Neural Network Model for Synthesis of Thermally Sprayed (Al/Al₂O₃) Composite Protective Coatings

Thamir Abdul-Jabbar Jumah¹, Saad Ali Ahmed²

¹Al-Nahrain University, College of Sciences, ²Baghdad University, College of Education Ibn-Haytham of Pure Science

*Corresponding author Email: drthamir05@yahoo.com

Abstract. Al₂O₃ and Al₂O₃–Al composite coatings were deposited on steel specimens using Oxy-acetylene gas thermal spray gun. Alumina was mixed with Aluminum in six groups of concentrations (0, 5, 10, 12, 15 and 20% ) Al₂O₃. Specimens were tested for corrosion using Potentiodynamic polarization technique. Further tests were conducted for the effect of temperature on polarization curve and the hardness tests for the coated specimens. At first, Modelling was carried out using MINITAB-19, least square method, as a 2nd degree nonlinear model, bad results were achieved because of the high nonlinearity. Better result was achieved using neural network fitting tool. The network was designed using five neurons in the hidden layer and the input was I input with two layers, the electrical potential and alumina concentration.

1. Introduction
Aluminium composites are widely used as anticorrosion material for marine applications. (Berenika et al., 2020) reviewed and summarized corrosion mitigation methods applied in the field of marine thermal spray coatings and the control parameters acting on the protection performance for aluminium thermally spray coatings used for steel [1].

The wetting behaviour between poly-crystalline alumina substrate and molten aluminium doped with magnesium and pure aluminium was studied. (Sangghaleh et. al. 2008) [2]. To improve wettability between Al₂O₃ and Al in the fabricating of composite by employing the infiltration method (Szafran et. al. 2006) [3]. The structural energetic and adhesion strength for both solid and liquid phases of Al/Al₂O₃ interfaces by using the reactive force field was studied by (Zhang et. al. 2006) [4]. Silicon based alloy and Al₂O₃ particles with volume fraction of (5, 10, 15) wt.% and size of 44, 85 and 125 µm, were Characterized by (Sevak et. al. 2006) [5]. Effect of polarization on stress corrosion cracking of aluminium alloy type7075 was studied by (Liu et. al. 2004) [6]. The corrosion behaviour of Al- Zn/Al₂O₃ in NaCl solution was investigated by (T.G.Durai et. al. 2008) [7]. They conclude that the corrosion depends on the weight fraction of the reinforcing particles.

(Edoziuno et al., 2020) reported that the optimization and development of predictive models for the corrosion inhibition of mild steel in Sulfuric acid by Methyl-5-benzoyl-2-benzimidazole Carbamate (Mebendazole). Design methodology, weight loss measurement, open-circuit potential analysis, Tafel...
polarization, etc. were used for the evaluation of inhibition efficiency of mebendazole for mild steel in H₂SO₄. The corrosion inhibition process parameters were optimized and predictive mathematical models developed using the Response Surface Methodology using the central composite design tool of Design Expert software version 11 [8].

Uang et al, reported the Cross-sectional FESEM views of the Al and Al-Al₂O₃ coatings deposited by flame spray, XRD patterns of the starting Al powder, and the Al-20 wt.%Al₂O₃ powder the flame spray Aluminium and the flame spray of Al-Al₂O₃ coatings. They concluded that aluminium-alumina composite coatings fabricated by thermal flame spraying have a hard skeleton structure, it is attributed to the distribution of alumina splats in coatings, the cost effective for this protective coating coatings is promising for potential applications as the barrier and sacrificial protective layers in the marine environment [9]. The aim of this project is improving the corrosion resistance of steel due to composite and thermally treatment.

2 Materials and methodology
2.1 Specimens Preparation
Corrosion Specimens were firstly slicing with dimension of about (2.5mm) thickness and (25mm) diameter. The specimens were cleaned carefully with distill water and then by alcohol solution. Grinding and polishing by metallographic papers of grits 1200 and 2000 were achieved. Finally, the specimens should have cleaned by rinsed in distill water and acetone to remove any traces of the cleaner and organic which it adherent, and then kept in desiccator according to the ASTM [10].

