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Research Article

OPTIMIZING THE COMPOSITION OF ELECTROPLATED NiCrAl COMPOSITE COATING

Kürşad Oğuz OSKAY*[1], Bilal DEMİREL[2]

[1]*Cumhuriyet University, Dep. of Metallurgical and Materials Eng.,SİVAS;* ORCID:0000-0003-4026-867X
[2]*Erciyes University, Dep. of Metarials Science and Eng.,KAYSERİ;* ORCID:0000-0002-5360-0630

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ABSTRACT

NiCrAl composite coatings were obtained by electro-deposition under direct current (DC) conditions from a Watt's bath containing suspended Cr, Al particles. Mathematical models were developed to simulate the electroplated composite coating. The models allow composition of the coatings to be predicted. The predicted values obtained were close to the experimental values, indicating the suitability of the models. The prediction made using Response Surface Method (RSM) was also supported by SEM photos. Three-dimensional surface plots were helpful for predicting results by performing only limited set of experiments.
Keywords: Electrodeposition, NiCrAl composite coating, RSM, central composite design, composition optimization.

1. INTRODUCTION

In recent years, research and development of metal matrix composite coatings (MMCs) have attracted special interest due to their expected engineering applications [1]. Co-electrodeposition of MMCs consisting of dispersed micron and submicron sized particles of oxides, carbides, borides, metals and some other organic and inorganic materials is a flexible and low cost method of composite coating [2]. Electrolytic co-deposition method is particularly suitable for the tubular structures with complex shapes and the internal surfaces of small tubes that are difficult or impossible to be coated through other coating methods. Furthermore, the coatings produced by this method have excellent surface quality and adhesion to substrate [3]. Although this process is widely adopted for the development of wear and corrosion-resistant coating [4],[5], the development of high temperature coatings is still an area of research. Several researchers have evaluated bond coatings for thermal barrier coating (TBC) by electrodeposition techniques [6]–[8]. In addition, Bates et. al. have performed an optimization study about incorporating CrAlY particles by using electroplating process [9]. In their study, composition of the coating was not optimized. However, bond coat composition is an important factor for TBC to provide oxidation resistance [10]. Oxidation resistance is associated with the evaluation of a thermally growth oxide (TGO) layer (especially α-Al_2O_3 scale) at the interface between the top-coat and the bond-coat [11]. The slow growing oxide layer (TGO) is achieved when the right composition of the bond

* Corresponding Author: e-mail: kursadoskay@gmail.com, tel: (352) 207 66 66 / 32933

coat is selected. The bond coats usually contain 18-30 wt.%Cr, 5-15 wt.%Al [12]. Hence, the aim of this work was to optimize the composition of NiCrAl by RSM technique. In most of the experimental studies, effects of the coating process parameters have been studied by using conventional methods. In these studies carried out, researchers have varied one factor at a time to analyze the effect of input process parameters on output quality characteristics or response. However, this technique requires a large number of experimental runs because only one factor is varied in each run, keeping all other factors constant. Therefore, these increased the cost and time [13]. On the other hand, in this technique, the interaction effects among various input process parameters are not considered. To overcome these kind of problems, some researchers have incorporated design of experiment methodologies such as Response Surface Methodology (RSM) [14].

2. EXPERIMENTAL

2.1. Materials and Methods

Nickel composite coating was prepared by using a Watts-type bath containing 240g/L Nickel Sulphate ($NiSO_4.6\ H_2O$), 50 g/L Nickel Chloride ($NiCl_2.6H_2O$), 40g/L Boric acid (H_3BO_3). Analytical reagents and distilled water were used to prepare the plating solution. A nickel sheet of 99.99% purity with dimensions of 250x300x100mm was used as anode and Inconel 718 with a radius of 200 mm used as the cathode. For deposition of composite coatings, Cr (40µm) and Al (5µm) particles were supplied from Merck and Alfa Aesar, respectively. Samples were cleaned and activated according to ASTM B343 procedure.

