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Corrosion Behavior of 3A21 Aluminum Alloy in Water-Ethylene Glycol Coolant under Simulated Engine Working Conditions

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In this work, the corrosion behavior of 3A21 aluminum alloy in ethylene glycol coolant was studied under simulated working conditions of automotive engine. The conditions changed alternately between 25°C and 88°C were used to simulate automobile engine usage scenarios. Various methods were used to evaluate polarization resistance, corrosion morphology, element characteristics of corrosion products and corrosion rate. The electrochemical impedance spectroscopy (EIS) demonstrated that polarization resistance first increased and then decreased with the increasing immersion duration at 25°C and 88°C due to the formation of aluminum alloy oxide film and Al-alcohol film. X-ray photoelectron spectroscopy (XPS) confirmed the existence of Al-alcohol film. Energy dispersive spectrometer (EDS) shown that the content ratio between oxygen and aluminum (O/Al) in corrosion products of aluminum alloy surface decreased with increasing concentration of ethylene glycol, while the ratio of C/O increased with the increasing concentration of ethylene glycol. The scanning electron microscope (SEM) results showed that there was pitting corrosion on the surface of 3A21 aluminum alloy. The results of mass loss corrosion experiments indicated that the corrosion rate of 3A21 aluminum alloy in ethylene glycol increased with the increasing of immersion duration and decreased with the increasing concentration of ethylene glycol. Corrosion rate decreased from 0.00512 g·h⁻¹·m⁻²(in 0% ethylene glycol coolant) to $0.00226 \text{ g}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ (in 65% ethylene glycol coolant) at 25°C-88°C alternately for 14 days. The mass loss corrosion rate decreased from 0.00908 $g \cdot h^{-1} \cdot m^{-2}$ (in 0% ethylene glycol coolant) to 0.00396 $g \cdot h^{-1} \cdot m^{-2}$ (in 65% ethylene glycol coolant) at 25°C-88°C alternately for 90 days.

Keyword: 3A21 aluminum alloy; Ethylene glycol coolant; Simulating condition; Automotive engine

1. INTRODUCTION

In recent years, the development of automobile industry is hindered by three problems which included energy, environment and safety. The researches of new materials and technology on automobile products are carried out around energy saving and environmental protection[1, 2]. Reducing the weight of cars is an effective way to reduce energy consumption. According to the survey, The energy consumption[3] of automobile could reduce by 6–7% when its weight decreased by 1000 kg. Aluminum alloy has the advantages of low density, good corrosion resistance and easy processing. It is gradually replacing carbon steels, stainless steels and other metals[4] to be applied in the engine fabrication and bodywork of automobile industry. It is generally agreed that aluminum alloy is an easy-passivated metal and the passivation film formed on its surface would protect the aluminum alloy substrate effectively. However, the passivation film[5, 6] could be damaged by chloride ions and other corrosive ions, resulting in pitting corrosion[7-9] and other local corrosions.

The engine is the heart of automobile. Considerable energy and heat generated in the running process of automotive engine system would cause the sharply rising of its heat flux density and further influenced the safety of engine. Therefore, cooling system and medium were adopted to ensure the cooling capacity of engine. Ethylene glycol coolant[10-13] has become the first choice of automotive engine owing to its low cost, brilliant chemical stability, excellent freeze resistance and the ability to prevent overheating. In the aluminum automobile engine cooling system, the passivation film on the surface of aluminum alloy was consisted of aluminum oxide and Al-alcohol film[14] in ethylene glycol cooling solution. The pitting corrosion sensitivity of Al-alcohol film[15] formed by aluminum and ethylene glycol was lower than that of oxide film, and it could enhance the corrosion resistance of aluminum alloy. However, ethylene glycol coolant would oxidize to produce glycolic and other oxidizing substances in the long-term cooling process, thus the corrosion sensitivity of aluminum alloy could enhance accordingly. Ethylene glycol is easy to be acidified to produce glycol aldehyde, glycol acid, oxalic acid and other substances during operation, which would accelerate the corrosion of aluminum alloy in the engine cooling system, further affecting the safe operation of automobile device and shortening its service life. Nowadays, the corrosion behaviors of aluminum alloy in the ethylene glycol cooling solution has gained increasing attention among the researchers and scholars.

