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RESEARCH

Multiple Roughness Characteristics of Chemically Deposited Ni-P-W Coatings

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A B S T R A C T

This paper presents an experimental study of multiple roughness characteristics of Ni-P-W coatings on a mild steel substrate. The different roughness parameters considered are centre line average roughness (R_a), root mean square roughness (R_q), skewness (R_{sk}), kurtosis (R_{ku}) and mean line peak spacing (R_{sm}). The aim of the present study is to optimize the coating process parameters based on Taguchi method and Grey relational analysis in order to obtain the particular bath composition which may be used to deposit Ni-P-W coatings with optimum roughness characteristics. Experiments are carried out based on the L_{27} Taguchi orthogonal design using the combination of three process parameters, namely, concentration of tungsten ion, concentration of reducing agent and concentration of nickel source. It is observed that concentration of tungsten ion has the most significant influence in controlling roughness characteristics of Ni-P-W coating. The surface morphology, composition and phase structure of coatings are also studied with the help of scanning electron microscopy, energy dispersive X-ray analysis and X-ray diffraction analysis respectively.

1. INTRODUCTION

Coatings process is the most effective method to improve the performance capabilities of metals, by allowing the mechanical properties of the substrate material to be maintained while protecting them against wear, friction or corrosion by a protective coating. Chemically deposited coatings have extensive use in different industrial applications such as the coatings in machinery construction, textile machinery, chemical and plastic industries, automobile industry, hydraulics, mining industry, oil and gas industries, electrical and electronic industries, aerospace and printing industry. This is particularly due to their excellent mechanical, physical, electrical, corrosion, and wear-resistance properties. This coating is different from the conventional electrolytic coating as the former does not require any electricity for its operation. It is an autocatalytic process where the substrate develops a potential when it is dipped in a solution called bath that contains a source of metallic ions, reducing agent, complexing agent, stabilizer and other components.

Due to the developed potential both positive and negative ions are attracted towards the substrate surface and release their energy through charge transfer process. An electrochemical model for the process of metal deposition was suggested by Paunovic and Saito on the basis of the Wagner–Traud mixed-potential theory of corrosion processes [1]. According to the mixed-potential theory of deposition, the overall reaction given by:

$$M^{z+}_{solution} + Red_{solution} \xrightarrow{\text{catalytic surface}} M_{lattice} + OX_{solution} \quad (1)$$

It can be decomposed into one reduction reaction, the cathodic partial reaction,

$$M^{z+}_{solution} + ze \xrightarrow{\text{catalytic surface}} M_{lattice} \quad (2)$$

and one oxidation reaction, the anodic partial reaction,

$$Red_{solution} \xrightarrow{\text{catalytic surface}} OX_{solution} + me \quad (3)$$

Where M is the metal ion, Red is the reducing agent and OX is the oxidation product of the reducing agent. This type of plating is becoming more popular method of coating due to low tool cost, low temperature process, good quality deposit with uniformity. The basic Ni–P coating has been used as a functional coating due to the advantage of surface roughness, friction, wear resistance and corrosion properties [2-4]. It is considered that the incorporation of a typically transition metal such as W, Co, Mn, Re and Mo in the binary Ni-P alloy could lead to superior properties than the binary Ni-P coating. So the research could be extended for the ternary Ni-P-M alloy where the M is the transition metal. Addition of a third element into the binary coating to form a ternary alloy coating such as Ni–Cu–P [5], Ni–Tio_2–P [6], Ni–W–P [7-11] has been studied. Pearlstein and Weightman [12] first presented the Ni-P-W ternary alloy in 1963 and since then, many investigations on Ni -W-P ternary alloy were reported. As tungsten, a refractory metal itself cannot be deposited from any aqueous solution. However tungsten alloys with the iron group transition metals can be readily deposited from aqueous solutions containing tungsten ion [13]. The incorporation of tungsten in to the nickel matrix led to the solute hardening and enhanced the hardness and also exhibits excellent properties such as mechanical properties, tribological properties and corrosion resistance.

Surface roughness has a large impact on the mechanical properties of a material. The manufacturing cost also increases with the decrease in roughness. So we need to optimize the controlling process parameters to obtain the surface roughness at desired level. However, a surface generated by machining is composed of a large number of length scales of superimposed roughness [14] which are generally characterized by three different types of parameters, viz., amplitude parameters, spacing parameters, and hybrid parameters. Amplitude parameters are measures of the vertical characteristics of the surface deviations, the examples of such parameters are centre line average roughness, root mean square roughness, skewness, kurtosis, peak-to-valley height, etc. Spacing parameters are the measures of the horizontal characteristics of the surface deviations, the examples of such parameters are mean line peak spacing, high spot count, peak count, etc. And the hybrid parameters are a combination of both the vertical and horizontal characteristics of surface deviations and examples of such parameters are root mean square slope of profile, root mean square wavelength, core roughness depth, reduced peak height, valley depth, peak area, valley area, etc. Thus it is not sufficient to describe the surface quality by considering only one parameter such as centre line average roughness (R_a), though it is the most commonly used roughness parameter.

