, the diameter of the capacitive arc increased with decreasing grain size. The diameter of the sample after heat treatment at 500 °C/1 h was the smallest, indicating the lowest protective effect of the passive film formed on the sample surface. The maximum phase angle was 80° in the intermediate-frequency region, indicating the formation of a stable passive film on the sample surface [29].

![EIS plots](image)

**Figure 6.** The electrochemical impedance spectra (EIS) of aluminum were obtained after 3 h of potentiostatic polarization in a 3.5 wt% NaCl solution: (a–c) Nyquist curves and (d–f) Bode curves.

In order to quantitatively analyze the EIS data obtained from the experiment, an equivalent circuit model was used to fit the impedance data, as shown in Figure 7. The model assumes the presence of a large number of point defects in the passive film, which enables the diffusion of ions from the solution to the alloy substrate. In the equivalent circuit model, $R_s$ represents the solution resistance, and $Q_1$ and $Q_2$ are the constant phase elements associated with the passive film capacitance and the double-layer capacitance, respectively. $R_1$ and $R_2$ are passive film resistance and charge transfer resistance, respectively. Polarization resistance $R_p$ ($R_p = R_1 + R_2$) is used to evaluate the corrosion resistance of materials. Figure 8 shows the variation in polarization resistance with applied film formation potential for samples with different grain sizes. The $R_p$ decreased from 14,400 $\Omega \cdot \text{cm}^2$ to 11,053 $\Omega \cdot \text{cm}^2$ as the grain sizes increased from 23 µm to 462 µm at a film formation potential of $-800 \text{ mV}_{\text{SCE}}$, indicating an increase in the corrosion resistance of the material with finer grains. In addition, the polarization resistance of all samples increased with increasing film-forming potential.

![Equivalent circuit](image)

**Figure 7.** Equivalent circuit for quantitative evaluation of the electrochemical impedance data.

The above results confirm that corrosion resistance is improved with decreasing grain size, which can be attributed to the higher grain boundary density. The grain boundary has a higher internal energy than the grains and exhibits stronger chemical activity [30], leading to faster formation of the passive films, which act as a barrier against corrosion and reduce the corrosion rate [31].
3.4. Semi-Conductive Property of the Passive Film

The electronic properties of the passive films formed on the samples at three different film-forming potentials in the 3.5 wt% NaCl solution were determined using Mott–Schottky measurements. According to the PDM, a large number of defects existing in the barrier layer of the passive film, including oxygen vacancies, cation interstitials, and cation vacancies, play important roles [3]. According to M-S theory, the capacitance is related to the electrode potential as follows:

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 e N_d} \left( V - V_{FB} - \frac{k_B T}{e} \right)$$  

where \( \varepsilon \) and \( \varepsilon_0 \) are the dielectric constant of the passive film (10 for the \( \text{Al}_2\text{O}_3 \) [17,30,31]) and the vacuum permittivity (8.854 \( \times \) 10\(^{-14} \) F cm\(^{-1} \)), respectively. \( N_d \) is the donor density (cm\(^{-3} \)), \( e \) is the electron charge (1.602 \( \times \) 10\(^{-19} \)C), and \( V \) is the applied potential. \( V_{FB} \), \( k_B \), and \( T \) are the flat band potential, Boltzmann’s constant (1.38 \( \times \) 10\(^{-23} \) J K\(^{-1} \)), and absolute temperature (K), respectively [20].

Figure 9 shows the Mott–Schottky curves for the passive films potentiostatically formed on samples with different grain sizes for 3 h in the 3.5 wt% NaCl solution. It can be seen that the slopes of the linear parts for \( C \)–2 and \( E \) are positive, indicating that the passive films on the surface of pure aluminum exhibit n-type semiconductor characteristics in the 3.5% NaCl solution. Therefore, oxygen vacancies and/or cation interstitials were the major defects in the passive films. The electronic properties of the passive films obtained on AA1050 in the 0.5 M \( \text{H}_3\text{BO}_3 \) + 0.1 M NaOH solution were similar [12,17,32]. Also, the slopes of the curves increased with increasing formation potential, indicating the donor density of the passive film decreased.