2.2 Composite
Spray powders of (Al/Al₂O₃) mixed were prepared for (Al₂O₃) concentration (0, 5, 10, 12, 15 & 20 wt.%) the rest is Al- powder. The percentage of cumulative particle size of Al- powder lied between (10-74) µm, while the particle size of Al₂O₃ lied between (5-45) µm. The powders were mixed carefully for 8 hr. before spraying process.

2.3 Thermal spray
Thermal spraying coating technique of (Al/Al₂O₃) composite for specimens surface of steel. Thermal spray gun with an Oxy-acetylene gas of pressure 5 bar was used. The operation conditions as follows: Substrate Temp 50 °C. Distance between the nozzle and substrate equal 15 cm. with two flame passes and 90° vertical spraying angle.

2.4 Potentiodynamic tests
Potentiodynamic polarization technique was carried out using WENKING Mlab multi channels potentiostat and SCI-Mlab corrosion measuring system from Bank Electroniks-Intelligent control GmbH, Germany 2007. The coating specimens achieved by the thermal spraying technique.

Corrosion tests were conducted electrochemically by Potentiodynamic method. It is a polarization technique in which the potential of the electrode is varied over a relatively large potential domain at a selected rate by the application of a current through the electrolyte. The research is conducted on potential domain of (-600~ -1300 mV). Calculation of polarization resistance is performed by illustrate Tafel curves. the anodic and cathodic slopes and the corrosion current (α, β and i₉) respectively were predicted from graphs. by substitution of these slopes in the equation (1) we got the polarization resistance. The prediction of these values is elucidated in figure 1'

\[ R = \frac{\alpha \beta}{2(\alpha+\beta)i_c} \]  

(1)
2-5 Hardness
The specimens are tested according to Vickers technique (HV) for hardness to conform the durability of the protective coating.

3 Results and discussion
3.1 Polarization analysis
Results of Aluminium / Alumina concentration effect are elucidated in figure 2. The figure shows the Potentiodynamic polarization curves of the coating samples acquired in (3.5M) NaCl solution. Tafel curves were illustrated from experimental data. The slopes of anodic and cathodic lines as well as the corrosion current is predicted. The polarization resistance was calculated using equation (1), the data is shown in ‘table 1’.

At the corrosion potential, the cathodic potential and anodic potentials are equal (see ‘table 1’). light implies that the higher electrical resistance exists at 10wt. % alumina, when spread in the aluminium it made splats and a hard Skeleton that improves the corrosion and erosion
resistance. The corrosion potentials of the (Al-Al₂O₃) composite coating and the (Al) coating show increased in the electrical potential and increase in the current density, (-1275mV) for Al only surface coating to (-1063mV) for (20% Al₂O₃), the current density of Al-Al₂O₃ composite protective coating, (2.95 µA/cm²) for Al only and (9.9 µA/cm²) for 20% Al₂O₃, this meant that adding alumina powder enhances the corrosion resistance.

Table 1. Corrosion resistance and Tafel line slopes for various alumina weight %.

| Al₂O₃% | α (Ω.cm²) | B (Ω.cm²) | i_c (A) | R(Ω.cm²) |
|--------|-----------|-----------|---------|-----------|
| 0      | 1086.957  | 1086.957  | 8E-6    | 2.95E+07  |
| 5      | 1123.596  | 561.5     | 1.10E-05| 1.48E+7   |
| 10     | 2778      | 1111.11   | 1E-5    | 3.45E+07  |
| 12     | 3111      | 1333.333  | 2E-5    | 2.03E+07  |
| 15     | -1086.96  | 766.6667  | 1.00E-06| 1.95E+7   |
| 20     | 782       | 252       | 9.90E-6 | 9.21E+6   |
Figure 2. Polarization curves
It is reasonably, increasing the temperature increase the corrosion as shown in figure 2. Temperature effects on polarization are shown in figure 3, increasing temperature speeds corrosion.