All the coatings were fabricated using DC electrodeposition method at the current density of $8A/dm^2$ with deposition time 45 min at 50 ^oC. The pH of the plating solution was maintained at 4 which was adjusted by adding sulphuric acid or sodium hydroxide when necessary. The composite plating were carried out in a beaker. The bath was stirred and heated by a magnetic stirrer. The microstructure of the coatings was analyzed using scanning electron microscope (LEO-440). EDX analysis and surface roughness measurements were measured from 5 different locations and the average value was taken.

3. RESULTS AND DISCUSSION

3.1. Construction of model equation and adequacy checking

Table 1. CCRD design for composition of composite coating

	Actual values of Variables			Observed			Predicted		
No.	Cr (g/L)	Al (g/L)	Stirring Rate (Rpm)	Ni (%)	Cr (%)	Al (%)	Ni (%)	Cr (%)	Al (%)
O1	20	12.5	100	46	26	28	46.75	25.88	27.83
O2	20	7.5	200	67	21	12	67.75	20.87	11.83
O3	10	12.5	200	74	10	16	74.75	9.88	15.83
O4	10	7.5	100	51	11	38	51.75	10.88	37.83
O5	7.9	10	150	40	19	41	36.75	19.13	41.17
O6	15	10	220	83	7	10	81.25	8.50	10.17
O7	15	6.5	150	58	22	20	60.75	22.19	20.17
O8	15	10	150	61	26	13	60.25	25.00	13.83
O9	15	10	79	24	57	19	39.25	41.50	19.17
O10	22	10	150	89	4	7	83.51	6.43	7.17
O11	15	13.5	150	57	20	23	59.75	20.21	23.00
O12	15	10	150	58	27	15	60.25	25.00	13.83

Table 1 shows the results of EDX analysis of CCRD experiments for studying the effect of factors, along with the predicted and observed responses. According to designed experimental data the models Eq. (1), the Ni composition of the coating, Eq. (2), the Cr composition of the coating, Eq. (3), the Al composition of the coating, obtained as:

$$R_{Ni} = +60.25 + 16.62x_1 - 0.35x_2 + 14.85x_3 + 3.85x_1x_2 - 0.85x_1x_3 + 19.62x_2x_3 \quad (1)$$

$$R_{Cr} = +25.00 - 4.60x_1 - 0.71x_2 - 11.67x_3 - 10.17x_1x_2 - 1.71x_1x_3 - 11.10x_2x_3 - 6.19x_1^2 - 1.94\,x_3^2 \quad (2)$$

$$R_{Al} = +13.83 - 12.02x_1 + 1.06x_2 - 3.18x_3 + 6.32x_1x_2 + 2.56x_1x_3 - 8.52x_2x_3 + 5.17x_1^2 + 3.92x_2^2 + 0.42x_3^2 \quad (3)$$

The model equations representing (R_{Ni}), (R_{Cr}) and (R_{Al}) are expressed as a function of x_1. x_2 and x_3 (in coded units) represent the values of Cr concentration (g/L) Al concentration (g/L) and stirring rate (rpm), respectively.

Table 2. ANOVA of the response surface model to predict Ni compositon of the composite coating

Factor	Sum of squares	Degree of freedom	Mean Square	*f* value	p-value
Model	2508.25	6	418.70	41.59	0.0004
Residual Error	50.25	5	10.05		
Lack of Fit	45.75	4	11.44	2.54	0.4355
Pure Error	4.5	1	4.5		
Total	2558.25	11			
R-Squared	0.9804		Pred R-Squared		0.8708
Adj R-Squared	0.9568		Adeq Precision		19.411

Table 3. ANOVA of the response surface model to predict Cr compositon of the composite coating

Factor	Sum of squares	Degree of freedom	Mean Square	*f* value	p-value
Model	1061.29	7	132.66	41.35	0.0055
Residual Error	9.63	4	3.21		
Lack of Fit	9.13	3	4.56	9.13	0.2279
Pure Error	0.5	1	0.5		
Total	1070.92	11			
R-Squared	0.9910		Pred R-Squared		0.9170
Adj R-Squared	0.9670		Adeq Precision		22.805

