Influence of the Altered Surface Layer on the Corrosion of AA5083

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The corrosion behavior of sensitized AA5083 in aerated and deaerated 3.5 wt% NaCl solutions has been studied. The results indicated that an altered surface layer (ASL) with a recrystallized microstructure having no β phase at the grain boundaries formed on sensitized AA5083 during polishing. The ASL prevented the exposure of β phase at the surface and its dissolution at the alloy open circuit potential, even though this potential was above the breakdown potential of bulk β phase. Selective dissolution of β phase was observed when a cathodic reaction caused an increase in localized pH near intermetallic particles or after removal of the ASL by etching to expose the grain boundary β phase. The different corrosion behavior of solutionized and sensitized AA5083 was clarified by testing etched samples. Removal of the ASL is therefore necessary to understand the initiation of intergranular corrosion on sensitized AA5083.

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Lightweight materials that provide good formability, high strength-to-weight ratio, weldability and corrosion resistance are desired for use in automotive and marine industrial and military applications. Wrought AA5XXX Al-Mg alloys are well known for these properties, and in recent years these materials have been used to replace heavier materials.1 However, Al-Mg alloys can be susceptible to intergranular corrosion (IGC) attack and intergranular stress corrosion cracking (IGSCC) because of sensitization, which involves the formation of the anodic β phase (Mg2Al3) along the grain boundary.2–4

When an Al-Mg alloy containing more than 3 wt% Mg is exposed to room temperature over long periods of time or an elevated temperature (60–180°C) over a shorter period of time, supersaturated Mg will diffuse to the grain boundary region and form β phase particles.5 Because the breakdown potential (Ebk) of β phase (−0.95 VSCE) is more negative than the open circuit potential (OCP) of the alloy (−0.78 VSCE), dissolution of β phase along grain boundaries can occur when the alloy is exposed in a corrosive environment. This phenomenon leads to IGC and also IGSCC when a tensile stress is present.6–9 Goswami et al. showed that the hardness of AA5083 gradually decreased with aging time,10 which indicates removal of the strengthening element Mg from solid solution. Searles et al. found that the ductility of sensitized AA5083 during constant extension rate testing increased when a potential below the pitting potential of β phase was applied to the sample compared to testing at the OCP.11 Jones et al. showed that the crack growth rates of AA5083 were faster at potentials above the OCP than at the OCP.12 Additionally, the crack growth rate in 3.5% NaCl + 0.01 M K2CrO4 solution for sensitized AA5083 was 350 times faster than for solution heat treated AA5083.8 These papers suggest that the mechanical and corrosion properties of AA5083 are highly affected by the formation of β phase along the grain boundaries.

The IGC penetration rate was found to be highly dependent on degree of sensitization (DoS), as measured by the nitric acid mass loss test (NAMLT).11,12 Galvanostatic and potentiostatic measurements on AA5083 samples showed a deeper penetration of intergranular corrosion in samples with higher DoS, longer exposure time, higher applied potential, or higher current. Formation of continuous β phase along grain boundaries provides a pathway for deeper penetration of intergranular corrosion attack in highly sensitized AA5083 samples.13 In the presence of a tensile stress, dissolution of β phase at grain boundaries might also cause IGSCC, leading to rapid failure. It is therefore critical to understand the corrosion behavior of β phase in alloys such as AA5083 with different DoS to prevent field failures.

However, previous studies on AA5083 have not shown strong evidence of selective β phase dissolution under free corrosion conditions.7–14–17 Many papers assume the dissolution of β phase will occur because its breakdown potential, Ebk, is lower than the OCP of the alloy.1,2,4,9,11,12,18 Lim et al. showed that an incubation time to cause local acidification by applying a potential close to or above the Eb of AA5083 was required to develop IGC on sensitized AA5083.11,12 At the OCP of AA5083 in aerated solutions, which is typically at least 100 mV more noble than the Ebk of β phase, selective dissolution of β phase is not observed.14 The only corrosion sites under these conditions were pits around intermetallic particles, such as Al6(Mn, Fe), which serve as cathodic sites and promote anodic dissolution around them at OCP.13,17 No clear explanation for the absence of IGC and β phase attack on sensitized AA5083 at its OCP has been provided in the literature.

Jones et al. found that the corrosion rate of AA5083 was decreased with aging in association with a shift in OCP to more negative potentials.8 They assumed that the shift in OCP occurred because of β phase precipitation, which protected aluminum cathodically. These authors further suggested that selective dissolution of β phase was not observed because the passive film formed on the β phase was as protective as that on the AA5083 matrix.

