Al-Mg alloys can precipitate β phase, Mg2Al3, along grain boundaries during long-term exposure to moderate temperatures, resulting in susceptibility to intergranular corrosion. It is of interest to investigate the corrosion inhibition of this alloy in this sensitized condition. Furthermore, recent work has shown that the presence of an altered surface layer (ASL) affects the corrosion behavior of polissed AA5083, making it difficult to determine the effectiveness of corrosion inhibitors. The combined effects of the presence of the ASL and inhibitors are not well understood. In this work, the effects of adding potassium chromate (K2CrO4), sodium silicate (Na2SiO3), and sodium vanadate (NaVO3) to NaCl solution were examined using electrochemical methods on sensitized and solutionized AA5083 with and without the ASL present on the surface. The ASL alone may protect the alloy depending on whether or not the alloy was sensitized. All of the tested inhibitors exhibited a suppression of the cathodic reaction, with chromate causing mixed inhibition on sensitized AA5083 without the ASL present. The composition and surface morphology of samples exposed to inhibitors were also investigated.  

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AA5083-H116 plates with thickness of 3 mm were purchased commercially. One group of as received sample plates was sensitized by heat-treatment at 100 °C for 30 days and air cooling to room temperature. The other group of plates was solutionized at 450 °C for 1.5 h, cold water quenched to room temperature, and stored in a refrigerator to prevent microstructural changes. The degree of sensitization (DoS) was tested with ASTM G67, and the average values of DoS were 1.2 and 64.2 mg/cm² for solutionized samples and sensitized samples, respectively. These findings support the descriptions of the two conditions as being solutionized and sensitized.

Electrochemical tests were performed in a flat-cell using a platinum-mesh counter electrode and a standard calomel reference electrode (SCE). AA5083 coupons were cut from the heat-treated plates into 2 cm × 2 cm (L-T) pieces. One group of samples was abraded to 1200 grit with silicon carbide (SiC) paper in ethanol-based lubricant to minimize corrosion, and then rinsed with DI water and ethanol (C₂H₅OH) and air dried. To investigate the effect of the ASL on the sample surface, the other group of samples was etched after polishing for 15 s in 5 wt% NaOH at 80 °C followed by DI water rinsing, desmutting in 70 wt% HNO₃ for 3 s, DI water rinsing again, ethanol rinsing, and then air drying. TEM analysis of the cross-section showed that the ASL was etched away by this procedure.

Cathodic and anodic potentiodynamic polarization measurements were performed separately on freshly prepared samples. The potential was scanned from the OCP after 1 hour of immersion at 10 mV/min in the anodic direction, and 18 mV/min in the cathodic direction. Each experiment was performed at least three times to check the reproducibility of the measurement. The curves presented in this work are representative results taken from replicated experiments for each condition.

Electrochemical impedance spectroscopy (EIS) measurements were performed in 3.5 wt% NaCl solutions with and without inhibitor addition. Solutionized and sensitized AA5083 plates were cut into 4.5 cm × 4.5 cm (L-T) pieces and abraded to 1200 grit. One group of samples was etched for ASL removal and the other group of samples remained as-polished. Ethch samples and as-polished samples will be referred to as “without ASL” and “with ASL” samples, respectively. Samples were exposed to the test solution for 7 days, and EIS measurements were performed once per day. A potential amplitude of 10 mV was applied around the open circuit potential over the frequency range from 10⁴ to 10⁻² Hz. The ZView analysis software was used to fit the data to a simplified Randles model equivalent circuit.

X-ray photoelectron spectroscopy (XPS) was performed to investigate the chemical nature of surfaces of AA5083 samples that had been immersed in 3.5 wt% NaCl with and without inhibitors for 7 days. A Kratos AXIS Ultra spectrometer with a monochromated Al X-ray source was operated at 12 kV. The samples were exposed to the ultra-high vacuum in the XPS chamber overnight before the analysis. Survey scans (0–1400 eV) and high resolution spectra of Mg 1s, Zn 2p, Cu 2p, O 1s, C 1s, Cl 2p, Al 2p, Cr 2p, Si 2p and V 2p were collected. The XPS spectra and analyze the chemical state of the elements. All reported binding energy values were rounded to 0.1 eV with a precision of ±0.2 eV. The analysis area was approximately 0.21 mm².

