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On the cathodic dissolution of Al and Al alloys

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ABSTRACT

The cathodic dissolution of aluminum and aluminum alloys is a potentially important but poorly understood phenomenon. In this work, the dissolution of pure Al and AA6061 aluminum alloy under cathodic polarizations was investigated. The dissolution rates of the base metal and minor alloying elements were measured in real time using atomic emission spectroelectrochemistry. These data were used to verify the stoichiometry of 4.62 ± 0.22 hydroxides per dissolved Al ion for pure Al. It was found that at high cathodic currents, the cathodic dissolution of SiO_2 was observed while Mg^{2+} species precipitated on the surface perhaps in the form of $MgSiO_3$. These precipitated solid phases did not alter the OH/Al stoichiometry. The $Al_n[Fe_m,Mn_{1-m}]Si$ phases appear to serve as local cathodes accelerating Al dissolution leading to the formation of "trenches" around the intermetallic particles.

1. Introduction

It is well known that the rate of Al corrosion increases with an increasing cathodic polarization, a phenomenon referred to as cathodic dissolution or cathodic corrosion of Al first described in the pioneering work of Caldwell and Alano [1]. This phenomenon may play an important role in the corrosion mechanism of Al during a number of situations including the trenching mechanism of localized corrosion which occurs around cathodic intermetallic particles [2], during galvanic coupling between Al rich paint pigments and an underlying steel surface [3], and when Al becomes the cathode when in contact with various materials such as Zn or Mg in automotive bodies [4]. Further, this phenomenon may also be observed for materials containing Al as a minor component. For example, a Zn–Al–Mg coating on steel (3–4% Al, 3–4% Mg) also showed the characteristic selective dissolution of Al at cathodic potentials and selective dissolution of Zn at open circuit [5]. Finally, the mechanism is an excellent test case for the use of electrochemical methods in corrosion research. Since this phenomenon involves an anodic reaction that *increases* with decreasing electrochemical potential, it is obvious that the standard mixed potential theory based upon the Tafel equations for the anodic and cathodic reaction, may not be directly applied. The use of polarization curves and/or polarization resistances to estimate the corrosion rate of Al containing materials with the standard Tafel model, should therefore be questioned.

In the recent work [6,7] we investigated the cathodic dissolution of Al, Al_2Cu and Al alloys in an initially neutral 3% NaCl electrolyte. The measured stoichiometry was found to be approximately 4.6 were the excess hydroxide was lost to diffusion. The objective of this work is to verify this stoichiometry and investigate the role of precipitated Mg and Si species on the overall stoichiometry with the idea of ultimately proposing a mechanistically derived rate law for the cathodic dissolution of aluminum. The necessity of a such a rate law for the numerical simulation of Al corrosion has been recently addressed [8,9]. In these works, a Tafel relationship for Al dissolution was assumed with the cathodic dissolution mechanism being taken into account by assuming a first order relationship between the exchange current and the hydroxide ion concentration.

Cathodic Al dissolution is highlighted by a small but significant literature [1,5–8,10–12] and references therein]. It is well accepted that the overall reaction is:

$$Al + 4H_2O + e^- \rightarrow Al(OH)_4{}^- + 2H_2. \quad (1)$$

while the elementary reaction scheme may be summarized as follows:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2. \quad (2)$$

$$Al + 3OH^- \rightarrow Al(OH)_3 + 3e. \quad (3)$$

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4{}^-. \quad (4)$$

The important point of reaction (3)–(4) is that Al dissolution is controlled by the properties of an intermediate hydroxide/oxide film, assumed for simplicity to be ($Al(OH)_3$ in reactions (3) and (4), although AlOOH and Al_2O_3 are other possible solid phases. The film

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may be considered to exist in a steady state between film formation (reaction (3)) and film dissolution (reaction (4)). Both reaction rates depend upon the rate at which hydroxide is produced at the interface (reaction (2)). Although a pure Al_2O_3 passive layer may be considered as essentially non-conducting, the film formed under these dynamic conditions is probably amorphous and porous, with limited protective properties that will depend upon the ratio of reactions (3) and (4).

Despite the importance of the kinetic rate law, few of the above cited references have presented data that would allow a precise determination of how the corrosion rate of Al varies with the cathodic current, a prerequisite for determining the rate law for Al dissolution. In the pioneering work on this subject Caldwell and Alano [1] did measure the steady state Al corrosion rate from mass loss measurements as a function of the cathodic current density. Although they did not calculate the dissolution stoichiometry from their data, an analysis of the linear region at low cathodic current densities from their published data would indicate a stoichiometry of 1.8 e^-/dissolved Al. This would imply that an excess of hydroxide is necessary to push reactions (3) and (4) to completion. Despic et al. [11] measured the efficiency of hydrogen production and found that the ratio H_2/e^- was between 1 and 1.3 at 20 °C to 30 °C demonstrating that the Faradaic efficiency of reaction 3 was below unity. More recently, Baek et al. [12] performed real time measurements of mass loss using a quartz crystal microbalance; however, they did not discuss the quantitative relationship between cathodic current and dissolution.

The novelty of the present work is to not only measure the relationship between hydroxide formation and Al dissolution but also to investigate the interplay between the dissolution and precipitation of Mg and Si components during the reaction. The AA6061 used here includes Mg, Si, Fe and other additives including Mg_2Si phase [13,14]. The formation of mixed Al–Mg oxidized species, often detected in corrosion products on Al–Mg compounds and on the Al alloys corroded in the presence of Mg^{2+}, could complicate the behavior of the system [15–17].

