Indian Journal of Chemical Technology
Vol. 24, March, 2017 pp. 162-168

Response surface methodology for manganese coating on AISI 430 and optimization of corrosion property

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Received 4 February 2014; accepted 5 December 2016

Pack cementation is a well known method for creation of diffusional coatings at low or high temperatures. The coating of manganese on AISI 430 alloy is applied and the corrosion properties of the coating have been investigated by electrochemical impedance spectroscopy (EIS) method. For modeling of variables that influences the corrosion properties of the coating, Box–Behnken experimental design and response surface methodology (RSM) is employed. The variables included amount of manganese in pack cementation mixture, amount of ammonium chloride and annealing temperature. The corrosion properties of Mn-coated samples have been investigated in NaCl 3.5 wt% solution. The results of EIS tests prove that Box–Behnken design (BBD) and response surface methodology could effectively be applied for modeling of Mn diffusional coating properties.

Keywords: Box–Behnken design, Manganese coating, Pack cementation, Electrochemical Impedance Spectroscopy (EIS), Corrosion

A common method to protect stainless steel alloys is the application of metallic protective coatings which act as a barrier against corrosive media like halides. Different methods include electroplating, electro-deposition, pack cementation and others are used for production of coating. Thermochemical surface treatment such as pack cementation has proved to be an efficient technique for depositing a uniform layer of diffusion coatings on steels or on other types of metal alloys[1-10].

Pack cementation is a relatively simple technique, which consists of immersing the component to be coated in a powder mixture in a sealed or semi-sealed retort. The pack normally consists of the coating element source, an activator, which is usually a halide salt, and an inert filler material, most often alumina, to prevent the source from sintering at high temperature[11,12]. The entire apparatus is placed inside a furnace and is heated in a protective atmosphere to a high temperature for a sufficient period of time. The pack cementation process is simple to reproduce.

Coatings containing manganese have significant effect on the oxidation and corrosion behaviour of steels[13-20]. In the previous work the effect of diffusional cobalt coating on the corrosion behavior of AISI 430 ferritic stainless steel was investigated[21]. In the present work pack cementation method is used for preparation of manganese coating on AISI430 stainless steel alloy for the protection of substrate against corrosion at low temperature. There are few studies aimed at understanding the effects of pack variables and deposition conditions on the corrosion properties of coating. Therefore a systematic method is accomplished to exactly realize the effect of processing variables on corrosion properties. These variables include percent of manganese (X1) and activator (X2) on pack cementation mixture as well as sintering temperature (X3). Since the thermochemical treatment of alloy steels at temperatures higher than 900°C can severely degrade their mechanical properties such as high temperature strength and creep resistance, X3 is taken below 900°C. Using Box-Benken design (BBD) and response surface method (RSM) it is possible to better understand the relationships between the factors (X1, X2, X3) and the response.

Experimental Section

Coating Preparation

Samples of AISI 430 stainless steel containing 17.4% Cr, 0.92% Mn, 0.85% Si, 0.12% C, 0.02% S, 0.03% P with Fe as remaining, were selected for this study. Coupons with a dimension of 10 mm × 10 mm × 2 mm (width × length ×

height) were obtained using a wire cut machine and ground with SiC paper of 320-1200 grit, ultrasonically cleaned in ethanol and dried. In order to deposit manganese on the substrate, pack cementation method was employed. Mn, Al_2O_3 and NH_4Cl powder were used as powder mixture in average size of 150 µm, 70-80 µm and 240 µm, respectively. Various amount of manganese, NH_4Cl and Al_2O_3 at different temperatures were used for coating of manganese onto AISI 430 stainless steel. After pack cementation treatment, the samples were removed from the pack and ultrasonically cleaned in ethanol to remove any embedded pack material.

Instrumentation

Microstructure and surface morphology of coatings were studied by scanning electron microscopy (SEM) (CamScan MV2300, England). The PARC 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% sodium chloride solution. The platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. A Lug in capillary with a porous tip was employed for minimizing contamination and preventing potential variation in the reference electrode, as well as to position it in the desired point of the cell. Impedance measurements were carried out at the OCP using a frequency response analyzer at the frequencies from 100 kHz to 10 MHz with an amplitude of 10 mvs, peak-to-peak. The exposed surface area of samples were 1 cm^2. Power suit software package was used to control the corrosion tests and results.

