# Response Surface Methodology Applied to Optimize the Experimental Conditions for Preparing Synthetic Rutile by Microwave Irradiation

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## ABSTRACT

In this paper, response surface methodology (RSM) was implemented to optimize the experimental conditions for preparing synthetic rutile from high titanium slag by microwave irradiation. The effects of the preparation variables, such as temperature, microwave power, and time, on synthetic rutile content in the product were systematically investigated. The interaction between the dependent and independent variables were carried out in the central composite design (CCD) method, which was part of RSM. The experimental data obtained were fitted with a second-degree polynomial equation using nonlinear regression analysis. According to results from analysis of variance (ANOVA), also part of RSM, $R^2$ value of 0.9691 indicated that predicted values are in good agreement with experimental values. The optimization process is obtained by solving the nonlinear regression equation and analyzing the response surface and contours. The optimum preparation conditions are obtained: synthetic rutile content of 88.61%, temperature of 1209 K, microwave power of 2.5 kW and time of 48 min. The specific polymorphic phase transition and the microstructure of synthetic rutile under the optimum condition are analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively.

**Keywords:** Response surface methodology, Central composite design, Synthetic rutile, Microwave irradiation

## 1. INTRODUCTION

It is known that titanium dioxide exists in three main phases: rutile, anatase and brookite /1/. Anatase and brookite are metastable phases, and their exothermic and irreversible conversions to rutile at high temperatures have been widely studied. Rutile is the major raw material for the production of $TiO_2$ pigment or $TiCl_4$ from which titanium metal is produced by reduction /2, 3/. $TiO_2$ has a number of very important applications in pigment production, as well as in the paper, plastics, rubber, and textile industries. The demand for $TiO_2$ pigment is increasing rapidly; however, the supply of high grade natural rutile is limited /4, 5/. Thus, producing synthetic rutile from abundantly available high titanium slag becomes a major alternative. However, conventional heating to transform anatase into rutile causes many problems, such as high energy consumption, and pollution /6, 7/.

Recently, microwave energy has been widely used in several fields of applications on both research and industrial processes /8/. In particular, microwave heating arises from the direct interaction of matter with electromagnetic energy and thus it offers a number of potential advantages over conventional heating. The main advantage of using microwave heating is that the treatment time can be considerably reduced, which in many cases results in the reduction of energy consumption /9, 10/. Therefore, the big thermal gradient from the interior of the materials to its cooler surface allows the reaction to proceed more quickly and effectively at a lower bulk temperature, giving rise to energy savings and processing time shortening /11, 12/.

Design of experiment (DOE) is applied to optimize a complex process. Using the DOE technique, one may obtain the optimum conditions associated with a specified property by performing much fewer experiments than the traditional single-variable method /13, 14/. Recently, many statistical experimental design methods have been developed for process optimization. These methods involve using mathematical models for designing chemical processes and analyzing the process results. Among them, RSM stands out as a popular method utilized in many fields /15/. RSM is a combination of mathematical and statistical technique that is useful for analyzing the effects of several independent variables on the system response without the need of the predetermined relationship between the objective function and the variables /16, 17/. Of RSM approach, CCD, the most commonly used for designing experiments, is adopted as the first step; then, ANOVA is efficiently utilized for selecting the most significant factors among numerous factors that are to be further analyzed in a response surface model. This RSM procedure has been successful in optimizing various kinds of chemical products.

The focus of this research was to optimize the preparation conditions of synthetic rutile from high titanium slag with high synthetic rutile content by microwave irradiation. Temperature, microwave power, and time are the main three dominant factors selected as independent variables for experiments. Synthetic rutile content was selected as a dependent variable affected by these factors. A five-level was chosen to study simultaneously the effects of three independent variables on dependent variable. The polymorphic phase transition and the microstructure of synthetic rutile under the optimum condition were then compared with those of original high titanium slag.

