The Effect of Processing Parameters on the Corrosion Resistance of Zn-Ni Coating

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ABSTRACT

The effect of processing parameters such as nickel ion concentration, zinc ion concentration, stabilizer ratio, brightener concentration and current density on the corrosion resistance of Zn-Ni coating has been investigated in this study by the Taguchi robust experimental design method. According to the experimental results, the corrosion resistance of the Zn-Ni coating was noted to be primarily affected by the Ni content in the coating, which was found to be strongly influenced by the current density and zinc ion concentration involved during the coating process. The achieved corrosion resistance of Zn-Ni coating was also found dependent upon the stabilizer ratio, brightener concentration and the interaction of nickel ion with zinc ion or brightener concentration involved during the electrodeposition process. The optimized parameters for the production of Zn-Ni corrosion resistant coatings are: the concentration of nickel ion - 2.0 g/l, stabilizer ratio - 6, the interaction between nickel ion and zinc ion - 2.0 and 6.5 g/l and the interaction between nickel ion and brightener - 2.0 g/l and 16 g/l. The second order regression equations have been developed to predict the required nickel content and the obtained corrosion resistance of the Zn-Ni coating.

Keywords: Zn-Ni coating, Corrosion resistance, Robust design method

實驗參數對鋅鎳合金腐蝕阻抗的效應

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摘　要

鋅鎳合金的腐蝕阻抗主要受鍍層內鎳含量的影響，同時也受實驗參數間接的影響；藉由田口實驗法可知影響實驗參數為鎳離子濃度、鋅離子濃度、鎳穩定劑量、光澤劑量及對鍍層內鎳含量及電流密度。本實驗結果，影響鍍層內鎳含量的顯著因子依序為電流密度及鍍液中鋅離子濃度。而影響腐蝕阻抗的重要參數，依序為鍍液中鎳離子濃度、鎳穩定劑量、鎳離子濃度與鋅離子濃度的交互作用、及鎳離子濃度與光澤劑量的交互作用。本研究對鍍層腐蝕阻抗的最佳操作條件為鎳離子濃度 2.0 g/l，鎳穩定劑量比 6，鎳及鋅離子交互作用濃度 2.0 及 6.5 g/l，以及鎳離子濃度與光澤劑量交互量 2.0 g/l 及 16 g/l。另外，亦發展出鋅-鎳鍍層之鎳含量與腐蝕阻抗的二次回歸式，藉此提供由實驗參數計算出鍍層內鎳含量及腐蝕阻抗。

關鍵詞：鋅鎳合金，腐蝕阻抗，田口實驗法

文稿收件日期 94.09.13; 文稿修正後接受日期 94.12.30.
Manuscript received Sep. 13, 2005; revised December 30, 2005

I. INTRODUCTION

Zinc electrodeposition has been widely used for the protection of ferrous metals in corrosion atmospheres [1, 2]. Theoretically, the zinc is sacrificially corroded while protecting the ferrous metal. Although pure zinc coating provides some capability for the protection of metal substrate, however, zinc is rapidly consumed in a severe corrosion environment. For this reason, the thickness of zinc coating has to be increased, which is not cost-effective and results in problems in forming and welding of the ferrous metal [3, 4]. Therefore, there are lots of R & D works, carried out during the last two decades, regarding to the production of zinc alloy coatings used to replace zinc coating [5-9]. The zinc alloy coatings, having high zinc content with less addition of noble metal, offer many excellent film characteristics such as superior corrosion resistance, chemical stability, weld-ability, paint-ability with reduced thickness. The zinc alloy coatings are able to provide good anodic protection of the ferrous metal and remains less active than zinc coatings. The Zn-Ni electrodeposition has been considered to be one of highly attracted zinc alloy coatings capable of providing high corrosion resistance [10-13].

The standard reduction potential of nickel ion is more positive than the zinc ion, so the nickel content is theoretically higher than the zinc content in the Zn-Ni coating prepared by the electrodeposition technique. However, the obtained composition of the coating produced in this study revealed the contrary result. The zinc content is shown higher than the nickel content in Zn-Ni coating. The corrosion resistance of Zn-Ni alloys is considered varied with the composition of coatings that is affected by processing parameters chosen for the electro-deposition. The coating composition is dependent upon various factors, which is related either to the noble metal content (Ni) in the Zn-Ni alloys, alloy morphology, density, and texture, or to the electrolytic conditions such as metal ion concentration of the solution [14-18], pH value [19], electrolyte temperature [20], current density [21], supplemented agent, and mechanical forces for the cell. Therefore, the corrosion resistance of Zn-Ni alloys is found indirectly affected by the operation parameters involved during electrodeposition process. In the last decade, various electrolytes with different bath composition [22-25] using different operation conditions [25, 26] have been employed to obtain Zn-Ni coatings with the favorable nickel percentage. However, these results are always under the dilemma of experiments due to the complicated electrodeposition conditions. Therefore, it is imperative to develop an effective and quick method to analysis the corrosion resistance of Zn-Ni coatings, achieved after the electro-deposition process.

