

Corrosion Behavior of Al7075, Ti-6Al-4V, and Sn-3.6Ag-1Cu Alloys in 3.0 wt.% Sodium Chloride Solutions Using Potentiodynamic Polarization Measurements

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Received: 11 February 2015 / Accepted: 13 March 2015 / Published: 23 March 2015

The corrosion behavior of Al7075, Ti-6Al-4V, and Sn-3.6Ag-1Cu alloys in 3.0 wt.% sodium chloride solution has been investigated using potentiodynamic polarization measurements. The galvanic coupling between Al7075 and Ti-6Al-4V alloys using tin-base alloy, copper, and copper coatings mixed with Sn-3.6Ag-1Cu interlayers at different bonding periods has been also carried out. The effect of bonding time on the galvanic corrosion between Al7075 and Ti-6Al-4V alloys in NaCl solution was also reported. It has been found that the corrosion of the individual alloys decreases in the order Al7075 > Sn-3.6Ag-1Cu > Ti-6Al-4V. Also, increasing the bonding time between Al7075 and Ti-6Al-4V alloys using Sn-3.6Ag-1Cu interlayer from 10 min to 60 min highly decreases their galvanic corrosion through decreasing their corrosion parameters, i.e., corrosion current density (j_{Corr}) and corrosion rate (R_{Corr}) as well as increasing their polarization resistance (R_p). On the other hand, coupling Al7075 and Ti-6Al-4V alloys via bonds made using copper interlayers and further copper coating with the combination of Sn-3.6Ag-1Cu interlayer increases the galvanic corrosion by increasing the values of j_{Corr} and R_{Corr} and decreasing the values of R_p . Therefore, bonding Al7075 to Ti-6Al-4V alloys using Sn-3Ag-1Cu thin interlayer was preferred over the copper interlayer and copper coatings in term of corrosion resistance in the chloride test solution.

Keywords: aerospace alloys; eutectic; interlayer; microstructure; polarization; solid solution

1. INTRODUCTION

The rapid oxidation of aluminum in air at room temperature results in the formation of a stable oxide film, which prevents the further oxidation of aluminum [1]. It is well known that aluminum has

excellent corrosion resistance in several media because of the stable oxide film that forms on its surface. Although, aluminum is an active metal in the galvanic series, once the oxide film forms, it provides excellent protection against further oxidation [2-4].

Aluminum alloy, Al7075, in particular contains major additions of zinc, magnesium, and copper in combinations that can lead to the existence of various levels of tensile strength. Because of the zinc content, the Al7075 alloy is considered nobler in comparison of pure aluminum. However, the Al7075 alloy is among the most susceptible aluminum alloys to stress corrosion cracking (SCC) and has a lower resistance to corrosion than those of the same series that do not contain copper. All 7xxx aluminum alloys are more resistant to general corrosion than 2xxx aluminum alloys, but less resistant than wrought alloys of other groups [5].

On the other hand, titanium alloys offer excellent resistance in many corrosive media. The protective TiO₂ film, which forms on titanium surface, provides good passivation that makes it stable over a wide values range for the pH, potential, and temperature. There, titanium can easily resist most of the reducing, neutral and oxidizing environments, even at high range of temperatures. As example, titanium shows high corrosion resistance in a temperature of up to 240 °C in dilute sulphuric acid solutions [6]. It is only under highly reducing conditions that the titanium oxide film breaks down and results in corrosion. Many of the industrial titanium alloys after their weldments, heat affected zones (HAZ), and castings, provide corrosion resistance almost equal to their base metal counterparts. This is usually results from the metallurgical stability of titanium alloys as well as the same protective oxide which, forms on titanium surfaces [7].

Titanium already has a wide range of applications that can be further expanded by alloying it with certain noble elements or by impressed anodic potentials to be used in the anodic protection process [8]. It has been reported [9] that titanium alloys have superior resistances to chlorides and various forms of localized corrosion. This is because it has the highest immunity to pitting and intergranular corrosion that result from the chloride ions attack. It is also highly resistant to crevice and stress corrosion cracking. This is why Ti is used in chloride salt solutions and other brines even in high concentration ranges and high temperatures. Very low corrosion rates can be expected in a solution of brine within the pH range of 3 to 11. It has been also reported [8] that metallic chlorides such as NiCl₂, FeCl₃, or CuCl₂, enhances the passivity of Ti to a lower pH level.

It is well known that when two dissimilar metals are coupled together, a galvanic cell is created, which leads to corrosion. Galvanic corrosion is an electrochemical process in which one metal corrodes preferentially when the couple is immersed in an electrolyte. In such a couple, one metal acts as the anode and the other acts as the cathode depending on their corrosion potentials. Furthermore, this galvanic corrosion is made more complex if a different intermetallic or several intermetallic layers form at the interface. These new layers could be more prone to corrosion than the base metals being joined [10]. Therefore, corrosion at the joint could result in failure within the joint. In designing a product made of dissimilar metals, it is normal practice to select a combination of metals with similar electrode potential. The other alternative is to electrically insulate each metal with an insulating material such as paint or plastic coating at the joints [11-13].

According to D. J. Bartlett [14], metals and alloys can be arranged in a galvanic series as per their potential in a given electrolyte against a standard reference electrode. When joining aluminum to

titanium, the galvanic series in sea water predicts that the aluminum part will act as the anode therefore, to design a joint between aluminum and titanium, the aluminum surface area should be larger than that of titanium in order to reduce the corrosion of the aluminum part, and therefore, increase the life of the joined product [10,15]. The objective of the present work was to study the corrosion of Al7075, Ti-6Al-4V, and Sn-3.6Ag-1Cu alloys in 3.0 wt.% NaCl solutions. The aim was also extended to report the galvanic corrosion created due to the coupling of Al7075 and Ti-6Al-4V alloys using Sn-3.6Ag-1Cu, copper, and copper-Sn-3.6Ag-1Cu interlayers at different bonding time. The work was carried out using the potentiodynamic polarization measurement technique.

