

Improvement of hydrogen embrittlement and stress corrosion cracking by annealing for Al-4.4Mg-0.6Mn alloy

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Abstract: With no annealing treatment, cathodic polarization trends in 5083F Al alloy revealed concentration polarization and activation polarization. However, the annealed specimens have lower current densities at corrosion protection potential compared to the non-annealed specimen. The results of SSRTs conducted in seawater at the applied potential range of -1.8 V to -0.5 V indicated that the maximum tensile strength, elongation, and time-to-fracture had high values at applied potentials of -0.7 to -1.4 V. The maximum tensile strength, elongation, and time-to-fracture decreased when the potential values were beyond this range in either anodic or cathodic direction. In general, the increased shear lip caused by annealing treatment indicates elongation. Time-to-fracture would likely increase with elongation. Potentials between -0.5 V to -0.6 V were found to be in the region of stress corrosion cracking. The corrosion protection zone was determined to be -0.7 V to -1.4 V because these potential ranges produced good mechanical properties. Potential less than -1.4 V produced a fractured surface with a mixture of dimples (ductile fractures) and a quasi-cleavage pattern resulting from the effects of hydrogen gas.

Key words: annealing; 5083F Al-Mg alloy; corrosion; seawater; slow strain rate tests

1 Introduction

The fiber-reinforced plastic (FRP) composite materials are susceptible to fire and are prohibited from use in high-speed passenger ships and cargo boats with gross tonnages in excess of 500 t. In addition, FRP ships such as small boats for fishing pose numerous problems from both the environmental and recycling perspectives. In particular, no methods exist to dispose these ships at the end of their service. The specific strength of Al ships is higher than that of steel ships. They are capable of high speed, and have increased load capacities, greater ease of recycling, and higher anticorrosion properties. Typically, user believe erroneous sense that corrosion of Al alloys does not occur in seawater by E –pH diagram on Al alloys, the corrosion prevention area is examined at around pH 8 in seawater but the Cl^- ions in seawater destroy the strong passive layer on the surface of Al alloys. In general, the corrosion of Al alloy occurs as like crevice corrosion, galvanic corrosion and pitting corrosion[1–5]. Among Al-Mg alloys (5××× series), 5083F, non-heat treated alloy, has the high strength in as-rolled condition. This high strength alloy has

electrochemical characteristics inferior to lower strength alloys because it contains considerable residual stress. Annealing heat treatment can improve the characteristics of stress corrosion cracking and hydrogen embrittlement by relieving residual stress.

This work investigates the electrochemical and mechanical properties of 5083F alloy specimens subjected to annealing treatment.

2 Experimental

The 5083F Al alloy has the composition of Si 0.09%, Fe 0.289%, Cu 0.018%, Mn 0.589%, Mg 4.449%, Cr 0.076%, Zn 0.005%, Ti 0.009% and Al balance, and the mechanical properties of tensile strength 319.2 MPa, yield strength 154.8 MPa, and elongation 23.7%. The specimens used for electrochemical tests in this investigation were mounted with epoxy resin with an exposed area of 100 mm², and then polished with 600# emery paper. The specimens were carefully degreased with acetone and distilled water. The polarization system consisted of a Pt coil which acted as a counter electrode, and an Ag/AgCl saturated KCl reference electrode. The tests were carried out at a scanning rate of 2 mV/s at

room temperature. The anodic and cathodic polarization tests were taken in the open circuit potential from -0.5 to 3.0 and 2.0 V (Ag/AgCl electrode), respectively. The specimens for mechanical property testing with size of $235\text{ mm}\times 4\text{ mm}\times 6\text{ mm}$ were machined. Notches with 1 mm in width and depth, were made on both sides of parallel parts of the specimens to cause a fracture. The specimens used for the slow strain rate tests (SSRTs) were also exposed to natural seawater. These were fitted with a jig for an Instron machine. The SSRT was carried out at a strain rate of 0.001 mm/min , during which a constant potential was maintained with a potentiostat/galvanostat apparatus.

