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RESEARCH ARTICLE - CHEMICAL ENGINEERING

Process Optimization of the Preparation of Vanadium Nitride from Vanadium Pentoxide

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Abstract Process optimization of vanadium nitride synthesis from vanadium pentoxide was attempted utilizing microwave carbothermal nitridation at atmospheric pressure using response surface methodology. The process variables that have significant influence on the quality of vanadium nitride such as the reaction temperature, reaction time and carbon addition ratio were investigated. The quadratic models were developed to evaluate the variables and optimize the process conditions, while the analysis of variance was utilized to identify the significant model parameters. The optimum conditions were identified to be a reaction temperature of 1400°C, reaction time of 240 min and carbon addition ratio of 0.29; the nitride and vanadium content in the vanadium nitride products was found to be 15.83 and 80.99 %, respectively. Experiments were repeated, and the results authenticated the optimized process conditions successfully.

Keywords Vanadium nitride · Microwave · Response surface methodology · Optimization

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1 Introduction

Vanadium nitrides are known for their quality of high thermal, mechanical, and chemical stability, which are being widely used in many fields especially in large quantities in steelmaking [1]. The wide application of vanadium nitride as an important steel- melting additive can be ascribed to two reasons: (1) the addition of vanadium nitride could improve the dispersion strengthening and grain refinement, thereby improving the strength, hardness, toughness, ductility, and thermal fatigue resistance of steels, (2) the addition of nitrogen in steel can reduce vanadium content of steel, which is an economical option for production of steel of same quality. Moreover, nitrogen can improve the phase distribution of vanadium in steel [2]. Therefore, it is desirable to have nitride content of the vanadium nitride higher than 10 wt%, while vanadium content in the range of 77–81 wt% based on the industry demand [3].

Nitride content is significantly influenced by the synthesis process and the process conditions. Different preparation methods of vanadium nitride are reported in the literatures. For example, Tripathy et al. [4] reported the nitridation as well as purity of vanadium nitride by using conventional carbonitrithermal nitridation with high-purity nitrogen for the preparation of vanadium nitride, and the product obtained had a nitrogen content of 20.98 wt%, while a nitriding time in excess of 3 h was needed. Yeh et al. [5] investigated the synthesis of vanadium nitride from vanadium powder compacts with gaseous nitrogen using self- propagating high-temperature synthesis, and the influences of the sample density, nitrogen pressure, diluent content and combustion temperature were studied as well. Advanced preparation methods including sol–gel [6], laser deposition [7] and microwave plasma technique [8] are applied to synthesis vanadium nitride power, but these methods generally

require expensive equipment, long preparation period and high production cost. Microwave carbonitrithermal nitridation was first attempted by Vaidhyanathan and Rao [9], who have reported shorter reaction duration; however, the reaction temperature was not measured accurately. Huang et al. [10] measured the surface temperature of the samples directly by an infrared pyrometer and have reported the effects of synthesis temperature, soaking time and initial concentration of carbon on the final nitrogen content. None of the above studies have reported optimized conditions for preparation of vanadium nitride with favorable vanadium and nitride content; hence, the present work attempts to optimize the process conditions using a process optimization tool response surface methodology (RSM) for synthesizing vanadium nitride by microwave-induced carbothermal reduction of vanadium pentoxide.

Response surface methodology (RSM) is considered to be a statistical and mathematical technique which is useful to develop, improve and optimize process. The main advantage of RSM is that it demands less number of experiments needed to assess the effect of multiple parameters and their interactions [6].

The focus of this research was to optimize the synthesis conditions of vanadium nitride with high nitride content and desirable vanadium content using RSM. A central composite design (CCD) was selected to design the experiments as well as to assess the effects of process variables such as the carbon addition, reaction time and reaction temperature on the nitride content and vanadium content. Empirical models correlating the responses to the process variables were developed and utilized for interpreting the data and optimizing the process conditions.