Results and Discussion

Potentiodynamic polarization measurements.— Figure 1 shows polarization curves in naturally- aerated 3.5 wt% NaCl solution for AA5083 samples with and without the ASL. Figure 1a shows that the corrosion current density decreased by about a factor of 10 as the result of a decrease in the cathodic current density and the pitting potential increased by about 50 mV after removing the ASL from a solutionized sample. As shown in Figure 1b, removing the ASL on sensitized AA5083 samples decreased the corrosion potential by 100 mV and increased the corrosion current density slightly as the result of an increase in the passive current density. This result indicates that the ASL on solutionized AA5083 sample is more reactive than the underlying bulk matrix, but the ASL on sensitized AA5083 sample is less reactive than the bulk matrix. As was reported in the previous study, β phase is not present at the grain boundaries in the ASL formed on the surface of sensitized AA5083 during polishing. This is the first reported instance of an ASL on an Al alloy being more corrosion resistant than the underlying material. Therefore, it is important to investigate efficiency of inhibitors on samples without an ASL.

The polarization curves shown in Figure 2 demonstrate the effect of adding 2 mM K₂CrO₄. The chromate acted as strong cathodic inhibitor on solutionized AA5083 samples both before and after etching to remove the ASL (Figure 2a). The cathodic reaction rate was reduced by about two orders of magnitude for both conditions and the OCP was lower on solutionized AA5083 with and without an ASL by about 150 mV and 400 mV, respectively. However, no change in pitting potential was observed. For sensitized AA5083 with no ASL, chromate addition led to mixed inhibition including strong anodic inhibition associated with an increased pitting potential (Figure 2b). The same amount of cathodic inhibition was observed for the non-etched AA5083 sample, but there was no evidence of an increase in pitting potential as shown in Figure 2a. Transmission electron microscopy (TEM) analysis confirmed that NaOH etching fully removed the ASL from the polished surface and exposed the grain boundary β phase to the corrosive environment. Therefore, it is expected that exposed β phase may interact with chromate and change the inhibition behavior on etched surfaces.

Figure 3 shows polarization curves for sensitized AA5083 in naturally aerated 3.5 wt% NaCl solution with varying concentrations of
In this case, the pH of the non-inhibited solution was adjusted to 12.2 because the pH of solutions with increasing addition of $\text{Na}_2\text{SiO}_3$ varied from 11.0 to 13.3. This increase in pH is due to the formation of silicic acid and hydroxyl ions from the reaction between silicate and water.31 On both solutionized (not shown) and sensitized AA5083 samples, silicate acted as a strong cathodic inhibitor and no evidence of anodic inhibition was found. The cathodic reaction rate was reduced by about two orders of magnitude for each silicate concentration, meaning that even a small amount can inhibit localized corrosion attack near Fe-rich intermetallic particles. As shown in Figure 3a, the OCP for samples with an ASL became more negative with increasing silicate concentration; the decrease was about 200 mV for an addition of 100 mM silicate. However, there was no significant change in OCP or in the polarization curves with varying silicate concentration for samples without the ASL (Figure 3b).

Figure 4 shows polarization curves for sensitized AA5083 in solutions containing vanadate. Like silicate, the addition of vanadate also resulted in cathodic inhibition but no anodic inhibition. The oxygen limiting current density was reduced slightly compared to the other inhibitors, but the hydrogen evolution rate was reduced by the same amount as for the other inhibitors. Figure 4a shows that a vanadate concentration of 10 mM had the strongest cathodic inhibition with a 100 mV negative shift in OCP for the sample with ASL. However, no dependence of the cathodic inhibition efficiency on vanadate concentration was observed after removing the ASL (Figure 4b). This change in behavior is likely again related to the etching process. Koroleva et al. studied the surface morphology change on aluminum alloys during NaOH etching, and found a high rate of dissolution of silicon-free intermetallic particles, which would be Fe-rich particles in AA5083.32 A reduced density at the surface of Fe-rich particles, which are cathodic to the matrix,33 will alter the surface activity compared to the surface before etching. The absence of an effect of varying silicate or vanadate concentration for etched samples might be the result of the reduced number of cathodic sites on the etched surface. This observation indicates that a small amount of inhibitor can provide enough inhibition to have good cathodic protection on samples both with and without etching to remove the ASL.

