

Corrosion behaviour of electrochemically joined aluminum and stainless steel

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Two dissimilar metals *viz.*, aluminum and stainless steel (SS) were joined electrochemically by heavy nickel deposition. Potential-time behavior, Tafel extrapolation method and galvanic coupling experiments were conducted to study the corrosion behavior of the three individual metals in 5% aqueous sodium chloride acidified with acetic acid, alone and in combination. The systems behaved differently in simple immersion test and on coupling with each other. In simple immersion test, nickel and SS were nobler to aluminum. Coupling of aluminum and nickel (bi-metallic) resulted in dissolution of both metals, the rate of nickel being lower. Potentiodynamic polarization experiments showed that the aluminum-SS bi-metallic system has the highest corrosion rate than aluminum-Ni or SS-nickel. Aluminum exhibits pitting type corrosion when coupled to nickel. Experiments with electroplated specimens and SEM analysis confirmed that in aluminum-nickel couple both metals corrode, the corrosion of nickel being considerably lower. Formation of elemental nickel on aluminum surface also confirmed the above result.

Keywords: Electrochemical joining, mass loss, corrosion current, galvanic couple, polarization technique

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Electrochemical joining of dissimilar metals is preferred when two difficult-to-plate metals need to be joined. In this context, conventional joining methods are not suitable due to metallurgical incompatibility. Since electroplating process can be done at room temperature, problems due to shrinkage stresses and distortions, associated with high temperature joining operations, are eliminated¹. The properties of the joints can be tailored to meet specific requirements and can be used on components of any size and shape². Because of these advantages, this method is gaining popularity in aerospace and nuclear programs, for example in heat shields, missile nose cone protection during reentry, solid motor cases with propellant grain insulation and nozzle system grown in place, jet nozzles with fuel partitions grown in place, linear accelerator structures with copper discs for regulating purposes and so on. Large diameter (1 meter) rings of 6061-T6 aluminum alloy have been joined to AM 363 stainless steel rings and are used for commercial production in some countries.

In the project on electrochemical joining for space applications, heavy nickel deposition was used to join aluminum and stainless steel, adopting suitable pre-

plating procedures and the strength of the joints were evaluated³. Determining the corrosion behaviour of such a tri-metallic joint needed special consideration since each metal will be influencing the corrosion behaviour of the other. So, corrosion of three different metals was studied individually and in combination with another metal and as three systems together, in a similar manner as reported earlier⁴. This paper presents the results of these studies.

Experimental Procedure

Corrosion experiments were conducted in aqueous 5% sodium chloride electrolyte acidified to pH 3 with glacial acetic acid. This solution is universally accepted for accelerated corrosion testing for electroplated nickel^{5,6} and hence should have strong corrosive effect on nickel. Since, the ultimate aim of the paper is to evaluate behaviour of the plated materials, this solution was chosen for the studies.

For open circuit potentials measurements aluminum (6061-T6) (Al), stainless steel (AISI type 316) (SS) and nickel (electrolytic) sheet (Ni) specimens of 1 inch² surface area were exposed as individual study metals in the above medium for 168 h, with potential monitoring after every 20h and finally estimating the weight loss of the metals in milligrams/day/square decimeter (mdd).

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In a separate experiment, the metals were coupled as Al-Ni, SS-Ni, and SS-Al and their mixed potentials with time and weight loss were estimated as above.

Galvanic current prevailing between the two coupled metals and three coupled metals (each 1 inch² exposed area) were monitored using a Zero Resistance Ammeter (ZRA) in the same electrolyte and the experiments were conducted for 168 h. The potential and current values were recorded.

For corrosion current density determinations, an electrochemical analyzer (Ecochemie auto lab 100 Potentiostat/galvanostat, Netherlands) was used. The individual metals in the above test medium were polarized from the open circuit potential (OCP) by about 200 mV on cathodic as well as anodic side at the rate of 10 mV/sec. A platinum foil and SCE were used as the auxiliary and reference electrodes respectively. The linear segments of the anodic and cathodic branches were extrapolated to OCP and from the Tafel slopes of the individual metals the corrosion current density i_{corr} and corrosion potentials E_{corr} were estimated.

In the same way, the above values were determined also for the bimetallic system in which 1 cm² of each electrode (total 2 cm² exposed area) was externally connected in the above test medium and treated as the working electrode.