## 2. EXPERIMENTAL

### 2.1 Materials

High titanium slag was prepared from ilmenite ore by carbothermal reduction in an electric arc furnace. The chemical composition of the high titanium slag was presented in **Table 1**. The slag contains 72.33% $TiO_2$, 17.79% $Ti_2O_3$, and 5.26% FeO. This slag was considered as high grade since it contains a relatively great amount of titanium. The slag also contains 1.04% MnO, 2.75% $Al_2O_3$, 2.30% MgO, 2.57% $SiO_2$ and minor elements such as S, P and C. The product was also analyzed for synthetic rutile content by the method in accordance with the recommended methods of National Standard of the People's Republic of China (GB/T).

**Table 1**

Chemical composition of high titanium slag (mass percentages)

| Species | $TiO_2$ | $Ti_2O_3$ | FeO | $Al_2O_3$ | $SiO_2$ | MnO | MgO | S | P | C |
|---|---|---|---|---|---|---|---|---|---|---|
| Mass % | 72.33 | 17.79 | 5.26 | 2.75 | 2.57 | 1.04 | 2.30 | 0.049 | 0.014 | 0.049 |

### 2.2 Instrumentation

SEM (XL30ESEM-TMP, Philips, Holland) was used to observe the microstructure morphology of the synthetic rutile obtained at different experimental conditions. Products were also analyzed by XRD (D/Max 2200, Rigaku, Japan) to detect the other coexisting mineral phase. XRD pattern was acquired using an X-ray diffractometer with CuKα radiation and a Ni filter operated at 35 kV, 20 mA and a scanning rate of 0.25 °/min.

The high titanium slag was treated using the self-made microwave heating equipment. Our microwave system consists of a magnetron, a power controller, a matched load, a wave guide, and a multi-mode cavity. Schematic diagram of the microwave heating equipment was shown in **Fig. 1** /18/. The microwave power supply for the microwave heating equipment consists of 2 magnetrons, which were cooled by water circulation, of 2.45 GHz frequency and 1.5 kW power; a ceramics tube, 50 mm (outer diameter) × 80 mm (inner diameter) × 600 mm (in length), was positioned at the center of the microwave stainless steel oven, by drilling holes on the side faces, with ends projecting on both sides; an attached infrared pyrometer (Marathon Series, Raytek, USA), which was used to monitor the temperature of the sample, has the circular crosswire focusing on the sample cross-section; a thermocouple (Shengyun Company, China) was also used to measure the temperature as a reference, thus when any temperature discrepancy arises, the latter was used as the correct temperature.

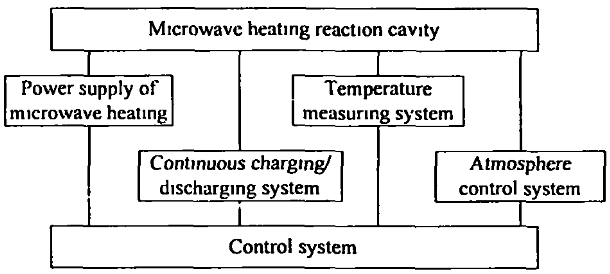


**Fig. 1:** Schematic diagram of the microwave heating equipment

## 2.3 Procedure

Prior to the use, high titanium slag was crushed and sieved to obtain particles of size less than 0.2 mm. Subsequently, high titanium slag was loaded on a ceramics boat which was placed inside a stainless steel tubular reactor, whose internal diameter is 38 mm. Then the samples were heated to 393 K at a heating rate of 278 K/min in the drying oven and held at this temperature for 120 min. After drying, the samples were cooled to room temperature. The total mass of sample taken was 100 g for each experimental run. The optimum experimental conditions for preparing synthetic rutile by microwave irradiation were determined using RSM. The desirable response is influenced by several independent variables and the objective is to optimize this response.

