Chlorination of Titanium Carbonitride (TiC$_{0.7}$N$_{0.3}$) for Production of TiCl$_4$

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Abstract. The chlorination of titanium carbonitride (TiC$_{0.7}$N$_{0.3}$) was conducted on the effect of temperature, reaction time and nitrogen gas flow rate for low-temperature production of titanium tetrachloride (TiCl$_4$). Statistical design of experiments (DOE) was employed to analyze the interaction of the parameters. The chlorinated samples were characterized by X-Ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis. The DOE results showed that the flow rate of nitrogen (N$_2$) gas was the most influential parameter followed by temperature and chlorination time. The highest weight loss for TiC$_{0.7}$N$_{0.3}$ sample was obtained to be about 79.52% at 500 °C for 60 minutes under N$_2$ gas with the flow rate of 200 mL.min$^{-1}$. The XRD patterns showed a strong decrease in intensity of TiC$_{0.7}$N$_{0.3}$ peaks. The XRD and SEM/EDX analyses also showed some free carbon in the residues after the chlorination process that could be formed from the chlorination of TiC in solid solution with TiN.

1. Introduction

Titanium carbonitride (TiCN) is a synthetic material commonly employed for coating of cutting tools. It has high cutting performance and can be used at high cutting speeds [1]. In synthesis of TiCN coatings, TiN and TiC have been used as starting material and prepared by sintering techniques [2, 3]. In addition, Mostert et al. [4], have reported that titanium carbonitride produced by reduction and nitridation of titanium dioxide, ilmenite and/or titanium slag could be chlorinated successfully at 200-500°C. In the low-temperature chlorination process, impurities normally do not react with chlorine gas to any significant extent or may become chlorinated at very slow rate [5-7]. The reason that chlorine gas was used is because of its high reactivity as well as the more environmentally friendly waste. The wastes generated from chlorine metallurgy routes, compared to those obtained from other processes, the chlorine and the chlorides in the effluents can be easily dissolved in water or precipitated and subsequently recycled in the same unit or otherwise [8, 9]. The overall chlorination reaction for Ti(C,N) can be written as below as Eq.(1).

Preliminary chlorination studies on nitrided ilmenite and Ti(O,C,N) has been reported elsewhere [10].
$\text{TiCN} (s) + 2\text{Cl}_2 (g) \rightarrow \text{TiCl}_4 (g) + C (s) + \frac{1}{2} \text{N}_2 (g), \quad \Delta G^\circ = -413.67 + 3.5 \times 10^{-3} T \text{ (kJ/mole)}$ (1)

2. Materials and Method

Titanium carbonitride powder was used as raw material in this study. The mean particle size of the TiC$_{0.3}$N$_{0.7}$ was about 40 μm. Aluminum powder (Sigma-Aldrich, CAS 7429-90-5) was used as a catalyst to speed up the reaction between hydrochloric acid (Sigma-Aldrich, CAS 7647-01-0) and potassium permanganate (Sigma-Aldrich, CAS 7722-64-7) to generate significant amounts of chlorine gas. Details of the thermodynamics calculation and experimental use of aluminum metal powder is given elsewhere [7]. Hydrochloric acid was used as scrubber to trap the TiCl$_4$ gas produced from the chlorination process. The solubility limit of TiCl$_4$ in 37 wt.% HCl at 20°C was [11]. The studied parameters were chlorination temperature, chlorination time and nitrogen (N$_2$) gas flow rate. The pellets were prepared using Specac Hand Press Machine and chlorinated at different chlorination temperatures (400-500 °C), chlorination time of 1-3 hours, and the N$_2$ gas flow rate of 200-300 ml.min$^{-1}$). A fully randomized factorial design with different parameters including temperature, chlorination time and flow rate of nitrogen gas (N$_2$) was applied to evaluate and optimize the chlorination process parameters. The design matrix for this study is presented in Table 1.

