Chlorination of Iron-Containing Nitrided Ilmenite Prepared by Carbothermal Process with Polystyrene and Coal

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Abstract. This work sheds light on the effect of carbothermal reduction and nitridation of ilmenite concentrate with the mixtures of Mukah coal and polystyrene as reducing agents under H₂/N₂ gas atmosphere on the chlorination process. Pre-reduced samples of ilmenite were chlorinated at 400-500°C for 1-3 hours without removing metallic iron. The characterization of the synthesized materials was made by X-ray diffraction (XRD), scanning electron microscopy (SEM), and inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses. Design of Experiment (DOE) analysis was also applied to evaluate the significant factors and their interactions in low-temperature chlorination process. Statistical analysis indicated that Mukah-Balingian coal-to-polystyrene (C/PS) ratio was the most significant factor influencing the chlorination results. In addition, the highest extent of chlorination ~ 95.01% was achieved with the highest carburized and nitrided samples at 500 °C for 1 hour. The present study can be useful for the chlorination of different types of pre-reduced ilmenite concentrates with high efficiency of titanium tetrachloride production.

1. Introduction

Ilmenite (FeTiO₃) composed of iron (Fe) and titanium oxide (TiO₂) is an important world reserve (~ 90%) for production of TiO₂ pigment and titanium metal [1, 2]. A number of procedures have been developed for upgrading titanium metal from FeTiO₃ and Ti ores [2-4]. Commercialized processes for upgrading ilmenite to synthetic rutile and separation of iron include but not limited to: (a) pyrometallurgical method in which a mixture of ilmenite concentrate and anthracite as reductant is charged into an electric arc furnace (EAF) to produce a slag containing about 86 %TiO₂ and pig iron. The slag is processed further for removing iron by acid leaching process using 18–20 % HCl solution at 125 °C for production of high-grade TiO₂ feedstock (~ 95 %TiO₂) by upgraded slag (UGS) process, and (b) Becher process that applies both pyro-, and hydrometallurgical routes for oxidation/reduction followed by the aeration acid leaching method using a solution containing ammonium chloride (NH₄Cl) ions as a catalyst to accelerate the metallic iron removal, respectively[2, 3, 5-8].

The study of extracting titanium metal from ilmenites of different grades and selective chlorination process of unreduced and/or reduced and nitrided ilmenite concentrates for developing a low-cost Ti metal technology has been a constant challenge for last decade due to a complex mineralogical composition of ilmenite ores[1, 3, 5, 6, 8-10]. Previously, high-grade TiO₂ feedstocks were chlorinated at high temperatures of about 900-1100 °C to produce titanium tetrachloride (TiCl₄) in which majority
of the impurities such as iron and other undesired metal oxides in feedstock were converted to metal chlorides [5]. However, the present study focused on the low-temperature chlorination of a mixture of Fe and titanium oxycarbonitride (TiO$_x$C$_y$N$_z$) synthesized by carbothermal reduction and nitridation (CTRN) process. In this work, Malaysian ilmenite concentrate was reduced and nitrided by using a mixture of Muka coal and polystyrene (PS) as an alternative reductant. The feasibility of the chlorination process of different mixtures of TiO$_x$C$_y$N$_z$ and metallic iron synthesized by CTRN process was investigated in production of TiCl$_4$ at low temperatures.

2. Experimental study

The raw Malaysian ilmenite concentrate was supported from Chee Ng Minerals Sdn. Bhd. located in Kampar, Perak. It was composed of Ilmenite, FeTiO$_3$ (ICSD# 98-001-7094), Iron oxide, Fe$_2$O$_3$ (ICSD# 98-009-8279) and small amounts of Protonstatite, Mg$_2$SiO$_4$ (ICSD# 98-001-2489). The ilmenite samples were mixed with 85% Mukah Coal + 15% Polystyrene (C85P15), 75% Mukah Coal + 25% Polystyrene (C75P25) and 65% Mukah Coal + 35% Polystyrene (C65P35) as reductants. In this work, titanium oxycarbonitride (TiO$_x$C$_y$N$_z$) and iron (Fe) mixtures with mean particle size of about 150 μm were synthesized by CTRN process from Malaysian ilmenite at 1250 °C under an H$_2$-N$_2$ atmosphere for 3 hours. The reduced and nitrided samples were uniaxially pressed under a pressure of 100 kPa into cylindrical pellets weighing about 2.0g. Pellets with different compositions were chlorinated under flowing nitrogen as carrier gas with a constant flow rate of about 20 ml/min at temperatures in the range of 400 to 500 °C for 1, 2 and 3 hours. The Cl$_2$ gas for this study was generated by the reaction between potassium permanganate (KMnO$_4$) and hydrochloric acid (HCl) by adding 0.5 g aluminium powder as catalyst to enhance the chlorine gas generation. The moist Cl$_2$ gas was also passed through concentrated sulfuric acid (1.0 M), and phosphorus pentoxide (P$_2$O$_5$) powder to remove moisture prior to the chlorination process. The produced TiCl$_4$ was captured by 37.0% hydrochloric acid, HCl Sigma-Aldrich (CAS# 7647-01-0) in the gas scrubbers and the liquid samples taken from the scrubbers were analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Perkin Elmer Optima 4300 DV ICP System). Phase characteristics of the unchlorinated and the residues obtained from the chlorination of the samples were carried out by using X-ray diffraction (Bruker D8-advance) and field emission scanning electron microscope (FESEM, Zeiss SUPRA 35VP) analyses. In addition, a fully randomized factorial design with various combinations of temperature, time and Muka coal to Polystyrene ratios was applied to evaluate and optimize the chlorination process. The design matrix as well as factors levels are presented in Table 1.