## 2.4 Experimental design

In this study, three operating factors, namely the temperature ($\chi_1$, K), microwave power ($\chi_2$, kW) and time ($\chi_3$, min) were chosen as independent variables, and dependent variable was the synthetic rutile content ($Y$). The range and levels of the variables investigated were listed in **Table 2**. Generally, a $2^n$ factorial runs with $2n$ axial runs and $n_c$ center runs (six replicates) for three independent variables (n=3) at two levels (low (-) and high (+)) was employed /19/. The total numbers of 20 experimental runs were performed, according to **Table 3**, to optimize the parameters, as calculated from Eq. (1) /20/.

$$N = 2^n + 2n + n_c = 2^3 + 2\times3 + 6 = 20 \quad (1)$$

**Table 2**

Variables and their corresponding levels in the experimental design

| Independent variables | Symbol | Coded variable levels | | | | |
|---|---|---|---|---|---|---|
| | | -1.682 | -1 | 0 | 1 | 1.682 |
| Temperature (K) | $\chi_1$ | 1020.73 | 1123.00 | 1273.00 | 1423.00 | 1525.27 |
| Microwave power (kW) | $\chi_2$ | 1.659 | 2 | 2.5 | 3 | 3.341 |
| Time (min) | $\chi_3$ | 6.36 | 20 | 40 | 60 | 73.64 |

**Table 3**

Central composite design matrix with three independent variables and results

| Run | Variables | | | Synthetic rutile Content, $Y$ |
|---|---|---|---|---|
| | Temperature $\chi_1$ (K) | Microwave Power $\chi_2$ (kW) | Time $\chi_3$ (min) | |
| 1 | 1123(-1) | 2(-1) | 20(-1) | 87.42 |
| 2 | 1423(+1) | 2(-1) | 20(-1) | 89.68 |
| 3 | 1123(-1) | 3(+1) | 20(-1) | 89.59 |
| 4 | 1423(+1) | 3(+1) | 20(-1) | 90.98 |
| 5 | 1123(-1) | 2(-1) | 60(+1) | 86.32 |
| 6 | 1423(+1) | 2(-1) | 60(+1) | 87.87 |
| 7 | 1123 (-1) | 3(+1) | 60(+1) | 86.52 |
| 8 | 1423(+1) | 3(+1) | 60(+1) | 89.42 |
| 9 | 1020.73(-1.682) | 2.5(0) | 40(0) | 86.23 |
| 10 | 1525.27(+1.682) | 2.5(0) | 40(0) | 90.56 |
| 11 | 1273(0) | 1.659(-1.682) | 40(0) | 87.72 |
| 12 | 1273 (0) | 3.341(+1.682) | 40(0) | 90.85 |
| 13 | 1273 (0) | 2.5(0) | 6.36(-1.682) | 90.68 |
| 14 | 1273 (0) | 2.5(0) | 73.64(+1.682) | 87.23 |
| 15 | 1273 (0) | 2.5(0) | 40(0) | 89.46 |
| 16 | 1273 (0) | 2.5(0) | 40(0) | 89.84 |
| 17 | 1273 (0) | 2.5(0) | 40(0) | 89.23 |
| 18 | 1273 (0) | 2.5(0) | 40(0) | 89.73 |
| 19 | 1273 (0) | 2.5(0) | 40(0) | 89.71 |
| 20 | 1273 (0) | 2.5(0) | 40(0) | 89.99 |

where $N$ is the total number of experimental runs and $n$ is the number of factors. For statistical calculations, the relation between the coded values and actual values are described in the following Eq. (2) /21/:

$$\chi_i = \frac{(A_i - A_0)}{\Delta A} \quad (2)$$

where $\chi_i$ is a coded value of the variable; $A_i$ is the actual value of variable; $A_0$ is the actual value of the $A_i$ at the center point; and $\Delta A$ is the step change of variable.

