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Stability analysis of the Mg₂Si phase in AA 6061 aluminum alloy.

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Abstract

The spent MTR fuel elements, manufactured with the aluminum-based alloy AA 6061, are stored under water in interim storage basins. In such conditions the AA 6061 is susceptible to degradation by localized corrosion processes which might be related to the behavior of second-phase particles present in the alloy.

According to its electrochemical behavior, the second-phase particles present in AA 6061 can be classified into cathodic or anodic in relation to the aluminum matrix.

In order to investigate the stability of the Mg₂Si phase, which dissolves in high purity water, immersion and polarization tests were carried out in alkaline solutions. SEM and EDS were used to analyze the second-phase particles after the tests.

It was determined that Mg₂Si phase particles are stable in solutions of pH 8 to 14, and undergo selective magnesium dissolution from pH 7 to lower values.

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1. Introduction

Among other applications, the aluminum-based alloy AA 6061 is used as cladding material for MTR

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(Material Test Reactor) fuel elements. Once removed from the reactor, the spent MTR fuel elements are stored under water in interim storage pools until stabilize for final disposition. Since these elements will be immersed in water for periods of time up to 30 years, it is important to study and to understand the corrosion processes that may induce degradation on the AA 6061 cladding.

Several authors have demonstrated that localized corrosion susceptibility of aluminum alloys is associated to the presence of second-phase particles in the alloy [Alodan and Smyrl, 1998; Nisancioglu et al., 1990; Liao et al., 1999]. The electrochemical behavior of second-phase particles depends mainly upon the potential difference between the particle and the matrix [Smialowska, 1999]. The second-phase particles in AA 6061 can be classified into two main kinds: active particles rich in magnesium, silicon and aluminum; and particles with iron, silicon and chromium which show cathodic behavior relative to the aluminum matrix [Alodan and Smyrl, 1998].

The behavior of second-phase particles present in aluminum alloys has been studied by several authors mainly in low conductivity or chloride-containing solutions. In previous research about the corrosion of the AA 6061 alloy in aerated high purity water and NaCl solutions at open circuit potential, it was found that the iron-rich particles act as cathodic sites promoting the oxygen reduction reaction, generating a localized pH increase that provokes aluminum dissolution around the particles [Rodriguez et al., 2009]. Aballe also found a kind of localized hemispherical attack surrounding the Al(Mn-Fe-Cr) precipitates when alloy AA 5083 corrodes freely in 3.5% NaCl solution [Aballe et al., 2001].

In AA 6061 alloy, it was found that Mg₂Si particles undergoes selective magnesium dissolution in high purity water ($\kappa = 0.05 \mu\text{S/cm}$; pH = 5.5) [Rodriguez et al., 2003]. This phase in AA 5083 alloy shows anodic behavior and undergoes partial magnesium dissolution during immersion tests in 0.5NaCl solutions [Yasakau et al., 2007]. Buchheit collected the corrosion potential values for intermetallic phases common in aluminum alloys and reported a value of $-1.98 V_{\text{SSE}}$ for the Mg₂Si phase in deaerated NaCl solution [Buchheit, 1995]. Alodan suggests that the electrochemical behavior of the Mg₂Si phase can switch from anodic to cathodic as the dealloying progresses [Alodan and Smyrl, 1998].

The main objective of this paper is to study the Mg₂Si phase behavior in chloride-free solutions and to analyze its stability as a function of the pH. In order to achieve this, immersion and polarization tests were carried out in solutions of different pH values prepared with NaOH and NaOH/KH₂PO₄. A brief discussion of the electrochemical behavior of the AA 6061 alloy in these solutions is also included.

2. Experimental

The AA 6061 alloy composition (in wt %) is as follows: Mg: 0.95-1.10; Si: 0.55-0.65; Fe: 0.15-0.45; Cu: 0.20-0.40; Cr: 0.10-0.20; Mn: 0.10; Zn: 0.25; Ti: 0.03-0.07; Al: balance. In a previous work, the following second-phases have been identified in the AA 6061 alloy: Al₃Fe, α -(Fe,Cr,Mn)₃SiAl₁₂, β -(Fe,Cr,Mn)₂Si₂Al₉, Si, Mg₂Si and π -(Fe,Cr,Mn)Mg₃Si₆Al₈. These phases are present as precipitates in the aluminum matrix [Rodriguez et al., 2003].