2 Experimental

2.1 Materials

Vanadium pentoxide (Dasgab Vanadium Co. Ltd, Sichuan, Industry grade, 98.15 wt%) was used as the starting material; carbon black (N220, Jinxiang Carbon Black Co.Ltd, China, Industry grade, 98.26 wt%) was used as reducing agent. Sinter atmosphere was created using flowing nitrogen gas (MESSER, Industry grade, Tianjin, 99.2 %). Polyvinyl alcohol was used as binder (Tianjin Rgent Chemicals Co. Ltd, Tianjin, AR, 97 %).

2.2 Equipment

The microwave furnace (Fig. 1), used for the present work, was designed and manufactured by MKW microwave applied technology Co. Ltd, Qingdao, China. It consists of a 2.45-GHz microwave generator with the ability to control the power output from 0–3 kW. The sinter cavity consists of an alumina tube ensuring a controlled atmosphere. The temperature of the samples was measured using thermocouple by touching the materials inside the furnace.

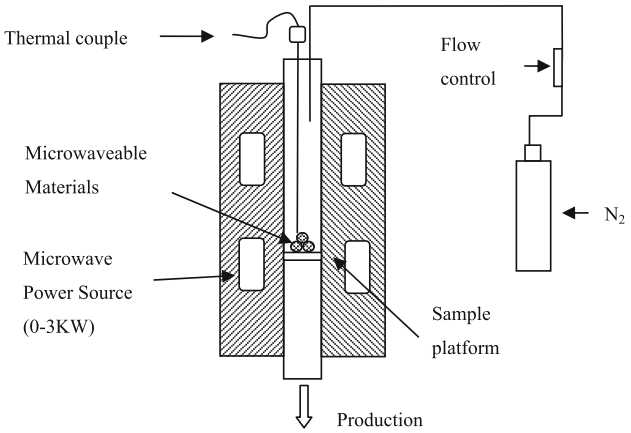


Fig. 1 Schematic diagram of shaft high-temperature microwave reactor

2.3 Procedure

Vanadium nitride samples were synthesized employing carbothermal reduction from V_2O_5 in nitrogen atmosphere, with a weight ratio of C/V_2O_5 varied in the range of 0.24–0.30. The mixture was blended with a binder (2 % polyvinyl alcohol in water) and pelletized into pellets of 24 mm diameter and 35 mm length under a dynamic load of 10 MPa. The degummed pellets were placed into the microwave reactor, with the flow of nitrogen at 50 L/h. The sample was heated to the desired temperature in the microwave reactor and retained in the reactor for the desirable amount of time. After sintering, the power was turned off and the sample was cooled down to 200 °C by continuing the nitrogen flow.

2.4 Sample Characterization

The nitrogen content was measured employing distillation–acid base titration analysis, while the vanadium content was measured employing acid base titration analysis [3]. X-ray diffraction (XRD) patterns were collected with a scintillation counter using Cu K_α radiation and recorded from 0° to 100° (2θ), with a step width of 0.4°.

2.5 Design of Experiment

The three independent variables studied were carbon addition (χ_1), reaction time (χ_2) and reaction temperature (χ_3). Table 1 lists the ranges and levels of three independent variables covered in the present work. The choice of range of these parameters was based on the preliminary experiments and literatures. A 2^3 full factorial CCD for the three vari-

Table 1 Independent variables and their levels used for central composite rotatable design

Independent variables	Code	Low actual	High actual	Low coded	High coded	Mean
Carbon addition	χ_1	0.25	0.29	−1.000	1.000	0.270
Reaction time (min)	χ_2	230	300	−1.000	1.000	265.000
Reaction temperature (°C)	χ_3	1300	1400	−1.000	1.000	1350.000

