Corrosion behavior of 3A21 aluminum alloy in ethylene glycol solution under different atmospheres

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Abstract
The corrosion behavior of 3A21 aluminum alloy in different concentrations of ethylene glycol solution under different simulated atmospheres was studied by electrochemical methods (potentiodynamic polarization and electrochemical impedance spectroscopy) and surface analytical techniques (metalloscopy and the scanning electron microscope equipped with energy-dispersive x-ray spectrometer). The electrochemical results showed that the corrosion of 3A21 aluminum alloy was affected by the concentration of ethylene glycol solution and atmosphere conditions, and the influence of atmosphere was different in different concentrations of ethylene glycol solution. The results were further confirmed by morphology analysis, and the formation of Al-alcoholized film on the surface of aluminum alloy was proved by element energy spectrum analysis, then the corrosion mechanism of 3A21 aluminum alloy was discussed.

1. Introduction
Aluminum alloys have attracted research interests because of their remarkably low densities, good workability, good corrosion resistance, and high electrical and thermal conductivities. These characteristics have effectively put them ahead of traditional metals such as stainless steel and cast iron in automobile engine cooling systems, aiding the reduction of automobile self-weight and ensuring the improvement of fuel efficiency [1, 2]. In the presence of oxygen, aluminum alloy undergoes passivation to form a dense film of aluminum oxide, thereby reducing the chemical reactivity of the surface and improving its corrosion resistance. However, the passive film on the surface of aluminum alloy can be destroyed in environments containing corrosive ions such as chloride ions. Long-term service of aluminum alloys in such corrosive environments could cause material failure [3, 4].

Ethylene glycol is widely used as an automobile engine coolant due to its good chemical stability, low cost, excellent antifreeze properties and the ability to prevent overheating [5–8]. As reported, an alcohol film can be formed with ethylene glycol being adsorbed on the surface of aluminum alloy, which inhibits the dissolution of the anode after oxygen has been consumed [9]. Compared to 3.5% NaCl solution, pure ethylene glycol can reduce the corrosion rate of the 5A06 aluminum alloy by inhibiting the anodic dissolution [10]. But different corrosion mechanisms of aluminum alloy in ethylene glycol have been reported at higher temperatures. Harrooni [11] proved that the adsorption of ethylene glycol can reduce the interfacial capacitance and thus reducing the corrosion rate of aluminum alloy. Zaharieva et al [12] discovered that the corrosion rate of aluminum alloy accelerated under the action of an aqueous solution of ethylene glycol–water mixture at a temperature of 130 °C after 172 h due to the ease of acidification of ethylene glycol to produce glycol aldehyde, glycolic acid, etc during its use as a coolant, which will ultimately cause corrosion of aluminum alloy in cooling systems [13, 14]. Recently, the effect of atmospheres on the corrosion behavior of aluminum alloy at high temperature has attracted much attention. Zhang et al [9] reported that the corrosion potential of aluminum...
alloy shifts positively and the anode current density decreased in the solution exposed to the air. However, the effects of atmospheric conditions on the corrosion behavior of aluminum alloys in ethylene glycol solution at high temperature are not sufficient at present.

In this study, the corrosion behavior of 3A21 aluminum alloy in ethylene glycol under different atmospheres (blank, N₂, O₂, and Air) was studied by using electrochemical method. The blank atmosphere refers to the condition that the test solution is in a static state, non-aerated. Nitrogen gas was introduced to reduce the dissolved oxygen concentration in the solution in order to investigate the corrosion behavior of 3A21 aluminum alloy in ethylene glycol solution under oxygen-deficient atmospheres. Oxygen was introduced to increase the dissolved oxygen concentration in the solution and permit test the corrosion of 3A21 aluminum alloy in ethylene glycol solution under oxygen-rich atmospheres. Air was introduced to study the corrosion behavior of 3A21 aluminum alloy in ethylene glycol solution under normal conditions, while the blank atmosphere was the solution without filling gas and considered as the control experiment. Then the influence of atmosphere (N₂, O₂ and Air) and solution concentration on the corrosion behavior of 3A21 aluminum alloy in ethylene glycol solution was discussed.

