

Chlorination of Titanium Oxycarbide and Oxycarbonitride

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The University of New South Wales
Faculty of Science
School of Materials Science and Engineering



CHLORINATION OF TITANIUM OXYCARBIDE AND OXYCARBONITRIDE

by

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Submitted in Partial Fulfilment of the
Requirements for the degree of
Doctor of Philosophy

23 March 2009

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*This thesis is dedicated
to my mother*

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The project undertook a systematic study of chlorination of titanium oxycarbide and oxycarbonitride with the aim to develop further understanding of kinetics and mechanisms of the chlorination reactions. The project studied titania, ilmenite ores, and synthetic rutile reduced by carbon in argon and nitrogen and chlorinated at different temperatures, gas flow rates and compositions. Chlorination of titanium sub-oxides, iron and impurities in ilmenite was also examined.

Chlorination of titanium oxycarbide $\text{Ti}(\text{O},\text{C})$ or oxycarbonitride $\text{Ti}(\text{O},\text{C},\text{N})$ can be implemented at 200 to 400 °C, while the commercial chlorination process in the production of titanium metal or titania pigment requires 800 to 1100 °C. This makes chlorination of $\text{Ti}(\text{O},\text{C})$ or $\text{Ti}(\text{O},\text{C},\text{N})$ an attractive technology in processing of titanium minerals.

Chlorination reaction is strongly exothermic, which increased the sample temperature up to 200 °C above the furnace temperature. The chlorination of $\text{Ti}(\text{O},\text{C})$ or $\text{Ti}(\text{O},\text{C},\text{N})$ was ignited at 150 °C to 200 °C depending on the sample composition. Their chlorination at 235 °C to 400 °C was close to completion in less than 30 min.

The chlorination rate of titanium oxycarbide or oxycarbonitride increased with increasing gas flow rate. Sample composition had a significant effect on the extent of chlorination. The optimum results were obtained for titanium oxycarbide or oxycarbonitride produced with carbon to titania molar ratio of 2.5; these samples contained no detectable excess of carbon or unreduced titanium suboxides.

In chlorination of reduced ilmenite ores and synthetic rutile, $\text{Ti}(\text{O},\text{C})$ or $\text{Ti}(\text{O},\text{C},\text{N})$, metallic iron and Ti_2O_3 were chlorinated. The rate and extent of chlorination of titanium increased with increasing carbon to TiO_2 ratio. Chlorination of Ti_2O_3 was slow relative to $\text{Ti}(\text{O},\text{C})$ or $\text{Ti}(\text{O},\text{C},\text{N})$ and iron; chlorination of impurity oxides such as MgO , SiO_2 and Al_2O_3 was not observed.

The project also examined chlorination of $\text{Ti}(\text{O},\text{C})$ or $\text{Ti}(\text{O},\text{C},\text{N})$ in ilmenite ore and synthetic rutile after removal of iron, which was achieved by aerated leaching of reduced samples in heated flask containing 0.37 M of ammonium chloride solution. Iron removal from the ilmenite ore or synthetic rutile resulted in higher rate and extent of chlorination of titanium oxycarbide or oxycarbonitride.

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ABSTRACT

The project undertook a systematic study of chlorination of titanium oxycarbide and oxycarbonitride with the aim to develop further understanding of kinetics and mechanisms of the chlorination reactions. The project studied titania, ilmenite ores, and synthetic rutile reduced by carbon in argon and nitrogen and chlorinated at different temperatures, gas flow rates and compositions. Chlorination of titanium sub-oxides, iron and impurities in ilmenite was also examined.

Chlorination of titanium oxycarbide $\text{Ti}(\text{O},\text{C})$ or oxycarbonitride $\text{Ti}(\text{O},\text{C},\text{N})$ can be implemented at 200 to 400 °C, while the commercial chlorination process in production of titanium metal or titania pigment requires 800 to 1100 °C. This makes chlorination of $\text{Ti}(\text{O},\text{C})$ or $\text{Ti}(\text{O},\text{C},\text{N})$ an attractive technology in processing of titanium minerals.

Carbothermal reduction process was implemented under argon or nitrogen atmosphere at 1450 °C with carbon to titania molar ratio from 1.5 to 4.5. Titanium oxides reduced in argon were converted to $\text{Ti}(\text{O},\text{C})$; reduction in nitrogen produced $\text{Ti}(\text{O},\text{C},\text{N})$. When C/TiO_2 molar ratio was below 2.5, reduction of titania was incomplete; at C/TiO_2 ratio above 2.5, the reduced sample contained unconsumed graphite. In the reduction of ilmenite ores and synthetic rutile, main phases in the reduced sample were $\text{Ti}(\text{O},\text{C})$ or $\text{Ti}(\text{O},\text{C},\text{N})$, metallic iron, graphite (for high C/TiO_2 molar ratio), and unreduced impurity oxides.

Chlorination was studied in a transparent quartz tube placed in a horizontal electric furnace in temperature programmed experiments with temperature ramping from 100 °C to 400 °C at the rate of 3 °C·min⁻¹ and isothermal experiments in the temperature range 200 °C to 500 °C. Titanium tetrachloride vapour was absorbed in two scrubbers containing hydrochloric acid solution. The extent and kinetics of chlorination were determined by analysing periodically concentration of liquid samples by using ICP-OES.

Chlorination reaction is strongly exothermal that increased the sample temperature up to 200 °C above the furnace temperature. The chlorination of $\text{Ti}(\text{O},\text{C})$ or $\text{Ti}(\text{O},\text{C},\text{N})$ was ignited at 150 °C to 200°C depending on the sample composition. Their chlorination at 235

°C to 400 °C was close to completion in less than 30 min. Chlorination in isothermal experiments with chlorine flow rate of 50 mL·min⁻¹ was affected by the reactant gas starvation. It was avoided when the chlorine flow rate was above 100 mL·min⁻¹. Chlorination of Ti(O,C) at 235 °C to 400 °C was close to completion in 30 min. In chlorination of Ti(O,C,N), close to completion reaction was achieved in 30 min at 235 °C, 25 min at 300 °C and 20 min at 400 °C.

The effect of gas flow rate in the range of 100 to 500 mL·min⁻¹ was studied at 300 °C using the Cl₂-N₂ gas mixture with constant chlorine partial pressure of 50 kPa. The chlorination rate of Ti(O,C) or Ti(O,C,N) increased with increasing gas flow rate. With 100 mL·min⁻¹ gas flow, the extent of chlorination after 30 min was 93 pct. The extent of chlorination of Ti(O,C) was close to 100 pct after 30 min of reaction when the gas flow rate was 200 mL·min⁻¹ and above. Sample composition had a significant effect on the extent of chlorination. The optimum results were obtained for Ti(O,C) or Ti(O,C,N) that was produced with carbon to titania molar ratio of 2.5; these samples contained no detectable excess carbon or unreduced titanium suboxides. Chlorination of these samples was close to 100 pct. Chlorination of titanium suboxides in incompletely reduced samples with low C/TiO₂ ratio was slow and had low extent.

In chlorination of reduced ilmenite ores and synthetic rutile, Ti(O,C) or Ti(O,C,N), metallic iron, and Ti₂O₃ were chlorinated. The rate and extent of chlorination of titanium increased with increasing carbon to TiO₂ ratio. Chlorination of Ti₂O₃ was slow relative to Ti(O,C) or Ti(O,C,N) and iron; chlorination of impurity oxides such as MgO, SiO₂ and Al₂O₃ was not observed.

The project also examined chlorination of Ti(O,C) or Ti(O,C,N) in ilmenite ore and synthetic rutile after removal of iron, which was achieved by aerated leaching of reduced samples in heated flask containing 0.37 M of ammonium chloride solution. Iron removal from the ilmenite ores or synthetic rutile resulted in higher rate and extent of chlorination of Ti(O,C) or Ti(O,C,N).

The project showed that titanium, iron and chromium in ilmenites could be extracted and chlorinated at low temperature. Crude products of volatile halides such as FeCl₃ (boiling point 315 °C), TiCl₄ (boiling point 136 °C), and CrO₂Cl₂ (boiling point 117 °C) can be

refined by distillation. TiCl_4 produced from low temperature chlorination can be employed in a novel process based on the continuous reduction of TiCl_4 with magnesium producing a titanium powder developed by the Light Metals Flagship of CSIRO, Australia.