Experiments were conducted to determine the i_{corr} and E_{corr} values in the above medium on nickel electroplated aluminum/stainless steel exposing 0.5 cm² each of nickel plated portion and the unplated portion on aluminum or stainless steel. Finally, the three metal systems viz., electrochemically joined SS and aluminum flats with nickel were treated as working electrodes and tested for their corrosion behaviour.

All experiments were conducted under quiescent condition and at room temperature. The schematic diagram of the circuits used in this study is shown in Fig. 1.

The corroded specimens were examined for their surface topography using Scanning Electron Microscope, to confirm the findings.

Results

In the open circuit potentials measurements of aluminum, SS and nickel in 5% NaCl solution acidified with acetic acid (pH 3.0), aluminum exhibited the least potential among the three followed by nickel. SS exhibited the highest values. At the end

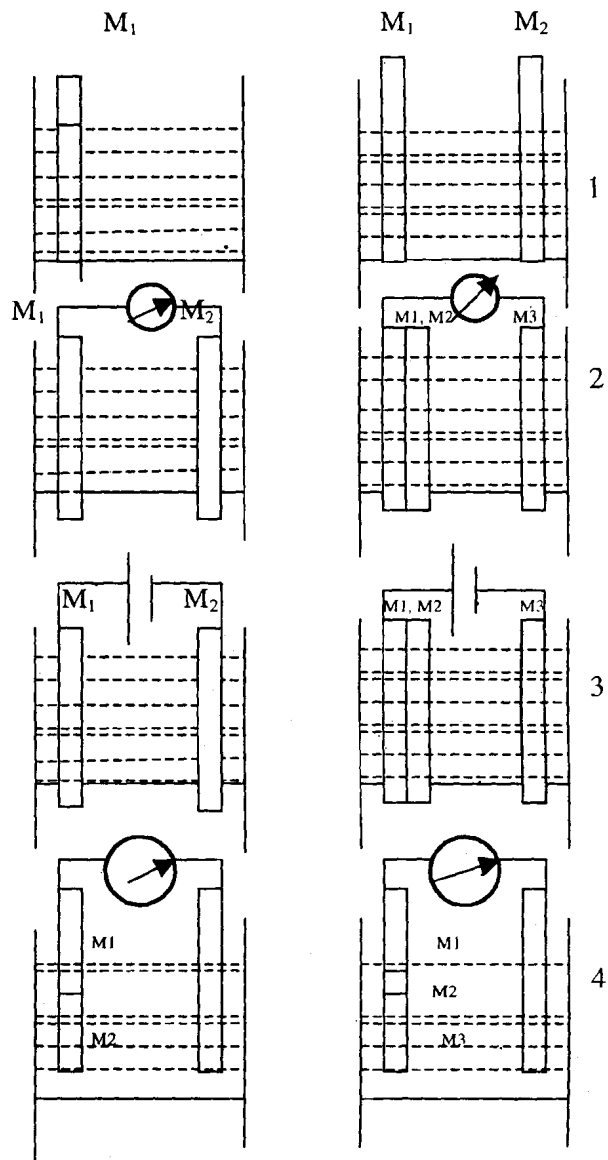


Fig. 1—Schematic diagram for the circuits used for the study (1) immersion (2) galvanic coupling study of bi and trimetallic systems (3) potentiodynamic polarization study of single and bimetallic system (4) potentiodynamic polarization study of plated systems.

of 168 h, nickel exhibited highest corrosion rate followed by aluminum. SS was found to possess least corrosion rate (Table 1).

Open circuit potentials of bimetallic couples were followed for 168 h. Aluminum-nickel, and aluminum-SS when immersed together showed almost the same behaviour. Their mixed potentials were in the range of -750 to -800mV whereas nickel-SS system exhibited the mixed potential of -0.27 at the time of start but decreased to -300mV in 35 h and got stabilized

around this value. This suggested that in aluminum-nickel and aluminum-SS systems, aluminum dissolved in preference and controlled the mixed potential value whereas in SS-nickel system, nickel dissolved preferentially.

In aluminum-nickel system, nickel showed a negative value for mass gain, which can be taken as no loss whereas aluminum exhibited a corrosion rate of 70.87 mdd. This suggested that in aluminum-nickel system aluminum acted anodically (Table 1). In presence of SS, aluminum experienced corrosion rate of 116.3 mdd and SS a negative value that can be assumed as no loss. In SS-nickel system nickel dissolved with a corrosion rate of 45.4 mdd and SS experienced negative rate that can be taken as no loss. Surface examinations of the nickel surface indicated pitting⁷ and that of aluminum surface, uniform dissolution (Fig. 2).

