Modelling of Carbothermal Reduction of TiO$_2$-Fe$_2$O$_3$ Composite with Compressed Natural Gas Using Design of Experiment

Nur Atiqqah Mohd. Moslim$^1$, Sivakumar Ramakrishnan$^{1*}$, Sheikh Abdul Rezan, Eltefat Ahmadi$^1$, Najwa Ibrahim$^1$, Norlia Baharun$^1$, M.N. Ahmad Fauzi$^1$, Abdul Rahman Mohamed$^2$

$^1$ School of Materials & Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, Nibong Tebal, Penang, Malaysia

$^2$ School of Chemical Engineering, Engineering Campus Universiti Sains Malaysia, Engineering Campus, Nibong Tebal, Penang, Malaysia

*Email: srsivakumar@usm.my

Abstract. An alternative way to process titanium minerals was investigated via carbothermal reduction/nitridation (CTR/N) by yielding titanium oxycarbonitride (TiO$_x$C$_y$N$_z$). Synthetic anatase (TiO$_2$) and hematite (Fe$_2$O$_3$) were mixed together with graphite/CNT mixture to study the reduction kinetics. The reduction process was carried out at 1150 – 1250 °C for 1 to 4 hours in a gas mixture of hydrogen, nitrogen and compressed natural gas. The carbon to reducible oxygen molar ratio (C:O$_{red}$) was varied in this experiment from 0.5 to 1.0. The extents of reduction and nitridation with the amount of free carbon deposited were studied using $2^3$ factorial design to define the optimum parameters in producing TiO$_x$C$_y$N$_z$. From Design Of Experiment (DOE) analysis, the most influential factor contributing to the extent of reduction was reduction time, followed by carbon to reducible oxygen molar ratio and reduction temperature subsequently. The highest extent of reduction was 92.68% which was obtained at 1150 °C for 4 hours using sample with C:O$_{red}$ of 1.

1. Introduction

Titania or titanium dioxide (TiO$_2$) exists in a number of crystalline forms; the most important of which are anatase, rutile and brookite. In this study, anatase, TiO$_2$ being used together with hematite, Fe$_2$O$_3$ to form TiO$_2$-Fe$_2$O$_3$ composite or synthetic ilmenite. The composite was reduced in reducing atmosphere to obtain titanium oxycarbonitride (TiO$_x$C$_y$N$_z$) which contains the phase of titanium oxide (TiO), titanium nitride (TiN), titanium carbide (TiC) and solid iron (Fe). At the very end of the carbothermal reduction of the TiO$_2$-Fe$_2$O$_3$ composite, high density of titanium oxycarbonitride (TiO$_x$C$_y$N$_z$) would be expected to be formed. Chlorination process is being carried out to form metal chlorides after carbothermal reduction. The decomposition of natural gas used in the experiment provides H$_2$ and CO gases for the reduction process (Lobo et al., 2013). One of the factors that would influence the reduction kinetics of TiO$_2$-Fe$_2$O$_3$ composite would be the presence of carbon source either in the form of coal, graphite or carbon nanotube. Design of Experiment (DOE) was used in this
study by incorporating $2^3$ factorial designed experiment including three center points. A kinetic model for cylindrical pellet sample was created using MATLAB software with respect to the physical and thermodynamic properties of the product and reactant. The reaction is expected to show the effects of the reduction time, reduction temperature and also the C:O$_{\text{red}}$ molar ratio contributed throughout the process.

