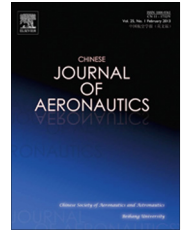




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Effect of temperature on corrosion behavior of 3003 aluminum alloy in ethylene glycol–water solution



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Abstract The effect of temperature on the corrosion behavior of 3003 aluminum alloy in ethylene glycol–water solution was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The surface characterization was observed and determined by scanning electron microscopy (SEM), atomic force microscopy (AFM) and energy dispersive spectrometer (EDS). The results demonstrate that the anodic aluminum dissolution and the cathodic oxygen reduction were accelerated by the increased temperature. However, as temperature was over 60 °C, the solubility and concentration of oxygen decreased, resulting in the inhibition of cathodic reaction. The cathodic reaction rate of 3003 aluminum alloy rose to the maximum at 60 °C. The Warburg impedance in Nyquist diagram diminished and then was replaced by a negative capacitance caused by the absorption of intermediate corrosion product on electrode. On the other hand, after potentiodynamic measurements, 3003 aluminum alloy suffered pitting corrosion. The dissolution of aluminum alloy around secondary phase particles expanded both horizontally and vertically. © 2016 The Authors. Production and hosting by Elsevier Ltd. on behalf of Chinese Society of Aeronautics and Astronautics. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Aluminum alloys are increasingly used in aerospace industries owing to their excellent properties of high strength-to-weight ratio and good formability.^{1–3} For example, the heat exchangers on the aircraft AC modules are made of the aluminum alloy rather than the other two types of commonly applied materials: the copper alloy and the stainless steel. However,

aluminum alloy corrosion occurs and is a major problem in the cooling system of aircraft engine block.^{4–6} It is due to a wide temperature range and complex components of coolant to which the aluminum alloy is exposed.^{7–9} The appropriate physical and chemical properties of heat coolant have been required to prevent malfunction of cooling system.^{10–12} Mixed with water, ethylene glycol is a popular coolant in heat exchanger¹³, because of its low cost and excellent freeze and heat-protection over a wide temperature range.^{14–17} The main composition of a conventional coolant consists of 30%–70% (by volume) ethylene glycol and some corrosion inhibitors.^{18–20} Common heat transfer fluids show a low aggressivity, unless pollution or high-temperature exposure (degradation) occurs.²¹ Coolant in the aircraft heat exchanger is always contaminated with chloride ions. In the presence of Cl[–], the

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corrosion resistance of aluminum and aluminum alloys decreased significantly and severe pitting corrosion was observed.²²

3003 aluminum alloy is considered as an advanced material for manufacturing aero heat exchangers.^{23–26} It has complex microstructure containing intermetallic particles and impurity precipitation in the aluminum matrix. These particles and precipitation can be either cathodic or anodic with respect to the matrix phase.^{27,28} Such complexities have made it challenging to understand the corrosion of 3003 aluminum alloy in cooling systems at different temperatures.

There were a few works in the study of corrosion of aluminum alloys in aqueous ethylene glycol solutions.²⁹ Liu and Cheng³⁰ found that the oxide film formed on aluminum depended on the dissolved oxygen in the solution. The cathodic reaction is dominated by the oxygen reduction in aerated solution.³¹ In the absence of oxygen, the main cathodic reaction is either reduction of water or reduction of ethylene glycol.³² However, few of them focused on the effect of temperature on the corrosion behavior of 3003 aluminum alloy in aero coolant systematically. It can provide useful data for material protection and design. In particular, the change in temperature may make a big difference to the inhibition effect of inhibitor. Therefore, it is necessary to study the effect of temperature on the corrosion behavior of 3003 aluminum alloy in the solution.

The present work studies the corrosion and electrochemical behavior of 3003 aluminum alloy in chloride-containing ethylene glycol–water solution at different temperatures by various electrochemical measurements, including corrosion potential, potentiodynamic polarization, cathodic polarization, electrochemical impedance spectroscopy (EIS). The geometrical parameters of pits are measured and analyzed. The surface morphology of aluminum electrode is characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The chemical composition is measured by an energy dispersive spectroscopy (EDS) combined.