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3. **Adipuri A.**, Zhang G., Ostrovski O. (2007), Chlorination of titanium oxycarbide produced by carbothermal reduction of rutile, *The 11th World Conference on Titanium*, Kyoto, Japan.
4. Zhang G., Dewan M.A.R., **Adipuri A.**, Ostrovski O. (2009), Synthesis and chlorination of titanium oxycarbide, *TMS Annual Meeting & Exhibition*, San Francisco, USA.
5. Rezan S. A., **Adipuri A.**, Zhang G., Ostrovski O. (2010), Carbothermal Reduction and Nitridation of Ilmenite Concentrates and Their Chlorination, International Mineral Processing Congress, Brisbane, Australia. *Abstract accepted*.
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CHAPTER 1. INTRODUCTION

Titanium, silver white metallic transition element of group IVB, is broadly used in manufacturing of metallic items, as a pigment, photocatalyst with numerous applications such as brick coating, water purification, or as photoelectrode for production of solar hydrogen (under development). It is the ninth most abundant element in the earth's crust, at approximately 0.62 pct, which is commonly occurred in nature as ilmenite, FeTiO_3 ; rutile (tetragonal TiO_2), anatase (tetragonal TiO_2), brookite (rhombohedral TiO_2); perovskite, CaTiO_3 ; sphene, CaTiSiO_5 ; and geikielite, MgTiO_3 [Donachie, 1988; Froes, 2001; Barksdale, 1949]. Rutile and ilmenite represent a major feedstock for commercial purposes [Dooley, 1975].

The mineral rutile consists mainly of TiO_2 (90 to 98 pct) with low content of iron impurities, while commercial ilmenite has between 35 to 65 pct TiO_2 with iron as the main impurity [Froes, 1997]. Ilmenite can be utilised directly in some processes although it is often beneficiated to synthetic rutile containing 85 to 96 pct TiO_2 by separating the titanium from impurities. Rutile world reserves are limited. Ilmenite, however, is more abundant and its world supplies are estimated to meet the world demand until twenty second century [Froes, 1997].

Australian deposits of ilmenite ore are among the largest in the world [Svoboda and Wilson, 1985]. Australia produces about 40 pct of the world's ilmenite and 25 pct of the rutile [Lyday, 1997]. Growth of titanium dioxide production with an average rate of 5 pct stimulates further increase in utilisation of Australian titanium resources. Processing of raw ilmenite to titanium dioxide pigment increases its value by over ten times [Anonymous, 1993].

Further potential increase in value of Australian titanium minerals is associated with production of titanium metal. Titanium metal has superior properties – high strength, low density, excellent corrosion resistance, extreme mechanical and thermal loading capacity and other. In 2008, the global titanium minerals market was estimated at approximately 5.9 million metric ton of TiO_2 units. Pigment industry is by far the largest consumer of titanium minerals with an estimated total world pigment production of approximately 4.7 million metric ton of TiO_2 [TZ Mineral International, 2009]. Titanium sponge production,

which is used mainly in the aerospace industry, as well as other industrial applications, was estimated at approximately 175 thousand metric ton in 2008 [TZ Mineral International, 2009]; what is a negligible amount in comparison with other light metals – aluminium and magnesium. The application of metallic titanium is limited by its high production cost. Most titanium metal goes into the aerospace industry. New opportunities for the use of titanium exist and will grow in automotive/transport sector, computer, chemical and electrical industries, recreational market if the production of titanium becomes cheaper [Department of Industry Science and Resources, 2001]. Radical technological advances are needed to cut the production cost by half – an issue remaining unresolved for more than fifty years.

A novel direct titanium extraction process termed as FFC Cambridge process, recently developed by Fray, Farthing, and Chen has provided impetus to the titanium research activity [Chen *et al.*, 2000]. As a result, several processes that enable titanium production directly from oxide such as: Ono Suzuki (OS) process, BHP Biliton Polar process, Electronically Mediated Reaction/Molten Salt Electrolysis (EMR/MSE) process, Preform Reduction Process (PRP), MER process, and MIR Chem process are under development [EHK Technologies, 2004]. The detailed explanations are given in *Section § 2.1*.

In general, most of direct reduction processes of titanium from its oxide has several drawbacks such as: requirement of expensive high grade titania feed, difficulties in scaling up to large quantity production, contamination of electrolyte which leads to low purity of titanium metal product, and low current efficiency.

A novel process based on the continuous reduction of titanium tetrachloride with magnesium, producing a titanium powder, has been developed by the Light Metals Flagship of the Australian Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia. Drawing on CSIRO's expertise in fluidised bed technology, researchers have developed the TiRO process, which cuts the cost of titanium metal production. This process enables the reaction to occur at a lower temperature and continuously in fluidised bed. The process occurred between the melting point of magnesium (650 °C) and the melting point of MgCl₂ (712 °C). The first step of this process is the reduction of TiCl₄ with magnesium metal in a fluidised bed to produce fine titanium particles. The particles are co-deposited with MgCl₂ in composite pellets that form in the bed. The second step is

separating the titanium from the MgCl_2 . A laboratory scale fluidised bed has been built and operated continuously for up to 60 h with a production rate of $5 \text{ kg}\cdot\text{day}^{-1}$ [Brooks *et al.*, 2007].

Currently commercial titanium metal production solely relies on chlorination of rutile and reduction of titanium tetrachloride, TiCl_4 . Chlorination of TiO_2 in the presence of coke or other reducing agents such as graphite or CO at temperature 800 to 1100 °C in a fluidised bed, leads to intermediate product TiCl_4 , which is subsequently reduced to titanium metal via Kroll (using magnesium) or Hunter process (using sodium). Alternatively, it is oxidised at 1000 °C to produce chlorine and pure TiO_2 as paint filler [Barksdale, 1949]. The chlorine is recycled at the chlorination step.

The reduction of TiCl_4 is a lengthy and expensive process. Nevertheless, this conventional method has several beneficial features. The TiCl_4 is in the liquid state at ambient temperature and it can be purified by distillation due to its high vapour pressure.

Impurities in natural or synthetic rutile are also chlorinated in the process of production of titanium tetrachloride at 800-1100 °C. These impurities could condense and clog the chlorinator [Dooley, 1975; Perkins *et al.*, 1961; Nieberlein, 1960]. Chlorination of impurities increases wastes generation, energy consumption, and production cost.

Chlorination of titanium oxycarbide $\text{Ti}(\text{O},\text{C})$ or oxycarbonitride $\text{Ti}(\text{O},\text{C},\text{N})$, can be implemented at much lower temperature between 200 and 500 °C [Nieberlein, 1957; Moster *et al.*, 1992; Van Vuuren and Stone, 2006; Smillie and Heydenrych, 1997]. In the low temperature chlorination, impurities do not chlorinate or chlorinate very slowly [Kanari *et al.*, 1999; Hitching and Kelly, 1982; Hunter *et al.*, 1973]. This permits selective chlorination of $\text{Ti}(\text{O},\text{C})$ or $\text{Ti}(\text{O},\text{C},\text{N})$, decreases the chlorine consumption and waste generation, and makes the whole technology of ilmenite processing more efficient and environmentally friendly.

No detailed investigation of kinetics and mechanisms of chlorination of $\text{Ti}(\text{O},\text{C})$ or $\text{Ti}(\text{O},\text{C},\text{N})$ under different operational conditions was reported in the literature. This project undertook a systematic study of chlorination of $\text{Ti}(\text{O},\text{C})$ and $\text{Ti}(\text{O},\text{C},\text{N})$ with the aim to develop further understanding of kinetics and mechanisms of chlorination process.

The project studied titania, ilmenite ores, and synthetic rutile reduced by carbon in argon and nitrogen and chlorinated at different temperatures, gas flow rates and compositions. Chlorination of titanium suboxides, iron and impurities in ilmenite was also examined.

The structure of dissertation is as follows. A survey of relevant literature is presented in Chapter 2. The experimental equipments and procedures employed in the study are described in Chapter 3. Chapter 4 and 5 presents results of chlorination of $\text{Ti}(\text{O,C})$ and $\text{Ti}(\text{O,C,N})$ produced from the carbothermal reduction of titania in argon or nitrogen atmosphere. Chlorination of reduced ilmenite ores and impurities are presented in Chapter 6. Finally, conclusions and suggestions for further work are presented in Chapter 7.

CHAPTER 2. LITERATURE SURVEY

The objective of this chapter is to provide a background on chlorination of titanium and its compounds. This chapter starts with the development of titanium production technology. It presents thermodynamics, kinetics and mechanisms of chlorination reactions and factors that influence the chlorination process.

2.1. Titanium Production Technology

2.1.1. Current Production Technology

Commercial titanium metal production relies on chlorination of rutile and reduction of titanium tetrachloride, TiCl_4 . As titanium metal has high affinity for oxygen, the reduction of titanium dioxide is not feasible as it requires high temperatures [Stwertka, 1998]. Titanium is therefore produced by chlorination of TiO_2 in the presence of coke or other reducing agents such as graphite or CO at temperature 800 °C to 1100 °C in a fluidised bed. This leads to intermediate product TiCl_4 , which is subsequently reduced to titanium metal via Kroll process (by using magnesium metal) or Hunter process (by using sodium metal). Alternatively, it can be oxidised at 1000 °C to produce chlorine and titanium dioxide pigment [Barksdale, 1949]. Almost 94 pct of all titanium minerals are processed to titania pigment [Froes, 2001].