2. **Experimental study**

Sample was prepared via wet mixing, sonication, drying, grinding and pellet pressing. The reduction process was carried out in H$_2$-N$_2$ and compressed natural gas (CNG) atmospheres. H$_2$ and N$_2$ gases both occupied the volume of 50% each and allowed to flow from the start to the end of experiment with total flow rate of 1.5 L/min. For CNG, it was purged at reduction temperature for 45 minutes. The flow rate for CNG was 0.15 L/min and occupied 10% of gas volume. Both heating and cooling rates for the furnace were adjusted at 10°C/min. Figure 1 shows the experimental setup of reduction process. This setup is the same for oxidation process except for the absence of CNG, H$_2$ and N$_2$ gas inlet because the process was being carried out in air only. The reduction process was carried out at 1150°C and 1250°C for 1 to 4 hours by using the samples with C:O$_{\text{red}}$ of 1:1, 0.75:1 and 0.5:1 while the oxidation process was carried out in open-end tube furnace at 850°C for 6 hours.

![Figure 1. Schematic diagram of reduction process](image)

3. **Result and discussion**

3.1 **Chemical reactions and equilibria**

The reactions occurred during the reduction process were studied using Outkompu HSC Chemistry software v6.00. The simulation and modelling of the chemical reactions used to predict the reactions that occurred at a certain temperature and gas atmosphere. Titanium oxycarbonitride (TiO$_x$C$_y$N$_z$) phase existed as a metastable solid solution phase between its boundary counter parts titanium carbide (TiC) and titanium nitride (TiN) [1]. For this reason, only TiC and TiN will take part in the reaction equilibrium of the reduction process. From the overall chemical reaction, natural gas which mainly composed of methane (CH$_4$) was assumed to be converted into hydrogen and carbon monoxide (CO). Study done by Wullenkord (2010) [6] proved that this argument is valid.

$$2\text{TiO}_2 + \text{N}_2(g) + 4\text{CH}_4(g) = 2\text{TiN} + 4\text{CO}(g) + 8\text{H}_2(g) \quad (\Delta G^\circ = -23.763 \text{ kcal/mole at } 1000^\circ\text{C}), \quad (1)$$

$$\text{Fe}_2\text{O}_3 + 3\text{H}_2(g) = 2\text{Fe} + 3\text{H}_2\text{O}(g) \quad (\Delta G^\circ = -1.957 \text{kcal/mole at } 600^\circ\text{C}), \quad (2)$$
The simulation proved that the above mentioned reaction occurs below 1000°C (1273 K) and thus agreeing to the actual reaction equation.

3.2 Statistical design of experiment (doe) analysis

Statistical design was performed to find the most and the least effective parameter in the carbothermal reduction of TiO$_2$-Fe$_2$O$_3$ composite powder. The experimental responses were fitted to a factorial model using Design-Expert v8.0.6.1. ANOVA (Analysis of Variance) was also performed to determine the best reduction condition, thus several types of graphs were analyzed. The experimental parameters are shown in Table 1 while the standard deviation and values of R-squared obtained from the responses and ANOVA are given in Table 2. From the value of R-squared in Table 2, it can be concluded that the experimental results are generally agree with the statistical model when the model have high R-squared value with 1 being the highest value.

**Table 1. Variable parameter used in Design of Experiment.**

| Variable parameter | Unit | Details |
|--------------------|------|---------|
| A                  | Reduction time | Hours | 1, 5 |
| B                  | Reduction temperature | °C | 1150, 1250 |
| C                  | C:O$_{\text{red}}$ molar ratio | - | 0.5, 1.0 |

**Table 2. Standard deviation and R-squared responses from the reduction process.**

| Response                | Standard Deviation | R-Squared |
|-------------------------|--------------------|-----------|
| Extent of reduction, $X_O$ | 3.87               | 0.9520    |
| Extent of nitridation, $X_N$ | 5.36               | 0.8060    |
| Carbon deposited, $C_{\text{deposited}}$ | 21.75               | 0.8310    |

The relationship between the responses and each of the parameters can be determined using Equations 1, 2 and 3. Negative values in the equation states that the single or a combination of parameters did not contribute much to increase the extent of reduction, extent of nitridation and carbon deposited. For example, the negative values of $-5.73 C$ and $-1.11 AC$ in Equation 3 indicated that factor $C$ and a combination of factor $A$ and $C$ did not have significant effect on the carbon deposited response.