It is also possible that an altered surface layer (ASL) forms on AA5083 during surface preparation by polishing such that β phase is not exposed at the surface. Samuels described different types of surface damage from several polishing mechanisms.19 He found that a plastically deformed surface layer is inevitably formed by mechanical processes on metals with face centered cubic crystal structure. ASLs have been found on alloys from other Al alloy systems, and they have different characteristics. Afseth et al. found that an ASL with a refined grain structure formed on AA3003 as the result of thermomechanical processing.20,21 Heat treatment at high temperature, such as a paint bake cycle, following deformation or a surface abrasion step results in the precipitation of a high density of secondary intermetallic particles and depletion of noble elements in solution. Under these conditions, the ASL is more active than the bulk matrix, which promotes filiform corrosion under the paint. Leth-Olsen et al. found a grain refined surface layer at the surface of cold rolled AA8006.22 Zhao and Frankel found that polished AA7075 had an ASL with a lower breakdown potential than the bulk matrix.23 Selective dissolution of the ASL occurred at potentials above the Eb of the ASL but below the Eb of the bulk matrix. Transmission Electron Microscopy (TEM) imaging of the very top layer of the polished sample showed an absence of hardening precipitates with Mg and Zn solute concentrated in bands along elongated grains. There is no evidence in the
literature of the formation of ASLs on AA5083. However, if an ASL forms on sensitized AA5083 during surface preparation steps such as polishing, it might prevent exposure of β phase at the surface, and thus protect the sensitized alloy from IGC.

In this work, potentiostatic tests were used to study selective dissolution of β phase in AA5083. Both highly sensitized AA5083 samples, which contained β phase along most of the grain boundaries, and fully solutionized AA5083 were tested. These materials should provide a good contrast in behavior to highlight the important parameters in β phase dissolution. The focus of this study was the early stages of β phase dissolution on the surface of AA5083 rather than the rate of IGC penetration after initiation, which has been studied in detail.11,21

Experimental

Materials.— Two plates of AA5083-H116 were procured commercially with thicknesses of 3.2 and 25.4 mm. One group of samples was solution heat treated at 450 °C for 1.5 h, cold-water quenched to room temperature, and stored in a refrigerator to prevent sensitization. The other samples were sensitized at 100 °C for 30 days without prior sensitization.

The β phase morphology and distribution for both conditions were assessed using phosphoric acid (H₃PO₃) etching. Samples were abraded to 1200 grit with silicon carbide (SiC) paper in a non-aqueous slurry to minimize the onset of corrosion, and rinsed with ethanol (C₂H₅OH). Then the samples were polished with 1 μm diamond paste, ultrasonically cleaned with ethanol, and air dried. Etching was performed for 2 min in 8.5 vol% H₃PO₃ at 50 °C followed by rinsing with deionized (DI) water and air drying.13 Etched samples were imaged using scanning electron microscopy (SEM).

Degree of sensitization.— ASTM G67, the standard method for the NAMLT,24 was used to measure DoS. The 25.4 mm thick plate was cut into 5 cm × 2 cm × 0.6 cm (L × T × S) samples for this test. As specified by the ASTM standard, the samples were immersed in 5% NaOH solution at 80 °C for 1 min, followed by a water rinse, immersion in HNO₃ for 30 s, a second water rinse, and then air drying. Samples were immersed in 70 wt% HNO₃ for 24 h at 30 °C, then brushed under DI water and recleaned using the C.1.1 procedure defined in ASTM G1.25 The sample was immersed for 10 min in a 1 L solution containing 50 ml of phosphoric acid, 20 g of chromium trioxide and DI water. The solution was maintained at a temperature of 80°C. The mass loss per unit area was calculated to determine the DoS.

Electrochemical testing.— Electrochemical tests were performed in a flat-cell using a saturated calomel reference electrode (SCE) and a platinum mesh counter electrode. The 3.2 mm thick plate was cut into 2 cm × 2 cm (L × T) for this test. Samples were abraded to 1200 grit with silicon carbide (SiC) paper in a non-aqueous slurry to minimize the onset of corrosion, and rinsed with ethanol (C₂H₅OH). Then the samples were polished with 3 μm diamond paste, ultrasonically cleaned with ethanol, and air dried before testing.

Scanning transmission electron microscopy.— Analysis by high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and X-ray energy dispersive spectroscopy (EDS) was used to characterize the surface microstructure. STEM sample foils were prepared from solutionized and sensitized samples in the as-polished and NaOH acid etched conditions. Platinum was deposited on the sample surface before sample lift-out to protect the top surface integrity. STEM samples of size 20 μm × 5 μm with thicknesses of 20–100 nm were prepared by an FEI Helios NanoLab 600 DualBeam focused ion beam (FIB). A Ga ion beam with a 30 kV acceleration voltage was used for sample lift-out and thinning; a final thinning by a 5 kV Ga ion beam was adopted to minimize ion damage. Ga has a strong tendency to penetrate into Al grain boundaries,26 making EDS quantification difficult. STEM imaging and EDS analysis were carried out on an FEI image-corrected Titan3TM G2 60-300 S/TEM equipped with a quad silicon drift detector at 300 kV. At sufficiently large detector collection angle, HAADF-STEM is a predominantly incoherent imaging mode, commonly referred to as “Z-contrast” imaging, in which the intensity of scattering depends strongly on the atomic number (approaching ∼Z²).27,28