Response surface methodology and statistical analysis

The aim of this work was to examine the effects of percentage of manganese (X_1) and activator (X_2) on pack cementation mixture as well as sintering temperature (X3) using a RSM approach. In addition, the RSM was also applied to identify the optimal conditions for the best corrosion properties, as measured by electrochemical impedance spectroscopy[22].

The preliminary range of the extraction variables was determined through a single-factor test, a BBD with three independent variables (X1, X2 and X3) at three levels was performed. For the statistical calculation, the variables were coded according to Equation 1.

$$X_i=(A_i-A_0)/\Delta A \qquad \ldots (1)$$

where Xi is a coded value of the variable, A_i is the actual value of the variable, A_0 the actual value of A_i at the centre point and ΔA is the step change of the variable. The range of independent variables and their levels are presented in Table 1, which is based on the results of preliminary experiments. As seen from Table 2, the complete design consisted of 15 experimental points, which were carried out in a random order.

If all variables are assumed to be measurable, the response surface can be expressed as Equation 2.

$$Y=f(X_1,X_2,X_3,\ldots,X_k) \qquad \ldots (2)$$

In Equation 2, Y is the answer of the system, and X_i is the variables of action, also called factors including sintering temperature, activator percent and Mn percent.

The intention was to optimize the response variable Y. It was 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 was required. Usually, a second-order model is utilized in response surface methodology as written in Equation 3.

$$\mathrm{Y} = \beta_o + \Sigma_{i=1}^{k} \beta_i X_i + \Sigma_{i=1}^{k}\beta_{ii}x_i^2 + \Sigma_{i-1}^{k-1}\Sigma_{j=2}^{k}\beta_{ij}x_i x_j + \varepsilon \qquad \ldots (3)$$

where X_1, X_2, . . . , X_k are the input factors that influence the response Y. The β_0, β_{ii} (i=1,2,. . . ,k) and β_{ij} (i=1,2,...,k; j=1,2,...,k) are unknown parameters and ε is a random error. The β coefficients, which

Table 1 — The levels of variables chosen for the trials.

	Low level (-1)	Low level (-1)	Low level (-1)
Concentration of manganese (%)	4	8	12
Concentration of activator (%)	1	4	7
Heat treatment temperature (°C)	700	800	900

Table 2 — Box–Behnken design with actual values for three size fractions

Run	Concentration of manganese	Concentration of activator	Heat treatment temperature	Results $\|Z\|\times10^6$ (Ohms)
1	4	4	700	17.2335
2	12	7	800	21.32211
3	4	4	900	38.1123
4	8	1	700	11.5546
5	8	4	800	31.5443
6	8	7	700	8.6577
7	12	1	800	26.7621
8	4	1	800	14.7821
9	8	7	900	26.8112
10	8	1	900	27.4333
11	12	4	700	40.5542
12	4	7	800	11.6553
13	12	4	900	43.5566
14	8	4	800	32.8774
15	8	4	800	33.7551

should be determined in the second-order model, are obtained by the least square method. The fitted polynomial equation was expressed as surface plots to envision the correlation between the response and experimental levels of each factor and to find the optimum conditions. The design Expert 7.1.3 software package was used to analyze the experimental data.

Results and Discussion

Corrosion results and Box-Behnken analysis

Electrochemical impedance spectroscopy (EIS) measurement is a non-destructive method for measuring corrosion rates of coatings. EIS measurements were conducted with the immersion of uncoated sample and coated samples at determined condition. The impedance plots of several experiments are shown on Fig. 1. The area under each impedance curve is a good feature to show the corrosion properties of the coating.

The sum of lZl values derived from power suit software package which were measured at 30 frequencies (from 10^5 Hz to 0.01 Hz step by step) are equivalent to that area and in this research is considered as result (R). The results of 15 experiments of BBD are shown in Table 3.