2.1.1.1. Ores Refining

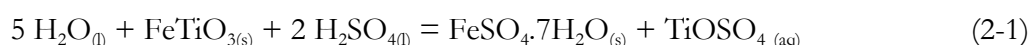
Ilmenite ore can be utilised for chlorination process although it is often beneficiated to synthetic rutile containing 85 to 96 pct TiO_2 by separating the titanium from impurities. Rutile world reserves are limited, ilmenite on the other hand is more abundant and its world supplies are estimated to meet the world demand until twenty second century [Froes, 2001]. The content of TiO_2 in the ores determines further processing steps. High grade ores such as rutile or synthetic rutile is refined to pigment-grade TiO_2 by chlorination, while lower grade ores are processed by the sulphate process [Froes, 2001].

At the present time, the main commercial routes for upgrading ilmenite into synthetic rutile are selective acid leaching (commonly known as a sulphate process), magnetic separation, selective chlorination with or without a reducing agent, or preferential reduction of iron in

the liquid or solid state and its removal into a metallic phase or by leaching [Froes, 2001; Van Deventer, 1998; Walker, 1967; Barksdale, 1949; Dooley, 1975; Town and Sanders, 1961; Graham, 1974; Becher *et al.*, 1965; Walpole and Winter, 2002; Verhulst *et al.*, 2002]. Ilmenite ores containing 50 to 60 pct of TiO_2 content is beneficiated by partial reduction, then leached with sulphuric or hydrochloric acid to yield synthetic rutile [Froes, 2001].

2.1.1.2. Sulphate Process

In the sulphate process, ilmenite ores are treated with sulphuric acid at temperature 150 to 180 °C [Froes, 2001]:



The precipitated $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is filtered and titanyl sulphate is hydrolysed at 90 °C to form insoluble titanyl hydroxide, $\text{TiO}(\text{OH})_2$ and sulphuric acid. $\text{TiO}(\text{OH})_2$ is then washed and calcined at 1000 °C to form TiO_2 [Froes, 2001].

2.1.1.3. Chloride Process

In the chlorination process, a high grade of titanium oxide ore is chlorinated in a fluidised bed reactor in the presence of coke at 800 to 1100 °C:



The non-volatile halides and unreacted solids are removed from volatile halides. TiCl_4 is separated from the other halides by double distillation [Weast, 1982]. Vanadium oxychloride, VOCl_3 , which has a boiling point close to TiCl_4 , is separated by complexing with mineral oil or copper, or reducing with H_2S to VOCl_2 . The TiCl_4 is finally oxidized at 985°C to TiO_2 and the chlorine gas is recycled [Haddeland and Morikawa, 1978; Minkler and Baroch, 1981]

With the stringent environmental control, chloride process is more favoured because it produces less waste. The sulphate process generates approximately six metric tonnes of waste per metric tonne of TiO_2 ; whereas only one metric tonne of waste is produced through the chloride process [Slatnick, 1994]. The chlorination process, commercialised by Du Pont in the early 1960s, produces a better quality pigment, requires less processing energy than the sulphate process ($1800 \text{ kWh}\cdot\text{t}^{-1}$ compared to $2500 \text{ kWh}\cdot\text{t}^{-1}$), and has less waste discharge [Haddeland and Morikawa, 1978; Anonymous, 1975]. However, the chloride process is unsuitable for direct processing of ilmenite ores. The impurities in ilmenites such as MgO and CaO can clog the chlorinator and cause high pressure drop

[Froes, 2001]. This condition could terminate the flow of fluid through the column, thereby collapsing the fluidised bed.

2.1.1.4. Commercial Process for TiCl_4 Reduction

In the 1990s and until these day, nearly all sponge titanium has been produced by the magnesium reduction process (commonly known as Kroll process), which is described by the following [Froes, 2001]:



The distilled TiCl_4 vapour is metered into a carbon-steel reaction vessel that contains liquid magnesium. An excess of 25 pct magnesium over the stoichiometric amount ensures that the lower chlorides of titanium (TiCl_2 and TiCl_3) are reduced to metal. The highly exothermic reaction is controlled by the feed rate of TiCl_4 at temperature approximately 900°C . The reaction atmosphere is helium or argon. Molten magnesium chloride is tapped from the reactor bottom and recycled using conventional magnesium-reduction methods [Froes, 2001]. The production is in batches up to 10 metric tons of titanium. The product is further processed to remove unreacted titanium chlorides, magnesium, and residual magnesium chlorides. These impurities are removed by acid leaching, vacuum distillation at 960 to 1020°C , or the argon sweep at 1000°C used by the Oregon Metallurgical Plant [Froes, 2001]. After purification, the titanium sponge is crushed, screened, dried, and placed in air-tight containers. The energy required to convert TiCl_4 to sponge by the leaching route was reported to be 37 kWh per kg of sponge [Anonymous, 1975]; while energy consumption using vacuum distillation was approaching 15 kWh per kg of sponge [Ikeshima, 1984].

2.1.1.5. Emerging Direct Reduction Technologies of Titanium from Its Oxide

A novel FFC Cambridge process for titanium metal production has been developed by Fray, Farthing, and Chen [Chen *et al.*, 2000]. In the FFC Cambridge process, metallic titanium is produced by electrochemical reduction of titania. TiO_2 cathode is immersed into a molten CaCl_2 electrolyte with a graphite anode. It was estimated that industrial titanium production using this method would cost one-third of that using the Kroll process [Freemantle, 2000]. A schematic diagram of experimental setup for FFC Cambridge process is shown in **Figure 2.1 (a)**. Chen, *et al.* (2000) reported that the removal of a small amount of oxygen from electrically insulating rutile produced a highly conducting Magnelli phase (TiO_{2-x}). The electrolysis process removes the oxygen from the cathode where it

dissolves in the electrolyte and is then removed as O_2 , CO or CO_2 at the anode. The duration of the process is between 24 to 48 hours with resulting oxygen level below 1000 ppm and nitrogen of 5 to 20 ppm [Chen, *et al.*, 2000]. The simultaneous reduction of several oxides allowed production of an alloy and intermetallic compound such as: Ti-6Al-4V, TiAl, NbTi, and NiTi [EHK Technologies, 2004]. This process, however, has several disadvantages. The long processes, the cost of manufacture of TiO_2 electrode, purity control of titanium are the limitations for this process [EHK Technologies, 2004; Takeda and Okabe, 2005].

A number of technologies for direct titanium production from oxide are also under development, including Ono Suzuki (OS) process, BHP Biliton Polar process, Electronically Mediated Reaction/Molten Salt Electrolysis (EMR/MSE) process, Preform Reduction Process (PRP), MER process, and MIR Chem process [EHK Technologies, 2004].

In OS process (**Figure 2.1 (b)**), TiO_2 is reduced calciothermally in Ca-CaO- $CaCl_2$ solution baths. The reductant calcium is produced by the electrolysis of molten $CaCl_2$ salt. Titania powder is supplied to the molten $CaCl_2$ salt, and TiO_2 is reduced by calcium. Ca^{+2} is reduced to Ca at the cathode and oxygen is produced at the anode, combining with carbon to form CO or CO_2 [Suzuki and Inoue, 2003]. It was found that when TiO_2 particles are in contact with the cathode, low oxygen content in titanium could be achieved, whereas if the particles are electrically isolated, only sub-oxides are produced. This is attributed to the high concentration of Ca on the cathode. As low as 2000 ppm of oxygen was achieved in 3 hours and 420 ppm in 24 hours [Suzuki and Inoue, 2003]. Although the production of titanium with low content of oxygen in reasonable times and moderate cost with this process appears feasible, the separation of the titanium product from the bath constituents and purification to very low chloride level is still to be addressed. Calcium is soluble in molten $CaCl_2$, which increases electrical conductivity of the melt. This however, decreases the current efficiency of the process.