Generally, there are several different approaches available for the experimental examination of the influence of processing parameters on the nickel content in Zn-Ni coatings, such as the simple one-factor-at-a-time approach, the full factorial design of experiments and the Robust Experimental

Design method. The one-factor-at-a-time approach requires the least runs of experiments but with low reproduction. The full-factorial experiment design conducts experiments under all combinations of factor levels, and thus needs a much larger number of experiments. The Robust Experimental Design method, known as Taguchi method, is one of the fractional factorial experimental design methods [27-29]. This method provides the efficient experimental analysis with much better accuracy.

Recently, The Robust Design has been widely and successfully applied in the experimental analysis [30-32]. The fundamental principle of Robust Design is to improve the quality of an experimental procedure by minimizing the effect of the causes of variation without eliminating the causes. The optimization is achieved with the result analyzed by experimental design method, which makes the performance minimally sensitive to the various causes of variation.

The two major tools used in the Robust Design to promote the accuracy and efficiency of the experimental procedure are: (1) signal-to-noise ratio, which measures quality about the experimental accuracy, and (2) orthogonal arrays, which are used to study many processing parameters simultaneously to minimize the experimental running. In recent years, several researchers have employed the Taguchi method with an orthogonal array to plan the experiment in their studies. The analysis of variance was also used to determine the significant factors and interactions among processing parameters on objective properties. The corrosion resistance of electrochemical deposition of Zn-Ni coating is affected by a complicated combination of processing parameters. Therefore, the objective of this study is to analyze the influence of processing parameters on the corrosion resistance for Zn-Ni alloys coating by Robust Design method. It is found that the nickel content of the coating directly influences the corrosion resistance of Zn-Ni coating. The second order regression equations are developed for predicting the nickel content in coating and its corrosion resistance.

II. THEORY OF ROBUST DESIGN METHOD

Robust Design involves three major steps, which can be divided as planning a matrix experiment, running the experiment, as well as analyzing and verifying the result.

2.1 Planning A Matrix Experiment

The identification of the experimental characteristics (corrosion resistance, y_i) and the objective function (S/N ratio, η) are the first step for planning a matrix experiment. The value of corrosion resistance is continuous and nonnegative, and it is desired to be as large as possible. This is a larger-the-better type problem. The objective function (S/N ratio, η), which is to be maximized in this case, is given by

$$\eta_i = \frac{S}{N} = -10\log\frac{1}{n}\sum_{i=1}^{n}\left[\frac{1}{y_i^2}\right] \qquad (1)$$

where

η_i = signal to noise ratio;

n: natural number (experimental times);

y_i: quality characteristic (polarization resistance) at level i.

The second step is to select the control factors (process parameters) and their levels. The factors and their levels for this experiment are presented in Table 1. Three-level of factors (A, B, C, D, and E) were selected and four interactions (A×B, A×C, A×D, and A×E) were estimated.

Finally, the matrix experiment was designed by orthogonal arrays. The selection of an orthogonal array depends on the number of factors, their levels and the desired interactions. In order to construct an orthogonal array to fit the requirement in this study, the total degrees of freedom (**df**) needs to be counted, which decides the minimum number of experiments that must be performed for all the selected control factors. The **df** for this experiment is calculated and shown in Table 2. The calculated value of **df** is 27, and at least 27 experiments must be carried out to estimate the effects of the factors and the desired interactions.

Table 1. Factor and levels of experiment

Factor	Level 1	Level 2	Level 3	Unit
A. Ni^{2+} Conc.	1.6	1.8	2.0	g/l
B. Zn^{2+} Conc.	6.5	8.0	9.5	g/l
C. Ni-T/Ni-S	2.0	4.0	6.0	ratio
D. Brightener	12.0	16.0	20.0	g/l
E. Current Density	1.0	3.0	6.0	A/dm^2

Table 2. The degrees of freedom for these experiments

Factor/Interaction	Degrees of freedom
Overall mean	1
A, B, C, D, E	5×(3-1)=10
A×B, A×C, A×D, A×E	4×(3-1) ×(3-1)=16
Total	27

2.2 Analyzing And Verifying The Result

In this stage, the results were analyzed to determine optimum levels of the control factors, and to predict the performance under these levels. In Robust design, S/N ratio and other summarized statistics are first computed for each experiment followed by performing the calculation of the factor effects and their analysis of variance (ANOVA). A better result of the interaction of the different factors on the objective function can be obtained by ANOVA. ANOVA is used in our experimental analysis to determine the relative magnitude of effect of each factor on the objective function and to estimate both the error variance for the factor effects and variance of the prediction error. In the ANOVA table, the relative magnitude of effect of each factor is determined by the F_0 value and $F_{0.95}(\beta, \gamma)$. If F0 value of a factor is larger than the $F_{0.95}(\beta, \gamma)$, then the factor effect is significant at 95 percent confidence level. Otherwise, the factor effect is insignificant. F_0 denotes the variance ratio that is the ratio of the mean square due to a factor and the error mean square, that is

$$F_0 = MS / MS_{error} \quad (2)$$

where

MS is the mean squares due to factor;

MS_{error} is the error mean square due to factor.