Abiola has found that aluminum alloy would have serious pitting corrosion in ethylene glycol coolant which contains common ions in water (such as chloride ion) [16].Meanwhile, the surface film of aluminum was no longer protective. Jin found that ethylene glycol coolant had a protective effect on aluminum alloy in the early stage of immersion corrosion, but ethylene glycol would oxidize to form by-products such as glycolic acid over time, which would cause severe corrosion of aluminum alloy[17]. Harrooni showed that the adsorption of ethylene glycol could reduce the interfacial capacitance, thereby reducing the corrosion rate of aluminum alloy[18]. Hu found that the 6063 aluminum alloy cold plate in the ethylene glycol coolant was mainly corroded by pitting corrosion, but the corrosion rate of the 6063 aluminum alloy cold plate decreased with the increase of immersion duration[19]. However, there is rare reports about the corrosion behaviors of aluminum alloy in ethylene glycol coolant under the actual working conditions of engine. The car will have two states during actual working: running and stationary.

At this time, the environment where the engine is located will change in temperature. Therefore, the study of temperature alternation can better simulate working conditions of automotive engine.

In this work, three temperature conditions were adopted to simulate the actual operating temperature of engine, they were 25°C, 25°C-88°C alternation (12 h at room temperature, 12 h at 88 °C) and 88°C. The change of polarization resistance of 3A21 aluminum alloy were carried out by electrochemistry in ethylene glycol coolant under various temperature, ethylene glycol concentration and immersion duration. The element characteristics of corrosion products are analyzed by XPS and EDS. The corrosion micro morphology was observed by SEM. Corrosion rate of 3A21 aluminum alloy were evaluated by mass loss corrosion test in ethylene glycol under different condition.

2. EXPERIMENTAL

2.1 Material and regent

3A21 aluminum alloy was used in the experiment. The main chemical composition is exhibited in Table 1.

Table 1. chemical composition of 3A21 aluminum alloy (wt.%)

Element	Si	Fe	Cu	Mn	Mg	Zn	Ti	Al
w.t%	0.6	0.7	0.2	1.0-1.6	0.05	0.1	0.15	Bal.

Two sizes of 3A21 aluminum alloy sheets were used in the experiment. Samples with a size of 50 mm×30 mm×10 mm were used to calculate the corrosion rate. While samples with a size of 10mm×5mm×5mm were used to observe the corrosion micro morphology and characterize the corrosion products. The side of each sample was drilled with a hole of 3 mm for hanging. Before immersion, the samples were polished by silicon carbide paper with 800 mesh. The samples were washed sequentially with acetone, absolute ethanol and deionized water to ensure a clean surface and then dried in air.

Anhydrous sodium sulfate, sodium chloride, sodium bicarbonate and ethylene glycol are all analytical pure (Chengdu Kelong Chemical Reagent Factory. China).The corrosion aqueous solution was prepared according to the standard (ASTM D1384-01)[20]. 148 mg anhydrous sodium sulfate, 165 mg sodium chloride and 138 mg sodium bicarbonate were dissolved into 1 L distilled water, then the solution contained 100 ppm chloride, sulfate and carbonate ions. The cooling solution of engine was ethylene glycol coolant that consisted of different ratios of corrosion aqueous solution and ethylene glycol. The concentrations of ethylene glycol coolant included 0 %, 15 %, 33.3 %, 50 % and 65 %. A 500 mL flat-bottomed jar was used to contain corrosive medium. In order to prevent the corrosive medium from evaporating, a condenser tube was used to condense and reflux the evaporating solution, and the interface between the jar and the condenser tube was sealed.

2.2 Electrochemical impedance spectroscopy tests

According to the results of static mass loss corrosion experiments, electrochemical impedance spectroscopy (EIS) of 14 days was performed at room temperature and 88°C to research the corrosion behavior of 3A21 aluminum alloy in ethylene glycol coolant over time.