In this regard, 2 mM concentration of silicate and vanadate were separately added to study the inhibition behavior on solutionized AA5083. As is shown in Figure 5, the inhibitors inhibited the cathodic reaction like they did on sensitized AA5083 samples. Figure 5a shows that the polarization curves for solutionized AA5083 with and without ASL in 3.5 wt% NaCl solution with silicate were almost identical, with a large decrease in passive current density and a clear decrease in pitting potential compared to the uninhibited cases. In Figure 5b, the sample without ASL showed a decrease in pitting potential of about 100 mV after adding vanadate, while the sample with ASL showed cathodic inhibition but not near the OCP. This behavior...
Figure 4. Polarization curves for AA5083-H116 in aerated 3.5% NaCl solution with varying NaVO$_3$ concentration on sensitized AA5083 samples. (a) with ASL, (b) without ASL.

Figure 5. Polarization curves for AA5083-H116 in 3.5% NaCl for solutionized AA5083 samples with and without ASL. (a) with 2 mM Na$_2$SiO$_3$, (b) with 2 mM NaV$_2$O$_5$.

is interesting because ASL on solutionized AA5083 is more active than the matrix.$^{29}$ It was observed that vanadate acted in an opposite manner on sensitized AA5083 samples than on non-sensitized samples. It was not as obvious as the effect on solutionized samples, but the pitting potential was about 30 mV higher with vanadate on the sensitized sample without the ASL than for the sample with an ASL. These observations were supported by EIS and XPS analyses.

The effects of 2 mM concentration of each of the inhibitors in 3.5 wt% NaCl solution on the anodic polarization curve for bulk β-phase are shown in Figure 6. No anodic inhibition was observed for any of the inhibitors. The breakdown potential for β phase was unchanged, and adding silicate increased the passive current density by about one order of magnitude, although this was likely the result of the higher pH with silicate. In conclusion, the corrosion resistance of β phase cannot be improved by any of these inhibitors, and the cathodic inhibition found with all three inhibitors on the sensitized AA5083 after etching was from interactions with the bulk matrix or cathodic intermetallic particles, not with grain boundary β phase.

Electrochemical impedance spectroscopy.— EIS was performed on solutionized and sensitized AA5083, both with and without an ASL, in NaCl solutions containing each of the inhibitors. The spectra were fitted to a simplified Randles circuit and the polarization resistance, $R_p$, was extracted. Figure 7 shows a summary of $R_p$ values at the end of the 7 day exposure in the various conditions, and Figure 8 shows SEM images after the 7 day exposure period. The $R_p$ values in Figure 7 show the average values and standard deviations from the replicated experiments. The SEM images in Figure 8 were collected from one group of immersed samples and were not repeated. Solutionized AA5083 samples without an ASL in non-inhibited solution showed higher $R_p$ than samples with an ASL present during the measurement. As indicated above, removing the active surface layer improves the corrosion resistance on solutionized samples. Sensitized AA5083 samples with the ASL showed similar or somewhat lower $R_p$ values than samples without an ASL, even though the exposure of grain boundary β phase by etching was expected to make the surface more active. It is possible that a layer of corrosion products blocked further exposure of β phase on grain boundaries in salt solution (Figure 8b), which made the surface similar to the one with no β exposure. Furthermore, Figure 8a suggests that cathodic corrosion around Fe-rich intermetallic particles might remove the ASL and expose β phase to the surface. These conditions may alter the surface condition for sensitized samples both with and without the ASL in non-inhibited solution.

Further examination of Figure 7 shows that adding chromate increased the $R_p$ of both solutionized and sensitized AA5083 samples by about one order of magnitude. Adding chromate can improve the corrosion resistance in all conditions. The behavior of $R_p$ after addition of silicate was similar to that of the chromate inhibitor for solutionized AA5083. Furthermore,
Figure 6. Polarization curve result in aerated 3.5 wt% NaCl solution on bulk \( \beta \) phase with various inhibitors.

Figure 7 shows that adding silicate increased \( R_p \) about one order of magnitude for solutionized AA5083 both with ASL and without the ASL. On the sensitized sample, the addition of silicate decreased the \( R_p \) by about one order of magnitude on the sample without ASL. This behavior is not predicted based on the polarization curves in Figure 3. The SEM images in Figures 8c and 8d show that silicate film was formed on the surface of the sensitized sample with the ASL but not without the ASL. It is not known why the silicate film was not formed on the sensitized sample without ASL, but the absence of this film might explain the small \( R_p \) measured for this condition.