| Factor             | Unit       | Level  | Low   | Medium | High  |
|--------------------|------------|--------|-------|--------|-------|
| Temperature        | ºC         |        | 400   | 450    | 500   |
| Soaking Time       | Minutes    |        | 30    | 45     | 60    |
| Flowrate of N$_2$  | cc/min     |        | 200   | 250    | 300   |

3. Result and Discussion

The highest weight loss was obtained for the sample chlorinated at 500 °C for 60 minutes when the flow rate of N$_2$ gas was 200 ml/min. The weight lost for this sample was about 79.52 wt.% obtained for experimental std #4 designated in table 1. Similarly, highest extent of chlorination of titanium (X$_{Ti}$) obtained was about 62.35% for experimental std #4 based on the ICP-OES data. Table 2 shows the weight reduction (X$_B$) and extent of chlorination (X$_{Ti}$) of the chlorinated samples at different conditions. As increase in temperature causes the gaseous reactant to possess more thermokinetic energy, hence higher extent of chlorination of TiC$_{0.7}$N$_{0.3}$.

| STD   | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 |
|-------|----|----|----|----|----|----|----|----|----|----|----|
| Weight lost*,\(\%\) | 63.90 | 69.33 | 74.88 | 79.52 | 9.25 | 21.59 | 28.11 | 45.02 | 47.82 | 44.65 | 52.02 |
| Extent of chlorination, X$_{Ti}$**,\(\%\) | 51.79 | 59.53 | 58.23 | 62.35 | 14.17 | 12.85 | 21.20 | 24.95 | 47.24 | 46.43 | 51.13 |
SEM / EDX analysis provides more detailed insights into the morphological changes in the chlorinated samples. The samples with lowest (STD #5), middle (STD #9) and highest (STD #4) weight lost were analyzed using SEM/EDX. The elemental analysis obtained is given in Table 3 above. It can be seen that with increasing concentration of detected surface chlorine atoms via EDX, the concentration of detected surface oxygen was also increasing. This implied that the TiCl$_4$ residue was trapped in the mesoporous product after chlorination. As the surface was exposed slowly to ambient conditions, it was being hydrolyzed, forming oxides of titanium by reaction in Eq. (2).

$$\text{TiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{HCl}, \quad \Delta G^\circ = -18.13 - 0.05T \text{ (kJ/mole)}$$

The surface morphology of the chlorinated samples shown in Figure 1. From these micrographs, it can be concluded that as the weight loss increased, the size of the pores being generated was also increasing. XRD analysis of the residue was used to determine the phases present in the samples after chlorination. The sample designated experimental std #3 showed highest weight loss, which indicated almost all of titanium being removed. Other samples showed similar trends, that with increasing weight loss, the TiC$_{0.7}$N$_{0.3}$ (ICSD 98-006-3229) XRD peaks intensity was lower. Selected XRD patterns are shown in Figure 2 at different temperature and N$_2$ gas flow rate. There were trace amount of TiO$_{0.33}$ (ICSD 98-001-4919) phase and TiCl$_3$ were observed in the residue obtained from the sample with highest extent of chlorination. This results showed that upon chlorination, TiC$_{0.7}$N$_{0.3}$ is being chlorinated into TiCl$_4$ or TiCl$_{2.3}$ (ICSD 98-000-3839). However, due to the porous nature of the chlorinated residual product, these titanium sub-chlorides were being trapped inside the pores. The TiC$_{0.7}$N$_{0.3}$ was not fully chlorinated due to this inadequate contact with

| Experimental Std Run | Elements | Weight lost, (%) |
|----------------------|----------|-----------------|
| Ti (wt. %) | Cl (wt. %) | O (wt. %) | C (wt. %) | N (wt. %) | |
| STD#5 | 73.15 | 03.21 | 00.00 | 15.40 | 08.24 | 9.26 |
| STD#9 | 12.16 | 18.17 | 10.42 | 39.84 | 19.41 | 47.83 |
| STD#4 | 65.89 | 02.78 | 07.15 | 13.95 | 10.23 | 79.52 |
Cl₂ gas and with subsequent contact with ambient moisture in air, it will eventually hydrolyzed into oxides of titanium by Eq. (4).

