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Corrosion and optimum corrosion protection potential of friction stir welded 5083-O Al alloy for leisure ship

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Abstract: Electrochemical tests were undertaken to determine the optimum conditions in seawater for corrosion protection of friction stir-welded 5083-O Al alloy. Polarization trend observations show that the limiting potential that avoids the effects of hydrogen embrittlement is -1.6 V, corresponding to the crossover point between concentration polarization and activation polarization. However, the optimum protection potential is between -1.5 and -0.7 V since the current density at these values is low in the potentiostatic tests. When a galvanic cell is formed in the seawater, the welds exhibit electrochemically stable trends. Welded parts in galvanic tests with various area ratios are stable and have excellent anticorrosion characteristics.

Key words: 5083-O Al alloy; electrochemical test; polarization; hydrogen embrittlement; optimum protection potential

1 Introduction

The composite fiber reinforced polymer(FRP) 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, such as those commonly used in coastal navigation. In addition, FRP ships are small. Like wooden vessels, larger craft cannot detect FRP ships by radar since their composite materials reflect radar waves poorly. According to data collected by the Ministry of Maritime Affairs and Fisheries, a large proportion of ship accidents involve these vessels, composing 72.4% of all marine accidents between 1998 and 2002 and approximately 58% of all collisions involving fishing boats[1]. In light of these considerations, aluminum offers a far better material for ship building than FRP does. Aluminum crafts require less fuel. They are capable of high speed; and have increased load capacities, greater ease of recycling, and high anticorrosion properties[2]. Ships constructed with 5000-series Al alloy suffer little corrosion in marine environments, with a coat of paint providing sufficient corrosion protection for the ship. However, considerable corrosion occurs at the welds, and problems exist with deformation due to the welding heat. Moreover, the mechanical strength near the welds is low.

In this work, several electrochemical tests were undertaken to determine the optimum conditions in seawater for corrosion protection of base metal and friction stir-welded(FSWed) 5083-O Al alloy.

2 Experimental

The main additional element of an Al-Mg alloy is Mg. These alloys have high strength and good welding properties. They are often used as materials for vessels and other marine structures since they have good corrosion resistance in seawater environments. Tables 1 and 2 show the mechanical properties and chemical composition of 5083-O Al alloy specimens. The probe used for the friction stir welding(FSW) is tool-grade steel (SK). The full-screw probe had a shoulder of 20 mm, a plunging depth of 4.5-4.7 mm, a length and diameter of 4.5 and 5.0 mm, respectively. The pitch of screw was 2.0 mm and the tilting angle when advancing was 2°. The 5083-O Al alloy specimens used for the electrochemical tests were mounted with epoxy resin to give an exposed area of 10 mm², and then polished with 600# emery paper. The specimens were carefully degreased with

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 Table 1 Mechanical properties of 5083-O Al alloy

Maximum tensile strength/MPa	Yield strength/MPa	Elongation/%
316.7	177.8	25.43

Table 2 Chemical composition of 5083-O Al alloy (massfraction, %)

Si	Fe	Cu	Mn	Mg
0.122	0.250	0.024	0.627	4.528
Cr	Zn		Ti	Al
0.076	0.023		0.011	Bal.

acetone and water, and the corrosion potential was measured over 24 h in natural seawater. The polarization system consisted of a Pt coil, which acted as a counter electrode, and a Ag/AgCl-saturated KCl as reference electrode. The tests were carried out at a scan rate of 2 mV/s at room temperature. Anodic and cathodic polarizations were created from the open-circuit potential (OCP) to +3.0 and -2.0 V, respectively, using a Ag/AgCl electrode (SSCE). In the potentiostatic tests, a variety of polarization potentials in seawater were applied for 20 min and evaluated in terms of variations in the current density with time and by ascertaining the current density remaining after 20 min at the applied potential. A Tafel analysis was performed under both anodic and cathodic conditions from the OCP up to ± 0.25 V with aeration. The corrosion potential and corrosion current density were determined from the Tafel analytical results by comparing with various reference specimens. The galvanic experiments between the base cm²) were evaluated for 24 h in seawater embrittlement.

3 Results and discussion

The mechanical properties of FSWed 5083-O Al alloy specimens were evaluated for various factors as traveling speed and rotation speed. The optimum corrosion protection potential for welds in seawater was identified from the lack of stress corrosion cracking and hydrogen under the condition of 124 mm/min and a rotational speed of 800 r/min. Therefore, the electrochemical tests were carried out under these conditions to evaluate the corrosion characteristics.