Results

Degree of sensitization.— Representative SEM micrographs of samples etched with 8.5% phosphoric acid at 50°C for 2 min are shown in Fig. 1. No evidence of attack was found for the solutionized condition, as shown in Fig. 1a. In contrast, samples sensitized by aging at 100°C for 30 days exhibited obvious etching at grain boundaries as well as some pits within the grains (Fig. 1b). These images suggest that the sensitization treatment caused the formation of β phase along all of the grain boundaries, resulting in a severely sensitized microstructure.

The ASTM G67 NAMLT test was performed on three samples from each heat-treatment condition. The average values of DoS were found to be 1.2 and 64.2 mg/cm² for solutionized and sensitized AA5083, respectively. ASTM G67 indicates that a sample is heavily solutionized if DoS is higher than 25 mg/cm²,24 supporting the designation of the samples from the two heat treatments as being solutionized or highly sensitized.

Anodic potentiodynamic polarization.— Fig. 2 shows potentiodynamic polarization curves of solutionized AA5083, sensitized AA5083 and bulk β phase in aerated 3.5% NaCl solution. Bulk β phase exhibited an active OCP of about −1.3 V SCE even in this aerated solution. A wide range of passivity was found prior to a clear E₀ associated with pitting. Solutionized AA5083 exhibited a relatively noble OCP with rapidly increasing current, which is indicative of spontaneous pitting. In other words, the OCP was just above the alloy E₀ because of the rate of oxygen reduction was greater than the passive current density, and the anodic and cathodic partial curves intersected in the pitting region. The OCP of sensitized AA5083 was about 50 mV
Representative potentiodynamic polarization curves of solutionized AA5083, sensitized AA5083, and bulk β phase in aerated 3.5% NaCl solution. The OCPs for both solutionized and sensitized AA5083 were more noble than the $E_b$ of bulk β phase by 120–150 mV. Any β phase exposed at the surface of sensitized AA5083 would be polarized well above its $E_b$ and thus would be expected to corrode quickly. However, this was not observed. Fig. 3 shows the surfaces of solutionized AA5083 and sensitized AA5083 before (Figs. 3a and 3b) and after (Figs. 3c–3f) 24 h of immersion at their OCP in aerated 3.5% NaCl solution. Figs. 3c and 3d show localized corrosion around Mn-rich intermetallic particles, which are cathodic to the matrix. IGC attack could be found on the sensitized sample after OCP immersion using SEM, Fig. 3f, but only at a few areas scattered across the sensitized sample. Most of area had localized corrosion in the form of trenching around intermetallic particles, of the type that was also seen on the solutionized sample (Fig. 3e).

Anodic potentiodynamic polarization curves for the same materials in deaerated solution are given in Fig. 4. The OCP values were lower than in the aerated solution as expected and a range of passivity below $E_b$ was evident for both alloys. The $E_b$ for sensitized AA5083 was slightly lower than that for solutionized AA5083. However, both materials showed only extensive pitting with no evidence of IGC after the test. The polarization curve for the bulk β phase was almost identical to that measured in aerated solution.

Cathodic polarization.—To further investigate the behavior of β phase, a constant potential of $-800$ mV SCE was applied to both sensitized and solutionized AA5083 for 24 h in deaerated 3.5% NaCl solution. Fig. 4 shows that the applied potential was in the passive region for AA5083 but above the $E_b$ of β phase. From the polarization curve for β phase in Fig. 4, the local current density associated with β phase

Figure 2. Representative potentiodynamic polarization curves of solutionized AA5083, sensitized AA5083, and bulk β phase in aerated 3.5% NaCl solution.

Figure 3. Images of AA5083 before and after immersion for 24 h in aerated 3.5% NaCl a) optical image of solutionized before immersion, b) optical image of sensitized before immersion, c) optical image of solutionized after immersion, d) optical image of sensitized after immersion, e) SEM images of solutionized after immersion, f) SEM images of sensitized after immersion.
Figure 4. Representative potentiodynamic polarization curves of solution-ized AA5083, sensitized AA5083, and bulk β phase in deaerated 3.5% NaCl solution. Dissolution would be expected to be very high rate at this potential, about $1.3 \times 10^{-3}$ A/cm², while the AA5083 matrix should be passive. However, the surfaces of sensitized and solutionized AA5083 samples had similar appearance following this potentiostatic treatment, Fig. 5. The optical microscopy images in Figs. 5a and 5b indicate that corrosion attack occurred mostly near intermetallic particles on both solutionized and sensitized samples. SEM analysis, Figs. 5c and 5d, indicated that β phase dissolved at a few sites on the sensitized sample, similar to what was found in the aerated solution.