3 Results and discussion

Figure 1 shows the cathodic polarization curves of 5083F Al alloy annealed for different time at $410\text{ }^{\circ}\text{C}$. All four specimens exhibited polarization trends, indicating effects of concentration polarization resulting from oxygen reduction and activation polarization resulting from hydrogen generation. The tests revealed that during the cathodic polarization of 5083F Al alloy, the concentration polarization resulting from oxygen reduction ($\text{O}_2+2\text{H}_2\text{O}+4\text{e}^-\rightarrow 4\text{OH}^-$) and the activation polarization resulting from hydrogen gas generation

($2\text{H}_2\text{O}+2\text{e}^-\rightarrow \text{H}_2+2\text{OH}^-$) had turning points of approximately -1.60 V (vs Ag/AgCl). ‘Turning point’ at the cathodic polarization curve means the potential between concentration polarization and activation polarization[6–7]. The as-received specimen had a high current density corresponding to the dissolved oxygen reduction reaction region compared to the heat-treated specimens. Annealing treatment improved anticorrosion properties during cathodic protection.

Figure 2 presents the potential at the turning point with heat treatment time for specimens annealed at $410\text{ }^{\circ}\text{C}$. Here, the turning point is an important index for evaluating hydrogen embrittlement. The cathodic protection potential is good condition with a high potential compared to the turning point of -1.6 V , as well as the region of dissolved oxygen reduction reaction. Higher values on the bar graph indicate strong resistance to hydrogen embrittlement during corrosion protection, since the turning point of -1.6 V has a low potential. As shown in Fig.2, the non-heat-treated specimens had a higher potential(noble potential) at the turning point than the heat-treated specimens, with the exception of specimens annealed for 20 min . Specimen annealed for 120 min had the lowest negative potential at the turning point. Therefore, the specimen annealed for 120 min was more resistant to hydrogen embrittlement.

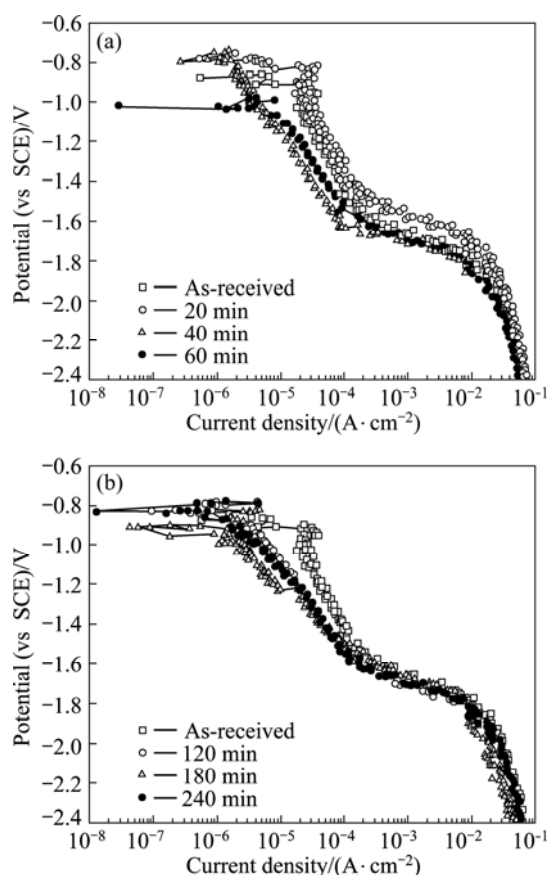


Fig.1 Cathodic polarization curves of 5083F Al alloy annealed at $410\text{ }^{\circ}\text{C}$ for different time

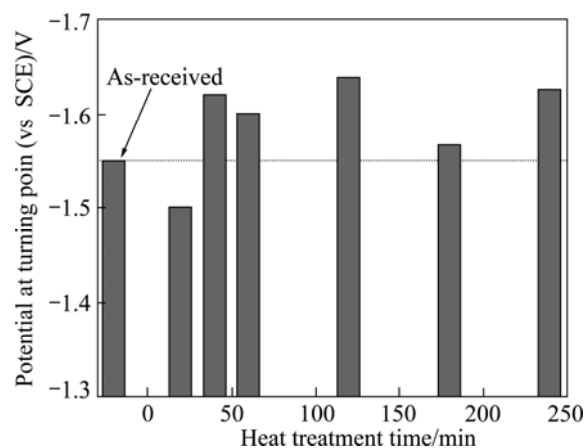


Fig.2 Comparison of potential at turning point with time for specimens annealed at $410\text{ }^{\circ}\text{C}$

Figure 3 compares the current density at a potential of -1.1 V with heat treatment time for specimens annealed at $410\text{ }^{\circ}\text{C}$. The current density at potential of -1.1 V is the cathodic protection range, i.e. the region of concentration polarization resulting from the dissolved oxygen reduction reaction[8]. Hence, a low current density indicates high resistance to corrosion. The anti-corrosion property is improved by heat treatment with the exception of specimen annealed for 20 min , since the current densities in the heat-treated specimens were lower than that in the non-heat-treated specimen. When

the electrochemical properties were tested in seawater, specimens annealed at 410 °C for 180 min had the lowest current density, and were therefore the most stable.