Table 4. ANOVA of the response surface model to predict Al compositon of the composite coating

Factor	Sum of squares	Degree of freedom	Mean Square	*f* value	p-value
Model	1259.833	9	138.3148	119.945	0.0083
Residual Error	2.333	2	1.041667		
Lack of Fit	0.083	1	0.083333	0.041	0.7532
Pure Error	2	1	2		
Total	1261.677	11			
R-Squared	0.9982		Pred R-Squared		0.9635
Adj R-Squared	0.9898		Adeq Precision		34.820

For the estimation of significance of the model, the analysis of variance (ANOVA) and the *f*-test were applied. The ANOVA of the regression models, which are presented in Tables 2-3 and 4, demonstrate that the models are highly significant as evident from the calculated *f*-values for (R_{Ni}), (R_{Cr}) and (R_{Al}), which are 41.59, 41.35 and 119.94, respectively. These values have a very low probability value 0.0004, 0.0055 and 0.0083. If the p-value is smaller than 0.05, the model is significant. The results indicated that the models used to fit the response variable were significant and adequate to represent the relationship between the response and the factors [15]. The lack of fit p-value of (R_{Ni}), (R_{Cr}) and (R_{Al}) are 0.435, 0.227 and 0.753, respectively, which imply that the lack of fits are insignificant. The corresponding variables would be more significant if the absolute *f*-value becomes greater and the p-value becomes smaller. The value of adjusted determination coefficient R^2_{adj} was found to be 0.9568, 0.9670 and 0.9898 for, (R_{Ni}), (R_{Cr}) and (R_{Al}) respectively. This means that the calculated model was able to explain 95.68%, 96.70% and 98,98% of the total variations in the system. “Adequate Precision” measures the signal to noise ratio. A ratio greater than 4 is desirable. Our ratios was found to be 19.411, 22.805, and 34.820 for (R_{Ni}), (R_{Cr}) and (R_{Al}), respectively. These models can be used to navigate the design space. All of these results show that the constructed models for composition of the coating are significant.

