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Response Surface Methodology for Optimum Hardness of TiN on Steel Substrate

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Abstract**—**Hard coatings are widely used in cutting and forming tool industries. Titanium Nitride (TiN) possesses good hardness, strength, and corrosion resistance. The coating properties are influenced by many process parameters. The coatings were deposited on steel substrate by changing the process parameters such as substrate temperature, nitrogen flow rate and target power in a D.C planer magnetron sputtering. The structure of coatings were analysed using XRD. The hardness of coatings was found using Micro hardness tester. From the experimental data, a regression model was developed and the optimum response was determined using Response Surface Methodology (RSM).

Keywords**—**Hardness, RSM, sputtering, TiN XRD.

I. Introduction

SURFACE coating, now-a-days, is widely used to improve the functionality of components. Physical Vapour Deposition (PVD) technique can be used to prepare tailor-made refractory coatings on cutting tool for metal machining. Owing to extreme hardness, high thermal and chemical stability, low electrical resistance Titanium Nitride (TiN) has been widely applied as a coating material ranging from hard and protective coatings on mechanical tools, decorative coatings to the diffusion barrier in microelectronic industry [1]. TiN coatings are also used for medical applications such as orthopaedic prostheses [2], cardiac valves [3], and dental prostheses [4]. The application of coatings based on nitrides has proved to be very successful in extending the life of cutting tool [5], [6]. Further, TiN film prevents penetration of relatively lower melting temperature materials such as aluminium and it protects against destitute reactors during the ultra-large scale integrated circuit fabrication process [7]. Even though TiN ceramic coatings on steel substrate can be done by PVD and CVD methods, PVD is a preferable technique due to its advantage that it will not have a chemical effect on the substance material composition because of low temperature processing. Although the growth and properties of TiN films deposited by sputtering type PVD technique have been extensively studied, the fundamental relations between deposition parameters and hardness are not yet fully understood. This work presents about developing a mathematical model for correlating the interactive and higher order influences of various PVD parameters on micro hardness of TiN coated on SS420 tool steel using Response Surface Methodology (RSM).

The TiN film properties are widely changed with various sputtering conditions [8]. The substrate roughness, substrate temperature, argon gas pressure, nitrogen flow rate, bias voltage, and coating thickness are some of the variables which would affect the structure, morphology, and mechanical properties of the coating. In most of the works, the average surface roughness of the substrate was taken as0.2 μm. The substrate temperature is important for hardness, adhesion, and structure of coating. The columnar structure changes into dense fibre structure when substrate temperature becomes higher than 0.3 T_m (T_m is the melting temperature of coating material) [9]. It was also established that the hardness of coating is not much affected by the coating thickness [10] Variations in both the substrate bias potential and the target power has a strong effect on the hardness and texture of the TiN coatings [11]. Similarly, nitrogen content influences the mechanical and structural properties of TiN coating [12]. Hence, the present work has been proposed to optimize the hardness of TiN with the effect of important input parameters substrate temperature, nitrogen flow rate and target power using Response Surface Methodology (RSM) [13].

II. Experimental Procedure

A. Sputtering Apparatus

TiN films were deposited on steel substrate using PVD planer magnetron sputtering equipment. The distance between the target and substrate was 60 mm. Initially the system was evacuated to base pressure of 6X 10 -6 mbar. The working pressure was maintained at 2 X 10-3 m bar. The substrate temperature was controlled in the range of 200, 300 and 400°C by external electronic controller. The argon flow rate was maintained at 20 sccm. The nitrogen flow rates were controlled by mass flow controller in between 2 sccm and 6 sccm. All the specimens were coated for 60 min.

B. Substrate and Target

The SS 420 steel specimens have been prepared for the dimensions of 20 x20 x 5 mm. The steel specimens were cleaned in a multi-stage cleaning process to remove soils, oils, fingerprints to produce an oxide free surface. The composition of steels used shown is in Table I. The 99.9% pure Ti target has been used. The diameter of target was 2 inch.