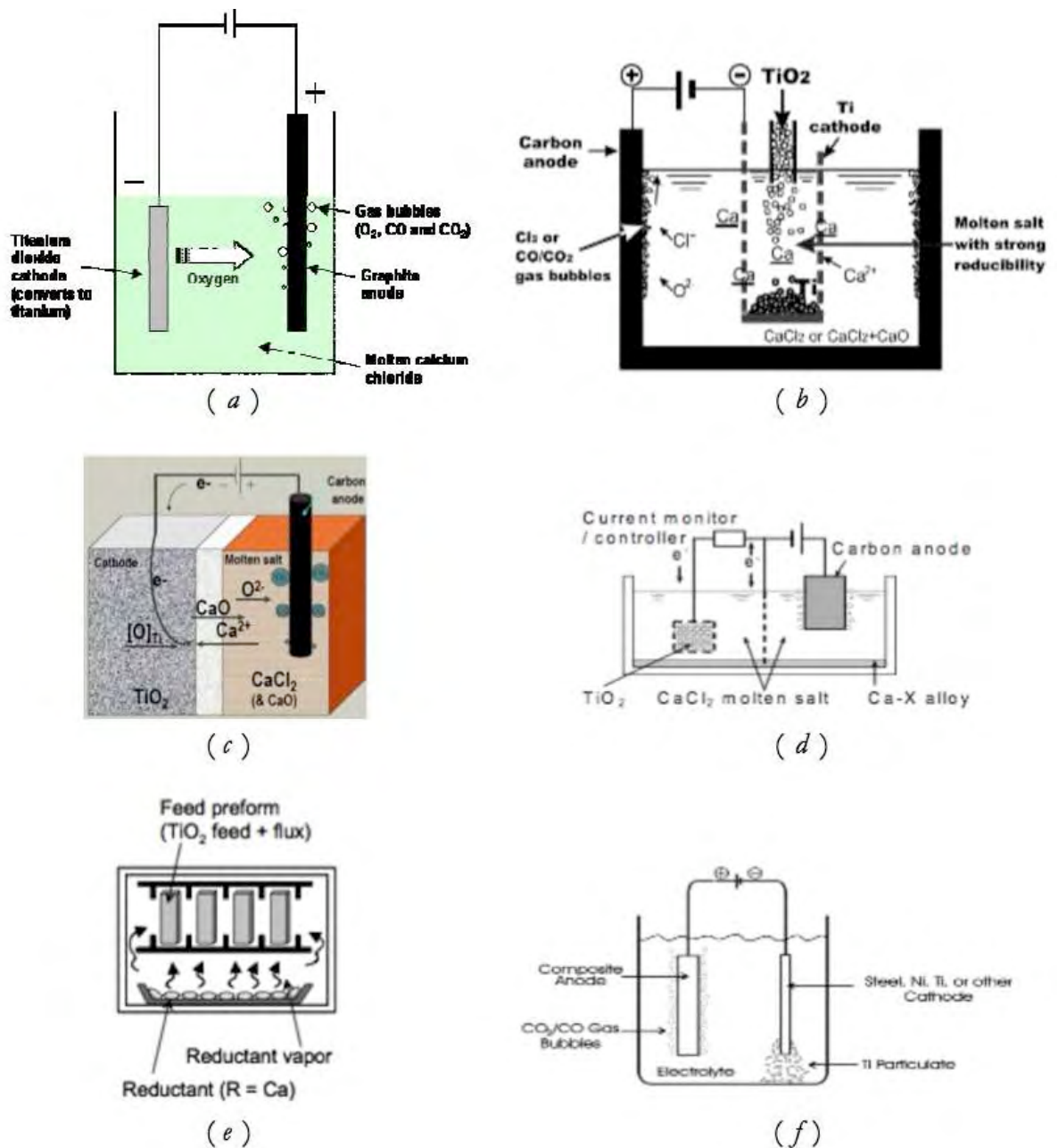


Figure 2.1. Schematic diagram of: (a) FFC Cambridge process [Chen *et al.*, 2000], (b) OS process [Suzuki and Inoue, 2003], (c) BHP Bilton Polar process [BHP Bilton, 2005], (d) EMR/MSE process [Abiko *et al.*, 2003], (e) PRP process [Okabe *et al.*, 2003], (f) MER process [Withers and Loutfy, 2003]

BHP Biliton Polar process (**Figure 2.1 (c)**) is claimed to work in the same way as the OS process where CaCl_2 is reduced to calcium which acts as a reductant. Its pilot plant has a capacity of producing $2 \text{ kg}\cdot\text{day}^{-1}$ of titanium [BHP Biliton, 2005]. As reduction reactions proceed, the titania progressively attains final product specifications, moving through a series of transitions to titanium metal.

The EMR/MSE process utilises an electronically mediated reaction in the metallothermic reduction. A schematic diagram of experimental setup for EMR/MSE process is shown in **Figure 2.1 (d)**. Titania powder or a preform is placed in a holder. An alloy of calcium with 18 mass pct of nickel is placed on the bottom of the reactor with carbon as the anode. This forms an electrochemical cell between TiO_2 cathode and Ca alloy. During this stage, TiO_2 is reduced and Ca ions are formed. With duration 2 to 4 hours, titanium was produced with impurity levels on the order of 0.15 to 0.2 wt pct Ca, 0.2 to 0.5 wt pct Fe, 0.04 to 0.16 wt pct Ni and 0.35 to 0.65 wt pct O_2 . The overall reaction of the FFC, OS, and EMR/MSE processes are identical.

In PRP process (**Figure 2.1 (e)**), TiO_2 and a flux of either CaO or CaCl_2 are formed into a pre-form and held with minimal contact in the space above a bath of molten Ca metal. The Ca metal vapour reacts with titania, forming Ti and CaO. Leaching and washing of the product produces titanium with oxygen content on the order of 2800 ppm. This process is essentially resistant to contamination and has flexible scalability since it is based on the metallothermic reduction using metal vapour.

In MER process (**Figure 2.1 (f)**), titania powder is mixed with carbonaceous material and binder, moulded into electrode form and heat treated to form a composite anode. Ilmenite can be used for iron containing alloys if the other impurities are tolerated. The composite anode contains a reduced TiO_2 as titanium oxycarbide. Ti^{+2} ions are released into the electrolyte, are further reduced and deposit as solid titanium on the cathode. Both CO and CO_2 are released at the anode. The form of titanium deposit is determined by salt composition and operating conditions. Powder with particle size from 1 to $125 \mu\text{m}$ has been produced.

In MIR-Chem process, TiO_2 is reacted with I_2 and CO gas forming TiI_2 and CO_2 . In the formation of TiI_2 , the process time is on the order of four days. Following this reaction, TiI_2 is thermally dissociated to titanium metal and I_2 , and the iodine is recycled.

In general, most of direct reduction processes of titanium from its oxide has several drawbacks such as requirement of expensive high grade titania feed, difficulties in scaling up to large quantity production, contamination of electrolyte which leads to low purity of titanium metal product, and low current efficiency.

2.1.1.6. Emerging Reduction Technologies of Titanium from TiCl_4

A number of technologies that use TiCl_4 as a feedstock have also been under development, including Armstrong/International Titanium Powder process, SRI International process, Idaho Titanium Technologies process, Vartech, CSIR, Ginatta, and CSIRO TiRO process [EHK Technologies, 2004; Brooks *et al.*, 2007].

In Armstrong/International Titanium Powder process, titanium metal is produced by the reduction of TiCl_4 with sodium. Liquid sodium is pumped through a cylindrical chamber containing a centreline second tube. TiCl_4 vapour is injected into the sodium stream through this nozzle. Reaction occurs immediately downstream with titanium powder being carried out in the excess sodium stream. Titanium, sodium, and sodium chloride are separated by filtration, distillation and washing. The powder produced has a purity level near to that of commercially pure Grade 1, including chlorine content of less than 50 ppm. The pilot plant with a full-scale reactor has achieved oxygen levels less than 1000ppm [EHK Technologies, 2004].

SRI International process utilises a high temperature fluidised bed to convert TiCl_4 and other metal chlorides to titanium or alloy that is deposited on a particulate substrate of the same material. This substrate is produced by crushing about 1 pct of the product to a smaller size and feeding back into the reactor. The feasibility of the alloy production has been demonstrated [EHK Technologies, 2004].

Idaho Titanium Technologies, Vartech, and CSIR process involves the thermal dissociation and reduction of TiCl_4 by hydrogen gas. It passes TiCl_4 through an electric arc in a vacuum chamber, which heats the vapour to over 3727 °C forming a plasma. A stream of

hydrogen carries the gas through the nozzle, where it expands and cools. The combined effect of rapid cooling (quenching), the reducing effect of hydrogen, and the formation of hydrochloric acid, prevent reversal reaction of titanium and chlorine. A very fine hydride powder is produced [EHK Technologies, 2004].

The Ginatta process utilises electrolytic process in which TiCl_4 vapour is injected into a molten halide electrolyte where it is absorbed. A multilayer cathodic interphase separates the molten titanium cathode from the electrolyte. This multilayer phase consists of ions of potassium, calcium, titanium, chlorine, and fluorine. The technology allows liquid titanium to be tapped continuously from the reaction vessel into a separate chamber [EHK Technologies, 2004].

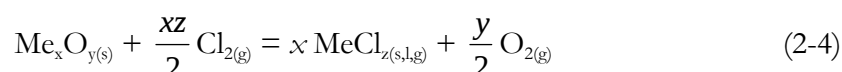
A novel process based on the continuous reduction of titanium tetrachloride with magnesium, producing a titanium powder, has been developed by the Light Metals Flagship of the Australian Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia. Drawing on CSIRO's expertise in fluidised bed technology, researchers have developed the TiRO process, which cuts the cost of titanium metal production. This process enables the reaction to occur at a lower temperature (650-712 °C) and continuously in fluidised bed. The process occurred between the melting point of magnesium (650 °C) and the melting point of MgCl_2 (712 °C). The first step of this process is the reduction of TiCl_4 with magnesium metal in a fluidised bed to produce fine titanium particles. The particles are co-deposited with MgCl_2 in composite pellets that form in the bed. The second step is separating the titanium from the MgCl_2 . A laboratory scale fluidised bed has been built and operated continuously for up to 60 h with a production rate of $5 \text{ kg}\cdot\text{day}^{-1}$ [Brooks *et al.*, 2007].