2. EXPERIMENTAL PROCEDURE.

There were two sets of samples in this research work. The first set consists of the base alloys, namely Al7075, Ti-6Al-4V and Sn-3.6Ag-1Cu alloys. Each alloy was polished to 1 μm finish then cleaned with acetone and mounted in epoxy. The bulk metal surface area of 0.56 cm^2 was exposed to the corrosion test. A second set of samples for corrosion testing consisted of the bonded Al7075 and Ti-6Al-4V samples using Sn-3.6Ag-1Cu interlayers and other bonded samples of Al7075 and Ti-6Al-4V with copper interlayers. The corrosion testing of bonded samples of Al7075 to Ti-6Al-4V using copper coatings with Sn-3.6Ag-1Cu interlayers was also compared. The bonded samples were also polished to 1 μm finish then cleaned with acetone and mounted in epoxy with an area of 0.465 cm^2 was exposed to the corrosion test. The surface ratio of Ti-6Al-4V to Al7075 was 2:1. The corrosion test was performed using a solution of 3.0% sodium chloride (NaCl, Merck, 99%), which was prepared by dissolving 30 g of NaCl in 1 L glass flask, to be a representative for the percent of chloride salt in the natural sea water.

An electrochemical cell with a three-electrode configuration was used; the alloy's sample rod; a platinum foil, and a saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. Potentiodynamic polarization curves as well as open-circuit potential (OCP) measurements for all samples were obtained using Gamry Instrument with Gamry Framework software. In order to get the steady state potential, the OCP vs. time curve was recorded and the step analysis of the test was 0.51 second. After reaching the steady state value of potential, the polarization curve was obtained by varying the potential between the reference electrode and the working electrode and measuring the current density using the counter electrode. All potentiodynamic polarization curves were obtained by scanning the potential in the forward direction at a scan rate of 0.001 V/s versus SCE reference electrode.

3. RESULTS AND DISCUSSION

3.1. Corrosion behavior of the base alloys

The corrosion behavior of Al7075, Ti-6Al-4V, and Sn-3.6Ag-1Cu alloys in aerated stagnant 3.0 wt.% NaCl solutions was measured using the potentiodynamic polarization method and the curves are shown in Fig.1, Fig. 2 and Fig. 3, respectively. The potentiodynamic polarization testing were conducted to measure the corrosion parameters such as corrosion potential (E_{Corr}), corrosion current

density (j_{Corr}), polarization resistance (R_p) and corrosion rate (R_{Corr}) for the three chosen alloys. These parameters, in addition to the Tafel (cathodic, β_c , and anodic, β_a) slopes are listed in Table 1. The values of E_{Corr} and j_{Corr} were evaluated from the cathodic and anodic curves by Gamry Instrument Framework software. The values of β_c and β_a were determined after at least 50 mV away from E_{Corr} and at least one decade of current densities (j_{Corr}). The R_p values for the different alloys corrosion were calculated from the Stern–Geary equation [16] using parameters listed in Table 1 as follows:

$$R_p = \frac{1}{j_{\text{Corr}}} \left(\frac{\beta_c \beta_a}{2.3 (\beta_c \beta_a)} \right) \tag{1}$$

The values of the corrosion rate (milli inches per year, mpy) were calculated according to the following equation [16]:

$$R_{\text{Corr}} = j_{\text{Corr}} \left(\frac{k E_w}{d A} \right) \tag{2}$$

Where, k is a constant that defines the units for the corrosion rate ($k = 128,800$ milli inches (amp cm year)), E_w the equivalent weight in grams/equivalent of the alloy, d the density in gcm^{-3} , and A the area of alloy electrode in cm^2 .

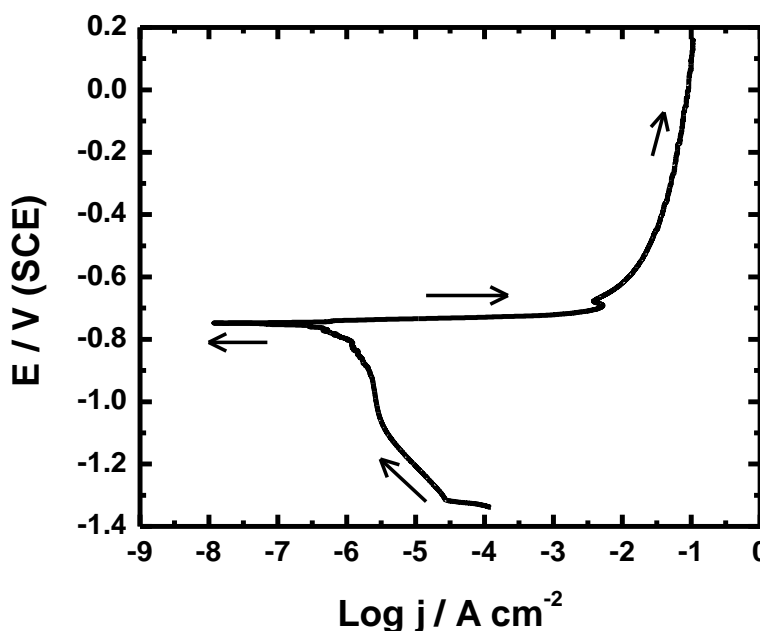


Figure 1. Potentiodynamic polarization curve obtained for Al7075 alloy in 3.0 wt.% NaCl solution.