2. Experimental procedure

2.1. Material
The chemical compositions (wt%) of 3A21 aluminum alloy is shown in table 1. 3A21 aluminum alloy sheet was cut into Φ 10 mm × 5 mm, and soldered to a copper wire. The specimen was embedded in epoxy resin leaving an exposed area of 0.785 cm² as the working area. Prior to each experiment, the sample was successively wet ground using silicon carbide abrasive paper with increased fineness until it reached 800 grits, degreased with acetone and absolute ethanol to remove oil, rinsed with distilled water and then air-dried.

2.2. Electrochemical equipment and measurements
A conventional three-electrode system was used in the experiment, in which, the working electrode (WE) was made by 3A21 aluminum alloy, a platinum sheet was used as the counter electrode (CE), while the reference electrode (RE) was a saturated calomel electrode. The electrochemical experiments were carried out by a potentiostat (Solartron SI 1287 Electrochemical interface/Solartron SI 1260 Impedance gain-phase analyzer), and controlled by Zplot and Corrware software.

According to ASTM D1384-01 [15], the corrosive solution was composed of 148 mg anhydrous sodium sulfate, 165 mg sodium chloride and 138 mg sodium bicarbonate, dissolved in 1 l distilled water. The solution contained 100 ppm chloride ion, sulfate ion and carbonate ion. Ethylene glycol solution was prepared in proportion with the corrosive ions and pure ethylene glycol. All the reagents were analytical grade. The concentration of aqueous ethylene glycol solution were 0%, 15%, 30%, 50%, 65%, and 80%, respectively. In the tests under different atmospheres (N₂, O₂, and Air), the gas was injected at a rate of 100 ml min⁻¹ for 30 min, and then the atmosphere was maintained at a low flow rate during the electrochemical experiment. The diagram of the experimental device is shown in figure 1.

Electrochemical tests were carried out at a temperature of 88 ± 1 °C. Before tests, the 3A21 aluminum alloy electrode was immersed in the ethylene glycol solution for 30 min to obtain stable corrosion potentials. EIS was carried out at the open circuit potential (OCP) with AC signals of 5 mV amplitude in a frequency range of 10 mHz ~ 10 kHz. The impedance spectra were fitted by ZSimpWin software. The potentiodynamic polarization test was conducted at a scan rate of 1 mV s⁻¹ in the potential range of −300 mV~+300 mV relative to OCP. All electrochemical tests were performed three times to ensure reproducibility of data.

2.3. Surface morphology analysis
The surface morphology of the each sample after electrochemical measurement was observed by metallographic scanning microscope (ZEISS Axio Vert.A1) and scanning electron microscope (SEM, TESCAN Vega-3 SBU) equipped with energy-dispersive x-ray spectroscopy (EDS, BRUKER D2-PHASER).

| Table 1. Chemical composition of the used 3A21 aluminum alloy (wt%). |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Element         | Si  | Fe  | Cu  | Mn  | Mg  | Zn  | Ti  | Al  |
| wt%             | 0.6 | 0.7 | 0.2 | 1.0-1.6 | 0.05 | 0.1 | 0.15 | Bal. |

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3. Results and discussion

3.1. Potentiodynamic polarization

The potentiodynamic polarization curves of 3A21 aluminum alloy in ethylene glycol under different atmospheres are shown in Figure 2. It can be clearly seen from Figure 2 that the corrosion potential ($E_{corr}$) of 3A21 aluminum alloy has a higher positive value in glycol aqueous solution than in corrosive water (0% ethylene glycol solution), and the corrosion current density ($I_{corr}$) decreases, which means that the ethylene glycol concentration has an effect on the corrosion of 3A21 aluminum alloy. This is owing to the addition of ethylene glycol reduces the conductivity and increases the viscosity of the solution, then the movement of ions becomes difficult, resulting in increased resistance to corrosion reactions, making corrosion difficult. On the other hand, ethylene glycol, as a polar organic substance, can be adsorbed on the metal surface to inhibit the corrosion of 3A21 aluminum alloy.