2. Experimental procedures

2.1. Electrodes and solutions

Test specimens were cut from a 3003 aluminum plate into cylinders of 10 mm diameter, with the chemical composition (wt%): Cu 0.2, Mn 1.5, Fe 0.70, Si 0.60, Zn 0.10, Mg 0.05, Ti 0.05, Cr 0.05 and aluminum in balance. The aluminum electrode was embedded in phenolic resin, leaving a working area of 0.785 cm². Electrical contact of the specimen was made from the rear by spot welding a cooper lead on to the back of the specimen. The non-working surface of the electrode was sealed in an epoxy resin. The exposed surface of each electrode was finished by wet-grinding with a series of emery papers from 400 grit to 5000 grit and then cleaned thoroughly with alcohol acetone and deionized water in turn. The base solution was a mixture of 50% ethylene glycol + 50% deionized water + 0.1 mol · L⁻¹ NaCl, simulating the aero coolant and the potential chloride contamination. Tests were performed at temperatures ranging from 30–80 °C, consistent with the typical operating temperature in the aero cooling system. The test temperature was maintained through a water bath controlled by a thermoelectric couple. All solutions were

made from analytic grade reagents and ultrapure deionized water.

2.2. Electrochemical measurement

Electrochemical measurements were conducted on a three electrode cell with the test specimen as working electrode (WE), a platinum as counter electrode (CE) and a saturated calomel electrode (SCE) as reference electrode (RE). Prior to electrochemical measurement, the specimen was immersed in the static solution for 3 h in order to obtain a steady corrosion potential. Open-circuit potentials were monitored prior to any polarization or impedance measurements.

Potentiodynamic scans were performed at a positive direction from -0.8 V(vs. SCE) to -0.45 V(vs. SCE) with a scan rate of 30 mV/min on Princeton 2273. Polarization stopped when the anodic current density exceeded 0.01 mA. The values of corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (b_a , b_c) were fitted and calculated through a Zview analytical software. Cathodic polarization was carried out by sweeping from -0.6 V(vs. SCE) negatively to about -1.3 V(vs. SCE).

All the EIS measurements were conducted at open circuit potential on CHI 660E (Hua Chen instrument corporation, Shanghai). Impedances were characterized over the frequency range from 100 kHz to 10 mHz, with the AC signal amplitude being ± 10 mV(vs. SCE). Equivalent circuit modeling was performed using ZsimpWin software.

For each temperature, at least three parallel valid samples were tested to ensure the reproducibility of the results. The sample data closest to the average level was the final data used in analysis. All the tests were performed open to air without agitation of the electrolyte.

2.3. Surface characterization

After potentiodynamic polarization, the 3003 aluminum electrode was removed from solution. Before AFM measurement the sample was cleaned by ultrasonic bath for 10 min to get rid of corrosion product, rinsed with deionized water and dried with cold air for atomic force microscopy (AFM) analysis. AFM analysis was conducted on a Veeco Dimension Icon operating in Tap Control mode under ambient conditions in air at a scan size of 30 $\mu\text{m} \times 30 \mu\text{m}$ to provide detailed topographic information. Images were analyzed by the AFM NanoScope Analysis software, version 1.40. And then a layer of gold was sprayed on the surface of the electrode to enhance the electrical conductivity prior to SEM (scanning electron microscopy) characterization conducted on CamScan3400. The morphological features of different regions of the electrode were characterized by SEM at 2000 \times magnification. Then, the total number and physical dimensions of pits located in the microscopical view were recorded without repetition. The number of pits was counted on the visual field of the microscopy. We chose ten visual fields of microscopy randomly on each sample under the same magnification, recorded the number of pits on it, and then calculated the number of pits on per mm². Elemental composition was measured with a combined EDS (energy dispersive spectrometer) instrument.

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