However, preparations of synthetic rutile by microwave irradiation were often considered to possess a nonlinear relationship between independent variables and dependent variables. Consequently, the general form of the second-degree polynomial is applied to fit the data into the equation by the nonlinear regression procedure. The model equation used for the analysis is given by Eq. (3) /22/.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i \chi_i + \sum_{i=1}^{k} \beta_{ii} \chi_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} \chi_i \chi_j \quad (3)$$

where $Y$ is the predicted response, $\beta_0$ is the constant coefficient, $\beta_i$ is the linear coefficient, $\beta_{ii}$ is the quadratic coefficients and $\beta_{ij}$ is the interaction coefficients, $k$ is the number of factors studied and optimized in the experiment, $\chi_i$, $\chi_j$ are the coded values of independent variables, and the terms $\chi_i \chi_j$ and $\chi_i^2$ represent the interaction and quadratic terms, respectively.

To carry out the RSM approach, 'Design Expert' software (version 7.1.5, STAT-EASE Inc., Minneapolis, USA) was used for regression and graphical analyses, from which the data was obtained. The maximum values of the synthetic rutile content were taken as the responses of the design experiment. Statistical analysis of the model was performed to carry out the ANOVA.

## 3. RESULTS AND DISCUSSION

### 3.1 Response surface analysis for the optimization of three factors

In order to search for the optimum conditions for the preparation of synthetic rutile, the optimized experimental independent variables and the corresponding synthetic rutile content are also shown in **Table 3**. CCD is used to calculate correlation between the synthetic rutile prepared variables and the synthetic rutile content. The synthetic rutile content is found to range from 86.23% to 90.98%. Runs 15–20 at the center point are used to determine the experimental error. According to the least squares method, the models are selected based on the highest order polynomials while the additional significant terms are also put into account and the models were not aliased. For the synthetic rutile content, the quadratic model is selected, as suggested by the software. The final empirical models in terms of coded factors after excluding the insignificant terms for the synthetic rutile content ($Y$) is shown in Eq. (4). Positive sign in the equation indicates synergistic effect, whereas negative sign indicates antagonistic effect.

$$Y = 89.72 + 1.13\chi_1 + 0.77\chi_2 - 0.98\chi_3 - 0.53\chi_1^2 - 0.21\chi_2^2 - 0.33\chi_3^2 + 0.06\chi_1\chi_2 + 0.10\chi_1\chi_3 - 0.22\chi_2\chi_3 \quad (4)$$

The results of the second-order response surface model fitting in the form of ANOVA are given in **Table 4**. The value of the determination coefficient ($R^2 = 0.9691$) indicates that the sample variation of 96.91% for synthetic rutile content is attributed to independent variables and only 3.09% of the total variations cannot be explained by the model. The value of the adjusted determination coefficient ($adj.R^2 = 0.9382$) is also very high to advocate for a high significance of the model. The statistical analysis of the coefficients of the model revealed that linear and quadratic terms are significant while the interaction coefficients were non-significant. It indicated that independent variables individually affected dependent variable.

The coefficient of variation (CV) indicates the degree of precision with which the experiments are compared. The lower reliability of the experiment is usually indicated with high value of CV. In the present case, a low CV (0.45%) indicated that the experiments performed are more precise and highly reliable. The "Lack of Fit F-value" of 0.1257 implies the lack of fit is not significant compared to the pure error, and the model fits well.

The adequacy of the models is further justified through ANOVA. The ANOVA of the quadratic model for synthetic rutile content is listed in **Table 5**. From the ANOVA of response surface quadratic model for synthetic rutile content, the Model F-value of 31.37 implied that the model is significant as well. The significance of each coefficient is determined by the p-value. The smaller the p-value ($p < 0.05$) is, the more significant the corresponding coefficient will be. In this case, $\chi_1$, $\chi_2$, $\chi_3$, $\chi_1^2$ and $\chi_3^2$ are significant model terms. From the statistical results obtained, it shows that the above models are adequate to predict the synthetic rutile content within the range of error.