![Figure 8](image_url)  
**Figure 8.** Variation in polarization resistance of samples at different annealing temperatures with the applied film formation potential.

![Figure 9](image_url)  
**Figure 9.** The Mott–Schottky curves of pure aluminum with different grain sizes after 3 h of potentiostatic polarization in a 3.5 wt% NaCl solution. The sample annealed at (a) 275 °C for 4 h, (b) 375 °C for 1 h, (c) and 500 °C for 1 h, respectively.
The point defect density $N_d$ in the passive films on the surface of samples with different grain sizes was calculated using Equation (1), and the results are shown in Figure 10 and Table 2. The values of $N_d$ are in the range of $10^{20}$–$10^{21}$ cm$^{-3}$, which is in agreement with other researchers’ results [17]. At the same film formation potential, $N_d$ decreased with decreasing grain size. The electron transfer was reduced due to the decrease in defect density in passive films, leading to a reduction in the electrochemical reaction [20,33]. The decrease in the $N_d$ value could reduce the electrochemical reactions at metal/solution interfaces, thus increasing the stability of the passive film [34]. This is consistent with the results of polarization and electrochemical impedance testing. Furthermore, the $N_d$ value decreased as the film formation potential increased. These results confirm that grain refinement could enhance the passive behavior of pure aluminum.

![Figure 10](image-url) The variation in defect density with film-forming potential for different grain sizes. The sample annealed at (a) 275 °C for 4 h, (b) 375 °C for 1 h, (c) and 500 °C for 1 h, respectively.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Formation Potential (mV SCE)</th>
<th>$i_{sc}$ ($10^{-6}$ A cm$^{-2}$)</th>
<th>$N_d$ ($10^{20}$ cm$^{-3}$)</th>
<th>$D_0$ ($10^{-17}$ cm$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>275 °C/4 h</td>
<td>-800</td>
<td>0.71 ± 0.09</td>
<td>3.82 ± 0.4</td>
<td>1.94 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>-900</td>
<td>0.46 ± 0.04</td>
<td>6.01 ± 0.7</td>
<td>1.34 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>-1000</td>
<td>0.19 ± 0.03</td>
<td>11.64 ± 0.5</td>
<td>0.52 ± 0.1</td>
</tr>
<tr>
<td>375 °C/1 h</td>
<td>-800</td>
<td>1.51 ± 0.05</td>
<td>4.46 ± 0.5</td>
<td>3.42 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>-900</td>
<td>0.87 ± 0.1</td>
<td>6.92 ± 1.0</td>
<td>1.97 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>-1000</td>
<td>0.54 ± 0.04</td>
<td>13.34 ± 0.7</td>
<td>1.23 ± 0.3</td>
</tr>
<tr>
<td>500 °C/1 h</td>
<td>-800</td>
<td>2.76 ± 0.08</td>
<td>4.64 ± 0.8</td>
<td>5.25 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>-900</td>
<td>2.04 ± 0.04</td>
<td>7.21 ± 0.7</td>
<td>3.88 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>-1000</td>
<td>1.73 ± 0.06</td>
<td>15.64 ± 1.1</td>
<td>3.29 ± 0.2</td>
</tr>
</tbody>
</table>

Since the solution often contains a large number of corrosive anions, such as halide ions (Cl$^-$), the anions are easily adsorbed at the oxygen-vacancy defect sites in the passive films, causing pitting corrosion in the alloys [5]. Therefore, the decrease in defect density can reduce the chloride ion absorption capacity of the passive films formed on their surface and reduce the occurrence of localized corrosion.