The present study aims at considering five different roughness parameters, viz., centre line average roughness (R_a), root mean square roughness (R_q), skewness (R_{sk}), kurtosis (R_{ku}) and mean line peak spacing (R_{sm}) for the surface texture generated in Ni-P-W coating. Taguchi method along with grey relational analysis is used to determine the suitable coating process parameters in order to obtain optimum surface roughness characteristics of these coatings. Taguchi method [15,16] is a powerful tool for design of high-quality systems based on orthogonal array (OA) experiments that provide much reduced variance for the experiments with an optimum setting of process control parameters. The OA requires minimum number of experimental runs. This method used a statistical measure of performance called signal-to-noise (S/N) ratios, which are logarithmic functions of the desired output to serve as objective functions for optimization. Three categories of S/N ratios are used; Lower the better (LB), Higher the better (HB) and Nominal the best (NB). The present study deals with optimizing the coating process parameters with an objective to optimize five roughness parameters of Ni-P-W coatings. This is a case of multi-response optimization. This type of problem cannot be handled by Taguchi method alone, since while optimizing, a higher S/N ratio for one response may correspond to a lower S/N ratio for another, thus optimization cannot be done until an overall evaluation of S/N ratio is done for all the parameters. Hence Grey relational analysis is introduced to convert the multi-response problem to a single response problem. Then Taguchi method is used to find the optimum combination of coating parameters. Since grey relational grade needs to be maximized, HB criterion needs to be used. After that Analysis of variance (ANOVA) was carried out to find the significant factors and their interactions on the overall grey relational grade. Finally a confirmation test is also conducted in order to verify the optimal combination of parameters. The surface morphology and composition are studied with the help of scanning electron microscopy (SEM), energy dispersed X-ray (EDX) analysis, and X-ray diffraction (XRD) analysis.

2. EXPERIMENTAL PROCEDURE

2.1 Coating deposition

Mild steel (AISI 1040) specimen of size 20 mm × 20 mm × 8 mm is used as the substrate material for the deposition of the Ni-P-W coating. Shaping, parting, milling processes are used accordingly for the preparation of the sample. The sample is then subjected to surface grinding process. The sample is mechanically cleaned from foreign matters and corrosion products. After that the MS sample is cleaned using distilled water. After that a pickling treatment is given to the specimen with dilute (50 %) Hydrochloric acid for one minute to remove any surface layer formed like rust followed by rinsed in distilled water and methanol cleaning. A large number of trial experiments are performed before deciding the bath composition.

Table 1 indicates the bath composition and the operating conditions for successful coating of Ni-P-W on the mild steel substrate.

Table 1. Chemical composition and operating condition.

Bath Constituents	Values
Nickel Sulphate (g/l)	20 – 30
Sodium Hypophosphite (g/l)	14 – 20
Sodium Citrate (g/l)	35
Ammonium Sulphate (g/l)	30
Lactic Acid (g/l)	5
Sodium Tungstate (g/l)	15 – 25
pH	7 – 8
Temperature	90 ± 2 °C
Duration of coating	3 hrs
Bath volume (ml)	200

Nickel sulphate is used as the source of nickel while sodium hypophosphite is the reducing agent. Sodium tungstate solution is used as the source of tungsten ion. The bath is prepared by adding the constituents in appropriate sequence. The pH of the solution is maintained around 7-8 by continuous monitoring with a pH meter. The cleaned samples are activated in palladium chloride solution at a temperature of 55 °C. Activated samples are then submerged into the chemical bath which is maintained at a temperature between 90-92 °C with the help of a hot plate cum stirrer attached with a temperature sensor submerged in the solution. The deposition is carried out for a period of 3 hours. The range of coating thickness is found to lie around 20-25 microns. After deposition, the samples are taken out of the bath and cleaned using distilled water. The electrode reactions in the deposition of ternary Ni-P-W are as follows [17]:

$$Ni^{2+} + 2e = Ni \quad (4)$$

$$WO_4^{2-} + 6e + 4H_2O = W + 8OH^- \quad (5)$$

$$H_2PO_2^- + 3OH^- = HPO_3^{2-} + 2H_2O + 2e \quad (6)$$

$$H_2PO_2^- + 2H^+ + e = P + 2H_2O \quad (7)$$

It is important to note that the present study does not consider the substrate roughness as the input variable. Thus it is essential that all samples after different stages of processing and prior to coating should have same roughness. But this is extremely difficult to achieve. Hence large numbers of samples are prepared and after all the processing prior to coating these are subjected to roughness evaluation. Only those specimens that show insignificant variation (less than 0.1 %) in roughness are used for coating deposition.

