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OPTIMIZATION OF CHEMICAL PRETREATMENT FOR REMOVING COBALT ON TUNGSTEN CARBIDE SUBSTRATE USING RESPONSE SURFACE METHODOLOGY

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Abstract

Diamond coating are commonly used in industries especially for application such as cutting tools, biomedical components, optical lenses, microelectronics, engineering, and thermal management systems. The diamond coating quality is strongly depending on substrate preparation prior to diamond coating. Thus, the several process parameters must be studied to obtain optimal parameters which lead high quality diamond coating. In this present work, an attempt was made to optimize pretreatment parameters namely temperature and time on cobalt removal of tungsten carbide. Full factorial experimental designs followed by Response Surface Methodology (RSM) were employed in this study to plan and analyze the experiment. The cobalt removal was the independent response variables. Empirical model was successfully developed to predict amount of cobalt removal on the substrate after single step etching process. Experimental results have shown that the temperature, time and time^2 are found to be the most significant factors for cobalt removal. Whereas for interaction of time and temperature were insignificant factors to influence cobalt removal. According to this study, the minimum cobalt content can be obtained at working temperature from 48° to 50°C for 3 minute.

Keywords: Diamond coating, RSM, full factorial design, tungsten carbides, cobalt removal

Abstrak

Salutan berlian biasa digunakan dalam industri terutama untuk aplikasi seperti alat memotong, komponen bioperubatan, kanta optik, mikroelektronik, kejuruteraan, dan sistem pengurusan haba. Kualiti salutan berlian adalah sangat bergantung kepada penyediaan substrat sebelum salutan berlian. Oleh itu, beberapa parameter proses perlu dikaji untuk mendapatkan parameter optimum yang dapat menghasilkan salutan berlian berkualiti tinggi. Dalam kajian ini, percubaan telah dibuat untuk mengoptimumkan parameter rawatan awal iaitu suhu dan masa pada penyingkiran kobalt tungsten karbida. reka bentuk eksperimen faktorial penuh diikuti oleh Metodologi Tindak balas Permukaan (RSM) telah digunakan dalam kajian ini untuk merancang dan menganalisis eksperimen. Penyingkiran kobalt adalah pemboleh ubah tindak balas bebas. model empirikal telah berjaya dibangunkan untuk meramalkan jumlah penyingkiran kobalt pada substrat selepas proses langkah pertama. Keputusan eksperimen telah menunjukkan bahawa suhu, masa dan masa^2 didapati menjadi faktor paling penting bagi penyingkiran kobalt. Manakala bagi interaksi masa dan suhu adalah faktor penting untuk mempengaruhi penyingkiran kobalt. Keputusan menunjukkan kobalt minimum boleh diperolehi pada suhu dari 48° ke 50°C selama 3 minit.