Table 2 Experimental design matrix and results

Std	Experimental variables			Yield	
	Carbon addition χ_1	Reaction time χ_2 (min)	Reaction temperature χ_3 (°C)	Nitride content Y_1 (wt%)	Vanadium content Y_2 (wt%)
1	0.25	230	1300	12.58	75.37
2	0.29	230	1300	11.62	77.46
3	0.25	300	1300	13.21	72.83
4	0.29	300	1300	12.82	84.07
5	0.25	230	1400	15.31	81.4
6	0.29	230	1400	14.78	78.82
7	0.25	300	1400	15.73	76.06
8	0.29	300	1400	15.39	84.3
9	0.24	265	1350	12.56	79.19
10	0.30	265	1350	12.01	83.08
11	0.27	206.14	1350	12.36	72.97
12	0.27	323.86	1350	13.94	76.32
13	0.27	265	1265.91	11.97	76.06
14	0.27	265	1434.09	16.63	83.78
15	0.27	265	1350	14.67	81.35
16	0.27	265	1350	14.65	81.5
17	0.27	265	1350	14.63	82.14
18	0.27	265	1350	14.68	81.45
19	0.27	265	1350	14.66	81.67
20	0.27	265	1350	14.59	79.99

ables, consisting of eight factorial points, six axial points and six replicates at the center points, was employed. The total number of experiments required was calculated based on the following equation [7],

$$N = 2^n + 2n + n_c \tag{1}$$

where N was the total number of experiment, n was the number of the factors and n_c was the number of repeat runs to estimate the experimental error. In total the number of experiments was estimated to be 20.

3 Result and Discussion

3.1 Development of Regression Model

A polynomial regression equation was developed using CCD relating the process parameters and the response variable. The nitride content was found to vary from 12 to 16.63 %, while the vanadium content was found to vary from 72.83 to 84.07 %. The appropriateness of the model equation representing the data and the significant model parameters were estimated using ANOVA. The complete design matrix together with the response values were detailed in Table 2. Experiment No. 15 ∼ 20 corresponded to repeat runs at the center point to determine the experimental error.

The final empirical models in terms of coded factors for nitride content (Y_1) and vanadium content (Y_2) are shown in Eqs. (2) and (3), respectively as,

$$Y_1 = 14.62 + 0.10\chi_1 + 0.39\chi_2 + 1.07\chi_3 + 0.36\chi_1\chi_2 + 0.38\chi_1\chi_3 - 0.37\chi_2\chi_3 - 0.73\chi_1^2 - 0.42\chi_2^2 - 0.05\chi_3^2 \tag{2}$$

$$Y_2 = 81.34 + 1.87\chi_1 + 0.72\chi_2 + 1.75\chi_3 + 2.50\chi_1\chi_2 - 0.96\chi_1\chi_3 - 0.49\chi_2\chi_3 + 6.480E - 003\chi_1^2 - 2.29\chi_2^2 - 0.42\chi_3^2 \tag{3}$$

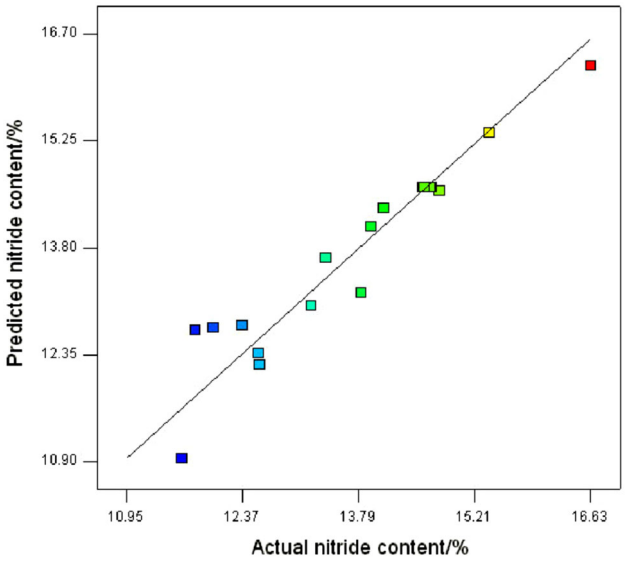


Fig. 2 Predicted versus experimental nitride content (wt%)

The quality of model developed was evaluated based on the correlation coefficient, R^2 and the standard deviation. The closer the R^2 value to unity and the smaller the standard deviation, the more accurate the response predicated by the model is. The R^2 value for Eqs. (2) and (3) was found to be 0.9152 and 0.9509 respectively. Figures 2 and 5 showed the ability of the model equation to predict the experimental result, which validated the appropriateness of model equation.

