Journal of Manufacturing Engineering, June, 2017, Vol. 12, Issue. 2, pp 68-76

OPTIMIZING IMMERSION CORROSION TEST PARAMETERS TO ATTAIN MINIMUM CORROSION RATE IN THE STIR ZONE OF FRICTION STIR WELDED AA6061 ALUMINIUM ALLOY

***Kamal Jayaraj R[1], Malarvizhi S[2] and Balasubramanian V[3]**

[1]Research Scholar, [2]Associate professor, [3]Professor, Centre for Materials Joining and Research (CEMAJOR), Department of Manufacturing Engineering, Annamalai University.

ABSTRACT

Joining of aluminium alloys has a wide application in automobile industries because of light weight and high specific strength. Compared to fusion welding process, friction stir welding (FSW) is widely adaptable to join aluminium and its alloy. In the FSW joint, grains are very finer in stir zone (SZ) compared to the other zones. The Chloride ion concentration, pH value and immersion time are reported to be the more influencing parameters on corrosion attack. The present work aims to identify the minimum corrosion conditions in the SZ of friction stir welded AA6061 aluminium alloys by statistical tools such as design of experiments (DoE), analysis of variance and response surface methodology (RSM). From the results, it is found that the chloride ion concentration has a greater influence on corrosion rate than the other two parameters.

Keywords: *Friction stir welding, AA6061 aluminium alloy, Response surface methodology, Corrosion rate.*

1.Introduction

Aluminium alloys are extensively used in automobile industries due to low density, high strength and excellent corrosion resistance [1-3]. Welding of aluminium alloys is quite difficult in fusion welding process because of its rapid formation of oxide films on its surface [4]. In order to overcome this problem the solid state welding is commonly used to join the aluminium alloys. Defects such as porosity and hot cracking are completely eliminated in this process due to low melting [5].

Friction stir welding (FSW) is one of the solid state welding techniques specially invented for joining aluminium alloys [6]. Generally, this weld exhibits three regions, namely stir zone (SZ), thermo-mechanically affected zone (TMAZ) and heat affected zone (HAZ). Among these three regions the grains are very fine in the SZ of the joint due to dynamic crystallization. Hence it is most important to study the corrosion behaviour of the SZ.

Immersion corrosion is one of the tests used to study the corrosion behaviour of the aluminium alloy by weight loss method [7, 8]. The corrosion behaviour of the material may vary depends upon the concentration of the solution, pH level and duration of exposure. Zaid et al., investigated the effects of pH and chloride concentration on pitting corrosion of AA6061 aluminum alloy and reported that the corrosion process is due to intense chemical dissolution by OH^- in alkaline solutions and at relatively lower in acidic solution [9].

In this respect, the present work is aimed to optimize the immersion corrosion test parameters to identify the minimum corrosion rate in the stir zone of friction stir welded AA6061 aluminium alloy. An empirical relationship is also developed to estimate the corrosion rate in the stir zone of friction stir welded AA6061 aluminium alloy joints.

2. Experimental Work

2.1 Fabrication of joints and specimen preparation

Rolled plates of AA6061-T6 aluminium alloy plates with a thickness of 6 mm were used in the present investigation and the chemical composition of the alloy in weight percentage is 0.6% Si, 0.25% Cu, 0.2% Cr, 1% Mg and balance Al. The plates were cut to the required size (150 mm x75 mm) by power hacksaw. A square butt joint was fabricated by FSW process. The initial joint configuration was obtained by securing the plates in position using mechanical clamps. The direction of welding was normal to the rolling direction of the plates. The single pass welding procedure was used to fabricate the joints. Schematic representation of AA6061 aluminium joint is shown in Fig. 1a. Taper