Kata kunci: Salutan berlian, RSM, reka bentuk faktor penuh, tungsten karbida

1.0 INTRODUCTION

Tungsten carbides are widely used in application of tools for metal cutting and rock drilling or wear parts for several decades [1]. This material is preferred used as a cutting tool material due to its high hot hardness and wear resistance properties over a wide range of temperatures [2]. Hard coating such as TiN, TiAlN, TiCN, diamond are commonly used to coat on the outer tool surface for improving tool life when machining hard and abrasive materials. Among these types of coating, diamond is considered the hardest but it is difficult to deposit directly on the cemented tungsten carbide due to the presence of cobalt which prevents a good adhesion between diamond layer and the substrate. The presence of cobalt as a binder material on the tungsten carbide surface retards the diamond growth and also promotes non-diamond formation on the WC substrate during diamond coating process [3]. Sub-standard diamond quality forms on the cutting tools will affect the tool life significantly. Realizing this issue, researchers have made many attempts to reduce cobalt contents on the WC substrate surface either using single-step or two-step pretreatments which involve mechanical and/or chemical etching methods. Between the two methods, chemical pretreatment seems giving a more consistent result. This method is also simple and relatively cheap to perform. The only drawbacks with chemical method are toxic and hazardous where it requires special cares during treatment. Acid concentration, etching time and temperature are among the parameters varied in chemical etching studies. Sarangi*et al.* [4] attempted to remove cobalt on WC surface at room temperature using acid solution of HCL + HNO3 + H_2O (1:1:1). They etched for fifteen minutes and able to remove cobalt contents to less than 1%. Kamia*et al.* [5] studied the effect of HNO_3 + H_2O (3:1) and Murakami's solutions on cobalt removal and surface roughness at room temperature respectively. They found that Murakami solutions were effective for roughening the substrate surface while the acid solution able to remove cobalt below 10% within 10 minutes. Several researchers made an attempt to conduct chemical pretreatment at elevated temperature. Tang *et al*. [6] and Ilias*et al.* [7] evaluated the effect of different nitric-hydrochloric acid solutions with and without water at high temperature respectively. They used these solutions to remove cobalt on the WC substrate prior to the diamond coating. Caro acid (H_2SO_4 + H_2O_2) has been quite commonly used by numerous researchers in the second step chemical pretreatment process for depleting cobalt from substrate surface [8-10]. However, up to the current literature the use of Caro acid at high temperature as a single acid solution for removing cobalt on WC substrate hardly been found. Most practices in the above studies the determination of significant chemical etching parameters involves the use of one-factor at a time (OFAT). This experimental approach is not only time consuming and exorbitant in cost but also neglects the effect of interaction between factors. The recent trend shows that the application of experimental design techniques using statistical methods has been increased steadily especially in planning experimental trials and analyzing results. Beltran-Heredia *et al.* [11] utilized Response Surface Methodology (RSM) approach for removing sodium dodecyl benzene sulfonate from water by means of a new tannin-based coagulant. Zheng and Wang [12] made similar efforts to optimize the removal of heavy metals using polyvinyl alcohol semi-IPN poly (acrylic acid)/tourmaline composite using RSM approach. Da'na and Sayari [13] employed full factorial design followed by RSM for optimizing of copper removal efficiency using aminopropyl-functionalized SBA-15 silica. Another worker Martín-Lara *et al.* [14] also used full factorial designs for optimizing the removal conditions of lead ions from aqueous solutions from three wastes of the olive-oil production. Apart from RSM and factorial design, Taguchi method also receives attentions from researchers to evaluate chemical experimental performances. Havuz*et al.* [15] employed L9 (34) Taguchi experimental plan for removing lead from decopperized anode slime in aqueous Na2CO3/HNO3 media. Gonzalez and Diaz [16] applied Taguchi L16 orthogonal array for removing acid orange 8 using guava seeds activated carbon. Recently, Ghasemi and Moradi [17] used Taguchi method is to evaluate the effect of design experiment and find contributions of temperature difference, composite layups, fiber volume fraction and number of thermal cycles subjected to thermal cycling on glass/epoxy composite components. The above literatures show that attempts to remove cobalt contents on WC substrate at high temperature using Caro acid as a single step pretreatment method are still scarce. Though statistical experimental design techniques have been applied successfully in many chemical removal studies but its application in cobalt removal on WC substrate is somewhat lacking. The aim of this research is to optimize the chemical pretreatment parameters in removing cobalt contents on WC substrate prior to diamond coating process. The chemical pretreatment parameters include etching time and temperature. RSM approach is used for planning the experimental trials and analyzing the significant parameters. It is expected that the findings from this experiment can be used for producing high quality of diamond coating on the tungsten carbide tools.

2.0 METHODOLOGY

2.1 Workpiece Material

The workpiece material used in this study was tungsten carbide (WC) with 6 % wt Co. The received WC bar was cut into cylindrical shape using a precision cutter to a dimension of ø12mm x 3mm thick. This material is suitable for a wide variety of cutting tool applications either in the form of insert or solid carbide mainly due to its high hardness, strength and wear resistance over a wide range of temperatures.

2.2 Chemical Pretreatment Preparation

The etchant used for treating cobalt on the WC substrate was Caro acid. This acid is a mixture of 88ml-30% hydrogen peroxide (H_2O_2) and 3ml-95% sulfuric acid (H_2SO_4). This solution has been used as a single step pretreatment process by several researchers for removing cobalt on WC substrate. All of them conducted their experiments at room temperature. In this work, the experiment was carried out above room temperature (35oC and 55oC) for increasing the cobalt removal rate. The etching time was varied from 1 to 3 minutes.