2.2 Selection of coating parameters

There are several factors which have impact on the characteristics of the chemical coating such as bath temperature, reducing agent concentration, nickel source concentration, stabilizer concentration, pH of the solution, substrate, bath load, etc. However, recent literature [18-20] shows that the three factors viz. concentration of nickel source (nickel sulphate, A), concentration of reducing agent (sodium hypophosphite, B) and concentration of tungsten source (sodium tungstate, C) are the most commonly used ones by the researchers to control the properties of this type of coating. Each process parameter has its specific role on the process and affects the process response variables. Nickel sulphate solutions supply free nickel ions in the bath. The reducing agent supplies the electrons for the reduction. At the same time some elements in the reducing agent can also be incorporated into the nickel deposit. The sodium tungstate solution supply free tungsten ions in the bath. Thus, in the present study these three factors are considered as the main design factors along with their interactions. Table 2 shows the design factors along with their levels.

Table 2. Design factors and their levels.

Design Factors	Unit	Levels		
		1	2	3
Concentration of source of nickel (nickel sulphate solution, A)	g/l	20	25[a]	30
Concentration of reducing agent (sodium hypophosphite solution, B)	g/l	14	17[a]	20
Concentration of source of tungsten (sodium tungstate, C)	g/l	15	20[a]	25

a: initial coating condition.

2.3 Roughness parameters

The present study is carried out to optimize the multiple roughness characteristics of Ni-P-W coatings. For this multi-response problem the following five roughness parameters are considered:

Centre line average roughness (R_a): It is also known as the arithmetic average height, defined as the average absolute deviation of the roughness irregularities from the mean line over one sampling length. R_a may be expressed in the form:

$$R_a = \frac{1}{L}\int_0^L |Z(x)|\,dx \qquad (8)$$

where Z(x) is the ordinate of the profile curve, x is the profile direction and L is the sampling length (shown in Fig. 1). The unit of R_a is micrometer (μm).

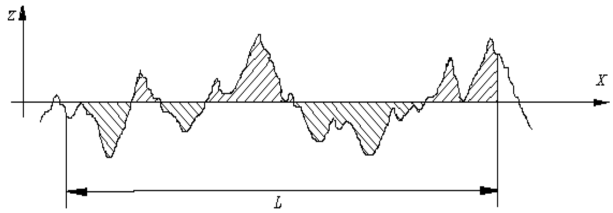

Fig. 1. Rough surface with a sampling length L.

Root mean square roughness (R_q): It represents the standard deviation of the distribution of surface heights. It is defined as the root mean square deviation of the profile from the mean line. This parameter is more sensitive than the centre line average and is mathematically expressed as:

$$R_q = \sqrt{\frac{1}{L}\int_0^L [Z(x)]^2\,dx} \qquad (9)$$

Skewness (R_{sk}): The skewness of a profile is the third central moment of profile amplitude probability density function, measured over the sampling length. It is a measure of the departure of a distribution curve from its symmetry and may be expressed in the form:

$$R_{sk} = \frac{1}{R_q^3 L}\int_0^L [Z(x)]^3\,dx \qquad (10)$$

It is a non-dimensional number, and for a symmetrical distribution such as the Gaussian distribution, R_{sk} = 0. A surface with positive skewness has a wider range of peak heights that are higher than the mean. A surface with negative skewness has more peaks with heights close to the mean as compared to a Gaussian distribution.

Kurtosis (R_{ku}): Kurtosis coefficient is the fourth central moment of profile amplitude probability density function, measured over the sampling length. It is a measure of the bump on a distribution curve and may be expressed in the form:

$$R_{ku} = \frac{1}{R_q^4 L}\int_0^L [Z(x)]^4\, dx \qquad (11)$$

It is also non-dimensional, and for a Gaussian distribution, R_{ku} = 3. R_{ku} > 3 means that the peaks are sharper than Gaussian and vice versa.

Mean line peak spacing (R_{sm}): It is defined as the mean spacing between peaks, with a peak defined relative to the mean line (a peak must cross above the mean line and then back below it). This parameter may be expressed in the form:

$$R_{sm} = \frac{1}{m}\sum_{n=1}^{m} S_n \qquad (12)$$

where m is the number of peak spacing and S is the spacing between two consecutive peaks. Its unit is in millimeters.