Figure 3 presents the variation of mixed potential values versus SCE and galvanic current of the aluminum-nickel couple (aluminum connected as anode and nickel as cathode) with time. The mixed potential, which was $-0.66V$ at the start gradually decreased with time and reached $-1.52V$ in 75 h and then showed oscillations representing onset of passivity followed by trans-passivity. In a Zero Resistance Ammeter (ZRA), to measure absolute current values the resistance of the system must be reduced to a minimum and this imposes some potential on the electrodes. Hence the measured galvanic potential would not be the correct one for drawing any conclusion. The galvanic current, which registered a slightly positive value at the start, decreased gradually, reached a negative value with a rapid decrease after 130 h. Both nickel and aluminum were found to experience corrosion rates of 468.66 and 343.08 mdd respectively (Table 2). When the current density prevailed at each electrode was calculated using this value, it was observed that the average current density at aluminum was around 3 mA/cm^2 and that at nickel was around 0.178 mA/cm^2 .

When nickel was coupled to SS, the mixed potential that was positive at the start, progressively decreased with time and reached $-0.41V$ at the end of 168 h, which corresponds to the open circuit potential of nickel suggesting a gradual increase in dissolution of nickel (Fig. 4). This was confirmed by corrosion rate measurements given in Table 2.

Table 1— Open circuit potentials of various systems in acidified 5% sodium chloride

System	Open circuit potential (mV Vs SCE)		Corrosion rate (mdd)
	Start potential	Potential after 168 h	
Nickel	-240	-335	75.53
SS	-70	-155	0.433
Aluminum	-770	-865	21.48
SS-nickel	-27	-357	Ni 45.4; SS -2.66
Aluminum-nickel	-756	-796	Al 70.87; Ni -5.98
SS-aluminum	-754	-784	Al 116.3; SS -5.76

Table 2— Galvanic behaviour of various systems coupled to nickel in acidified 5% sodium chloride

System	Potential (mV Vs SCE)		Corrosion rate (mdd)
	Initial	Final	
SS-nickel	33	-414	Ni 53.4; SS -0.89
Aluminum-nickel	-661	-1279	Ni 468.66; Al 343.08

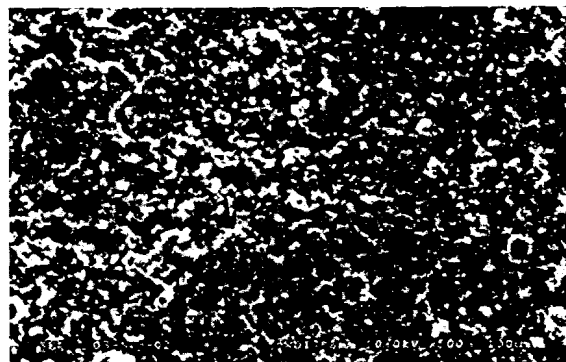


Fig. 2—SEM micrograph showing corrosion of aluminum after immersion test.

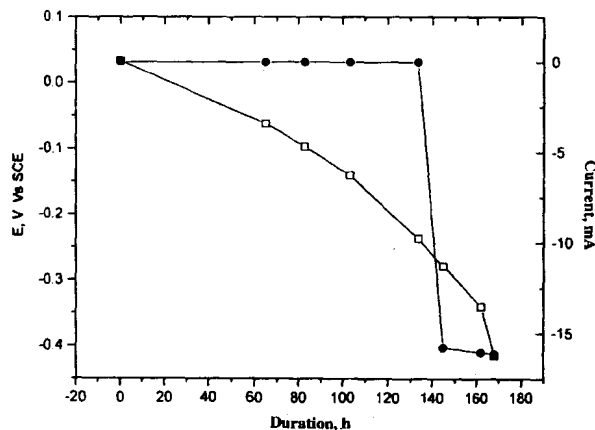


Fig. 3—Galvanic current and potential measurements for Aluminum versus Nickel in acidified 5% sodium chloride. (□) Potential (•) Current.