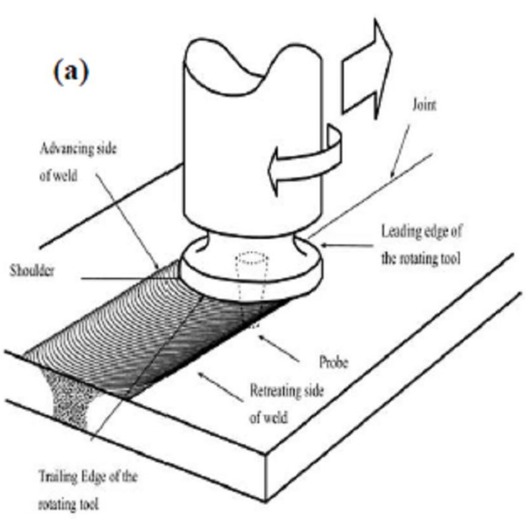
**Corresponding Author - E- mail: jayaraj_kamal@yahoo.co.in*

cylindrical tool made of super high speed steel was used to fabricate the joints (Fig. 1b). A computer numerical controlled friction stir welding machine (22 kW; 4000 rpm; 60 kN) was used to fabricate the aluminium joints. From previous investigation [10], the optimized FSW parameters were obtained and they were used in this investigation is listed in Table 1. From the fabricated joints, the specimens were extracted from weld nugget region for conducting immersion corrosion tests with the dimensions of 15 x 15 x 6 mm. The scheme of extraction of immersion corrosion test samples is shown in Fig.1c. Then the specimens were grounded with 600#, 800#, 1200# and 1500# grit SiC paper. Finally, it was cleaned with acetone and washed in distilled water and then dried by warm flowing air before immersing in the prepared NaCl solution. The photograph of the olished immersion corrosion test specimen is shown in Fig. 1d. The optical micrograph of the parent metal and stir zone of friction stir welded joint are shown in Fig. 2.

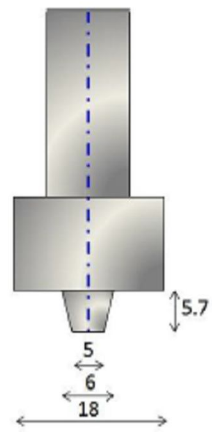
Table 1. Optimized welding conditions and process parameters used to fabricate the joints

Tool rotational speed,	Tool travel speed, mm/min	Axial force, kN	Tool shoulder diameter,	Tool pin diameter,	Tool pin length, mm	Tool pin profile
1000	30	5.5	18	5-6	5.7	Taper cylind rical

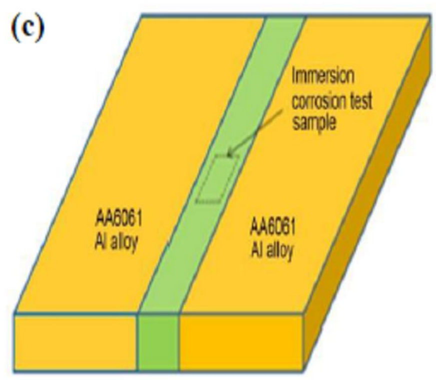
(a)



(b)



(c)



(d)

Fig.1 Experimental details (a) Schematic diagram of FSW joint (b) Tool dimensions (c) Specimen extraction scheme and (d) Dimension of immersion test specimen.

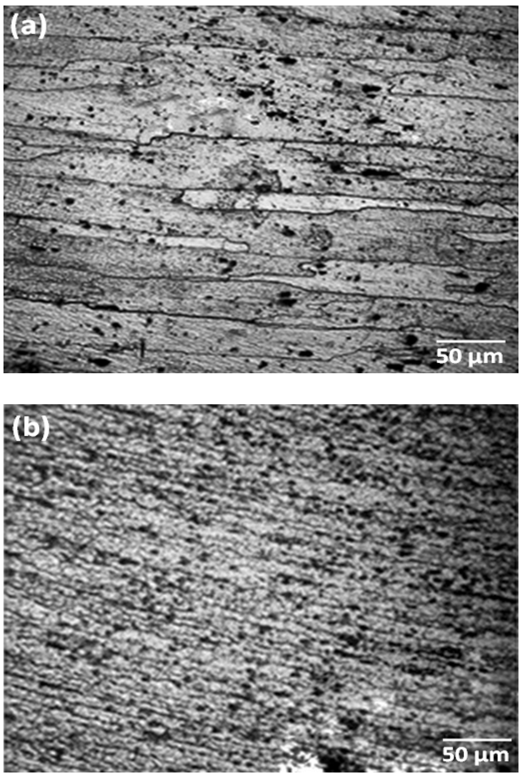


Fig 2. Optical micrograph of (a) AA6061 aluminium and (b) stir zone of friction stir welded joint.

