

Effect of Process Parameters on Corrosion Resistance of Ni-P-Al₂O₃ Composite Coatings Using Electrochemical Impedance Spectroscopy

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Received 9 February 2015; accepted 25 February 2015

Abstract

Electroless nickel composite coatings are developed by incorporating soft/hard particles into Ni-P coatings, to improve mechanical as well as tribological properties. The objective of the present work is to investigate the effect of various coating process parameters on the corrosion behavior of Ni-P-Al₂O₃ composite coating deposited on mild steel substrate. The electrochemical impedance spectroscopy test is used to evaluate the corrosion behavior of the heat treated composite coatings at various annealing temperatures (300 °C, 400 °C, and 500 °C). Corrosion properties, charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}), are optimized using Taguchi based grey relational analysis to improve the corrosion resistance of the coating. Concentration of nickel source, concentration of reducing agent, concentration of alumina particles and annealing temperature, are considered as a main design factor for optimization of electrochemical properties. Analysis of variance (ANOVA) is used to find out the optimum combination of coating process parameters. From ANOVA result, it is found that the concentration of Al₂O₃ particles and annealing temperature have significant influence on the corrosion resistance of the composite coatings. Concentration of reducing agent has moderate influence on the corrosion resistance. Surface morphology of the coated surface is studied using SEM (scanning electron microscopy) and chemical composition of the coating is studied using EDX (energy dispersive X-ray analysis). The XRD (X-ray diffraction analysis) is used to understand the phase transformation behavior of the composite coatings.

Keywords: Ni-P-Al₂O₃ composite coating, corrosion, electrochemical impedance spectroscopy, optimization.

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Introduction

Electroless nickel coatings are not only used for environmental protection of base metal but also to protect it from corrosion and wear. Most machine parts, tools and equipments in the industries are affected due to environmental changes, corrosion, erosion, wear and friction. It is essential to protect the machine tools, equipments and materials from corrosion, wear and erosion. It may be achieved by applying specific coatings on the base material to protect them from corrosion and environmental changes and also to increase hardness, wear and friction resistance. Ni-P electroless plating is one of the most important surface-engineering technology, which is applied in industrial fields. Composite coatings are more popular in various industries like as mechanical, chemical, automobile, textile, aerospace, etc., due to excellent mechanical and tribological properties [1]. Electroless nickel plating is a metal deposition process involving chemical reaction. It is an auto-catalytic chemical technique used to deposit layers of nickel and phosphorus on ferrous or non-ferrous solid substrates. This process relies on the presence of a reducing agent, which reacts with metallic ions to deposit metal. When the substrate is dipped in the electroless bath, it develops potential. Due to this, negative and positive ions are attracted towards the surface of the substrate and release the energy by charge transfer process. Electroless bath consists of source of metallic ions, source of reducing agent, complexing agent, wetting agent, stabilizer, and pH controlling agent. The electroless Ni-P coatings containing more than 7% phosphorus have an excellent corrosion resistance. Therefore, these coatings are used in industries which have corrosive environments such as in mining, chemical, textile, oil and gas, etc. In general, electroless coating is divided into four group viz., pure nickel coatings, alloy and poly alloy coatings, composite coatings, and nano coatings [2]. These coatings have uniform thickness across all the surfaces irrespective of complex geometry and sharp edges.

Incorporation of fine inert (soft/hard) particles into electroless nickel coatings yields electroless nickel composite coatings. In composite coatings, second phase particles are deposited on the surface of the substrate and are well embedded in the Ni-P matrix during the deposition process. To improve corrosion resistance, lubricity and to reduce friction, soft particles like as PTFE, MoS₂, HBN, and graphite are introduced in the electroless Ni-P coatings. On the other hand, hard particles like as SiC, WC, Al₂O₃, Si₃N₄, CeO₂, TiO₂, ZrO₂, and diamond, etc., are incorporated in the electroless Ni-P coatings to increase hardness, wear resistance, corrosion resistance, and frictional resistance [3]. To get excellent properties, the second phase particles must be uniformly distributed during the deposition process otherwise, due to non-uniform distribution of particles, numerous defects are formed because of segregation and agglomeration of composite or nano particles with high surface energy and activity in the electroless bath [4]. The tribological and mechanical properties of composite coatings are significantly improved with appropriate heat treatment at and above 400 °C for one hour [5]. Various hard particles like, SiC, TiC, TiB₂, B₄C

particles are normally used as reinforcement phase. Out of these particles Al_2O_3 is widely used because of its high elastic modulus, strength retention at high temperature, and high wear resistance [6]. Usually, the presence or availability of composite particles in the electroless Ni-P composite coatings depends on incorporation of particles on the coating surface and holding time of the particle on the coating surface [7]. Deposition rate, incorporation rate of the composite particles, roughness and hardness of the composite coating depend on the concentration of alumina particles in the electroless bath [8]. Corrosion resistance of electroless Ni-P coatings is higher than chromium alloy and pure nickel. In a particular environment higher corrosion resistance is due to amorphous nature and the passivity of the Ni-P coating [9]. Various factors such as phosphorus content, porosity of the coating and heat treatment of the coating significantly affect the corrosion resistance of the composite coating. The porosity of the composite coating is increased with increase in the surface roughness. Roughness of the coating depends on the mechanical preparation of the surface of the substrate and deposition of the second phase particles on the coated surface of the sample. The porous composite coatings have lower corrosion resistance as compared to non-porous composite coatings. Hence, to avoid the porosity of the coating, the second phase particles must be uniformly distributed over the coated surface of the sample. Wetting agents play important role in the deposition of the composite coating. In the presence of wetting agent, the second phase particles get uniformly distributed over the coated surface and it also improves the corrosion resistance of the composite coating. Recently, much attention is being paid on composite coatings due to their excellent performance, instead of Ni-P and Ni-B coatings [4].