However, the change of corrosion potential and corrosion current density with the concentration of ethylene glycol shows different trends under different atmospheres as shown in Figure 2, which shows that the atmosphere conditions also have an impact on the corrosion of 3A21 aluminum alloy in ethylene glycol solution. The polarization parameters were obtained by fitting the linear Tafel segments of the potentiodynamic polarization curves, figures 3 and 4 show the changes of corrosion potential and Corrosion current density of 3A21 aluminum alloy under different atmospheres at 88°C with the concentration of ethylene glycol solution, respectively.

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As figure 3 depicts, the corrosion potential of 3A21 aluminum alloy in ethylene glycol solution under oxygen atmosphere and under air atmosphere increases firstly with the increase of ethylene glycol concentration and then tends to be stable at 50% of the V/V concentration of ethylene glycol, while the corrosion potential of 3A21 aluminum alloy in ethylene glycol solution under blank atmosphere (static state, non-aerated) and under nitrogen atmosphere increases at first and then decreases. The different trend may reflect the different corrosion mechanism of 3A21 aluminum alloy in ethylene glycol solution under different atmospheres.

According to figure 4, the corrosion current density decreases with the increase of ethylene glycol concentration in the same atmosphere, and the possible causes have been described previously. This is similar to the effect of 1,2-propanediol on Mg alloy as reported by Wang et al [16]. Furthermore, it is also noted that, compared with other ventilation conditions, the corrosion current density of 3A21 aluminum alloy is smaller under blank atmosphere (static state, non-aerated) when the V/V concentration of ethylene glycol is 0% and 15%, this corresponds to the larger corrosion potential in the same case in figure 3. This may be due to that the aeration accelerates the movement of ions in the solution and makes the formation of corrosion product film difficult. The V/V concentration of ethylene glycol is 30%, it may be a critical point, when the concentration is further increased to 50%, oxygen and air accelerate the corrosion of 3A21 aluminum alloy, and the effect of
oxygen is more significant, while nitrogen has a certain inhibition effect on the corrosion of 3A21 aluminum alloy. Ventilating oxygen or air can increase the concentration of oxygen in the test solution, it is well known that oxygen as depolarizer can promote the progress of the cathode reaction so as to accelerate the occurrence of corrosion reaction, while the positive shift of corrosion potential may be related to the corrosion products on the surface of aluminum alloy. Since deaeration with nitrogen leads to the reduction of cathode oxygen is inhibited, however, in the high concentration of ethylene glycol solution, the ethylene glycol could be adsorbed on the
metal surface, being advantageous for forming an Al alcoholized film, then inhibiting the corrosion of 3A21 aluminum alloy.

3.2. Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy (EIS) of 3A21 aluminum alloy in ethylene glycol solution under different atmospheres at 88 °C are shown in figure 5. It is obvious that the concentration of ethylene glycol and the atmosphere conditions significantly affect the corrosion mechanism of 3A21 aluminum alloy in ethylene glycol solution, as a result, the Nyquist diagrams of 3A21 aluminum alloy in ethylene glycol solution under different atmospheres show different shapes and trends. The impedance spectra of 3A21 aluminum alloy in ethylene glycol solution under blank atmosphere (static state, non-aerated) and under nitrogen atmosphere only show an imperfect semicircle, but the impedance spectra of 3A21 aluminum alloy consists of a high-frequency semicircle and a low-frequency inductive loop under air or oxygen atmosphere with high V/V concentration of oxygen.
ethylene glycol. The appearance of inductive loop is usually related to the adsorption and desorption of ions or pitting of metals, as aluminum and its alloy are prone to pitting, the inductance is more likely to be caused by pitting of aluminum alloy.