2.4 Planning of experiments

Design of experiments (DOE) is the method to provide maximum amount of conclusive information from the minimum amount of experimental run, time, energy, money, or other limited resource. By applying this technique, it is possible to reduce the required time and number of experiments significantly for experimental investigations. In Taguchi method, an orthogonal array (OA) is employed to reduce the number of experiments for determining the optimal coating process parameters. An OA requires the minimum number of experimental trials to determine the main effect as well as interaction effects of parameters simultaneously. The choice of a suitable OA design depends on the total degrees of freedom (DOF) required for studying the main and interaction effects. DOF refers to the number of fair and independent comparisons that can be made from a set of observations. In present study, to check the DOFs in the experimental design, for the three-level test, the three main factors take 6 [3 × (3 − 1)] DOFs. The DOF for three second order interactions (A × B, A × C, B × C) is 12 [3 × (3 −1) × (3 − 1)] and the total DOFs required is 18 (6+12). Here the L_{27} OA has been selected because as per Taguchi method, the total DOFs of selected OA must be greater than or equal to the total DOFs required for the experiment. The L_{27} OA along with the column assignments are shown in Table 3. In the array, the 1st column is assigned to concentration of source of nickel (nickel sulphate, A), the 2nd column is assigned to concentration of reducing agent (sodium hypophosphite, B), the 5th column is assigned to concentration of source of tungsten (sodium tungstate, C) while the rest of the columns are assigned to the two-way interactions of the factors and error terms. Here each column represents a specific factor, each row represents an experimental run and the cell values indicate the factor settings for the run. The cell values in the main factor columns (A, B and C) indicate their levels (1, 2 and 3) while the same in the interaction indicate the combination of the levels of the main factors concerned. The cell values in interaction columns and error columns are used in ANOVA for determination of their percentage contribution to the total effect.

2.5 Roughness measurement

A stylus type profilometer, Talysurf (Taylor Hobson, Surtronic 3+) is used to measure the roughness of the coated surface. The profilometer is set to a cut-off length of 0.8 mm, Gaussian filter, and traverse speed 1 mm/s with a traverse length of 4 mm. Roughness measurement on the coatings is repeated for five times at different locations on same surface and the average of four measurements is recorded. The parameter evaluations are microprocessor based. The measured profile is digitized and processed through the dedicated advanced surface finish analysis software *Talyprofile* for evaluation of the roughness parameters.

2.6 Composition study

Energy dispersive X-ray analysis (EDAX Corporation) is performed to determine the composition of the coating in terms of the weight percentages of nickel, phosphorous and tungsten. The EDX analysis is done on the coatings developed from the bath consisting of different concentrations of sodium tungstate (tungsten ions) in order to capture the range of tungsten content in the coatings. Scanning electron microscopy (SEM) (JEOL, JSM-6360) is used on as-deposited samples in order to observe the surface morphology. An XRD analyzer (Rigaku, Miniflex) is used for the identification of phase of the compounds in the coatings.

Table 3. L_{27} Orthogonal Array with main parameters and interactions.

	COLUMN NUMBERS												
TRIAL NO.	1 (A)	2 (B)	3 (A×B)	4 (A×B)	5 (C)	6 (A×C)	7 (A×C)	8 (B×C)	9	10	11 (B×C)	12	13
1	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

3. RESULTS AND DISCUSSION

3.1 Grey relational analysis for roughness characteristics

The present study deals with the optimization of the coating process parameters by minimizing of the five roughness parameters (R_a, R_q, R_{sk}, R_{ku}, and R_{sm}) simultaneously. Thus it is a case of multi-response optimization which cannot be solved by Taguchi method alone. Hence the Grey relational analysis [21] is used together with Taguchi method to solve the problem. The first step in grey relational analysis is to perform the grey relational generation in which the results of the experiments are normalized in the range between 0 and 1. Then the second step is to calculate the grey relational coefficient from the normalized data to represent the correlation between the desired and actual experimental data. The overall grey relational grade is then computed by averaging the grey relational coefficient corresponding to each performance characteristic. Furthermore, a statistical ANOVA [22] is performed to find which process parameters are statistically significant. The optimal combination of the process parameters can be predicted by the grey relational analysis and statistical ANOVA. Finally, a confirmation experiment is performed to verify the optimal process parameters obtained from the analysis. All the statistical analyses in the present study are performed using Minitab [23]. Table 4 represents the experimental results for the five roughness parameters. The roughness parameters R_a, R_q, and R_{sm} need to be minimized while R_{sk} and R_{ku} are to be targeted at 0 and 3, respectively. However, it is seen from the data in Table 4, that R_{sk} is always positive and R_{ku} is greater than 3 for the present chapter. Thus all the five roughness parameters are optimized with the objective LB.

In grey relational analysis, the normalized data processing for five roughness parameters considered in the present study, corresponding to lower the better criterion, can be expressed as:

$$x_i(k) = \frac{\max y_i(k) - y_i(k)}{\max y_i(k) - \min y_i(k)} \tag{13}$$

where xi (k) is the value after the grey relational generation, min y_i (k) is the smallest value of y_i (k) for the kth response, and max y_i (k) is the largest value of y_i (k)for the kth response: R_a (k = 1), R_q (k = 2), R_{sk} (k = 3), R_{ku} (k = 4) and R_{sm} (k = 5).

