CHLORINATION OF NITRIDED MALAYSIAN ILMENITE CONCENTRATE REDUCED WITH POLYPROPYLENE AND COAL

by

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LIST OF SYMBOLS

^{o}C	Percentage
%	Carbon, Hydrogen , Nitrogen and Sulphur analysis of PP and Mukah coals (carbon sources)
±	Plus-minus
μm	micrometre
cm	centimetre
g	gram
kJ	kilojoule
J	Joule
θ	Theta - Angle of incidence
L	Litre
ml	Millilitre
min	minutes
W_f	Weight final of sample
W_i	Weight initial of sample
K	Kelvin
atm	atmosphere
O_i	Oxygen initial content
O_f	Oxygen final content
ΔG^o	Delta G^o
Wt	weight
hrs	hour
ppm	Part per million

Å	angstrom
λ	Wavelength
X	Weight loss
X_N	Extent of nitridation
X_O	Extent of reduction
X_{Ti}	The extent of chlorination or percentage of titanium extraction
R_{wp}	Weighted profile factor
GoF	Goodness of Fit

LIST OF ABBREVIATION

AQ-2	Anthraquinone-2-sulfonic acid sodium salt monohydrate
CHNS	Carbon Hydrogen Nitrogen Sulphur
CTRN	Carbothermal reduction and nitridation
DOE	Design of Experiment
EDX	Energy-dispersive X-ray Spectroscopy
Fe	Iron
Fe2O3	Hematite
Fe3O4	Magnetite
Fe_2TiO_5	Pseudobrookite
FeTiO3	Ilmenite
FTIR	Scanning Electron Microscope
H_2	Hydrogen gas
H_2SO_4	Sulphuric acid
HCl	Hydrochloric acid
ICP	Inductively Coupled Plasma
$KMnO_4$	Potassium permanganate
P_2O_5	Phosphorus pentoxide
PP	Polypropylene
N_2	Nitrogen gas
NH_4Cl	Ammonium chloride
MB	Mukah Balingan coal
SEM-EDX	Scanning electron microscope-energy dispersive x-ray
TGA	Thermal gravimetric analysis

Ti	Titanium
TiC	Titanium Carbide
$TiCl_4$	Titanium Tetrachloride
TiN	Titanium Nitride
TiO_2	Titanium Dioxide / rutile
$TiO_xC_yN_z$	Titanium Oxycarbonitride
UV-Vis	Ultraviolet–visible spectroscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
-γFe2O3	Magnetite

PENGKLORINAN KONSENTRAT ILMENIT NITRIDA MALAYSIA OLEH PROSES PENURUNAN BERSAMA POLIPROPILENA DAN ARANG

ABSTRAK

Penghasilan $TiO_xC_yN_z$ daripada ilmenit Malaysia dan pengklorinan pada suhu rendah untuk menghasilkan $TiCl_4$ telah diteliti dalam projek ini. Objektifnya adalah untuk meningkatkan teknologi altenatif bagimenghasilkan $TiCl_4$. Kesan terhadap masa CTRN, ratio karbon kepada oksigen dan penambahan plastik PP kedalam arang bagi pembentukan Fe dan $TiO_xC_yN_z$ daripada ilmenit telah dikaji. Reka bentuk Eksperimen (DOE) telah ditugaskan untuk mereka bentuk parameter dalam proses CTRN Proses CTRN telah dilakukan pada suhu 1150 dan 1250 °C di bawah atmosfera H2-N2 untuk 60 dan 180 min. Campuran ratio karbon kepada oksigen bermula dari ratio 3.0 dan 7.0. Peratus X_o and X_N meningkat apabila kandungan PP kepada arang meningkat daripada 25 wt. %, 60 wt. % and 100 wt. %. Analisis SEM/EDX menunjukkan produk disintesis oleh 60 wt. % and 100 wt. % mempunyai mikrostruktur yang unik iaitu zarah Fe sfera. Zarah Fe sfera ini boleh dipisahkan dengan mudah daripada fasa $TiO_xC_yN_z$. Peratus X_O and X_N yang paling tinggi masing-masing adalah 93.15% dan 93.85% bagi C7PP1004. Selepas proses CTRN, pembuangan Fe dilakukan selama 8 jam dengan larut lesap jenis Becher pada 70 °C dengan kehadiran NH4Cl dan 0.1 wt. % AQ-2 sebagai pemangkin yang efektif. Sekali lagi DOE digunakan dalam pengklorinan untuk merancang percubaan experiment. Mekanisma pengklorinan nitrida ilmenit telah dikaji pada 300 – 400. Peratus Xti daripada $TiO_xC_yN_z$ pada 300 C ialah 84.00% dan pada 400 C ialah 88.70 dalam masa 60 minit. Ketulenan $TiCl_4$ adalah 97% adalah dihasilkan daripada nitrida ilmenit Malaysia. Oleh itu, projek ini menunjukan proses CTRN, proses larut lesap