2.2 Determination of the limits of corrosion test parameters

From the literature [11], the predominant factors that have greater influence on the corrosion rate of aluminium alloy were identified. They are: (i) pH value, (ii) chloride ion concentration and (iii) immersion time. Large numbers of trial experiments were conducted to identify the feasible testing conditions using FSW joint under immersion environment and the following inferences are obtained:

(i) If the pH value of the solution was <3, the transmutation in chloride ion concentration did not considerably affect the corrosion.
(ii) If the pH value was in between 3 and 11, there was inhibition of the corrosion process and stabilization of the protective layer.
(iii) If the pH value was >11, then the corrosion was resisted by the active protective layer.
(iv) If the chloride ion concentration was <0.2 mol/L, then there was no noticeable corrosion occured in the weld nugget.
(v) If the chloride ion concentration was in between 0.2 and 1 mol/L, then there was a moderate fluctuation in the corrosion rate.
(vi) If the chloride ion concentration was >1 mol/L, then the rise in corrosion rate may falter and decrease slighter.
(vii) If the immersion time was <4 hours, the surface was entirely covered with thick and rough corrosion products.
(viii) If the immersion time was in between 4 and 12 h, then the track of the corrosion can be predicted.
(ix) If the immersion time was >12 h, then the tracks of corrosion film were difficult to identify.

2.3 Selection of experimental design matrix

The range of individual factors was wider, therefore a central composite rotatable three-factor, five-level factorial design matrix was selected to minimize number of experiments. The experimental design matrix consisting 20 sets of coded conditions, comprising a full replication three-factor factorial design of eight points, six star points, and six center points was used. Table 2 presents the range of factors considered and Table 3 shows the 20 sets of coded and actual values used to conduct the experiments. The lower and upper limits of immersion corrosion test parameters were coded as -1.682 and +1.682, respectively. In this manner, the 20 experimental runs took into consideration for the estimation of the linear, quadratic, and two-way interactive effects of the variables. The method for designing such a matrix is managed with elsewhere [12, 13]. The coded values of intermediate levels can be ascertained from the relationship.

$$X_i = \frac{1.682\,[2X - (X_{max} + X_{min})]}{X_{max} - X_{min}} ------(1)$$

Where X_i is the required coded value of a variable X and X is any value of the variable from X_{min} to X_{max}; X_{min} is the lower level of the variable; X_{max} is the upper level of the variable.

Table 2. Important factors and their levels

S.No.	Factor	Notation	Unit	Levels				
				-1.68	-1	0	+1	+1.68
1	Chloride ion con.	C	mol/L	0.2	0.36	0.6	0.84	1
2	pH value	P	-	3	4.62	7	9.38	11
3	Immersion time	T	hours	4	5.62	8	10.38	12

Table 3. Design matrix and experimental results

Experimental number	Coded values Conc. (C)	pH (P)	Time (T)	Actual values Conc. (C)	pH (P)	Time (T)	Corrosion rate (mm/year)
1	-1	-1	-1	0.36	4.62	5.62	0.0178
2	+1	-1	-1	0.84	4.62	5.62	0.0242
3	-1	+1	-1	0.36	9.38	5.62	0.0098
4	+1	+1	-1	0.84	9.38	5.62	0.0171
5	-1	-1	+1	0.36	4.62	10.38	0.0113
6	+1	-1	+1	0.84	4.62	10.38	0.0187
7	-1	+1	+1	0.36	9.38	10.38	0.0047
8	+1	+1	+1	0.84	9.38	10.38	0.0119
9	-1.682	0	0	0.20	7.00	8.00	0.0065
10	+1.682	0	0	1.00	7.00	8.00	0.0188
11	0	-1.682	0	0.60	3.00	8.00	0.0203
12	0	+1.682	0	0.60	11.00	8.00	0.0089
13	0	0	-1.682	0.60	7.00	4.00	0.0214
14	0	0	+1.682	0.60	7.00	12.00	0.0113
15	0	0	0	0.60	7.00	8.00	0.0148
16	0	0	0	0.60	7.00	8.00	0.0149
17	0	0	0	0.60	7.00	8.00	0.0148
18	0	0	0	0.60	7.00	8.00	0.0143
19	0	0	0	0.60	7.00	8.00	0.0153
20	0	0	0	0.60	7.00	8.00	0.0148