In statistic, the F_0 value is often compared to the quantities of a probability distribution called the F-distribution to determine the degree of confidence and whether a particular factor effect is significant or not. MS is obtained from the sum of squares due to factors (SS_A) divided by the degree of freedom which is expressed as

$$MS = SS_A / df \quad (3)$$

and

$$SS_A = \sum_{i=1}^{3} (R_{p_{Ai}} - \mu)^2 \times 9 \quad (4)$$

$$\mu = \frac{1}{n} \times \sum_{i=1}^{n} R_{p_i} \quad (5)$$

where

SS_A: the sum of squares due to factor A;

df: degree of freedom of all factors;

$R_{p_{Ai}}$: object function (Ni%, or R_p) about the factor A in level i;

R_{p_i}: object function (Ni%, or R_p) in level i;

μ: the overall mean value of R_{pi} for the experimental region.

Finally, from the ANOVA table, a better result of the interaction of the different factor on the objection function (Ni%, or R_p) can be clearly obtained.

III. Experimental Details

The electrolyte involved during the electro-deposition was prepared using the experimental grade chemicals and de-ionized water. The basic bath composition contains 1.6 to 2.0 g/L of Ni^{2+} as $NiSO_4$ and Zi^{2+} ranged from 6.5 to 9.5 g/L. The Ni-T (triethanolamine) is a stabilizer for stabilizing nickel ion of the electrolyte. The Ni-S (sulfosalicyclic acid) is the supplemented agent for nickel ion of the electrolyte. The Ni-T/Ni-S ratio is ranged from 2 to 6. The brightener comprised the organic compounds: ethoxy-lated nonyl- phenol with 15 ethylene oxide groups, C_9H_{19}-C_6H_4-O-$(CH_2CH_2O)_{15}$, ranged from 12 to 20 g/l.

The electrolyte temperature was controlled by a constant-temperature water bath at 18℃. Solution pH value was adjusted with NaOH at 13. The substrate is low-carbon steel (10×6.5×0.1cm) and the anode was nickel's electrode with dissolubility. The electroplating time and current density are set at 30 minutes and varied from 1.0 to 6.5 A/dm^2, respectively.

Experiments were carried out in an electrochemical cell of the capacity of one liter with the agitation controlled by an agitator. Electrodeposition were performed using an Hokuto Denko current pulse generator HC-113, to prepare the Zn-Ni coating under the different conditions such as electrolytic concentration of metal ion, current density, and additives agent. X-ray Photoelectron Spectroscopy (Fisher Scope X-ray 1010 System) was used to analyze the composition of the Zn-Ni coating after the electrodeposition.

Furthermore, the corrosion resistance test was carried out after the electrodeposition of Zn-Ni coatings. The polarization resistance performed by an EG & G273 Potentiostat was conducted to examine the corrosion resistance of the coating. The corrosion solution selected is 3.5 wt% NaCl. The scanning rate of polarization resistance is 1 mV/s between the interval of ±10 mV. The corrosion resistance was defined as Rp $\equiv \triangle E/\triangle i_{app}$, in which $\triangle E$ and $\triangle i_{app}$ was the variance of voltage and current, respectively. Finally, A salt spray test for these coating was also conducted to investigate the corrosion resistance in 5 wt% NaCl solution at temperature 35℃. The specimens were arranged in a salt spray cabinet and exposed in accordance with ASTM B-117.

IV. Results and Discussions

Table 3 shows the experimental results of the Ni content in the coating and corrosion resistance (R_p) with the corresponding value of S/N value, respectively. Table 4a, 4b show the interactions of the different factors from the ANOVA table, analyzed by the robust experimental design method. In this ANOVA table, the significant factors on the Ni content in the coating are ordered as the applied current density in this experiments (E) and the concentration of zinc ion in the electrolyte (B) at 95 percent confident level respectively. As well as, the significant factors on the corrosion resistance are ordered as the concentration of nickel ion in the electrolyte solution (A), the stabilizer is added in the electrolyte solution (C), the interaction of nickel ion with zinc ion in the electrolyte solution (AB) and the interaction of nickel ion with brightener in the electrolyte solution (AD), also at 95 percent confident level. Figures 1a and 1b show the variation of the S/N ratio and the factors affecting the Ni content and polarization corrosion resistance (R_p) in the coating, respectively.

Table 3. Corrosion resistance and nickel content of coating with S/N ratio

NO	Rp (Ω)	MSD of Rp	S/N of Rp	Nickel (%)	MSD of %	S/N of %
1	315.0	1.01E-05	49.97	7.95	0.0158	18.01
2	89.3	12.55-05	39.01	7.15	0.0197	17.09
3	318.7	0.98E-05	50.07	7.83	0.0164	17.87
4	119.6	6.99E-05	41.56	8.04	0.0155	18.11
5	87.5	13.07-05	38.84	4.61	0.0477	13.21
6	57.7	30.05-05	35.22	6.39	0.0245	16.11
7	29.9	111.8-05	29.52	6.56	0.0232	16.34
8	32.4	95.02-05	30.22	6.59	0.0230	16.38
9	123.0	6.61E-05	41.80	3.61	0.0777	11.10
10	85.3	13.76-05	38.61	9.36	0.0114	19.42
11	82.4	14.74-05	38.32	9.03	0.0123	19.11
12	84.7	13.93-05	38.56	6.07	0.0272	15.66
13	51.0	38.49-05	34.15	8.38	0.0143	18.44
14	93.9	11.35-05	39.45	7.43	0.0182	17.40
15	206.2	2.35E-05	46.29	8.07	0.0154	18.14
16	52.3	36.59-05	34.37	7.93	0.0160	17.97
17	59.5	28.25-05	35.49	4.82	0.0433	13.64
18	303.0	1.09E-05	49.63	6.47	0.0240	16.21
19	55.8	32.17-05	34.93	10.89	0.0084	20.74
20	121.4	6.78E-05	41.68	7.42	0.0184	17.36
21	285.5	1.23E-05	49.11	9.48	0.0112	19.52
22	230.5	1.887E-05	47.25	8.54	0.0137	18.63
23	248.6	1.62E-05	47.91	8.23	0.0149	18.28
24	267.4	1.39E-05	48.54	5.51	0.0331	14.81
25	310.0	1.04E-05	49.83	5.47	0.0344	14.63
26	178.9	3.12E-05	45.05	6.81	0.0216	16.65
27	318.7	0.98E-05	50.07	7.78	0.0166	17.81