Table 4. Experimental results for roughness parameters.

Sample No	R_a (μm)	R_q (μm)	R_{sk}	R_{ku}	R_{sm} (mm)
1	0.41	0.52	1.05	5.56	0.146
2	0.43	0.57	0.65	6.71	0.133
3	0.62	0.85	3.97	7.39	0.141
4	0.41	0.53	1.1	6.77	0.183
5	0.46	0.59	0.65	7.77	0.199
6	0.46	0.61	1.95	5.26	0.169
7	0.4	0.53	2.59	5.8	0.173
8	0.43	0.59	3.04	7.03	0.153
9	0.39	0.49	0.43	4.07	0.15
10	0.35	0.44	0.59	3.52	0.226
11	0.48	0.59	0.4	3.73	0.222
12	0.39	0.57	2.17	5.9	0.167
13	0.29	0.38	1.61	7.28	0.117
14	0.63	0.75	1.12	5.79	0.183
15	0.36	0.45	0.91	6.51	0.151
16	0.61	0.73	1.07	6.68	0.055
17	0.61	0.79	1.43	7.49	0.053
18	0.62	0.8	0.9	5.34	0.058
19	0.44	0.56	1.08	6.29	0.127
20	0.45	0.59	1.22	6.86	0.065
21	0.97	1.32	1.54	9.95	0.08
22	0.45	0.58	1.08	7.91	0.081
23	0.44	0.55	0.8	5.92	0.147
24	0.76	1.08	3.07	6.63	0.149
25	0.49	0.68	2.92	3.01	0.106
26	0.41	0.52	1.08	9.16	0.093
27	0.48	0.62	1.03	6.61	0.102

An ideal sequence is x_0(k) (k = 1, 2, 3, 4, 5) for the responses. The definition of grey relational grade in the course of grey relational analysis is to show the relational degree between the 27 sequences [x_0(k) and x_i (k), i = 1, 2, 3, ..., 27]. The grey relational coefficient ξ_i (k) can be calculated as

$$\xi_i(k) = \frac{\Delta_{\min} + \xi\Delta_{\max}}{\Delta_{oi}(k) + \xi\Delta_{\max}} \tag{14}$$

Where, $\Delta_{oi} = \| x_o(k) - x_i(k) \|$ is the difference of the absolute value between x_0(k) and x_i(k), Δ_{min} and Δ_{max} are respectively the minimum and maximum values of the absolute differences (Δ_{0i}) of all comparing sequences. ξ is a distinguishing coefficient, 0 ≤ ξ ≤ 1, the purpose of which is to weaken the effect of Δ_{max} when it gets too big, and thus enlarges the difference significance of the relational coefficient. The grey relational coefficients are calculated for the experimental data using ξ = 0.5. The grey relational grade γ_i is obtained by averaging the grey relational coefficient as follows:

$$\gamma_i = \frac{1}{n}\sum_{k=i}^{n} \xi_i(k) \tag{15}$$

where n is the number of process responses. Higher value of grey relational grade implies stronger relational degree between the ideal sequence x_0(k) and the given sequence xi(k).

3.2 Analysis of signal to noise ratio

The simple average method was used as traditional method for calculating the desirable factor levels, which can not capture the variability of the results within a trial condition. That is why in the present study the S/N ratio analysis is preferred herewith the grey relational grade as the performance index. The S/N ratio is treated as a response (output) of the experiment, which is a measure of variation when uncontrolled noise factors are present in the system. The S/N ratio for grey relational grade is calculated using HB (Higher the better) criterion and is given by:

$$S/N = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y^2}\right) \tag{16}$$

where y is the grey relational grade and n is the number of observations. The grey relational grade along with their order is shown in Table 5.

Table 5. Grey relational grade and its order.

Sample No	Grey relational grade	Order
1	0.6601976	9
2	0.660217	8
3	0.4557636	26
4	0.6189975	18
5	0.6057328	19
6	0.5814263	22
7	0.5871752	21
8	0.5459982	23
9	0.7607874	2
10	0.7691565	1
11	0.69988	4
12	0.5927954	20
13	0.7238593	3
14	0.5453674	24
15	0.6888198	5
16	0.6557611	10
17	0.6239647	17
18	0.672073	7
19	0.6388215	15
20	0.6817227	6
21	0.4744742	25
22	0.655133	12
23	0.6536595	14
24	0.437106	27
25	0.654945	13
26	0.6556523	11
27	0.6343589	16

The response table for the mean of grey relational grade is shown in Table 6. The response table compares the relative magnitude of the effects which includes ranks based on Delta statistics. The Delta statistic is the highest average for each factor minus the lowest average for the same. For factor A, the delta value is calculated as (0.6635 – 0.6085 = 0.055), similar calculation is performed for the other factors. Ranks are assigned on the basis of delta values.