2.4 Corrosion rate evaluation

NaCl solutions with concentrations of 0.2, 0.36, 0.6, 0.84 and 1 mol/L were prepared. The pH value was measured using a digital pH meter and varied from 3 to 11 as prescribed by design matrix. By addition of HCl and H_2SO4 in the NaCl solution the pH level was varied to acidic and basic respectively. The corrosion rate of the weld nugget region was calculated by weight loss method. The initial weight (w_0) of the specimen was measured before immersing into the NaCl solution and kept in the solution for 4 to 12 hours. Then the specimens were removed from the solution and washed with distilled water, then dried by warm air and measured the final weight (w_1). The weight loss (W) was measured using the following expression,

$$W = (w_0 - w_1) \text{ --------- } (2)$$

The corrosion rate was calculated as per the ASTM-G31 standard using the following equation,

$$\text{Corrosion rate (mm/year)} = \frac{8.76 \times 10^4 \times W}{A \times D \times T} \quad (3)$$

Where 'W' is the weight loss in grams, 'A' is the surface area of the specimen in cm^2, 'D' is the density of the material in g/cm^3 and 'T' is the immersion time in hours.

2.5 Developing an empirical relationship

To correlate the immersion corrosion test parameters and the corrosion rate, a second order quadratic model was developed. The response (corrosion rate) is a function of chloride ion concentration (C), pH value (P), and immersion time (T). Hence it can be expressed as

$$\text{Corrosion rate} = f\{C, P, T\} \text{ ---------- } (4)$$

The empirical relationship should include main and interaction effects of all factors and hence the selected polynomial are expressed as

$$Y = b_0 + \Sigma b_i x_i + \Sigma b_{ii} x_i^2 + \Sigma b_{ij} x_i x_j \text{ ------ } (5)$$

For three factors, the selected polynomial could be expressed as

$$CR = b_0 + b_1(C) + b_2(P) + b_3(T) + b_{12}(CP) + b_{13}(CT) + b_{23}(PT) + b_{11}(C^2) + b_{22}(P^2) + b_{33}(T^2) - - - - - (6)$$

Where b_0 is the average of responses (corrosion rate) and b_1, b_2, b_3,…,b_{11}, b_{12}, b_{13},…,b_{22}, b_{23}, b_{33}, are the coefficients that depend on their respective main and interaction factors, which were calculated using the expression given below,

$$B_i = \Sigma (X_i, Y_i)/n - - - - - - - - - - - - - - (7)$$

Table 4 Calculated values of coefficients

Coefficient	FactorEstimate
Intercept	519.58
C	1743.54
P	1665.01
T	1120.28
CP	0.45
CT	1.25
PT	4.04
C^2	88.54
P^2	1.32
T^2	39.26

Where 'i' varies from 1 to n, in which X_i is the corresponding coded value of a factor and Y_i is the corresponding response output value (corrosion rate) attained from the experiment and 'n' is the total number of combinations considered. All the coefficients were calculated by applying central composite face centered design using the Design Expert statistical software package. The significance of each co-efficient was calculated by student's t-test and p-values, which are presented in Table 4; Values of "Prob >F" less than 0.05 indicate that the model terms are significant. After determining the significant coefficients (at 95 % confidence level), the final relationship was developed by using these coefficients. The final empirical relationship derived by the above method to estimate the corrosion rate in the stir zone of friction stir welded AA6061 aluminium joint is given below,

$$Corrosion\ rate,(mm/year) = 0.015 + 3.580*10^{-3}(C) - 3.498*10^{-3}(P) - 2.869*10^{-3}(T) + 7.500*10^{-5}(CP) + 1.250*10^{-4}(CT) + 2.250*10^{-4}(PT) - 7.853*10^{-4}(C^2) - 9.584*10^{-5}(P^2) + 5.229*10^{-4}(T^2) \quad (8)$$

The analysis of variance (ANOVA) technique was used to find the significant main and interaction factors. The ANOVA results for second order response surface model fitting are given in the Table 5. The determination coefficient (r^2) indicated the goodness of fit for the model. The model F-value of 519.58 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case C, P, C^2, T^2 is significant model terms.