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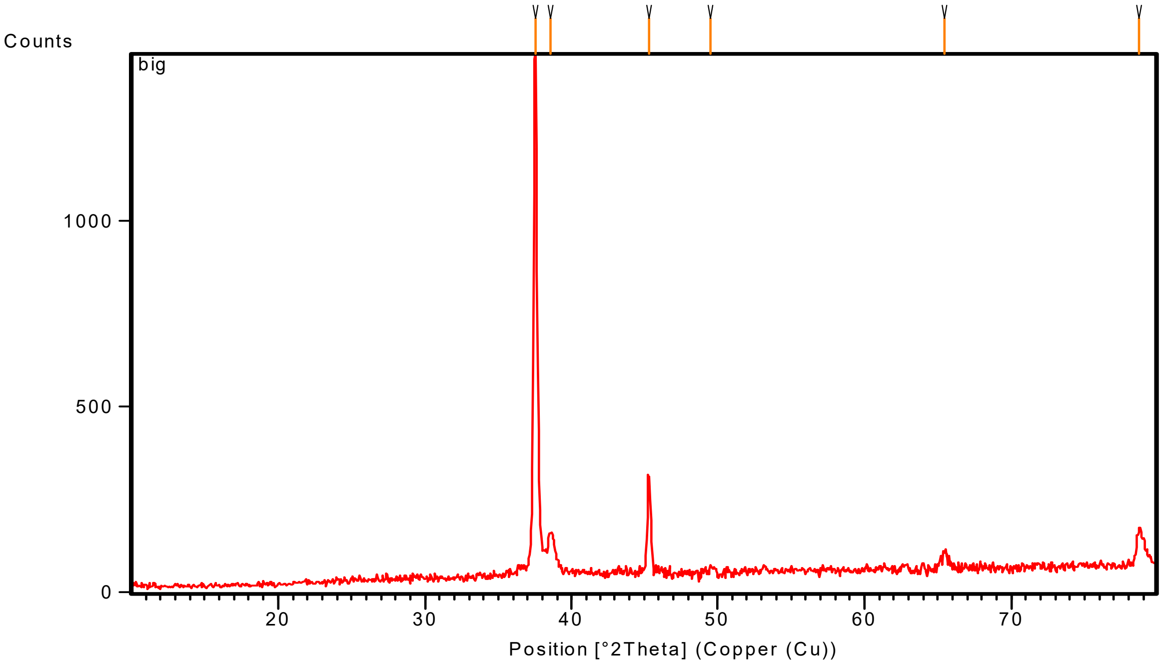

Fig. 1 XRD pattern of TiN deposited under temp 300°C, N_2 6sccmand power 300watts