Fig.1 presents the potential variation for base metal and a FSWed 5083-O Al alloy specimen in seawater. In the early stages of the test, the potential in FSWed part and base metal reached a maximum value of -0.668 V and -0.718 V at an immersion time of 600 s. Afterwards, the potential shifted abruptly in the negative direction. The potential stabilized after an immersion time of 5 000-7 000 s, and then increased slowly with time since Al and Al alloys do not corrode due to the formation of anticorrosive films, such as Al_2O_3 and Al_2O_3 · $3H_2O$, in neutral solutions. At the end of the test, the potentials of the welded part and base metal in seawater were -0.720 V and -0.744 V, respectively. The base metal has more active potential compared with the FSWed part. It is suggested, therefore, that galvanic corrosion of welded part did not occur. Thus, the electrochemical reaction for 5083-O Al alloy in seawater was reasonably stable.



Fig.1 Comparison of potential for base metal and welding metal parts of FSWed 5083-O alloy specimen in seawater

Fig.2 depicts the anodic polarization curves of base metal and a FSWed 5083-O Al alloy specimen in seawater. The passivity phenomenon was not observed. An increase in the current density occurred with increasing potential both for welding metal and base metal. Therefore, it was impossible to obtain anodic protection, and stress corrosion cracking was expected to create a weak specimen. The current density in friction stir welded part of the anodic polarization curves was greater than that in base metal of 5083-O Al alloy in seawater. This suggests that stress corrosion cracking in base metal is beneficial compared with that in friction stir welded parts. In the previous investigation[2–3], a high-strength 7075 Al alloy among the 1050, 5456, and 7075 Al alloys had the highest current density. This alloy



Fig.2 Anodic polarization curve for base metal and welding metal parts of FSWed 5083-O alloy specimen in seawater

is most prone to stress corrosion cracking and hydrogen embrittlement because the residual stress is high, which not only gives a high strength, but also increases the hardness compared with 1050 and 5456 Al alloys. In comparison, the 5456 alloy is less prone to stress corrosion cracking and hydrogen embrittlement in seawater due to its low current density. The current density of 7075 alloy was higher than that of 1050 and 5456 alloys. Till now, the stress corrosion cracking characteristics for specimens have been analyzed using anodic polarization curves, but in the present study, potentiostatic tests were also performed over a period of 1200 s at a variety of applied potentials to examine this behavior in detail.

Fig.3 shows the time-current density curves from the potentiostatic tests for base metal of 5083-O Al alloy at the anodic polarization potential in seawater. An applied potential of 0.5-1.5 V corresponded to the range in which the current density increased with the potential due to the active dissolution reaction of the anodic polarization curve. The results verified that the current density increased with the applied potential increasing. The current densities after immersion for 1 200 s had high values of 0.1 A/cm² under all conditions. At applied potentials from -0.5 to 0 V (see Fig.3(b)), which were higher than the OCP, the current density was high and continued to increase as the potential shifted in the noble direction, similar to the anodic polarization curve. The highest current density at the range from -0.8 to -0.6 V was obtained at -0.6 V. The current density at an applied potential of -0.7 V had almost stable value from the early stages of the test to approximately 200 s, but the current density at -0.8 V fluctuated for approximately 100 s before stabilizing. The current densities at applied potentials of -0.7 and -0.8 V had low values. The current density increased as the potential shifted to more noble values for both the anodic polarization curve and the potentiostatic tests at various applied potentials. The current density had low values close to the OCP. Corrosion of Al similar to hydrogen generation occurred at potentials in both acidic and alkaline solutions, as defined from the φ -pH diagram for Al, which was derived from the protection range since the pH of seawater is approximately 8.0[4]. However, the passivity phenomenon did not occur due to the destruction of the passivity film by the Cl⁻ differing from that of Al in other neutral solutions. Up till now, various Al corrosion trends have been explored using anodic polarization. However, the concentration polarization caused by the dissolved oxygen reduction reaction and activation polarization caused by hydrogen generation are best understood by means of a cathodic polarization analysis. Thus, we sought to ascertain the optimum protection potential range with respect to both hydrogen embrittlement and stress corrosion cracking.