2.3 Experimental Plan

In this investigation, two factors were studied (temperature and time) and their low and high levels are summarized in Table 1. A 22 full factorial design with three center points were used as a screening process to determine the significant factors. Then it is followed by factorial design augmentation technique for optimizing the process when a curvature is detected in the predicted model. Augmentation plan is carried out using Central Composite Design (CCD) method to perform additional experiments followed by analysis of variance (ANOVA) and confirmation runs. In the absence of curvature, steepest of ascend step will be used to modify the experimental plan. These procedures are summarized as shown in Figure 1.

Table 1 Factors and levels for response surface study

Factor	Low level (-1)	Centre point (0)	High level (+1)
A-Temperature °C)	35	45	55
B-Time (Minutes)	1	2	3

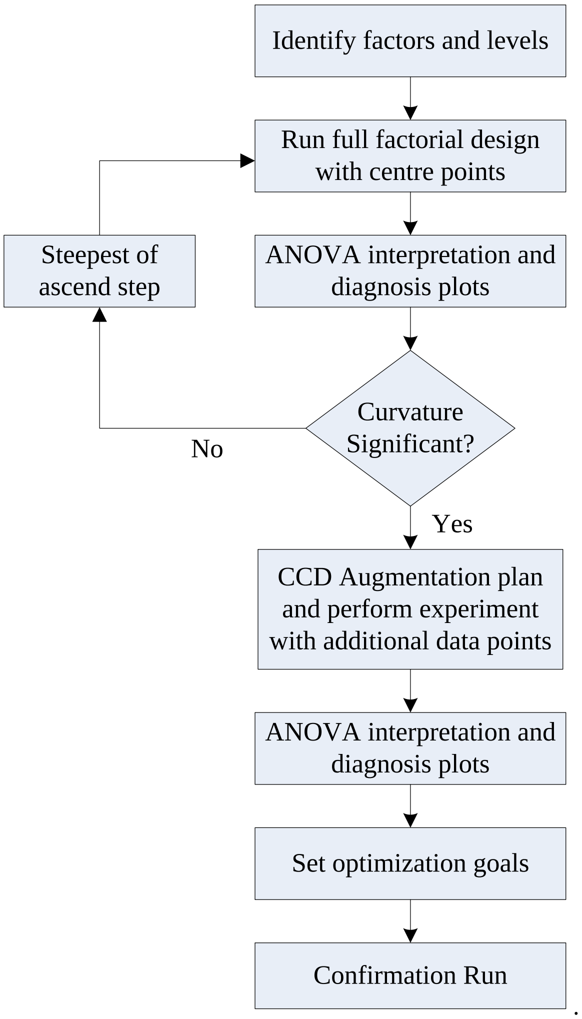


Figure 1 Flow chart of RSM experimental procedure.

Design Expert version 6 was used to generate the experimental plan for full factorial design with two replicates as shown in Table 2. The design involves 11 runs and the response variable measured was the percentage of cobalt removal. The center points generated in the experimental plan are 2 minutes and 45°C etching time and temperature respectively.

3.4 Experimental Procedure

After cutting, all WC samples were blasted for 10 seconds using Blasting Wear Tester (BWT) to roughen the substrate surface. The abrasive used during blasting was Al_2O_3 with #180 grit size. Prior to chemical etching, all samples were cleaned with acetone to remove other contaminants left on the surface. Subsequently, the samples were etched in Caro acid solution under ultrasonic vibration at varied temperatures and times following the conditions given in Table 2 earlier. After etching, the samples were rinsed using distilled water and compressed air was used to dry the samples. The cobalt contents were measured using Energy Dispersive X-ray (EDAX) technique, the function that is available within the Scanning Electron Microscopy (SEM) equipment. The effectiveness of the chemical pretreatment process is judged based on the ability of reducing cobalt contents on the substrate from 6% to less than 1%.