It is worth mentioning that the obtained potentiodynamic polarization curve obtained for Al7075 alloy shown in Fig. 1 is similar in shape to the results obtained in previous research for the potentiodynamic polarization curves for 5083 and 1100 aluminum alloys in sea water [17]. It is clearly seen from Fig. 1 that the current decreases with increasing potential in the cathodic branch until it reaches to the corrosion current density, where the cathodic reaction for aluminum in near neutral

solutions is primarily the reduction of oxygen followed by its adsorption through these two reactions [18];

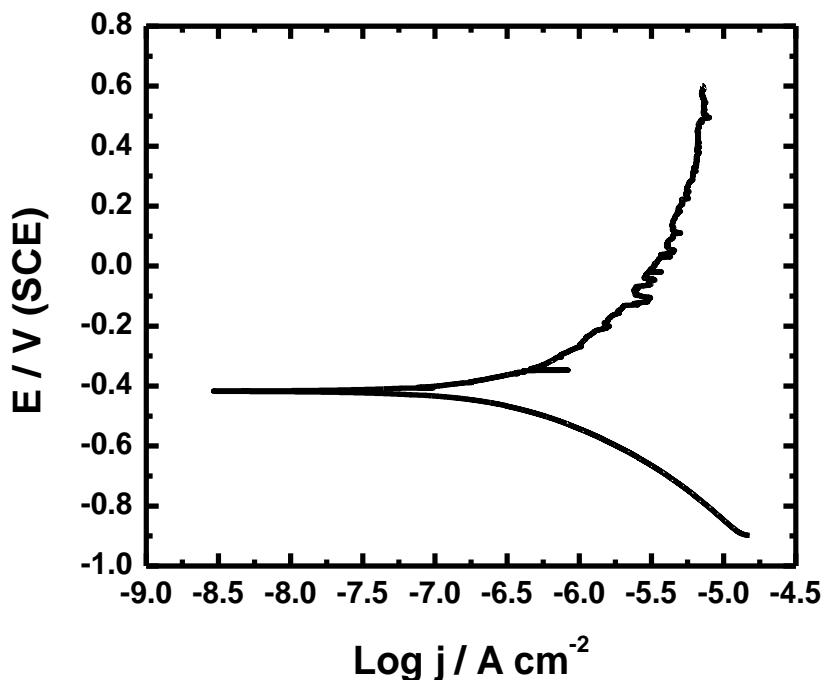
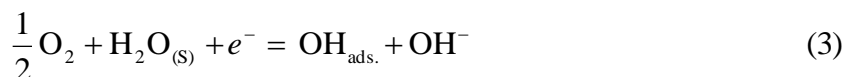
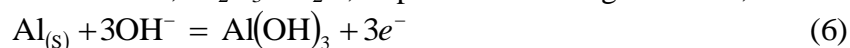


Figure 2. Potentiodynamic polarization curve obtained for Ti-6Al-4V alloy in 3.0 wt.% NaCl solution.

With the increase of the applied potential in the anodic branch, the current rapidly increases just after the corrosion potential. This is due to the dissolution of metallic aluminum (Al^0) into aluminum cations (Al^{3+}) according to the following equation [18];



The current then stays almost unchanged with large increase in the applied potential in the passive region seen on the curve. This is because the formation of aluminum hydroxide, $Al(OH)_3$, which may form in the early stages of the anodic reaction before the transformation of this hydroxide into aluminum oxide, $Al_2O_3 \cdot 3H_2O$, as per the following reactions,



On the other hand, the potentiodynamic polarization curve obtained for the Ti-6Al-4V alloy (Fig. 2) showed less corrosion compared to that recorded for Al7075 alloy (Fig. 1) and even for the Sn-3.6Ag-1Cu interlayer (Fig. 3). This was confirmed by the data listed in Table 1. Where, the values of j_{Corr} and R_{Corr} obtained for Ti-6Al-4V alloy recorded the lowest and the value of R_p was the highest. Also, the value of E_{Corr} was the less negative, -0.42 V vs. SEC. The polarization measurements thus indicated that the three alloys have relative nobility and corrosion decreases in the order; Ti-6Al-4V <

Sn-3.6Ag-1Cu < Al7075. These results agree with the galvanic series in sea water for aluminum, titanium and tin based on the measurement of the corrosion potential [19].

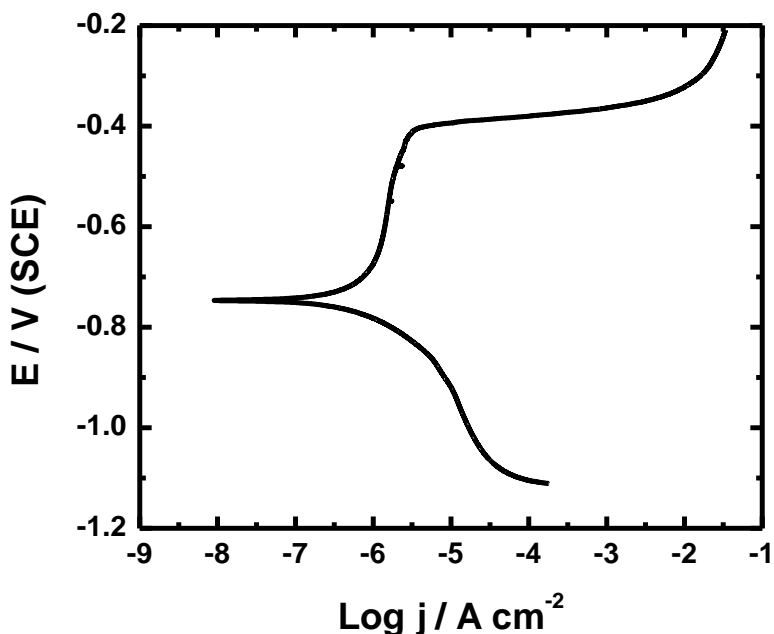


Figure 3. Polarization curve obtained for Sn-3.6Ag-1Cu alloy in 3.0 wt.% NaCl solution.

