On the Cathodic Corrosion of Aluminum and Aluminum Alloys

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Electrochemical methods are frequently used to assess the corrosion rate of aluminum and aluminum alloys. However, the interpretation of electrochemical experiments in neutral pH electrolytes may be complicated due to a well known but poorly understood phenomenon, referred to as cathodic dissolution or cathodic corrosion, for example see [1]. This refers to the fact that the rate of Al dissolution will actually increase with an increasing cathodic polarization in contradiction with conventional assumptions in the electrochemical analysis of corrosion phenomena such as the Stern-Geary equation. This phenomenon may play an important role during the corrosion of Al in situations in which Al becomes the cathode when coupled to other materials such as galvanized steel or with more noble phases within the alloy matrix. Nevertheless, the mechanisms and kinetics of the cathodic Al dissolution have not been well characterized and are not considered during the interpretation of electrochemical kinetic data or efforts to model Al corrosion.

In this presentation we discuss recent work on the mechanism and kinetics of cathodic aluminum corrosion. The simultaneous measurement of Mg, Si and Al dissolution rates, v_M, together with the potential and the total electrochemical current density were performed simultaneously with *atomic emission spectroelectochemistry* (AESEC) [4]. The pH evolution of the electrolyte was also monitored downstream from the flow cell. The aim of this study is to distinguish the role of Al and alloying elements (such as Si, Mg, Fe, Cu) on the elementary corrosion phenomena (dissolution, surface oxide formation, precipitation) by simultaneous, *in-situ* measurement of the elementary dissolution rates for Al, pure Al_2Cu intermetallics, and various Al alloys were investigated in an initially neutral 3% NaCl electrolyte. Previously published work [2,3] will be reviewed and new work with AA6061, an alloy increasingly favored in vehicle design, will be presented for the first time.

The results are consistent with an overall reaction stoichiometry of

$$Al + 3OH^- \rightarrow Al(OH)_3 + 3e^- \qquad [1]$$

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^- \qquad [2]$$

The measured stoichiometry was found to be approximately 4.7, independent of the nature of the alloy or the magnitude of the cathodic current. It is estimated that the excess hydroxide was lost to diffusion. A typical stoichiometry analysis of the Al dissolution rate versus cathodic current is shown in Fig. 1. These results represent measurements of the steady state reaction rates performed under potentiostatic conditions for the alloy AA6061.

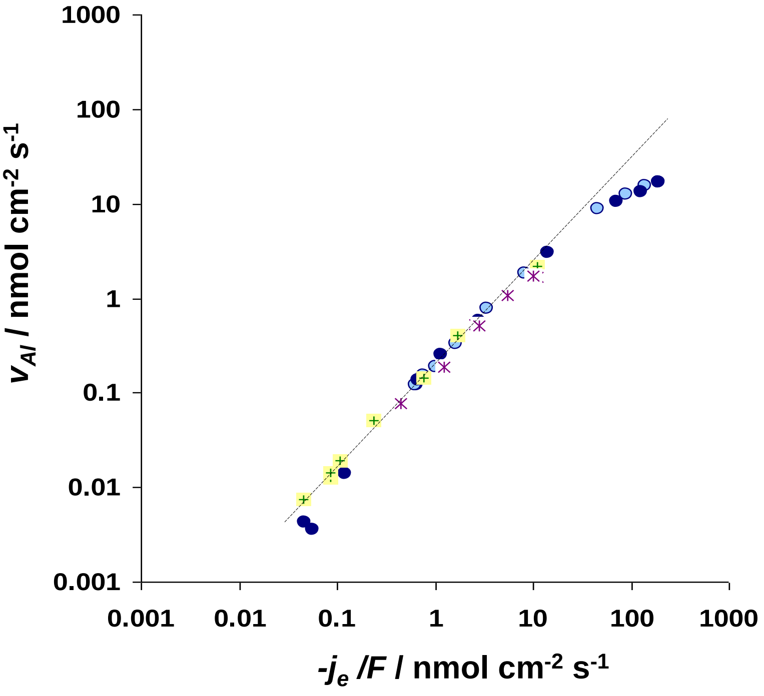

Figure 1. The dissolution rate of Al as function of cathodic current.

During the corrosion of Al alloys, Mg^{2+} and Si^{2+} compounds precipitate on the surface of the material. The quantity of these precipitates was estimated from consideration of the bulk stoichiometry and the relative dissolution rates. Fig. 2A gives the quantity of residual Mg^{2+} as a function of applied potential for two different potentiostatic programs: "Direct" implies a cathodic potential step from open circuit to the test potential while "Activation" implies first a potential step from open circuit to a high cathodic potential (to activate the aluminum), followed by an anodic step to the test potential. The "activated" program results in a higher cathodic current due to the activation of the Al and to the formation of a residual Mg-Si rich oxide/hydroxide film on the surface. The quantity of precipitates may be estimated by considering the bulk composition of the alloy and the relative dissolution rates. As shown in Fig. 2b, it was found that these precipitates did not have a measurable effect on either the kinetics of the cathodic reaction or the OH/Al dissolution stoichiometry.

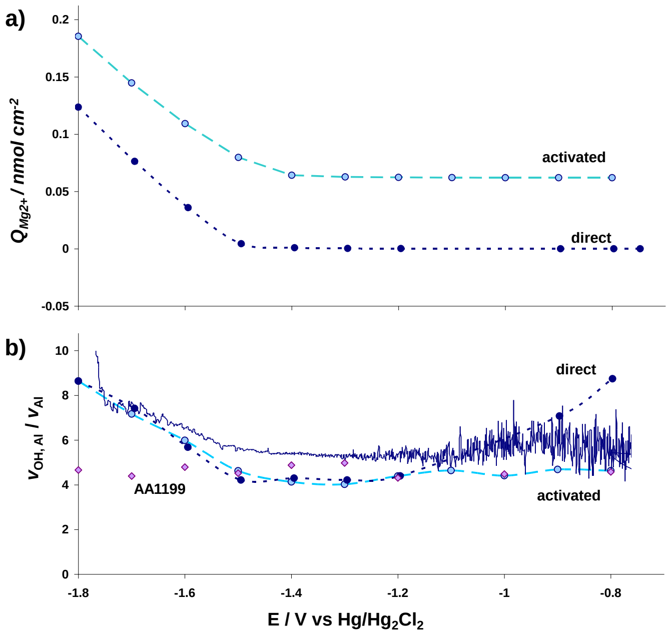

Figure 2. (a) - Amount of $Mg(OH)_2$ formed on the surface of AA6061 during potentiostatic experiment, (b) - $\nu_{OH,Al}$ / ν_{Al} as a function of potential in the cathodic domain for AA6061 (direct potential step is represented by filled circles and with preactivation is represented by empty circles) and 99.99% Al (AA1199 alloy) for both the direct and pre-activated experiment. For pure Al only the direct program was used.

The results of this work will be interpreted in terms of a simple kinetic model for the cathodic corrosion of Al while taking into account the variation of Al^{3+} and Mg^{2+} solubility with pH. Al^{3+} is relatively insoluble at neutral and slightly acid pH resulting in the passivation of Al metal over this pH range. At higher pH, Al^{3+} is soluble as $Al(OH)_4^-$. Mg^{2+} however is highly soluble in acid and neutral solution but becomes insoluble at higher pH. Moreover, the presence of Cu in the alloy or intermetallic is also important for Al dissolution because of the acceleration of the cathodic water decomposition to hydroxide.

References

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