![Figure 2](image)

**Figure 2.** XRD patterns of (a) raw TiCN and the residues obtained from the chlorination (b) at 400 °C for 60 min with 200 ml/min (std #3) and (c) at 450 °C for 45 min with 250 ml/min (std#10)

Statistical design study was carried out using Design Expert v8.0.6 using a factorial model to determine the interaction and the most influential factors in chlorination of TiC₀.₇N₀.₃. Results obtained are shown Table 2 in the previous section. Then, ANOVA (Analysis of Variance) and model graph analysis was performed in order to interpret the experimental results based on factorial model. The model graphs analysis used in this study included perturbation plots, and 3D cube plot. The results were expressed in the form of percentage of weight lost (wt. %) and Xₜ, or percentage of titanium being extracted. ANOVA was performed to analyze the results obtained and the respective standard deviation and correlation factor (R²) for weight loss (%) is 4.4 and 0.9731 respectively, while standard deviation for extent of chlorination was 6.21 and 0.8239 respectively. The predicted value and actual value is shown in Figure 3(a)-(b). It can be seen that in both figures, the experimental data point lies around the predicted linear line and evenly distributed. Hence it can be stated that 95% confidence level can be claimed in experimental data fitting within the range of the parameters investigated.

![Figure 3](image)

**Figure 3.** Graph of predicted value against actual value of (a) percentage of weight reduction (wt.%) (b) extent of chlorination, Xₜ

The perturbation plots for both responses are shown in Figure 4(a)-(b). From these figures, it can be seen that chlorination temperature and time had a positive impact on the percentage of weight loss, while N₂ flow rate had a negative effect on the weight loss. From the magnitude of the slopes for all 3 factors, N₂ gas flow
rate showed the highest negative gradient compared to other factors. This implied that it had the most significant effect on the percentage of weight loss and XT. It can also be easily explained by the dilution of reactant gas namely Cl₂, which caused the reaction to have slower kinetics. Same trend can be observed for the XT data. However, it should be noted that none of the XT exceeded 65% which was rather moderate when compared to chlorination of titanium oxycarbonitride [6, 12]. A possible explanation for this was due to the bonding energy of titanium carbonitride (TiC₀.₇N₀.₃) compared to titanium oxycarbonitride (TiOₓCᵧNₘ). In the latter, the electronic bandgap was less than pure TiC and TiN whereas for TiC₀.₃N₀.₇, the bandgap was about 5.52 eV [13]. Electronic bandgap is an indication of the strength of the chemical bonds between the atoms. The higher bandgap for TiC₀.₇N₀.₃ made it more unfavorable for the removal for Ti via TiCl₄ formation.

Figure 4. Perturbation plots for (a) weight loss and (b) XT

4. Conclusion

Titanium Carbonitride (TiC₀.₇N₀.₃) used in this study was obtained via carbothermal reduction and nitridation of titanium metal with carbon and N₂ gas. It can served as a model for chlorination studies on nitrided ilmenite which contains titanium oxycarbonitride (TiOₓCᵧNₘ). The TiC₀.₃N₀.₇ was chlorinated to form TiCl₄ and C at various reaction temperatures, chlorination times and N₂ gas flow rates. The response of the study was percentage of weight lost and XT. Based on the findings of this paper, the most significant parameter was N₂ gas flow rate, followed by temperature and chlorination time. The maximum weight lost obtained was 79.52% whereas the highest XT was 62.36%. These results were obtained by at 500 °C at 60 minutes of chlorination time with 20 ml.min⁻¹ of N₂ flow rate. From the XRD analysis, samples chlorinated over 45 minutes was contaminated by traces of TiO₂ due to the exposure to ambient moisture. The findings for this work will enable the production of TiCl₄ and nanoporous carbon from TiC₀.₇N₀.₃. It will also serve as good representative for chlorination of titanium oxycarbonitride with low oxygen fraction in nitrided ilmenite.
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