Table 1. Parameters obtained from polarization curves shown in Fig. 1, Fig. 2 and Fig. 3 for the different electrodes immersed in in 3.0 wt.% NaCl solutions.

Electrode	Polarization parameters					
	$\beta_c / \text{Vdec}^{-1}$	$E_{\text{Corr}} / \text{V}$	$j_{\text{Corr}} / \text{Acm}^{-2}$	$\beta_a / \text{V dec}^{-1}$	$R_p / \text{k}\Omega\text{cm}^2$	$R_{\text{Corr}} / \text{mmy}^{-1}$
Al7075 alloy	0.260	-0.745	7.18×10^{-7}	0.065	31.5	0.308
Ti-6Al-4V alloy	0.100	-0.430	2.57×10^{-7}	0.160	104.1	0.054
Sn-3.6Ag-1Cu alloy	0.090	-0.760	5.51×10^{-7}	0.085	34.5	0.286

3.2. Galvanic corrosion of Al7075 and Ti-6Al-4V alloys coupled by Sn-3.6Ag-1Cu interlayer.

In order to report the galvanic corrosion between Al7075 and Ti-6Al-4V alloys coupled by Sn-3.6Ag-1Cu interlayer in 3.0 wt.% NaCl, potentiodynamic polarization measurements at room temperature were carried out. The coupling between the aluminum and tin alloys was made by bonding the tin base interlayer between them for periods of time varied from 10 min to 60 min. Fig. 4 shows the shape of the bonded Al7075 and Ti-6Al-4V alloys using Sn-3.6Ag-1Cu interlayer during the potentiodynamic polarization test. The image depicted in Fig. 4 shows that the Al7075 surface looked

darker than its original color during the corrosion test, which indicates that corrosion occurred at the Al7075 alloy structure when coupled with the Ti-6Al-4V alloy.

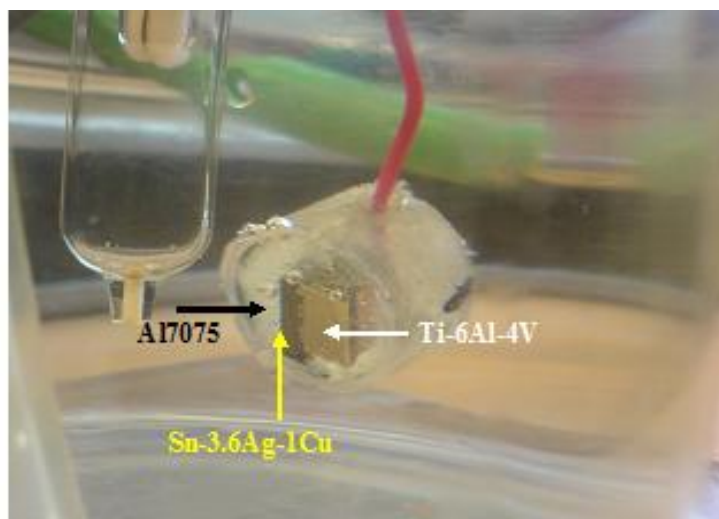


Figure 4. Image of the bond made using Sn-3.6Ag-1Cu interlayer between Al7075 and Ti-6Al-4V alloys during the polarization test.

The potentiodynamic polarization curves obtained for the bonds made using Sn-3.6Ag-1Cu interlayer between Al7075 and Ti-6Al-4V alloys at 10, 20, 30, 40, 50 and 60 min are shown in Fig. 5 to Fig. 10, respectively.

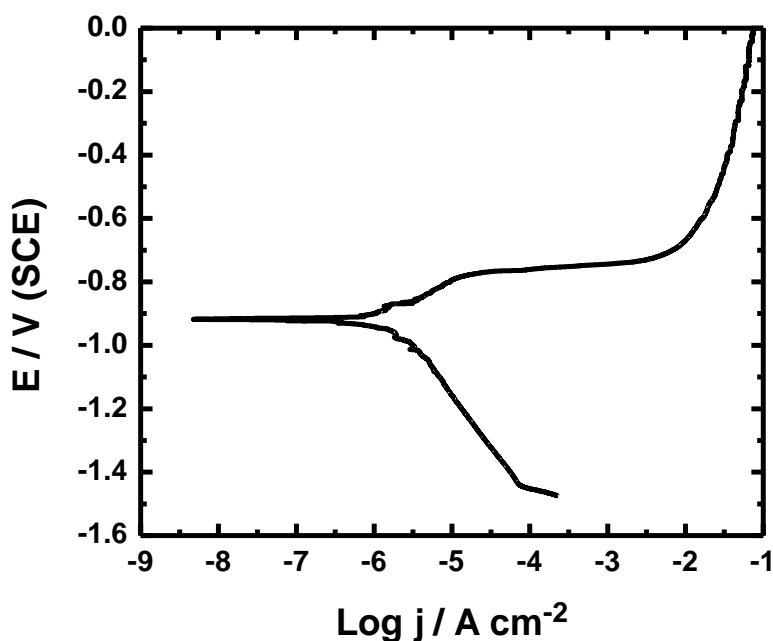


Figure 5. Potentiodynamic polarization curve in 3% NaCl for bond made using Sn-3.6Ag-1Cu interlayer at 10 min.