dan proses pengklorinan boleh menjadi kaedah menghasilkan $TiCl_4$ daripada ilmenite Malaysia.

CHLORINATION OF NITRIDED MALAYSIAN ILMENITE CONCENTRATE REDUCED WITH POLYPROPYLENE AND COAL

ABSTRACT

The production of Titanium Oxycarbonitride ($TiO_xC_yN_z$) from Malaysian ilmenite and its chlorination at low temperatures for production of Titanium Tetrachloride ($TiCl_4$) was studied in this project. The objective was to improve an alternative technology for production of $TiCl_4$. The effects of carbothermal reduction and nitridation (CTRN) on parameters of time, carbon to oxygen molar ratio ($C:O_{red}$) and the addition of waste PP plastic into coal (PP:MB coal) on the formation of Fe and $TiO_xC_yN_z$ from ilmenite were investigated. Design of Experiments (DOE) was assigned to design the parameters in CTRN process. The CTRN process was done at temperature of 1150 and 1250 °C under H_2-N_2 atmosphere for 60 and 180 min. A mixture of $C:O_{red}$ molar ratio ranging from 3.0 and 7.0 ratios. The extent of reduction (X_O) and the extent of nitridation (X_N) was increasing as increase PP:MB coal content from 25 wt. %, 60 wt. % and 100 wt. %. SEM/EDX analyses showed that the product synthesized by 60 wt. % and 100 wt. % PP had a unique microstructure in which is spherical Fe particles. This spherical Fe can be easily separated from $TiO_xC_yN_z$ phase. The highest X_O and X_N were 93.15% and 93.85%; respectively for C7PP1004. After CTRN process, Fe removal was carried out for 8 hours by an aeration leaching Becher type process at 70 °C in the presence of NH_4Cl and 0.1 wt. % AQ-2 as the effective catalysts. Again DOE was used in chlorination to design the experiment run. The parameters for chlorination were time (30 min and 60

min),temperature (300 °C and 400 °C) and N_2 gas flowrate (200 mL/min and 400 mL/min). The X_{Ti} moderately increased with increasing the temperature and decreasing flow rate of N_2 gas from 200 mL/ min to 400 mL/min. The highest weight loss and X_{Ti} of $TiO_xC_yN_z$ at 300 °C and 400 °C were 84.0% and 88.7 % in 60 minutes, respectively. The $TiCl_4$ with the purity of about 97% was eventually produced from Malaysian ilmenite. Therefore, project demonstrated that the process of CTRN, leaching process and chlorination process could be a feasible method in production of $TiCl_4$.

CHAPTER ONE

INTRODUCTION

1.1 Research background

Titanium is a metallic element commonly known as Ti in the periodic table. Titanium is silver in colour and has a lustrous appearance (Ewald et al., 2006). It is known to be highly resistant to corrosion due to their stable passive layer, and it is chemically inert (Schmutz et al., 2008). Although Ti on its own has many uses, Ti compound such as TiO_2, TiN, and TiC are also useful in various industries. For example, TiC is used in the groundwork of ceramic materials, which are regularly used in machine steel materials with high cutting speed (Ghidiu et al., 2014). Generally, Ti metal can be alloyed with aluminium (Al) and Fe, among other metals, to form durable and lightweight alloys for most engineering and construction industries. Derived Ti compounds mentioned above are also economically in demand. Concerning w TiO_2 pigment, mainly used by paint, paper and cosmetics industry for its high index of refraction (2.55-2.733) and light-scattering ability (El-Sherbiny et al., 2014).On the other hand, the composition of TiN and TiC are known to have a hardness equivalent of 9 to corundum in the Mohs Scale (Tabor, 2000). This makes the latter excellent for manufacturing and machining industries.