Abdel Salam Hamdy et al. [10] have observed the improvement in corrosion resistance (100 times) of the coatings, in the presence of alumina particles as compared to steel substrate. The surface resistance of Ni-P coating is $0.78 \times 10^4 \Omega\text{-cm}^2$ and for composite coatings it is $7.00 \times 10^4 \Omega\text{-cm}^2$. Bigdeli and Allahkaram [11] have found increase in corrosion resistance (R_c) with decrease in the constant phase elements (CPE) of the Ni-P and Ni-P-SiC composite coatings. The Ni-P-SiC composite coating has higher corrosion resistance as compared to Ni-P coating, due to reduction in effective metallic area for corrosion. Zarebidaki et al. [12] have confirmed that the corrosion resistance of Ni-P-SiC coating depends on the dispersion of nano particles throughout the coating. At higher concentration, SiC particles are agglomerated on the coated surface, which provokes the porosity of the composite coating. On the basis of Nyquist plot, it is confirmed that Ni-P coatings have better corrosion resistance as compared to Ni-P/nano-SiC composite coatings. The porosity of the composite coatings is decreased with increase in incorporation of alumina particles in the composite coatings, which improves the corrosion resistance of the coating. Whereas Stankiewicz et al. [13] have observed that the addition of zirconium oxide in Ni-P and Ni-P-W coatings adversely affect corrosion resistance after 1 hour immersion in 3.5% NaCl medium, Allahkaram et al. [14] have found that addition of nano-particles in Ni-P coating reduces the effective metal area, which is prone to corrosion. The charge transfer resistance (R_{ct}) of a

nano composite coating is higher than that of Ni–P coating, meaning that the composite coating has higher corrosion resistance than the electroless nickel coating. The corrosion resistance of EN silicon carbide composite coatings depends on the spreading of nano particles throughout the coatings. Parveen et al. [15] have found the improvement in corrosion resistance of zinc coating in the presence of carbon nanotube particles.

The corrosion resistance of a coating depends on various factors such as phosphorus content, type of corrosion solution and incorporation of second phase particles in Ni–P coatings. Zarebidaki et al. [16] have observed that the proper heat treatment of the coating significantly improves the coating density and structure. The experimental results show that the Ni–P–CNT composite coating has better corrosion resistance as compared to Ni–P coating. Corrosion resistance of the Ni–P coating is reduced due to increase in effective metallic area. Lee [17] has performed immersion tests in 3.5 wt.% NaCl solution for different test durations (one hour to 720 hours). The experimental result shows that the Ni–P–CNT composite coating has higher corrosion shield compared to Ni–P/nano composite coating. It might be due to denser and uniform distribution of composite particles with higher phosphorus content. Novakovic and Vassiliou [18] have found that, after vacuum heat treatment, a composite coating has less corrosion resistance as compared to electroless Ni–P coating and observed the same trend for as-deposited Ni–P coating with higher corrosion resistance as compared to annealed Ni–P coating.

To identify the basic characteristics of the corrosion behavior of the coated surface in different corrosive environments, the measurement of electrochemical corrosion is very essential. From literature review on Ni–P coating, it is confirmed that the dissolution of nickel ions occurs at open circuit potential, leading to the enrichment of phosphorus on the surface layer. During chemical reaction the phosphorus available on the coated surface reacts with water from the electrolyte to form a layer of adsorbed hypophosphite anions, which blocks the supply of water to the electrode surface and forms a passive nickel film. Electroless Ni–P coatings are known as barrier coating, which protects the surface of the specimen by sealing it off from corrosive environments. Corrosion resistance of the coating also depends on the amorphous structure and passivity of the electroless coating. Amorphous alloys offer better corrosion resistance as compared to crystalline or polycrystalline materials.

Different electrochemical tests, namely, potentiodynamic polarization test and electrochemical impedance spectroscopy tests are used to study the corrosion behavior of electroless nickel coatings. The resistance of the coatings towards corrosion is evaluated on the basis of different corrosion parameters obtained from such tests such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), charge transfer resistance (R_{ct}), double-layer capacitance (C_{dl}), and corrosion rate (R_c), etc. The present study deals with the assessment of corrosion behavior of Ni–P–Al₂O₃ composite coating using electrochemical impedance spectroscopy (EIS) technique. EIS is a non-destructive technique often used to understand the corrosion behavior in electrochemical systems and is best suitable for the electrochemical characterization of the coating deposited on the metal

surface. It provides the exhaustive data on the usefulness of coating over a relatively small area. It also indicates the occurrence of the rate of corrosion, and moisture content in the coating. To maximize the corrosion resistance (R_{ct} and C_{dl}) of the composite coating, the process parameters are optimized in order to identify the optimum combination of parameters using Taguchi method with grey relational grade. Analysis of variance (ANOVA) is used to observe the level of significance of the process parameters and their interactions. The surface morphology and composition of Ni-P-Al₂O₃ coatings are studied with the help of scanning electron microscopy (SEM), energy dispersed X-ray analysis (EDX) and X-ray diffraction analysis (XRD).

Experimental details

Parameters selection and coating deposition

Effective deposition of the coating on the surface of the substrate depends on the preparation of the substrate. Hence, it is important to prepare the substrate surface very carefully and properly. In the present work AISI 1040 (mild steel) of size 20 mm × 20 mm × 2 mm is used as substrate material for Al₂O₃ composite coatings. Different machining processes such as shaping, parting, milling and grinding processes are used accordingly for the preparation of the substrate. The substrate is mechanically cleaned to remove foreign matters and corrosion products, and after that cleaned with de-ionized water. Sequentially a pickling treatment is given to the substrate with dilute hydrochloric acid (50 % HCl and 50% de-ionized water) for short duration of time to remove any surface layer formed like rust followed by rinsing with de-ionized water and methanol cleaning. To start the coating deposition quickly, the specimen is activated using a warm palladium chloride solution, maintained at 55 °C. The activated substrate is then dipped into the electroless bath maintained at 85 °C and the coating is carried out for three hours duration. For every substrate the constant deposition time is maintained to get uniform thickness of the coating. The coating thickness is found in the range of 28–32 microns. After the completion of the coating deposition process, the samples are cleaned with distilled water and wrapped with soft tissue paper.

Fig. 1 shows the schematic experimental setup for electroless Ni-P-Al₂O₃ composite coating. It consists of a heater with a magnetic stirrer (IKA[®] RCT basic). A fixed rigid stand is provided to grip and support the substrate and a glass coated temperature sensor. Chemical solution for electroless bath (200 mL) is poured into the glass beaker (250 mL size) placed on the heating plate. With the help of a temperature sensing knob, the temperature is set at 85 °C and a stirrer speed is set with the help of a speed setting knob at 150 rpm. The function of PTFE coated magnetic stirrer is to maintain the composite particles in suspension without agglomeration at the bottom of the glass beaker. The stirrer speed is fixed after a large number of iterations to avoid the decomposition of the electroless bath due to the agglomeration of particles.