**Figure 2** shows the predicted values versus the experimental values for synthetic rutile content. Actual values are the measured response data for a particular run, and the predicted values are evaluated from the model and generated by using the approximating functions. It could be seen that the predicted values obtained is quite close to the experimental values, and such a tendency of the linear regression fit does exist. The fitted regression equation showed the fitting is good.

**Table 4**

Analysis of variance (ANOVA) for the quadratic model

| Source of variation | Degrees of freedom | Sum of squares | Mean square | F-value | p-value |
|---|---|---|---|---|---|
| Mean | 9 | 44.1741 | 4.9082 | 25.57 | 0.000 |
| Linear | 3 | 38.4331 | 12.8110 | 66.73 | 0.000 |
| Square | 3 | 5.2546 | 1.7515 | 9.12 | 0.003 |
| Interaction | 3 | 0.4863 | 0.1621 | 0.84 | 0.500 |
| Residual Error | 9 | 1.41 | 0.16 | | |
| Lack-of-Fit | 5 | 1.15 | 0.23 | 3.47 | 0.1257 |
| Pure Error | 4 | 0.26 | 0.066 | | |
| Total | 19 | 46.09 | | | |

$R^2 = 0.9691$; $adj.R^2 = 0.9382$; CV =0.45%

**Table 5**

Model coefficients and significance of regression coefficient for synthetic rutile content

| Source | Coefficient | Standard error of coefficient | Degrees of freedom | Sum of squares | Mean squares | F-value | p-value |
|---|---|---|---|---|---|---|---|
| Model | 89.72 | 0.16 | 9 | 44.30 | 4.92 | 31.37 | 0.000 |
| $\chi_1$ | 1.13 | 0.11 | 1 | 17.33 | 17.33 | 110.47 | 0.000 |
| $\chi_2$ | 0.77 | 0.11 | 1 | 8.06 | 8.06 | 51.38 | 0.000 |
| $\chi_3$ | -0.98 | 0.11 | 1 | 13.04 | 13.04 | 83.10 | 0.000 |
| $\chi_1^2$ | -0.53 | 0.10 | 1 | 4.00 | 4.00 | 25.48 | 0.001 |
| $\chi_2^2$ | -0.21 | 0.10 | 1 | 0.65 | 0.65 | 4.13 | 0.103 |
| $\chi_3^2$ | -0.33 | 0.10 | 1 | 1.57 | 1.57 | 9.98 | 0.018 |
| $\chi_1\chi_2$ | 0.06 | 0.14 | 1 | 0.028 | 0.028 | 0.18 | 0.712 |
| $\chi_1\chi_3$ | 0.10 | 0.14 | 1 | 0.081 | 0.081 | 0.51 | 0.532 |
| $\chi_2\chi_3$ | -0.22 | 0.14 | 1 | 0. 38 | 0.38 | 2.41 | 0.191 |

**3.2 Interactions among the factors**

The interaction effects of independent variables and optimum levels of the variables are determined by the response surface curves and contours. The response surface curves and contours are represented in **Figs. 3-5.**

In **Fig. 3**, the response surface and contours show interaction between microwave power and temperature. The effects of microwave power and temperature are studied and found to have significant effects on the response. The time is fixed at zero level. It can be seen from **Fig. 3**, the shape of the contours show a positive interaction between the two variables. Synthetic rutile content increases with increasing microwave power and temperature. The highest synthetic rutile content value is obtained when both variables are at the maximum point within the range studied.