MSD: Mean Square Deviation

Table 4a. Analysis of variance (ANOVA) for nickel content of coating

Factor	Degree of freedom	MS	F_0	$F_{0.95(\beta,\gamma)}$
A	2	0.26442	2.27119	5.719
B	2	3.11762	26.77792	5.719
AB	4	0.02874	0.24682	4.313
C	2	0.16617	1.42731	5.719
AC	4	0.04366	0.37503	4.313
D	2	0.53332	4.58081	5.719
AD	4	0.00751	0.06449	4.313
E	2	10.18587	87.48869	5.719
AE	4	0.07847	0.67399	4.313

MSE=(2A+4AB+2C+4AC+2D+4AD+4AE)/22 =0.116

$F_{0.95(2,25)}$=5.719　　$F_{0.95(4,25)}$=4.313

Significant factors：E、B

MSE: Mean Square Error

Table 4b. Analysis of variance (ANOVA) for Rp

Factor	Degree of freedom	MS	F_0	$F_{0.95(\beta,\gamma)}$
A	2	14.257	7.018	3.74
B	2	0.783	0.385	3.74
AB	4	7.864	3.871	3.11
C	2	10.848	5.340	3.74
AC	4	1.120	0.551	3.11
D	2	1.952	0.961	3.74
AD	4	6.929	3.411	3.11
E	2	0.130	0.064	3.74
AE	4	4.558	2.244	3.11

MSE=(2B+4AC+2D+2E+4AE)/14=2.031

$F_{0.95(2,14)}$=3.74　　$F_{0.95(4,14)}$=3.11

Significant factors：A、AB、C、AD

MSD: Mean Square Deviation

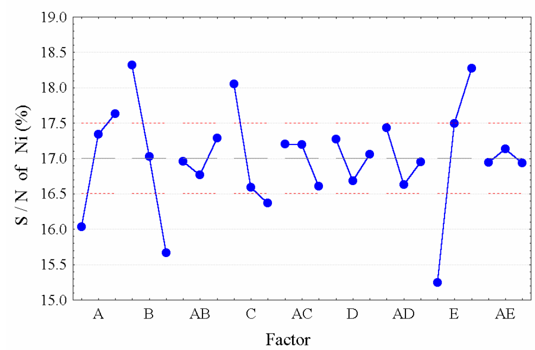

Fig. 1a. S/N ratio vs. factor effects of the nickel content in the coating.

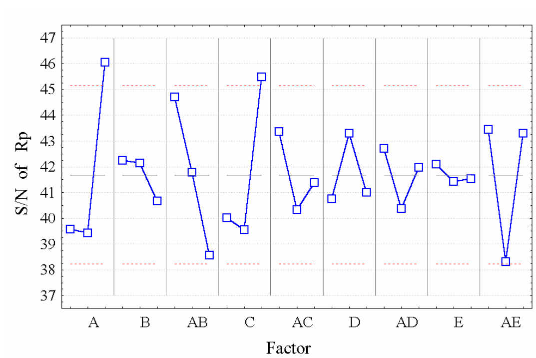

Fig. 1b. S/N ratio vs. factor effects of the corrosion resistance (Rp) of the coatings.

Figure 2 reveals the effect of the applied current density on the nickel content in the obtained Ni-Zn coating. The nickel content of the coating is show to be increased with the increasing of applied current density.

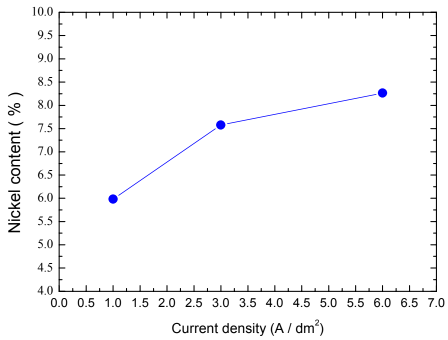

Fig. 2. The effect of the applied current density on the nickel content in the obtained Ni-Zn coating.

Figure 3 shows the influence of the zinc ion concentration in the electrolyte on the nickel content of the coating. The nickel content of the coating is note to be increased with the decreasing of the zinc ion concentration in the electrolyte. A higher applied current density (E3) and a lower concentration of zinc ion (B1) in the electrolyte are shown better for producing higher Ni content in the Zn-Ni alloy.