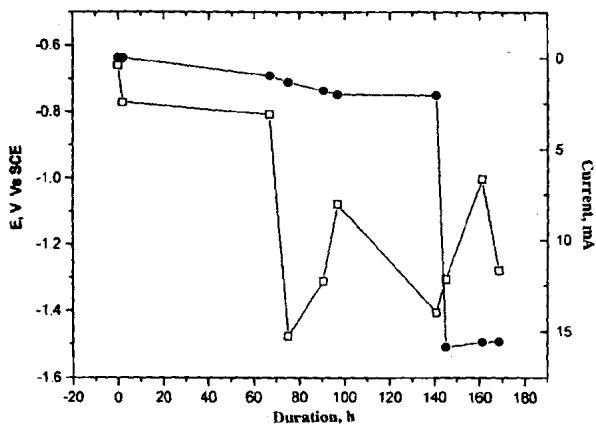


Fig. 4—Galvanic current and potential measurements for SS versus Nickel in acidified 5% sodium chloride. (□) Potential (•) Current.

Table 3—Parameters derived from polarization curves for the corrosion of various systems in acidified 5% NaCl

System	E_{corr} mV vs SCE	Tafel slopes mV/decade		Corrosion current density $\mu\text{A}/\text{cm}^2$
		Anodic	Cathodic	
SS	-417	40	40	0.35
Nickel	-425	50	40	15.0
Aluminum	-795	50	50	900
Aluminum-nickel	-770	30	30	870
Aluminum-SS	-785	30	30	1250
Nickel-SS	-420	50	40	8

Figure 5a-c presents the potentiodynamic polarization curves for aluminum, nickel and SS in acidified 5% NaCl solution (against platinum counter electrode). Aluminum exhibited highest corrosion current density followed by nickel and SS (Table 3).

The potentiodynamic polarization curves for bimetallic systems are given in Fig. 6a-c (against platinum counter electrode). Aluminum-SS couple showed highest corrosion current density. Aluminum-nickel couple exhibited moderate, while SS-nickel couple the least corrosion current density. The corrosion potentials recorded for Al-SS and Al-Ni couples corresponded to that of aluminum while for Ni-SS couple it was nearer to that of nickel (Table 3).

Figure 7a-c presents the polarization curves for electroplated nickel with other metallic couples. Nickel plated aluminum exhibited a corrosion current density of $70 \mu\text{A}/\text{cm}^2$ while nickel plated SS offered more than ten times less corrosion current density. When aluminum and SS were joined by heavy nickel

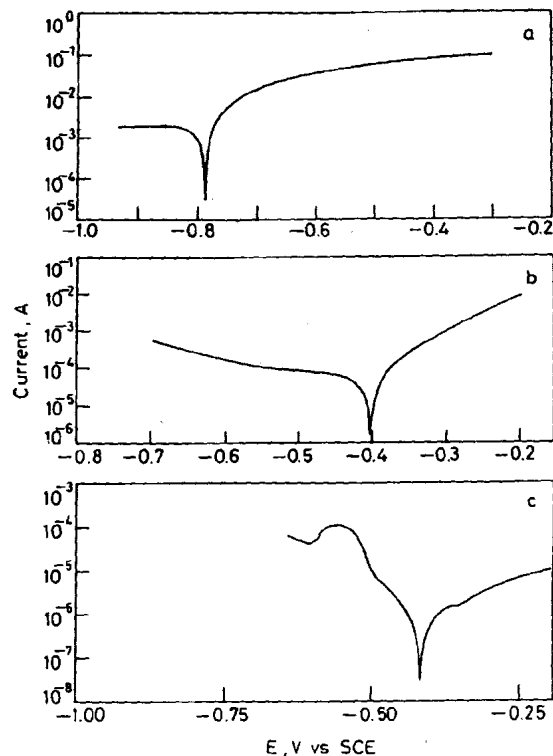


Fig. 5—Potentiodynamic polarization behaviour of (a) Al (b) Nickel (c) SS in the above medium with Platinum counter electrode, Scan rate 10mV/s.