Aballe et al. polarized AA5083 in aerated solution at a potential below the OCP, $-840$ mV_SCE, and then allowed the sample to sit in the free corrosion condition. The sample exhibited pitting attack, which was not found for a sample immersed into the test solution without any pretreatment. It was assumed that an oxide film covering the surface of AA5083 protected the sample surface from corrosive environment and did not allow pitting attack.

The effects of prior cathodic pretreatment were investigated by applying two different potentials below the OCP ($-800$ and $-850$ mV_SCE) for 11 h on sensitized and solutionized samples in aerated NaCl solution. Optical microscopy images of the sample surfaces are given in Fig. 6. Comparison of Fig. 6b and Fig. 5b indicates that the surface morphology after treatment at $-800$ mV_SCE on sensitized AA5083 was very different with oxygen present in the solution; black lines in Figs. 6b and 6d are evidence of IGC resulting from selective dissolution of β phase along grain boundaries. These features were not observed for the solutionized samples, as shown in Figs. 6a and 6c. Instead, the periphery of intermetallic particles was corroded on solutionized samples.

The currents measured during polarization at $-800$ and $-850$ mV_SCE in aerated solution are shown in Fig. 7. The current from sensitized samples at $-800$ mV_SCE was significantly higher than for the solutionized sample, as shown in Fig. 7a. The measured current in both cases was anodic because of a shift of the OCP early in the test. The higher current for the sensitized sample was apparently associated with β phase dissolution, as shown in Fig. 6b. It is interesting that the IGC in this sample was found only near intermetallic particles. The reduction of oxygen at intermetallic particles should increase the local pH.

Figs. 6c and 6d show the surface after polarization at $-850$ mV_SCE in aerated solution for 11 h. IGC was observed on the sensitized sample as shown in the circled area, but the extent of IGC and the number of IGC sites were less than at $-800$ mV_SCE because the driving force to dissolve β phase was less at the lower potential. As shown in Fig. 7b, the current was cathodic throughout the charging period, and larger for the sensitized sample even though this sample exhibited β phase dissolution in this condition.

Local pH increases associated with oxygen reduction appear to play an important role in the dissolution of β phase on polished sensitized AA5083 in an aerated solution. Cathodic polarization of sensitized samples in deaerated 3.5% NaCl solution was investigated to see if similar attack could be generated. Fig. 5 showed that polarization at $-0.8$ V_SCE for 24 h resulted only in attack near the intermetallic particles. However, after polarization at $-1.3$ V_SCE for 10 min, IGC was observed on the sensitized sample near the intermetallic particles as was observed at higher potentials in the aerated solution, Fig. 8b. Numerous small pits could also be found in circular regions surrounding the intermetallic particles on both solutionized (Fig. 8a) and sensitized samples. The remainder of the surface away from the particles was not corroded in both types of samples. The SEM images in Figs. 8c and 8d show the sample surface of solutionized and sensitized samples after polarization at $-800$ mV_SCE for 24 h. These images indicate that corrosion attack occurred near intermetallic particles on both solutionized and sensitized samples.
polarization at $-1.3 \text{V}_{\text{SCE}}$ for 1 h. Solutionized AA5083 samples only exhibited dishing near Mn-rich intermetallic particles, while IG attack was observed around these sites for the sensitized AA5083 samples.

**STEM analysis of AA5083 altered surface layer.**—As mentioned above, the absence of IGC at potentials above the $\beta$ phase breakdown potential might be associated with the presence of an ASL preventing the exposure of $\beta$ phase at the surface. The high pH associated with cathodic reactions might result in cathodic corrosion that was sufficient to remove the ASL and result in $\beta$ phase exposure at the surface. STEM analysis of the near surface region was performed to investigate the presence of an ASL. Fig. 9 shows that an ASL around 1 $\mu$m in thickness did form on the as-polished surface of both sensitized and solutionized AA5083. The microstructure of this layer was small, recrystallized grains that were not elongated in the rolling direction as were the grains in the bulk matrix. Additionally, the grain boundaries in the bulk matrix became deformed and did not continue straight through the ASL to the surface. $\beta$ phase was not found on the grain boundaries in the ASL, as would be expected for recrystallized grains. Evidence for the absence of grain boundary $\beta$ phase is provided by Fig. 10a, which presents an HAADF STEM image and EDS mapping of the ASL of polished sensitized AA5083. Evidence for the absence of grain boundary $\beta$ phase is provided by Fig. 10a, which presents an HAADF STEM image and EDS mapping of the ASL of polished sensitized AA5083. The Mg count on the recrystallized grain boundaries in the ASL on the sensitized alloy was lower than that in the grains, similar to that observed in the bulk under the ASL in the solutionized AA5083 as shown in Figure 10b. Because the recrystallized ASL had no $\beta$ phase at the new grain boundaries, the continuous pathway of $\beta$ phase to the surface was interrupted and $\beta$ phase was not exposed at the surface of the sensitized alloy after polishing.