These complications may to a certain extent be predicted by the pH dependence of the solubilities of Al^{3+}, Mg^{2+} and SiO_2. Al^{3+} is relatively insoluble at neutral and slightly acid pH resulting in the passivation of Al metal over this pH range. Al^{3+} and SiO_2 are insoluble at neutral pH but soluble at higher pH with the predominant solution species as $Al(OH)_4{}^-$ [18] and $SiO(OH)_2{}^-$/$SiO_2(OH)_2{}^{2-}$, respectively. Mg^{2+} however is highly soluble in acid and neutral solution but becomes insoluble at higher pH [19]. The situation is more complex when Mg^{2+} and SiO_2 are present simultaneously because of the formation of various Mg silicates. According to equilibrium calculations using Hydra-Medusa software (Fig. 1), the pH of Mg^{2+} precipitation is shifted from about pH = 9.5 to pH = 7.2 due to the formation of $Mg_3Si_4O_{10}(OH)_2$. At higher pH, the $Mg_3Si_4O_{10}(OH)_2$ decomposes into $Mg_3Si_2O_5(OH)_4$ with the release of $SiO_2(OH)_2{}^{2-}$.

The Cu and Fe in the alloy or as an intermetallic [20,21] should remain in the metallic state throughout the cathodic potential range, however, they will nevertheless affect Al dissolution because of their accelerating effect on the cathodic water decomposition to hydroxide [7,22].

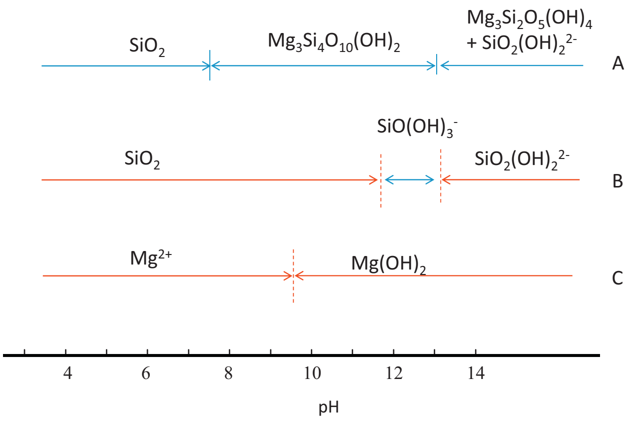

Fig. 1. Predominant equilibrium species predicted for (A) 0.01 M Mg^{2+} + 0.02 M $Si(OH)_4$, (B) 0.02 M $Si(OH)_4$, (C) 0.01 M Mg^{2+} using the Hydra-Medusa software and associated database of equilibrium constants at 25 °C. The complexes used in the simulation include. Mg species alone: $Mg_4(OH)_4{}^{4+}$, $MgOH^+$, $Mg(OH)_2$; Si species alone: $Si_2O_2(OH)_5^-$, $Si_2O_3(OH)_4^{2-}$, $Si_3O_6(OH)_3^{3-}$, $Si_4O_7(OH)_5^{3-}$, $Si_4O_8(OH)_4^{4-}$, $SiO(OH)_3^-$, $SiO_2(OH)_2^{2-}$, SiO_2 (am), SiO_2 (cr); Mixed Mg–Si species: $Mg(HSiO_3)_2$, $Mg(HSiO_3)_2$, $MgHSiO_3)^+$, $MgSiO_3$, $Mg_2Si_3O_{7.5}(OH){:}3H_2O$, Mg_2SiO_4, $Mg_3Si_2O_5(OH)_4$, $Mg_3Si_4O_{10}(OH)_2$, MgO, $MgSiO_3$.

2. Measurement principles

2.1. Rate and concentration relationships

The principle of the AESEC (atomic emission spectroelectrochemistry) measurement has been previously described in detail [3,7,8]. Briefly, it consists of an electrochemical flow cell combined with an inductively coupled plasma optical emission spectrometer (ICP-OES). In the cell, reactions between a sample and an aggressive electrolyte occur, leading to the production of dissolved ions. The concentrations of these ions are measured in real time downstream from the cell with ICP-OES. The instantaneous dissolution rate of an element M in the cell, ν_M, is directly related to the downstream concentration (in nmol s^{-1} cm^{-2}) as

$$\nu_M = C_M \frac{f}{A}. \tag{5a}$$

$$j_M = zF\nu_M. \tag{5b}$$

where *f* is the flow rate of electrolyte (in this work, approximately 3.0 cm^3 min^{-1}, but measured independently for every series of experiments), C_M is the instantaneous concentration of element M (mol cm^{-3}), and *A* is the exposed surface area (0.51 cm^2). C_M is measured from the emission intensity at a specific wavelength using normal quantitative procedures for ICP-OES spectrometry. The rate of dissolution may also be expressed as an equivalent current density, j_M, by Eq. (5b) where *z* is the charge on the ion and *F* is the Faraday constant.

The total electrical current between working and counter electrodes, i_e (measured by the electrometer of potentiostat), is the sum of the cathodic current, i_c, and the anodic current, i_a (Eq. (6)):

$$i_e = i_c + i_a. \tag{6}$$

The major cathodic reactions in neutral electrolyte are H_2O and O_2 reduction. Each of these reactions leads to the formation of one OH^- per electron.

It is of interest to estimate the total cathodic reaction rate as the rate of hydroxide production, ν_{OH}, and the extent of formation of precipitated corrosion product films. This can be done considering the steady state values of the total current density, j_e and the steady state elemental dissolution rates, ν_M, with m = Al, Mg, Si, (combined with our knowledge of the bulk composition of the alloy). If we assume that the aluminum oxide film growth is at steady state, the total instantaneous Al oxidation rate, ν°_{Al}, will be equal to the instantaneous dissolution rate, ν_{Al}:

$$\nu^\circ_{Al} = \nu_{Al}. \tag{7}$$

It is also reasonable to assume that Mg and Si are oxidized as rapidly as they are exposed by dissolving Al. Under this condition,