Values greater than 0.1000 indicate the model terms are not significant. To improve the model, the reduction of many insignificant model terms is required. The "Lack of Fit F-value" of 0.97 implies the Lack of Fit is not significant relative to the pure error. There is a 51.10% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good. The "Pred R-Squared" of 0.9900 is in reasonable agreement with the "Adj R-Squared" of 0.9959."Adeq Precision" measures the signal to noise ratio, a ratio greater than 4 is desirable. A ratio of 88.806 indicates an adequate signal. Each observed value (actual value) is compared with the predicted value which is calculated from the model and it is shown in the Fig.3.

Table 5. ANOVA test results

Source	Sum of squares	Df	Mean square	F value	p-value Prob>F	
Model	**4.693E**	**9**	**5.215E**	**519.58**	**< 0.0001**	**significant**
C	**1.750E**	***1***	**1.750E**	**1743.54**	**< 0.0001**	
P	**1.671E**	***1***	**1.671E**	**1665.01**	**< 0.0001**	
T	**1.124E**	***1***	**1.124E**	**1120.28**	**< 0.0001**	
CP	**4.500E**	***1***	**4.500E**	**0.45**	**0.5183**	
CT	**1.250E**	***1***	**1.250E**	**1.25**	**0.2905**	
PT	**4.050E**	***1***	**4.050E**	**4.04**	**0.0723**	
C^2	**8.887E**	***1***	**8.887E**	**88.54**	**< 0.0001**	
P^2	**1.324E**	***1***	**1.324E**	**1.32**	**0.2775**	
T^2	**3.940E**	***1***	**3.940E**	**39.26**	**< 0.0001**	
Residual	**1.004E**	**10**	**1.004E**			
Lack of Fit	**4.953E**	***5***	**9.907E**	**0.97**	**0.5110**	***not significant***
Pure Error	**5.083E**	***5***	**1.017E**			
Cor Total	**4.703E**	**19**				

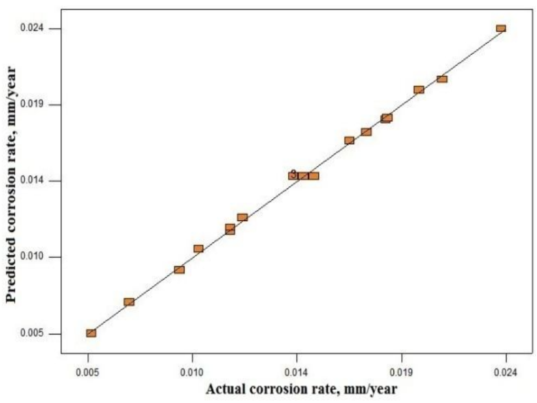


Fig. 3 Correlation graph

3. Estimating minimum corrosion rate conditions

The main and interaction effects of the corrosion process parameters were computed and plotted in the form of perturbation plots, as shown in Fig. 4. The perturbation plot is a most important pictorial representation which shows silhouette views of the response surface [14, 15]. It can be used to compare the individual and combined effects of all factors at a particular point in the RSM design space. For response surface designs, the perturbation plot shows how the response changes as each factor moves from the chosen reference point, while all other factors remain constant at the reference value.