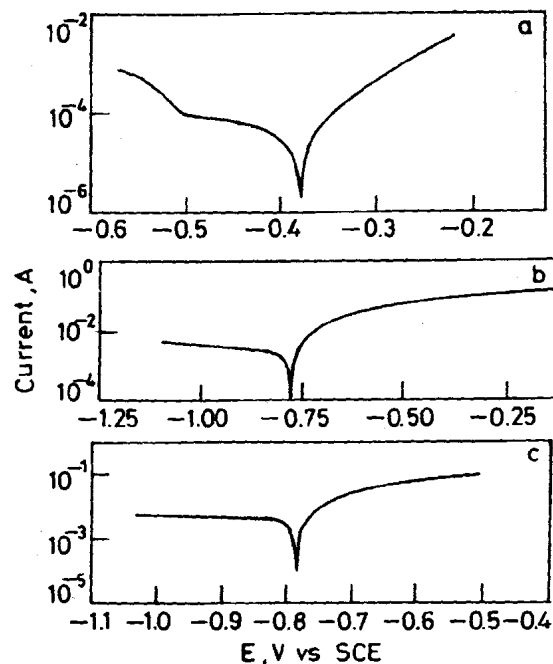


Fig. 6—Potentiodynamic polarization behaviour of (a) SS-Ni (b) Al-Ni (c) SS-Al in the above medium with Platinum counter electrode, Scan rate 10 mV/s.

electro deposition, the corrosion current density recorded was $150 \mu\text{A}/\text{cm}^2$ (Table 4).

The nickel-plated aluminum surface showed corroded portions of both the metals. Pitting and non-uniform etching along with the precipitation of elemental nickel was observed on aluminum while uniform corrosion with corrosion products are observed on nickel (Fig. 8a & b).

Discussion

It is well known that when couples/joints of galvanically dissimilar metals are exposed to a corroding medium, the nobler metal gets cathodically protected at the expense of the baser member provided their corrosion potentials are sufficiently apart. Associated cathodic current polarizes both members. Their compromise potential is governed predominantly by anodically dissolving baser member of the coupled joint. However, concentrations of ionic species in contact with the surfaces of bi/tri-metallic couples exposed to corrosive medium, polarization

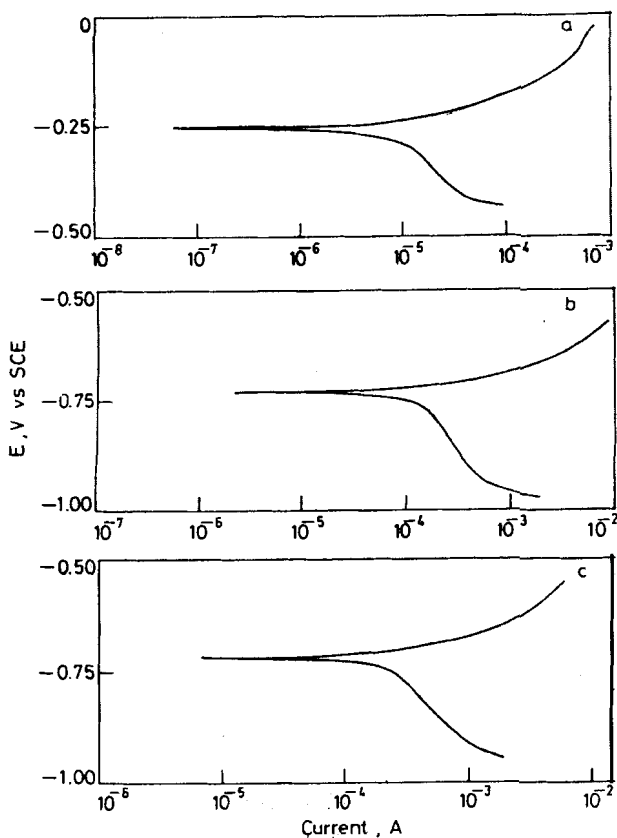


Fig. 7—Potentiodynamic polarization behaviour of nickel-plated (a) SS (b) Al (c) SS-Al joined by nickel with platinum counter electrode, Scan rate 10 mV/s.

Table 4—Parameters derived from E-logi curves for the corrosion of various plated systems in acidified 5% NaCl

System	E_{corr} , mV vs SCE	Tafel slopes mV/dec		I_{corr} $\mu\text{A}/\text{cm}^2$
		Anodic	Cathodic	
Ni deposited SS	-250	59	59	6
Ni deposited Al	-750	39	46	70
Al-SS (joined) by nickel deposit	-740	52	30	150