Table 2 Completed design layout for factorial design

Std no	Run	Block	Factor	
			A-Temp (Deg C)	B-Time (Min)
1	1	1	35.00	1.00
2	4	1	35.00	1.00
3	3	1	55.00	1.00
4	11	1	55.00	1.00
5	10	1	35.00	3.00
6	7	1	35.00	3.00
7	5	1	55.00	3.00
8	2	1	55.00	3.00
9	9	1	45.00	2.00
10	6	1	45.00	2.00
11	8	1	45.00	2.00

3.0 RESULTS AND DISSCUSION

The results from the etching trials conducted as per the experimental plan are shown in Table 3. These response values (% Co contents) were input into the Design Expert Version 6 software for further analysis.

Table 3 Experimental results

Std no	Run	Block	Factor		Cobalt Contents (%)
			A-Temp (Deg C)	B-Time (Min)	
1	1	1	35.00	1.00	0.88
2	4	1	35.00	1.00	0.84
3	3	1	55.00	1.00	0.72
4	11	1	55.00	1.00	0.67
5	10	1	35.00	3.00	0.4
6	7	1	35.00	3.00	0.43
7	5	1	55.00	3.00	0.35
8	2	1	55.00	3.00	0.42
9	9	1	45.00	2.00	0.63
10	6	1	45.00	2.00	0.65
11	8	1	45.00	2.00	0.68

3.1 ANOVA Analysis ForFactorial Design

Analysis of variance (ANOVA) was performed after completing the experimental runs. For ensuring a good model, tests for significance of the regression model and the individual model coefficients need to be performed. An ANOVA table is usually used to present these results. Table 4 shows the ANOVA results for the response, i.e. percentage of cobalt removed on the WC substrate when varying the etchant temperature and etching time. The value of "Prob> F" in Table 4 for the model is less than 0.05, which indicates that the model is significant. It is a desirable condition as the terms in the model have a significant effect on the response. Similarly, the main effect of etching time (B), etching temperature (A) and two level interactions of etching time and temperature are significant model terms. Based on the "F" value, the main effect of etching time (B) is found to be the most significant factor than the etching temperature (A) and their interaction (AB) in removing cobalt. It can be translated that etching time plays major role than acid temperature in removing cobalt contents on the substrate surface. The smaller the "Prob> F" value and the larger magnitude of "F' value, the more significant is the corresponding coefficient. Thus, in this work, the order of significance can be ranked as follows: B > A > AB. The lack of fit is also not significant, which is desirable as we want a model that fits. The R2-value calculated in Table 4 for this response is 0.98, approaching to unity which is most desirable. It implies that about 98% of the variability in the data is explained by the model. This also confirms the model provides an excellent explanation of the relationship between the investigated factors and the response. The difference between the predicted R2 and the adjusted R2 is in reasonable agreement. Adequate precision measures the signal to noise ratio. Basically, it compares the range of the predicted value at the design point to the average prediction error. A ratio of greater than 4 is desirable which represents adequate model discrimination. The adequate precision value for this case is well above 4. ANOVA results in Table 4 indicate there is a significant curvature effect for the cobalt removal. The presence of curvature hinted that the tested independent variables are already within the optimum region and thus necessary to consider factorial design augmentation by adding points to fit the data to a second-order or quadratic model. This is a common method for continuing experimentation after initial factorial screening process has revealed critical factors that lead to optimization process. The final augmentation step in this case uses a standard central composite design (CCD). This is a part of the response surface methods (RSM) to plan additional points and fits the results to the quadratic polynomials. The CCD has been the most accepted experimental design for developing second-order models. Table 5 shows the default augment plan based on CCD with $a = 1$ and their results. This plan creates seven more points to be added on the existing data, i.e. four points on the face centered CCD (standard number from 12-15) plus another three center points (standard number from 16-18). All additional points are grouped in Block 2.

Table 4 ANOVA table for full factorial (Response: Cobalt Content)

Source	Sum of squares	d.f.	Mean square	F	Prob.> F
Model	0.31	3	0.10	100.74	< 0.0001
A	0.019	1	0.019	18.35	0.0052
B	0.29	1	0.29	275.08	< 0.0001
AB	9.112E-003	1	9.112E-003	8.79	0.0251
Curvature	9.100E-003	1	9.100E-003	8.78	0.0252
Pure Error	6.217E-003	6	1.036E-003		
Cor Total	0.33	10			
Std. Dev.	0.032	R^2	0.9805		
Mean	0.61	Adj R^2	0.9708		
C.V.	5.31	Pred R^2	0.9310		
PRESS	0.023	Adeq Prec	21.888		