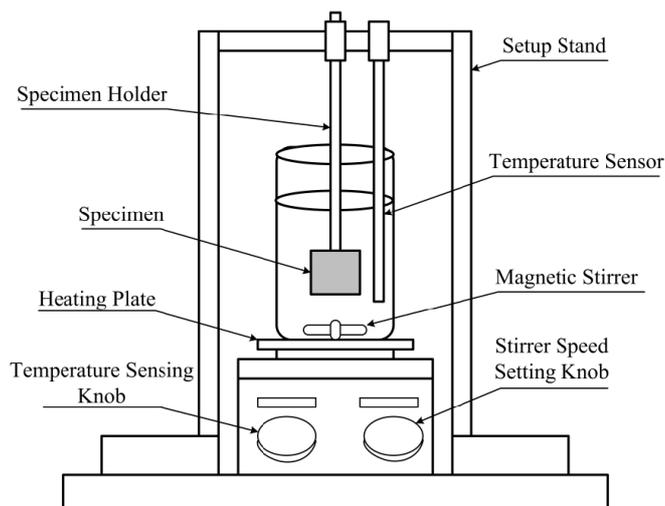


Figure 1. Experimental setup for electroless Ni–P–Al₂O₃ composite coating.

The operating conditions and the ranges of chemicals used in electroless bath for electroless Ni–P–Al₂O₃ composite coatings are selected after several trials. The three important coating parameters are varied and the others are kept constant for coating deposition. The electroless bath composition and operating conditions used for the deposition of the electroless Ni–P–Al₂O₃ composite coatings are shown in Table 1. To have better suspension of the second phase alumina particles and to avoid agglomeration of particles, a specified amount of surfactant SDS (Sodium Dodecyl Sulphate) is added to the electroless nickel poly alloy bath. About 50 mL of electroless nickel solution containing the required amount of alumina powder are thoroughly mixed using a Magnetic stirrer (Remi make 2MLH) to get a uniform suspension of particles in the solution. At first a Ni–P layer is deposited in the first hour to prevent the porosity of the coating and then the solution containing Al₂O₃ particles and surfactant is introduced into the same bath for subsequent 2 hours for Ni–P–Al₂O₃ co-deposition.

Table 1. Electroless bath composition and operating conditions.

Bath composition		Operating conditions	
Nickel sulphate	35, 40, 45 g/L	pH	4.5-5.0
Sodium hypophosphite	15, 20, 25 g/L	Temperature	85±2 °C
Al ₂ O ₃ powder	5, 10, 15 g/L	Bath volume	250 mL
Tri sodium citrate	15 g/L	Stirrer speed	150 rpm
Sodium acetate	5 g/L	Deposition time	3 hours
Sodium dodecyl sulphate	0.2 g/L	Annealing temp.	300 –500 °C
Lead acetate	2 mg/L		

During a chemical reaction within the electroless bath, nickel sulphate, which is used as a source of metallic ions, supplies the nickel ions in the solution. In the same bath sodium hypophosphite (used as a reducing agent) reduces the nickel ions from their positive valence state to zero valence state. At the given

temperature the chemical reaction between nickel sulphate and sodium hypophosphite is quite fast and tremendous, which results in instant decomposition of the electroless bath. Consequently, complexing agents (tri sodium citrate and sodium acetate) are used to slow down the chemical reaction into a feasible form. Complexing agent forms metastable complexes with nickel ions and releases them slowly for the reaction, which helps to maintain the stability of the electroless bath. Even though the complexing agents have performed their duty in the electroless bath, there remains a possibility of decomposition of the chemical solution. In such situations the stabilizer (Lead acetate) plays an important role in the stabilization of the electroless bath for total duration of coating. To increase the wettability and surface charge of alumina particles, surfactant Sodium Dodecyl Sulphide is used in the electroless bath. The imperative functions of the surfactant are to reduce the surface tension of the liquid, easy dispersion of the particles and to reduce the interfacial tension between the solid and liquid surfaces. Surfactant reduces the agglomeration of the particles and electrostatic adsorption of suspended particles on the substrate [19]. To understand the effect of heat treatment on the corrosion resistance of the composite coatings, the coated samples are annealed in a box furnace for 1 hour at different temperatures (300 °C, 400 °C and 500 °C) according to the Orthogonal Array (OA). After annealing, the samples are cooled to room temperature without application of any artificial cooling.

Parameters optimization process and design of experiments

During coating deposition several factors like nickel source concentration, reducing agent concentration, pH of the solution, bath temperature, stabilizer and surfactant concentration, concentration of second phase particles and substrate material affect the coating characteristics. To obtain an optimum combination for maximum corrosion resistance, various coating parameters are varied within the specific range. From literature review, it is seen that three factors viz. nickel sulphate (A), sodium hypophosphite (B) and concentration of second phase particles, i.e., Al₂O₃ particles (C), are the most commonly used by the researchers to control the properties of the composite coatings [19-21]. Besides, heat treatment (annealing) is found to have great effect on the corrosion resistance of the coating. Therefore, annealing temperature (D) is considered as the fourth parameter in the experimental design to study its effect on the corrosion resistance of the coating. The different design factors and their levels are shown in Table 2.

Table 2. Design parameters and their levels.

Design factors	Designation	Unit	Levels		
			1	2	3
Nickel sulphate solution	A	g/L	35	40*	45
Sodium hypophosphite solution	B	g/L	15	20*	25
Concentration of source of Al ₂ O ₃	C	g/L	5	10*	15
Annealing temperature	D	°C	300	400*	500

* = initial condition

The present work considers the optimization of the corrosion behavior of electroless Ni-P-Al₂O₃ composite coating using a grey based Taguchi method [22] that uses loss function to measure the quality characteristics. The value of the loss function is transformed into a statistical measure, called as signal to noise ratio (S/N ratio). It is the ratio of the desirable value or signal to standard deviation or noise. S/N ratio can effectively consider the variation encountered in a set of trials. On the basis of the objective of the experimental work, the S/N ratios are classified into three basic criteria: lower-the-better (LB), higher-the-better (HB) and nominal-the-best (NB). A larger S/N ratio represents minimization of noise factors. The combination of parameter levels which gives a maximum S/N ratio is known as the optimum combination of parameter levels. The present work is related to assessment of corrosion characteristics by measuring the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}). Because of using two different corrosion characteristics, it becomes a complex multivariate problem, which cannot be solved by Taguchi method. It may be possible that higher S/N ratio of one response variable corresponds to the lower S/N ratio of the other. Grey relational analysis [23] is an efficient tool which is used for the overall evaluation of the S/N ratio to optimize the multiple response characteristics. The optimization of the process is performed in a range of steps. In the first step the results of the experiments are normalized in the range of one and zero by performing the grey relational generation. In the next step grey relational coefficients are calculated with the help of normalized data. The normalized data represent the correlation between actual experimental data and desired experimental data. In the third step grey the relational grade is calculated by averaging the grey relational coefficients. The grey relational grade is treated as the overall response of the process instead of multiple responses of charge transfer resistance and double layer capacitance.