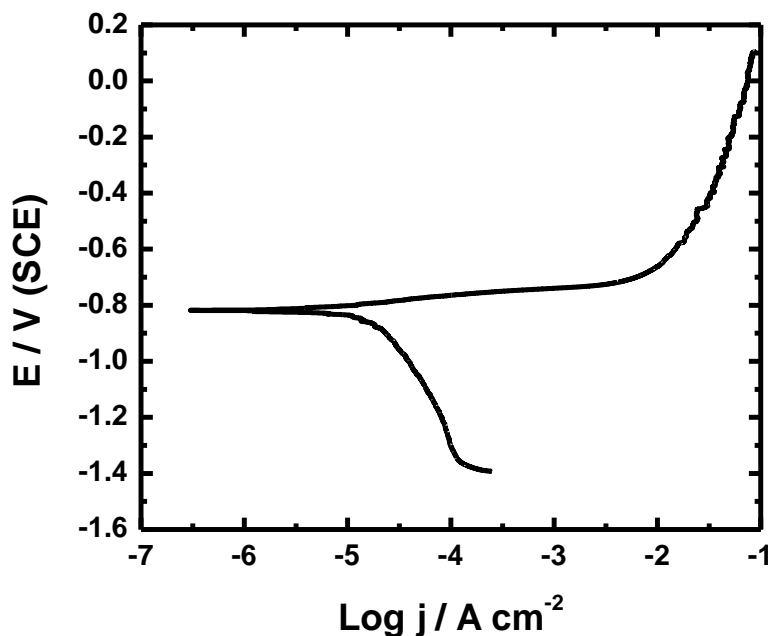


Figure 6. Potentiodynamic polarization curve in 3% NaCl for bond made using Sn-3.6Ag-1Cu interlayer at 20 minutes.

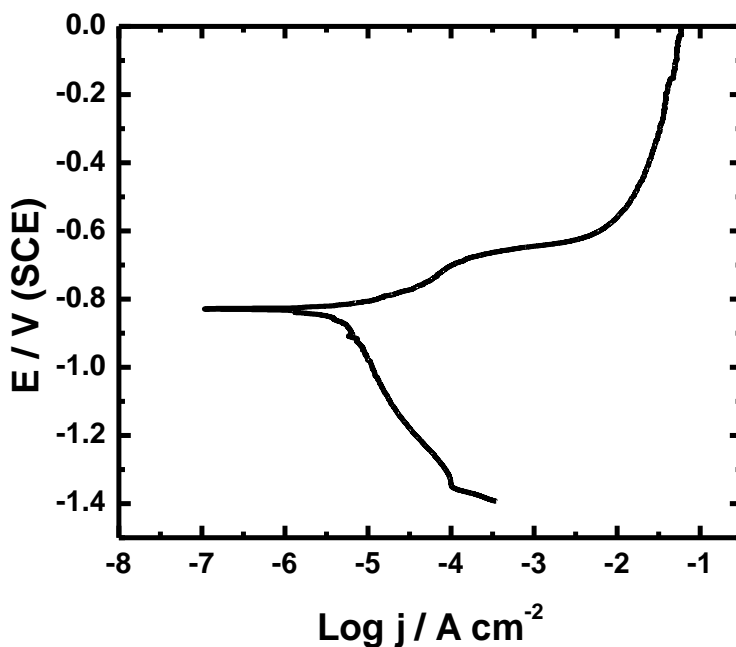


Figure 7. Potentiodynamic polarization curve in 3% NaCl for bond made using Sn-3.6Ag-1Cu interlayer at 30 minutes.

The values of β_c , β_a , E_{Corr} , j_{Corr} , R_p and R_{Corr} obtained from the polarization curves for the coupled alloys after the different bonding periods are listed in Table 2. These parameters were obtained as in the case of the individual alloys listed in Table 1. Fig. 5 clearly shows that the polarization curve of the coupled alloys is different from the polarization curves obtained for the individual alloys shown

in Fig. 1, Fig. 2 and Fig. 3. This is due to the occurrence of galvanic corrosion, which accelerated the corrosion of Al7075 alloy, while decreased the corrosion of Ti-6Al-4V alloy.

It is also seen from Fig. 6 that increasing the bonding time to 20 min decreases the corrosion of the coupled materials by decreasing the corrosion current density, j_{Corr} , and also shifting the value of E_{Corr} to the less negative direction. Further increasing the bonding time to 30, 40, 50, and 60 min decreased the corrosion by further decreasing the values of j_{Corr} and R_{Corr} , while increasing the values of polarization resistance (R_p). This effect was also noticed to decrease both the cathodic and anodic currents for the coupled alloys.

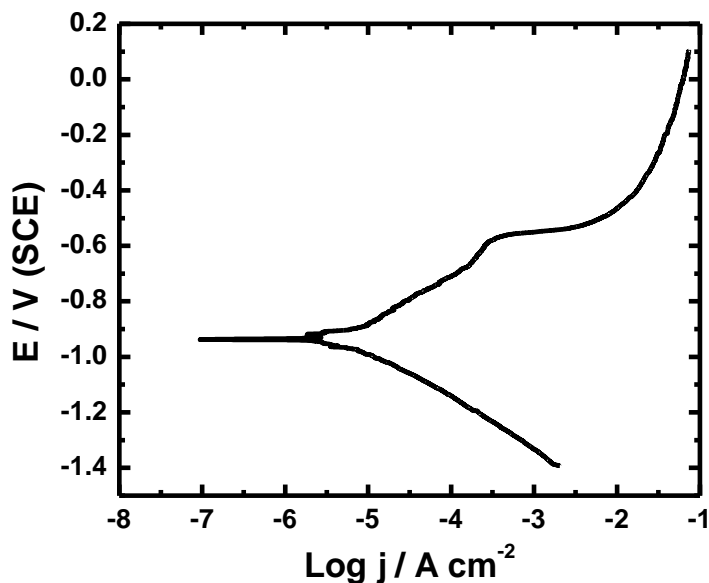


Figure 8. Potentiodynamic polarization curve in 3% NaCl for bond made using Sn-3.6Ag-1Cu interlayer at 40 minutes.