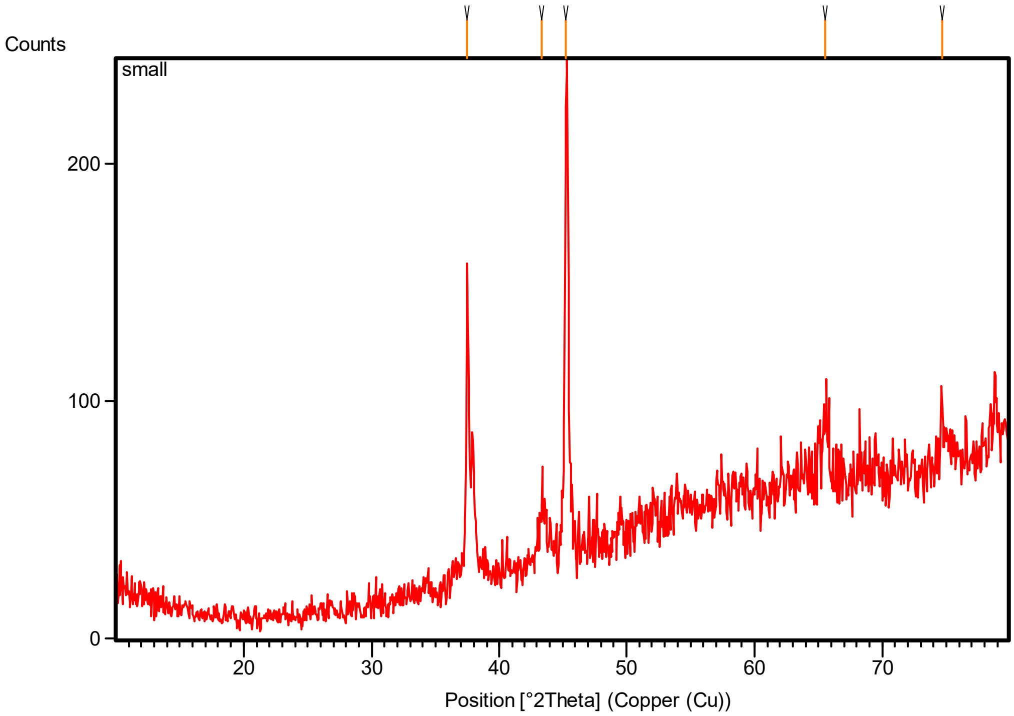

Fig. 2 XRD pattern of TiN deposited under temp 400°C, N2 6sccm and power 200watts

TABLE I
COMPOSITION OF TARGET MATERIAL

Material	Composition			
	C	Mn	Si	Cr
SS420	0.15	1	1	12-14

III. RESULT AND DISCUSSION

A. Structure Analysis Using XRD

X-ray analysis was conducted in PANalytical-X'Pert Pro using CuKα (1.514 θ) with θ-2θ scan mode and a thin film attachment with a parallel plate collimator 0.18°. Fig. 1 exhibits TiN (111) formed at 37.49°C with the crystal size of

571 [Å] which was coated at substrate temperature at 300°C, N_2 at 6 sccm and power at 300W.

Fig. 2 is the XRD pattern of sample coated at a temperature of 400°C, N_2 at 6 sccm and power at 200W. It is evident from Fig. 2 that high intensity of reflection occurs at (200) plane with smaller crystallite size of 481 [Å] which is less than previous one and has more hardness.

B. Microhardness Tester

The micro hardness of as-deposited films was measured with a Vickers indenter. The average hardness value was measured at five different locations with the load of 25 gf.

C. Response Surface Analysis

The RSM is an important tool of Design Of Experiment (DOE) in which the maximum or minimum value of the response is obtained for the input variables. It is a collection of mathematical and statistical techniques for the modeling and analysis of problems based on statistical design of experiments and least square error fitting. It is extensively, used where several input variables influence the process.

The relationship between the response y and the controllable input variables ($\xi_1, \xi_{2 \ldots} \xi_{k,}$) is as,

$$Y = f(\xi_1, \xi_2, \ldots \ldots \xi_k) + \xi \tag{1}$$

ξ includes the measurement error and other inherent errors in the system or process. Generally, ξ is treated as a statistical error, which has normal distribution of mean zero and variance σ. The first order model is used to approximate the true response surface in relatively small region where there is little curvature of the independent variable space. In the vicinity of the optimal point, a second order regression model is generally found adequate

The second-order model is widely used in response surface methodology for the following reasons.

1. The second-order model is very flexible as an approximation to the true response surface. It can take on a wide variety of functional forms, so it will often work as an approximation to the true response surface
2. It is easy to estimate the parameters (the β's) in the second-order model.
3. There is considerable practical experience indicating that second-order models work well in solving real response surface problems.

The second order response surface representing the output (Y) can be expressed as a function of substrate temperature, nitrogen flow rate and power of target. The relationship between the output and processing parameters has been expressed as:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \cdots + \beta_k X_k + \beta_{11} X_1^2 + \ldots + \beta_{kk} X_k^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \ldots + \beta_{k-1,k} X_{k-1} X_k + \varepsilon \tag{2}$$

where Y is the corresponding response, β_0 is constant called the intercept of the plane and β_1, $\beta_{2\ldots}$, β_9 are regression coefficient that depends on main effects. The β_0 coefficients used in (2) can be calculated using least square techniques. The terms X_1, $X_2$and X_3 are the input variables, X_1^2, X_2^2 and X_3^2 are the square terms and X_1X_2, $X_2\ X_3$ and $X_1\ X_3$ are interaction terms respectively for input variables. To test the fit of the model, the value of R^2 was calculated which measures percentage of the variation of data that is explained by the regression equation. The value of R^2 approaches to unity, the better the response model fits the actual data.

The experimental design to fit a second-order response in RSM should possess.

