Production of cobalt anti-corrosion coating on AISI 430 steel–Optimization using Box–Behnken experimental designs

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Corrosion-resistant cobalt coating has been prepared by the pack-cementation method on AISI 430 ferritic stainless steel. In order to investigate the corrosion properties of the coating, the polarization technique is employed using a 3.5 wt. % NaCl solution. Experimental design with a response surface methodology and a Box-Behnken design is used to investigate the effective parameters of the coating process. In this method, three factors, namely cobalt concentration, activator concentration, and heat treatment temperature, have been examined at three levels, and the optimized conditions for the corrosion properties of the coating are obtained. The surface morphology of the cobalt coating is characterized by scanning electron microscope. In addition, the chemical composition and structure of the coating are analyzed by EDS and XRD. The results show that the statistical model is valid when it comes to describing the corrosion properties of the coating using various variables. Optimized conditions to achieve excellent corrosion-resistant coating have been obtained using the variables 10.63% cobalt, 2.90% activator, and 840°C temperature for the heat treatment.

Keywords: AISI 430 ferritic stainless steel, Box-Behnken design, Corrosion, Cobalt, Pack-cementation method

Stainless steels represent one of the most popular metallic materials, although it is well known that they suffer from different forms of localized corrosion. This is mainly due to halide ions, which are especially prevalent in chloride solution. Halide ions are very dangerous and lead to the degradation and failure of structural stainless steels in service¹. As corrosion is mostly a surface phenomenon, corrosion resistance is closely related to the composition and structure of surface films on metals. Various techniques have been developed to apply protective coatings to ferritic stainless steels in order to enhance their corrosion properties. These include slurry coatings²⁻⁵, anodic electrodeposition⁶⁻⁷, and cathodic electrodeposition of particular metals or alloys, followed by annealing/oxidation in air⁸⁻¹⁰, sol-gel¹¹ and pack-cementation¹²⁻¹⁶. According to literature survey, no research has been done on cobalt coatings on any alloy using the pack-cementation method for corrosion resistance applications.

Experimental design methodology is a cost-effective way for extracting the maximum amount of information and can save the cost of experiment and time. Response surface methodology (RSM), a common method of experimental design, is a set of statistical and mathematical technique that is valuable for the analyzing and modeling engineering phenomena in which a response of interest is influenced by several variables. The objective of response surface methodology is to optimize the response surface that is influenced by various process parameters and to quantify the relationship between the controllable input parameters and the obtained response surfaces. Using response surface methodology the number of experiment decreases. The main objective of this work is to provide better understanding about the relationships between the various variables.

To study the relationships between several control variables and to lower the number of runs, the Box-Behnken design (BBD) of experiment has been used. Response surface method is not commonly used by researchers in coating-corrosion studies. However, it is an interesting tool when numerous variables could affect the response. The study of the corrosion properties of cobalt coating produced by the pack-cementation method at low temperature has not been
reported elsewhere. The purpose of this study was to investigate the corrosion properties of cobalt coating, employing the polarization technique. The parameters selected for optimization were concentration of cobalt \( (x_1) \), concentration of activator \( (x_2) \), and heat treatment temperature \( (x_3) \). The corrosion performance of this coating was evaluated by a resistance polarization technique in 3.5 wt. % NaCl solutions.

The effective factors of the pack-cementation process used in cobalt coating were the amount of salt activator contained in the pack powder, concentration of cobalt, and heat treatment temperature. This type of coating is usually employed at a high temperature, but this study shows that pack-cementation coating can also be carried out at a low temperature.

**Experimental Procedure**

**Coating preparation**

AISI 430 stainless steel measuring 10 mm×5 mm×2 mm with a chemical composition of 17.4% Cr, 0.92% Mn, 0.85% Si, 0.12% C, 0.02% S, and 0.03% P, and Fe as the remainder, were selected for the study. The steel samples were polished with 320-1200 grit paper, ultrasonically cleaned in ethanol, and then dried. In order to deposit cobalt onto the substrate, the pack-cementation method was employed. The Co, Al\(_2\)O\(_3\), and NH\(_4\)Cl powder with an average size of 1.0, 70–80, and 240 µm respectively, were used as the powder mixture. All the chemicals were procured from Merck with above 99.99% purity. Cobalt was deposited onto the surface of AISI 430 steel using the pack-cementation method by vary the salt activator concentration in the pack powder, deposition temperature, and deposition time. After the pack-cementation treatment, the samples were removed from the pack and ultrasonically cleaned in ethanol to remove any embedded pack material. Table 1 shows the actual experimental design matrix (based on the Box-Behnken design model) and various conditions at which coating is formed; this matrix was created using Design Expert 7.1.3 software. The source of the Design Expert Software is SPSS 17. In each experimental run, the process variable conditions given in the design matrix were maintained.