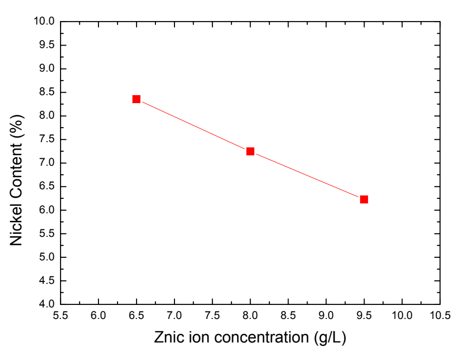

Fig. 3. The influence of the zinc ion concentration in the electrolyte on the nickel content of the coating.

In the alkaline bath of this Zn-Ni electrodeposition, the nickel ion and zinc ion are easily to form the metal hydroxides, $Ni(OH)_2$ and $Zn(OH)_2$. These metal hydroxides hinder the reduction of nickel ion in this electrochemical reaction. However, the mechanism of zinc ion reduction is favorable for continuously forming the Zn $(OH)_2$ and Zn metal [21]. The zinc hydroxide is a medium material in the reduction of zinc ion. The current efficiency is about 45-80% in an alkaline bath of the Zn-Ni electrochemical reaction [26]. The current density is increased to enhance the reaction rate of hydroxide ion, OH^-, and form the H_2O. As well as, it decreases the reaction rate of Zn $(OH)_2$. Therefore, the increase of applied current density is shown able to promote the reduction of nickel ion. Furthermore, the reduction rate of zinc ion may be alleviated by the decrease of the zinc ion concentration in the electrolyte. So, the smaller concentration of zinc ion in the electrolyte is more preferred for resulting in higher Ni content in Zn-Ni alloy.

The corrosion resistance of zinc phosphating coating on low carbon steel samples were investigated by conducting the salt spray test, based on the ASTM B-117 standard, with the Elite Salt Spray Tester using 5 wt % of neutralized salt solution (NSS) at the temperature of 35 ± 1°C. When the red rust occur on the sample, the salt spray test will stop and record the test time.

Figure 4 shows the relationship between the corrosion resistance and the nickel ion concentration in the electrolyte.

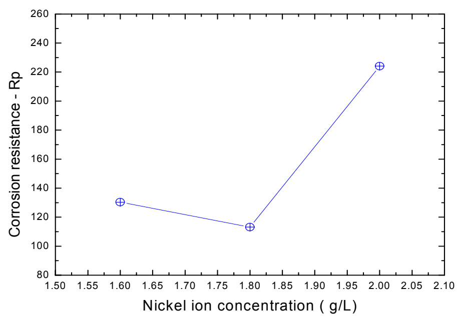

Fig. 4. The relationship between the corrosion resistance and the nickel ion concentration in the electrolyte.

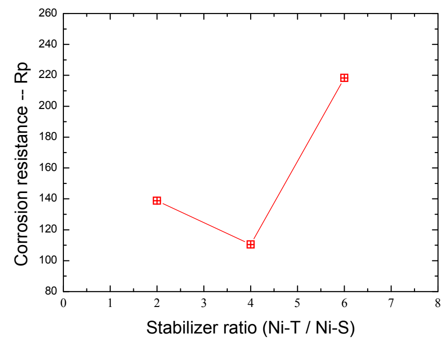

Fig. 5. The dependence of the corrosion resistance on the amount of stabilizer ratio in the electrolyte.

The corrosion resistance keeps almost a constant value at lower nickel ion concentration, then, it abruptly increases with the increasing of nickel ion concentration in the electrolyte.

Figure 5 shows the dependence of the corrosion resistance on the amount of stabilizer ratio in the electrolyte. The corrosion resistance is show to be increased as the stabilizer ratio is increased. A higher concentration of nickel ion in the electrolyte solution is shown preferred for resulting in higher Ni content in the Zn-Ni coatings after the electrodeposition process, so factor A promotes the ability of corrosion resistance. The optimum condition of factor A is the nickel ion concentration (A3) at 2.0 g/l. Literature [23] concerning the zinc-nickel system indicated that it showed the maximum corrosion resistance in the coatings obtained with the nickel content set at about 10-15% and an inferior corrosion resistance in the ones achieved with the nickel content set below 5%.

Under a lower concentration of nickel ion, the nickel content in the Zn-Ni coating obtained is about 4%. The corrosion resistance is also affected by the morphology of the coating. Therefore, the corrosion resistance keeps almost a constant value at lower nickel ion concentration and is fast enhanced at higher nickel ion concentration. The stabilizer is added in the electrolyte solution to stable the nickel ion of the solution in order to inhibit the formation of $Ni(OH)_2$ [23, 25], so factor C is also favors the Ni content of the Zn-Ni alloys. The optimum condition of factor C - the stabilizer ratio (C3) is at 6. The interaction of the nickel ion and zinc ion (AB) in the electrolyte is also an important factor affecting the corrosion resistance of the coating. These two metal ions compete each other affecting the amount of nickel content achieved in this electrochemical system. The optimum condition of factor AB - the interaction of nickel ion with zinc ion (A3B1) is at both 2.0 and 6.5 g/l. Factor D is the brightener aimed to uniform the primary current distribution and secondary current distribution, so a uniformed coating is obtained in this electrodeposition process. Factor D will indirectly assist the reduction of nickel ion (A) to achieve uniformly dispersed Zn-Ni alloys. The uniform morphology is favorable for the enhancing corrosion resistance of this coating. The optimized condition of factor AD - the interaction of nickel ion with the brightener (A3D2) is at 2.0 and 16 g/l.