A traditional three-electrode system was used in the experiment, in which the working electrode (WE) was made of 3A21 aluminum alloy, the platinum sheet was used as the counter electrode (CE), and the reference electrode (RE) was a saturated calomel electrode. EIS analysis was performed by using a potentiostat and impedance gain phase analyzer (Solartron SI 1287/Solartron SI 1260) controlled by Zplot and Corrware softwares to evaluate the corrosion behavior of 3A21 aluminum alloy.

The electrochemical tests were carried out at 88±1°C. Before testing the AC impedance, a 30 mins open circuit potential (OCP) test was performed on the 3A21 aluminum alloy to obtain a stable corrosion potential. Next, an alternating current impedance (EIS) test was performed with an AC signal of 5 mV amplitude in the frequency range of 10 mHz to 10 kHz. The AC impedance data was fitted by ZSimpWin software.

2.3 Surface analysis after corrosion

The surface element of every sample after corrosion was tested by Energy dispersive X-ray spectrometer (EDS, BRUKER D2-PHASER). The samples of 3A21 aluminum alloy immersed in 0% and 65 % ethylene glycol coolant at 88 °C for 14 days was tested by Multifunctional surface analysis electronic energy spectrometer (XPS, Kratos XSAM800). The corrosion morphology of every sample after immersion experiments was observed by scanning electron microscope (SEM, TESCAN Vega-3 SBU).

The chromium trioxide-phosphoric acid solution was prepared before SEM tests. 980 g phosphoric acid solution of 1:19 was prepared, and 20 g chromium trioxide was completely dissolved into above solution. The samples after EDS and XPS tests were immersed in chromium trioxide-phosphoric acid solution at 80 °C for 5 min, and a soft eraser was used to remove their surface dirt. Next, the samples were degreased with acetone and absolute ethanol, washed with distilled water, and then dried in air. The obtained samples were characterized by SEM to observe the corrosion morphology on their surface.

2.4 Corrosion rate test

Conditions with different temperature were chosen to simulate the actual operating situation of engine. 25°C, 88°C and 25°C~88°C alternation (12 h at room temperature, 12 h at 88°C). The static mass loss corrosion test was carried out in various immersion duration (14 d and 90 d). The formula for calculating the mass loss corrosion rate is as follows:

$$V = \frac{W_0 - W_t}{St}$$
 1.

V is the mass loss corrosion rate, W_0 is the initial weight of matrix, W_t is the weight of the

substrate after removing the corrosion products. S is the total surface area of the testing sample. t is the immersion duration.

3. RESULTS AND DISCUSSION

3.1 EIS measurements

The AC impedance of 3A21 aluminum alloy immersed in ethylene glycol coolant for 14 days was shown in Fig 1 and Fig 2. After different immersion duration, the Nyquist diagram of 3A21 aluminum alloy in different concentrations of ethylene glycol coolant at 88 °C had a similar pattern, all diagrams exhibited incomplete semicircles.



Figure 1. The Nyquist diagrams of 3A21 aluminum alloy in ethylene glycol coolant under different immersion duration at 25 °C: (A) 0%,25°C; (B) 33.3%,25°C; (C) 65%,25°C.



Figure 2. The Nyquist diagrams of 3A21 aluminum alloy in ethylene glycol coolant under different immersion duration at 88 °C: (A) 0%,88°C; (B) 33.3%,88°C; (C) 65%,88°C.



Figure 3. The equivalent circuits used to fit the EIS data for 3A21 aluminum alloy in ethylene glycol coolant under different immersion duration at 88 °C.

The Warburg impedance appears in the impedance spectrum when the V/V concentration of ethylene glycol was 0% at temperature of 25°C, and the oxygen concentration diffusion reaction was occurred at this time.

At 25 °C, the equivalent circuit of 3A21 aluminum alloy immersed in glycol coolant for 14 days was shown in Fig 4 (A). R_s was the solution resistance, R_p was the polarization resistance, CPE (denoted by C_c) was the capacitance of oxide film, and W was Warburg impedance [21].