**Microscopy, surface morphology and corrosion analysis**

The microstructure and surface morphology of the samples were studied by SEM (scanning electron microscopy, CamScan MV2300, England). An EG&G Model 263A potentiostat was used for the corrosion studies. Measurements were carried out in a three-electrode cell assembly containing a 3.5% NaCl solution. A platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. Polarization curves were achieved at a speed of 1 mv/s.

**Response surface methodology and statistical analysis**

The preliminary range of the extraction variables was determined through a single-factor test; a Box-Behnken design was used with three independent variables namely, cobalt concentration \( (x_1) \), activator concentration \( (x_2) \) and heat treatment temperature \( (x_3) \) at three levels. For the statistical calculation, the variables were coded according to the following equation:

\[
x_i = \frac{A_i - A_n}{\Delta A}
\]

... (1)

where \( x_i \) is the coded value of the variable; \( A_n \) the actual value of the variable; \( A_0 \), the actual value of \( A_i \) at the centre point; and \( \Delta A \), the step change of the variable. In this study, concentrations of cobalt and the activator, as well as heat treatment temperature, were selected as independent variables \( (x_1, x_2, x_3) \) respectively and the corrosion current was the dependent output response of the system. Table 2

<table>
<thead>
<tr>
<th>Run</th>
<th>Concentration of cobalt, %</th>
<th>Concentration of activator, %</th>
<th>Heat treatment temperature, °C</th>
<th>Corrosion current, A/cm²</th>
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<td>4.1E-009</td>
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<td>650</td>
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<td>650</td>
<td>5.9E-009</td>
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<td>8</td>
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<table>
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<th>Category</th>
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<th>Low level (-1)</th>
<th>Low level (-1)</th>
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<tr>
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<td>12</td>
</tr>
<tr>
<td>Concentration of activator, %</td>
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<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Heat treatment temperature, °C</td>
<td>650</td>
<td>750</td>
<td>850</td>
</tr>
</tbody>
</table>

Table 2—Levels of variables chosen for the trials
shows the independent variables, experimental range, and levels of the design model.

If all variables are assumed to be measurable, the response surface can be expressed as

$$ Y = f(x_1, x_2, x_3, \ldots, x_k) \quad \ldots (2) $$

where $Y$ is the answer of the system, and $x_i$ represents the variables of action, also called factors. The purpose of this is to optimize the response variable $y$. It is assumed that the independent variables are continuous and controllable by experiments with negligible errors. A suitable approximation for the true functional relationship between independent variables and the response surface is required. Usually, a second-order model like Eq. (3) is utilized in an response surface methodology, as shown below:

$$ Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \varepsilon \quad \ldots (3) $$

where $x_1, x_2, \ldots, x_k$ are the input factors that influence the response $Y$. $\beta_0, \beta_i (i=1,2,\ldots,k)$ and $\beta_{ij}$ $(i=1,2,\ldots,k ; j=1,2,\ldots,k)$ are unknown parameters, while $\varepsilon$ is random error. The $\beta$ coefficients, which should be determined in the second-order model, are obtained by the least square method.

The fitted polynomial equation is expressed as surface plots in order to visualize the relationship between response and experimental levels of each factor and to realize the optimum conditions. The Design Expert 7.1.3 software package was used to analyze the experimental data. $p$-values less than 0.05 were considered to be statistically significant.

Experimental statistical methods are often used in the design of experiments, and the significant factors of the preparatory conditions can be tested by analysis of variance. This is also a reliable method to simplify the process of identifying the most influential preparation variables, and the optimal preparatory conditions are singled out.

The aim of optimization was to determine the optimized conditions of the experimental variables. The three variables were selected to identify the optimal conditions for a higher corrosion resistance of cobalt coating using the Box-Behnken design and response surface methodology.

**Results and Discussion**

The Box-Behnken design is used to determine the response (corrosion current) for different variables of pack-cementation coating preparation (concentration of cobalt, concentration of activator, heat treatment temperature. The objective of the experimental design was to optimize the reaction conditions for maximizing corrosion current. As the classic method of optimization cannot examine all the possible combinations of independent variables, and the full factorial method is too difficult to perform, therefore the use of appropriate statistical experiment design tools for optimization is necessary. The use of Box-Behnken design for finding optimum levels of selected variables is well established. Response surface methodology allows calculation of the optimum levels of various process parameters based on a few sets of experiments.

Figure 1 shows the polarization curves. As can be seen, the corrosion current of the uncoated sample is equal to $7e^{-8}$. The corrosion current represents the corrosion properties of samples; it is well-known that as the corrosion current decreases, the corrosion resistance increases.

The statistical results of the recommended model for the Box-Behnken design created using the design expert software are shown in Table 3. The results for the $p$-value, $F$-value, and $r^2$ (0.8577) show that the model is reliable. $F$-value is calculated by model
mean square divided by residual mean square and shows the effect of curvature relative to the background noise. A large number (ratio) means that curvature is a significant contributor to the overall variance. The *F*-value is used to test the significance of adding new model terms to those terms already in the model. In statistical hypothesis testing, the *p*-value is the probability of obtaining a test statistic at least as extreme as the one that was actually observed. The model *p*-value should be less than 0.05 to be strongly significant, between 0.05 and 0.10 is marginally significant.