Furthermore, the 3-D figures of reaction surface were introduced in order to easily visualize the interaction between two factors. Figure 6 shows the variation of the corrosion resistance of the Zn-Ni alloy with the interaction between nickel ion concentration and zinc ion concentration in electrolyte.

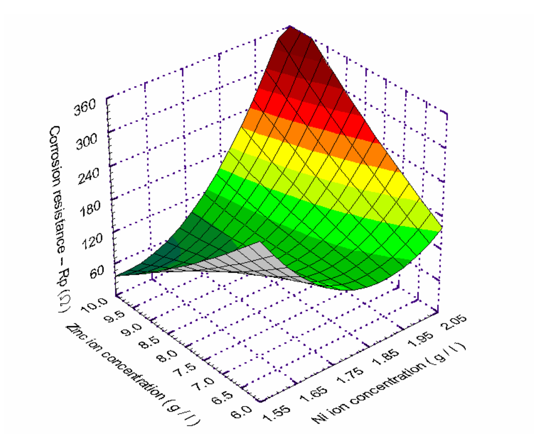

Fig. 6. The response surface shows the variation of corrosion resistance of the Zn-Ni alloy with the interaction between the concentration of nickel ion and zinc ion in electrolyte.

The corrosion resistance is linearly affected by the variation of the zinc ion under a lower concentration of nickel ion in the electrolyte. At the middle concentration of nickel ion in the electrolyte, the corrosion resistance almost keeps constant. At the highest concentration of nickel ion in the electrolyte, the corrosion resistance has proved to be improved by the interaction of the reduction of nickel ion and zinc ion in this electrochemical process. Although, the nickel content of the Zn-Ni coating is the most important factor on the corrosion resistance of the coating, but, the other factors such that of the texture, the morphology of the coating, are also shown to affect the corrosion resistance of the coating. The interaction of the reduction of nickel ion and zinc ion (AB) in this electrochemical process may result in the alteration of the morphology of the Zn-Ni alloy.

Figure 7 shows the variation of the corrosion resistance of the Zn-Ni alloy with the interaction between nickel ion concentration and brightener. The corrosion resistance of the Zn-Ni alloy is promoted by the interaction of the increased nickel ion concentration and brightener. However, the morphology of the coating is affected by the increase of nickel ion concentration.

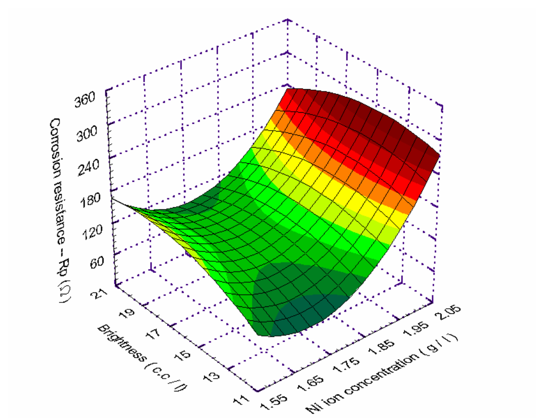

Fig. 7. The response surface shows the variation of corrosion resistance of the Zn-Ni alloy with the interaction between the nickel ion and brightener concentration.

Although, the corrosion resistance of the coating is complicatedly affected by the nickel content, texture, morphology of the coating. The nickel content in this alloy is the main influential processing parameter on the chemical characteristics of Zn-Ni alloy. A regression equation is introduced to estimate the effect of significant experimental parameters on the nickel content, shown as below,

$$Ni(\%) = 11.781 - 1.033\times B + 0.020\times B^2 + 1.2513\times E - 0.114\times E^2 \quad (6)$$

Similarly, a regression equation is introduced to estimate the effect of significant experimental parameters on the obtained corrosion resistance, shown as below,

$$Rp = 5028.774 - 5548.8\times A + 1601.806\times A^2 - 116.403\times C + 17.0347\times C^2 + 1.3809\times AB + 0.3508\times AD \quad (7)$$

These regression equations show some trends to obtain the better chemical characteristics of Zn-Ni alloy. The lower zinc concentration, higher nickel concentration, and higher stabilizer ratio introduced in the electrolyte bath incorporated with higher applied current density are shown favorable for enhancing the nickel content and corrosion resistance of Zn-Ni layer.

A salt spray test of the Zn-Ni coating is carried out to check the experiments of polarization corrosion resistance. Table 5 and figure 8 shows the variation and correlation of corrosion resistance with the nickel content in the coating. Both the trend of the time to red rust corrosion and the polarization corrosion resistance are consistence with the nickel content of the coating. The result shows that the Robust design analysis can efficiently improve the experiment running and accuracy involved in the investigation of the corrosion resistance of Zn-Ni alloy.