At 88 °C, the equivalent circuit of 3A21 aluminum alloy immersed in glycol coolant for 14 days was shown in Fig 4 (B). In the equivalent circuit diagram, R_s is the solution resistance, Q_f and R_f represent the capacitance and resistance of oxide film, respectively. C_d is the electric double layer capacitor, and R_{ct} is the charge-transfer resistance. The ideal capacitance in this circuit uses a constant phase angle element (CPE)[22] represented by Q, and the coated capacitor uses the constant phase angle element to express its impedance value. The capacitive element is represented by the following equation[23, 24].

$$Z_Q = \frac{1}{Y_0(jw)^n}$$
 2.

where *j* is an imaginary unit $(j^2 = -1)$ and *w* is the angular frequency $(w = 2\pi f).Y_0$ denotes a frequency-independent constant; and $n (1 \le n \le 1)$ is the parameter of CPE[25].

The calculation formula of polarization resistance of 3A21 aluminum alloy in glycol coolant under different immersion duration, $R_p=R_f+R_{ct}$, the polarization resistance R_p indicated the corrosion resistance of 3A21 aluminum alloy in glycol coolant[26, 27]. A higher R_p meant better corrosion resistance of 3A21 aluminum alloy in glycol coolant.



Figure 4. The *R*_p of 3A21 aluminum alloy in ethylene glycol coolant after different immersion duration:(A) 25 °C (B) 88 °C

The fitting results of polarization resistance R_p of 3A21 aluminum alloy in ethylene glycol coolant at various immersion durations were shown in Fig 4. As shown in Fig 4 (A), R_p first increased and then gradually decreased with increasing of immersion duration. R_p increased significantly from 44.27 k $\Omega \cdot cm^{-2}$ to 64.2 k $\Omega \cdot cm^{-2}$ in 0% ethylene glycol when the immersion duration reached 2 hours. R_p increased significantly from 284.78 k $\Omega \cdot cm^{-2}$ to 969 k $\Omega \cdot cm^{-2}$ in 33.3% ethylene glycol and increased significantly from 436.4 k $\Omega \cdot cm^{-2}$ to 1190 k $\Omega \cdot cm^{-2}$ in 65% ethylene glycol coolant when the immersion duration reached 24 hours. As shown in Fig 4 (B), R_p first increased and then gradually decreased with increasing immersion duration in 33.3% ethylene glycol and 65% ethylene glycol coolant, and it

increased significantly to 70.49 k Ω ·cm⁻² (in 33.3% ethylene glycol) and 109.784 k Ω ·cm⁻² (in 65% ethylene glycol) when the immersion duration reached 2 hours. The results demonstrated, the aluminum would form an oxide film and an alcoholic film with ethylene glycol to protect matrix at initial immersion after 3A21 aluminum alloy was immersed in ethylene glycol coolant. And the R_p decreased with the increasing of immersion duration, because ethylene glycol has begun to oxidize and destroy the oxide film on the surface of aluminum alloy. In corrosion aqueous solution (0 % ethylene glycol), R_p increased gently with increasing immersion duration. However, Rp showed an obvious increase when the reimmersion duration increased from 24 to 168 hours, and then it decreased with increasing immersion duration. The result indicated that an oxide film layer formed on the surface of aluminum alloy at initial immersion duration, which played a role in protecting aluminum alloy matrix. As the immersion duration further increased, the active ions in corrosion aqueous solution would destroy the oxide film layer on the surface of aluminum alloy, leading to a decrease of R_p. The results similar to the study of Jin [17]. Jin and Zaharieva both found that the oxidation by-products of ethylene glycol were one of the main reasons for the increased corrosion susceptibility of AA6061 aluminium alloy in ethylene glycol coolant. This may be one of the reasons for the reduced corrosion resistance of 3A21 aluminum alloy in ethylene glycol solution[17, 28].

3.2 Surface element analysis after corrosion

Fig 5 and Fig 6 respectively showed the XPS results of 3A21 aluminum alloy in 0% and 65% ethylene glycol coolant after immersion at 88 °C. In Fig 5 and Fig 6, XPS characterization has obtained detailed information on the surface composition and elemental analysis of 3A21 aluminum alloy in 0% and 65% ethylene glycol coolant at 88 °C. The characteristic signals of O, C and Al elements could be clearly seen in the XPS spectrum of 3A21 aluminum alloy (Fig. 5 A and Fig. 6 A).