Macdonald [5] used the point defect model to explain the formation of passive films and the diffusion of ions in the film. The physicochemical reactions occurring within the passive film in this model are shown in Figure 11. Reactions 3 and 6 suggest that oxygen vacancies were generated at the metal/film interface and annihilated at the film/solution interface, resulting in the growth of passive films on the metal surface [5]. A key parameter to describe the diffusion of point defects within the passive film is the diffusion coefficient of point defect ($D_0$), which is an important factor influencing the growth of the passive film. The passive film formed on pure aluminum in the 3.5%NaCl solution has n-type semiconducting characteristics, with oxygen vacancies or cationic interstices primarily...
serving as electron donors. However, it is not possible to distinguish the contributions of oxygen vacancies and cationic interstices to the measured diffusion coefficients. Therefore, the diffusion coefficient is considered to be a combination of these two types of point defects. The relationship between defect density and formation potential is given in Equation (2) [19]:

\[
N_d = \omega_1 \exp(-bE) + \omega_2
\]

where \(\omega_1, \omega_2, \) and \(b\) are constants determined from experimental data [19,30]. Based on the above relationship, a nonlinear fitting of the experimental data of the defect density and film formation voltage in Figure 7 was performed using Origin software (2022). The diffusion coefficients were calculated according to the Nernst–Plank equation (Equation (3)) [31]:

\[
D_0 = \frac{i_{ss}RT}{4eF\omega_1\omega_2}
\]

where \(i_{ss}\) is the steady-state passive current density, \(R\) is the gas constant (8.314 J·mol\(^{-1}\)K\(^{-1}\)), \(F\) is the Faraday constant (96,500 C·mol\(^{-1}\)), and \(\omega_L\) is the electric field strength within the passive film (approximately \(6 \times 10^{10}\) V·cm\(^{-1}\)).

The steady-state current density of all samples under different applied potentials was obtained using the results of electrochemical testing. According to Equation (3), the values of \(D_0\) of the passive films formed on the samples with different grain sizes under different formation potentials are given in Table 2. At the film formation potential of 

\(-800\) mV\(_{SCE}\), the \(D_0\) values for the three samples with different grain sizes are \(1.94 \times 10^{-17}\), \(3.42 \times 10^{-17}\), and \(5.25 \times 10^{-17}\) cm\(^2\)s\(^{-1}\), respectively. The \(D_0\) of the passive film on fine-grained surfaces was smaller than that on coarse-grained surfaces.

At the initial stage of film formation, the grain boundaries could act as a short-range diffusion pathway. Fine-grained aluminum metal has more grain boundaries, making it easy for the film to form. The passive elements could rapidly form a stable passive film. Following the establishment of the passive layer, it served as an effective barrier against reactions on the metal surface. The subsequent decrease in reaction rates led to a reduction in the diffusion coefficient. Additionally, it was observed that the diffusion coefficient of oxygen vacancies increased with the rise in film formation potential. This increase in the diffusion coefficient accelerated the transfer of the point defect in the passive film and promoted the growth of the passive film.
4. Conclusions

The effects of grain size on the corrosion behavior of high-purity aluminum and the defect density and diffusion coefficient of surface passive films have been studied. The following conclusions can be drawn:

(1) Three different samples with mean grain sizes of 23 ± 11, 134 ± 52, and 462 ± 203 µm were formed using cold deformation and recrystallization annealing.

(2) With decreasing grain size, the $i_{corr}$ decreases from 0.069 µA/cm$^2$ to 0.038 µA/cm$^2$ in the 3.5% NaCl solution, suggesting that the corrosion resistance tended to increase with decreasing grain size.

(3) The passive film formed on the surface of the samples with fine grains of 23 µm has a lower defect density of $3.82 \times 10^{20}$ cm$^{-3}$, confirming that there are fewer point defects in the passive films after grain refinement. The films with fewer defects on the surfaces of fine-grain samples play an important role in improving the corrosion resistance of materials.

(4) The diffusion coefficients of point defects of the samples with grain sizes of 23 µm and 462 µm are $1.94 \times 10^{-17}$ and $5.25 \times 10^{-17}$ cm$^2$/s, respectively. The reduction in the diffusion coefficient with decreasing grain size tends to reduce the ion transfer between the film and solution, inhibiting electrochemical reactions.

(5) The grain refinement significantly improved the corrosion resistance performance of high-purity aluminum. The result is strictly applicable to the passive behavior of metals with low defect density in a particular environment.

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Conflicts of Interest: Author Dejing Zhou was employed by the company Yin Bang Clad Material Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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