Table 5 Completed design layout for RSM

Std no	Run	Block	Factor		Cobalt Contents %
			A-Temp. (Deg C)	B-Time (min)	
12	15	2	35.00	2.00	0.8
13	18	2	55.00	2.00	0.7
14	17	2	45.00	1.00	0.72
15	12	2	45.00	3.00	0.35
16	14	2	45.00	2.00	0.69
17	16	2	45.00	2.00	0.71
18	13	2	45.00	2.00	0.72

3.2 ANOVA Analysis for Response Surface Methodology

Results of augmenting at star points shown in Table 5 were input into the Design Expert software for model fitting. Analysis of these results follows automatically the RSM approach. Examination of this fit summary output revealed that the quadratic model is statistically significant for the percentage of cobalt removal. Hence, this model is used to represent the response for further analysis. An ANOVA table again is used to evaluate the significance of the proposed regression model, individual model coefficients and lack-of-fit test. Table 6 shows the ANOVA table for the response surface, quadratic model for cobalt removal. The value of “Prob> F” in Table 6 is for the model and all others model terms are significant. Among the five main effects, the etching time (B) is the most significant term based on the highest F-value. The ranking of model terms is as follows: $B>B^2>A>A^2>AB$. This indicates that etching time (B) has the greatest influence on the cobalt removal as compared to temperature (A) and the interaction effect (AB). In other word, a little change in etching time will affect drastically in cobalt removal rate. Though AB seems to be significant here, but interaction plot in Figure 2 proves otherwise. The parallel two curve plots indicate AB interaction term is not significant. The lack of fit is also not significant, which is desirable as we want a model that fits. The R^2 is high (0.99) closed to 1, which is also desirable. The difference between the Pred R^2 is in reasonable agreement with the Adj R^2. Adequate Precision that measures the signal to noise ratio is greater than 4 which is good. The following equations are the final empirical models in terms of coded and actual factors for the percentage of cobalt removal:

- Cobalt removal in terms of coded factors :

  $$Co = +0.68 - 0.054A - 0.19B + 0.067A^2 - 0.15B^2 + 0.028AB \quad (1)$$

- Cobalt removal in terms of actual factors :

  $$Co = +2.32662 - 0.071527Temp + 0.27380\,Time + 6.73632E\text{-}004Temp^2 - 0.14764Time^2 + 2.75000E\text{-}003Temp.Time \quad (2)$$

Table 6 ANOVA table for RSM (Cobalt Removal)

Source	Sum of squares	d.f.	Mean square	F	Prob.> F
Model	0.47	5	0.094	178.02	< 0.0001
A	0.029	1	0.029	55.14	< 0.0001
B	0.37	1	0.37	704.30	< 0.0001
A^2	0.013	1	0.013	24.81	0.0004
B^2	0.063	1	0.063	119.19	< 0.0001
AB	6.050E-003	1	6.050E-003	11.44	0.0061
Residual	5.818E-003	11	5.289E-004		
Lack of Fit	1.384E-003	3	4.614E-004	0.83	0.5125
Pure Error	4.433E-003	8	5.542E-004		
Cor Total	0.50	17			
Std. Dev.	0.023	R^2	0.9878		
Mean	0.63	Adj R^2	0.9822		
C.V.	3.66	Pred R^2	0.9668		
PRESS	0.016	Adeq Prec	35.012		