Currently commercial titanium metal production solely relies on carbochlorination of rutile and reduction of titanium tetrachloride. Chlorination of TiO_2 in the presence of coke or other reducing agents such as graphite or CO at temperature 800 to 1100 °C in a fluidised bed, leads to intermediate product TiCl_4 , which is subsequently reduced to titanium metal via Kroll (using magnesium) or Hunter process (using sodium). At these temperatures impurities are also chlorinated. Chlorination of titanium oxycarbide $\text{Ti}(\text{O},\text{C})$ or oxycarbonitride $\text{Ti}(\text{O},\text{C},\text{N})$, can be implemented at much lower temperature in the range

200 to 400 °C. At these temperatures, impurities do not chlorinate or chlorinate slowly [Kanari *et al.*, 1999; Hitching and Kelly, 1982; Hunter *et al.*, 1973].

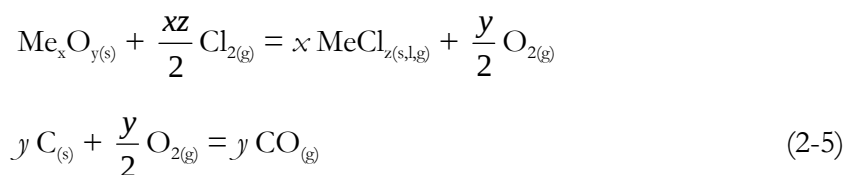
2.2. Thermodynamics and Kinetics of Chlorination Reactions

When a metal oxide exposed to an atmosphere with a sufficient chlorine partial pressure at elevated temperature, the metal reacts producing a metal chloride [Manukyan and Martirosyan, 2003].



where x, y are the stoichiometric coefficients, and z is the valence of the metal, Me.

In order to promote further reaction, oxygen must be continuously removed as soon as it is formed. This can be achieved by adding reductant carbon to the reaction mixture [Manukyan, Martirosyan, 2003]. When carbon is employed, the oxygen is removed as CO_2 or CO depending on the temperature of the reaction.



The most common chlorinating agents for rutile or ilmenite in industrial application are Cl_2 and HCl [Kanari *et al.*, 1999; Habashi, 1986]. The other possibilities include COCl_2 , CCl_4 , hexachloroethane and trichloroethylene that are produced in methane chlorination processes, as well as some by-products of processes for the synthesis of chloroprene and chloroparaffins [Lavecchia *et al.*, 1993].

Chlorination processes for extraction of valuable metals from mineral ores generally divided into: (a) *Direct chlorination* in which all the components of the ore are chlorinated and then separated in the gaseous state. In this process, most impurities are also chlorinated. (b) *Selective chlorination* in which only one or more components of the ore are chlorinated based upon the different forming affinity, leaving behind an enriched metal residue [Habashi, 1986]. Selective chlorination process is considered to be more economical and environmental friendly given that it operates at lower temperature,

produces less waste, and further separations of its gaseous products are generally not necessary. Attempts have been made to suppress the total chlorination by adding a controlled amount of reducing agents, by proper choice of a chlorinating gas, or by operating at specific temperature [Athavale and Altekhar, 1971].

Nowak (1969) patented a process for extractive metallurgy based on chlorine affinity series tabulated in **Table 2.1**. This process involved chlorination of metal oxide using other metal chloride with lower affinity for chlorine. Nowak used SiCl_4 to purify ore of Fe_2O_3 by converting Fe_2O_3 to FeCl_3 ; he also studied reaction of SiCl_4 with alumina.

Table 2.1. Comparison of chloride forming affinity for various metal elements at 600-1300°C [Nowak, 1969^(a); Medynski, 1976^(b)]*

1300 °C ^(a)	950 °C ^(b)	800 °C ^(a)	600 °C ^(a)
Pb	Ca	Cu	Cu
Zn	Cu	Zn	Ca
Co	Pb	Co	Pb
Ni	Zn	Sn	Zn
Sn	Mn	Ni	Mn
Fe	Bi	Fe	Bi
Ti	Ni	Ti	Ni
Ge	Fe	Ge	Mg
Al	Sn	Al	Sn
Si	Mg	Si	Fe
V	Ti	S	Cr
P	Cr	V	Zr
S	Zr	P	Ti
	Al		Al

* The elements are listed in order of decreasing chloride affinity

Figure 2.2 and **Table 2.2** show standard Gibbs free energy and enthalpy changes of various reactions as functions of temperature. The Gibbs free energy change itself does not give an indication for the reaction rate, as it is strongly dependent on the kinetic factors. It is quite common that chlorination reactions are thermodynamically feasible at low temperatures; the chlorination temperature is dictated by the kinetics of the reaction. This

is seen for carbochlorination of TiO_2 ; the Gibbs free energy change of the chlorination reaction is negative even at 0 °C (Figure 2.2); however, TiO_2 carbochlorination temperature is above 800 °C.

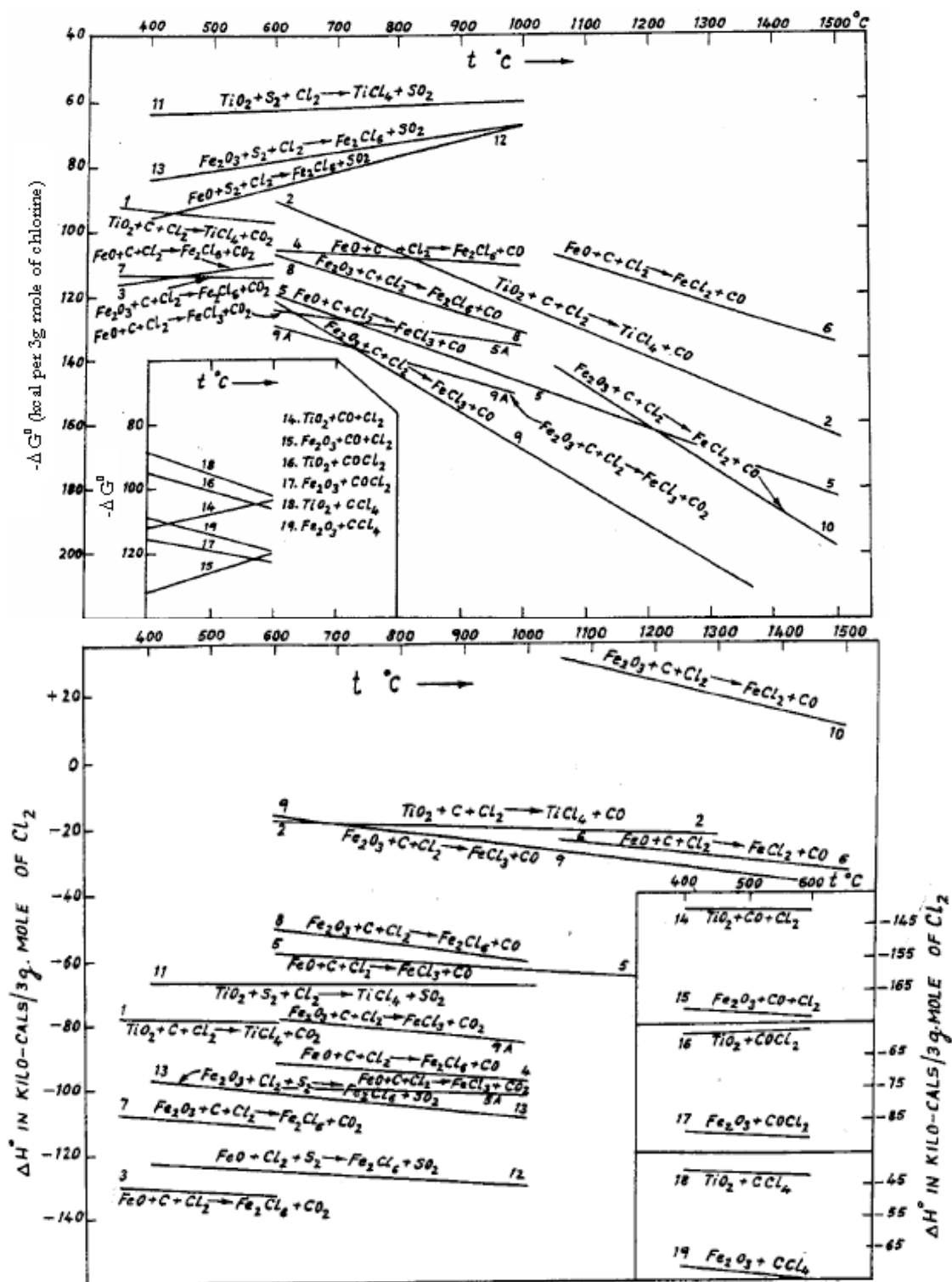


Figure 2.2. Standard free energy and enthalpy changes of various reactions as a function of temperature [Patel and Jere, 1960]