A statistical technique, analysis of variance (ANOVA), is performed to find the significant parameters of the experiment. The optimum combination of the coating process parameters is predicted with the help of ANOVA and grey relational analysis. Finally, a confirmation test is conducted to verify the optimum process parameters obtained from the analysis. In the present work, corrosion behavior of electroless Ni-P-Al₂O₃ composite coating is studied with the help of electrochemical impedance spectroscopy. Charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) are obtained from the Nyquist plot. R_{ct} and C_{dl} are taken as the response variables for the current study. A higher value of R_{ct} and lower value of C_{dl} indicate better corrosion resistance of the composite coating.

Design of Experiment (DOE) is a systematic and rigorous approach that provides the maximum amount of conclusive information from limited experimental runs. The DOE of the present study includes an orthogonal array (OA) based on the Taguchi method to reduce the number of experiments for the optimization of the coating process parameters.

Table 3. Design factors and interactions in L_{27} orthogonal array.

Trial No.	Column numbers												
	1 A	2 B	3 AxB	4 AxB	5 C	6 AxC	7 AxC	8 BxC	9 D	10	11 BxC	12	13
1		1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	2	2	2	2	2	2	2	2	2
3	1	1	1	1	3	3	3	3	3	3	3	3	3
4	1	2	2	2	1	1	1	2	2	2	3	3	3
5	1	2	2	2	2	2	2	3	3	3	1	1	1
6	1	2	2	2	3	3	3	1	1	1	2	2	2
7	1	3	3	3	1	1	1	3	3	3	2	2	2
8	1	3	3	3	2	2	2	1	1	1	3	3	3
9	1	3	3	3	3	3	3	2	2	2	1	1	1
10	2	1	2	3	1	2	3	1	2	3	1	2	3
11	2	1	2	3	2	3	1	2	3	1	2	3	1
12	2	1	2	3	3	1	2	3	1	2	3	1	2
13	2	2	3	1	1	2	3	2	3	1	3	1	2
14	2	2	3	1	2	3	1	3	1	2	1	2	3
15	2	2	3	1	3	1	2	1	2	3	2	3	1
16	2	3	1	2	1	2	3	3	1	2	2	3	1
17	2	3	1	2	2	3	1	1	2	3	3	1	2
18	2	3	1	2	3	1	2	2	3	1	1	2	3
19	3	1	3	2	1	3	2	1	3	2	1	3	2
20	3	1	3	2	2	1	3	2	1	3	2	1	3
21	3	1	3	2	3	2	1	3	2	1	3	2	1
22	3	2	1	3	1	3	2	2	1	3	3	2	1
23	3	2	1	3	2	1	3	3	2	1	1	3	2
24	3	2	1	3	3	2	1	1	3	2	2	1	3
25	3	3	2	1	1	3	2	3	2	1	2	1	3
26	3	3	2	1	2	1	3	1	3	2	3	2	1
27	3	3	2	1	3	2	1	2	1	3	1	3	2

For successful completion of the experiments it is very essential to choose the proper orthogonal array. It allows to compute the total degree of freedom (DOF) of main and interaction effects via a minimum number of experimental trials. In the present experiment, four process parameters are used with three levels, therefore the total DOF considering the individual factors and their interaction is 20. Hence the L_{27} OA is chosen which has 27 rows corresponding to the number of experiments and 26 DOF with 13 columns. The L_{27} OA is shown in Table 3. Each row in the table represents the specific combination of the experimental run and each column represents a specific factor or interactions. The cell value indicates the level of the corresponding factor or interaction assigned to that column. The experimental run is controlled by the setting of the design factors and not by the interactions.

Electrochemical study

The electrochemical impedance spectroscopy (EIS) test of heat-treated electroless Ni-P- Al_2O_3 composite coated samples is carried out using a potentiostat (Gill AC) of ACM instrument, UK. The test is conducted using 3.5%

NaCl solution as electrolyte at ambient temperature of 30 °C. The electrochemical cell consists of three types of electrodes. A saturated calomel electrode (SCE) is used as reference electrode, which provides a stable ‘reference’ against which the applied potential may be accurately measured. A platinum electrode works as counter electrode or auxiliary electrode, which provides the path for the applied current into the solution. The coated specimen is used as working electrode. The design of the cell is such that only an area of 1 cm² of the coated surface is exposed to the electrolyte.

Fig. 2 shows an equivalent electrical circuit model, which is used to arouse and fit the corrosion property parameters. In the circuit the charge transfer resistance (R_{ct}) is represented by the resistance of electron transfer during the electrochemical reaction course. The double layer capacitance (C_{dl}) is correlated to delamination of the coating. Solution resistance (R_s) is referred to the resistance between the work electrode (WE) and the reference electrode. The values of charge transfer resistance and double layer capacitance are calculated from the Nyquist plot by fitting a semicircle using the accompanying software.

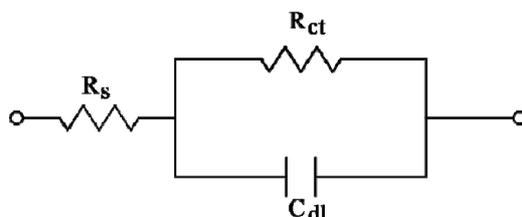


Figure 2. Equivalent circuit of EIS of Ni–P–Al₂O₃ composite coating.

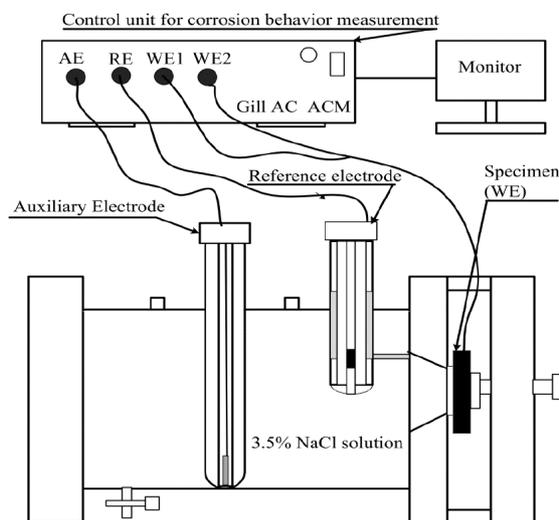


Figure 3. Experimental setup for electrochemical impedance spectroscopy test.

The experimental setup of the electrochemical impedance spectroscopy test is shown in Fig. 3. A settling time of 15 minutes is assigned before every test in order to stabilize the open circuit potential (OCP). The potentiostat is controlled with the help of a sophisticated desktop computer, which also collects and stores the data of EIS test. During the test the applied frequency of corrosion setup is

varied from 10 KHz to 0.01 Hz. The Nyquist plot obtained from the EIS test appears in a single semicircle. The semicircle in the high frequency region signifies the charge control reaction and is quite consistent [14].