AA 6061 samples of 15mm x 25mm were cut from a 1.5mm thickness plate coming from remnants of the manufacture of Argentine MTR fuel elements, in the region where no fissile material is present. All specimens were ground up to 1500 SiC paper lubricated with water, and further polished with 3 μm and 1 μm diamond paste. The diamond polishing stage was performed in ethanol to avoid magnesium dissolution.

Considering that the Mg₂Si phase undergoes magnesium dissolution in water (pH = 5.5), polarization and immersion tests were carried out in NaOH and NaOH/KH₂PO₄ solutions with pH values from 14 to 7. NaOH/KH₂PO₄ solution was selected due to its buffering capacity between pH 6 and 8, and because KH₂PO₄ inhibits oxide growing on aluminum [Zhang et al., 2009; Aziz et al., 1965].

Potentiokinetic polarization tests were performed in NaOH solutions of pH 11 ($\kappa = 2.34 \text{ mS/cm}$) and 14

($\kappa = 5.38$ mS/cm) and in NaOH/KH₂PO₄ solutions of pH 7 ($\kappa = 4.15$ mS/cm), pH 8 ($\kappa = 7.12$ mS/cm), pH 9 ($\kappa = 8.24$ mS/cm), pH 11 ($\kappa = 12.7$ mS/cm) and pH 14 ($\kappa = 14.8$ mS/cm) at a scan rate of 0.23 mV/seg, from $-2.1 V_{SSE}$ to $-0.4 V_{SSE}$. The open circuit potential (OCP) was allowed to stabilize during 1 hour prior to the polarization.

Immersion tests were performed during 4 hours at OCP in NaOH and NaOH/KH₂PO₄ solutions of pH values from 7 to 14. OCP was recorded as a function of immersion time.

All tests were carried out in deaerated solutions by nitrogen bubbling and at room temperature. A three electrode cell was used, with a saturated mercury sulfate electrode (SSE, $E = +0,640 V_{SHE}$) as reference and a platinum wire as the counter electrode.

After concluding the tests, samples were observed with Scanning Electron Microscopy (SEM) and the Mg₂Si phase particles were analyzed through Energy Dispersive Spectroscopy (EDS). As a means to evaluate the magnesium dealloying in the Mg₂Si phase particles, the ratio Mg/Si (in atomic %) was calculated for each analyzed particle and it was compared to the Mg/Si value obtained for Mg₂Si particles in as-polished samples: 1.2 ± 0.3 (atomic %).

3. Results

The results of the polarization tests carried out in deaerated NaOH and NaOH/KH₂PO₄ solutions are shown in Fig. 1. In NaOH pH 11 solution the test was performed in duplicate. In NaOH at pH 11 and 14 (Fig. 1a) evolution of hydrogen was observed since immersion of the samples (OCP $\sim -1.7 V_{SSE}$ at pH 14 and $-1.75 V_{SSE}$ at pH 11) and up to a potential value of $-1.4 V_{SSE}$ at pH 14 and to $-1.6 V_{SSE}$ at pH 11. Cathodic limit currents of $0.2 \text{ mA}\cdot\text{cm}^{-2}$ and $2 \text{ mA}\cdot\text{cm}^{-2}$ were measured for the tests in pH 11 solution, whereas a value of cathodic current of $20 \text{ mA}\cdot\text{cm}^{-2}$ was detected in pH 14 solution. In Fig. 1a it can be seen that both the cathodic current of hydrogen evolution and the anodic current increased when pH increased from 11 to 14. For both pH values, the E_{CORR} (potentiokinetic corrosion potential) showed good agreement with the respective OCP values. In the test performed in NaOH at pH 14 a limit anodic current of $4 \text{ mA}\cdot\text{cm}^{-2}$ was obtained, which resulted higher than the anodic limit currents measured in the tests performed in NaOH pH 11 solution ($0.3 \text{ mA}\cdot\text{cm}^{-2}$ and $30 \mu\text{A}\cdot\text{cm}^{-2}$). These anodic current values do not correspond to passivity.