Table 2.2. Standard Gibbs free energy change and enthalpy change for various chlorination reactions [Patel and Jere, 1960]

$$\Delta G_T^0 = \left(\Delta H_0^0 - \Delta aT \ln T - \frac{\Delta b}{2} T^2 + \frac{\Delta c}{2T} + IT \right) \times 4.184 \text{ kJ}$$

$$\Delta H_T^0 = \left(\Delta H_0^0 + \Delta aT + \frac{\Delta b}{2} T^2 + \frac{\Delta c}{T} \right) \times 4.184 \text{ kJ}$$

No.	Reaction	ΔH_0^0	Δa	$\frac{\Delta b}{2} \times 10^3$	$\Delta c \times 10^{-5}$	I	Calculated Range of Temperature °K
A) Chlorine as chlorinating agent							
a) Carbon (graphite) as reducing agent							
1)	$3/2 \text{ TiO}_2(c) + 3\text{Cl}_2(g) + 3/2 \text{ C} = 3/2 \text{ TiCl}_4(g) + 3/2 \text{ CO}_2(g)$	-73989	-5.57	+0.735	-5.115	-63.57	573 to 873
2)	$3/2 \text{ TiO}_2(c) + 3\text{Cl}_2(g) + 3\text{C} = 3/2 \text{ TiCl}_4(g) + 3\text{CO}(g)$	-9720	-7.17	-0.18	-10.995	-140.8	above 873
3)	$2\text{FeO}(c) + 3\text{Cl}_2(g) + \text{C} = \text{Fe}_2\text{Cl}_6(g) + \text{CO}_2(g)$	-122079	-10.77	-1.14	-2.86	-59.7	573 to 873
4)	$2\text{FeO}(c) + 3\text{Cl}_2(g) + 2\text{C} = \text{Fe}_2\text{Cl}_6(g) + 2\text{CO}(g)$	-79179	-11.84	-1.75	-6.78	-111.6	873 to 1273
5)	$2\text{FeO}(c) + 3\text{Cl}_2(g) + 2\text{C} = 2\text{FeCl}_3(g) + 2\text{CO}(g)$	-47076	-9.84	-1.75	-6.78	-151.1	above 873
5A)	$2\text{FeO}(c) + 3\text{Cl}_2(g) + \text{C} = 2\text{FeCl}_3(g) + \text{CO}_2(g)$	-89975	-8.77	-1.14	-2.86	-99.17	873 to 1273
*6)	$3\text{FeO}(c) + 3\text{Cl}_2(g) + 3\text{C} = 3\text{FeCl}_3(g) + 3\text{CO}(g)$	-829	-13.53	-2.58	-9.15	-181.1	1323 to 1773
7)	$\text{Fe}_2\text{O}_3(c) + 3\text{Cl}_2(g) + 3/2 \text{ C} = \text{Fe}_2\text{Cl}_6(g) + 3/2 \text{ CO}_2(g)$	-99181	-7.51	-7.25	-6.364	-74.01	573 to 873
8)	$\text{Fe}_2\text{O}_3(c) + 3\text{Cl}_2(g) + 3\text{C} = \text{Fe}_2\text{Cl}_6(g) + 3\text{CO}(g)$	-34912	-9.11	-8.17	-12.244	-151.2	873 to 1273
9)	$\text{Fe}_2\text{O}_3(c) + 3\text{Cl}_2(g) + 3\text{C} = 2\text{FeCl}_3(g) + 3\text{CO}(g)$	-2808	-7.11	-8.17	-12.244	-190.6	above 873
9A)	$\text{Fe}_2\text{O}_3(c) + 3\text{Cl}_2(g) + 3/2 \text{ C} = 2\text{FeCl}_3(g) + 3/2 \text{ CO}_2(g)$	-67077	-5.51	-7.255	-6.364	-113.5	873 to 1273
*10)	$3/2 \text{ Fe}_2\text{O}_3(c) + 3\text{Cl}_2(g) + 9/2 \text{ C} = 3\text{FeCl}_3(g) + 9/2 \text{ CO}(g)$	65571	-9.43	-12.2	-17.346	-240.5	1323 to 1773
b) Sulfur as reducing agent							
11)	$3/2 \text{ TiO}_2(c) + 3\text{Cl}_2(g) + 3/4 \text{ S}_2(g) = 3/2 \text{ TiCl}_4(g) + 3/2 \text{ SO}_2(g)$	-63432	-5.09	1.68	-3.488	-31.86	673 to 1273
12)	$2\text{FeO}(c) + 3\text{Cl}_2(g) + 1/2 \text{ S}_2(g) = \text{Fe}_2\text{Cl}_6(g) + \text{SO}_2(g)$	-114818	-11.11	-0.51	-1.775	-43.52	673 to 1273
13)	$\text{Fe}_2\text{O}_3(c) + 3\text{Cl}_2(g) + 3/4 \text{ S}_2(g) = \text{Fe}_2\text{Cl}_6(g) + 3/2 \text{ SO}_2(g)$	-88326	-8.03	-6.31	-4.737	-48.96	673 to 1273
c) CO (g) as reducing agent							
14)	$3/2 \text{ TiO}_2(c) + 3\text{Cl}_2(g) + 3\text{CO}(g) = 3/2 \text{ TiCl}_4(g) + 3\text{CO}_2(g)$	-138414	-3.96	+1.65	+0.765	+14.96	673 to 873
15)	$\text{Fe}_2\text{O}_3(c) + 3\text{Cl}_2(g) + 3\text{CO}(g) = \text{Fe}_2\text{Cl}_6(g) + 3\text{CO}_2(g)$	-163606	-5.9	-6.34	-0.484	+4.54	673 to 873
B) $\text{COCl}_2(g)$ as Chlorinating agent							
16)	$3/2 \text{ TiO}_2(c) + 3\text{COCl}_2(g) = 3/2 \text{ TiCl}_4(g) + 3\text{CO}_2(g)$	-59690	-0.66	+3.21	+3.135	-55.08	673 to 873
17)	$\text{Fe}_2\text{O}_3(c) + 3\text{COCl}_2(g) = \text{Fe}_2\text{Cl}_6(g) + 3\text{CO}_2(g)$	-84883	-2.6	-4.78	+1.886	-65.48	673 to 873
C) $\text{CCl}_4(g)$ as Chlorinating agent							
18)	$3/2 \text{ TiO}_2(c) + 3/2 \text{ CCl}_4(g) = 3/2 \text{ TiCl}_4(g) + 3/2 \text{ CO}_2(g)$	-34877	-7.97	-0.14	-5.325	-131.6	673 to 873
19)	$\text{Fe}_2\text{O}_3(c) + 3/2 \text{ CCl}_4(g) = \text{Fe}_2\text{Cl}_6(g) + 3/2 \text{ CO}_2(g)$	-60068	-9.91	-8.125	-6.574	-142.0	673 to 873
*Hypothetical, $\text{FeCl}_3(g)$ as product of reaction.							

2.2.1. Chlorination of TiO_2

Chlorination of titania (which is a refined form of rutile) is exothermic reaction; it has been intensively investigated in the high temperature range of 800 to 1500 °C [Rao, 1988; Habashi, 1986; Froes, 2001]. At temperature below 800 °C, the rate of the chlorination reaction was found to be too slow [Medynski, 1956]. The standard Gibbs free energy change, ΔG° at temperature 1000 °C indicates that chlorination of TiO_2 in Reaction (2-7) is not thermodynamically feasible without the addition of a reducing agent such as carbon shown in Reaction (2-8):



In the absence of carbon, Zverev and Barsukova (1960) reported that the reaction started at 800 °C only with continuous removal of gaseous products. Rapid reaction was observed at 1200 °C [Zverev and Barsukova, 1960]. Introducing a reducing agent as in the case of Reaction (2-7), will reduce oxygen potential favouring chloride formation, prevent the reversal reaction, and reduce initiation reaction temperatures and energy consumption [Barksdale, 1949; Gamboa *et al.*, 1999]. Zverev and Barsukova (1960) reported that carbochlorination of titania was initiated at 500 °C and achieved rapid reaction at 700 °C.