Table 6. Response table for the grey relational grade.

Level	A	B	C
1	0.6085	0.6259	0.6627
2	0.6635	0.6122	0.6302
3	0.6095	0.6434	0.5886
Delta	0.055	0.0312	0.074
Rank	2	3	1
Total mean grey relational grade = 0.627167			

Figs. 2 and 3 shows the main effects and interaction plots between the process parameters respectively.

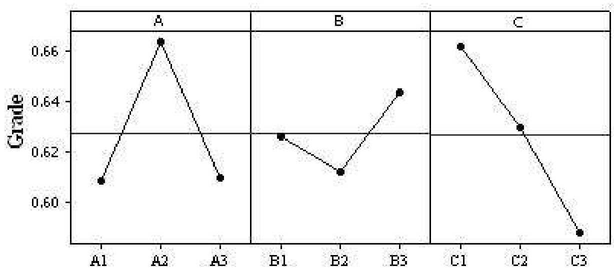

Fig. 2. Main effects plot for mean grey relational grade.

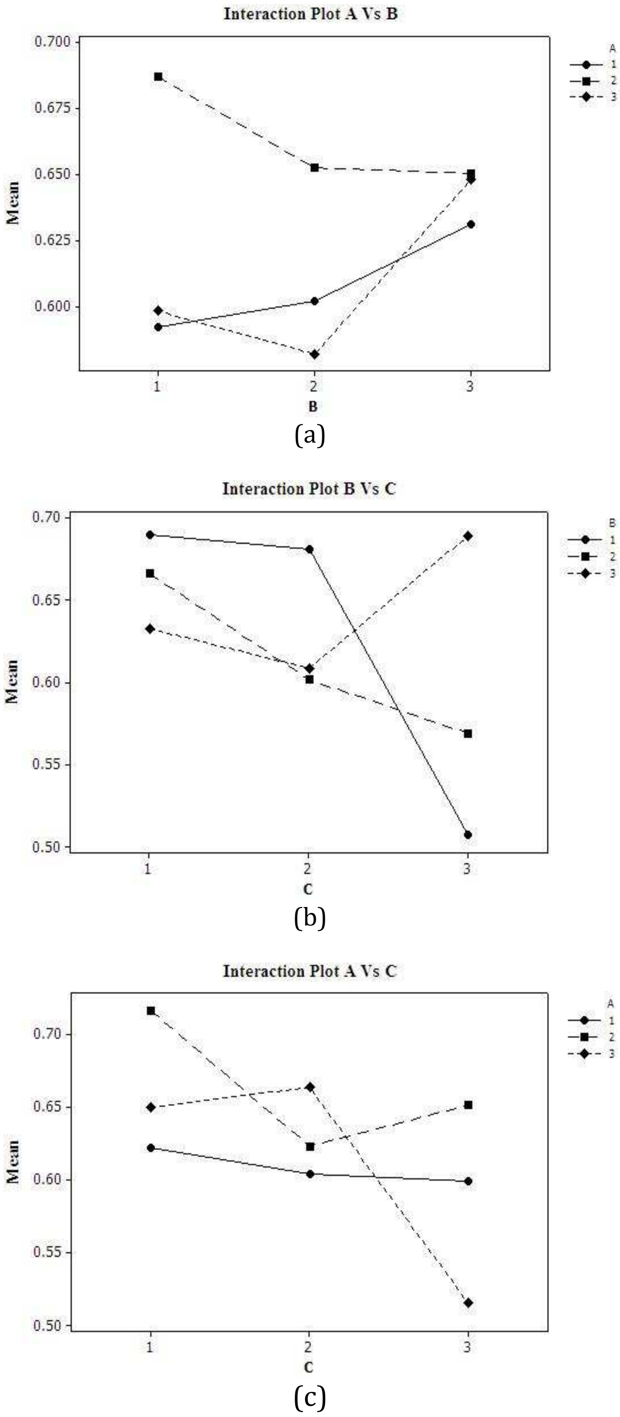

Fig. 3. Interaction effect plots for the mean of grey relational grade (a) A Vs B, (b) B Vs C, (c) B Vs C.