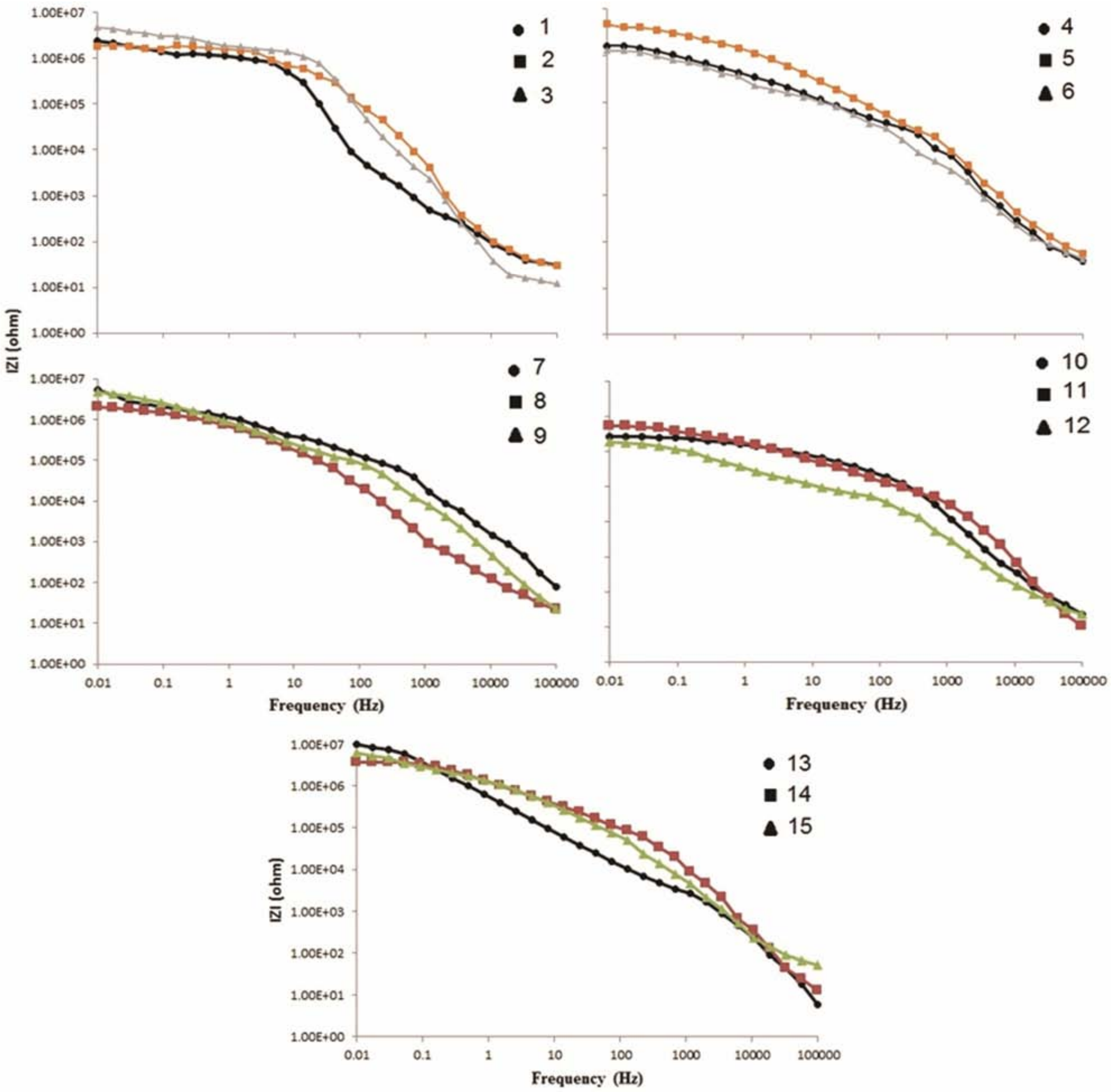

Fig. 1 — The impedance spectra of uncoated sample and coated samples under different conditions given in Table 2.