According to whether there is inductive impedance in the impedance spectrum, the EIS data for 3A21 aluminum alloy in ethylene glycol solution under different atmospheres was fitted by two equivalent circuits as shown in figure 6.

In the equivalent circuits, $R_s$ is solution resistance, $Q_f$ and $R_f$ respectively represent the capacitance and resistance of oxide film, $C_d$ is electric double layer capacitor, $R_{ct}$ is charge-transfer resistance and $L$ is inductance. To improve the accuracy of the simulation, a surface inhomogeneity factor and a possible diffusional factor were included. The ideal capacitance in this circuit uses a constant phase element (CPE) [17] which is denoted by $Q$.

The capacitive element is expressed by the following equation [18, 19]:

$$Z_Q = \frac{1}{Y_0(j\omega)^n}$$

where $j$ is an imaginary unit ($j^2 = -1$) and $\omega$ is the angular frequency ($\omega = 2\pi f$). $Y_0$ denotes a frequency-independent constant; and $n$ (1 $\leq n \leq 1$) is the parameter of CPE [20]. The value of polarization resistance $R_p = R_f + R_{ct}$ represents the corrosion properties of the 3A21 aluminium alloy [21, 22], and the fitted results of polarization resistance are presented in figure 7.

In general, the polarization resistance increases with the increase of glycol concentration, when the V/V concentrations of ethylene glycol are 0% and 15%, the values of polarization resistance is larger than that of gas filled condition, but when the V/V concentration is up to 50%, oxygen and air reduce the value of polarization resistance, while nitrogen increases it, this corresponds to the change trend of current density in figure 4, and the reasons have been described previously.

3.3. Analysis of corrosion morphology

In order to further investigate the influence of glycol concentration and atmosphere conditions on the corrosion behavior of 3A21 aluminum alloy, the metalloscope micrographs of 3A21 aluminum alloy after electrochemical measurement in 0% and 30% ethylene glycol solutions under different simulated atmospheres are shown in
Figure 8. It can be seen from figure 8 that there are many obvious pits on the surface of 3A21 aluminum alloy in 0% ethylene glycol solution (corrosive water) in all the experimental atmospheres, on the contrary, the surface of 3A21 aluminum alloy sample is flat without obvious corrosion in 30% ethylene glycol solution, which indicates that ethylene glycol inhibit the corrosion of 3A21 aluminum alloy. Meanwhile, it can also be found from figure 8 that the number of pits increased for the specimens tested under aeration conditions. All of these are consistent with the results of polarization curves and electrochemical impedance spectrum.

Figure 9 gives the SEM morphology of 3A21 aluminum alloy after electrochemical measurement in 0% and 30% ethylene glycol solutions under different simulated atmospheres. Compared with the metallographic test results, the SEM images are clearer. Obviously, aeration accelerated the corrosion of 3A21 aluminum alloy in blank solution (static state, non-aerated), while ethylene glycol inhibited the corrosion of 3A21 aluminum alloy, and there is obvious corrosion product film on the surface of 3A21 aluminum alloy in 30% ethylene glycol solution. Under the experimental conditions, oxygen and air can promote the corrosion of aluminum alloy, and oxygen has a bigger impact, however, nitrogen inhibited the corrosion of aluminum alloy in 30% glycol solution to some extent. The results of SEM are consistent with those of electrochemistry and similar to those in literature reported by Zhang [23].