**Figure 7.** Measured current during polarization of AA5083 in aerated 3.5% NaCl solution. a) $-800 \text{ mV}_{\text{SCE}}$ b) $-850 \text{ mV}_{\text{SCE}}$. 

**Figure 6.** Optical microscope images of AA5083 after potentiostatic polarization for 11 h. a) solutionized at $-800 \text{ mV}_{\text{SCE}}$ b) sensitized at $-800 \text{ mV}_{\text{SCE}}$ c) solutionized at $-850 \text{ mV}_{\text{SCE}}$ d) sensitized at $-850 \text{ mV}_{\text{SCE}}$. 

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Figure 8. Images after polarization of AA5083 in deaerated solution at $-1.3 \ \text{V}_{\text{SCE}}$. a) optical image of solutionized sample b) optical image of sensitized sample c) SEM image of solutionized sample d) SEM image of sensitized sample.

Figure 9. Images of the surface of AA5083 sample that was cut perpendicular to short traverse direction after polished to 3 $\mu$m. a) HAADF image of sensitized AA5083. b) HAADF image of solutionized AA5083.

Figure 10. A HAADF image of AA5083 surface and corresponding EDS maps for the surface region of a sample polished to 3 $\mu$m. a) sensitized AA5083 sample. b) solutionized AA5083 sample.
Discussion

The objective of this study was to determine why β phase dissolution is not observed during open circuit immersion of highly sensitized AA5083. Understanding this behavior is critical in understanding IGC and IGSCC, but has not been explained by previous studies on AA5083.5,6

It is well known that β phase influences the mechanical properties and corrosion behavior of AA5083. β phase dissolution is thought to be the first phase to be attacked in a corrosive environment because of its low Eq. The lack of extensive IGC associated with β phase dissolution at the OCP of sensitized AA5083 was shown in Fig. 3. Furthermore, large differences in the potentiodynamic polarization curves for sensitized and solutionized AA5083 samples that might be expected if there was extensive β phase dissolution in the sensitized sample were also not observed, as shown in Figs. 2 and 4. On the other hand, Figs. 6 and 8 show the IGC was initiated around intermetallic particles on sensitized samples when cathodic current was applied. As described above, these observations can be explained by an ASL that is present on as-polished samples.

and is removed near the cathodic sites, i.e. intermetallic particles, by the application of cathodic current to result in exposure and dissolution of the β phase. Baek and Frankel studied the phenomenon of cathodic corrosion using an electrochemical quartz crystal microbalance (EQCM) at cathodic potentials on thin films of pure Al, Al-4Cu, and Al-Cu.29 They found that the magnitude of true cathodic corrosion was significantly larger than the measured net cathodic current during cathodic polarization owing to simultaneous anodic dissolution.

The reactions associated with cathodic corrosion of AA5083 are shown in Eqs. 1–4. During cathodic polarization, the primary cathodic reaction, oxygen reduction, occurs primarily at the active cathodic sites, the intermetallic particles, to result in the generation of hydroxide ions, Eq. 1. In the high pH region near the intermetallic particles, the hydroxide ions chemically dissolve the aluminum oxide layer on the alloy surface by Eq. 2. The fresh Al surface is extremely reactive so it immediately oxidizes to reform the oxide layer, Eq. 3. The sum of Eqs. 2 and 3 provide the net reaction of Al dissolution that occurs during cathodic corrosion, Eq. 4.

Dissolution of Al according to Eq. 4 as the result of alkalization of the electrolyte near cathodic particles can apparently lead to sufficient loss of metal to remove the approximately 1 μm thick ASL, expose β phase particles at the grain boundaries and cause IGC. The application of a specific potential was not the critical step, as polarization at −800 mV SCE in aerated solution resulted in IGC, but polarization at the same potential in deaerated solution did not.

In AA2024-T3, intermetallic particles containing Al, Cu, Mn, and Fe serve as cathodic sites and promote dissolution of the matrix leaving slight trenches surrounding particles.30 Furthermore, trenching and cavity formation on AA2024-T3 surfaces can be inhibited by buffering the solution.31 By preventing local changes in pH, corrosion attack around the intermetallic particles is not possible. To examine β phase dissolution in a buffered test solution, experiments were performed on sensitized AA5083 in a 3.5% NaCl solution containing 0.1 M boric acid (H3BO3) resulting in a pH 4.85 buffer. The sample was polarized in this solution at −1.3 V SCE for 10 min in the deaerated condition, the behavior was significantly different compared to that in the un-buffered NaCl solution. After a few seconds of polarization in the un-buffered solution, the current density increased steadily, reaching −9.4 μA/cm² after 600 s, Fig. 11a. In contrast, the current density in the buffered solution was rather constant and much lower, −0.35 μA/cm² after 600 s. Furthermore, the surface of sensitized samples after polarization at this potential in buffered solution had a very different appearance than the sample polarized in the non-buffered solution, which was shown in Fig. 8b. The buffering action of the solution prevented a local increase in pH at the Mn-rich intermetallic particles, and essentially no attack was observed.