The EIS results for the solutions containing vanadate were different than for the other inhibitors. EIS measurement on the solutionized sample without ASL was not possible because the OCP was not stable for the entire exposure period. As a result, there is no bar for this condition in Figure 7a. The solutionized sample with ASL exhibited a decrease in \( R_p \) with vanadate addition. For the sensitized samples in vanadate solution, a higher \( R_p \) was measured without the ASL than with the ASL, but both are lower than for the uninhibited control samples. These results are in contrast to those in solutions with chromate and silicate, which exhibited better inhibition on the surface without ASL for solutionized samples and for sensitized samples with the ASL. Figures 8e and 8f are SEM images of the surface of sensitized samples with and without ASL, respectively, after 7 days in 3.5 wt% NaCl with 2 mM vanadate. The SEM image in Figure 8e shows that a vanadate film covered the Fe-rich intermetallic particles on the sample with ASL, which helped to provide cathodic inhibition. However, a vanadium product covered the entire surface on the sample without the ASL.

Figure 7. Impedance data summary of polarization resistances after 7 day immersion. (a) solutionized AA5083. (b) sensitized AA5083.

Figure 8. Scanning electron microscope images of sensitized AA5083 samples after 7 days immersion in each solution condition. (a) with ASL in non-inhibited 3.5 wt% NaCl. (b) without ASL in non-inhibited 3.5 wt% NaCl. (c) with ASL in 2 mM silicate. (d) without ASL in 2 mM silicate. (e) with ASL in 2 mM vanadate. (f) without ASL in 2 mM vanadate.

Figure 9. XPS spectra showing the Zn 2p\(^{3/2}\) and Cu 2p\(^{3/2}\) on solutionized and sensitized AA5083 after sample preparation.
ASL (Figure 8f). Small cracks in the SEM image provided evidence of this film, which likely cracked as a result of the vacuum conditions during SEM imaging. The differences in film coverage resulted in better corrosion protection on the surface with no ASL. The measured $R_p$ values with vanadate were lower than with other inhibitors by one or two orders of magnitude. It is possible that pits formed during long term immersion and the local pH decrease at the pits, which favored the formation of unprotective decavanadate. Iannuzzi et al. found that metavanadate transformed to orange decavanadate when added to solution of pH 3 or less and that this form was an ineffective inhibitor. After 7 days of immersion, the surface of sample with no ASL had areas with orange color corrosion products, which is consistent with the poor corrosion resistance of this condition. It is not clear why vanadate behaved differently on the sample with no ASL.

X-ray photoelectron spectroscopy — XPS was used to characterize the surfaces of samples after 7 days of exposure. Note that the XPS characterization was performed on one group of immersed samples.

Figure 10. XPS Spectra showing the (a) Al 2p on solutionized AA5083 (b) Cr 2p with chromate on solutionized and sensitized AA5083, (c) Si 2p with silicate on solutionized and sensitized AA5083, (d) V 2p with vanadate on solutionized AA5083, and (e) V 2p with vanadate on sensitized AA5083.
and was not replicated. For the samples before immersion, the atomic percentage of Mg was highest on sensitized AA5083 without the ASL, indicating that removal of the ASL made the surface more reactive by allowing β phase to be exposed to the corrosive environment. Furthermore, Zn and Cu were detected only after the surface had been etched with 5 wt% NaOH to remove the ASL, as shown in Figure 9. The presence of these species will affect the corrosion behavior of AA5083 because Zn activates Al, and Cu enhances the cathodic reaction on the surface. Because solutionized and sensitized samples behaved so differently, and Zn and Cu species were present on both surfaces, the influence of these species will not be considered in detail in this work.

Exposing samples to non-inhibited NaCl solution seemed to form a thick layer of corrosion product covering the surface area because of the decrease in the content of alloying elements at the surface. Zn and Cu were not detected on samples without ASL after 7 days exposure in non-inhibited solution, while samples without ASL exposed in the inhibitor-modified solutions had those elements present.

Figure 10a shows the Al⁰ peak was not found on a sample immersed in inhibitor-free solution, whereas a strong Al⁰ peak was observed for the sample exposed to a solution with chromate, indicating a thin surface oxide layer. The data in Figure 10a are from solutionized AA5083 with ASL, but other samples exhibited the same tendency.