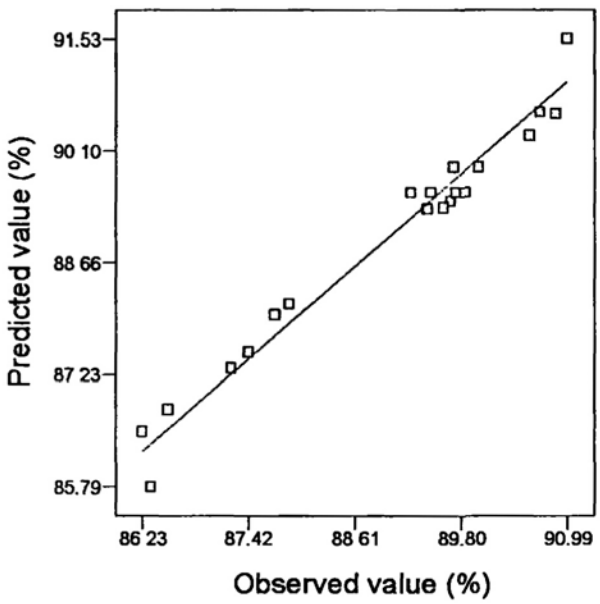


**Fig. 2:** Observed and predicted values of synthetic rutile content

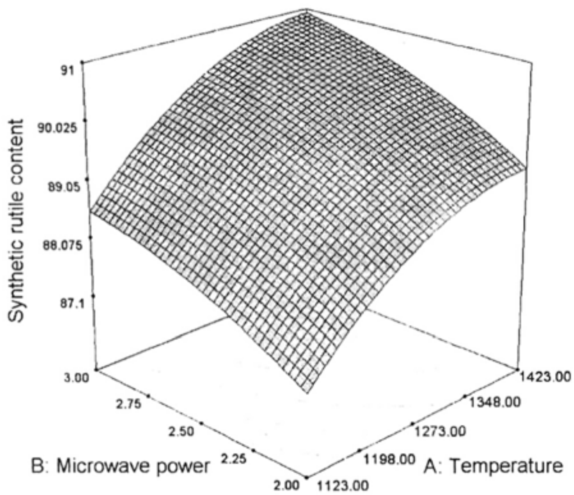


**Fig. 3:** Response surface and contours of microwave power vs. temperature on synthetic rutile content

The response surface curve for the interaction of time and temperature at zero level of microwave power is illustrated in **Fig. 4**. Only the low time and high temperature are beneficial for synthetic rutile content. **Figure 5** shows the effect of time and microwave power on synthetic rutile content at zero level of temperature. It can be seen that the highest synthetic rutile content can be obtained with minimum level of time but maximum level of microwave power. The response surface curves are plotted to demonstrate the interaction between independent variables and to determine the optimum level of each independent variable for maximum response.