Microstructure and characterization study

Energy dispersive X-ray analysis (EDAX Corporation) is used to find out and verify the weight percentage of nickel, phosphorus, aluminum oxide, and oxygen in the composite coating. Scanning electron microscopy (JEOL, JSM-6360) is used to observe the surface morphology of the composite coating before and after heat treatment. SEM is done in order to investigate the effect of heat treatment on the electroless Ni-P-Al₂O₃ composite coatings. The phase compositions of composite coatings before and after heat treatment are detected using an X-ray diffraction analyzer (Rigaku, Ultima III).

Results and discussion

Microstructure study and characterization of the Ni-P-Al₂O₃ composite coating

SEM micrographs of as-deposited and heat treated Ni-P-Al₂O₃ composite coatings are shown in Fig. 4. From the figure it is confirmed that the surface of the as-deposited composite coating has a smooth surface with uniform distribution of alumina particles with no porosity. The alumina particles are properly embedded on the surface of the alloy coating. The uniform distribution of the composite particles along with the smooth surface of the coating is due to the use of surfactant (SDS) in the electroless bath. After heat treatment of the composite coating at 400 °C, the globules of nickel and phosphorus are seen with embedded alumina particles. The globules become more compact due to heat treatment, which further reduces the porosity of the coating. This may be the reason for increase in corrosion resistance of the composite coating.

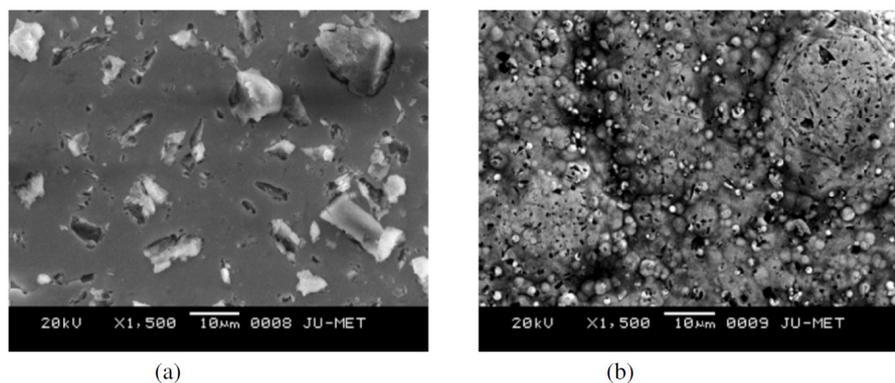


Figure 4. SEM image of (a) as deposited, and (b) heat treated Ni-P-Al₂O₃ composite coating.

Fig. 5 shows the EDAX analysis of as deposited and heat treated Ni-P-Al₂O₃ composite coating. The compositional analysis of the coatings deposited at different concentrations of nickel sulphate, sodium hypophosphite, and Al₂O₃ particles is carried out using energy dispersive X-ray analysis. From analysis, it is confirmed that the composite coating deposited using 5 g/L of Al₂O₃ particles

in the bath has 78.07 wt% of nickel, 6.67 wt% of phosphorus, 8.74 wt% of oxygen, and 6.52 wt% of alumina particles. Similarly, the composite coating deposited using 10 g/L of Al_2O_3 particles in the bath has 72.46 wt% of nickel, 6.92 wt% of phosphorus, 11.06 wt% of oxygen, and 9.56 wt% of alumina particles. It means that the amount of alumina particles in the composite coating increases with increase in Al_2O_3 particles in the electroless bath.

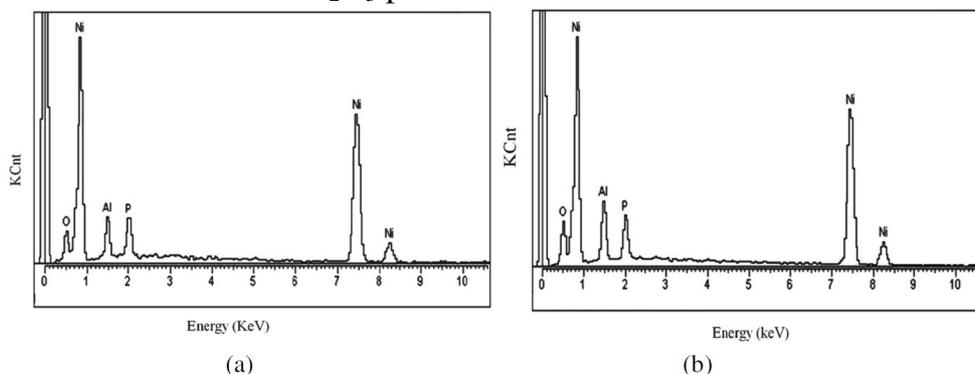


Figure 5. EDX analysis of composite coating (a) with 5 g/L, and (b) with 10 g/L of Al_2O_3 particles.

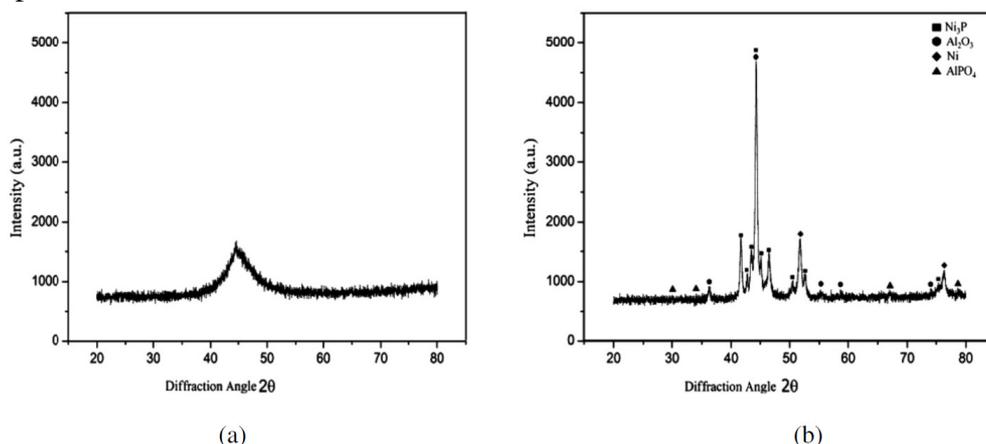


Figure 6. XRD plots of Ni-P- Al_2O_3 composite coating (a) as deposited, and (b) annealed at 400 °C.