\[
\text{Extent of reduction, } X_O = 74.54 + 7.97A - 1.52B + 4.73C - 4.05AB + 1.07AC + 2.30BC + 0.074ABC \quad (1) 
\]

\[
\text{Extent of nitridation, } X_N = 43.03 + 2.78A + 2.04B + 3.03C - 3.95AB + 0.70AC - 2.67BC + 0.59ABC \quad (2) 
\]

\[
\text{Carbon deposited} = 45.49 + 22.21A + 8.84B - 5.73C + 16.28AB - 1.11AC - 1.50BC - 0.075ABC \quad (3) 
\]

Where $A$ is reduction time, $B$ is reduction temperature and $C$ is C:O$_{\text{red}}$ molar ratio. From Equations 1, 2 and 3 can be observed that the interactions among the three factors can be significant and greater or less than expected from each factor separately [5]. This situation can also be used to explain the influencing factors for carbon deposited where higher carbon to reducible oxygen molar ratio should result in higher amount of carbon deposited.
3.3 Effect of reduction temperature and time

Table 3 presents the data for extent of reduction at different reduction times. The results show that the extent of reduction of the samples with 1:1 C:O_red increased with reduction time for both temperatures. Extent of reduction was the highest (92.68%) when the reduction process was carried out at 1150°C for 4 hours compared to the other samples reduced in other conditions. At higher temperatures, more carbon was produced from the thermal cracking of the methane gas from CNG which causes high amount of carbon deposition on the surface of the pellets. The excessive amount of carbon deposited would then hinder the reduction process [3].

Table 3. Data for extent of reduction, X_O of TiO_2-Fe_2O_3 composite with 1:1 molar ratio of reducible oxygen.

| Temperature, °C | 1150 | 1250 |
|----------------|------|------|
| Reduction time, h | 1 | 4 | 1 | 4 |
| Extent of reduction, % | 85.84 | 92.68 | 69.94 | 86.29 |

Longer reduction times allow more reduction of the sample to occur until the reaction completed at some extent. It enables higher amount of hydrogen and carbon to be formed when the reduction time is increased. As carbon forms, reduction extent also increases. The newly formed carbon will aid in the reduction process by acting as reductant [2].

3.4 Effect of carbon to reducible oxygen molar ratio

The effect of carbon to reducible oxygen molar ratio on TiO_2-Fe_2O_3 reduction at 1150°C was carried out in 1 to 4 hours. CNG was purged during the reduction (soaking) time for 45 minutes. Carbon nanotube (CNT) was used as carbon source that function as reductant in the reduction process. Lower extent of reduction obtained when performing the reduction without carbon source. This argument proves to valid from the study by Yin et al. (2016) [7]. From Table 4, it can be seen that higher extent of reduction obtained when using sample of 1:1 carbon to reducible oxygen molar ratio. By adding reductant in the sample, the reduction process can occur faster and more efficiently.

Table 4. Data for extent of reduction with different C:O_red molar ratio at 1150 °C.

| C:O_red molar ratio | 0.5:1 | 1:1 |
|---------------------|------|-----|
| Reduction time, h   | 1 | 4 | 1 | 4 |
| Extent of reduction, X_O | 63.78 | 66.64 | 85.84 | 92.68 |

3.5 Phase development in reduction of TiO_2-Fe_2O_3 composite in H_2-N_2-CNG atmosphere

Phase detected by XRD analysis indicates that titanium oxycarbonitride (TiOCN) formed at the end was in solid solution. Figure 2 shows the differences between the XRD patterns of raw material and samples that was reduced at different temperatures. The ICDD number for TiN and solid Fe in the reduced sample are 98-008-9933 and 98-008-7922 respectively. The figure clearly shows a higher amount of solid iron (Fe) was produced. Iron (III) oxide have lower reduction temperature in the range of 220-680°C [4] (Pineau et al., 2006). This temperature is much lower than the reduction temperature of titanium dioxide which is the reason why titanium dioxide did not convert into titanium metal even when reduced at 1250°C. The effects of carbon to oxygen reducible molar ratio on the extent of reduction are presented in Figure 3. From the XRD result, high amount of titanium nitride was formed when reduction of sample with C:O_red of 1:1 was executed at high temperature. Reduction increases
when temperature was increased. After 1 hour, TiN peak was more affirm at reduction temperature of 1250°C compared to 1150°C.

