THE OPTIMAL CORROSION INHIBITION OF ALUMINUM IN 0.1M NaCl SOLUTION

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ABSTRACT

The central composite rotable design technique was employed to investigate the influence of time of immersion and the ratio of $CoCl_2/NiCl_2$ blend as inhibitor on the corrosion behavior of aluminum alloy in 0.1 M air-saturated NaCl solution. The experimental results yielded the following coded 2nd order equation with a correlation coefficient of 0.97, and F-value = 16.7.

$$CR\ (gmd) = 0.045 - 0.045X_1 + 0.025X_2 - 0.035X_1X_2 + 0.13X_1^2 - 0.007X_2^2$$

The effect of time of immersion and inhibitor concentration ratio was found to decrease the corrosion rate leading to a minimum rate under certain operating conditions.

INTRODUCTION

One of the main types of corrosion that is commonly found in aluminum is the pitting corrosion. Its occurrence can be lowered or minimized in many ways: improved design of components, increasing the purity of the metal, and alter the solution. The last possible way is the limiting step in our case. If it is not possible, then the solution must be modified by the use of inhibitors[1,2].

The chemicals used as inhibitors in corrosion inhibition may be either anionic or cationic components, the anionic can function through the formation of an insoluble precipitate or storing electron coordination bonding of an adsorbed film[3]. Chemical cationic inhibition has also along history, beginning from the early work of Evans[4], with zinc cations, followed by others[5,6], to study a range of metal cation known to produce insoluble hydroxides.

Few workers have studied the chemical inhibition of aluminum alloys. Bird and Evans[7], have reported that ferrous salts were effective in corrosion inhibition of Al-Mg alloys in NaCl solution media. Others[3] have found that the AA aluminum alloy is inhibited by the addition of ferrous chloride to the solution.

The aim of the present work is to investigate the corrosion inhibition of the AA7075 aluminum alloy in sodium chloride solution by the addition of a blend of $CoCl_2$ and $NiCl_2$ as ratio's to the environment, for different times of immersion, besides their simultaneous effect (i.e., inhibitor concentration and time) on the corrosion rate using central composite rotatable design (CCRD) technique[9,9].

EXPERIMENTAL WORK

High strength AA7075 aluminum alloy having the following chemical composition (in wt.%) was used: Si (0.4%), Fe (0.5%), Mn (0.3%), Mg(2-2.9%), Cr (0.18-0.28%), Zn (5-6.1%), Ti (0.2%), and the remainder Al (90.32%).

Specimens about 3 x 1 x 0.33 cm were cut from the aluminum alloy with a small hole about 1 mm OD near the 1 cm side end for suspending.

The specimens were first degreased with analar benzene and acetone, then abraded in sequence under running tap water using emery paper of grade Nos., 220, 320, 400, and 600 then washed with running tap water followed by distilled water, dried with clean tissue, immersed in acetone and benzene, dried again, kept in a disicator over silica gel until using. The dimensions of each sample were measured with a digital vernier to 2nd decimal of millimeter and accurately weighted to the 4th decimal of gram.

Weight losses were determined after the removal of the corrosion products in chromic-phosphoric acid solution, as outlined in ASTM-G1-1972[4]. All tests were conducted in 0.1 NaCl solution with diffeent ratios of Co^{+2}/Ni^{+2+} ranging from (0-1) added to the solution as $CoCl_2$ and $NiCl_2$.

Constant immersion conditions were obtained by suspending the specimen on nylon thread in 100 cm^3 of salt solution exposed to laboratory air.

RESULTS AND DISCUSION

The investigation was started by experimenting in stationary at different times of immersion (i.e., 3-15 day). The results obtained as corrosion rate (g/m^2.day) versus time are shown in Fig. (1), which reveal a decrease in corrosion rate of AA7075 aluminum alloy in 0.1 M NaCl with time generally in uninhibited solutions.

The second step of the experimentation was performed in order to evaluate the simultaneous effect of time and inhibitor concentration on the corrosion behavior of the aluminum alloy. The program was executed in three sequential parts following the method of central composite rotatble design as shown in Table (1).

The data obtained were analyzed by regression the corrosion rates against time of immersion and inhibitor blend concentration[10].