3.2 Nitride Content Analysis

Analysis of variance (ANOVA) was carried out to justify the adequacy of the model. The ANOVA for the quadratic model for nitride content is listed in Table 3. ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variances for the purpose of testing hypotheses on the model parameters. The ANOVA symbolizes the regression equation adequacy in relating the process variables and the response. The F value indicates the ratio of mean square of the model term to the mean square of the residuals, while the p value (Pro $>$ F) <0.05 indicated that the model terms were significant.

The validation of the model is an important procedure, since an inadequate model could lead to misleading results. The F-value of 11.98 and (Pro $>$ F) of 0.0003 implied that the model was statistically significant. Based on the p values (Pro $>$ F) listed in Table 3 for each of the model parameters, the insignificant parameters could be identified. The model parameters which had a p value in excess of 0.05 were considered to be statistically insignificant and identified to be χ_1, $\chi_1\chi_2$, $\chi_1\chi_3$, $\chi_2\chi_3$ and χ_3^2.

Figure 3 was a contour map, showing the effect of carbon addition and the reaction temperature at the mid-range of the reaction time. It could be observed that the nitride content increased with increase in the reaction temperature, while the carbon addition had an optimal value. Huang et al. [10] reported that the atoms of nitrogen, carbon and oxygen were all located in the same position of fcc lattice, and a low carbon addition may lead to residual oxygen in the product due to the shortage of carbon for reduction, while high carbon addition may lead to the formation of a vanadium–carbon solid solution in the residual carbon content. Figure 4 shows that the highest nitride content appeared at high reaction temperature of 1400 °C, indicating the increase in the nitride content with increase in the reaction temperature. However, the nitride content was found to reduce beyond an optimum reaction time, obvious at higher temperature in excess of 1400°C, which could possibly be attributed to two influences during the reaction. On one hand, the presence of trace amount of oxygen in the nitrogen utilized and longer reaction time would prolong the contact of vanadium nitride products with the oxygen, thus, the product would possibly be oxidized into vanadium oxide at longer reaction times [11]. On the other hand, during the carbothermal nitridation process at

Table 3 Analysis of variance (ANOVA) for response surface quadratic model for nitride content

Source	Sum of squares	Degree of freedom	Mean square	F value	Prob $>$ F
Model	30.61	9	3.40	11.98	0.0003
χ_1	0.014	1	0.014	0.51	0.4917
χ_2	2.13	1	2.13	7.49	0.0210
χ_3	15.54	1	15.54	54.78	<0.0001
$\chi_1\chi_2$	1.04	1	1.04	3.68	0.0841
$\chi_1\chi_3$	1.15	1	1.15	4.04	0.0721
$\chi_2\chi_3$	1.07	1	1.07	3.78	0.0805
χ_1^2	7.68	1	7.68	27.08	0.0004
χ_2^2	2.60	1	2.60	9.15	0.0128
χ_3^2	0.035	1	0.035	0.12	0.7311