Figure 5. XPS survey spectra of 3A21 aluminum alloy in 0% ethylene glycol coolant at 88 °C for 14 days: (A)XPS energy spectrum; (B) O 1s; (C) C 1s; (D) Al 2p.



Figure 6. XPS survey spectra of 3A21 aluminum alloy in 65% ethylene glycol coolant at 88 °C for 14 days: (A) XPS energy spectrum; (B) O 1s; (C) C 1s; (D) Al 2p.

In Fig 5 B, three peaks located at 530.35 eV, 531.63 eV and 532.8 eV was attributed to O1s spectrum. The peak at 530.49 eV belonged to the surface lattice oxygen, and the peak at 531.7 eV was assigned to oxygen vacancy on the Al_2O_3 surface[29] while the peak at 532.87 eV was ascribed to adsorbed oxygen[30].

Table 2. The element (at.%) of 3A21	aluminum alloy immersed	d in ethylene glycol coo	ant for 14 days
at 88°C.			

<i>C</i> (V/V%)	С	0	Al	Si	Mn
0%	-	50.23	47.95	1.39	0.44
15%	25.21	33.16	40.51	0.74	0.38
33.3%	28.85	28.75	41.34	0.88	0.19
50%	24.74	29.04	44.56	1.25	0.41
65%	34.55	25.79	38.71	0.6	0.36



Figure 7. The element ratio of 3A21 aluminum alloy immersed in ethylene glycol coolant for 14 days at 88°C: (A)O/Al; (B)C/O.

A similar situation appeared at 530.49 eV, 531.7 eV and 532.87 eV in Fig 6 B. In Fig 5 C, only one peak of C1s spectrum at 284.83 eV was attributed to carbon functional groups of C-C. The appearance of this peak was due to the introduction of polluting carbon. In Fig 6 C, two peaks of C1s spectrum at 284.81 eV and 286.49 eV were attributed to carbon functional groups of C-C and C-O, respectively[31]. The Al 2p spectrum[32] had a main peak at the binding energy of 74.38 eV and 74.21 eV, which belonged to the Al³⁺ in Al₂O₃. The functional group C-O and adsorbed oxygen indicated that an alkoxide film was adsorbed on the surface of the 3A21 aluminum alloy. The Al³⁺ and oxygen vacancy proved that aluminum oxide was formed on the surface of aluminum alloy.

At various temperature (25 °C, 25°C-88 °C alternation and 88°C), 3A21 aluminum alloy was immersed in different concentrations of ethylene glycol coolant after 14 days, the corrosion products elements on its surface was exhibited in Table 2, and the elements ratios of corrosion products was depicted in Fig 7. As the concentration of ethylene glycol rose, the content ratio between oxygen and aluminum (O/Al) on the surface of aluminum alloy decreased.



Figure 8. The element ratio of 3A21 aluminum alloy after immersed in different concentrations of ethylene glycol coolant and different temperature conditions for 90 days: (A)O/Al; (B)C/O.

Table 3. The element (at.%) of 3A21 aluminum alloy after immersed in different concentrations of
ethylene glycol coolant and different temperature conditions for 90 days.

temperature (°C)	<i>C</i> (V/V%)	C(at.%)	O(at.%)	Al(at.%)	Si(at.%)	Mn(at.%)
	0%	2.39	70.28	26.89	0.13	0.18
25°C	33.3%	5.91	12.61	79.50	1.91	-
	65%	11.10	11.69	74.59	2.13	0.49
	0%	10.67	47.18	39.79	1.94	-
25°C -88°C	33.3%	8.59	39.01	49.8	1.65	0.31
	65%	15.97	18.88	63.01	1.51	0.42
	0%	7.59	50.16	33.74	5.84	0.32
88°C	33.3%	12.62	39.32	42.84	4.92	0.21
	65%	19.64	29.98	48.28	1.46	0.27

This might be due to the added ethylene glycol weakened the oxidation reaction of aluminum alloy. C element was appeared on the surface of aluminum alloy after the addition of ethylene glycol, which indicated that ethylene glycol would form Al-alcohol with the aluminum alloy to protect matrix. Similar to Cheng[14, 33] who by 3003 aluminum alloy during ethylene glycol coolant found that the passivation film formed is mainly composed of aluminum oxide and Al-alcohol thin film, and exhibits the characteristics of an n-type semiconductor.

