

CORROSION BEHAVIOUR OF ELECTROCHEMICALLY JOINED ALUMINUM AND TITANIUM

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ABSTRACT

Two dissimilar metals, viz. aluminum and titanium, 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 titanium 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-titanium bi-metallic system has higher corrosion rate than aluminum-nickel or titanium-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, corrosion current, galvanic couple, polarization technique.

INTRODUCTION

Electrochemical joining of dissimilar metals is preferred when two difficult-to-plate metals need to be joined. In this context, conjoining 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 eliminated. The properties of the joints can be tailored to meet specific requirements and can be used on components of any size and shape [1,2]. Because of these advantages, this method is gaining popularity in aerospace and nuclear programs. for example in heat shields, for 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 our project on electrochemical joining for space applications, heavy nickel deposition was used to join aluminum and titanium, adopting suitable pre-plating procedures and the strength of the joints were evaluated [3]. Defining the corrosion behavior of such a tri-metallic joint needed special consideration since each metal will be influencing the corrosion behavior of the other. So, corrosion of three different metals was studied individually and in combination with another metal and as three system, together, in a

SCHEMATIC DIAGRAM OF THE CIRCUITS USED

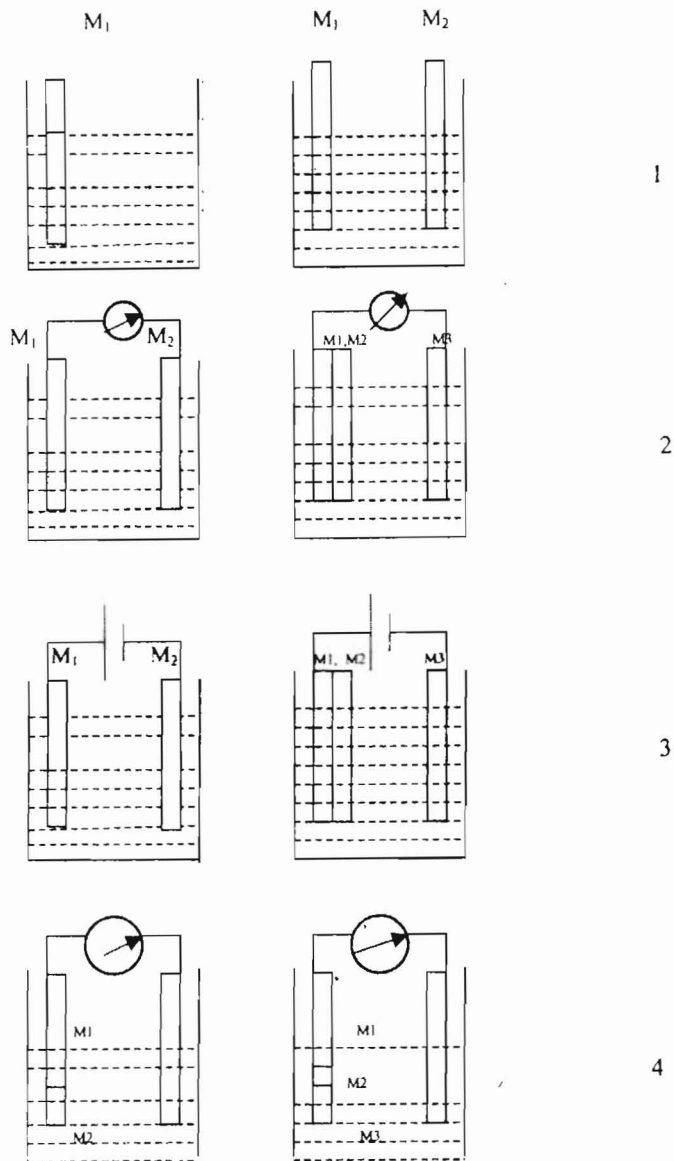


Fig 1 : Schematic diagram for the circuits used for the study (1) immersion (2) galvanic coupling study of bi and trimetallic systems (3) potentiodynamic polarization study of single and bimetallic system (4) potentiodynamic polarization study of plated systems.

similar manner as reported earlier [4]. This paper presents our recent observations.

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 the behaviour of the plated materials, this solution was chosen for the studies.

For open circuit potentials measurements aluminum (6061-T6) (Al), titanium (ASTM Grade II) (Ti) 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 corrosion rate from the weight loss of the metals [7].

In a separate experiment, the metals were coupled as Al-Ni, Ti-Ni, and Ti-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 hours. The potential and current values were recorded in these experiments also.

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 slope 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 / titanium exposing 0.5 cm² each of nickel plated portion and the unplated portion on aluminum or titanium. Finally, the three metal systems viz., electrochemically joined titanium and aluminum Ti-Al flats with nickel were treated as working electrodes and tested for their corrosion behavior.