Geological occurrences of Ti comes in various minerals, such as Anatase, Brookite, Ilmenite, Leucoxene, Perovskite, Rutile and Sphene. However, given the amount of Titanium in these minerals, only Ilmenite and Rutile are considered to be economically viable to be mined. According to the Mineral Commodity Summary

(Ober, 2018), Asia countries were listed for Rutile world production but not listed for Ilmenite world production. Although not listed, production of Ilmenite in Malaysia does exist. Ilmenite is obtained in the form of tin mining run-off, commonly known to the locals as "Amang" (Zulfahmi et al., 2012, Kiong and Hoe, 2003). Large tin mining plants in Perak and Selangor are setting these "Amang" aside for any potential refining ore beneficiation process. An alternative to "Amang", Ilmenite in Malaysia can be found in alluvial and hard rock deposits. Such deposits are located in Langkawi (Begum et al., 2016, Hassan, 1987) and also Terengganu (Yeap, 1977). However, traditional mining appears not to be lucrative due to the exhaustion of high-grade reserves and low ilmenite prices, According to US Geological survey the estimated value of titanium mineral concentrates consumed in the United States in 2017 was $561 million (Ober, 2018). Now, with the improvement in mineral processing, ilmenite reserves in Malaysia has a bright future as it may be used for producing Ti metallic products.

This research was conducted to investigate the production of $TiCl_4$ from $TiO_xC_yN_z$ in Malaysian ilmenite supplied by Chee Ng Minerals Sdn. Bhd from Kampar, Perak. Ilmenite ore was a major raw material for titania pigment and titanium metal production. The general chemical composition of ilmenite is iron titanium oxide, $FeTiO_3$. Ilmenite concentrates can be nitrided to $TiO_xC_yN_z$ in the H_2-N_2 gas mixture at 1200 ^{o}f (Rezan et al., 2011). This project aimss to convert Malaysian ilmenite to $TiO_xC_yN_z$ by CTRN with different blends of coal with waste PP. The goal of using PP was used as reductant agent to replace coal as primary reductant agent due to the higher cost of coal. After CTRN, the product sample was leached for 8 hours of leaching time and 0.1 wt. % of catalyst Anthraquinone-2-sulfonic acid sodium salt monohydrate (AQ-2) to enhance metallic iron removal as a retarded agent in the chlorination process. The leached samples then were chlorinated in a horizontal furnace to produce $TiCl_4$ at a low temperature of 400 ^oC

The project analyzes all the relevant kinetic data by a statistical DOE. Therefore, the study of CTRN and chlorination was undertaken with the aim to develop further understanding mechanisms of Malaysian ilmenite into $TiO_xC_yN_z$ and $TiCl_4$ as intermediary products in the Ti metal production cycle. The project studied Malaysian ilmenite ores which are the primary ore of Ti. The usage of titanium metals is limited because of its high production cost. Production of titania white pigments and titanium metal includes processing of titanium minerals to $TiCl_4$. The commercial chlorination process in the production of Ti metal or TiO_2 pigment requires 800-1100 ºC. However, the chlorination of $TiO_xC_yN_z$ produced from ilmenite can be implemented at 200-350 ºC (Ahmadi, 2017). Low-temperature chlorination can improve the efficiency of production of $TiCl_4$. This makes chlorination of $Ti(O_xC_y N_z)$ an attractive technology in processing of titanium minerals (Li et al., 2012).

1.2 Objectives

There were 3 objectives for this project. The objectives were listed below:

i. To investigate the effect of CTRN with PP as a new innovative reductant.
ii. To study the efficiency of iron removal in nitrided Malaysian ilmenite by aeration leaching process in NH_4Cl solution
iii. To improve the production $TiCl_4$ from Malaysian Ilmenite after CTRN by chlorination process at lower temperature

iv. To determine the most significant factors in the CTRN process and chlorination process by Design of Experiment (DOE)