In the main effects plot if the line for a particular parameter is near horizontal, the parameter has no significant effect. On the other hand, a parameter for which the line has the highest inclination will have the most significant effect. It can be easily observed from the main effects plot that parameter C (concentration of tungsten source) is the most significant parameter while parameter A (concentration of nickel source) also has a quite significant effect on the response. But parameter B (concentration of reducing agent) has almost no effect. Interaction plots are constructed by plotting the average response values at each factor level combination. In case of interaction, if the lines are parallel, it indicates that there is no interaction between the factors, but if the lines are non-parallel it indicates the presence of interaction between the factors. And if the lines intersect it indicates that strong interaction exist between the two factors. From Fig. 3, it can be seen that there is strong interaction between the parameters B and C, and there is moderate interaction between A*B and A*C. Thus from the present analysis it is clear that the concentration of reducing agent (B) and concentration of tungsten source (C) are the most influencing parameters for roughness optimization of Ni-P-W coatings. Since higher grey relational grade indicates that the system tends optimality, the optimal condition for each parameter is taken at those points where the mean grey relational grade is found to be the maximum. From Fig. 1, it is seen that plot for parameters A, B and C reach maximum at levels 2, 3 and 1 respectively. Hence the optimal combination of coating process parameters is given as A2B3C1.

3.3 Analysis of Variance (ANOVA)

The significance level of each of the process parameters in the performance characteristics can be investigated with the help of ANOVA. This is accomplished by separating the total variability of the response which is measured by the sum of the squared deviations from the total mean of the response, into contributions by each of the process parameters and the error. In the present study, ANOVA is performed using Minitab. ANOVA results for grey relational grade are shown in Table 7.

ANOVA calculations are based on the F-ratio, which is the ratio between the regression mean square and the mean square error, here for factor A the mean square is 0.008917 and the value of mean square error is 0.003412, so the F-ratio is (0.008917/0.003412) = 2.61. The F-ratio, also called the variance ratio, is the ratio of variance due to the effect of a factor and variance due to the error term. This ratio is used to measure the significance of the parameters under investigation with respect to the variance of all the terms included in the error term at the desired significance level δ. If the calculated value of F-ratio is higher than its tabulated value, then the factor is significant at the desired δ level. In general, when the F-value increases, the significance of the parameter also increases.

Table 7: Results of ANOVA for grey relational grade.

Source	DF	SS	MS	F	% Contri-bution
A	2	0.017833	0.008917	2.61*	10
B	2	0.004397	0.002199	0.64	2.5
C	2	0.024801	0.012401	3.63*	14
A*B	4	0.007816	0.001954	0.57	4.5
A*C	4	0.030026	0.007507	2.2	17
B*C	4	0.063041	0.01576	4.62*	36
Error	8	0.027293	0.003412		
Total	26	0.175208			

* Significant parameters ($F_{0.25,2,8}$ = 1.66, $F_{0.05,4,8}$ = 3.84).

ANOVA table shows the percentage contribution of each parameter. It is clear from the above table that parameter C (concentration of tungsten source) has got the most significant influence on roughness at the confidence level of 75 % within the specific test range. Also parameter A (concentration of nickel source) is significant at the same confidence level. The interaction between the concentration of reducing agent and concentration of tungsten source (B*C) has significant effect on the roughness characteristics of Ni-P-W coating, where the interaction between the concentration of nickel source and the concentration of tungsten source (A*C) has got some contribution in controlling the roughness characteristics.

3.4. Validation Test

In Taguchi method after the optimal level of process parameters has been found out, the final step is to predict and verify the improvement of the performance characteristic using the optimal level of the process parameters. The estimated grey relational grade, $\hat{\eta}$ using the optimal level of the process parameters can be calculated as:

$$\hat{\eta} = \eta_m + \sum_{i=1}^{o} (\overline{\eta}_i - \eta_m) \quad (17)$$

where, η_m is the total mean grey relational grade, $\overline{\eta}_i$ is the mean grey relational grade at the optimal process parameter level and o is the number of the main design process parameters that significantly affect the friction characteristics of Ni-P-W coating. Table 8 shows the comparison of the estimated grey relational grade with the actual grey relational grade using the optimal parameters. The improvement of grey relational grade from initial to optimal condition is 0.1105, which is about 18 % of the mean grey relational grade and is a significant improvement.

Table 8. Results of validation test.

Level	Initial parameter	Optimum parameter	
		Prediction	Experiment
	A2B2C2	A2B3C1	
R_a	0.63		0.61
R_q	0.75		0.73
R_{sk}	1.12		1.07
R_{ku}	5.79		6.68
R_{sm}	0.183		0.055
Grade	0.54536	0.699033	0.65576

3.5. Structural aspects and composition study

The energy dispersive x-ray analyzer (EDX) is used to confirm the presence of nickel, phosphorous and tungsten and also the percentages of the elements in the deposits. The EDX analysis of coated sample is shown in Fig. 4.