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

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 Hrs	
Nickel	-240	-335	75.53
Aluminum	-770	-865	21.48
Titanium	-147	-322	0.87
Aluminum-Nickel	-756	-796	Al 70.87; Ni 5.98
Ti-Ni Couple	-27	-394	Ni 40.4; Ti 5.97

Table 2 - Galvanic Behavior of Various Systems Coupled to Nickel in Acidified 5% Sodium Chloride

System	Cell Voltage (mV)		Corrosion rate (mdd)
	Initial	Final	
Nickel	-240	-335	75.53
Aluminum	-770	-865	21.48
Titanium	-147	-322	0.87
Aluminum-Nickel	-756	-796	Al 70.87; Ni 5.98
Ti-Ni Couple	-27	-394	Ni 40.4; Ti 5.97

RESULTS

In the open circuit potentials measurements of aluminum, titanium and nickel in 5% NaCl solution acidified with acetic acid (pH 3.0), aluminum exhibited the least potential among the three followed by nickel. Titanium exhibited the highest value initially which decreased considerably after 168 h. and reached value similar to nickel. At the end of 168 h, nickel exhibited highest average corrosion current followed by aluminum. Titanium was found to show least corrosion current (Table 1).

Open circuit potentials of bimetallic couples were followed for 168 h. Aluminum-nickel showed a mixed potential of around -750 to -800mV where as nickel-titanium system exhibited the mixed potential of -0.27 at the time of start but decreased to -300mV in 35h and got stabilized around this value. This suggested that in aluminum-nickel system aluminum dissolved in preference and in aluminum-titanium system, nickel dissolved in preference and controlled the mixed potential value. Aluminum- titanium system showed an erratic behavior.

In aluminum-nickel system, nickel showed a negligible mass gain, which can be taken as no loss where as aluminum exhibited a corrosion rate of 70.87 mdd. This suggested that in aluminum-nickel system aluminum acted anodically (Table. 1). In presence of titanium, nickel experienced corrosion rate of 40mdd and titanium a negligible value of around 5mdd.

Table 2 presents the variation of galvanic 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 tranpassivity. 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 hours. When the current rate prevailed at each electrode was calculated using this value, it was observed that the average current rate at aluminum was around 468mdd and that at nickel was around 343 mdd (Table 2).

Table 3 presents the potentiodynamic polarization data for aluminum, nickel and titanium

Table 3 - Parameters derived from E-Log I Curves for the corrosion of variuos systems in Acidified 5% NaCl

System	E_{corr} mV Vs SCE	Tafel Slopes Anodic Cathodic mV/dec		Corrosion current density $\mu\text{A}/\text{cm}^2$	
		Anodic	Cathodic	Anodic	Cathodic
Al	-795	50	50	900	900
Ti	-100	50	60	0.8	0.8
Ni	-405	50	40	15.0	15.0
Ti-Ni	-400	40	30	12.5	12.5
Al-Ni	-770	30	30	870	870

Table 4 - Parameters Derived from E-Logi Curves for the corrosion of various systems in Acidified 5% NaCl

System	E_{corr} mV Vs SCE	Tafel Slopes mV/dec		Corrosion current density $\mu\text{A}/\text{cm}^2$	
		Anodic	Cathodic	Anodic	Cathodic
Ti-Ni deposited	-250	107	65	1.0	1.0
Al-Ni deposited	-750	39	46	70	70
T-Al Ni-deposited	-720	52	50	140	140

in acidified 5% NaCl solution (against platinum counter electrode). Aluminum exhibited highest corrosion current density followed by nickel and titanium (Table 3). The potentiodynamic polarization data for bimetallic systems are given in the same table (against platinum counter electrode). Aluminum-nickel couple showed highest corrosion current density while titanium-nickel couple exhibited a moderate value. The corrosion potentials recorded for Ti-Ni and Al-Ni couples corresponded to that of nickel and aluminum respectively.

Table 4 presents the polarization data for electroplated nickel with other metallic couples. Nickel plated aluminum exhibited a corrosion current density of $70\text{mA}/\text{cm}^2$ while nickel plated titanium offered only $1.0\text{mA}/\text{cm}^2$. When aluminum and titanium were joined by heavy nickel electrodeposition, the corrosion current density recorded was $140\text{mA}/\text{cm}^2$ (Table 4).

DISCUSSION

It is well known that when couple 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 the 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 behaviour of the concerned metals, as well as associated IR drop

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 titanium is the least. Even in presence of another metal like titanium or nickel, aluminum functions as the anodic material and undergoes weight loss which is more in presence of titanium than nickel.

In galvanic coupling experiment, aluminum- nickel couple showed mixed potential which corresponds to aluminum. 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 titanium nickel the potentials are well separated and titanium easily forms oxide so that nickel showed higher 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-titanium couple, though both are oxide-forming materials, the film on titanium is more strong making aluminum to corrode faster. In aluminum-nickel 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 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 bielectrodes with platinum counter electrode. Moreover, in polarization studies, the weight loss experienced by each metal was not estimated source the duration is small. From this we can conclude 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.

CONCLUSION

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

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ENGINEER'S GUIDE TO SPRAY TECHNOLOGY AND NOZZLES

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The guide describes spray characteristics and patterns. This is followed by descriptions of key performance considerations, including nozzle capacities, pressure drops, spray angle and coverage, spray drop size, impact, operating pressure and specific gravity. Nozzle wear, materials of construction of nozzles as well as factors affecting spray nozzle performance are described in a simple manner.

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