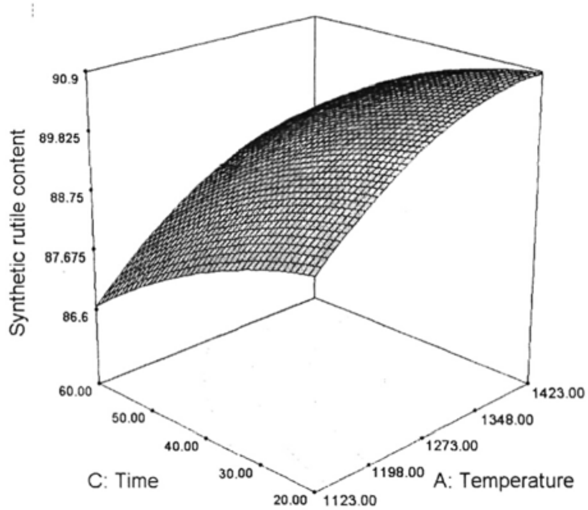


**Fig. 4:** Response surface and contours of time vs. temperature on synthetic rutile content

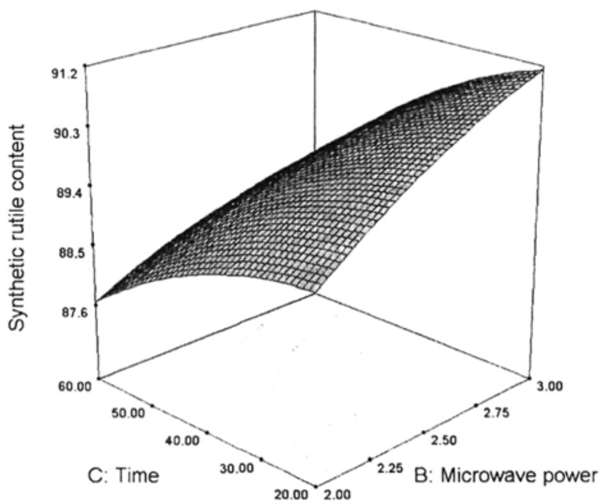


**Fig. 5:** Response surface and contours of time vs. microwave power on synthetic rutile content

### 3.3 Process optimization and characterization of synthetic rutile

The validation of the model is carried out under predicted conditions. Synthetic rutile is prepared under the experimental condition given in **Table 6**. The predicted synthetic rutile content is 88.61% while the experimental date was 87.95%. The optimum preparation conditions of synthetic rutile content are obtained in the condition of 1209 K temperature, 2.5 kW microwave power, and 48 min time. As a result, the model from response surface methodology is considered to be accurate and reliable for predicting synthetic rutile content.

**Table 6**
Validation of the model

| Temperature | Microwave Power | Time | Synthetic rutile content | |
|---|---|---|---|---|
| $\chi_1$ (K) | $\chi_2$ (kW) | $\chi_3$ (min) | Predicted | Experimental |
| 1209 | 2.5 | 48 | 88.61 | 87.95 |

In the present study, high titanium slag is characterized by XRD before and after the optimum preparation conditions. The results are shown in **Fig. 6** and **Fig. 7**. Through investigation, it can be seen from **Fig. 6** that anatase and iron titanium oxide are the main crystalline compounds in the high titanium slag; in addition, a minor amount of rutile is present. The iron titanium oxide has the strongest diffraction peak at $2\theta = 25.26^{\circ}$, which is close to the strongest diffraction peak of anatase at $2\theta = 25.30^{\circ}$, so the two peaks are overlapped. Synthetic rutile obtained under the optimum preparation conditions is characterized by XRD, which is shown in **Fig. 7**. It can be found from **Fig. 7** that the diffraction peaks of rutile gradually broadened and their intensities increased under microwave irradiation. The rutile has the strongest diffraction peak at $2\theta = 27.44^{\circ}$. All the X-ray diffraction peaks of sample matched well with those of the standard XRD pattern of rutile phase. It can be further inferred from **Fig. 7** that anatase is completely converted to synthetic rutile.

**Figures 8** and **9**, respectively, show the SEM images of high titanium slag and synthetic rutile obtained under the optimum preparation conditions. It can be seen from **Fig. 8**, some of the particles in the high titanium slag appeared well crystallized and their surfaces are smooth. **Figure 9** shows a synthetic rutile particle with a very complex trelliswork structure. During microwave irradiation, some pores will be opened up leading to an increase in the surface area. The brighter needle-like crystals are found to be titanium oxide minerals. However, there are numerous darker grains embedded in the structure.