At various temperature (25 °C, 25°C-88°C alternation and 88°C). After 3A21 aluminum alloy was immersed in different concentrations of ethylene glycol coolant for 90 days, the corrosion products elements on the surface of 3A21 aluminum alloy was indicated in Table 3. The elements ratios of corrosion products on the aluminum alloy were shown in Fig 8. As depicted in Table 3, oxygen element could be detected on the surface of 3A21 aluminum alloy after it was immersed in ethylene glycol coolant for 90 days, demonstrating aluminum oxides would generate on the surface of aluminum alloy. It can be seen in Fig. 8 (A), the composition of oxide on the surface of aluminum alloy would be different with various elements ratios of oxygen and aluminum. In solution (0 % ethylene glycol coolant), the O/Al ratio was obviously higher than in other ethylene glycol coolant, and the corrosion products on the surface of aluminum alloy were mainly aluminum oxide. After the addition of glycol coolant, the ratio

of O/Al decreased at different degrees due to that the adsorbed ethylene glycol on the surface of aluminum alloy might hinder its oxidation. As the concentration of glycol coolant increased, the C/O ratio of corrosion products would enlarge, because the adsorption of ethylene glycol on the aluminum alloy surface made it easier to from Al-alcohol film. As exhibited in Fig 8, in corrosion solution (0 % ethylene glycol coolant), O/Al ratio showed a decreased trend with increasing temperature. A higher temperature would cause the reduction of dissolved oxygen and increased the diffusion of oxygen molecules in solution, further influenced the oxidation of aluminum alloy. The little C element in corrosion products might be introduced during grinding. In 33.3 % glycol coolant, the O/Al ratio would decrease with increasing temperature as well as C/O ratio. The increasing temperature increased the oxidation of aluminum alloy and reduced the formation of Al-alcohol film. The same phenomenon appeared in 65 % glycol coolant, a higher temperature could increase the oxidation of ethylene glycol coolant, a higher temperature could increase the oxidation of ethylene glycol coolant, and reduced the formation of Al-alcohol film on the surface of aluminum alloy.

3.3 Surface morphology analysis after corrosion

The corrosion behavior of 3A21 aluminum alloy in different concentrations of glycol coolant was studied at various time and temperatures. The hanging film experiment was carried out to obtain SEM images of 3A21 aluminum alloy after immersing in different concentrations of ethylene glycol coolant for 14 days at different temperatures (25 °C, 25 °C -88 °C alternation and 88 °C). As depicted in Fig 9, group A was the test result at 25 °C, B was that at 25 °C -88 °C alternately while C was that at 88 °C. At same temperature, as the concentration of glycol coolant increased, the size and number of pits on the surface of 3A21 aluminum alloy decreased. In the immersion experiment, 3A21 aluminum alloy had better pitting corrosion resistance with the addition of glycol coolant. In same concentration of ethylene glycol coolant, the pits on the surface of 3A21 aluminum alloy increased with the increase of temperature. It might be because a higher temperature made ethylene glycol easier to be oxidized into glycolic acid, oxalic acid and other substances, which would damage the oxide film and Al-alcohol film on the surface of 3A21 aluminum alloy, leading to aggravation of pitting corrosion.





Figure 9. Scanning electron micrograph of 3A21 aluminum alloy after immersed in different concentrations of ethylene glycol coolant and different temperature conditions for 14 days