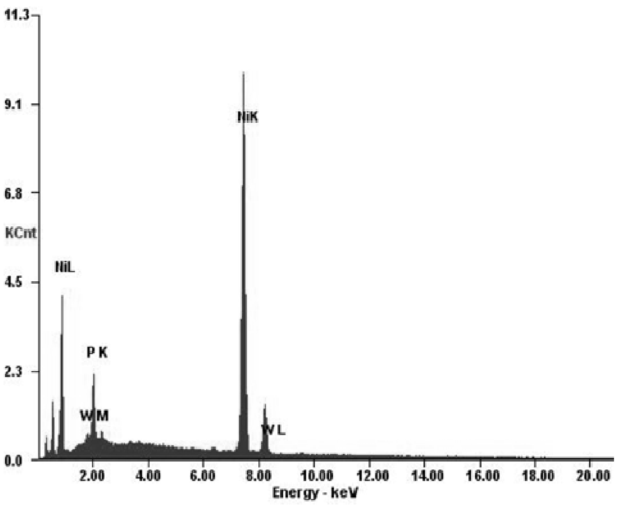

Fig. 4. EDX spectra of coated surface.

The weight percentage of tungsten is found to be 3.81 - 6.60 and that for phosphorous is 0.65 - 7.62, the remaining is mostly nickel. The scanning electron microscopy (SEM) of the sample is shown in Fig. 5.

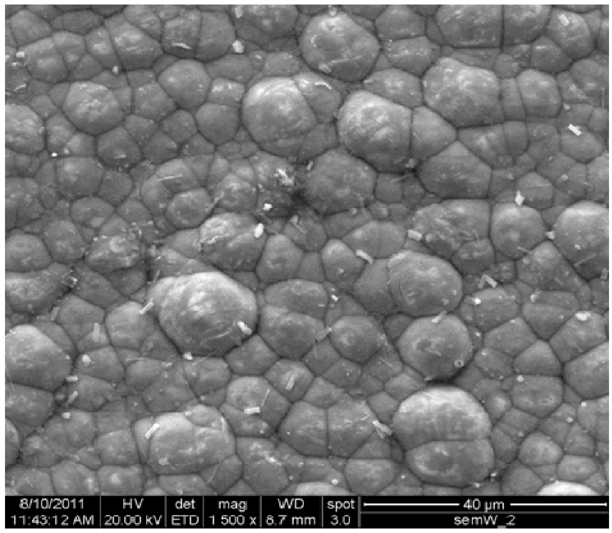

Fig. 5. SEM image of Ni-P-W coated surface

From the figure it is evident that the surface is covered with globular particles with almost no porosity. The surface is optically smooth with no surface damage. X-ray diffraction analysis was also performed to study the structural aspects of the coated surface. It is observed that the as deposited surface shows mostly amorphous behaviour but there is very small existence of crystalline peak which means the deposited surface is a mixture of crystalline and amorphous structure as shown in Fig. 6.

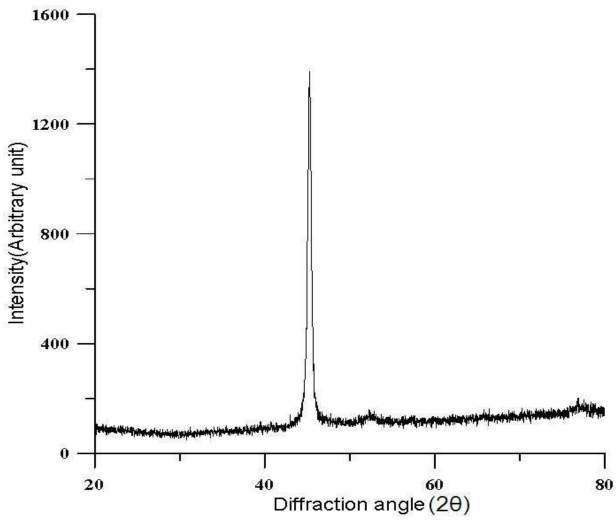

Fig. 6. XRD plot of as deposited coating.

4. CONCLUSION

In the present study, Taguchi orthogonal array in conjunction with grey relational analysis is used to optimize the coating process parameters (concentration of nickel source, concentration of reducing agent and concentration of tungsten source) together in order to optimize multiple roughness parameters (R_a, R_q, R_{sk}, R_{ku}, R_{sm}) of Ni-P-W coatings. The optimal combination of coating parameters is obtained as A2B3C1.

ANOVA result indicates that concentration of tungsten source (C) is the most important parameter that significantly affects the roughness characteristics. Also the concentration of nickel source is quite significant at the same level of confidence. The improvement of the grey relational grade from the initial condition to the optimal condition is found to about 18 %. From the EDX analysis it is clear that the coating is pure ternary and consists of nickel, phosphorous and tungsten.

The XRD plots reveal that the coating is a mixture of amorphous and crystalline structure. From the surface morphology captured by SEM it is seen that there are many globular particles on the surface of the substrate with no surface damage. Also the coating is dense with low porosity.

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