Figure 4 presents the anodic polarization curves of 5083F alloy at 410 °C with annealing time. The anodic polarization and corrosion potential trends did not differ greatly with annealing conditions. The tests revealed that the annealed specimens had lower corrosion current densities than the as-received specimen. Annealing treatment improved current densities, but similar current densities were observed for current densities greater than

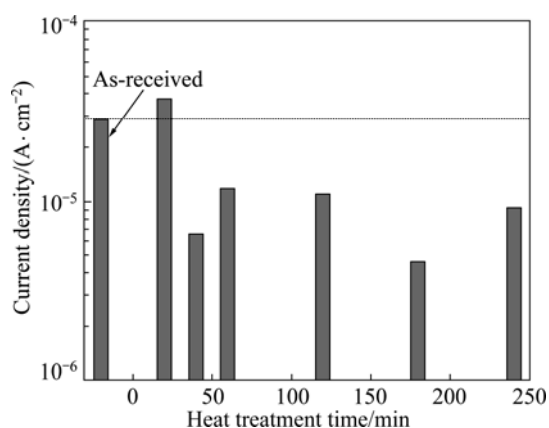


Fig.3 Comparison of current density at potential of −1.1 V with time for specimens annealed at 410 °C

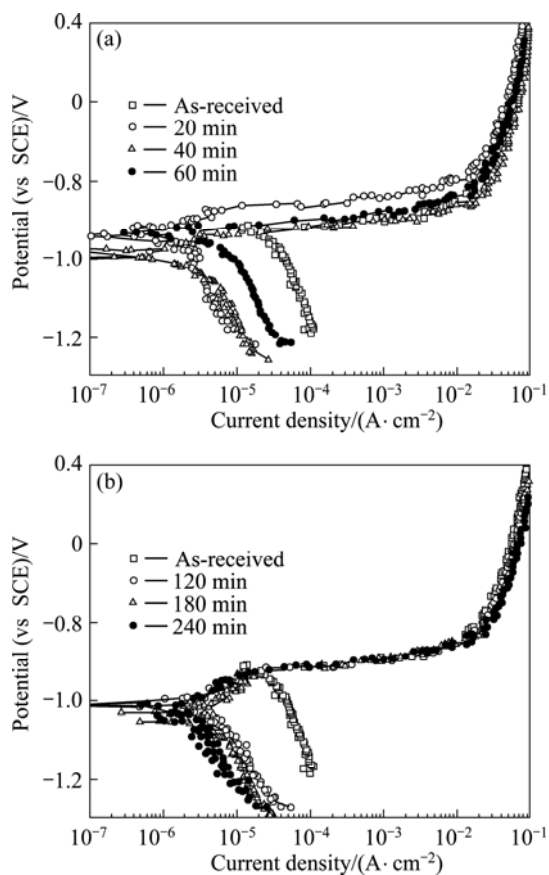


Fig.4 Anodic polarization curves of 5083F Al alloy annealed at 410 °C for different time

−0.65 V. Therefore, annealing treatment did not seem to have an effect on stress corrosion cracking under these conditions. Stress corrosion cracking phenomenon yielded similar trends at values greater than −0.65 V in the anodic direction.

Figure 5 compares the corrosion current density with heat treatment time for specimens annealed at 410 °C. The corrosion current density was calculated using Tafel analysis with anodic and cathodic polarization curves around the OCP. Resistance to corrosion is greater for low bar graph values, since the corrosion rate is low. Therefore, heat treatment improved the anti-corrosion properties because it lowered the corrosion current density. The lowest corrosion current density appeared after the specimen was annealed for 20 min. Comparison of the various properties revealed that 120 min was the optimal time of heat treatment at 410 °C. Therefore, next SSRTs were carried out at 410 °C for 120 min.