All of the observations are consistent with the removal of an ASL by cathodic corrosion during polarization in unbuffered solution at −1.3 V SCE. However, the polarization curves for bulk β phase indicate that this phase should not exhibit attack at this low potential. To understand why IGC was observed in the unbuffered case at this low potential, the effect of pH on β phase behavior must be considered. Birbilis et al. showed the anodic current density of bulk β phase at −1.3 V SCE is strongly dependent on pH: < 1 μA/cm² at pH 5.5 and > 10 μA/cm² pH 10.32 This supports the experimental results from buffered and un-buffered solutions in that the change in local pH to remove the altered surface layer was the key factor in understanding β phase dissolution.

The STEM studies provided clear evidence of an ASL on polished AA5083 samples. Several papers have shown that ASLs can form on aluminum alloys as the result of high shear stress processes, such as polishing and rolling.19–23 The mechanism of microstructure change during polishing has been studied previously.19,23 Heat generated during polishing was shown to cause recrystallization of the
surface microstructure. This theory is supported by the TEM observations in Figs. 9 and 10, which show the presence of subgrains and recrystallized grains after polishing. ASLs on other Al alloys exhibit higher susceptibility to corrosion than the underlying matrix.\textsuperscript{20–23} The HAADF-STEM image in Fig. 9 of polished AA5083 shows an ASL with small grain size and also that the grain boundaries in the bulk matrix did not continue in this region. Additionally, Fig. 10a shows that the grain boundaries in the ASL on the heavily sensitized alloy had lower Mg concentration than in the grains, which was a condition similar to the solutionized sample in Fig. 10b. The shear deformation during polishing caused redistribution of Mg from the β phase at the prior grain boundaries and recrystallization to form the small-grained ASL. The newly formed grain boundaries in the recrystallized region had no β phase because those boundaries had not experienced the temperatures and times required for sensitization. The ASL then prevented the expected selective dissolution of β phase by blocking the exposure of the β phase to the environment at the surface.

Samples were etched in NaOH to study the effects of removing the ASL on the corrosion behavior of AA5083. Koroleva et al. showed that aluminum alloys can be controllably etched by immersion in sodium hydroxide solution.\textsuperscript{34} In this study, polished AA5083 samples were etched for 10 s to fully remove the 1 μm ASL. The L-T surface of both sensitized and solutionized AA5083 samples were polished to 3 μm, and etched in 5 wt% NaOH for 10 s at a temperature of 80°C followed by desmutting in reagent grade HNO₃ for 3 s. Optical profilometry analysis was performed at the edge of the etched region where a lacquer layer had been applied to mask off the original surface. As shown in the topographic map in Fig. 12a and the line scan in Fig. 12b, a layer approximately 1.2 μm thick was removed from the surface, which is sufficiently deep to remove the entire altered surface layer. A few small pits (<1 μm in depth) were present on the etched surface. Nonetheless, it can be assumed that the exposed surface after etching represented the unaltered AA5083 base alloy in either the sensitized or solutionized condition. STEM investigation on sensitized AA5083 after etching verified the full removal of ASL with etching process. Figure 13a clearly shows no evidence of ASL on the top of the etched surface. The recrystallized grains shown in Figure 9a were not found, and only bulk matrix remained at the surface.

Further evidence for the exposure of grain boundary β phase after etching is provided by Fig. 13b, which presents an HAADF-STEM image of the ASL free sensitized AA5083 surface and corresponding EDS maps. The red box in Figure 13b shows that a line of high Mg concentration associated with β phase on a grain boundary continued to the top surface. The etched surfaces were then potentiostatically polarized at −800 mV\textsubscript{SCE} in aerated 3.5% NaCl. Fig. 14a shows the measured current for solutionized AA5083 in the as-polished as well as the polished and etched conditions. The nominal currents for both conditions were small and negative, with anodic current transients associated with metastable pitting. The as-polished condition exhibited larger and more numerous transients and a lower cathodic current. In contrast, a large difference was measured for sensitized AA5083 in the two conditions, as shown in Fig. 14b. The as-polished sensitized sample had a nominal current that started out negative and became positive with time. The etched sensitized sample exhibited a large and positive current that was 20× larger than that for the as-polished sample after 1 h of polarization. This difference was apparently associated with the dissolution of β phase that was exposed at the surface after removal of the ASL.
Fig. 14. Measured current during polarization of AA5083 in aerated 3.5% NaCl solution at −800 mV SCE before and after etching. a) Solutionized AA5083. b) Sensitized AA5083.