X-ray diffraction (XRD) analyzer (Rigaku, Ultima III) is used for identification of different compounds in the electroless Ni-P- Al_2O_3 composite coating. Fig. 6 shows XRD plots of as deposited and heat treated composite coatings. From the plots it is confirmed that in as-deposited condition the phase is mostly amorphous in nature, as a single broad peak is available at diffraction angle of 44.468. After heat treatment at 400 °C for one hour, the amorphous phase of composite coating is converted into crystalline phase. Different peaks are seen at different diffraction angles. The highest peak of Ni_3P with Al_2O_3 is observed at the diffraction angle of 44.320. Ni_3P peaks are also observed at the diffraction angles of 43.1, 43.5, 43.74, 44.26, 45.04 and peaks of Al_2O_3 are observed at diffraction angles of 37.06, 53.46, 55.7, and 77.28. Similarly, peaks of Ni are observed at diffraction angles of 52.18, and 77.38.

Coating process parameter optimization and confirmation test

The present work deals with two responses, charge transfer resistance and double layer capacitance, for optimization of the corrosion resistance of Ni–P–Al₂O₃ composite coatings. Grey analysis is a technique which converts a multi response (variable) problem into a single response problem. The experimental data for charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) of the electrochemical impedance test are given in Table 4. The particular sets of analysis are performed to convert the given multiple responses into a single performance index, called as grey relational grade.

Table 4. Experimental results of EIS test.

Sr. No.	$R_{ct} \times 10^5$ ($\Omega\text{-cm}^2$)	$C_{dl} \times 10^{-5}$ (F)	Sr. No.	$R_{ct} \times 10^5$ ($\Omega\text{-cm}^2$)	$C_{dl} \times 10^{-5}$ (F)
1	1.929	0.4257	15	1.362	0.2898
2	4.948	0.13457	16	5.015	0.259
3	99.44	0.0544	17	29.27	0.3437
4	15.74	0.2501	18	541.7	0.07228
5	5.991	0.1647	19	8.181	0.1193
6	8.376	0.1358	20	31.74	0.2217
7	5.782	0.01924	21	36.29	0.1186
8	4.148	0.1502	22	1.176	0.4544
9	88.63	0.0488	23	25.58	0.3484
10	0.4508	0.1681	24	33.51	0.2178
11	2.18	0.2597	25	6.526	0.3451
12	10.67	0.1478	26	24.37	0.1626
13	20.8	0.17	27	7.31	0.10749
14	32.98	003948			

Experimental results of the linear normalization, i.e., charge transfer resistance and double layer capacitance in the range of zero and one are vital for generating the grey relational coefficient. A material will have a lower tendency to corrode if R_{ct} value tends to be a higher and C_{dl} to be a lower value. From Table 4 it is observed that the values of charge transfer resistance for all experiments are positive, hence higher the better criterion is used for normalization. Similarly, for all values of double layer capacitance lower the better criterion is used.

The expressions for higher the better and lower the better criterion are given below.

Equation for higher the better:

$$x_i(k) = \frac{y_i(k) - \min y_i(k)}{\max y_i(k) - \min y_i(k)} \quad (1)$$

Equation for lower the better:

$$x_i(k) = \frac{\max y_i(k) - y_i(k)}{\max y_i(k) - \min y_i(k)} \quad (2)$$

where $x_i(k)$ is the value after grey relational generation, while $\min y_i(k)$ and $\max y_i(k)$ are the smallest and largest values of $y_i(k)$ for the k_{th} response. The data after grey relational grade are shown in Table 5.

Table 5. Grey relational analysis for R_{ct} and C_{dl} .

Sr.	Normalized value		Δ value		Grey coefficient	
	R_{ct}	C_{dl}	R_{ct}	C_{dl}	R_{ct}	C_{dl}
1	0.0027311	0.065952753	0.997269	0.934047247	0.333941349	0.348663547
2	0.0083089	0.734971045	0.991691	0.265028955	0.335190046	0.653570034
3	0.1828902	0.919202133	0.81711	0.080797867	0.379619086	0.860884704
4	0.0282479	0.469482489	0.971752	0.530517511	0.339731147	0.485193114
5	0.0102359	0.665732144	0.989764	0.334267856	0.335623618	0.599327898
6	0.014642423	0.732144499	0.985358	0.267855501	0.336619281	0.651164183
7	0.009849807	1.000000000	0.99015	0.000000000	0.335536647	1.000000000
8	0.006830865	0.699053222	0.993169	0.300946778	0.334858248	0.624261204
9	0.162917931	0.932070962	0.837082	0.067929038	0.373948624	0.880391681
10	0.000000000	0.657918926	1.000000	0.342081074	0.333333333	0.593767056
11	0.003194832	0.447421638	0.996805	0.552578362	0.334044811	0.475024015
12	0.018880767	0.704568435	0.981119	0.295431565	0.337582545	0.628589588
13	0.03759673	0.653552716	0.962403	0.346447284	0.341902955	0.590704241
14	0.060100227	0.1291479	0.9399	0.8708521	0.347246391	0.364736648
15	0.001683513	0.378251678	0.998316	0.621748322	0.333707868	0.445732782
16	0.008432715	0.449030242	0.991567	0.550969758	0.335217864	0.475751082
17	0.053245714	0.25438919	0.946754	0.74561081	0.345601188	0.40140949
18	1.000000000	0.878113797	0.000000	0.121886203	1.000000000	0.804005617
19	0.014282146	0.770061587	0.985718	0.229938413	0.336537653	0.684989296
20	0.057809231	0.534745841	0.942191	0.465254159	0.346694772	0.517998286
21	0.06621571	0.77167019	0.933784	0.22832981	0.348727492	0.686502177
22	0.001339863	0.000000000	0.99866	1.000000000	0.333631347	0.333333333
23	0.046428152	0.243588565	0.953572	0.756411435	0.343980245	0.39795881
24	0.061079444	0.543708061	0.938921	0.456291939	0.3474827	0.522852886
25	0.011224405	0.251171983	0.988776	0.748828017	0.335846451	0.400375386
26	0.044192583	0.670557956	0.955807	0.329442044	0.343452021	0.602814872
27	0.012672906	0.79720103	0.987327	0.20279897	0.33617353	0.711440997

The grey relational coefficient is calculated from the normalized value and the equation for the grey relational coefficient is as follows.

$$\xi_i(k) = \frac{\Delta_{\min} + \xi \Delta_{\max}}{\Delta_{oi}(k) + \xi \Delta_{\max}} \quad (3)$$

where $\Delta_{oi} = \|x_o(k) - x_i(k)\|$ is the difference of the absolute value between $x_o(k)$ and $x_i(k)$. Δ_{\min} and Δ_{\max} are the minimum and maximum values of the absolute differences (Δ_{oi}) of all comparing sequences. The overall multiple response characteristics evaluation is based on the grey relational grade and is calculated as follows:

$$\gamma_i = \frac{1}{n} \sum_{k=1}^n \xi_i(k) \tag{4}$$

where n is the number of process responses. The grey relational grades are considered in the optimization of multi-response parameter design problem. The values of grey relational grade are shown in Table 6.