3.2 Hardness

Hardness of the tested specimens is enhanced according to the results tabulated in ‘table 2’. It was done by that the Vickers method for micro hardness analysis. The method is based on an optical measurement system. A square base pyramid shaped diamond is used for testing in the Vickers scale. A test force of (50 gf) load was used to perform the test. A schematic drawing for the test indenter is shown in figure 4.

![Vickers test indenter](image)

**Figure 4. Vickers test indenter**
Table 2. Hardness of Aluminum thermal spray coating

| Al₂O₃ (wt.%) | Hardness (HV) |
|-------------|---------------|
| 0           | 85            |
| 5           | 90            |
| 10          | 95            |
| 12          | 100           |
| 15          | 105           |
| 20          | 95            |

One can conclude that the coated specimens by alumina particles act as obstacles against any mechanical deformation such as indentation and dislocation when the additives increase up to 15%. The resultant is when the specimens coated by ceramic such as Al/Al₂O₃. Increasing alumina which is less in particle size will decrease the porosity and increase the adhesion strength and that is reflected increase in the hardness. Adding more alumina increase the brittleness of the surface and decrease the hardness.

3.3 Microstructure analysis:
The microscopic photographs revealed the implies grains of different concentrations of alumina on the substrate. The aluminium metal matrix composites reinforce with Al₂O₃ of different weight fraction, will be reinforced the protection layer anti-corrosion as shown in ‘figure 5’, the thermally sprayed Al-Al₂O₃ coating, respectively. Compared with the thermally sprayed Al coating, the composite coating is much denser. The larger grain size of alumina on surface could be attributed to the accumulation of the molten droplets onto substrate surface, and this state may be due to the flight length of droplet [1,3]. For the Al-Al₂O₃ composite coatings, it is clear that alumina barriers are equally distributed in the coating [7,8] ‘figure 6’, showing undetectable defects at Al/Al₂O₃ interfaces. While in ‘figure 6’, the Al/Al₂O₃ does not cover the substrate evenly and different spots shown [2,9]. ‘Figure 7’ Shows the microscopic image of surface after corrosion occurrence. The present experiment shows that the corrosion resistance is reduced with increasing volume portions of alumina particles. This state is attributed to the Galvanic coupling in between alumina and matrix [8,9].
Figure 5. Microscopic image: Al$_2$O$_3$ material at the steel surface.

Figure 6. Microscopic image: sample sprayed with 7% Al$_2$O$_3$
3.4 Statistical analysis
Treatment of results are carried out through Minitab and MATLAB as mentioned below.

3.4.1 Minitab:
Response surface design is created using statistical software (Minitab- 19) : model is created for electrical potential as a function of aluminium concentration and electrical anode and cathode current density. It is appeared that the square of weight percent, the interaction between weight percent and cathodic current, and the interaction between anodic and cathodic current has significant values.
‘Table. 2’ Response surface analysis X: Alumina %, IA: Anodic current density, IC, cathodic current density, E: electrical potential [11].
Response Surface Regression: $E$ versus $X$, $IA$, $IC$