3.2. Microstructural study and the effect of factors on the responses (R_{Ni}), (R_{Cr}), (R_{Al})

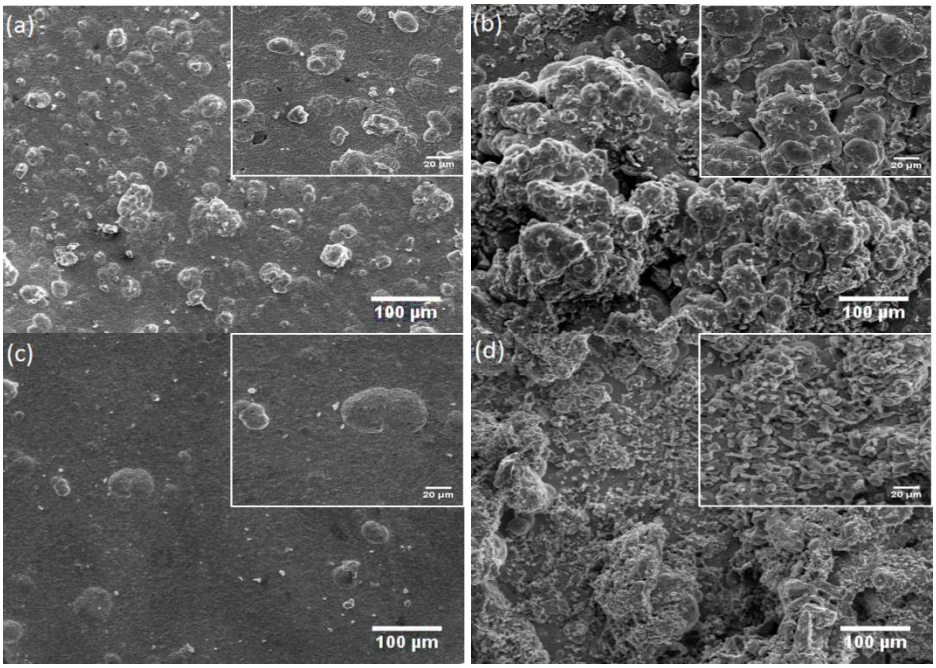

Figure 1. Surface morphology of the coatings a)O6 sample (Cr:15g/L, Al:10g/L, Stirring rate: 220rpm)b)O8 sample (Cr:15g/L, Al:10g/L, Stirring rate: 150rpm) c)O10 sample (Cr:22g/L, Al:10g/L, Stirring rate: 150rpm) d)O11 sample (Cr:15g/L, Al:13.5 g/L, Stirring rate: 150 rpm)

Figure 1 shows the surface morphology of NiCrAl composite coatings. It is clear that the concentration of the Cr particles and stirring rate of the electrolyte have a strong effect on the surface morphology of the coating. According to SEM images, both Cr and Al particles are well incorporated in the Ni matrix. The composition of Cr (%) coating decreases with the increase of stirring rate from 150 to 220 rpm as seen in Figure 1 (b) and (a). The reason for the decreasing trend of the co-deposition can be explained as follows. High stirring speed gives rise to high impinging velocity of the particles towards the cathode. When the particles hit the cathode surface faster, the amount of chromium in the coating decreases because nickel atoms do not have enough time to wrap around these particles. Hence, the amount of incorporated particles decrease [16].

In order to gain a better understanding, the interaction effects of factors on responses three-dimensional (3D) response surface plots for the measured responses were formed based on the model equations Eqs. 1-3. Since each model had three factors, one factor held constant concentration and stirring rate. As seen in Figure 4 (a), Cr composition increases with decreasing stirring rate at low Cr concentrations, but the increment decreases slightly after Cr concentration reaches approximately 15g/L. In addition, response surface plot (Figure 4(a)) supports SEM images. When the Cr concentration of the electrolyte was increased to 15-22 g/L at 150 rpm, the amount of Cr deposition on the coating decreased resulting from the excessive Cr particles addition into the electrolyte. This reveals that the nickel ions dissolving from anode cannot cover all Cr particles [17]. As shown in Figure 2 the granular particles are uniformly distributed on the coarse particles. The EDX analysis showed that the fine granular particles are Al and the coarse particles are Ni coated Cr particles. It can be observed from SEM images that increasing the Al

particles concentration 10g/L to 13.5 g/L in the electrolyte at 150 rpm resulted in increasing the composition of Al content. This result can be verified by response surface plot in Figure 5 (b). On the other hand, as seen in Figure 5 (a) high stirring speed decreases the amount of Al in the coating.

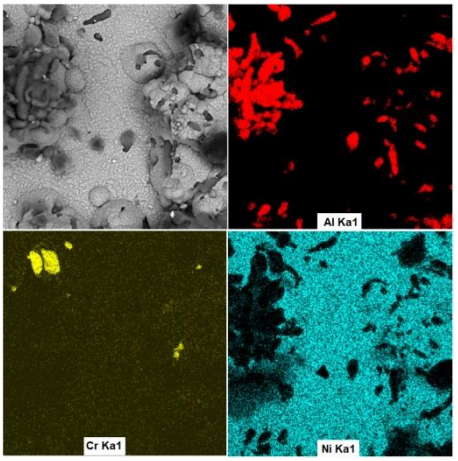

Figure 2. EDX mappings images of the NiCrAl coating.

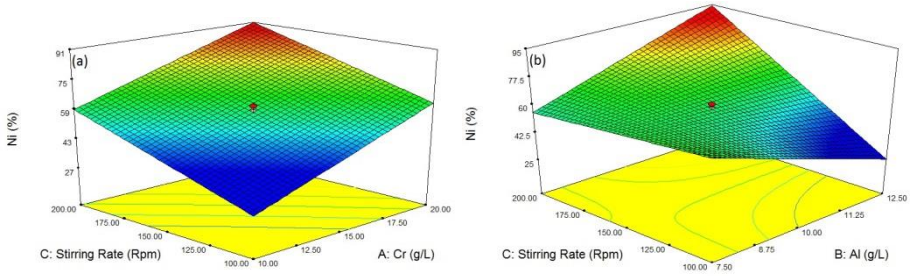

Figure 3. Response surface plots showing the effect of two factors on composition of Ni (the other two variables are held at center level).