### Table 1. The design matrix as well as factors levels

| Run (#) | Temperature (°C) | Time (hr) | Coal to Polystyrene ratio |
|---------|------------------|-----------|--------------------------|
| 1       | -                | -         | -                        |
| 2       | +                | -         | -                        |
| 3       | -                | +         | -                        |
| 4       | +                | +         | -                        |
| 5       | -                | -         | +                        |
| 6       | +                | -         | +                        |
| 7       | -                | +         | +                        |
| 8       | +                | +         | +                        |
| 9       | 0                | 0         | 0                        |
| 10      | 0                | 0         | 0                        |
| 11      | 0                | 0         | 0                        |

| Factors Code | Units | Levels |
|--------------|-------|--------|
| Temperature  | A °C  | 400 450 500 |
| Time         | B hr  | 1 2 3     |
| Coal to Polystyrene | C ratio | C85P15 C75P25 C65P35 |
3. Results and discussion

The reduced and nitrided samples were characterized by XRD method. The rietveld refinement method was also applied for the quantitative phase analysis of XRD patterns of the samples. The results for the extents of reduction, nitridation and carburization were determined based on the elemental analysis of the samples by CHN and LECO analyses, and identified phases by XRD analysis are summarized in Table 2.

![Table 2](#)

| Sample  | X₀, % | Xₙ, % | Xₓ, % | Identified phases from XRD | Rwp (%) | GoF |
|---------|-------|-------|-------|-----------------------------|---------|-----|
| C85P15  | 88.74 | 76.74 | 2.74  | 80.8 TiO₂; C₁₀N₁₃ + 19.2 Fe | 8.89-3.05 |     |
| C75P25  | 86.66 | 74.50 | 0.83  | 79.3 TiO₂; C₁₀N₁₃ + 20.7 Fe | 8.82-2.86 |     |
| C65P35  | 86.09 | 73.87 | 0.30  | 81.1 TiO₂; C₁₀N₁₃ + 18.9 Fe | 7.49-2.03 |     |

The XRD patterns revealed that titanium oxycarbonitride, TiOₓCᵧN_z (ICSD# 98-008-9933) and iron, Fe (ICSD# 98-002-2044) were the main phases for the reduced and nitrided samples using the mixtures of Muka coal and polystyrene as reductants. The results were also in agreement with the previous findings which reported the main phases after carbothermal reduction and nitridation of titania and ilmenite were TiO₂CₓNᵧ and Fe phases [8, 11].

The reduced samples were chlorinated in a tube furnace at 400-500 °C for 1-3 hours in order to produce TiCl₄ solutions. Table 3 summarizes the quantitative analyses of the solid residues collected from alumina crucibles after the chlorination of the pellets containing metallic Fe and TiOₓCᵧN_z at various operating conditions based on the XRD patterns for the highest and lowest chlorination times and temperatures. The phases determined in the solid residues were TiCl₃ (ICSD# 98-004-8808), SiO₂ (ICSD# 98-002-8673), TiO₂ (ICSD# 98-007-6757), Ti₃O₇ (ICSD# 98-007-1966) and Fe₂O₃ (ICSD# 98-001-2634). As is observed in Table 3, small amounts of titanium sub-oxides were also formed that can probably due to the aluminum catalyst used for Cl₂ gas generation producing oxygen gas as explained by Eqs.(1-3) [5, 12].

\[
\text{K}_2\text{MnO}_4 + 4\text{HCl} \rightarrow \text{MnCl}_2 + 2\text{H}_2\text{O} + 1.5\text{Cl}_2 (g);
\Delta G^0 = 13.437 - 0.1178T \text{kJ/mol} \quad (\text{Eq.1})
\]

\[
\text{K}_2\text{MnO}_4 + 8\text{HCl} (g) + \text{Al} \rightarrow \text{MnCl}_2 + 2\text{KCl} + \text{Cl}_2 (g) + 4\text{H}_2\text{O} + \text{AlCl}_3;
\Delta G^0 = 140.38 - 0.1746T \text{kJ/mol} \quad (\text{Eq.2})
\]

\[
2\text{KMnO}_4 + 2\text{Al} + 2\text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + 2\text{K}_2\text{O} + \text{O}_2 (g) + \text{Al}_2\text{O}_3 + 2\text{H}_2 (g);
\Delta G^0 = 210.58 - 0.0386T \text{kJ/mol} \quad (\text{Eq.3})
\]