Table 3 — Statistical results of recommended model for Box–Behnken design

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	1711.896	5	342.3791	87.17024	< 0.0001	significant
A-A	317.6688	1	317.6688	80.87896	< 0.0001	
B-B	18.25829	1	18.25829	4.648588	0.05	
C-C	419.2452	1	419.2452	106.7405	< 0.0001	
AC	79.89142	1	79.89142	20.34048	0.0015	
B^2	876.8318	1	876.8318	223.2427	< 0.0001	
Residual	35.34936	9	3.927706			
Lack of Fit	32.87098	7	4.695854	3.789449	0.2246	not significant
Pure Error	2.478383	2	1.239192			
Cor Total	1747.245	14				

From the experimental results listed in Table 2 and using Equation 3, the second-order response functions can be expressed as a function of X_1, X_2 and X_3. The relationship between response and variables were achieved as Equation 4.

$$R = -133.30505 + 10.51357X_1 + 13.11894\ X_2 + 0.16177X_3 - 0.011173X_1.X_3 - 1.7028\ X^2{}_2 \quad \ldots (4)$$

Statistical results of recommended model for Box–Behnken design are shown in Table 3. In this case A, C, AC, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The "Lack of Fit F-value" of 3.79 implies that the Lack of Fit is not significant relative to the pure error. There is a 22.46% chance that a "Lack of Fit F-value" this large could occur due to noise. No-significant lack of fit is good, because it is necessary for the model to fit.

The model adequacy was checked by an F-test and the determination coefficient R^2. The analysis of variance showed that this regression model was significant (P-values< 0.0001), with F-values of 87.17024. The fitness of the model was further confirmed by a satisfactory value of the determination coefficient, which was calculated to be 0.9798, indicating that about 97% of the variability in the response could be predicted by the model. For a valid model, R^2 should be more than 0.6.

Table 4 shows a review of important statistical analysis of the model. R-squared is the multiple correlation coefficient computed as $1\text{-}SS_{residual}/(SS_{model} + SS_{residual})$. The predicted R-squared of 0.9138 is in reasonable agreement with the adjusted R-squared of 0.9685. Adjusted R-squared is a measure of the amount of variation about the mean explained by the model.

Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of the model is 26.445 that indicates an adequate signal. This model can be used to navigate the design space.

The C.V % (coefficient of variation) of the model is 7.69 that shows the model is efficient. C.V% is the error expressed as a percentage of the mean. It is computed as 100 × (Std Dev)/(Mean). The dependent mean is the average of all the values for this particular response and for this model equals to 25.77.

Table 4 — Important statistical analysis of the model

Std. Dev.	1.98
R-Squared	0.9798
Mean	25.77
Adjusted R-Squared	0.9685
C.V. % (Coefficient of Variation)	7.69
Predicted R-Squared	0.9138
PRESS	150.62
Adequate Precision	26.445

A measure of how well a particular model fits each point in the design; the coefficients for the model are calculated without the first point. This new model is then used to estimate the first point and calculate the residual for point one. This is done for each data point and the squared residuals are summed.

The correlation between the predicted and experimental responses can be visualized through linear relations. The higher values of R-squared indicate that the predicted conditions using the Box - Behnken model were an index for accuracy for experimental usage.

The effect of each variable on the result is shown in Fig. 2 and Fig. 3. Fig. 2 shows the effect of X_1 and X_3 on the result at constant activator of 4%.

It is obvious that result (R) decreases with lowering X_1 and X_3. This means that corrosion properties are enhanced with higher X_1 and X_3 values. The effect of X_1 and X_2 is shown in Fig. 3. This figure represents that an average content of activator about 4% in pack cementation mixture can produce a coating with the best corrosion properties.

The results show that the concentration of manganese is an important parameter which affects the quality of the coating, as does activator concentration and heat treatment temperature. Increasing the Mn content in the pack-cementation mixture enhances the corrosion properties of the coating. A low concentration of manganese results in

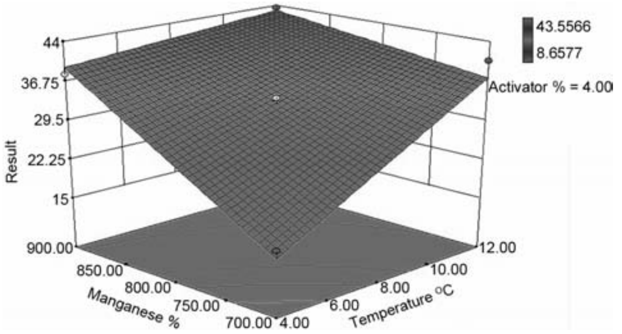

Fig. 2 — Response surface plots showing the effect of manganese content (X_1) and heat treatment temperature (X_3) on result at constant activator content of 4%.