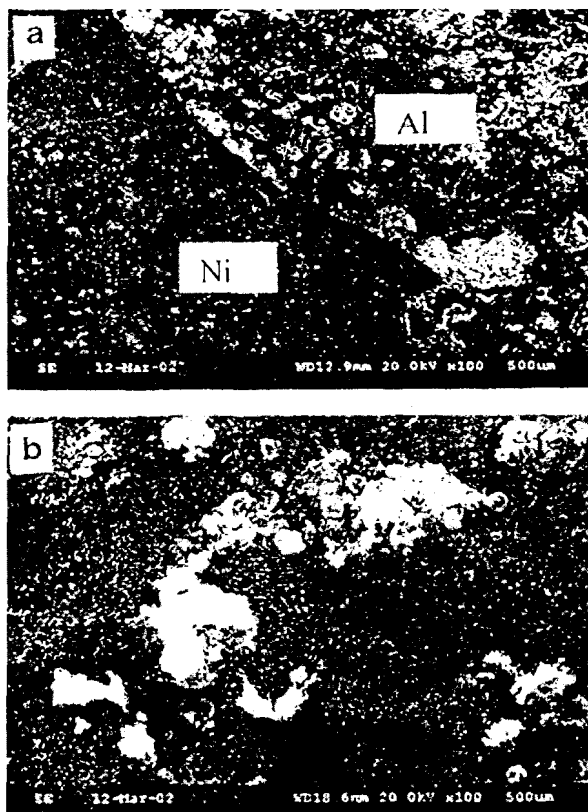


Fig. 8—SEM micrographs of (a) nickel-plated Al showing corrosion products on both metals; pitting type corrosion in aluminum and precipitated elemental nickel; (b) nickel-plated aluminum showing non-uniform etching and nickel corrosion products.

behaviour of the concerned metals, as well as associated IR drop etc, also contribute to the overall compromise potential and corrosion rate. Preferential greater corrosion rate of the anodic member includes contributions from the factor of associated activation and concentration polarization and also of the nature of the thin-filmed cathodic surface^{8,9}.

Results obtained in immersion tests as single metal as well as in combination indicate that aluminum is the most reactive metal of the three and SS is the least. Even in presence of another metal like SS or

nickel, aluminum functions as the anodic material and undergoes weight loss which is more in presence of SS than nickel. This can be understood by the difference in their open circuit potentials, which is more between aluminum and SS than Al and nickel.

In galvanic coupling experiment, aluminum-nickel couple showed mixed potential which corresponds to aluminum but showed oscillations. The current registered was very low initially and showed a steep increase after 130 h. This suggested that when aluminum and nickel are coupled, the mixed potential at the initial stages was not sufficient to protect nickel so that both metals underwent dissolution till a value sufficient to protect nickel cathodically is reached. Black smut of elemental nickel formed on aluminum after the experiments confirmed the dissolution of both metals. In the case of SS-nickel the potentials are well separated so that nickel alone showed dissolution.

In potentiodynamic polarization studies in acidified 5% NaCl solutions, at pH 3 the most common cathodic reaction is hydrogen evolution. In a quiescent electrolyte, the hydrogen evolution is under diffusion control and the corrosion of a metal is mainly decided by its anodic reaction.

In aluminum-SS couple, though both are oxide-forming materials, the film on SS is more strong making aluminum to corrode faster. In aluminum-Ni couple, the observations in open circuit potential measurements do not agree with those of galvanic coupling where both metals exhibited weight loss. It could be inferred that in immersion testing, the metals are not connected and in polarization studies while scanning the potential some anodic current is impressed on the electrodes. But, in galvanic coupling both metals are electrically connected without applying any current and the current prevailing is only the corrosion current. Moreover, in the latter case, nickel is the counter electrode whereas in polarization studies the metals under study are treated as bi-electrodes with platinum counter electrode. In polarization studies, the weight loss experienced by each metal was not estimated since the duration is small. From this it can be concluded that in a nickel-aluminum couple, particularly in acidified sodium chloride, there is a possibility for dissolution of nickel also with a considerably low current compared to aluminum due to the inadequate protection offered. The dissolution of nickel is

confirmed by the presence of elemental nickel on aluminum surface after the test. SEM micrographs of the surface of a tri-metallic system of aluminum-SS joined by heavy nickel electro-deposition further support this behaviour.

Conclusion

The corrosion studies of aluminum, SS and nickel in acidified sodium chloride solution as individual, bimetallic and trimetallic systems indicated that in nickel-SS and aluminum SS couples SS remains protected allowing nickel or aluminum to corrode. Aluminum-nickel couple also showed dissolution of aluminum in immersion as well as potentiodynamic polarization tests. However, galvanic coupling experiments followed by weight loss measurements indicated noticeable but less significant corrosion of nickel also along with aluminum indicating that in this test media the protection offered by aluminum to nickel is marginal. The results are confirmed by surface examination also.

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