![Table 3](#)

| Run (#) | Identified phases from XRD | Rwp (%) | GoF | Extent of chlorination, (%) |
|---------|-----------------------------|---------|-----|-----------------------------|
| C3      | 0.9 TiCl₃+32.6 SiO₂+66.4TiO₂ | 7.40-1.08 |     | 94.98                       |
| C4      | 0.8 TiCl₃+5.2SiO₂+94.0TiO₂  | 8.83-1.92 |     | 94.68                       |
| C5      | 59.6 TiCl₃+30.8SiO₂+9.5Ti₁O₅ | 10.68-2.68 |     | 89.50                       |
| C8      | 4.0 TiCl₃+7.4 SiO₂+88.7Fe₂O₃ | 6.86-1.24 |     | 88.92                       |

3
Figure 1. DOE results for (a) Perturbation plots, (b) and (c) 3D surface maps of time and temperature in response to the extents of chlorination of the iron-containing samples reduced with lowest and highest ratios of C/PS in reductant, respectively.

Figure 1 shows the perturbation plots and 3D surface maps of time and temperature in response to the extents of chlorination for the reduced and nitrided samples with lowest and highest ratios of Muka coal-to-polystyrene (C/PS) in required reductants, respectively. The C/PS ratio, denoted as C in the perturbation plots, had the highest gradient and indicated the most significant factor effect on the process, as shown in Figure 1(a). Chlorination time (factor B) showed the lowest gradient among the investigated factors. However, decreasing the chlorination time to 1 hour at 400 °C resulted in TiCl$_3$ formation which was one of the remarkable findings of the present study as compared with the chlorination of the iron-free titanium oxycarbonitride samples[8, 12]. It is observed from Figures 1(b)-(c) that the extents of chlorination increased with increasing C/PS ratios. The chlorination of TiO$_x$C$_y$N$_z$ proceeds by the chlorination of TiC, TiN and TiO phases, and the standard Gibbs free energy change for TiC chlorination is more negative than TiN and TiO phases. Thus, the samples with high carbon content could be easily chlorinated at this range of temperature although it may have significant impact on the mass transfer of gaseous reactants and products. At the chlorination condition, Fe contents of the samples were converted into ferric chloride (FeCl$_3$). The NaCl trap inside an alumina fiber was utilized to reduce the FeCl$_3$ accumulation at the outlet of the chlorination reactor to minimize iron contamination in TiCl$_4$ product. A liquid phase between NaCl and FeCl$_3$ can occur at temperatures of above 157°C [13], and this technique was used to prevent the contamination of TiCl$_4$ product from undesired FeCl$_3$ (g) formed from the iron in chlorination of TiO$_x$C$_y$N$_z$.

The results of the present work obviously indicated that the carbothermal reduction and nitridation of the samples with a mixture of coal-to-polystyrene in high ratios were more feasible. Moreover, the presence of iron in the reduced samples had remarkable impact on the composition of the chlorination
resultant. More importantly, the TiCl$_3$ phase was determined to be formed at lowest chlorination temperature and time of about 400 °C and 1 hour; respectively, rather than TiCl$_4$ formation based on the rietveld refinements of XRD patterns presented in Table 3. From the DOE analysis, it can be concluded that there was a remarkable agreement between the estimated values and actual responses which can validate the statistical analyzing method. The SEM images of as-received ilmenite, nitrided ilmenite and the chlorinated samples are presented in Fig. 2. The morphology of nitrided ilmenite and chlorinated samples observed to be porous in structures.

![SEM images](image)

**Figure 2.** SEM images of (a) as-received ilmenite, (b) nitrided ilmenite and (c) chlorinated sample.

4. Conclusion

In summary, chlorination of titanium oxycarbonitride samples obtained from carbothermal reduction and nitridation were performed at temperature of about 400 - 500 °C for 1-3 hours. The results showed that approximately 95% of titanium compounds including titanium carbide and titanium nitride and oxides were chlorinated and transformed into TiCl$_4$ and TiCl$_3$. Metallic iron was transformed into FeCl$_3$ which was trapped by using NaCl at the end of chlorination reactor. The extents of chlorination increased with increasing temperature and increasing the C/PS ratio in reductant. Based on the experimental results, it was observed that C/PS ratio had the most significant effect towards the chlorination process. The highest extent of chlorination of 95.01% was obtained at 500 °C for 1 hour with a C/PS ratio of 1.90.
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