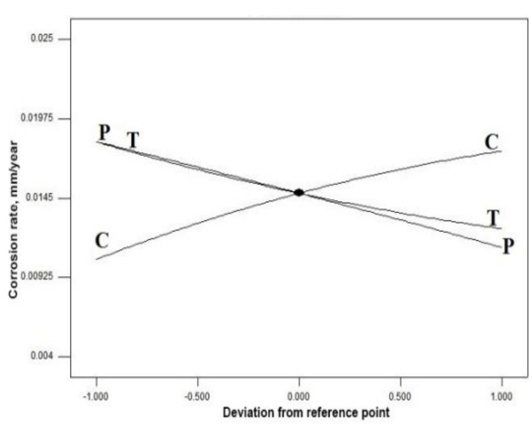


Fig.4 Perturbation graph

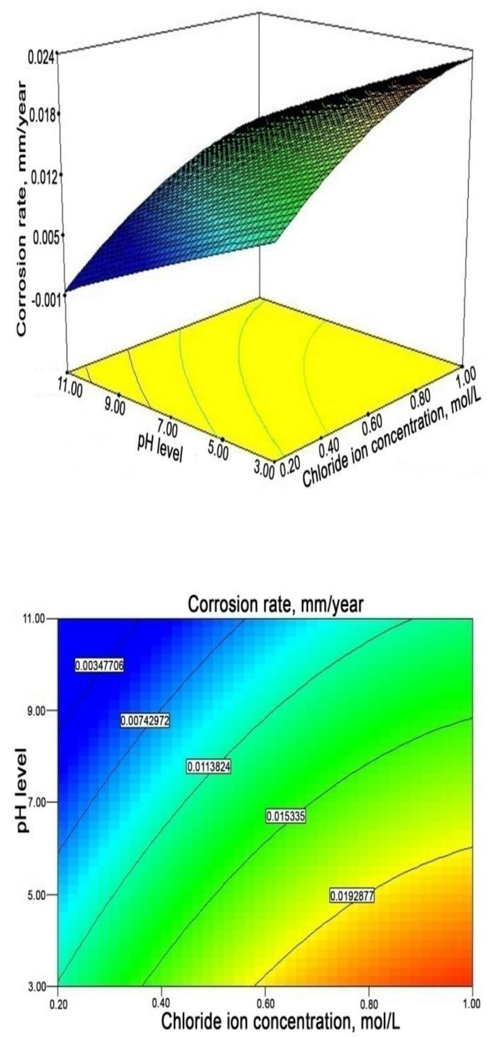
From the perturbation graph and response surface graphs (Fig.4 & Fig.5), it can be observed that when the corrosion rate decreases linearly with increase in pH value and immersion time. It may be due to dissolution of aluminium in aqueous solutions takings by the reduction of water to produce aluminium hydroxide ($Al(OH)_3$) and hydrogen gas (H_2). These reactions are reported to be insensitive to oxygen concentration [16]. Highly acidic solutions are aggressive to AA6061 aluminum alloy, hence a very high corrosion rate observed at pH 3.

The metal get started to passivate after some time it will prevent the metal from further corrosion. It was also observed that the corrosion rate typically increased with the increase in concentration of NaCl solution. The increase in corrosion rate with increasing chloride ion concentration may be attributed to the participation of chloride ions in the dissolution reaction. Chloride ions are aggressive for aluminum alloys. The adsorption of Cl^- ions to O_2 covered Al^+ surface transforms $Al(OH)_3$ to easily soluble $AlCl_3$.

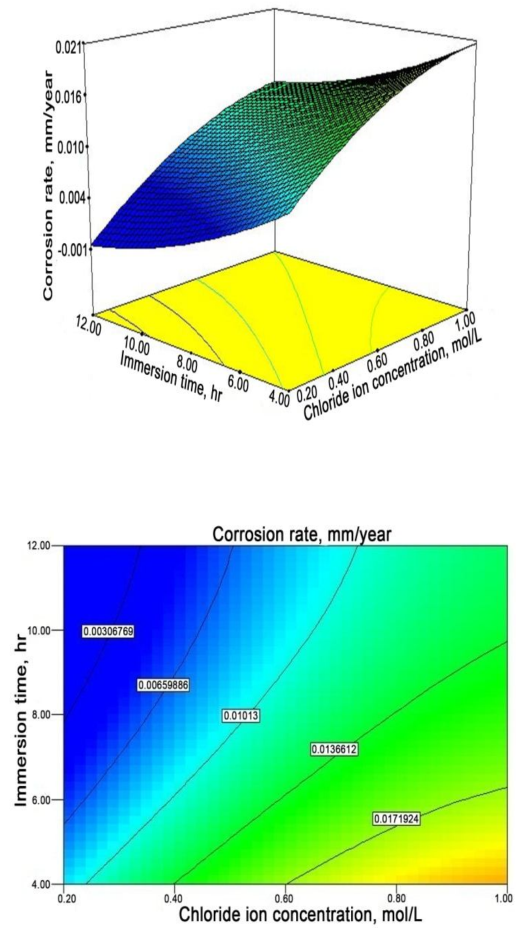
From the surface and contour plots the minimum corrosion rate conditions were identified as shown is Fig. 5. The least point in response plot shows the minimum achievable corrosion rate. A contour plot is formed to display the minimum corrosion rate parameter setting visually for second order responses, such a plot can be more complex compared to the simple series of parallel lines that can occur with first order models. It is generally important to characterize the response surface in the immediate vicinity of the point immediate the stationary point found. To classify whether the stationary point is a minimum response or maximum response or a saddle point by the identification; it is straightforward to analyze it through a contour plot. Contour plot is one of the 2D graphical representation plays a very important role in the study of a response surface. It is clear from that when the corrosion rate decreases with increase in pH value and immersing time. Correspondingly, the corrosion rate increases with increase in chloride ion concentrations.

