The role of chloride ions and pH in the corrosion and pitting of Al–Si alloys

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Abstract

The role of chloride ions in the pitting corrosion of some Al–Si alloys was investigated by chemical, polarization and EIS measurements, as well as SEM studies. Differences in corrosion rates of pure aluminium and the alloys are discussed. The capacitive behaviour of the oxide covered surface is replaced by resistive behaviour as immersion time increases in HCl solutions. At neutral pH corrosion currents increase then decrease with chloride ion concentrations. Pitting by chloride ions initiates more readily in acidic media.

1. Introduction

Aluminium finds extensive applications in the automotive industry as a result of emphasis on weight reduction to allow decreases in fuel costs. Thin and reproducible oxide layers form on aluminium after mechanical polishing and are stable under atmospheric conditions but thicken rapidly in solution so that the oxide reaches about 1000 times thicker (about 5000 nm) than the layer formed in air [1]. Corrosion of aluminium is thought to occur by ionic migration followed by dissolution at the oxide/electrolyte interface [2]. Due to its relative mechanical weakness it is usually strengthened by alloying, which may cause reduced corrosion resistance. The Al–Si alloys are among the most important commercial alloys. Al–Si is a simple eutectic system with two solid solution phases, the eutectic composition is 12.2 ± 0.1 at % Si [3]. Silicon exhibits low solubility in aluminium, < 0.1 wt % at 150 °C [3]. The presence of many alloying additives with limited solubilities in aluminium has been shown to promote localized corrosion [4]. Although aluminium passivates in H2SO4 due to formation of a porous oxide film [5], HCl gives rise to rapid aluminium corrosion [6]. The presence of chloride ions in aqueous media in contact with aluminium metal [7] or aluminium alloys [8], causes pitting attack. The presence of chloride ions was found to accelerate the corrosion of aluminium in aqueous media; the corrosion depended strongly on the pH of the solution [6]. Also, in acidic and alkaline media, where the solubility of aluminium oxide is enhanced, aluminium corrodes more rapidly [9]. Thus, the passivation of aluminium can be suppressed by lowering or increasing the pH, as well as by addition of chloride ions [6, 10]. In this study, the role of chloride ions and pH on the passivation and corrosion of some Al–Si alloys is investigated.

2. Experimental details

Analyses of the three Al–Si alloys and commercially pure aluminium are given in Table 1. According to the Al–Si phase diagram [3] alloy I is a hypoeutectic alloy (Al + eutectic), alloy II is almost formed of the eutectic, while III is a hypereutectic alloy (Si + eutectic).

Samples used in chemical measurements were 5 cm long and 1 cm in diameter. Electrodes used in potentiostatic polarization and electron impedance spectroscopy, (EIS), were in the form of rods embedded in glass tubes just larger than the sample and fixed with Araldite adhesive (Ciba Geigy, Switzerland) so that when immersed in the test solution the area exposed was 0.785 and 0.204 cm2 in polarization and EIS measurements, respectively. The electrodes were previously polished mechanically with finer grade of emery paper up to 4/0, washed with deionized water and rinsed with the test solution. The samples used in chemical measurements were mechanically polished and washed with deionized water decreased with acetone and dried with air, and immersed immediately in the test solution. All reagents were A.R. grade (BDH) except HCl (Fluka) and boric acid (Merck).

Experiments were carried out at a constant temperature of 30 ± 0.2 °C, adjusted by using an ultrathermostat (Julabo μ 3, no. 8311). Solutions were unstarred and, in polarization experiments were deaerated by ultra pure nitrogen (99.999% purity). The reference electrode was Ag/AgCl, and the auxiliary electrode a Pt wire in polarization measurements or a Pt sheet (about 4 cm2) in EIS.
Table 1. Composition of Al–Si alloys and pure Al (by weight percent)