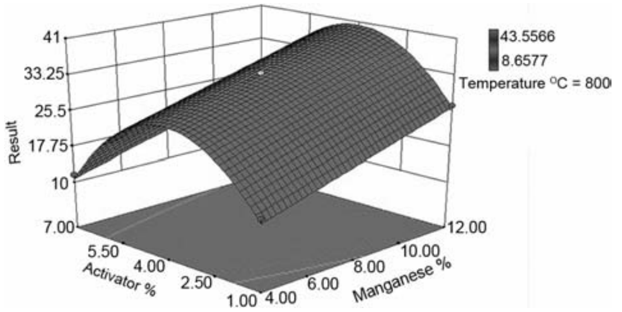

Fig. 3 — Response surface plots showing the effect of manganese content (X_1) and activator content (X_2) on heat treatment temperature of 800°C.

low thickness, and possibly increases the number of voids and cavities. For corrosion purposes, a minimum thickness of the coating is required. It was also found that improper amount of NH_4Cl in the pack mixture (lower or higher) results in a porous coating with many voids and cavities, causing lower corrosion resistance. Low amount of activator result to a low thickness of coating and a high amount of activator leads to a high thickness of coating. The growth of a thick coating may offer an effective protection with long term durability. However, the presence of voids reduces the coating adhesion and its corrosion protection. Furthermore, voids, which may be created near the interface of the coating-substrate, eliminate the positive role of such thick coating and additionally, decrease the adherence of coating on the substrate. The formation of voids is rather attributing to the Kirkendall effect which results from the high activator concentration[10]. High activator contents cause the diffusion of the elements very fast during the deposition, which create coating cavities and discontinuities. A minimum temperature of at least 800°C is required to activate the chemical reaction in order to deposit Mn onto the surface. A higher deposition temperature results in a thicker layer and also better barrier properties which results on better corrosion properties.

Table 5 — Conditions at which verification tests have been done and results

	Conditions of verification tests			Results derived from model	Results derived by experiment	Relative errors
	X1	X2	X3			
1	4.6	5.4	874	32.71305	31.2	4.8
2	8.3	6.6	706	15.10669	16.7	9.5
3	11.5	4.6	673	34.31466	31.9	7.5
4	6.2	3.5	723	23.81169	24.7	3.5
5	9.5	5.8	834	31.77403	29.8	6.6

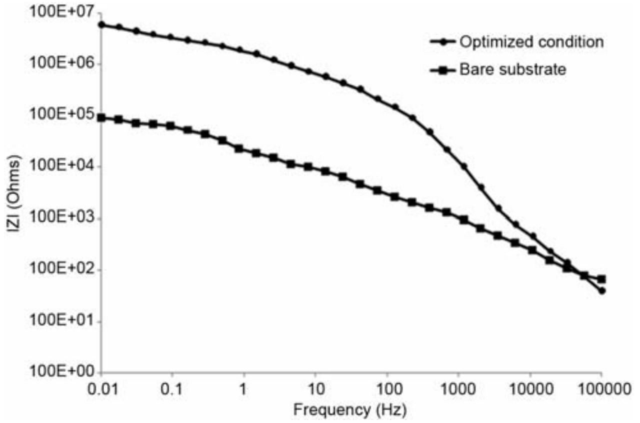

Fig. 4 — Bode diagram of optimized coating in comparison with bare substrate.

Verification and Optimization

In order to validate the model, five more experiments were carried out at random conditions and the experimental results are compared with statistical results developed by the model. The results are shown in Table 5. The relative error is calculated by Equation 5. Results show that the relative errors are low and therefore the model could be used to explain important process variables that affect corrosion properties of Mn pack cementation coating.

$$\text{Relative error} = \frac{(\text{Statistical result from model - actual result from experiment})}{\text{actual result from experiment}} \quad \dots (5)$$

The optimized condition suggested by software that shows the highest value of result and best corrosion properties is $X_1 = 12$, $X_2 = 3.85$, $X_3 = 900$. The desirability of the optimized condition is 0.986 and the result is 43.0564 ohms. Desirability is an objective function that ranges from zero outside of the limits to one at the goal. The numerical optimization finds a point that maximizes the desirability function. The EIS spectra of the coating prepared at optimized condition compared with bare AISI 430 substrate is shown in Fig. 4.