At various temperature (25 °C, 25 °C -88 °C alternation and 88 °C), The SEM images of 3A21 aluminum alloy immersed in different concentrations of ethylene glycol coolant after 90 days were depicted in Fig 10, after removing the corrosion products, there are a few small pits (below 2 μ m) of

various degree appeared on the surface of aluminum alloy in different concentrations of glycol coolant. However, obvious pits (2~10µm) appeared on the surface of aluminum alloy in corrosion solution (without ethylene glycol coolant), and the number of pits increased. At 25°C -88 °C alternation, after removing the corrosion products, corrosion pits (about $2 \sim 12 \mu m$) appeared obviously after the aluminum alloy was immersed in the corrosion aqueous solution. After aluminum alloy was immersed in ethylene glycol coolant of different concentrations, the size of surface corrosion pits was reduced, but its number is obviously increased. At 88 °C, pits of different degree appeared on the surface of aluminum alloy after removing corrosion products $(2 \sim 20 \mu m)$. Esenin[34] found that the pitting corrosion of aluminum alloy becomes worse with the increase of temperature in aqueous ethylene glycol solutions. We found a similar pattern in this study. As shown in Fig 10, after the corrosion products were removed, aluminum alloy would have corrosion pits of different degrees on its surface after immersion at different temperatures and various glycol concentrations for 90 days, indicating that the surface of aluminum alloy had localized corrosion dominated by pitting. Liu[35] found that pitting of aluminum alloys in aqueous ethylene glycol solutions occurs mainly because the chloride ions attack and replace the oxygen vacancies in the oxide film, causing localized detachment of the oxide film. The corrosion pit acted as an active area on the surface of aluminum alloy and formed a tiny battery with the aluminum alloy matrix, causing galvanic corrosion and accelerating the corrosion of the pit. With the addition of glycol coolant, the pitting corrosion on the aluminum alloy surface would be reduced to varying degrees.





Figure 10. Scanning electron micrograph of 3A21 aluminum alloy after immersed in different concentrations of ethylene glycol coolant and different temperature conditions for 90 days

3.4 Mass loss corrosion rate

The corrosion behavior of 3A21 aluminum alloy in different concentrations of ethylene glycol coolant was studied at various time and temperatures. The hanging film experiment was carried out to obtain corrosion rates of 3A21 aluminum alloy after immersing in different concentrations of ethylene glycol coolant for 14 days at different temperatures (25 °C, 25 °C-88°C alternation and 88°C). As shown in Fig 11 (A), at 25°C, as the concentration increased, the corrosion of 3A21 aluminum alloy showed a downward trend. At 25°C-88°C alternately, the corrosion of 3A21 aluminum alloy decreased with the increase of ethylene glycol concentration. When the concentration of ethylene glycol coolant increased from 0% (corrosion solution) to 15%, the mass loss corrosion rate of 3A21 aluminum alloy decreased from 0.00512 g·h⁻¹·m⁻² to 0.00256 g·h⁻¹·m⁻². However, there was an opposite trend which the mass loss corrosion rate of 3A21 aluminum alloy increased from 0.00256 $g \cdot h^{-1} \cdot m^{-2}$ to 0.00308 $g \cdot h^{-1} \cdot m^{-2}$ when the concentration of ethylene glycol coolant increased from 15% to 30%, and then the corrosion of 3A21 aluminum alloy further decreased with the increasing concentration. Finally, the mass loss corrosion rate decreased to 0.00226 g·h⁻¹·m⁻² in 65% ethylene glycol coolant. An inflection point appeared in 15% ethylene glycol coolant. Compared with the corrosion solution, the addition of ethylene glycol will reduce the corrosion rate of aluminum alloys. It is similar to the research found by Zhang[36]. It might be because that an Al-alcohol film would form on the surface of the aluminum alloy after the addition of ethylene glycol. The synergistic effect between Al-alcohol film and oxide film work increased protecting the surface of the aluminum alloy. At 88 °C, the corrosion of 3A21 aluminum alloy exhibited a similar trend to that at 25 °C. The corrosion rate of 3A21 aluminum alloy decreased significantly with the increasing concentration, especially at 0%-15% and 50%-65%, the two concentration transition points have changed obviously. Ethylene glycol was easier to be oxidized to form organic acids such as oxalic acid at higher temperature. As the immersion progressed, ethylene glycol would gradually acidify and further increased the corrosion of 3A21 aluminum alloy. Therefore, at the same concentration, the corrosion of aluminum alloy would be more serious at 88°C and 25°C -88°C than at room temperature. The increasing temperature would not only speed up the diffusion of oxygen molecules in the solution, but also reduce the concentration of oxygen molecules as well as accelerating the oxidation of ethylene glycol. Therefore, the corrosion of aluminum alloy at 88°C would be more serious than in 25°C-88°C at the same concentration.