Table 6. Grey relational grade and its order.

Sr. No.	Grey relational grade	Order	Sr. No.	Grey relational grade	Order
1	0.341302	27	15	0.38972	21
2	0.49438	08	16	0.405484	19
3	0.620252	04	17	0.373505	22
4	0.412462	18	18	0.902003	01
5	0.467476	13	19	0.510763	07
6	0.493892	09	20	0.432347	17
7	0.667768	02	21	0.517615	06
8	0.47956	11	22	0.333482	27
9	0.62717	03	23	0.37097	23
10	0.46355	15	24	0.435168	16
11	0.404534	20	25	0.368111	24
12	0.483086	10	26	0.473133	12
13	0.466304	14	27	0.523807	05
14	0.355992	25			

As the grey relational grade is to maximized, the S/N ratio is calculated using higher the better criterion which is given by:

$$S/N \text{ ratio} = -10 \log \left[\frac{1}{n} \sum \frac{1}{y^2} \right] \tag{5}$$

where y is the observed data and n is the number of observations. As the experimental design is orthogonal, it is possible to separate out the effect of each coating parameter at different levels. The mean grey relational grade for three levels of the four factors is summarized in Table 7. All the calculations are performed with the help of Minitab software [24]. The response table shows the average of the selected characteristic for each level of the factors. The ranks shown in the table are based on Delta statistics and it compares the relative magnitude of effects. The Delta statistics is the difference of highest average and lowest average of each factor. Ranks are assigned on the basis of Delta values; rank 1 is assigned to the highest Delta value, rank 2 is assigned to next highest

value, and so on. Fig.7 shows the main effects plot for mean S/N ratio and Fig. 8 shows the interaction plots between the process parameters.

Table 7. Mean response table for grey relational grade.

Level	A	B	C	D
1	0.511584689	0.474203	0.441025322	0.4276613
2	0.471575415	0.413941	0.427988478	0.4463871
3	0.44059957	0.535616	0.554745874	0.5497113
Delta	0.07098512	0.121675	0.126757397	0.1220499
Rank	4	3	1	2
Total mean grey relational grade = 0.474586558				

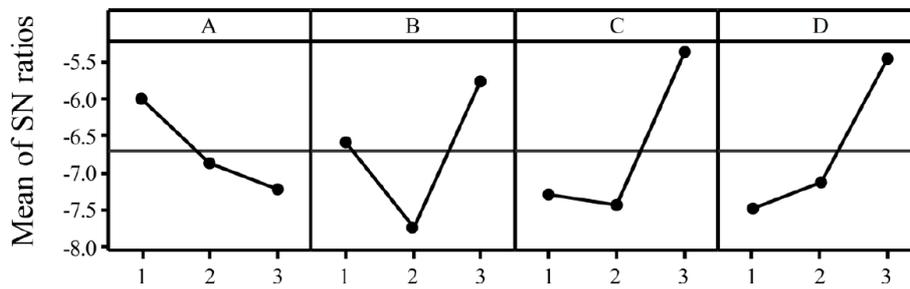


Figure 7. Main effects plot for mean S/N ratio.

If the line for a particular parameter in the main effect plot is horizontal, it means that the parameter has no significant effect. On the other hand, if the line has maximum inclination to horizontal line, it means that the parameter has the most significant effect. From Fig. 7 it is clear that annealing temperature (parameter D) has a significant effect, the concentration of Al₂O₃ particles (parameter C) has the most significant effect and the reducing agent (parameter B) has a moderate significant effect. Parameter A is less significant due to less inclination to the horizontal line. Increase in the corrosion resistance of the composite coating in the presence of Al₂O₃ particles has also been observed earlier. In Ni-P-(Al₂O₃-TiC) composite coating, the corrosion resistance is increased in presence of Al₂O₃ particles upto a certain level of particle concentration in the bath and after that it gets decreased [6]. In a further case [3], the researchers have observed that the corrosion resistance is increased with increase in Al₂O₃ particles.

Interactions between parameters A, B and C are shown in Fig. 8. From the plots it is observed that almost all lines are intersecting to each other, i.e., all factors have some amount of interaction between each other. From the figure it is seen a considerable interaction between parameters B and C and between parameters A and C. Thus, from the present analysis, it is confirmed that annealing temperature and concentration of Al₂O₃ particles are the significant parameters for the corrosion characteristics of Ni-P-Al₂O₃ composite coatings. In Taguchi method, optimum level of combinations is selected for those levels, which are having higher S/N ratios. In the present study the optimal combination is found to be A1B3C3D3.

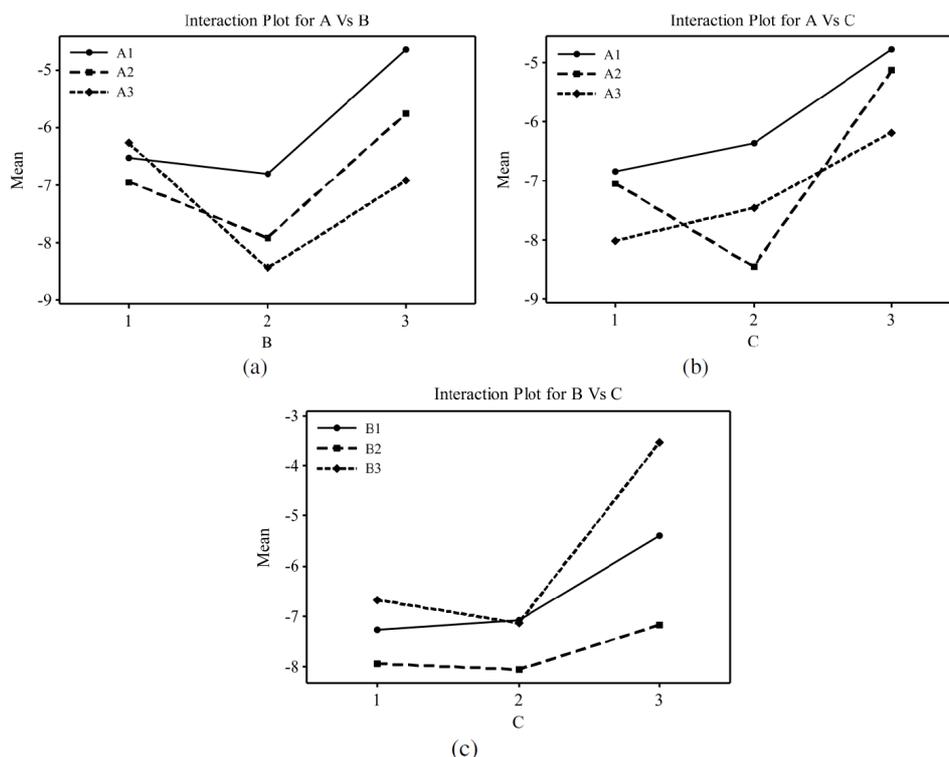


Figure 8. Interaction plots, (a) between A and B, (b) between A and C, and (c) between B and C.