1. At least three levels of each design variable,
2. At least 1 + 2k + k(k – 1)/2 distinct design points.

In this work, 27 design points were chosen to fit the response in design space for the 3 design variables at 3 levels.

The process variables are fixed at the following 3 levels is given in Table II.

TABLE II
LEVELS OF PROCESS PARAMETERS

Factor	Level 1	Level 2	Level 3
Substrate Temperature (°C)	200	300	400
Nitrogen flow rate (sccm)	2	4	6
Power (watts)	100	200	300

The response of the process hardness value was determined through the 27experiments with full factorial is given in Table III.

TABLE III
LEVELS OF PROCESS PARAMETERS

Run order	Substrate temperature (°C)	Nitrogen flow rate (sccm)	Power (watts)	Hardness (VHN)
1	400	2	300	440
2	300	4	100	440
3	200	6	300	490
4	400	4	100	420
5	200	4	200	470
6	300	6	100	510
7	300	4	300	470
8	300	6	200	580
9	200	2	100	350
10	200	2	200	380
11	400	6	300	530
12	400	6	200	620
13	400	6	100	480
14	300	6	300	520
15	400	2	200	380
16	200	4	100	430
17	200	2	300	370
18	300	2	100	350
19	200	6	100	460
20	400	2	100	370
21	300	4	200	490
22	300	2	200	410
23	200	4	300	420
24	400	4	200	580
25	400	4	300	480
26	300	2	300	380
27	200	6	200	520

The optimization analysis is carried out using Design-Expert® package.

The second order (quadratic) model for the hardness of coating has been developed at 95% confidence level. The output of model summary statistics is given in Table IV.

TABLE IV
MODEL SUMMARY STATISTICS

Source	Std. Dev	R-Squared	Adjusted R-Squared	Predicted R-Squared	Press
Linear	38.18	0.7580	0.7265	0.6760	44898.21
2FI	39.63	0.7733	0.7053	0.5860	57363.74
Quadratic	27.89	0.9046	0.8540	0.7432	35586.49
Cubic	26.67	0.9487	0.8666	0.5521	62061.21

From Table IV, R-Squared value of 0.9046 suggests the Quadratic Model fit for the design. The value for Adj R-Squared is 0.8540.

The model presented high determination coefficient (R^2 = 90.46) explaining 90% of the variability in the response which indicates the goodness of fit for the model and high statistical significance of the model. It shows the high correlation exist between the experimental and predicted values. Also, the adjusted R^2 (85.4%) value is very close to the predicted R^2 that shows that the unnecessary terms are not added in the model.