Figure 1b presents the polarization curves obtained in deaerated NaOH/KH₂PO₄ solutions. The E_{CORR} in the pH 7, 8 and 9 solutions were about $-1.55 V_{SSE}$ and about $-1.75 V_{SSE}$ in pH 11. In NaOH/KH₂PO₄ solutions of

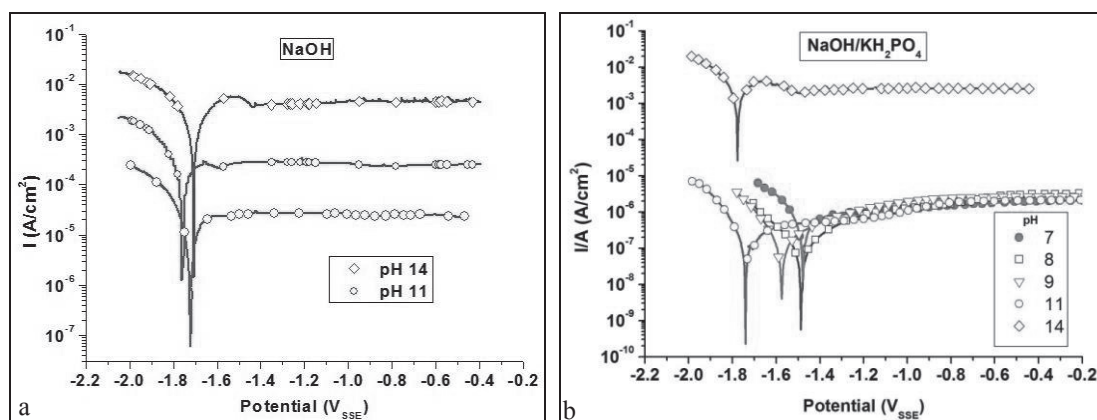


Fig. 1: Polarization curves in deaerated solutions of: (a) NaOH; (b) NaOH/KH₂PO₄.

pH 7, 8, 9 and 11 a cathodic limit current of $\sim 10 \mu\text{A}\cdot\text{cm}^2$ and an anodic limit current of $\sim 2 \mu\text{A}\cdot\text{cm}^2$ were measured. This anodic current value corresponds to a passive current. In NaOH/KH₂PO₄ of pH 14, the E_{CORR} was $-1.75 V_{\text{SSE}}$ and a limit anodic current of $3 \text{ mA}\cdot\text{cm}^2$ was detected.

SEM images of the samples after polarization in NaOH solutions are shown in Fig. 2. The polarization in NaOH of pH 14 and 11 had an effect of dissolution of the aluminum matrix similar to a chemical etching, being more severe in pH 14. Protruding of intermetallic phases were observed in the surface of the samples.

The particles shown in Fig. 2 with sizes from 1 to 10 μm and round edges correspond to the Mg₂Si phase. After the polarization tests in NaOH/KH₂PO₄ solutions of pH from 7 to 11, no oxide growing was detected, and the surface of the samples remained as brilliant as in the as-polished condition. In pH 14 the surface of the sample showed aluminum dissolution, similar to that observed in NaOH solution of pH 14.

The OCP vs. time records obtained during 4 hours of immersion in deaerated solutions of NaOH and NaOH/KH₂PO₄ at different pH values are presented in Fig. 3. In NaOH solutions (Fig. 3a) values of $\sim -1.80 V_{\text{SSE}}$ for pH 10, 11 and 14 and $\sim -1.70 V_{\text{SSE}}$ for pH 7, 8 and 9 were observed. In the case of NaOH/KH₂PO₄ solutions, OCP was $\sim -1.7 V_{\text{SSE}}$ at pH 9, 10, 11 and 14, and increased up to $-1.40 V_{\text{SSE}}$ at pH 7 (Fig. 3b).