Fig.3 Time—current density curves in potentiostatic experiment during 1 200 s for 5083-O alloy at anodic polarization potential in seawater

Fig.4 presents the cathodic polarization curves of base metal and a FSWed 5083-O Al specimen in seawater. The polarization trends show the effects of concentration polarization due to oxygen reduction $(O_2+2H_2O+4e^-\rightarrow 4OH^-)$ and activation polarization due to hydrogen generation $(2H_2O+2e \rightarrow H_2+2OH^-)$. For cathodic polarization of Al, however, the crossover point between the reactions was not clear; therefore, it was recast to allow for a mutual comparison. The crossover points in FSWed parts and base metal for 5083-O Al alloy was approximately -1.60 V, which is the limiting potential that prevents hydrogen embrittlement due to overprotection. The range over which concentration



Fig.4 Cathodic polarization curves for base metal and welding metal parts of FSWed 5083-O alloy specimen in seawater

polarization due to the dissolved oxygen reduction reaction occurs corresponds to the cathodic protection potential. This potential ranges in base metal and FSWed part were from -0.845 to -1.6 V and from -0.767 to -1.6 V, respectively. In a previous investigation[5], the crossover points for 1050, 5456, and 7075 alloys occurred at approximately -1.66, -1.7, and -1.64 V, respectively. The 5456 alloy had the lowest potential, while the 7075 alloy had the highest, which indicated that the 7075 alloy was most weakened by hydrogen embrittlement. During the polarization tests for the 5456 Al alloy, the destruction and formation of the passivity film in the anodic polarization curve were repeated. The current density at the potential that generated hydrogen gas increased abruptly in the cathodic polarization curve. The electrochemical properties of the 7075 alloy, when compared with those of the 1050 and 5456 alloys, inferred that the high strength of the metal occurred with considerable residual along stress The electrochemical properties of the 5456 alloy made it superior to the 7075 alloy, and the 5456 alloy also exhibited repeated repassivity following destruction of its passive film when subjected to anodic polarization. The current density at the potential in which hydrogen was generated during cathodic polarization increased abruptly. The current densities in FSWed parts and base metal at anodic polarization curves are greater than those of dissolved oxygen reduction during cathodic polarization. This implies that, economically, cathodic protection is more beneficial than anodic protection. However, we also investigated if improvements in corrosion resistance could be obtained when Al is subjected to friction stir welding in order to relieve the residual stress due to heat[6]. Upon close examination, anodic protection of friction stir welding on the 1050 Al specimen was found to be more economical than that offered by cathodic protection. The current density for

the potential at which hydrogen is generated during cathodic polarization increased abruptly. Investigations on hydrogen embrittlement of high-strength steel[7–8] showed that the change from concentration polarization to activation polarization occurs at -1~000 mV (vs SCE). A potential of -900 mV (vs SCE) can also be included in the range at which concentration polarization occurs because the reaction involves the reduction of dissolved oxygen. However, hydrogen embrittlement can also occur at -900 mV when atomic hydrogen is present. To examine the possible effects of atomic hydrogen, potentiostatic experiments were conducted on the 5083-O specimen.

Fig.5 shows the time—current density curves from the potentiostatic tests over a period of 1 200 s for base



Fig.5 Time—current density curves in potentiostatic experiment for 5083-O alloy at cathodic polarization potential in seawater

metal of 5083-O Al alloy at the cathodic polarization potential in seawater. The applied potentials from -1.4 to -1.0 V corresponded to the concentration polarization from the dissolved oxygen reduction reaction, when the current density increased with shifts in the negative potential direction of the cathodic polarization curve. The current density in the potentiostatic tests slowly increased as potential became more negative. This range provided cathodic protection due to the low current density. The results for the applied potentials from -1.7to -1.5 V (see Fig.5(b)), which span the crossover between concentration polarization and activation polarization, are shown in Fig.4. The current density increased as the potential became more negative. Atomic hydrogen was generated $(H^++e \rightarrow H)$ or molecular hydrogen was produced from atomic hydrogen (H⁺+e+H \rightarrow H₂, H+H \rightarrow H₂) in this potential range, accelerating the activation polarization and increasing the current density. Atomic hydrogen affected the potential at which the crossover occurred. The applied potentials from -2.0to -1.8 V, which corresponded to activation polarization by hydrogen gas, had high current densities. Large amounts of hydrogen gas were observed with the naked eye while the test was performed. Therefore, this potential range provided an equivalent effect as the range that produced atomic hydrogen.