Figure 11. Mass loss corrosion rate of 3A21 aluminum alloy in different concentrations of ethylene glycol coolant at different temperatures: (A)14D (B)90D

The corrosion rate of 3A21 aluminum alloy immersed in different concentrations of ethylene glycol coolant for 90 days was tested at different temperatures (25°C, 25°C-88°C alternately, and 88°C) through the static coupon experiment. As shown in Fig 11 (B), the corrosion rate of 3A21 aluminum alloy at same temperature decreased with increasing concentration in the mass loss corrosion of immersion. The corrosion rate decreased from 0.00908 g·h⁻¹·m⁻² to 0.00396 g·h⁻¹·m⁻² When the concentration of ethylene glycol coolant increased from 0% (corrosion solution) to 65% at 25°C-88°C alternately. However, the corrosion rate of 3A21 aluminum alloy would increase with the increasing temperature in the same glycol concentration.

4. CONCLUSIONS

(1) The results of electrochemical impedance spectroscopy indicated that polarization resistance R_p of aluminum alloy increased remarkably after the addition of ethylene glycol at 25°C and 88 °C as well as corrosion resistance. At the same concentration, the polarization resistance R_p would increase sharply when the immersion duration reached 24h (25°C) or 2h (88°C). R_p increased significantly to 969 k $\Omega \cdot cm^{-2}$ (in 33.3% ethylene glycol) and 1190 k $\Omega \cdot cm^{-2}$ (in 65% ethylene glycol) when the immersion duration reached significantly to 70.49 k $\Omega \cdot cm^{-2}$ (in 33.3% ethylene glycol) and 1190 k $\Omega \cdot cm^{-2}$ (in 33.3% ethylene glycol) and 1190 k $\Omega \cdot cm^{-2}$ (in 65% ethylene glycol) and 109.784 k $\Omega \cdot cm^{-2}$ (in 65% ethylene glycol) when the immersion duration reached 2 hours at 88°C. The immersion duration might be the critical factor for the formation of aluminum alloy oxide film and Alalcohol film.

(2) The XPS showed that Al-alcohol film was formed on the surface of the aluminum alloy after corrosion. The EDS results showed that the O/Al ratio on the surface of aluminum alloy would decrease with increasing concentration of ethylene glycol. Because ethylene glycol was adsorbed on the surface of aluminum alloy and reduced the oxidation reaction. However, the O/Al ratio on the surface of

aluminum alloy decreased with increasing temperature. It might be because ethylene glycol was easier to be oxidized into glycolic acid, oxalic acid and other substances when temperature was increased, which would destroy the oxide film and Al-alcohol film on the surface of aluminum alloy.

(3) The results of SEM demonstrated the surface of aluminum alloy was easier to form obvious pitting corrosion with increasing immersion duration. At 25 °C, there was no obvious pitting corrosion formed on the surface of aluminum alloy after the addition of ethylene glycol. When the temperature changed alternately between 25 °C and 88 °C, some small pitting corrosion formed on the surface after the addition of ethylene glycol. And obvious pitting corrosion formed when the temperature reached 88 °C.

(4) In ethylene glycol coolant, the mass loss corrosion rate of aluminum decreased with the increasing concentration. The mass loss corrosion rate decreased from 0.00512 g·h⁻¹·m⁻² to 0.00226 g·h⁻¹·m⁻² When the concentration of ethylene glycol coolant increased from 0% (corrosion solution) to 65% at 25°C-88°C alternately for 14 days. The mass loss corrosion rate decreased from 0.00908 g·h⁻¹·m⁻² to 0.00396 g·h⁻¹·m⁻² When the concentration of ethylene glycol coolant increased from 0.00908 g·h⁻¹·m⁻² to 0.00396 g·h⁻¹·m⁻² When the concentration of ethylene glycol coolant increased from 0% (corrosion solution) to 15% at 25°C-88°C alternately for 90 days. The mass loss corrosion rate increased with the increasing immersion duration.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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