Jena *et al.* (1998) studied kinetics of carbochlorination of TiO_2 using graphite powder in the temperature range of 500 °C to 1000 °C. In this temperature range, Jena *et al.* (1998) suggested that of the reaction of TiO_2 chlorination followed a topochemical reaction model, $1-(1-\alpha)^{1/3} = kt$. He presented the chlorination reaction at temperature below 700 °C by equation 2-9 [Jena *et al.*, 1998; Chase, 1998]:

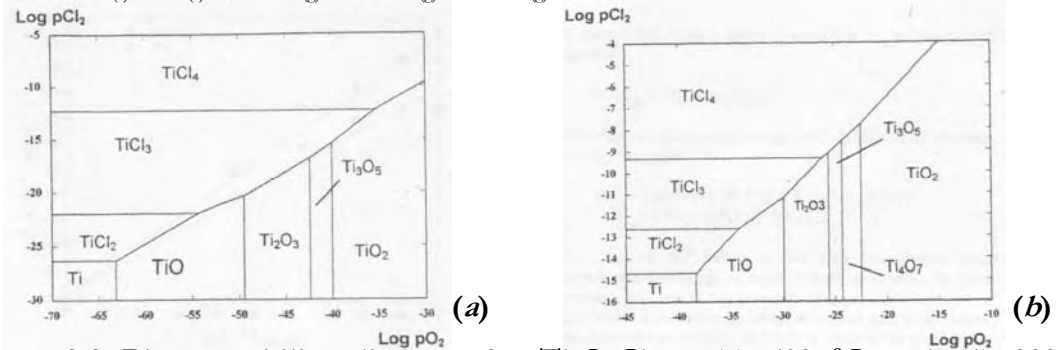
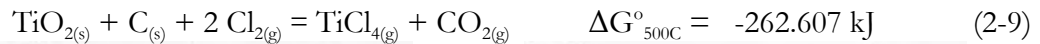


Figure 2.3 Phase stability diagram for Ti-O-Cl at (a) 500 °C and (b) 900 °C [Kubaschewski *et al.*, 1993]

Based on the kinetic results and phase stability diagram for Ti-O-Cl shown in **Figure 2.3**, Jena *et al.* (1998) suggested that Reaction (2-9) could proceed through the following reactions [Jena *et al.*, 1998; Chase, 1998]:



At 500 to 600 °C, Jena *et al.* (1998) suggested that Reaction (2-10) is the rate-controlling step. However, the standard Gibbs free energy change for Reaction (2-10) shows that the formation of TiCl₂ is not favourable at 500 °C. The boiling points of intermediate chlorides are also high (1500 °C and 960 °C for TiCl₂ and TiCl₃, respectively) and may not be easily removed by flowing gas as previously suggested by Jena *et al.* (1998). This could indicate that chlorination of titania could proceed only through Reaction (2-8) without the formation of intermediates TiCl₂ and TiCl₃.

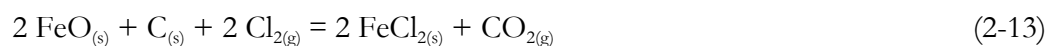
Noda (1955) investigated the carbochlorination of rutile briquettes using solid carbon. He discovered that the reaction is a first order surface reaction that depends heavily on chlorine concentration. The rate determining factors are the chemical reaction at temperature under 900 °C and the laminar film diffusion above this temperature.

Lin and Chiu (1988) studied kinetics of carbochlorination of rutile pellet using petroleum coke, amorphous graphite, and crystallised graphite in the temperature range 655 °C to 1130 °C. It was found that the chlorination rate was increased by increasing reaction temperature, carbon to TiO₂ molar ratio, and increasing chlorine partial pressure.

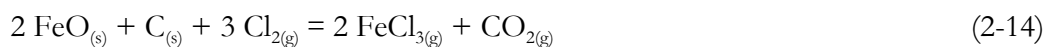
Morris and Jensen (1976) investigated carbochlorination of rutile using CO and carbon using fluidised bed. They found that temperature has appreciable influence on the reaction rate. CO and Cl₂ partial pressures also affect the rate. Fluidising gas velocity and the bed height have small effect on the reaction rate.

2.2.2. Chlorination of Ilmenite

Perkins *et al.* (1961) investigated carbochlorination of Idaho ilmenite ore in a moving bed at temperature 1000 °C. They found that when ilmenite ores with high iron contents are chlorinated, the following additional reactions become significant [Perkins *et al.*, 1961]:



For temperature below 1000 °C, the reactions favoured the formation of ferric chloride [Perkins *et al.*, 1961]:



Kanari *et al.* (1999) studied carbochlorination of wüstite and hematite with CO by thermogravimetric analysis using non-isothermal conditions up to 1000 °C. The wüstite started to react with CO and Cl₂ at temperature lower than 250 °C, producing ferric chloride and hematite (wüstite reacting with ferric chloride formed ferrous chloride and hematite; ferrous chloride then reacted with chlorine to form ferric chloride). Carbochlorination of hematite began at temperature of 550 °C with ferric chloride as main product. Kanari *et al.* (1999) observations were corroborated by the work of Okahara and Iwasaki (1970) and Fruehan and Martonik (1973).

Fruehan and Martonik (1973) investigated chlorination of Fe₂O₃, NiO, and NiFe₂O₄ at 800 °C to 1200 °C. They indicated that chlorination of Fe₂O₃ leads to several products such as FeCl_{2(s)}, Fe₂Cl_{6(g)}, and FeCl_{3(g)}. For the temperature range in their investigations, formation of FeCl₃ is thermodynamically most favoured thermodynamically [Fruehan and Martonik, 1973]. At temperature higher than 414 °C, FeCl₃ decomposes with formation of FeCl₂ [Patel and Jere, 1960]. FeCl₂ has melting point of 674 °C and boils at 1024 °C [Aylward and Findlay, 1994]. Thus, the FeCl₂ presence in the state of liquid in the reactor can cause a collapse of the fluid bed. The boiling point of FeCl₃ is 315 °C, lower than that of FeCl₂.

The solid impurities formed in the condensate when ilmenite is directly chlorinated may be as much as 50 pct by weight [Perkins *et al.*, 1961]. Therefore TiCl₄-FeCl₃ mixture is not fluid and cannot be handled by conventional condensing systems, thus either a trap for FeCl₃, or a special condensing system is necessary. With the differences in the boiling point between TiCl₄ and impurities, distillation is generally used for purification of TiCl₄. **Figure 2.4 and Figure 2.5** present vapour pressure and boiling temperatures of common impurities of halides, respectively. The volatility of the halides and the difference in their vapour pressure can be employed in separating the halides.

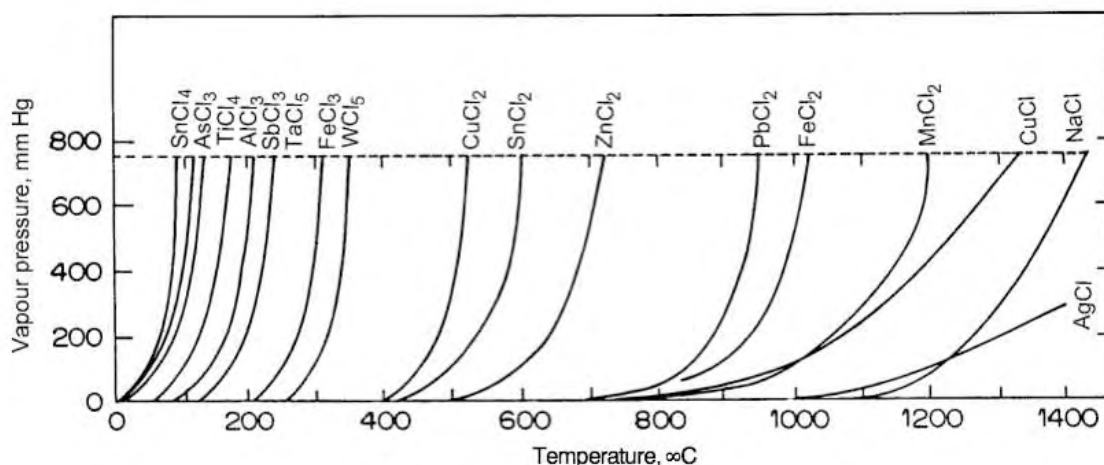


Figure 2.4. Vapour pressure of common impurities of halides [Gupta, 2003]