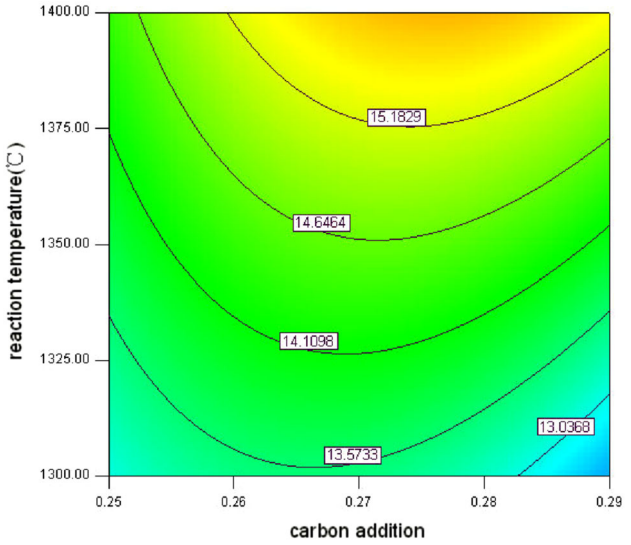


Fig. 3 Contour map of nitride content, effect of reaction temperature and carbon addition, at reaction time of 265 min

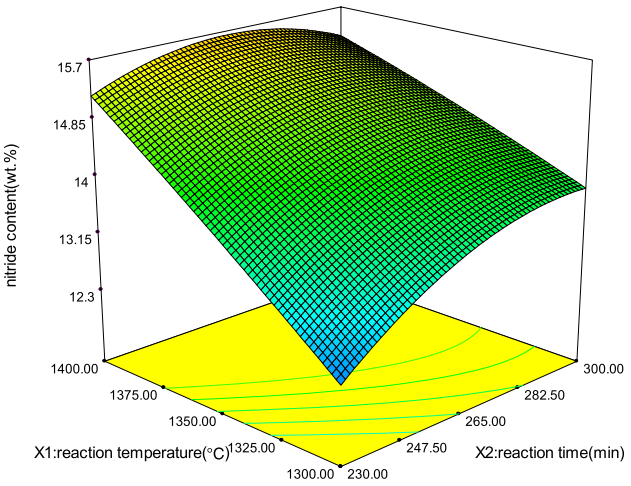


Fig. 4 Three-dimensional response surface plot of nitride content, effect of reaction temperature and reaction time, at carbon addition ratio of 0.27

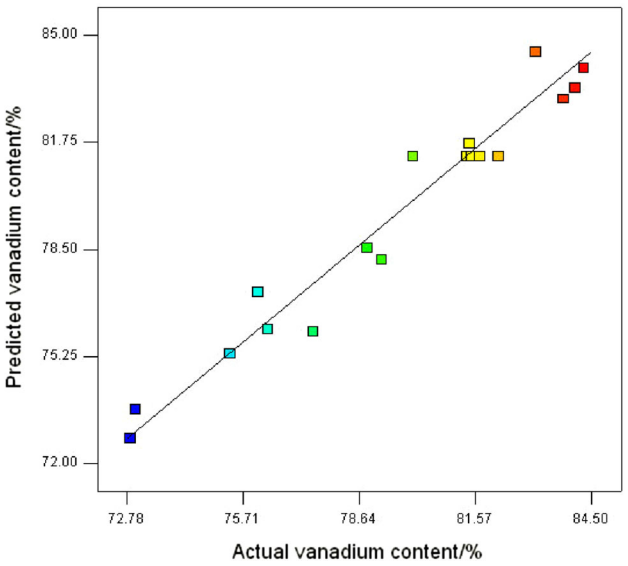


Fig. 5 Predicted versus experimental vanadium content (wt%)

Table 4 Analysis of variance (ANOVA) for response surface quadratic model for vanadium content

Source	Sum of squares	Degree of freedom	Mean square	F value	Prob > F
Model	232.49	9	25.83	21.51	<0.0001
χ_1	47.73	1	47.73	39.75	<0.0001
χ_2	7.10	1	7.10	5.91	0.0354
χ_3	71.59	1	41.59	34.64	0.0002
$\chi_1\chi_2$	49.85	1	49.85	41.52	<0.0001
$\chi_1\chi_3$	7.35	1	7.35	6.12	0.0328
$\chi_2\chi_3$	1.93	1	1.93	1.61	0.2335
χ_1^2	6.05E^{-004}	1	6.05E^{-004}	5.039E^{-004}	0.9825
χ_2^2	75.45	1	75.45	62.83	<0.0001
χ_3^2	2.58	1	2.58	2.15	0.1734