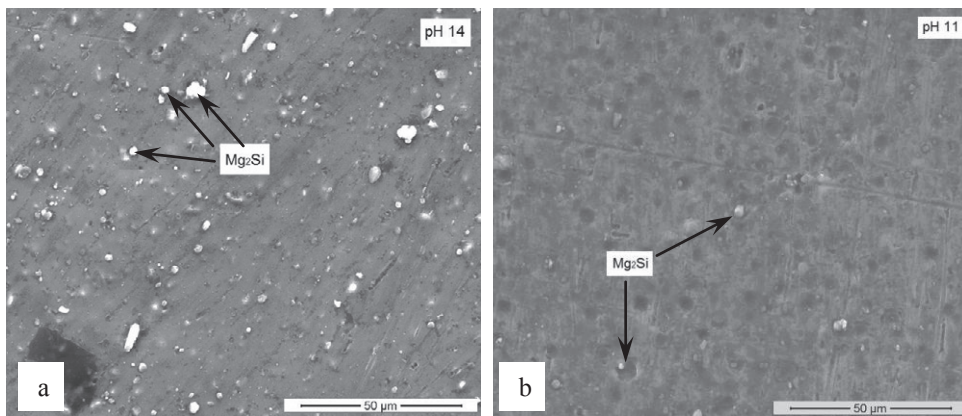


Fig. 2: SEM images of samples after polarization in: (a) NaOH pH 14; (b) NaOH pH 11.

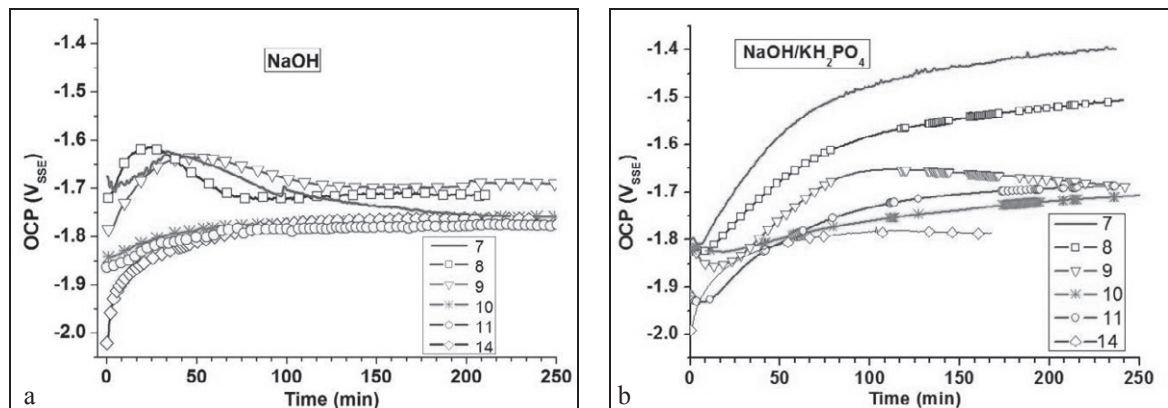


Fig. 3: OCP vs. time records for immersion tests in: (a) NaOH; (b) NaOH/KH₂PO₄.

After concluding the immersion tests, the samples were observed with SEM and the Mg_2Si phase particles were analyzed through EDS. The ratio Mg/Si (in atomic %) was calculated for about fifteen particles in each sample. The plot in Fig. 4 shows the Mg/Si values calculated for these particles after 4 hours of immersion in NaOH and NaOH/ KH_2PO_4 solutions. The data presented for NaOH at pH 14 and 11 correspond to particles analyzed after the polarization curves shown in Fig. 1a. As a means to evaluate the magnesium dealloying in the Mg_2Si phase, the values of Mg/Si were compared to those obtained in the as-polished samples: $Mg/Si=1.2\pm 0.3$ (atomic %). Values of Mg/Si ratio below this range indicate magnesium dealloying. In Fig. 4 it can be clearly seen that at a pH value of 7 the Mg_2Si phase presents depletion in magnesium, while at pH 8 this cannot be confirmed. The magnesium dealloying at pH 8 seems to depend on the solution.