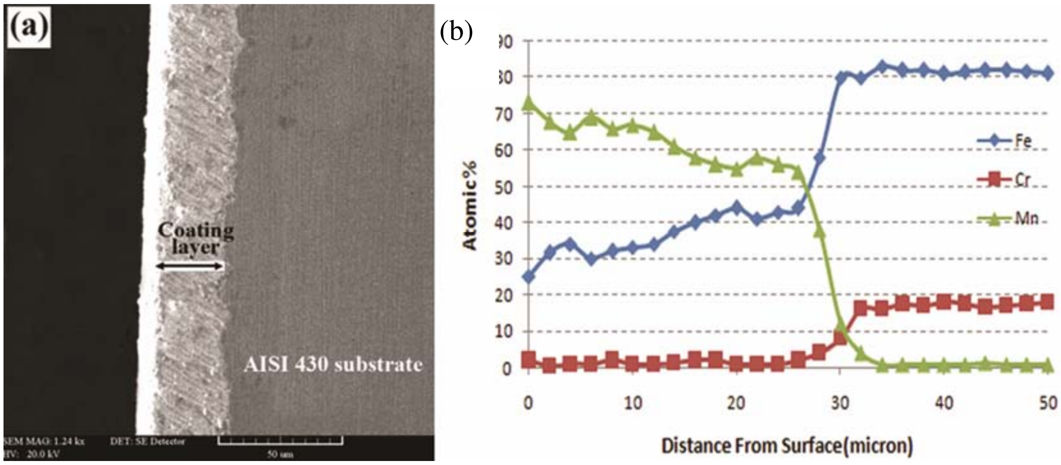

Fig. 5 — SEM cross section image (a) and elemental distribution (b) of manganese coated sample at optimized condition.

Figure 5 shows cross section SEM image (Fig. 5a) and concentration profile of the major elements in the coating layer measured by EDS (Fig. 5b). The coated layer (Fig. 5a) showed complete adherence to the surface and no spalling was observed on cooling and heating, which is attributed to a good thermal match between the scale and the substrate. XRD diffraction pattern of coated specimen is shown on our previous research[9]. It has been shown that the identified phases included $FeMn_3$ and $FeMn_4$. During the experiment, the active Mn was probably created by the following reactions:

$$NH_4Cl[g] \rightarrow NH_3[g] + HCl[g] \quad \ldots (6)$$

$$2\,NH_3[g] \rightarrow N_2[g] + 3H_2[g] \quad \ldots (7)$$

$$2HCl[g] + Mn[s] \rightarrow MnCl_2[g] + H_2[g] \quad \ldots (8)$$

$$MnCl_2[g] + H_2[g] \rightarrow 2HCl[g] + [Mn] \quad \ldots (9)$$

and therefore the formation of $FeMn_3$ and $FeMn_4$ based on the active Mn is carried out through the following reactions:

$$3[Mn] + [Fe] \rightarrow FeMn_3[s] \quad \ldots (10)$$

$$4[Mn] + [Fe] \rightarrow FeMn_4[s] \quad \ldots (11)$$

There are ferrite and FeCr peaks that related to the substrate. The presence of Al_2O_3 was believed to be the residue filler (Al_2O_3) material remained after cleaning or the entrapped Al_2O_3 in the coating during the growth of coating layer. From previous research it could be find out that the surface of the coated specimen is homogeneous and relatively dense and that the grains are bonded together[9]. Some pores were also observed which may be due to the remained ethanol after the pack treatment that caused to the creation of these pores.

Conclusion

The response surface methodology led to the development of an empirical polynomial model for the corrosion properties of pack cementation method coating. The model was able to foresee the result (the area under bode diagram at electrochemical impedance spectroscopy tests) by changing processing conditions, including Mn%, activator% and sintering temperature. These conditions have significant effects on the corrosion properties. Using the surface plots in RSM was effective for estimating the effect of three independent variables.

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