Table (1) Results of corrosion experiments of Al-alloy in 0.1 M NaCl according to CCRD method

Run No.	Coded variables		Real variables		CR (gmd)
	X_1 (day)	X_2 (Co/Ni)	X_1 (day)	X_2 (Co/Ni)	
1	-1	-1	4.76	0.146	0.2040
2	-1	+1	4.76	0.854	0.3530
3	+1	-1	13.2	0.146	0.0565
4	+1	+1	13.2	0.854	0.0661
5	-1.414	0	3	0.5	0.388
6	+1.414	0	15	0.5	0.2139
7	0	-1.414	9	0	0.0138
8	0	+1.414	9	1	0.0406
9	0	0	9	0.5	0.0446
10	0	0	9	0.5	0.0543
11	0	0	9	0.5	0.0401
12	0	0	9	0.5	0.0406

The following equation was obtained:

$$CR\ (gmd) = 0.045-0.045X_1 + 0.025X_2 - 0.035X_1X_2 + 0.13X_1^2 - 0.007X_2^2 \qquad (1)$$

Where X_1 and X_2 are coded variables representing the time of immersion and the blend inhibitor concentration ratio respectively, while the relationship between the coded levels and the corresponding real process variables is expressed as follows:

$$X_1 = \frac{t-9}{4.243};\ X_2 = \frac{c-0.5}{0.354} \qquad (2)$$

From statistical point of view, the above obtained equation has a correlation coefficient 0.97 which is useful and adequately described the corrosion behavior of Al-alloy within the specified conditions of the variables.

The variation of corrosion rate with any of the two independent variables can be easily realized by keeping one at a time constant, and for conditions which were not tried experimentally but within the specified limits of the variables as given in Figs. (2, and 3).

Figures 2 and 3 indicate the presence of a minimum in the response function (i.e., corrosion rate) as a function of both variables. Therefore, equation (1) was differentiated to calculate the optimum conditions which were found to be X_1 = 0.0647 coded (i.e., t=12.07) and X_2 = 0.7245 coded (i.e., c=0.7565 Co^{+2}/Ni^{+2} ratio).

In Fig. (4), the response surface of the objective function (i.e., corrosion rate) was plotted in three dimensions which clearly shows the area of optimal corrosion behavior of AA aluminum alloy 7075 as a function of both variables.

It is well known that great many variables might influence the corrosion mechanism as well as the corrosion rates and that and procedure which would save experimental effort while still yielding the desired information would be of great help. It was therefore decided to attempt the use of statistical method of experimental design in the study.

The variation of corrosion rate generally changed from an initial high value to a lower value between 0.82 and 0.68 g/m^2.day within 12 day of contact with solution, then the corrosion rate began to increase again when the time of contact with solution was 15 day. In the present Al/NaCl solution system, the following reactions take place:

$$Al \rightarrow Al^{+3} + 3e^- \qquad (3)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (4)$$

$$2H^+ + 2e^- \rightarrow H_{2(g)} \qquad (5)$$

So, the decrease in corrosion rate shown in Fig. (1) can be attributed to the formation of a natural insoluble and protective oxide/hydroxide films on the surface of the alloy, then the corrosion resistance of AA7075 alloy decreases noticeably (i.e., after 12 days immersion, when the pH value changes away from the near natural conditions due to oxygen reaction) and hydroxide layer dissolution[11,12], or due to the change of reaction mechanism and the nature of the formed film.

The regression equation (1) relate corrosion rate of the AA7075 alloy to immersion time and Co/Ni ratios as two variables and give a better insight into the relative effects of these variables on the corrosion process.

The effect of immersion time on the corrosion rate of AA7075 alloy at different inhibitor blend ratios of Co/Ni is shown in Fig. (2). It is clear that the addition of different inhibitor blend ratios of Co/No, generally reduces the corrosion rate (i.e., the longer the time of immersion until about 10 days (coded 0.645), the higher the inhibitor blend ratio added, the lower the corrosion rate), then the corrosion rate generally increased with all inhibitor ratios added after 10 days.

Arnott and coworkers[13-15] have found that the corrosion rate of AA7075 alloy in NaCl solutions (measured by weight loss) is decreased by addition of many cationic chlorides to the solution.

Fig. (3) shows the effect of inhibitor blend on corrosion rate at different immersion times. It's clear that increasing inhibitor blend ratios have no effect on metal protection for about 5 days of contact with the solution (i.e., the higher the inhibitor blend ratios the higher the corrosion rate for about 5 days). It can be concluded that within this time of immersion the pitting corrosion occurs, because the process of film formation and its growth besides the metal dissolution at the metal surface are kinetically related in such away that complete re-passivation does not occur[16,17].