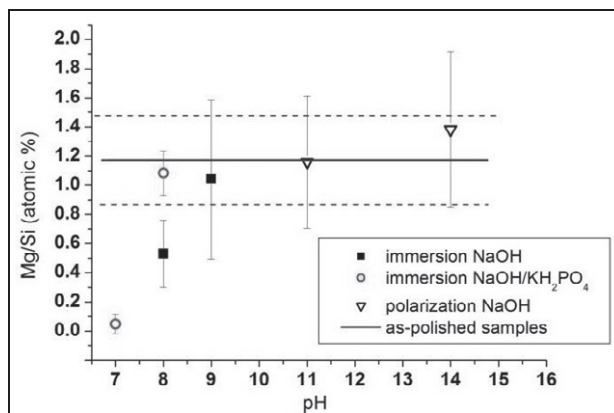


Fig. 4: Variation of the Mg/Si ratio as a function of pH.

After 4 hours of immersion in NaOH solutions of pH 8, 9 and 10, the SEM images of the samples showed oxide formation (Figs. 5a and 5b) and dissolution of the aluminum matrix around iron-containing cathodic particles with the characteristic morphology of localized alkaline attack [Rodriguez et al., 2009].

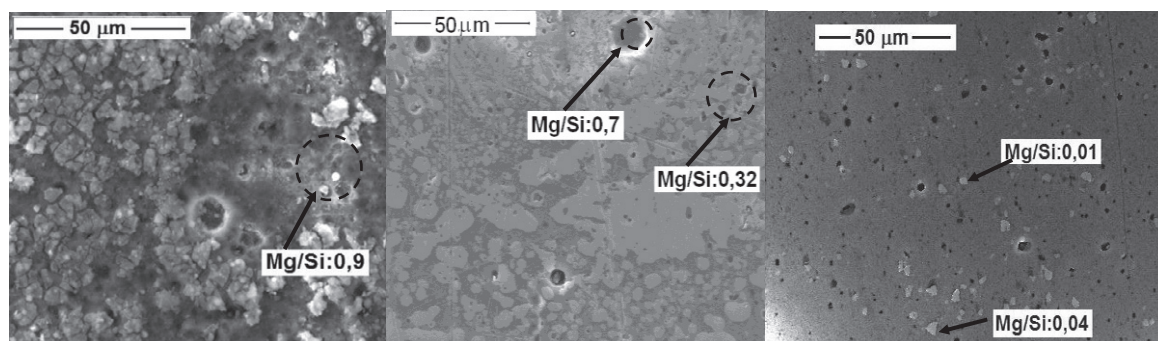


Fig. 5: SEM images of samples after immersion tests: (a) NaOH pH 10; (b) NaOH pH 8; (c) NaOH/ KH_2PO_4 pH 7.

In Fig. 5b it can be seen that the Mg_2Si particles on the surface exhibit dealloying ($Mg/Si: 0.32$) whereas for the particles of this phase located within the cavities, where the pH is well above the pH of the bulk solution due to the alkaline attack, the Mg/Si value does not show significant difference with the reference

value of 1.2 ± 0.3 .

In samples submitted to immersion tests in NaOH/KH₂PO₄, no oxide growing was detected and alkaline attack was inhibited due to the buffering capacity of these solutions (Fig. 5c), thus allowing better observation and quantification of the Mg₂Si particles. The SEM image in Fig. 5c, corresponding to a sample immersed for 4 hours in the pH 7 NaOH/KH₂PO₄ solution, shows a free oxide surface with Mg₂Si particles depleted in magnesium and small cavities produced after the detachment of these particles.

4. Discussion

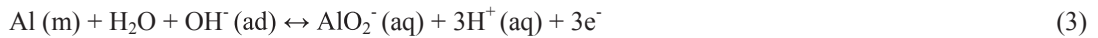
An oxide film is formed spontaneously on the aluminum surface in air or aqueous solutions and exists even under cathodic polarization. The oxide film formation in water can be described by:



In alkaline solutions the surface oxide film is dissolved chemically due to the OH⁻ attack:



where OH⁻(ad) is the adsorbed hydroxide ion and AlO₂⁻ is the soluble specie aluminate. By combining Eqs. (1) and (2) the dissolution reaction of aluminum is obtained:

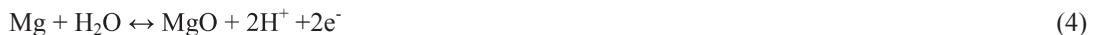


Equations 1 and 2 take into account the reaction of electrochemical formation of the oxide and the chemical dissolution of the surface oxide layer [Moon and Pyun, 1997]. According to Eq. 3, the concentration of AlO₂⁻ and H⁺ increases with an increase in the pH. Both the cathodic and anodic limit currents are a function of the hydroxide concentration (OH⁻). This fact explains the increase in both limit currents, cathodic of hydrogen evolution and anodic of aluminum dissolution, observed in the polarization curves in NaOH (Fig. 1a) when pH increases from 11 to 14. This observation was also made by Moon and Pyun [Moon and Pyun, 1997].

The results of polarization tests in NaOH/KH₂PO₄ showed a passive anodic limit current of $\sim 2\mu\text{A}\cdot\text{cm}^{-2}$ in solutions of pH values 7 to 11 (Fig. 1b); and no oxide formation was observed in these samples. Comparing the results obtained in the polarization tests in pH 11 solution, it can be deduced that the aluminum corrosion at this pH value depends on the electrolyte. The differences observed in both polarization tests in pH 11 NaOH solutions might be attributed to variations in the surface finish of the samples.

The polarization test performed in NaOH/KH₂PO₄ at pH 14 showed a limit current of $3\text{mA}\cdot\text{cm}^{-2}$, similar to the value obtained in pH 14 NaOH solution. The KH₂PO₄ inhibition efficiency in alkaline solutions depends both on the concentrations of KH₂PO₄ and NaOH species. Increasing the NaOH concentration leads to a decrease in the inhibition efficiency [Aziz et al., 1965].

The stability of the Mg₂Si phase is determined by the magnesium reactivity in aqueous solutions. In acid solutions, the magnesium dissolves as Mg⁺⁺ with hydrogen evolution, while at pH values above 8.5 it reacts with water generating an oxide or hydroxide layer. This latter reaction can be described by the equation:



The equilibrium potential values for the reaction in Eq. 4 range from $-3 \text{ V}_{\text{SSE}}$ at pH 8.5 to $-3.3 \text{ V}_{\text{SSE}}$ at pH 14 [Pourbaix, 1966]. The OCP values presented in Figs. 3a and 3b are well above the equilibrium potential for

Mg/MgO, so it can be deduced that there is a magnesium oxide layer covering the Mg₂Si particles during the immersion tests. According to Pourbaix, MgO is stable in alkaline media, but it undergoes chemical dissolution to Mg⁺⁺ ions at pH values lower than 8.5. Dissolution of the MgO at these pH values in turn generates magnesium depletion in the Mg₂Si phase particles.

The results in the present paper show that the dissolution of MgO and the magnesium dealloying in the Mg₂Si phase occur at pH 7. This observation is in good agreement with the pH value calculated from thermodynamic data (pH=8.5) [Pourbaix, 1966] and confirms the results found after 20 days immersion tests in high purity water (pH 5.5) in which a 100 % magnesium dealloying was detected in Mg₂Si particles in AA 6061 alloy [Rodriguez et al., 2003].

The stability of the Mg₂Si particles located within the cavities generated during the localized alkaline attack (Fig. 5b) suggests, according to the plot in Fig. 4, that the pH value within these cavities is greater than 8. Using a selective microelectrode, Park measured a pH value of 9.5 around the Al₃Fe phase in contact with the AA 6061 alloy in 0.6M NaCl aerated solution [Park et al., 1996]. This observation leads to conclude that, when Mg₂Si phase precipitate associated to cathodic particles, the localized alkalization inhibits the dealloying of this phase.

Dealloying was not observed in Mg₂Si particles after anodic polarization up to -0.4 V_{SSE} in NaOH solutions of pH 11 and 14 (Fig. 1a) indicating that the stability of this phase does not depend on the potential.

5. Conclusions

- Mg₂Si phase is stable in solutions of pH from 8 to 14. At pH values lower than 8, it undergoes selective magnesium dealloying.
- When Mg₂Si phase is associated to cathodic particles, the localized alkalization inhibits the magnesium dealloying.
- Magnesium dissolution in Mg₂Si phase does not depend on the potential.

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