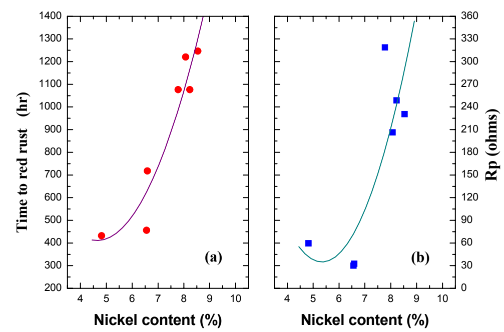

Fig 8. The relation of nickel content vs. corrosion resistance of the Zn-Ni alloy which using (a) salt spray test and (b) polarization test.
(a) $Y = 1681.636 - 546.814X + 58.817X^2$
(b) $Y = 749.869 - 267.617X + 25.041X^2$

IV. CONCLUSIONS

The Robust design method can be applied to effectively find the important factors affecting the nickel content and corrosion resistance of the Zn-Ni coating which leads to its optimized processing parameters. It is found that the significant factors on the Ni content in the coating are found to be the current density (E) and zinc ion concentration of the electrolyte (B). In addition, the significant factors on the corrosion resistance of Zn-Ni coating are found to be nickel ion concentration (A), stabilizer ratio (C), the interaction of nickel ion with zinc ion in the electrolyte (AB), and the interaction of nickel ion with brightener (AD). The optimum conditions for producing required nickel content in Zn-Ni coatings are: the applied current density, 6 A/dm^2; and the zinc concentration, 6.5 g/l. The optimum conditions for producing the preferred corrosion resistance of Zn-Ni coatings are: the concentration of nickel ion 2.0 g/l, stabilizer ratio 6, the interaction of nickel ion with zinc ion, 2.0 and 6.5 g/l, as well as the interaction of nickel ion with the brightener, 2.0 g/l and 16 g/l.

The corrosion resistance of the coating is complicatedly affected by the nickel content, texture, and morphology of the coating. The nickel content in the coating is the main influential processing parameter on the chemical characteristics of Zn-Ni coating. The second order regression equations are introduced to estimate the effect of processing parameters on the nickel content and corrosion resistance of Zn-Ni coating, shown as below:

$$Ni(\%) = 11.781 - 1.033\times B + 0.020\times B^2 + 1.2513\times E - 0.114\times E^2 \quad (8)$$

$$Rp = 5028.774 - 5548.8\times A + 1601.806\times A^2 - 116.403\times C + 17.0347\times C^2 + 1.3809\times AB + 0.3508\times AD \quad (9)$$

A salt spray test of the Zn-Ni coating is carried out to investigate its corrosion resistance. It is prove that both the time for the red rust corrosion and the polarization corrosion resistance are consistence with the nickel content of the coating.

REFERENCES

[1] Adaniya, T., Omura, M., Matsudo, K., and Naemura, H., “Development of Corrosion-Resistant Electrogalvanized Steel,” Plating and Surface Finishing, Vol. 68, No. 6, pp.96-99, 1981.

[2] Harvey, G. J. and Richard, P. N., “Zinc-Based Coatings for Corrosion Protection of Steel Sheet And Strip,” Metals Forum, Vol. 6, No. 4, pp.234-247, 1983.

[3] Arita, M., Matsuoka, K., Inoue, H., Naito, S., Shibata, T., and Ohnaga, K., “Thickness Distribution of Anti-Corrosive Coating Film for Offshore Structure Use,” Transactions of the Iron and Steel Institute of Japan, Vol. 27, No.5, pp.154, 1986.

[4] Knyazeva, V. V., Stepanok, N. A., and Orlov, V. A., “Protective Capacity of Zinc Silicate Coatings in Damage of Them,” Soviet Materials Science, Vol. 22, No.6, pp. 629-630, 1986.

[5]Adaniya, T., Hara, T., Sagiyama, M., Homa, T., and Watanabe, T., “Zinc-Iron Alloy Electroplating on Srip Steel,” Plating and Surface Finishing, Vol. 72, No. 8, pp.52-56, 1985.

[6] Verberne, W. M. J. C., “Zinc-Cobalt Alloy Electrodeposition,” Transactions of the Institute of Metal Finishing, Vol. 64, No. 1, pp.30-32, 1986.

[7] Sagiyama, M., Urakawa, T., Adaniya, T., Hara, T., and Fukuda, Y., “Electrodeposition of Zinc-Manganese on Steel Strip,” Plating and Surface Finishing, Vol. 74, No. 11, pp. 77-82 1987.

[8] Short, N. R., Abibsi, A., and Dennis, J. K., “Corrosion Resistance of Electroplated Zinc Alloy Coatings,” Transactions of the Institute of Metal Finishing, Vol. 67, No. 3, pp.73-77, 1989.

[9] Phan, N. H., Schwartz, M., and Nobe, K., "Electrodeposition for Fe-Ni-Co Alloys Part I. Direct Current Deposition," Journal of Applied Electrochemistry, Vol. 21, No. 8, pp.672, 1991.

[10] Abibsi, A., Dennis, J.K. and Short, N.R., "Effect of Plating Variables on Zinc-Nickel Alloy Electrodeposition," Transactions of the Institute of Metal Finishing, Vol. 69, No. 4, pp. 145-148, 1991.

[11] Albalat, R., Gomez E., Muller, C., Pregonas, J., Sarret M., and Valles, E., "Zinc-Nickel Coatings-Relationship Between Additives and Deposit Properties," Journal of Applied Electrochemistry, Vol. 21, No. 1, pp. 44-49, 1991.