Fig. 15 shows potentiodynamic polarization curves of solutionized and sensitized AA5083 before and after etching in aerated 3.5% NaCl solution. The OCP of sensitized and solutionized samples in the as-polished condition were only different by 50 mV and the difference in E_b was even less. The similar E_b was likely the result of a similar ASL on both samples. The polarization curves after removal of the ASLs by etching were quite different. The etched solutionized sample exhibited a lower OCP and a passive region prior to breakdown, which occurred at an E_b that was about 50 mV higher than that for the as-polished condition. The higher E_b suggests that defects on the polished surface were removed by etching. Etching also had a strong influence on the polarization behavior of the sensitized sample. The OCP for the etched sample was significantly lower and the passive current density was significantly higher. However, in contrast to the solutionized samples, the E_b of sensitized samples decreased by about 50 mV after etching. Exposing β phase on the etched surface shifted the OCP toward the corrosion potential of β phase. Fig. 14 clearly shows that removal of the ASL by etching results in clear differentiation of the corrosion behavior of solutionized and sensitized AA5083, which is not present for the as-polished condition.

In conclusion, these results indicate that the ASL on solutionized AA5083 is more active than the bulk matrix whereas the ASL on sensitized AA5083 is more corrosion resistant than the bulk matrix. This is apparently the first time that an ASL on an Al alloy was found to be less susceptible than the underlying matrix and is the result of the elimination of the very susceptible sensitized structure at the surface. This layer does not play a major role in stress corrosion cracking because the underlying sensitized microstructure is exposed after the attack penetrates through the thin surface layer. However, this work clearly shows that the corrosion behavior of polished samples does not represent the true behavior of the bulk matrix because of the presence of ASLs, and removal of these layers is necessary to study initiation of IGC in sensitized AA5083 at the OCP.

Conclusions

To understand selective dissolution of β phase in AA5083, sensitized and solutionized samples that were as-polished or polished and etched were polarized in aerated or deaerated 3.5% NaCl solution. Optical microscopy, SEM and STEM were used to analyze the surface morphology after the experiments to verify dissolution of β phase. The following conclusions can be made:

1. IGC did not occur on polished sensitized AA5083 during open circuit exposure even though the potentials were well above the breakdown potential for bulk β phase, and polarization to higher potentials resulted in the formation of pitting rather than IGC.

2. Cathodic polarization resulted in evidence of IGC near Mn-rich intermetallic particles.

3. The surface layer on polished sensitized AA5083 had a different microstructure with smaller grain size and no β phase precipitation on grain boundaries. This layer blocked the exposure of β phase to the environment.

4. Cathodic polarization resulted in cathodic corrosion near Mn-rich intermetallic particles, which removed the altered surface layer and initiated β phase dissolution on polished sensitized AA5083 samples.

5. Removal of the altered surface layer by alkaline etching resulted in clear differentiation of the corrosion behavior sensitized AA5083 by exposing grain boundary β phase.

6. The ASL on solutionized AA5083 was more active than the bulk matrix, but the ASL on sensitized AA5083 was more protective than the bulk matrix.