By analyzing the response surface and contour plots as shown in Fig.5 (a-c), the minimum achievable corrosion rate value is found to be 0.0040 mm/year. The corresponding parameters that give up this minimum value are chloride ion concentration of 0.21 mol/L, pH value of 7.15 and immersion time of 10.58 hr. The lower F ratio value implies that the respective levels are less significant. From the F ratio value, it can be concluded that the immersion time is contributing the minor factor to corrosion attack, followed by chloride ion concentration and pH value for the range considered in this investigation. Fig. 5 (a-c) indicates the response surface and contour plots representing the interaction effect of any two input parameters on the corrosion rate.

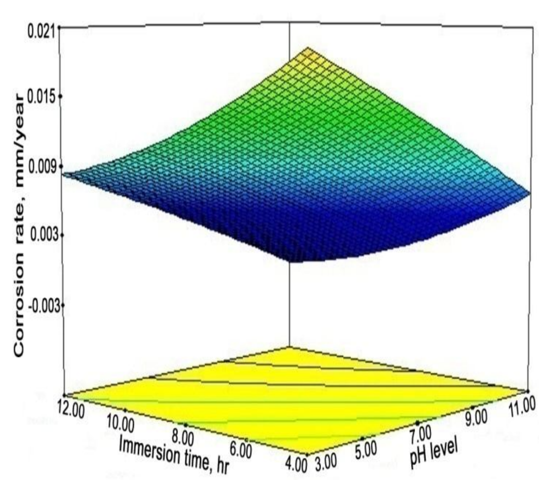
To validate the developed relationship, three confirmation experiments were conducted by varying the concentration of chloride ion, pH and immersion time and the values were chosen randomly within the range of test parameters presented in Table 3. The actual response was calculated from the average of three measured results. Table 6 summarizes the experimental values, predicted values and the variations. The validation results revealed that the developed empirical relationship is quite accurate as the variation is ±2 %.

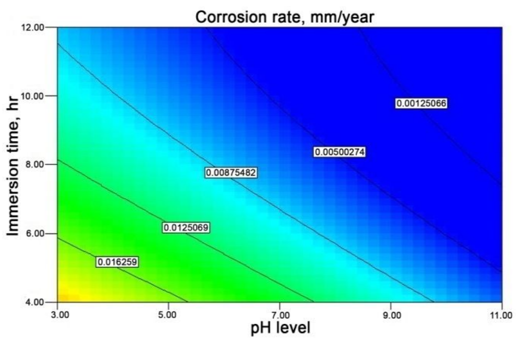


(a) Interaction effect of chloride ion concentration and pH.



(b) Interaction effect of chloride ion concentration and immersion time.





(c) Interaction effect of pH and immersion time.
Fig. 5 Response surface graphs and contour plots

Table 6. Validation of test results

Si.No	Chloride ion concentration, (mol/L)	pH	Immersion time, (hr)	Actual corrosion rate (mm/year)	Predicted corrosion rate (mm/year)	Variation (%)
1	0.4	5	6	0.0168	0.0171	-1.77
2	0.5	4	11	0.0155	0.0152	+1.28
3	0.9	9	7	0.0170	0.0173	-1.75

Fig. 6 shows the scanned images of the corrosion test specimens exhibited minimum and maximum corrosion rates. In both the conditions, the stir zone of FSW joint doesn't corrode severely, this may be due to passivation of oxide films on the surface it shielded the metal from corrosion. From all the conditions, minimum corrosion attack observed at a chloride ion concentration of 0.36 mol/L, pH of 9.38 and immersion time of 10.38 hours. Fig. 6(a), stir zone of AA6061 aluminium is exposed to NaCl solution, there was no visible corrosion attack is observed.