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Co</th>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy I</td>
<td>7.0</td>
<td>0.048</td>
<td>0.004</td>
<td>0.001</td>
<td>-0.02</td>
<td>0.023</td>
<td>0.136</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>Alloy II</td>
<td>11.0</td>
<td>0.123</td>
<td>0.014</td>
<td>0.002</td>
<td>-0.05</td>
<td>0.073</td>
<td>0.113</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>Alloy III</td>
<td>22.0</td>
<td>0.282</td>
<td>0.021</td>
<td>0.007</td>
<td>-0.05</td>
<td>0.385</td>
<td>0.179</td>
<td>0.056</td>
<td>Balance</td>
</tr>
<tr>
<td>Pure Al</td>
<td>-</td>
<td>0.002</td>
<td>0.003</td>
<td>0.100</td>
<td>-0.05</td>
<td>0.011</td>
<td>0.179</td>
<td>0.082</td>
<td></td>
</tr>
</tbody>
</table>

Potentiostatic polarization was carried out using an AMEL potentiostat, (model 533, Italy) with positive feedback for $iR$ drop compensation. EIS measurements were carried out by employing an impedance spectrum analyser (Thales IM 6, Germany) connected to a Samsung computer (Sync Master 15 GLi). All experiments were in the frequency range 100 kHz to 0.1 Hz. The input signal amplitude was 10 mV peak to peak in both the high and low frequency ranges. Scanning electron microscopy, (SEM), of the electrode surface was carried out using a Jeol/JSM T20 (Japan) scanning electron microscope. The alloys were etched in a solution formed of conc. HF (10 ml) + conc. HCl (15 ml) + 90 ml H$_2$O, while pure Al was etched in 15% NaOH. SEM for the alloys and for pure Al was also conducted after immersion of the polished samples for 90 min in 0.5 M HCl. Energy diffraction X-ray analysis (EDX) was carried on the samples before and after immersion in 0.5 M HCl. The EDX unit was attached to Jeol/JSM-5400 (Japan) scanning electron microscope.

The pH of the sulphate solution was adjusted at pH 2, 7 or 10 by addition of carbonate free NaOH. The Jenway pH meter (model 3015) was calibrated before and after each measurement with National Institute of Standards and Technology (NIST) solutions (pH 4.01 and 6.865).

3. Results and discussion

3.1. Effect of HCl concentration

The results of polarization measurements for the three alloys in HCl solutions are shown in Figure 1. At the lowest Cl$^-$ concentration, a more or less passive behaviour is detected for alloy I (Figure 1(a)) around a current density of 0.14 mA cm$^{-2}$, followed by a sharp current increase at $-0.57$ V, which indicates onset of localized attack, or pitting. The passive region may be attributed to existence of the air formed oxide film [11]. The oxide film cannot be ignored, even in highly acidic media, such as HCl [12].

At the potential at which pitting starts, $E_{pit}$, the potential current relationship tends to assume a zero slope. In the potential region bounded by $E_{pit}$ and the onset potential for hydrogen evolution the aluminium corrosion resistance has been reported to be greatest [13].

The corrosion potential, $E_{corr}$, was obtained by the Tafel extrapolation. $E_{corr}$ shifts to less negative potentials with increase in HCl concentration. This is due to the decrease in pH. The aluminium surfaces are positively charged in acid media, since the pH of the potential of zero charge (p.z.c.) for aluminium at the oxide/solution interphase in 9.0–9.1 [14]. Thus, as the pH decreases, the alloy surface acquires a less negative potential.

With increasing acid concentration the cathodic branch showed a marked increase in c.d. for the three alloys, while $E_{pit}$ was found to shift to more negative values. This caused a decrease in the passive range bounded by $E_{pit}$ and $E_{corr}$, which is attributed to a greater number of defects in the oxide layer. The spectra obtained in an EIS study on the corrosion behaviour of aluminium indicated that the electrochemical processes in the passive region are controlled mainly by multistep dissolution, ionic migration through the oxide layer and the influence of chloride ions [15]. This passive region was previously attributed to the existence of an oxide film on the metal surface [11]. At $E_{pit}$ the passive oxide film is replaced by an unstable salt film which undergoes dissolution easily above $E_{pit}$ [16]. At high anodic

![Fig. 1. Polarization curves for alloy (a) I, (b) II and (c) III as a function of HCl concentration: (1) 0.10, (2) 0.025, (3) 0.05, (4) 0.15, (5) 0.25 and (6) 0.50 m.]