7. For the IGC study of AA5083, removing altered surface layer is necessary for understanding the selective dissolution mechanism of β phase.
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References
1. J. L. Searles, P. I. Gouma, and R. G. Buchheit, Stress corrosion cracking of sensitized AA5083 (Al-4.5Mg-1.0Mn). Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 32(11), 2859 (2001).
2. J. R. Pickens, J. R. Gordon, and J. A. S. Green, The effect of loading mode on the stress-corrosion cracking of aluminum alloy 5083. Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 14(5), 925 (1983).
3. T. D. Burleigh, The postulated mechanisms for stress-corrosion cracking of aluminum alloys - A review of the literature 1980–1989. Corrosion, 47(2), 89 (1991).
4. D. R. Baer, Influence of Mg on the corrosion of Al. Journal of vacuum science and technology A, 18(31), 151 (2000).
5. Y. Zhong, M. Yang, and Z. K. Liu, Contribution of first-principles energetics to Al-Mg thermodynamic modeling. Calphad: Computer Coupling of Phase Diagrams and Thermochemistry, 29(4), 303 (2005).
6. N. Birbilis and R. G. Buchheit, Electrochemical characteristics of intermetallic phases in aluminum alloys - An experimental survey and discussion. Journal of the Electrochemical Society, 152(4), B140 (2005).
7. R. H. Jones, Role of Mg in the stress corrosion cracking of an Al-Mg alloy. Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 32(7), 1699 (2001).
8. R. H. Jones, J. S. Verano, and C. F. Windisch, Stress corrosion cracking of Al-Mg and Mg-Al alloys. Corrosion, 60(12), 1144 (2004).
9. A. J. Davenport, Yudie Yuan, and R. Ambut, Intergranular Corrosion and stress corrosion cracking of sensitized AA5182. Materials Science Forum, 519–521, 641 (2006).
10. R. Goswami, Microstructural Evolution and Stress Corrosion Cracking Behavior of Al-5083. Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 42A(2), 348 (2011).
11. S. Jain, Spreading of intergranular corrosion on the surface of sensitized Al-4.4Mg alloys: A general finding. Corrosion, 59, 136 (2012).
12. M. L. C. Lim, J. R. Scully, and R. G. Kelly, Intergranular Corrosion Penetration in an Al-Mg Alloy as a Function of Electrochemical and Metallurgical Conditions. Corrosion, 69(1) 35 (2013).
13. R. Goswami, Precipitation behavior of the beta phase in Al-5083. Materials Science and Engineering a: Structural Materials Properties Microstructure and Processing, 527(4-5), 1089 (2010).
14. A. Aballe, Localized alkaline corrosion of alloy AA5083 in neutral 3.5% NaCl solution. Corrosion Science, 43, 1657 (2001).
15. A. Aballe, Influence of the degree of polishing of alloy AA 5083 on its behavior against localised alkaline corrosion. Corrosion Science, 46, 1909 (2004).
16. K. A. Yasakan, Role of intermetallic phases in localized corrosion of AA5083. Electrochimica Acta, 52(27), 7651 (2007).
17. M. Bethencourt, The influence of the surface distribution of Al6(MnFe) intermetallic on the electrochemical response of AA5083 aluminum alloy in NaCl solutions. Materials Science Forum, 289–292, 567 (1998).
18. E. H. Dix, W. A. Anderson, and M. B. Shumarker, Influence of service temperature on the resistance of wrought aluminum-magnesium alloys to corrosion. Corrosion, 15(2), 19 (1959).
19. L. E. Samuels, Metallographic polishing by mechanical methods. 4 ed 2003, Materials Park, OH: ASM international.
20. A. Afseth, Effect of heat-treatment on filiform corrosion of aluminum alloy AA3005. Corrosion Science, 43(11), 2093 (2001).
21. A. Afseth, Effect of heat-treatment on electrochemical behaviour of aluminum alloy AA3005. Corrosion Science, 44(1), 145 (2002).
22. H. Leth- Olsen, J. H. Nordlien, and K. Nisancioglu, Filiform corrosion of aluminum sheet. III. Microstructure of reactive surfaces. Corrosion Science, 40(12), 2051 (1998).
23. Z. Zhao and G. S. Frankel, On the first breakdown in AA7075-T6. Corrosion Science, 49(7), 3064 (2007).
24. G67, A., “Standard test method for determining the susceptibility to intergranular corrosion of 5xxx series aluminum alloys by mass loss after exposure to nitric acid”. West Conshohocken, PA: ASTM International, 2004.
25. G1-03, A., “Standard Practice for preparing, cleaning, and evaluating corrosion test specimens”, (West Conshohocken, PA: ASTM International, 2011).
26. R. C. Hugo and R. G. Hoagland, The kinetics of gallium penetration into aluminum grain boundaries - In situ TEM observations and atomistic models. Acta Materialia, 48(8), 1949 (2000).
27. E. J. Kirkland, R. F. Loane, and J. Silcox, Simulation of annular dark field STEM images using a modified multislice method. Ultramicroscopy, 2(3), 17 (1987).
28. R. F. Loane, P. Xu, and J. Silcox, Incoherent imaging of zone axis crystals with adf STEM. Ultramicroscopy, 40(2), 121 (1992).
29. Y. Baek and G. S. Frankel, Electrochemical Quartz Crystal Microbalance Study of Corrosion of Phases in AA2024. Journal of the Electrochemical Society, 150(1), B1 (2003).
30. G. S. Chen, M. Gao, and R. P. Wei, Microconstituent-induced pitting corrosion in aluminum alloy 2024-T3. Corrosion, 52(1), 8 (1996).
31. J. C. Seegmiller, R. C. Bazito, and D. A. Buttry, Visualization of cathode activity for Fe-rich and Cu-rich intermetallic particles via cathodic corrosion from dioxygen reduction at aluminum alloy 2024-T3. Electrochemical and Solid State Letters, 7(1), B1 (2004).
32. J. A. Lyndon, Electrochemical behavior of the beta-phase intermetallic (Mg2Al) as a function of pH as relevant to corrosion of aluminum-magnesium alloys. Corrosion Science, 70, 290 (2013).
33. D. M. Turley and L. E. Samuels, The nature of mechanically polished surfaces of copper. Metallography, 14(4), 275 (1981).
34. E. V. Koroleva, Surface morphological changes of aluminum alloys in alkaline solution: effect of second phase material. Corrosion Science, 41(8), 1475 (1999).