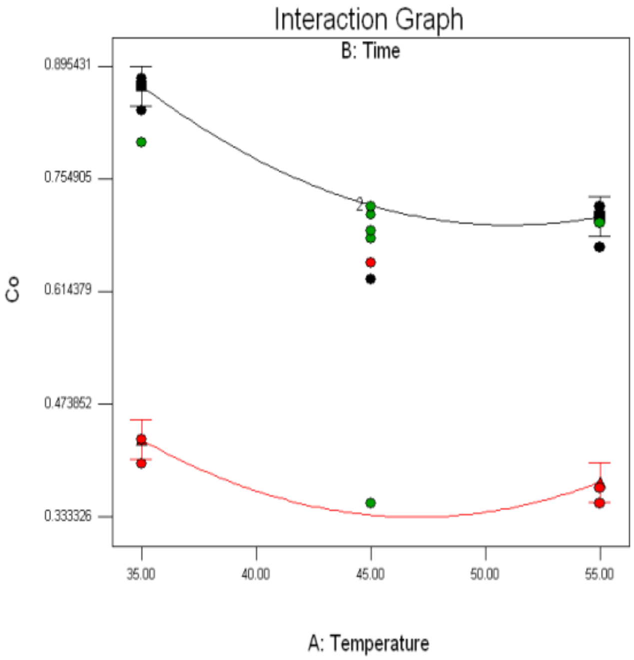
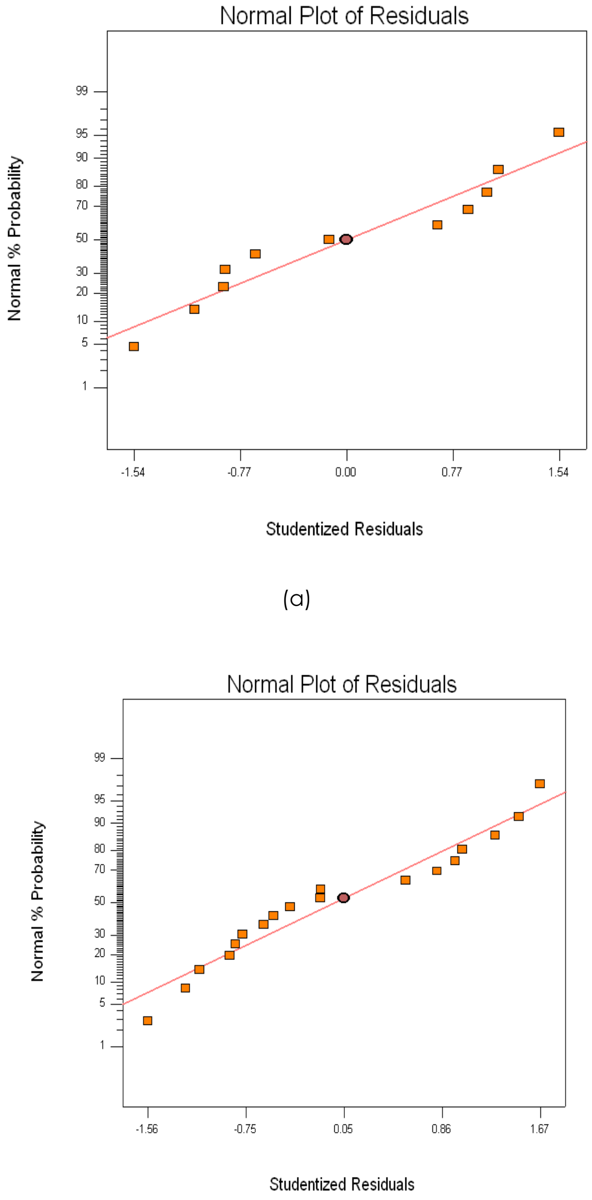


Figure 2 Interaction plot of AB term

3.3 Statistical Assumptions Validation

Two plots are used for checking the statistical assumptions in both experimental designs; 1) normal probability plot of residuals and 2) the plot of residuals versus predicted response. Figure 3a and 3b show the normal probability plots of residuals for cobalt removal under full factorial and RSM experimental designs respectively. In both cases, the plots exhibit no major deviations from the normal line. This implies that the errors are normally distributed. An extension to this, Figure 4a and 4b illustrate the plots of residuals versus the predicted response under full factorial and RSM designs respectively. As can be seen in both figures, there is no obvious increase in residuals as the predicted value increases. These suggest that the models proposed are adequate and there is no reason to suspect any violation of the independence or constant variance assumption.