[12] Fratesi, R. and Roventi, G., " Electrodeposition of Zinc-Nickel Alloy Coatings From a Chloride Bath Containing NH_4Cl," Journal of Applied Electrochemistry, Vol. 22, No. 7, pp. 657-662, 1992.

[13] Lin, Y. P. and Robert, S. J., "Electro-deposition of Corrosion-Resistant Ni-Zn Alloy, I. Cyclic Voltammetric Study," Journal of the Electrochemical Society, Vol. 140, No. 5, 1299-1303, 1993.

[14] Pushpavanam, M. and Balakrishnan, K., "Zinc-Nickel Alloy Electrodeposition From Uncomplexed Acid Bath," Journal of Applied Electrochemistry, Vol. 26, No. 3, pp.283-290, 1996.

[15] Wu, Z., Fedrizzi, L., and Bonora, P.L., "Electrochemical Studies of Zinc-Nickel Codeposition in Chloride Baths," Surface and Coatings Technology, Vol. 85, No. 3, pp.170-174, 1996.

[16] Miranda, F. J., Fabri Barcia, O. E., Mattos, O. R., and Wiart, R., "Electrodeposition of Zn-Ni alloys in sulfate electrolytes," Journal of the Electrochemical Society, Vol. 144, No. 10, pp. 3449-3457, 1997.

[17] Benballa, M., Nils, L., Sarret, M., and Muller, C., "Zinc-Nickel Codeposition in Ammonium Baths," Surface and Coatings Technology, Vol. 123, No. 1, pp. 55-61, 2000.

[18] Beltowska-Lehman, E., Ozga P., Swiatek Z., and Lupi C., "Influence of Structural Factor on Corrosion Rate of Functional Zn-Ni Coatings," Crystal Engineering, Vol. 5, No. 3-4, pp. 335-345, 2002.

[19] Abd El Rehim, S. S., Fouad E. E., Abd El Wahab, S. M., and Hassan H. H., "Electroplating of Zinc-Nickel Binary Alloys From Acetate Baths," Electrochimica Acta, Vol. 41, No. 9, pp.1413-1418, 1996.

[20] Fabri Miranda, F. J., Barcia, O. E., Diaz, S. L., Mattos, O. R., and Wiart, R., "Electrodeposition of Zn-Ni Alloys in Sulfate Electrolytes," Electrochimica Acta, Vol. 41, No. 7, pp.1041-1049, 1996.

[21] Baldwin, K. R., Smith, C. J. E., and Robinson, M. J., "Study Into The Electrodeposition Mechanisms of Zinc-Nickel Alloys From An Acid-Sulphate Bath," Transactions of the Institute of Metal Finishing, Vol. 72, No. 2, pp.79-88, 1993.

[22] Loewenstein, L. M., Charpin, F., and Mertens, P. W., "Competitive Adsorption of Metal Ions Onto Hydrophilic Silicon Surfaces From Aqueous Solution," Journal of the Electrochemical Society, Vol. 146, No. 2, P.719-727, 1999.

[23] Rajendran, S., Bharathi, S., and Vasudevan, T., "Electrodeposition of Zinc-Nickel Alloy From a Cyanide-Free Alkaline Plating Bath," Transactions of the Institute of Metal Finishing, Vol. 78, No. 3, pp.1129-133, 2000.

[24] Pushpavanam, M., Sheela, G., and Pushpavanam, S., "Zinc-Nickel Alloy Electrodeposits for Water Electrolysis," International Journal of Hydrogen Energy, Vol. 27, No. 6, pp. 627-633, 2002.

[25] Sohi, M. H. and Jalali, M., "Study of the

Corrosion Properties of Zinc-Nickel Alloy Electrodeposits Before and After Chromating," Journal of Materials Processing Technology, Vol. 138, No. 1-3, pp. 63-66, 2003.

[26] Kalantary, M. R., "Zinc Alloy Electrodeposits For Corrosion Protection," Plating and Surface Finishing, Vol. 81, No. 2, pp. 80-88, 1994.

[27] Kenney, J. M. and Cabana, L. R., "Robust Factorial Designs For Manufacturing Quality," American Society for Quality Control, 41st Annual Quality Congress Transactions, pp.227-235, 1987.

[28] Dowey, S.J. and Matthews, A., "Taguchi and TQM. Quality issues for surface engineered applications," Surface & Coatings Technology, Vol. 110, No. 1-2, pp.86-93, 1998.

[29] Jiang, M. and Komanduri, R., "Application of Taguchi Method for Optimization of Finishing Conditions in Magnetic Float Polishing (MFP)," Wear, Vo. 213, No. 1-2, pp.59-71, 1997.

[30] Ghani, J. A., Choudhury, I. A., and Hassan, H. H., " Application of Taguchi method in the optimization of end milling parameters," Journal of Materials Processing Technology, Vol. 145, No. 1, pp.84-92, 2004.

[31] Gentili, G. B., Cerretelli, M., and Cecchi, L., "Coated Conical Antennas For Automotive Application," Journal of Electromagnetic Waves and Applications, Vol. 18, No. 1, pp.85-97, 2004.

[32] Kuo, S. L., "The Influence of Process Parameters on the MoS_2 Content of Ni-MoS_2 Composite Coating by the Robust Design method," Journal of the Chinese Institute of Engineers, Vol. 27, No. 2, pp. 243-251, 2004.