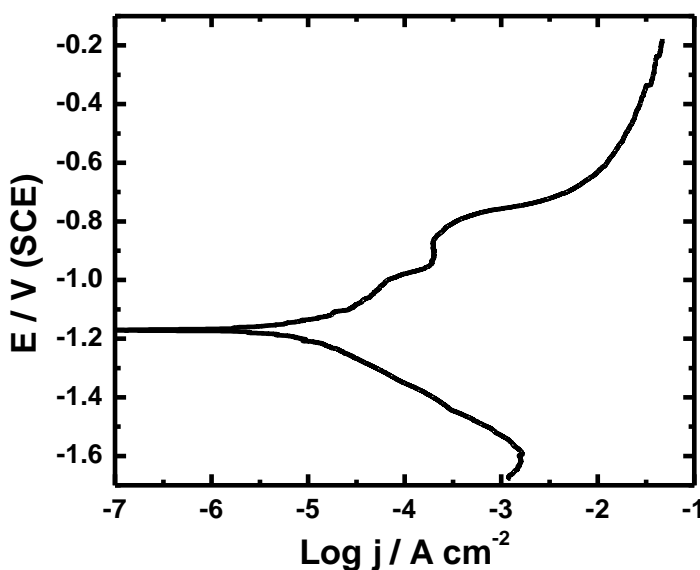


Figure 9. Potentiodynamic polarization curve in 3% NaCl for bond made using Sn-3.6Ag-1Cu interlayer at 50 minutes.

The effect of increasing the bonding time was further confirmed by the values of the corrosion parameters listed in Table 2. The values of j_{Corr} were noticed to largely decrease with increasing the bonding time and this is due to the decrease of the severity of the galvanic corrosion between Al7075 and Ti-6Al-4V alloys. As a consequence, the values of R_{Corr} also decreased and that leads in turn to increasing the values of R_p .

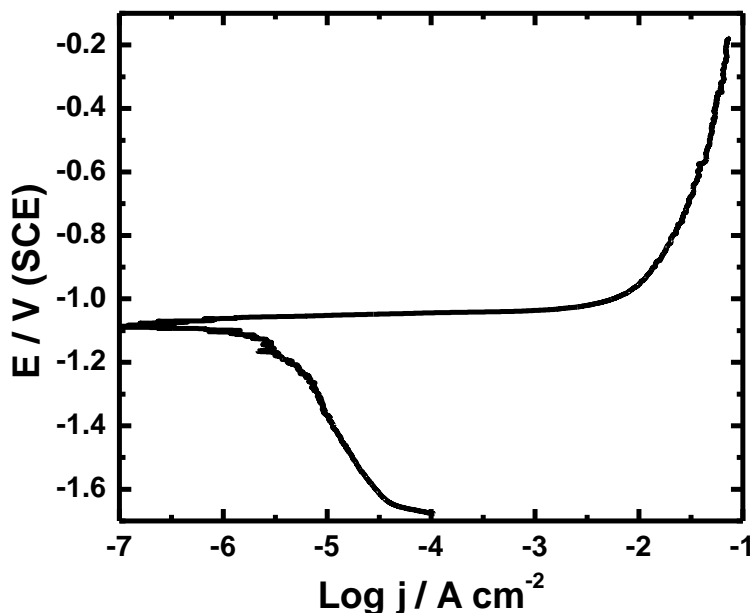


Figure 10. Potentiodynamic polarization curve in 3% NaCl for bond made using Sn-3.6Ag-1Cu interlayer at 60 minutes.

Table 2. Parameters obtained from polarization curves shown in Fig. 5 to Fig. 10 for the bond made using Sn-3.6Ag-1Cu interlayer at different periods and immersed in 3.0 wt.% NaCl solutions.

Bonding time	Polarization parameters					
	$\beta_c / \text{Vdec}^{-1}$	$E_{\text{Corr}} / \text{V}$	$j_{\text{Corr}} / \text{Acm}^{-2}$	$\beta_a / \text{V dec}^{-1}$	$R_p / \text{k}\Omega\text{cm}^2$	$R_{\text{Corr}} / \text{mmy}^{-1}$
10 min	0.320	-0.995	3.38×10^{-6}	0.110	10.530	1.7542
20 min	0.330	-0.830	3.16×10^{-6}	0.180	16.025	1.6401
30 min	0.320	0.850	2.23×10^{-6}	0.145	16.094	1.1574
40 min	0.140	-1.132	1.99×10^{-6}	0.165	16.547	1.0328
50 min	0.185	-1.175	1.99×10^{-6}	0.155	17.494	1.0328
60 min	0.220	-1.090	6.94×10^{-7}	0.060	29.534	0.3602

The best bonding time that decreased the corrosion of the coupled alloys was 60 min, where the values of j_{Corr} and R_{Corr} were the lowest and the value of R_p was the highest. This concludes that coupling the Al7075 and Ti-6Al-4V alloys by Sn-3.6Ag-1Cu interlayer leads to the occurrence of

galvanic corrosion via increasing the corrosion of Al7075 alloy and protecting Ti-6Al-4V alloy and this corrosion decreased remarkably by increasing the bonding time particularly at 60 min, which could be due to the homogenization with bonding time. However, other reasons such as phases formed at the joint and polarization effects at the joint could contribute to this behaviour. It was also noticed that there is a shift in the values of E_{Corr} to the more negative potentials, especially with the elongation of the bonding time, > 20 min. This indicates that there is a decrease in the cathodic reaction with respect to bonding time.