(a)

(b)

Figure 3 Normal probability plot of residual for cobalt removal under (a) Full factorial design, (b) RSM

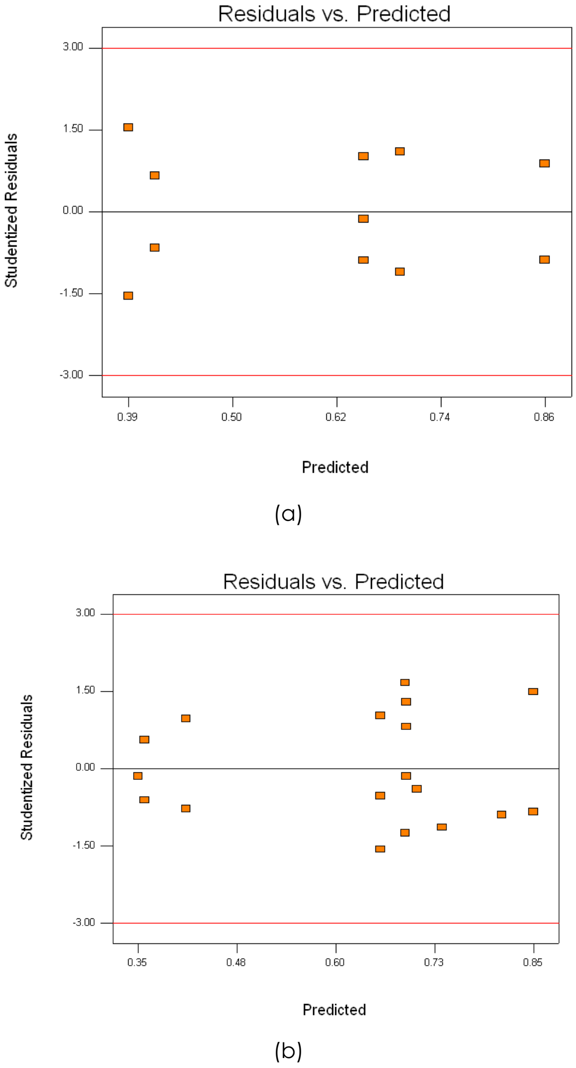


Figure 4 Plot of residual versus predicted response for cobalt removal under (a) Full factorial design, (b) RSM

3.4 Effect of Temperature and Time on Cobalt Removal

Figure 5 shows a 3D response surface and contour plot for cobalt content. The 3D response surface shows a curvature profile in accordance to the quadratic model fitted. It is clearly seen in these two figures, the cobalt content tends to decrease with increase the temperature in the region from 35^0 C to 50^0 C. After that the cobalt slightly increases again with the increasing of the temperature in the rest of the region. The cobalt content reaches minimum on the substrate surface when the etching time is at 3 minutes and the etching temperature is between 45^0 C and 50^0 C. This suggests that the temperature has less significant effect on cobalt removal as compared to the changes in etching time. A slight increase in etching time from 2.5 to 3 minutes at 45^0C, the cobalt reduces by 38%. While changing temperature from 45^0C to 50^0 C for 3 minutes etching, the cobalt only reduces by 1.2%. This finding is consistent with the earlier ANOVA analysis where temperature (A) and second order temperature are less significant compared to etching time (B) and second order etching time terms. Similarly, it also shows a weak relationship of temperature and time (AB) interaction.