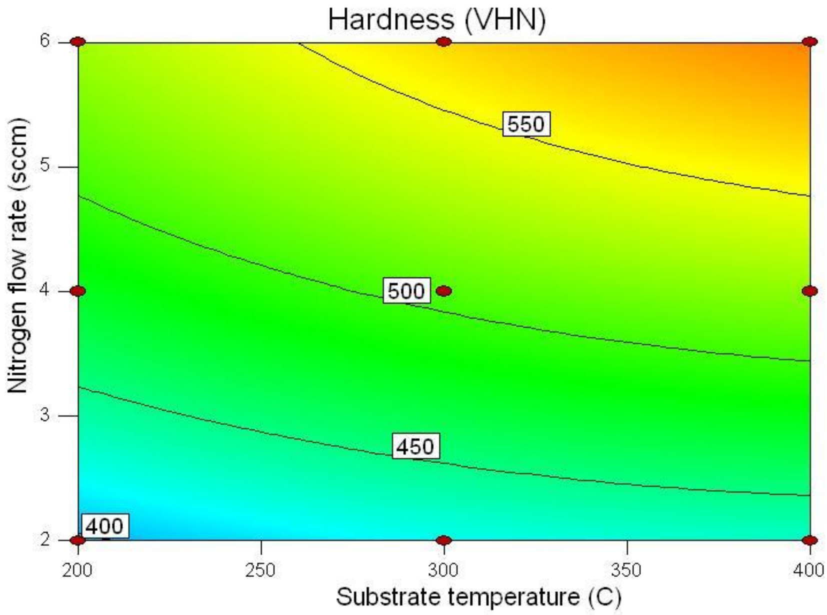

Fig. 3 Hardness for variation of Temperature and nitrogen flow

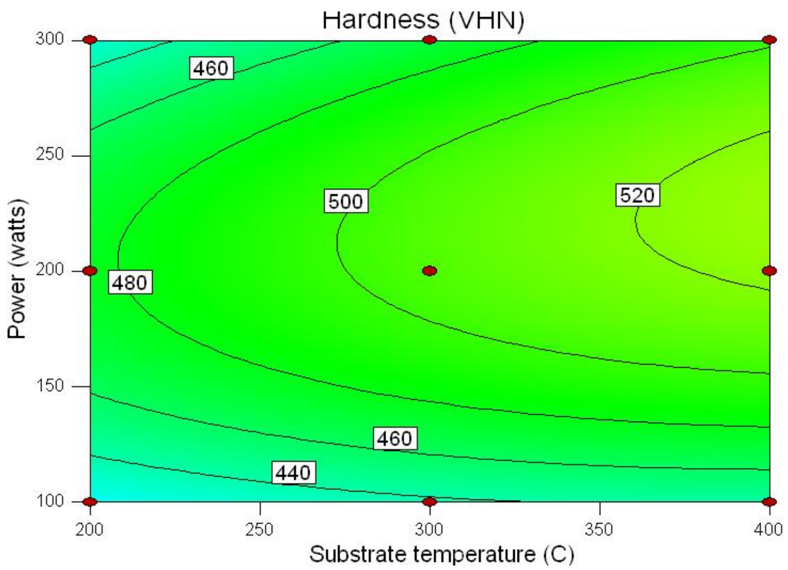

Fig. 4 Hardness for variation of Temperature and Power of target

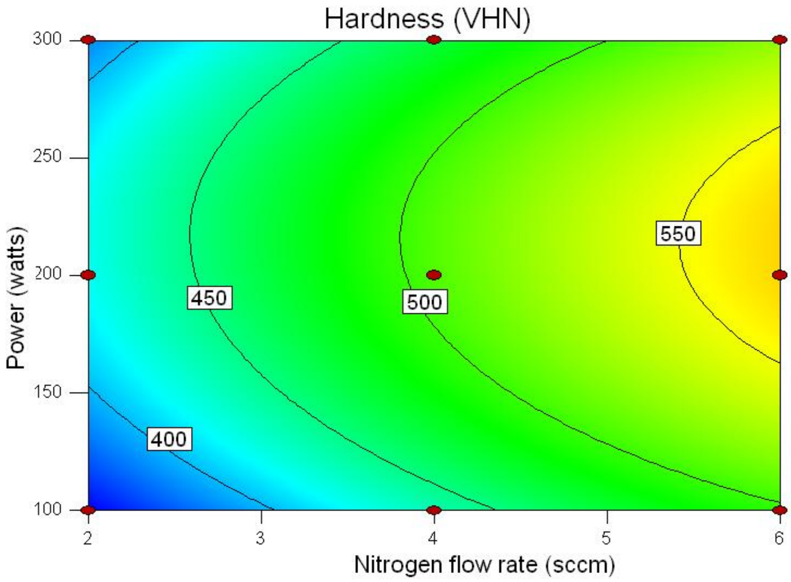

Fig. 5 Hardness for variation Nitrogen flow and Target Power

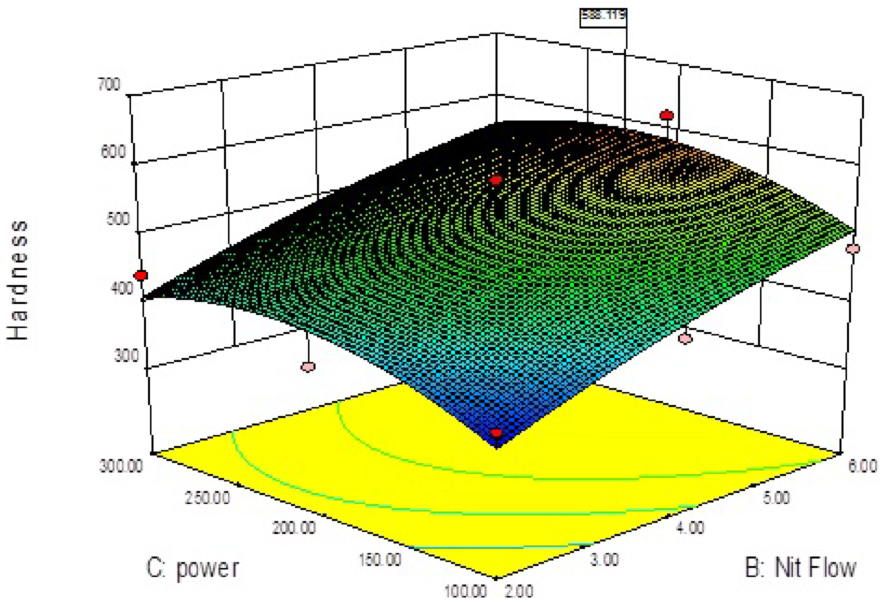

Fig. 6 Surface Plot with N_2 and Power

From Table V, the Model F-value of 17.90 implies that the model is significant and the variation due to noise is only 0.01%. If P value of model is less than 0.05 (95% confidence level), significance of corresponding term is established and the model has a significant effect on the response. The Values of "Prob> F" less than 0.0500 indicate model terms are significant. In this case A, B, C, C^2 are significant model terms.

The model for hardness (uncoded) is shown in (3):

$$Hardness = 34.25 + 0.24 * A + 58.19 * B + 1.97 * C + 0.029167 * A * B + 1.66E - 003 * A * C - 0.0125 * B * C - 6.11E - 004 * A2 - 3.611 * B2 - 5.277E - 003 * C2 \quad (3)$$

The equation shows that the factors influence the hardness of coating in the order of N_2, power and temperature.

The contour plots are two-dimensional graphs that show contours of constant response for the two design variables, while the other design variables are held constant.