From the experimental results derived from Fig. 1 and Eq. (3), the second-order response functions representing corrosion can be expressed as a function of *x*₁, *x*₂, and *x*₃. The relationship between the response and the variables attained is shown in below equation:

\[
i_{\text{corrosion}} = (8.41736\times10^{-9}) - (5.84375\times10^{-10} \times x_1) + (3.66528\times10^{-9} \times x_2) + (6.95833\times10^{-12} \times x_3) - (8.08333\times10^{-12} \times x_2 \times x_3) - (4.11111\times10^{-10} \times x_2)\]

… (4)

This model is useful as an approximation of the true response surface in a relatively small region, and it is widely used in response surface methodology for the following reasons:

(i) The second-order model is too flexible and can take on a wide variety of functional forms, so it will frequently work well as an estimate of the true response surface.

(ii) It is easy to estimate the parameters in the second-order model. The method of least squares can be used for this purpose.

(iii) There is considerable practical experience indicating that second-order models work well for solving real response surface problems.

The *r*² is obtained from comparison between actual values from the experimental data and the predicted values from the model. The *r*² value is equal to 0.85; this is within the acceptable range. Figure 2 shows the effect of concentration of cobalt (*x*₁) and concentration of activator (*x*₂) on corrosion current at constant heat treatment temperature (752°C). It is obvious that *i*ₙ₉*₉₉* decreases with increasing *x*₁; however, the behavior of *x*₂ is complicated. On increasing *x*₂, the corrosion current first decreases and then increases. This means that the corrosion resistance is enhanced with higher *x*₁ values and with average *x*₂ values.

The results show that the concentration of cobalt is an important parameter that affects the quality of coating, as does activator concentration and heat treatment temperature. Increasing the Co content in the pack-cementation mixture enhances the resistance of the coating. A low concentration of cobalt results in low thickness, and possibly increases the number of voids and cavities. For corrosion purposes, a

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of square</th>
<th>df</th>
<th>Mean squares</th>
<th><em>F</em>-value</th>
<th><em>p</em>-value (prob &gt; F)</th>
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<td>5.09</td>
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<td><em>x</em>₂²</td>
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<td>10.15</td>
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<td>4.623E-018</td>
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<td>1.0000</td>
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<tr>
<td>Lack of fit</td>
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<td>5.249E-018</td>
<td>21.42</td>
<td>0.1649</td>
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<tr>
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<td>13</td>
<td></td>
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<td>1.0000</td>
</tr>
</tbody>
</table>
minimum thickness of the coating is required. It is also found that an unsuitable amount of NH$_4$Cl in the pack mixture (lower or higher) results in a porous coating with many voids and cavities, causing lower corrosion resistance. A minimum temperature of at least 800°C is required to activate the chemical reaction in order to deposit Co onto the surface. A high deposition temperature results in a thicker layer.

Verification and optimization

To verify the model, five additional tests were carried out using random conditions; the statistical results developed by the model were compared with the experimental results (Table 4). The relative error was calculated by Eq. (5). The results show the low relative error; and therefore, this model could be used to describe the important process variables that affect the pack-cementation method. Equation (5) is given below:

\[
\text{Relative error} = \frac{\text{Statistical result from model} - \text{Actual result from experiment}}{\text{Actual result from experiment}} \quad \ldots (5)
\]

To optimize the coating corrosion resistance, it is desirable to minimize the corrosion current $i_{\text{cor}}$. In this case, the optimum conditions are found to be $x_1 = 10.63$, $x_2 = 2.90$, and $x_3 = 840.78$, with the highest desirability at 1. The response predicted by the model is $i_{\text{cor}} = 2.43205 \times 10^{-9}$.

In order to verify the optimization of $i_{\text{cor}}$, an experiment was carried out at optimized conditions,
and then the final optimal number was compared with the experimental data under the same conditions. As shown in Fig. 1, $i_{\text{corrosion}}$ at optimized condition is 2.3E-9; therefore, the relative error for $i_{\text{corrosion}}$ is 5.6%.

Figure 3 shows a cross-sectional SEM image. The deposited layer shows good adherence to the substrate. Figure 4 shows an XRD diffraction pattern of a coated specimen. The identified phases include CoCr and CoFe. Ferrite and FeCr peaks come from the substrate. The surface of the coated specimen (Fig. 5a) is homogeneous, relatively dense, and rough. Figure 5b shows a SEM micrograph of a coated surface sample under high magnification, and demonstrates that the grains are bonded together.

**Conclusion**

The predicted values of $i_{\text{corrosion}}$ achieved using the model equations are found to be in good agreement with its experimental values ($r^2$ value of 0.85). The predicted models are presented as three-dimensional graphs to shows the effect of the variables on $i_{\text{corrosion}}$. This study show that response surface methodology and Box-Behnken design could well be applied for the modeling of the corrosion properties of the coating.

**Acknowledgement**

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**References**