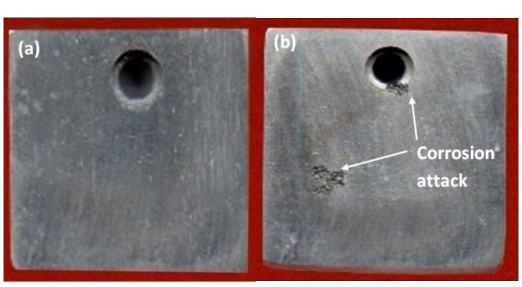


Fig. 6 Scanned image of the corrosion test specimens (a) Minimum corrosion attack (Run 1) and (b) Maximum corrosion attack (Run 6).

Hence, maximum corrosion attack observed at a chloride ion concentration of 0.84 mol/L, pH of 4.62 and immersion time of 5.62 hours. In Fig. 6(b) the surface of the stir zone is experiencing very lesser amount of corrosion attack when it is involved to immersion test.

3.Conclusions

(i) An empirical relationship was developed to estimate the corrosion rate in the stir zone of friction stir welded joint of AA6061 aluminium alloy at 95% of confidence level. The relationship was developed incorporating the chloride ion concentration, pH value in NaCl solution and immersion time using statistical tools, such as design of experiments and regression analysis.

(ii) From ANOVA results, it is found that the chloride ion concentration is having greater effect (F=1743.54) and immersion time is having comparatively lower effect (F= 1120.28) on corrosion rate.

(iii) Minimum corrosion rate of 0.0040 mm/year was attained under the immersion corrosion test conditions of 0.21 mol/L chloride ion concentration, 10.58 pH and 8.58 hr immersion time.

Acknowledgements

The authors wish to express sincere thanks to Council of Scientific and Industrial Research (CSIR), New Delhi for the financial support to carry out this investigation through sponsored project No. 22(0615)/13/EMR-II dated 26.02.2013.

References

1. *Hatch J.E (1984), "Aluminum Properties and Physical Metallurgy," ASM ,Ohio, US, p. 424.*

2. *Mondolfo LF (1979), Aluminum alloys: structure and properties. London: Butterworths.*

3. *Davis J R (1999), Corrosion of aluminum and aluminum alloys. Materials Park, OH: ASM International.*

4. *Totten G E and MacKenzie D S (2003), Handbook of aluminum. New York ; Basel: M. Dekker.*

5. *Xiao R and Zhang X (2014), "Problems and issues in laser beam welding of aluminum–lithium alloys," Journal of Manufacturing Processes, Vol. 16(2), 166–175.*

6. *Mishra R S and Ma Z Y (2005), "Friction stir welding and processing," Materials Science and Engineering: R: Reports, Vol. 50(1–2), 1–78.*

7. *Vilaça P and Thomas W (2011), "Friction Stir Welding Technology", 85–124.*

8. *Vargel C (2004), Corrosion of aluminium, 1st ed. Amsterdam ; Boston: Elsevier.*

9. *Zaid B, Saidi D, Benzaid A and Hadji S (2008), "Effects of pH and chloride concentration on pitting corrosion of AA6061 aluminum alloy," Corrosion Science, Vol. 50(7), 1841–1847.*

10. *Elangovan K, Balasubramanian V and Valliappan M (2008), "Influences of tool pin profile and axial force on the formation of friction stir processing zone in AA6061 aluminium alloy," The International Journal of Advanced Manufacturing Technology, Vol. 38(3–4), 285–295.*

11. *Bailey R, Pidaparti R, Jayanti S and Palakal M (2000), "Corrosion prediction in aging aircraft materials using neural networks," in 41st Structures, Structural Dynamics, and Materials Conference and Exhibit.*

12. *Khuri A I and Mukhopadhyay S (2010), "Response surface methodology," Wiley Interdisciplinary Reviews: Computational Statistics, Vol. 2(2), 128–149.*

13. *Miller I, Freund J E, and Johnson R A (1994), "Miller and Freund's Probability and statistics for engineers", Englewood Cliffs, N.J: Prentice Hall.*

14. *Box G E P and Draper N R (1987), "Empirical model-building and response surfaces", New York: Wiley.*

15. *Myers R H, Montgomery D C and Anderson-Cook C M (2016), "Response surface methodology: process and product optimization using designed experiments".*

16. *Jones R (2001), "Environmental Effects on Engineered Materials. Hoboken", Marcel Dekker Inc.,.*

Nomenclature

Symbol	Meaning	Unit
C	Chloride ion concentration	mol/L
P	pH	-
T	Time	hr
CR	Corrosion rate	mm/year