Figure 10b shows a peak associated with possibly either Cr(OH)₃ or Cr₂O₃ at a binding energy of 577.9 eV, which was evidence of a reduced chromate species. Formation of the Cr(III) species can block electron transfer and consequently decrease the oxygen reduction reaction kinetics. A small shoulder on the high binding energy side the Cr(III) peak is tentatively assigned to Cr(VI). As shown in Figure 7, a higher polarization resistance was measured on the solutionized AA5083 without an ASL than with an ASL in the chromate solution. The Cr(III) concentrations on the surfaces of solutionized AA5083 with and without an ASL were 2.4% and 3.9%, respectively. This suggests that the higher Cr(III) concentration provided better protection to the solutionized sample. However, on the sensitized AA5083, a lower Cr(III) concentration was observed on the sample with an ASL, which had higher polarization resistance.

An Si peak was observed after exposure in a solution containing silicate at a binding energy of 102.2 eV, as Figure 10c shows. This binding energy is consistent with aluminosilicate species containing Na⁺ with tetrahedral aluminum.

Figure 10 also shows evidence for the presence of Na⁺. A mechanism of Al alloy corrosion inhibition by silicate at high pH has been proposed. At high pH, aluminum oxide becomes chemically unstable, dissolving to form aluminate ions, which then react with silicate anions in solution to form aluminosilicate species. Na⁺ ions could act as a coagulating agent between alumina-silicate and the alumina oxide surface, which might both be negatively charged. This mechanism explains continuous growth of a silicate layer with time to form a protective film over the aluminum alloy. The effect of ASL on the corrosion inhibition by silicate is related to the amount of Si detected with XPS as the samples with more Si exhibited higher measured Rₑ as described in Figure 7.

As described above, vanadate influenced the corrosion resistance differently than the other inhibitors. A lower polarization resistance was measured on the solutionized sample with an ASL than without an ASL in solution with vanadate. Additionally, the sensitized sample without an ASL had a lower corrosion rate than the sample with an ASL. As shown in Figures 10d and 10e, the 2p peaks exhibited different amounts of V⁵⁺ (517.2 eV) and V⁴⁺ (516.0 eV). The ratios of V⁴⁺/V⁵⁺ for sensitized AA5083 with and without an ASL were 3.2 and 3.1, respectively. On the solutionized sample without an ASL, less V⁴⁺ species were observed. However, the ratio was the same on solutionized samples. The reduction of vanadate species on the surface may affect corrosion protection, but the surface reaction and product causing the inhibition on the AA5083 are unknown.

In conclusion, these experimental results indicate that chromate has the highest inhibition efficiency among the three inhibitors tested on solutionized and sensitized AA5083 with and without ASL present on the surface. Silicate provides good protection and is a possible substitute as a non-chromate inhibitor for solutionized AA5083. However, vanadate provides better protection for sensitized AA5083 than silicate, especially when grain boundary β phase is exposed by etching away the ASL. This work clearly shows that the corrosion and inhibition behaviors measured on the ASL of polished AA5083 are significantly different from those of the bulk matrix. Therefore, it is important to recognize the presence and study the influence of ASLs on aluminum alloys to understand the true corrosion behavior of the alloys.

Conclusions

The inhibition of AA5083 by different inhibiting compounds was investigated, and the role of the ASL formed during polishing was assessed. Testing was performed on solutionized and sensitized samples, before and after removing the ASL, in 3.5 wt% NaCl solution containing K₂CrO₄, Na₂SiO₃, or NaVO₃ inhibitors. The following conclusions can be made:

1. Addition of inhibitors to NaCl solution provided effective corrosion inhibition for AA5083, but was different before and after removing the ASL.

2. All of the tested compounds provided cathodic inhibition, and chromate exhibited additional anodic inhibition on sensitized AA5083 without an ASL as indicated by an increase in the pitting potential.

3. The bulk matrix of solutionized AA5083 (without an ASL) exhibited better corrosion resistance than samples with an ASL in non-inhibited NaCl solution and with chromate and silicate additions.

4. Sensitized AA5083 with an ASL exhibited higher corrosion resistance than without an ASL in non-inhibited NaCl solution and with chromate and silicate additions.

5. Vanadate provided better inhibition for solutionized AA5083 with an ASL condition, and without an ASL for sensitized AA5083.

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