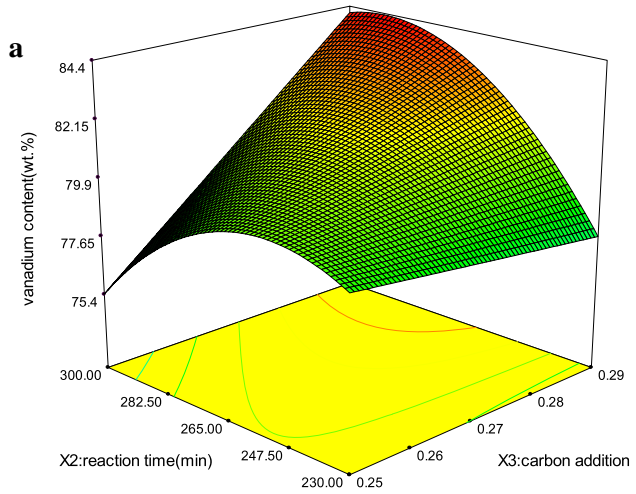
atmospheric pressure, vanadium carbide would first appear as intermediate product, which finally reacted with nitrogen to produce vanadium nitride. Higher reaction would favor the generation of vanadium carbide instead of vanadium nitride, which resulted in the decrease in nitrogen content [12].

The reaction temperature was found to be the most significant variable among the three variables to the response due to the smaller p value compared with the reaction time. The rate of de-oxygenation by carbon was expected to increase with the reaction temperature as the diffusion rate of carbon would be higher at high temperature. Similar observations on the change of nitride content at high reaction temperature were also reported by Ortega et al. [8] and Vaidhyanathan et al. [9].

3.3 Vanadium Content Analysis

The ANOVA for response surface quadratic model of vanadium content is presented in Table 4; the model F-value of 21.51 and a p value <0.0001 implied the appropriateness of the model and its statistical significance. Based on the parameter p values, the model terms χ_1, χ_2, χ_3, $\chi_1\chi_2$, $\chi_1\chi_3$ and χ_2^2 were found to be significant, while the terms $\chi_2\chi_3$, χ_1^2 and χ_3^2 were insignificant having negligible effect on the response variable.

Three-dimensional response surface plot of vanadium content with respect to the process variables is shown in Fig. 6a, b. The vanadium content was found to increase with increase in all three process variables, carbon addition, reaction time and reaction temperature. As compared to all three process variables, carbon addition seemed to be most significant evidenced from the sharp increase in the vana-



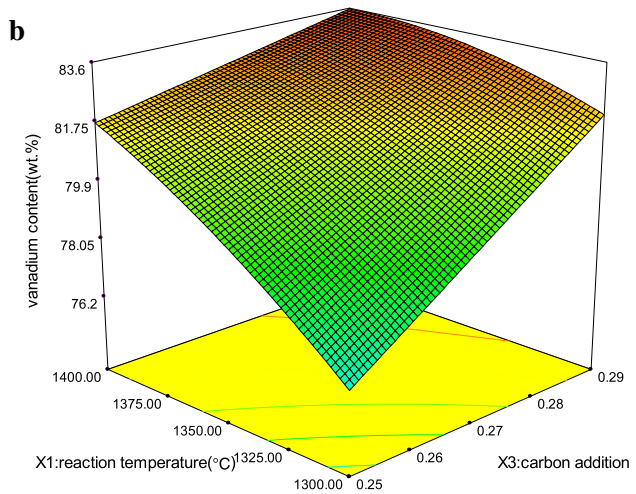


Fig. 6 Three-dimensional response surface plot of vanadium content. **a** Effect of reaction time and carbon addition at reaction temperature of 1350°C. **b** Effect of reaction temperature and carbon addition at reaction time of 265 min