3.3. Corrosion behavior of the bonds made using copper interlayer and copper coating/tin based interlayer.

The potentiodynamic polarization curve for bonds made using a copper interlayer between Al7075 and Ti-6Al-4V alloys at 30 min is shown in Fig. 11. For this bonding time, a complete dissolution of the copper interlayer was obtained and duly a small quantity of copper remained at the joint region because 30 min was the optimum bonding time for diffusion bonding using copper interlayer. Also, the potentiodynamic polarization curve for bond made using copper coating together with Sn-3.6Ag-1Cu interlayer at 60 min, which was the optimum bonding time for diffusion bonding using copper coatings and Sn-3.6Ag-1Cu interlayer is shown in Fig. 12. The corrosion parameters obtained from the polarization curves shown in Fig. 11 and Fig. 12 are listed in Table 3.

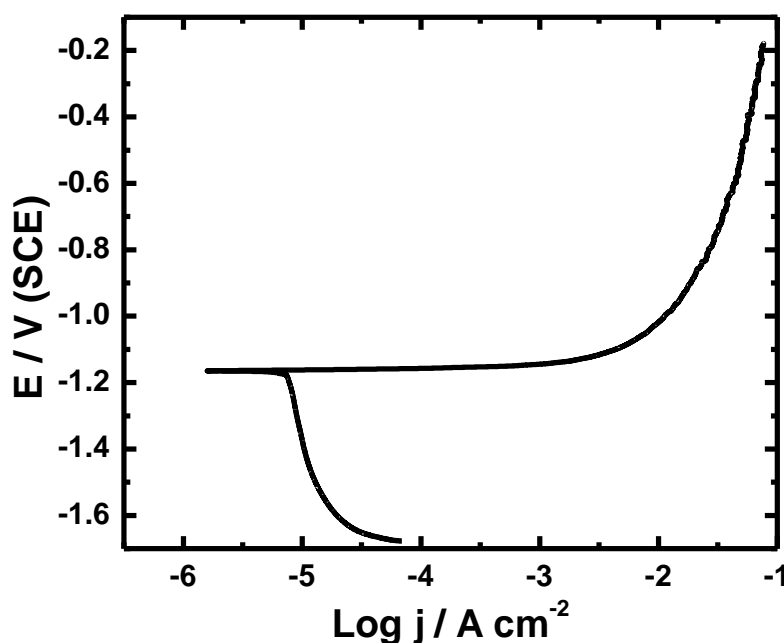


Figure 11. Potentiodynamic polarization curve in 3% NaCl for bond made using copper interlayer at 30 minutes.

It is obvious that the presence of copper increased the corrosion rate of the bonds and this was in agreement with a previous study on the effect of copper content on corrosion behaviour of 7xxx aluminum alloys [20]. The study found out that the corrosion potential increased with increasing

copper content. Also, there are two breakdown potentials; the first was corresponded to transient dissolution resulted from the attack of the fine hardening particles and the surrounding solid solution in a thin surface layer. On the other hand, the second breakdown potential was associated with combined intergranular and selective grain attack [20]. Therefore, in this work when using bonds made by either copper interlayer or copper coatings, the corrosion rate would be much higher than the corrosion rate using tin base interlayer due to the corrosive effect as a result of the diffusion of copper in Al7075 alloy. Adding the tin base (Sn-3.6Ag-1Cu) interlayer further led to more corrosion damage and this was confirmed by the parameters listed in Table 3. It is seen from Table 3 that j_{Corr} and R_{Corr} recorded higher values and lower R_p values compared to those obtained for the individual alloys (Table 1) and also in the presence of Sn-3.6Ag-1Cu interlayer without copper (Table 2).

In sea water there is a well-known series, which arranges the different metals and alloys based on the measurement of their corrosion potentials. In this series, the more noble metal will become the cathode (no dissolution), while the less noble metal will corrode and become the anode. The higher the difference in potential between the metals or alloys listed in this series means a greater degree of galvanic incompatibility when coupled. Accordingly, this series shows that titanium is nobler than copper, copper is nobler than tin, and tin is nobler than aluminum [21]. Previous work on the galvanic corrosion of the Al-Ti cell showed that the corrosion only occurred at the bondpad edge [10]. The moisture maybe trapped at the bondpad edge and enhances corrosion at this region. Therefore, there is a desire for complete contact between the joining surfaces in order to prevent voids forming at the contacting bond edges.