Figure 6 compares the effects of applied potential on the maximum tensile strength and yield strength when SSRTs were performed in seawater. Applied potentials between −1.4 and −0.7 V resulted in a greater maximum tensile strength than the other applied potentials. The

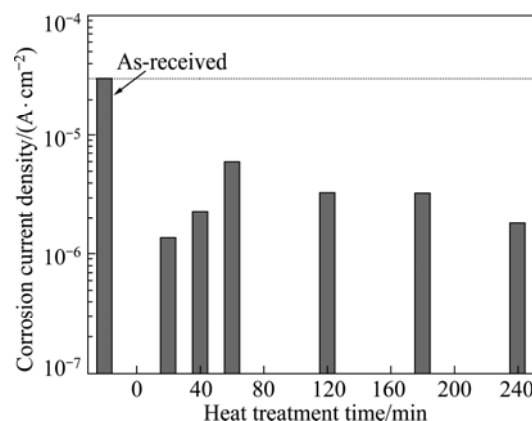


Fig.5 Comparison of corrosion current density with annealing time at 410 °C

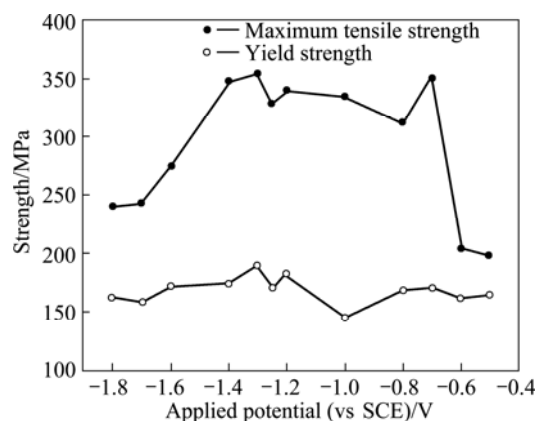


Fig.6 Effects of applied potential on maximum tensile strength and yield strength of annealed 5083F alloy when SSRTs were performed in seawater

applied potential of -0.7 V resulted in the greatest maximum tensile strength, while potential of -0.8 V produced the lowest values between the applied potential of -1.4 and -0.7 V. This phenomenon was likely a result of pitting generated by penetration of Cl^- because it was close to the natural potential in seawater. The maximum tensile strength decreased when the potential was beyond this range in either the anodic or cathodic directions. When the potential shifted to the anodic direction, the tensile strength decreased due to an active dissolution reaction. For yield strength, unlike the maximum tensile strength, no consistent trend was observed. A potential of -1.3 V produced the highest yield strength while a potential of -1.0 V produced the lowest. Previous investigations of hydrogen embrittlement in high strength steel exposed to a seawater were not able to find any correlation among tensile strength, yield strength, and applied cathodic potential, regardless of the welding method or any post-welding heat treatment[9–10].

Figure 7 shows the effects of applied potential on elongation and time-to-fracture of 5083F alloy when SSRTs were performed in seawater. Applied potentials between -1.4 and -0.7 V produced greater elongation than other conditions; the results were similar to the results for maximum tensile strength tests. In particular, the applied potential of -1.4 V yielded the greatest elongation. The elongation decreased when the potential shifted beyond this range in either the anodic or cathodic

directions. Therefore, the potential of -1.4 to -0.7 V corresponded to the protection potential range. Annealing treatment caused greater reduction in hydrogen embrittlement than in stress corrosion cracking because its anodic polarization potential produced greater elongation. Potentials from -1.4 to -0.7 V produced greater times-to-fracture than other conditions. These results were similar to the maximum tensile strength and elongation test results. Time-to-fracture decreased when the potential shifted to more anodic or cathodic values beyond the range of -1.4 to -0.7 V.

Figure 8 shows photographs of fractured specimens

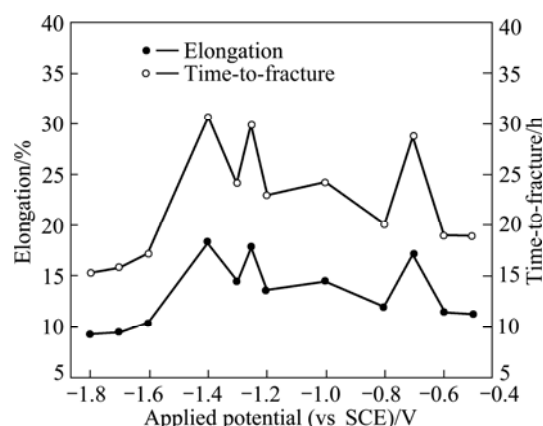


Fig.7 Effects of applied potential on elongation and time-to-fracture of annealed 5083F alloy when SSRTs were performed in seawater