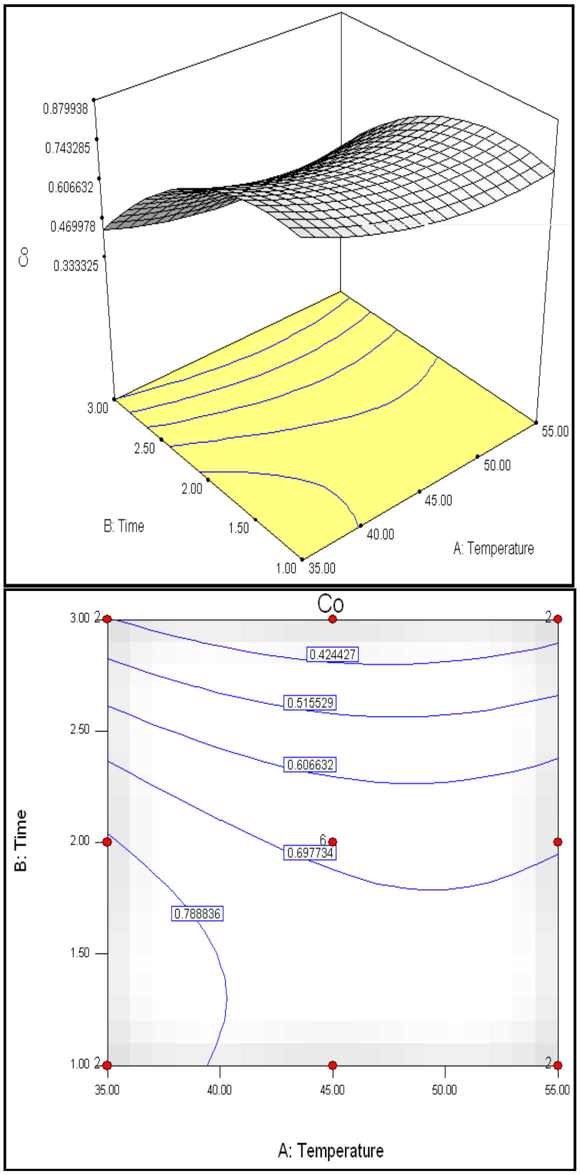


Figure 5 Surface and contour plot for cobalt content

3.5 Optimization Goal Setting Process

The optimization process can be done either by numerical or graphical. Graphical method can only be used when more than one response involved to perform overlay plot of the responses and thus irrelevant for this work. Table 7 shows the goal setting for optimizing the cobalt removal process based on numerical method. In order to maximize the productivity, time and temperature must be set as low as possible. The cobalt contents also must be set minimum within the possible range of less 1% to ensure good adherence of diamond coating on the substrate surface. Based on the goal setting, the software suggests five (5) possible optimal solutions as shown in Table 8.

Table 7 Optimum goals setting for cobalt removal

Item	Goal	Lower Limit	Upper Limit	Importance
Temperature	Minimize	35	55	3
Time	Minimize	1	3	3
Cobalt	Minimize	0.35	0.88	5

Table 8 Possible optimal etching parameters for removing cobalt contents on WC substrate

No.	Temperature	Time	Cobalt Content	Desirability
1	50.33	2.99	0.347164	1.000
2	50.81	2.99	0.347282	1.000
3	46.49	2.99	0.339588	1.000
4	45.74	2.97	0.349169	1.000
5	48.47	3.00	0.336608	1.000

3.6 Confirmation Run

Several confirmation runs need to perform in order to verify the adequacy of the model developed (equations 1 and 2). The Design Expert software suggests possible optimal parameters for the confirmation runs with the expected results as summarized in Table 8. However, these fractional values only serve as a guideline for running the confirmation runs. The nearest integer values for the temperature and time should be used instead of decimal points to make it more realistic. Table 9 shows the revised confirmation runs conditions together with the experimental results. Each condition was decided within the range of experimental trials and did not overlap with the existing design points. Point predicted capability of the software was used to predict the response (cobalt) within 95% predicted interval (PI). The residual and percentage error were calculated based on the difference between predicted and the actual percentage of cobalt contents left on the substrate surface. From the confirmation runs, the percentage errors of cobalt contents were less than 10 % and all the actual cobalt contents were still within 95% of PI. This indicates that the developed empirical model is reasonably accurate for the investigated response under this study.

Table 9 Confirmation tests results for cobalt removal

No.	Temp.	Time	Cobalt removal			
			Actual cobalt	Predict cobalt	Residual	Error (%)
1	40	3	0.41	0.37	0.04	9.76
2	50	1	0.73	0.70	0.03	4.11
3	48	3	0.31	0.33	-0.02	6.45
4	50	3	0.31	0.34	-0.03	9.68

4.0 CONCLUSIONS

Several conclusions can be drawn to describe the effect of pretreatment parameters, i.e. temperature and time, on the tungsten carbide surface. The main effect of etching temperature (A), time (B) and second order of time (B^2) are the most significant factors that influence the cobalt removal. The ranking of importance among the significant factors follows this order: $B>B^2>A>A^2$. The interaction between temperature and time (AB) is found insignificant to influence the cobalt removal. The confirmation runs prove that the optimum condition for achieving minimum cobalt content on the tungsten carbide substrate when it is etched at 48-50°C for 3 minutes. The empirical model developed is reasonably accurate for predicting the cobalt removal.

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