ANOVA is useful to investigate the effect of the process parameters and of their significance level. This technique gives various important conclusions based on analysis of the experimental data. ANOVA separates the total variability of the response into contribution of each of the factors and the error. A sophisticated software Minitab is used to obtain the results through ANOVA with the S/N ratio. ANOVA results for the corrosion behavior of the composite coatings are shown in Table 8. ANOVA calculations are based on the F-ratio or variance ratio. It is used to measure the significance of the parameters under investigation with respect to variations of all the terms included in the error term at the desired significance level. If the calculated value is higher than the tabulated one, the factor is significant at the desired level. The ANOVA table shows the percentage contribution of each parameter. From the table it is observed that parameter C (concentration of Al_2O_3 particles) has the most significant effect on the corrosion behavior at the confidence level of 95% within the specific test range. The annealing temperature (D) and concentration of reducing agent (B) are significant at 90% confidence level. Among the interactions, the interaction of parameters between B and C has a significant contribution. The percentage contribution of the factors and interactions are calculated to know the influence of the process parameters. From ANOVA table it is clear that parameter C has the largest contribution (23.071%) followed by parameter C (20.50%). Among interactions, B×C interaction has the highest contribution (9.74%).

In the final step, confirmation results of optimum parameters are calculated by Taguchi method. The confirmation test is performed by conducting the

experiment with optimal settings of the factors and levels previously calculated. The predicted values of the S/N ratio at the optimum level $\hat{\eta}$ is calculated as

$$\hat{\eta} = \eta_m + \sum_{i=1}^o (\bar{\eta}_i - \eta_m) \quad (6)$$

where η_m is the total mean grey relational grade, $\bar{\eta}_i$ is the mean grey relational grade at optimal level, and 'o' is the number of main design parameters that significantly affect the corrosion resistance of Ni-P-Al₂O₃ composite coating. The results of the validation test are shown in Table 9. The significant improvement in grey relational grade from initial to optimum condition is 0.2768, which is about 41.21% of the mean relational grade. Nyquist plots for the Ni-P-Al₂O₃ composite coatings developed at initial and optimum condition are shown in Fig. 9.

Table 8. Results of ANOVA for corrosion behavior.

Source	DOF	SS	MS	F	% contribution
A	2	0.022797397	0.011398698	1.38193575	6.010317266
B	2	0.6662394	0.03331197	4.038729754 *	17.56476941
C	2	0.087509283	0.043754641	5.304794999 *	23.07099177
D	2	0.077768204	0.038884102	4.71429278 *	20.50284883
AxB	4	0.020034634	0.005008659	0.67247742	5.281941212
AxC	4	0.018138814	0.004534704	0.549785617	4.782126151
BxC	4	0.036943327	0.009235832	1.119748497	9.739757468
Error	6	0.049488783	0.00824813		13.04724788
Total	26	0.379304382			100.0000000

*Significant at 95% and 90% confidence level ($F_{2, 6, 0.05} = 5.1433$ and $F_{2, 6, 0.10} = 3.4633$)

Table 9. Results of confirmation test.

	Initial condition	Optimum condition	
		Prediction	Experimentation
Level	A2B2C2D2	A1B3C3D3	A1B3C3D3
$R_c \times 10^5$ ($\Omega\text{-cm}^2$)	0.663		13.7
$C_{dl} \times 10^{-5}$ (F)	0.0278		0.00183
Grade	0.3949	0.6909	0.6717
Improvement of grey relational grade = 0.2768			

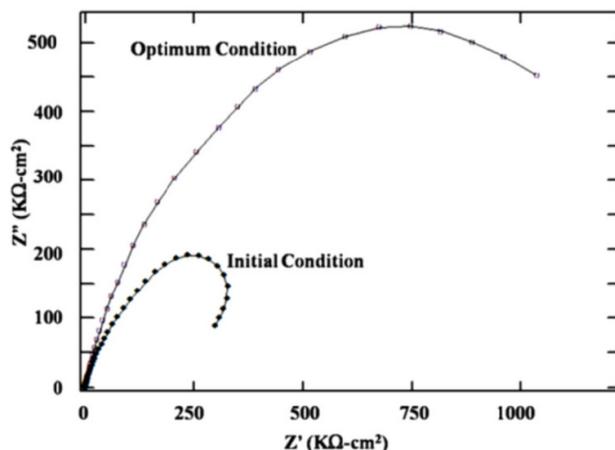


Figure 9. Nyquist plots at initial and optimum condition for composite coatings.

From the plots it is confirmed that the semicircle for optimum condition is larger than that of initial condition. Therefore the corrosion resistance at optimum condition is higher than that of initial condition.

Conclusion

Taguchi method in combination with grey relational analysis is used in order to optimize the electrochemical parameters of electroless Ni–P–Al₂O₃ composite coating using electrochemical impedance spectroscopy test in 3.5% NaCl solution. The optimum parameter combination is found to be A1B3C3D3. At optimum combination, the nickel concentration is 35 g/L, the reducing agent concentration is 25 g/L, the concentration of Al₂O₃ particles is 15 g/L, and the annealing temperature is 500 °C. From ANOVA results it is confirmed that the concentration of Al₂O₃ particles and the annealing temperature have the most significant influence on corrosion resistance of the composite coating. The interaction between the reducing agent and the concentration of Al₂O₃ particles has good significant effect among the interactions. The corrosion resistance of the composite coating improves with increase in alumina content and annealing temperature at 500 °C. The improvement in the grey relational grade from initial condition to optimal condition is found to be 41.21%. The coating composition is studied using EDX analysis. The micro structural analysis and crystallization behavior of the coating is studied with the help of SEM and XRD analysis. From SEM micrograph, it is confirmed that the alumina particles are uniformly distributed over the smooth coated surface without porosity. From EDX analysis, it is confirmed that the coating is deposited with the alumina particles, nickel, phosphorus and oxygen. From XRD plots it is confirmed that the as deposited composite coating has amorphous structure and it converts into a crystalline structure after heat treatment at 400 °C with Ni₃P as a major compound.

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