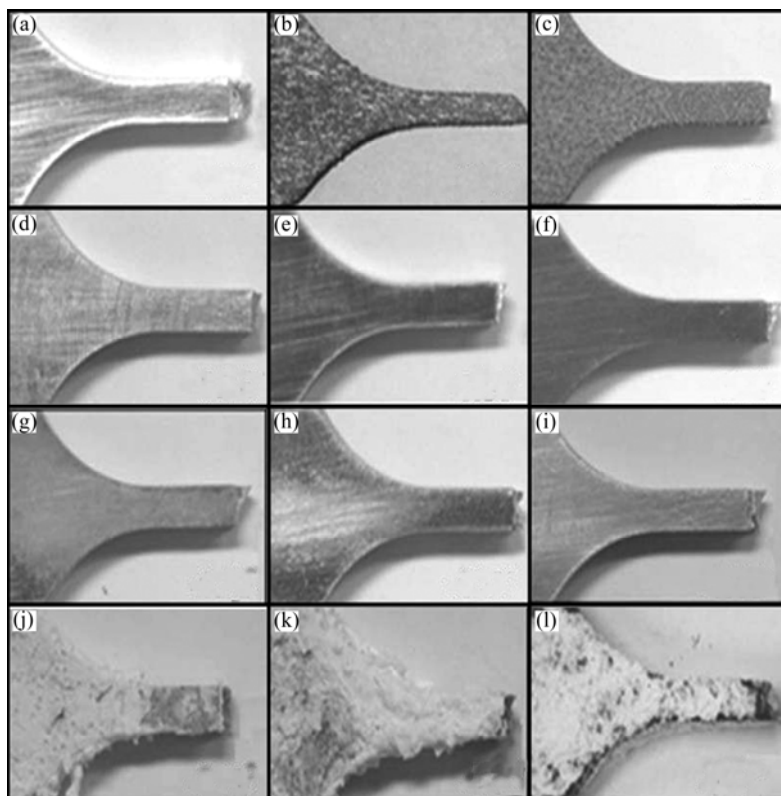


Fig.8 Photographs of fractured specimens after SSRTs performed at various applied potentials for annealed 5083F in seawater: (a) In air; (b) -0.5 V; (c) -0.6 V; (d) -0.7 V; (e) -0.8 V; (f) -1.0 V; (g) -1.2 V; (h) -1.3 V; (i) -1.4 V; (j) -1.6 V; (k) -1.7 V; (l) -1.8 V

after the SSRTs were performed at various applied potentials in seawater. The applied potential of -0.5 V presents due to the active dissolution reaction in parallel parts of the specimens. Corroded features due to pitting were observed at applied potentials of -0.5 and -0.6 V. The dissolution phenomenon was more evident at -0.5 V than at -0.6 V because of the high current density in the anodic polarization curve. In addition, the fractured specimens obtained at -0.7 V were very clean due to perfect protection, while those obtained at -1.8 to -1.6 V had a white coating consisting of a calcareous deposit composed of $\text{Mg}(\text{OH})_2$ and CaCO_3 , which was formed at the cathode surface due to the cathodic protection in seawater[11–14]. The film composed of CaCO_3 and $\text{Mg}(\text{OH})_2$ provides the corrosion

resistance. However, a uniform electrodeposition coating does not form at potentials below -1.6 V due to the lack of time. Therefore, it was concluded that the mechanical properties at such potentials were poor because the effect of hydrogen gas generation exceeded that of electrodeposition.

Figure 9 presents fractography analyses after SSRTs at various potentials in seawater. Fractograph observed in air revealed dimples (ductile fractures) and considerable shear lip. A mixture of dimples and quasi-cleavage (QC) was observed at potentials of -0.5 and -0.6 V, while potentials of -1.4 to -0.7 V, i.e. the protection zone, generally produced dimple fractures and a considerable quantity of shear lip. Potentials less than -1.6 V yielded a surface with a mixture of fractures, but mainly a