Analysis of Variance

| Source             | DF | Adj SS    | Adj MS    | F-Value | P-Value |
|--------------------|----|-----------|-----------|---------|---------|
| Model              | 9  | 0.000142  | 0.000016  | 17.48   | 0.000   |
| Linear             | 3  | 0.000057  | 0.000019  | 20.99   | 0.000   |
| $X$                | 1  | 0.000000  | 0.000000  | 0.51    | 0.478   |
| $IA$               | 1  | 0.000001  | 0.000001  | 0.67    | 0.415   |
| $IC$               | 1  | 0.000002  | 0.000002  | 2.36    | 0.129   |
| Square             | 3  | 0.000006  | 0.000003  | 2.77    | 0.048   |
| $X^2$              | 1  | 0.000025  | 0.000025  | 5.84    | 0.018   |
| $IA^2$             | 1  | 0.000001  | 0.000001  | 0.87    | 0.354   |
| $IC^2$             | 1  | 0.000000  | 0.000000  | 0.03    | 0.858   |
| 2-Way Interaction  | 3  | 0.000008  | 0.000003  | 2.82    | 0.045   |
| $X^*IA$            | 1  | 0.000000  | 0.000000  | 0.11    | 0.741   |
| $X^*IC$            | 1  | 0.000005  | 0.000005  | 5.09    | 0.027   |
| $IA^*IC$           | 1  | 0.000000  | 0.000000  | 0.26    | 0.611   |
| Error              | 68 | 0.000062  | 0.000001  |         |         |
| Total              | 77 | 0.000203  |           |         |         |

The model summary values are shown in ‘Table 3’, the fitting of model gives $R^2 = .69$ but the predicted values for $R^2$ is less than (0.5), the fitting is not satisfied.

Table 3. Model Summary

| $S$     | R-sq | R-sq(adj) | R-sq(pred) |
|---------|------|-----------|------------|
| 0.0009511 | 69.76% | 65.75% | 48.79% |

The regression equation is:

$$E = -0.031 + 0.00195X - 0.0032IA - 0.023IC - 0.000011X^2 + 0.0136IA^2 + 0.0059IC^2 + 0.000181X^2IA + 0.001171X^2IC - 0.0209IA^2IC$$

3.5 Neural Networks

3.5.1 Temperature effects by neural networks:

Three temperature sets were treated 298 °K, 308 °K and 318 °K. They were treated separately to ensure the accuracy and monitoring the results using MATLAB, 2017b neural networks Fitting tools. The artificial neural network which was used for nonlinear modelling of electrical potential with the current density is shown in figure 8. The architecture is used for all temperatures [11].
The RMS and R values for the three temperature ranges are listed in ‘Table. 4’.

| T (°K) | Samples | MSE         | R        |
|-------|---------|-------------|----------|
| 298   | Training 6 | 4.94706e-3  | 0.989944 |
|       | Validation 2 | 0.189061    | 1.000000 |
|       | Testing 2    | 6.32511e-2  | 1.000000 |
| 308   | Training 6 | 1.45586e-21 | 1.000000 |
|       | Validation 2 | 3.18962e-1  | 0.999999 |
|       | Testing 2    | 0.158381     | 1.000000 |
| 318   | Training 6 | 3.27960e-4  | 0.99261  |
|       | Validation 2 | 1.98587e-3  | 1.000000 |
|       | Testing 2    | 0.701652     | 1.000000 |

It was shown in ‘Table. 4’, at validation a reverse fitting sign. That is mean a change from cathode protection to anodic region. In figure 9, the three temperature zones are shown for the experimental and neural network output for the current density versus potential.

**Figure 8. Neural network fitting function.**

**Figure 9.** a Errors at 298°K
3.5.2 Corrosion resistance by Neural Networks

A new ANN is designed to model the current density as a function of the electrical potential, and the weight fraction. The neural network is designed to accept three inputs, alumina wet percent, current density and electrical potential, the output of the network is the electrical resistance to corrosion. The data used for training the network is highly nonlinear, MINITAB statistical software failed to model it, so we tried with neural networks. Multi hidden layers succeeded in achieving this target. Three hidden layers was good choice for this duty, the 1st hidden layer contains 12 neurons, the 2nd hidden layer includes 10 neurons and the 3rd has 12 neurons. All of them are (tansig) type activation function. The output layer has one neuron of linear type. The architecture of the neural network is shown in figure 10. Number of Neurons is was set by trial.
Inputs for the neural network are Alumina content, current density and the electrical potential. It was considered the electrical resistance is a function of these three inputs. The network gives good results, so it is important to thought of new terms.

\[ \text{ANN} = f(E, i, x_{Al2O3}) \]

The output of the ANN is \( R \).