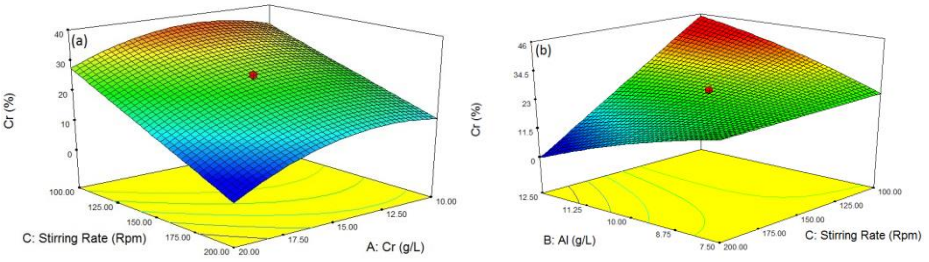

Figure 4. Response surface plots showing the effect of two factors on composition of Cr (the other two variables are held at center level).

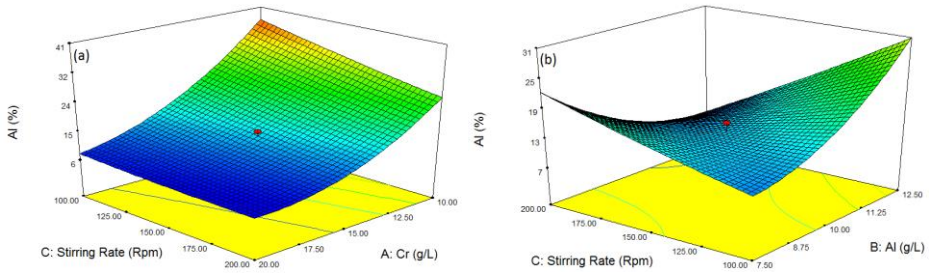

Figure 5. Response surface plots showing the effect of two factors on composition of Al (the other two variables are held at center level).

3.3. Optimization Studies

The experimental and predicted values are shown in Table 1. The table shows a close proximity of the model prediction with the experimental data signifying the validity of the regression model. Optimization studies were carried out using Eqs. 1-3. The range of the chemical composition of the coating were selected to be 18 to 30 wt.% Cr, 5 to 14 wt.% Al [12]. Based on Design expert trial software the optimum conditions were listed in Table 5.

Table 5. Optimum compositions for NiCrAl composite coating

Cr (g/L)	Al (g/L)	Stirring Rate (Rpm)	Cr (%)	Al (%)	Surface Roughness Ra (µm)
15.57	7.87	175	24.61	13.95	11.10
14.65	11.66	165	18.37	13.75	8.91
16.65	9.65	155	21.88	10.05	10.11

4. CONCLUSIONS

1. The present study aimed to optimize the composition of Cr, Al elements of the coating produced by electroplating. The commercial bond coat composition was obtained using electroplating method. It is easy and cost effective method to produce bond coats for thermal barrier coatings.

2. The results showed that stirring rate had significant effect of the composite coating. Lower stirring rate increases co-deposition of Cr particles. The maximum Cr deposited experiment was O9 sample (Cr (15g/L), Al (10g/L) and stirring rate (80rpm)).

3. The optimum values were determined as Cr : 15.57 (g/L), Al : 7.87 (g/L) and stirring rate : 175 (rpm).

4. CCRD was employed for modelling and optimizing the particle concentration of the electrolyte. The predicted values obtained using the model equations were in agreement with the observed values. This study demonstrates that the response surface methodology can be used for optimizing the composition of the electroplated coating.

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