These response contours can help in the prediction of response at any zone of the experimental domain. The effects of the coating parameters on responses are presented as contour plots in Figs. 3-5.

Figs. 6 and 7 show that maximum hardness of 588.19 can be achieved with respect to the process variables of temperature at 400°C, N_2 6 sccm and power at 224 watts, which correlate with the results of XRD.

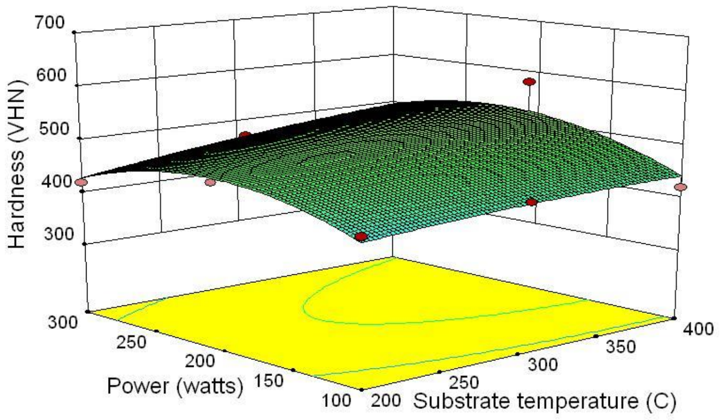

Fig. 7 Surface Plot with Temperature and N2

TABLE V
ANOVA FOR RESPONSE SURFACE QUADRATIC MODEL

Source	Sum of Squares	df	Mean Square	F value	p-value F>0.001
Model	1.253E+005	9	13926.54	17.90	< 0.0001
A -Temperature	9338.89	1	9338.89	12.01	0.0030
B-Nitrogen flow rate	91022.22	1	91022.22	117.01	< 0.0001
C-Power	4672.22	1	4672.22	6.01	0.0254
AB	408.33	1	408.33	0..52	0.4786
AC	1633.33	1	1633.33	2.1	0.1655
BC	75	1	1008.33	1.165439	0.2954
A2	224.07	1	224.07	0.096	0.5984
B2	1251.85	1	1251.85	1.61	0.2217
C2	16712.96	1	16712.96	21.49	0.0002
Residual	13224.07	17	777.89		
Cor.total	1.386E005	26			

D.Model Checking

Generally a model adequacy investigated by examination of residuals. For the model to be adequate the pattern of residuals plot should be structure less.