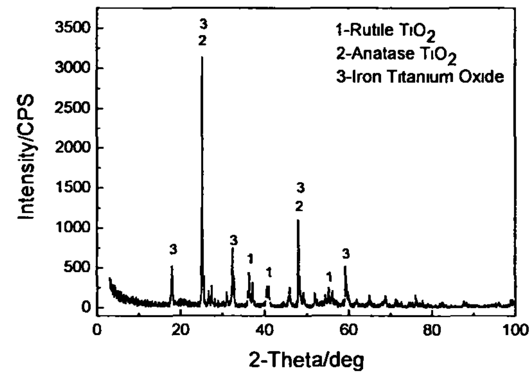


**Fig. 6:** XRD patterns of high titanium slag

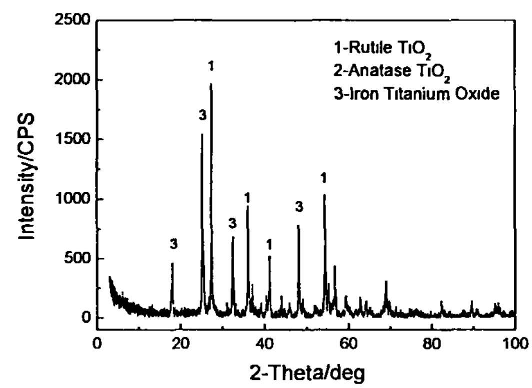


**Fig. 7:** XRD patterns of synthetic rutile prepared under the optimum preparation conditions

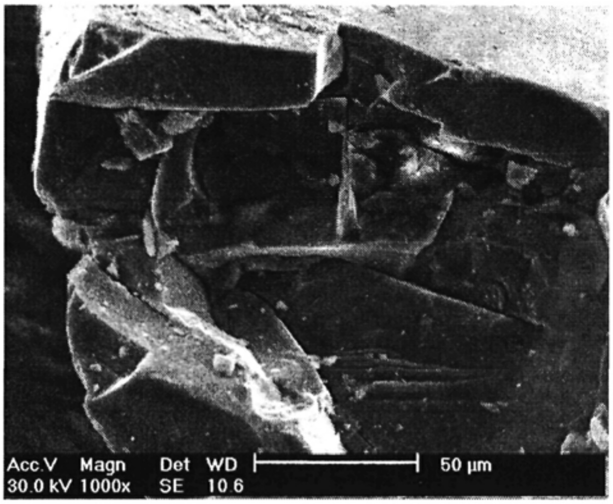


**Fig. 8:** SEM of high titanium slag

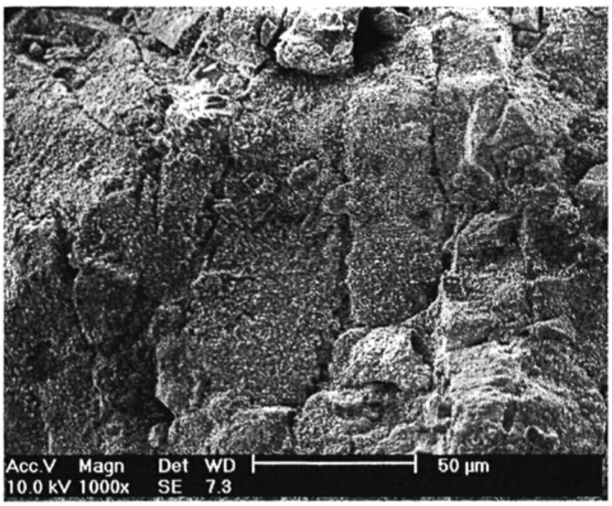


**Fig. 9:** SEM of synthetic rutile prepared under the optimum preparation conditions

## 4. CONCLUSIONS

Response surface methodology may be summarized as a collection of experimental strategies, mathematical methods and statistical inference for constructing and exploring an approximate functional relationship between a response variable and a set of independent variables. The effects of three synthetic rutile preparation conditions: temperature, microwave power and time, on the synthetic rutile content are studied by conducting a CCD and ANOVA. The second-degree polynomial equation is developed to fit the relationship between independent variables and dependent variable. The $R^2$ value is 0.9691, a relatively high value indicating that there is a good agreement between the experimental values and the predicted ones from the response surface models.

The optimum conditions for the preparation of synthetic rutile from high titanium slag by microwave irradiation is obtained with temperature of 1209 K, microwave power of 2.5 kW and time of 48 min. The optimum synthetic rutile content is 88.61% and the polymorphic phase transition of titanium dioxide from anatase to rutile also occurs under such optimum conditions. The experimental values are found to agree satisfactorily with the predicted values. These results implicate that the optimization using a response surface methodology based on the central composite design are effective and efficient with the estimation of the optimum conditions of the maximum synthetic rutile content.

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