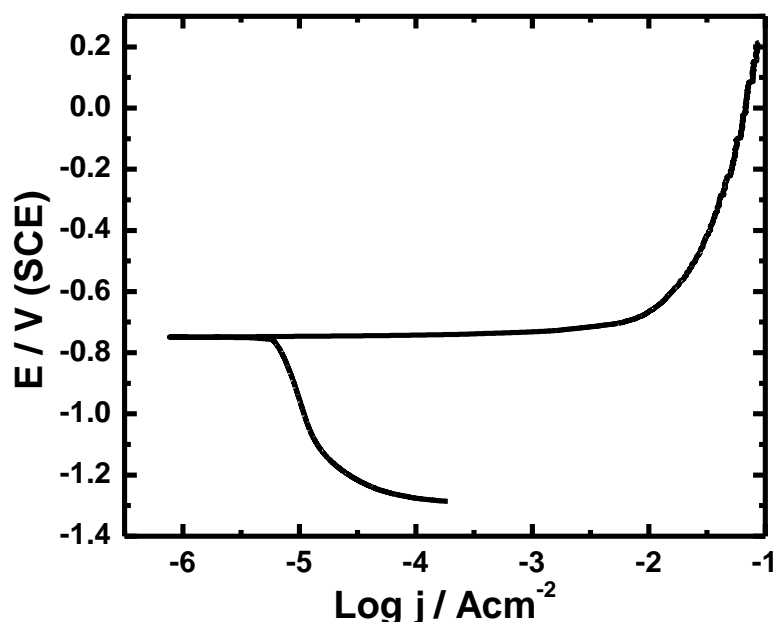
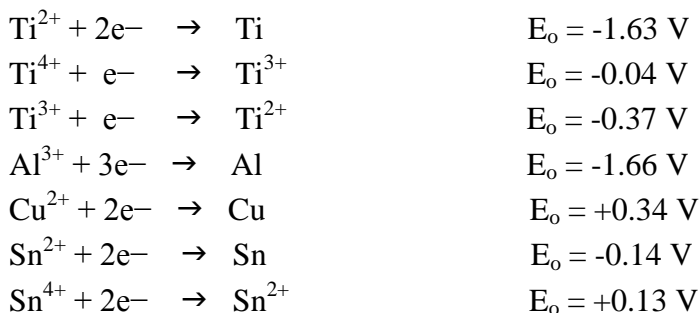


Figure 12. Potentiodynamic polarization curve in 3% NaCl for bond made using copper coatings and Sn-3.6Ag-1Cu interlayer at 60 minutes.

Titanium is a transition metal and has an electron configuration of: $1S^2 2S^2 2P^6 3S^2 3P^6 4S^2 3D^2$. Therefore, its electron configuration can give rise to possible oxidation states, namely Ti^{+} , Ti^{2+} ,

Ti³⁺ and Ti⁴⁺. The standard electrode potentials, E_o at 298 K have been established [22] and for the system in our case the values are:



The potential difference is a driving force for the corrosion process. Based on the above E_o values regarding titanium, only high oxidation states of Ti³⁺ and Ti⁴⁺ are possible and will be involved for the Ti-Al galvanic cell. For the galvanic corrosion in the Al-Ti cell, the difference of E_o value considering the Ti⁴⁺ oxidation reaction and the aluminum oxidation reaction is 1.62 V. Based on the standard electrode potentials it is predicted that aluminum will act as the anode in all bonds and this was also observed visually during the potentiodynamic polarization experiments.

Table 3. Parameters obtained from polarization curves shown in Fig. 11 and Fig. 12 for the bond made using copper and copper/tin base interlayers immersed in 3.0 wt.% NaCl solutions.

Bonding time	Polarization parameters					
	$\beta_c / \text{Vdec}^{-1}$	$E_{\text{Corr}} / \text{V}$	$j_{\text{Corr}} / \text{Acm}^{-2}$	$\beta_a / \text{V dec}^{-1}$	$R_p / \text{k}\Omega\text{cm}^2$	$R_{\text{Corr}} / \text{mmy}^{-1}$
30 min (Cu interlayer)	0.330	-1.170	7.49×10^{-6}	0.245	8.1621	3.8873
60 min (Cu/Sn base interlayer)	0.330	-1.145	7.96×10^{-6}	0.240	7.5894	4.1313

4. CONCLUSION

The potentiodynamic polarization method was applied to study the corrosion behavior of the Al7075, Ti-6Al-4V, and Sn-3.6Ag-1Cu alloys in 3.0 wt.% NaCl solutions at room temperature. The study was extended to investigate the effect of the chloride solution on the severity of the galvanic corrosion of Al7075 and Ti-6Al-4V alloys after bonding them together using Sn-3.6Ag-1Cu, copper, and copper coating incorporated with Sn-3.6Ag-1Cu interlayers at different bonding periods varied from 10 min to 60 min. It was concluded that the corrosion of the base alloys decreases in the order, Al7075 > Sn-3.6Ag-1Cu > Ti-6Al-4V, which is in a good agreement with the order of alloys in the galvanic series in sea water. Bonding the alloys using tin base interlayer for different periods led to the occurrence of galvanic corrosion due to the increased corrosion of Al7075 alloy because of being the anode and the protection of Ti-6Al-4V alloy as it behaved as the cathode. It was also found that the

increase of bonding time using Sn-3.6Ag-1Cu interlayers decreases the galvanic corrosion as a result of the chemical homogenization effect of the joint region between Al7075 and Ti-6Al-4V alloys. Moreover, the corrosion study of bonds made using copper interlayer showed that copper significantly increased the corrosion rate of the bonds, which was further increased using copper coating and Sn-3.6Ag-1Cu interlayers. This result supports the fact that the presence of copper increased the corrosion rate of the diffusion bonds of Al7075 alloy to Ti-6Al-4V alloy. Therefore, these results suggest that the corrosion resistance of joints made between Al7075 to Ti-6Al-4V using Sn-3.6Ag-1Cu interlayer is the most preferable with respect to good resistance to corrosion.

ACKNOWLEDGEMENTS

This project was supported by NSTIP strategic technologies program number (11-ADV1853-02) in the Kingdom of Saudi Arabia.

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