The normal probability plot of the residuals of RSM (Fig. 8) shows that the residuals lie reasonably close to a straight line implying that errors are distributed normally and giving support that the terms mentioned in the model are significant.

A graph of the predicted response values versus the actual response values is shown in Fig. 9. It helps to detect a value, or group of values, that are not easily predicted by the model. The figure also shows any abnormal in response.

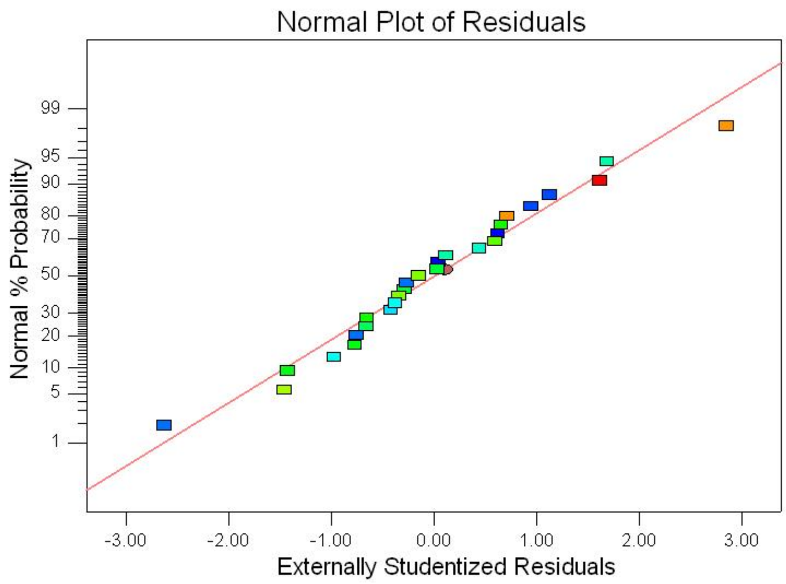

Fig. 8 Normal Plot of residuals

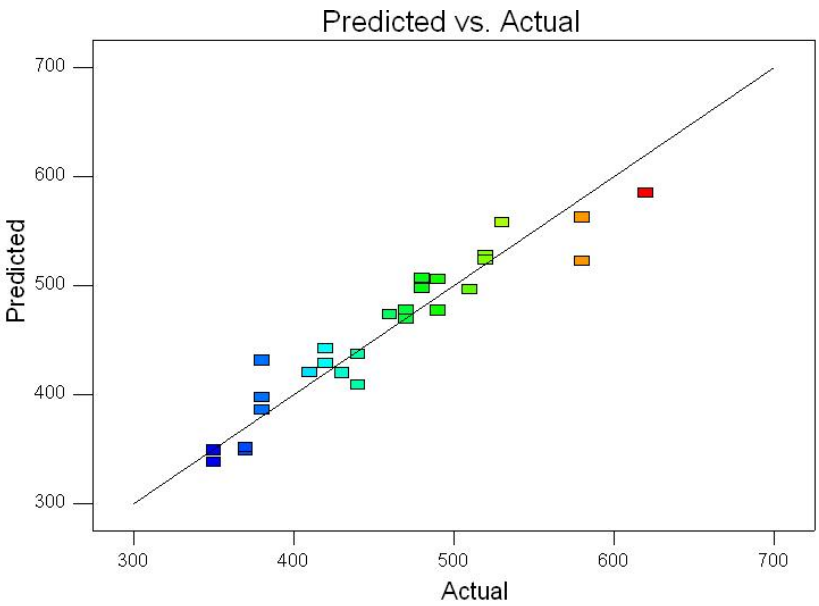

Fig. 9 Predicted Value vs Actual

IV. Conclusion

1. The ANOVA proved that the quadratic model for the hardness of coating is valid at 95% confidence level.
2. Through ANOVA, it is to be concluded that percentage of contribution of factors to the hardness of coating in sequence, is nitrogen flow rate, power and substrate temperature.

The RSM model predicts the optimum hardness value of 588.19 for the process variables substrate temperature at 400 C, N_2 at 6ssccm and target power at 224 watts which is confirmed with the XRD results.

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