Figure 2. XRD patterns of raw material and reduced samples with 1:1 carbon to reducible oxygen molar ratio for 1 hours in H2-N2-CNG atmosphere at different temperature.

Figure 3. XRD patterns of raw material and reduced samples at 1150°C for 1 hour in H2-N2-CNG atmosphere with different molar ratio.

Figure 4. XRD patterns of raw material and reduced sample with 1:1 carbon to reducible oxygen molar ratio at 1150°C in H2-N2-CNG atmosphere for different duration.

The effects of carbon to reducible oxygen molar ratio shown in Figure 4. Almost like the effect of temperature, larger ratio of carbon results in higher extent of reduction. At 1150°C, TiN peaks shows an increment in the intensity. The presence of active carbon enhanced the reaction kinetics in the sample. This led to high formation of TiN in the compound. Initially, titanium dioxide and hematite formed ilmenite-hematite solution from mixing process. When reduced at high temperature, TiO2 and Fe2O3 convert into another stable phase which is titanium nitride and solid iron.
Figure 4 shows the XRD pattern of raw material, 1 hour reduced sample and 4 hours reduced sample. This pattern however indicates differences in the amount of phases occur when reduced at 1 hour and 4 hours. High amount of TiN formed when reduced for 4 hours compared to the sample that reduced for 1 hour. Longer duration has provided more opportunity for the sample to be reduced at high temperature.

4. Conclusion

In this paper, three parameters were arranged using Design of Experiment. With respect to the response of extent of reduction, reduction time behaves as the most influential factors compared to reduction temperature and carbon to reducible oxygen molar ratio. The highest extent of reduction of 92.68% was obtained at 1150°C with 4 hours reduction time and carbon to reducible oxygen molar ratio of 1:1. It can be concluded that the extent of reduction was increasing with reduction time, carbon to reducible molar ratio and reduction temperature.

Acknowledgement

The authors gratefully acknowledge the financial support from Universiti Sains Malaysia (USM) Fellowship, APEX (1002/JHEA/ATSG4001). This work was also financially supported by USM and Ministry of Higher Education (MOHE) of Malaysia through the following research grants: Fundamental Research Grant Scheme (FRGS) (No. 203/PBAHAN/6071364) and (203/PBAHAN/6071261) from MOHE, USM Research University Individual (RUI) grant (No. 1001/PBAHAN/814273) and Nippon Sheet Glass Research Grant (NSGRG) (No. 304/PBAHAN/650360/N120). Special thanks to USM technicians Mr. Shahrul and Mr. Syafiq for supporting the experimental work.

References

[1] Ramakrishan S, Kwok T C, and Hamid S A R S A 2016 AIP Conference Proceedings 175 6050001
[2] Ibrahim N S C, Ramakrishnan S, Baharun N, Hamid S A R S A, Alizadeh R, and Roohi P 2015 Materials Science Forum 819 6
[3] Zhang G and Ostrovski O 2000 Metallurgical and Materials Transactions B 31129
[4] Pineau A, Kanari A and Gaballah I 2006 Thermochimica Acta 447 89
[5] Telford J K 2007 Johns Hopkins Apl Technical Digest 27 224
[6] Wullenkord M, Funken K H, Sattler C, and Pitz-Paal R 2010 18th World Hydrogen Energy Conference 3 201
[7] Yin T W, Ramakrishnan S, Hamid S A R S A, Noor A F M, and Shoparwe N I 2016 Journal of Physics: Conference Series 822 012063