dium content with increase in the carbon addition. The atoms of oxygen, nitrogen and carbon were located in the same position of face-centered cubic and the atom of vanadium combines with oxygen, nitrogen and carbon, respectively. As the carbon addition increased, the oxygen atoms were increasingly replaced by carbon atoms and the carbon atom was less than the oxygen atom (12–16); it contributed to the increase in vanadium content. The reaction temperature also had a significant effect on the response for the reasons as stated in the previous section.

3.4 Process Optimization

As seen from the analysis of the data, the process parameters affected the response variable differently, with certain parameters having an optimum value. Since the objective of the present work was to maximize the nitride content and

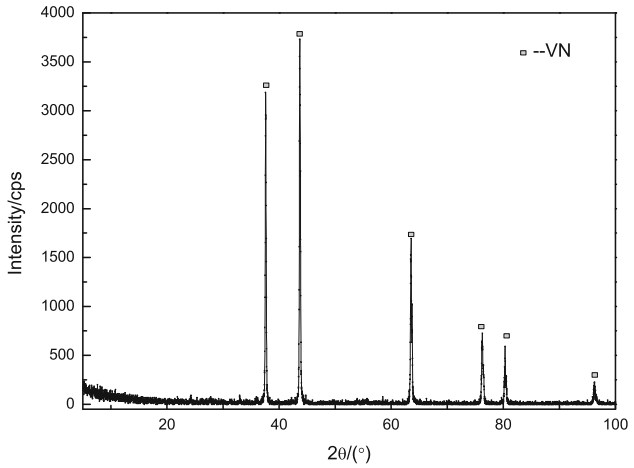


Fig. 7 XRD pattern of vanadium nitride

vanadium content within 77–81 wt%, the function of desirability was applied using Design Expert software version, 7.1.5 (STAT-EASE Inc., Minneapolis, USA). The optimum conditions of process variables were estimated to be a reaction temperature of 1400°C, reaction time of 240 min and carbon addition of 0.29. The nitride content and the vanadium content under the optimized conditions were estimated to be 15.83 and 80.99 %. In order to confirm the authenticity of the optimized condition estimated by the software, experiments were repeated under the optimized conditions, and the nitride content was found to be 16.1 %, while the vanadium content was 79.5 %, validating the optimization exercise.

3.5 Characterization of the Optimally Prepared Vanadium Nitride

Figure 7 shows the XRD pattern of vanadium nitride sample prepared under the optimum experimental conditions of reaction temperature: 1400°C, reaction time: 240 min and carbon addition: 0.29. The XRD patterns was obtained with a scintillation counter using Cu K_α radiation and recorded from 0° to 100° (2θ), with a step width of 0.4°. From the pattern, the synthesis product was found to possess excellent phases-purity.

4 Conclusion

1. A central composite design was conducted to study the effects of three vanadium nitride synthesis variables, which were the carbon addition, reaction time and reaction temperature, on the nitride content and vanadium content of the product. Quadratic models were developed to correlate the process variables with the two responses.

2. Through analysis of the response surfaces derived from the models, reaction temperature and reaction time were found to have significant effect on nitride content, while all the three variables were found to be significant for vanadium content.
3. Process optimization was performed using the Design Expert software and the optimized process conditions for maximizing the nitride content, and the optimal vanadium content was found to be a carbon addition of 0.29, reaction time of 240 min and reaction temperature of 1400°C, resulting a product with nitride content of 15.83 wt% and vanadium content of 80.99 wt%, the repeated experiments carried out confirmed the authenticity of the optimized conditions with products containing nitride of 16.1 wt% and vanadium of 79.5 wt%.
4. From the XRD pattern, the prepared vanadium nitride was found to possess excellent phase purity.

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