1.3 Problem statement

Due to the high production cost of TiO_2 white pigments and Ti metal, the usage of titanium was limited. This also includes the processing of Ti minerals to it titanium tetrachloride ($TiCl_4$) production. The commercial chlorination process in the production of Ti metal or TiO_2 pigment requires a temperature range of 800 ˚C to 1100 ˚C of for the reaction to be favourable (Noubactep, 2009). By producing $TiO_xC_yN_z$ via CTRN of ilmenite in the H_2-N_2 gas atmosphere, it will allow the production of $TiCl_4$. However, the existence of metallic Fe after CTRN with $TiO_xC_yN_z$ will affect the formation of $TiCl_4$. Therefore aeration leaching method called Becher process was used to remove the metallic Fe in nitrided ilmenite to increase the efficiency of the $TiCl_4$ production from $TiO_xC_yN_z$. $TiCl_4$ can be produced bychlorination at a lower temperature in the range of 200 ˚C to 350 ˚C. Titanium metal can now be produced from $TiCl_4$ by pure magnesium metal reduction at a lower cost due to low-temperature synthesis of $TiCl_4$. In the lower temperature of chlorination, impurities will not chlorinate or chlorinate very slowly (Adipuri, 2011). This permits selective chlorination of $TiO_xC_yN_z$, decreases chlorine gas consumption and waste generation, and makes the whole technology of ilmenite processing more efficient and environmentally friendly. The low temperature of chlorination will lower the cost of production of Ti metal.

1.4 Research Scopes

Currently, an innovative method used for production of hydrogenated titanium (TiH_2) sponge by reacting $TiCl_4$ and liquid Mg under an H_2 atmosphere. The cost of this process is considerably lower (20%) than the cost of dominant Ti sponge production by Mg reduction through the Kroll process (Duz etal., 2013; Duz et al., 2017). However, literature survey shows that it could be lowered by using the chlorination of $TiO_xC_yN_z$ at lower temperature (200-500 °C) (Adipuri et al., 2008; Adipuri et al., 2009). In this study, the preparation of $TiO_xC_yN_z$ by CTRN of ilmenite followed by Fe removal through the aeration leaching process and continue with chlorination can be done at low temperature.

The CTRN process is newly developed for the synthesis of TiO_xC_y and/or $TiO_xC_yN_z$ from $FeTiO_3$ and has been well studied at different atmospheres (Ar, CO, CH4, N_2 and H_2-N_2) (Dewan et al., 2010; Rezan et al., 2012b; Rezan et al., 2012c). In the synthesis of $TiO_xC_yN_z$ by CTRN process of $FeTiO_3$, graphite has typically been used as the main reductant in the 50 vol.% H_2–N_2 gas mixture (Rezan et al., 2011; Rezan et al., 2012a). However, the use of waste plastics as a source of carbon in CTRN of ilmenite, in literature only addressed for polyethylene terephthalate (PET) that had been done by Ahmadi (2017). Unfortunately PET only contains about 62.5% C compared to PP which contains about 85% of C. PP is the most common plastics going into landfills, are widely used in packaging applications and are encountered on a daily basis (Reis et al., 2011). Thus, ecological options for recycling waste plastics are strongly required for economic and environmental

In this research, ilmenite from Malaysia was converted to metallic Fe and $TiO_xC_yN_z$ in the first stage, then after Fe removal, chlorination process at low temperature was performed to synthesize pure $TiCl_4$ from $TiO_xC_yN_z$. No detailed investigations were found on CTRN of the ilmenite concentrate from Malaysia particularly with utilization of PP as an alternative reductant and its effect on the morphology of nitrided ilmenite. The effect of utilization of waste plastics on the extent of CTRN as well as its effect on microstructure of nitride ilmenite needs more investigation.

The research investigated the processing of $TiO_xC_yN_z$ from the ilmenite concentrate recovered from tin tailing of tin-ore processing plants in Malaysia by CTRN and chlorination. The effect of CTRN parameters ($C:O_{red}$ molar ratio, PP:MB coal ratio, temperature and time) on the formation of Fe and $TiO_xC_yN_z$ phases in CTRN and production of $TiCl_4$ in low-temperature chlorination process were investigated in this research.

1.5 Thesis outline

This thesis was organized into five chapters:

i. Chapter 1 is the introduction of this study. The general idea of the recent work was presented with a synopsis of the research background. The problem statement was highlighted, and the related info regarding the research area were given details. Furthermore, the research objectives were listed.

ii. Chapter 2 is the literature review. This section consists of a short introduction of Ti metal and its application in the industrial world. Then, the most common Ti mineral, which is the ilmenite was further described with focus on Malaysian ilmenite. A literature review on the synthesizing ilmenite ores by addition of waste polymer to $TiO_xC_yN_z$ with importance on using CTRN was also presented. Also, the most important parameter for production of