Fig.6 shows the current density at the end of the 1 200 s potentiostatic test for base metal of 5083-O Al alloy. The current density at an applied potential of -0.7V had the lowest value. As the potential shifted in the more negative direction, the current density increased. In general, current densities that show polarization due to the dissolved oxygen reduction reaction are low, and high current densities are observed at potentials that are lower than the crossover point (-1.6 V). In our tests, a potential of -0.7 V gave a low current density. The current density increased considerably as the applied potential shifted in the noble direction. The current density at which pitting occurred was high due to stress corrosion cracking. Therefore, the potential range that did not produce stress corrosion cracking and hydrogen embrittlement was from -1.5 to -0.7 V. The current density for passivity in anodic polarization was greater than that of dissolved oxygen reduction during cathodic polarization, which implies that economically, cathodic protection is more beneficial than anodic protection [9-10]. According to the criteria for cathodic protection given by England (CP 1021)[11], the protection potential of Al is from -0.85 to -1.1 V (vs SSCE), with pitting not occurring at a cathodic polarized potential of about 0.15 V. During potential measurement experiments conducted over 24 h in this study, at potential range from -0.75 to -0.72 V, agreement was found with England's criteria for cathodic protection for 5083-O alloy, the current densities remain low at all potentials. The polarization curves for Tafel analysis of a FSW 5083-O Al alloy specimen in seawater is shown in Fig.7. A passivity trend in the anodic polarization curve was not present above the OCP. The pitting potentials of FSWed part and base metal were identified at approximately -0.658 V and -0.665 V, respectively, and pitting increased the current density over a large scale. Concentration polarization due to the dissolved oxygen reduction reaction was observed from the cathodic polarization curve. The results obtained from the Tafel analysis indicated a low corrosion current density. The specimen was stable electrochemically and had good corrosion esistance properties.



Fig.6 Current density after 1 200 s potentiostatic experiment for base metal and FSWed parts in seawater



Fig.7 Polarization curves for Tafel analysis of base metal and welding metal parts of FSWed 5083-O specimen in seawater

Table 3 lists the results of the Tafel analysis in detail. The electrochemical behaviors of FSWed part were excellent compared with those of 5083-O Al alloy base metal.

Fig.8 compares the galvanic current for different area ratios (welding metal to base metal) of a FSWed specimen. A remarkably high current $(1.6 \times 10^{-5} \text{ A})$ was observed for small area ratios of 1:20 in the early stages of the tests. The current decreased with the immersion

Table 3 Result obtained from Tafel analysis of base metal and

 FSWed specimen of 5083-O alloy

Metal	Corrosion potential/V	Corrosion current density/($A \cdot cm^{-2}$)	Pitting potential/V
Base metal	-0.835	2.8×10^{-7}	-0.665
Welding metal	-0.813	1.8×10^{-7}	-0.658



Fig.8 Comparison of galvanic current for area ratios (WM:BM) of FSWed specimen

time and stabilized after 10 000 s. For an area ratio of 1:10, the highest current was obtained at 6 000 s. The current then decreased slowly with time and reached a stable value at 10 000 s, similar to the smaller area ratio. However, for an area ratio of 1:5 and 1:1, the current was low in the early stages of the test, although a higher current was obtained for an area ratio of 1:5 compared to 1:1 (see Fig.8(a)). Fig.8(b) compares the current obtained after 86 400 s galvanic tests. A low current was obtained for an area ratio of 1:1; and this increased for area ratios of 1:10 and 1:20. In general, corrosion occurred at the weld than at the base metal. When the potential at the weld is low compared with the base metal, concentration corrosion occurs at the weld. Fortunately, the welds in this investigation had higher potentials compared with the base metal, indicating that the base metal corroded.

4 Conclusions

The cathodic protection method was beneficial for 5083-O Al alloy in seawater. From observing the polarization trends, the limiting potential that did not cause stress corrosion cracking or hydrogen embrittlement was -1.6 V, which corresponded to the crossover point between concentration polarization and activation polarization. However, the optimum protection potential was between -1.5 and -0.7 V since these potentials produced low current densities in the potentiostatic tests, indicating cathodic protection. Concentration polarization due to the dissolved oxygen reduction reaction was observed over a wide range of conditions. When a galvanic cell was formed in the seawater, the weld exhibited stable electrochemical trends. Moreover, welded parts in galvanic tests with various area ratios were stable and had excellent anticorrosion characteristics.

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