As shown in figure 10, EDS analyses suggest the formation of oxide films on the surface of 3A21 aluminum alloy after electrochemical measurement in 0% ethylene glycol solutions under the different simulated atmospheres, the content of oxygen in corrosion products is almost the same, this may be due to the corrosion products under the experimental conditions are the same, all of which are aluminum oxides.
However, figure 11(a) shows the element proportion of O/Al on the surface of 3A21 aluminum alloy is much higher under oxygen and air atmospheres than that under nitrogen atmosphere, it is also larger than that in the blank atmosphere (static state, non-aerated), it is proved that filling oxygen/air promotes the formation of
oxidation products on the surface of 3A21 aluminum alloy. Carbon element was detected on the surface of 3A21 aluminum alloy samples in 30% ethylene glycol solution, this confirmed the formation of Al-alcoholized film on the surface of 3A21 aluminum alloy, the high element ratio of C/O in figure 11(b) means that the
aluminum alloy surface is easier to form Al-alcoholized film under nitrogen filling condition, then the corrosion of 3A21 aluminum alloy is inhibited. The results of EDS support the electrochemical test results mentioned above.

Figure 10. (Continued.)
3.4. Corrosion mechanism of 3A21 aluminium alloy in ethylene glycol solution

Usually, the corrosion processes of the aluminium alloy mainly includes anodic dissolution of aluminum and cathodic oxygen reduction. In the anode, hydroxide ions are used by the oxidation of Al to form Al oxide that consists of $\text{Al}_2\text{O}_3$, $\text{AlO(OH)}$, and $\text{Al(OH)}_3$ [17]. The oxidation film can improve the corrosion resistance of the aluminum alloy. Dissolved oxygen in the solution will diffuse to the surface of aluminium alloy, and become reduced to hydroxide ion at the cathode. In addition, Al-alcohol film can be formed on the surface of aluminium alloy in ethylene glycol solution.

The electrochemical reactions of aluminum alloy in corrosive water solution were as follows [24, 25]:

Anodic reaction:

$$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}$$

(2)

$$\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3$$

(3)

Cathodic reaction:

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \rightarrow 4\text{OH}^-$$

(4)

In the 0% ethylene glycol solution (corrosive aqueous solution), the oxidation film defect sites on the surface of the aluminum alloy is adsorbed by $\text{Cl}^-$ ions. Hence, the following chemical reaction occurred [26, 27]:

$$\text{Al(OH)}_3 + 3\text{Cl}^- \rightarrow \text{AlCl}_3 + 3\text{OH}^-$$

(5)

The aeration can cause the $\text{Cl}^-$ ions in the solution to diffuse more easily onto the surface of the aluminum alloy, accelerating the formation of pits.

The electrochemical reactions of 3A21 aluminum alloy in ethylene glycol–water solution were as follows [28–30]:

Anodic reaction:

$$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}$$

(6)

$$\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3$$

(7)

$$\text{Al}^{3+} + \text{OHCH}_2\text{CH}_2\text{O}^- \rightarrow \text{Al(OHCH2CH2O)}_3$$

(8)

Cathodic reaction:

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \rightarrow 4\text{OH}^-$$

(9)

$$\text{CH}_2\text{CH}_2\text{(OH)}_2 + \text{e} \rightarrow \text{OHCH}_2\text{CH}_2\text{O}^- + \text{H}$$

(10)

With the addition of ethylene glycol, the surface of the aluminum alloy did not only formed an oxide film but also formed an Al-alcohol film. Al-alcohol film and oxide film belong to the competitive relationship, and the atmosphere condition and ethylene glycol concentration will affect the formation of Al-alcohol film.
4. Conclusions

(1) The concentration of ethylene glycol solution affected the corrosion behavior and mechanism of aluminum alloy, with the increase of ethylene glycol concentration, the corrosion of aluminum alloy was inhibited, and it was also conducive to the formation of Al-alcoholized film.

(2) The influence of atmosphere conditions on the corrosion behavior of 3A21 aluminum alloy was related to the concentration of glycol solution, the corrosion behavior and mechanism of 3A21 aluminum alloy were different under different atmospheres. Under the research conditions, oxygen and air promoted the corrosion of 3A21 aluminum alloy, while in the high concentration of glycol solution, nitrogen inhibited the corrosion of 3A21 aluminum alloy.

(3) The morphology analysis confirmed the electrochemical test results and the formation of Al-alcoholized film.

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