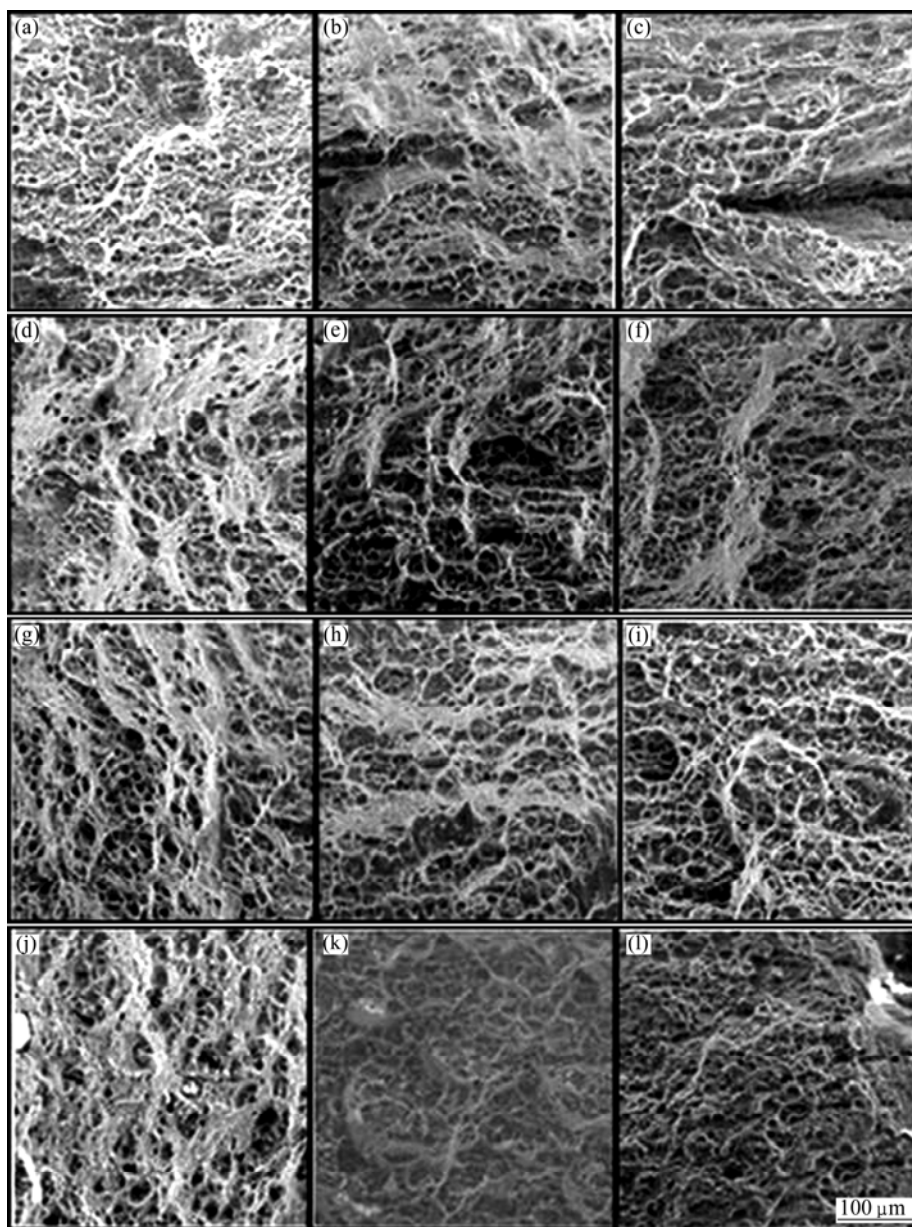


Fig.9 Fractography analyses after SSRTs at various potentials for annealed 5083F in seawater: (a) In air; (b) -0.5 V; (c) -0.6 V; (d) -0.7 V; (e) -0.8 V; (f) -1.0 V; (g) -1.2 V; (h) -1.25 V; (i) -1.3 V; (j) -1.4 V; (k) -1.6 V; (l) -1.7 V

considerable amount of QC. In general, increased shear lip resulting from annealing treatment indicates elongation. Time-to-fracture would likely increase with elongation.

4 Conclusions

The electrochemical and mechanical experiments were taken to determine the optimum annealing conditions on corrosion characteristics of Al alloys in seawater. The electrochemical experimental results indicated optimum annealing time of 120 min at 410 °C. According to the result of SSRT in seawater, the elongation, time-to-fracture and the amount of dimples for the annealed specimens at optimum condition (between -1.4 and -0.7 V) were increased. The maximum tensile strength, elongation and time-to-fracture were decreased when the potential shifted beyond this range in either the anodic or cathodic directions. From the fractured surface at potential below -1.4 V, the mixture of dimple (ductile fracture) and quasi-cleavage pattern with the effect of hydrogen gas was observed.

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