Fig. (3) shows also that for immersion time of (9-13 days), the film formed by the inhibitor blend depends on the kinetics of all reactions that cause film growth relative to all the reactions, that promotes metal dissolution (i.e., increasing the inhibitor blend ratio during this immersion time will lead to a decrease in corrosion rate).

The situation reversed again for immersion time of 15 days (i.e., increasing inhibitor ratios become insignificant and its increase lead to an increase in corrosion rate). This confirms the presence of a minimum in the corrosion rate as a function of both variables.

Finally, the inhibitor blend ratio (ppm Co^{+2}/1000 ppm Ni^{+2}) was evaluated at 0.5 ratio in three immersion times (i.e., 3, 9, and 15 days) using the well known mathematical expression.

$$\%\theta = 1 - \frac{\omega_1}{\omega_2}$$

It was found that the maximum inhibition efficiency is obtained at 0.5 ratio and immersion time of 9 days (i.e., 93.5%) which confirms the optimum conditions of about 10 days obtained from regression equation (1).

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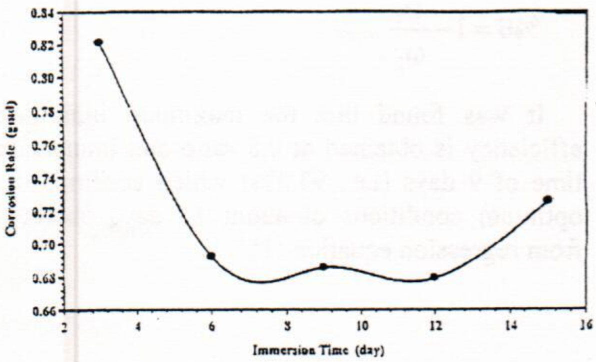

Fig. (1) Corrosion rate of aluminum alloy (AA7075) in 0.1M NaCl solution as a function of immersion time

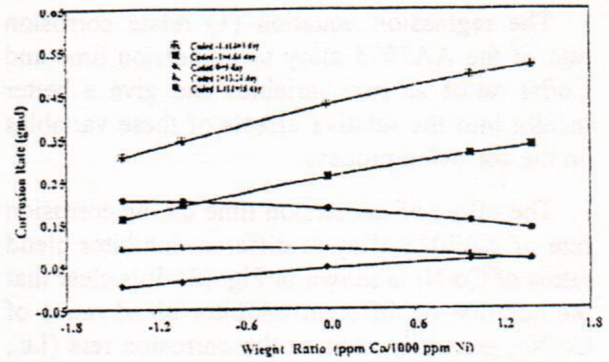

Fig. (3) Corrosion rate by weight loss of aluminum alloy AA7075 in 0.1M NaCl solution as a function of Co/Ni weight ratio at different immersion time

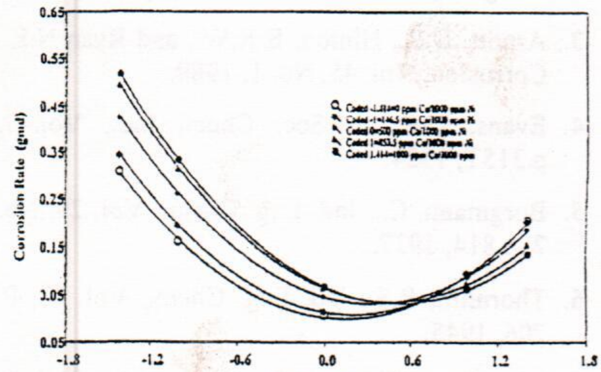

Fig. (2) Corrosion rate by weight loss of aluminum alloy AA7075 in 0.1 NaCl solution as a function of immersion time at different Co/Ni ratio

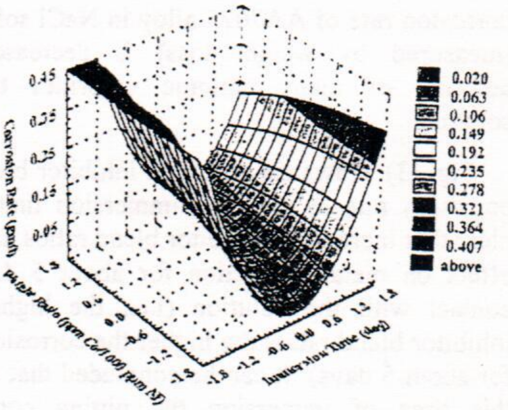

Fig. (4) Corrosion rate (surface response) for two variables experiments