A neural network is trained with 70% of input data, while the rest is 25% for validation and 15% for test. Good results were achieved for this highly nonlinear behaviour with experimental disturbances, RMS an R values for training, validation and test [12,13].

Comparing the neural network output with the experimental result shows complete alignment as shown in figure 11.

Figure 11. Neural network and experimental values of current density data series

Regression plots are shown in figure. 12.
4. Conclusions
1- Corrosion rate is enhanced as the weight percentage of alumina
2- Alumina particles act as obstacles to dislocate movement and in the same time acts to increase the surface hardness.
3- Thermal spraying by gun is efficient technique and low cost for applies the coating.
4- Neural was better method than modeling such nonlinear corrosion case.
References

[1] B. S. Gerstenkorn 1, S. Paul and A. J. Davenport 1,: Sacrificial Thermally Sprayed Aluminium Coatings for Marine Environments: A Review, Coatings, Vol. 267, pp. 1-19, 2020.

[2] A. Sangghaleh and M. Halali, : An investigation on the wetting of polycrystalline alumina and aluminum , journal of material and technology, Vol. 197, pp. 156-160, 2008.

[3] K. Konopka and M. Szarfran, : Fabrication of Al2O3 composites by infiltration method and their characteristic, journal of material processing technology, Vol. 175, pp. 266-270, 2006.

[4] Q. Zhang and Cagin: adhesion and nonwetting – wetting transition in the Al/α-Al2O3 interface, physical review 69(4). Art, No. 045423. ISSN 0163 1829 , 2006.

[5] H. Sevik and S. Can Kurnaz, : properties of alumina particulate reinforced aluminum alloy produced by pressure die castin, Vol.27, pp. 676 683, 2006.

[6] L. Ji-hua and L. pei-ying,: effect of polarization on SCC of 7075 aluminum alloys, materials forum journal, Vol.28, 2004.

[7] T.G.Durai , Karabi, and S. Das,: corrosion behavior of Al- Zn/ Al2O3, Journal of Alloys and Compounds, VOL. 462, ,PP. 410-415, 2008.

[8] S.K.Chaudhury and S.C.Panigrah, :Role of processing parameter on micro structural evaluation of spray formed Al-2Mg alloy and Al- 2Mg- TiO2 of composite, Journal. of materials processing technology, Vol. 182, pp. 343-351, 2007.

[9] "Optimization and development of predictive models for the corrosion inhibition of mild steel insulphuric acid by methyl-5-benzoyl-2-benzimidazole carbamate (mebendazole)," Cogent Engineering, vol. 7, 2020.

[10] ASTM G1-3 Standard practice for preparing, cleaning and evaluating corrosion test specimens; ASTM International; west conshohocken, PA,USA, 2003.

[11] F. T. M.Noori:, Experimental,kinetic, isotherm and quantum chemical calculation; corrosion inhibitor for mild steel in acidic medium, Journal.WULFENIA, Vol. 23, No. 2, pp. 493-500, 2016.

[12] J. Huang, Y. Liu, J. Yuan, and H. Li, :Al/Al2O3 Composite Coating Deposited by Flame Spraying for Marine Applications: Alumina Skeleton Enhances Anti-Corrosion and Wear Performances, J Therm Spray Tech Journal of Thermal Spray Technology, Vol. 23, pp. 676-683, 2014.

[13] Edgar, T. F. Optimization of chemical processes / Thomas F. Edgar, David M. Himmelblau, Leon S. Lasdon.-2nd ed. p. cm.-(McGraw-Hill chemical engineering series,) ISBN 0-07-039359, 2012.