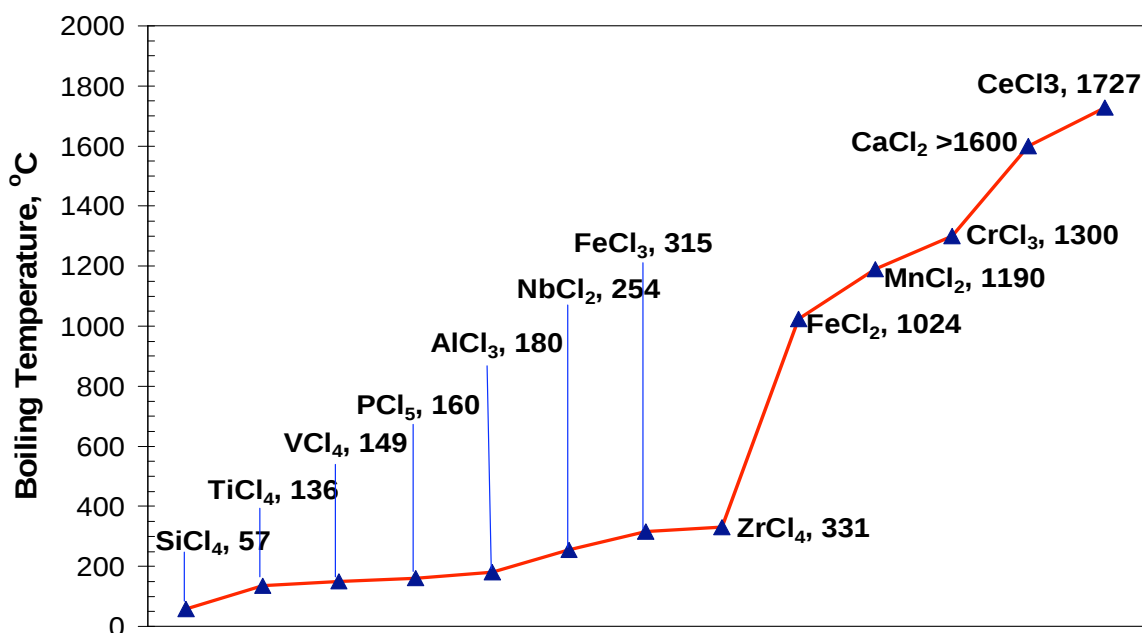
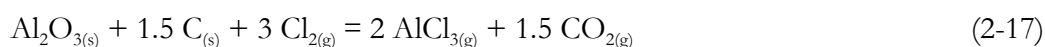
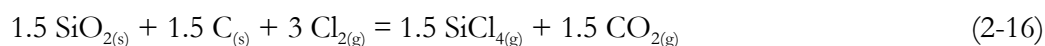
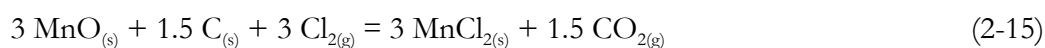


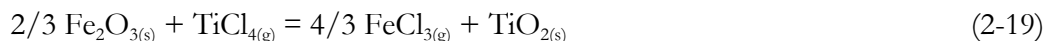
Figure 2.5. Boiling temperature of common impurities of halides [Aylward and Findlay, 1994]

Impurities such as manganese oxide, silica, and alumina were carbochlorinated. Carbochlorination of MnO was reported to start at 250 °C, SiO₂ at 1200 °C, and Al₂O₃ was reported to start at 800 °C. [Zverev and Barsukova, 1960; Titi-Manyaka and Iwasaki, 1973].



At temperature of 1000 °C during carbochlorination of TiO₂, the presence of TiCl₄ vapour could further chlorinate other impurities that have higher chlorine affinity as indicated by

Noda (1950), Habashi (1986), and Nowak (1969). The ignition temperatures for Reactions (2-18) to (2-21), however were not reported.



The AlCl_3 and SiCl_4 formed from Al_2O_3 and SiO_2 are able to chlorinate TiO_2 and other impurities that have higher chloride affinity. However, the content of these chlorides at temperatures of titania chlorination is small and these reactions have no practical significance. Constant removal of gaseous products from the reactor also ruled out the possibilities of chlorination of impurities by TiCl_4 , AlCl_3 , or SiCl_4 .

2.2.3. Selective Chlorination of Ilmenite

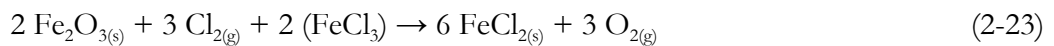
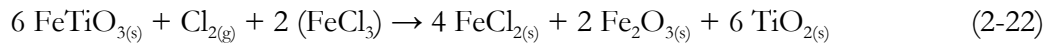
Selective chlorination is a process in which one or more components of the ore are chlorinated leaving behind an enriched metal residue. In iron selective chlorination, iron is extracted as volatile iron chlorides leaving behind enriched TiO_2 residues.

Titanium can be also selectively chlorinated from ilmenite. However, this requires two steps process which involves carbothermic reduction followed by low temperature chlorination. Selective chlorination which is generally employed in ilmenite beneficiation, has been extensively studied. Smillie *et al.* (1997) investigated process developed for selective chlorination of low-grade titanium-containing ores. The ore is first subjected to carbothermal reduction under nitrogen in which the titanium oxide is converted to carbonitride. Titanium carbonitride chlorinates at much lower temperature of 350 °C. At this temperature, the other oxides are not reactive and therefore a relatively pure titanium tetrachloride product can be obtained. A study of chlorination of ilmenite in this project does not support this finding.

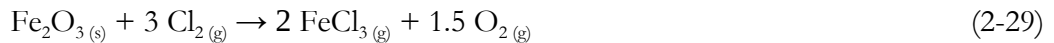
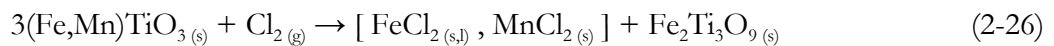
Mostert *et al.* (1992) and Van Vuuren and Stone (2006) developed processing of titanium minerals using reduction and nitridation of titanium oxides. Titanium oxide in titanium ores and slags can be nitrided at temperatures of 1000 to 1800 °C. Optimal chlorination temperature was found between 200 and 500 °C. At these temperatures, Van Vuuren and Stone (2006) had indicated that only the reduced metal oxides such as titanium, iron, and vanadium were selectively chlorinated leaving residues of CaO , MgO , SiO_2 and Al_2O_3 .

Brandstatter (1985) developed a technology, in which titanium in ilmenite ore and slag was carburised at 1700-2000 °C. The process described by Nanjo *et al.* (1988) is similar to that suggested by Brandstatter (1985), but used anatase as a raw material and lower carburisation temperature (1200-1300°C). Anatase is one of the three mineral forms of titanium dioxide, the other two being brookite and rutile [Donachie, 1988; Froes, 2001; Barksdale, 1949]. Iron or iron carbide formed during the carbothermal reduction were separated from titanium carbide by crushing and magnetic separation [Brandstatter, 1985; Nanjo *et al.*, 1988]. Brandstatter (1985) and Nanjo (1988) found that the chlorination temperature was 200 to 500 °C. The process described by Brandstatter (1985), carburised ilmenite ore at much higher temperature than the work in this project, which was at 1450 °C.

Rhee and Sohn (1990*a*, 1990*c*) investigated the kinetics of selective chlorination of ilmenite ore in a fluidised bed by CO-Cl₂ gas mixture in the temperature range 650 °C to 850 °C. The experiments were conducted in a shallow fluidised bed to minimise heat and mass transfer resistance. For selective chlorination of iron, they suggested that the partial pressure of oxygen should be in the range 10⁻⁸ to 10⁻³ atm while the chlorine partial pressure in the range of 10⁻² to 1 atm. This could be achieved by using high chlorine flow rate or by vacuum treatment. The reaction mechanism for selective chlorination of iron from ilmenite ore was represented by [Rhee and Sohn, 1990*a*]:



Fouga *et al.* (2007) also proposed a mechanism of selective iron or manganese chlorination of ilmenite ores based on thermogravimetric analysis at 600 °C to 850 °C. It is described by Reactions (2-26) to (2-29). Unlike Rhee and Sohn (1990*a*), their reaction mechanism did not take into account the effect of ferric chloride on chlorination of ilmenite.



Kelley *et al.* (1954) showed that ilmenite is stable even up to its melting point (1367 °C) and does not decompose into constituent oxides. Most of the reaction products of chlorination of ilmenite in the presence of reducing agents will be in equilibrium with their dissociation products depending on the temperature.

The experimental work by Rhee and Sohn (1990a) was used to model carbochlorination of ilmenite [Rhee and Sohn, 1990b]. They calculated activation energy of 37.2 kJ·mol⁻¹ in the temperature range of 650 °C to 850 °C [Rhee and Sohn, 1990b]. Yang and Hlavacek (1998) found that activation energy for chlorination of TiO₂ was 54.4 - 73.4 kJ·mol⁻¹ by Cl₂-CO and 6.9 - 19.3 kJ·mol⁻¹ by Cl₂-C. The activation energy calculated by Yang and Hlavacek (1998) is comparatively low for chemically controlled process and could indicate pore diffusion limitation. Low activation energy was also found in chlorination of other metal oxides: 58.2 kJ·mol⁻¹ for ZnO [Matsuura and Tsukihashi, 2006], 49 kJ·mol⁻¹ for MgO [Kanari and Gaballah, 1999], 18.3 kJ·mol⁻¹ for ZrO₂ with petroleum coke as reductant [Jena *et al.*, 1999], 23.81 kJ·mol⁻¹ for Ga₂O₃ [Gonzalez *et al.*, 2005], 57-115 kJ·mol⁻¹ by CCl₄ for Nb₂O₅ [Jena *et al.*, 1997], 110 kJ·mol⁻¹ by Cl₂-CO for Ta₂O₅ [Allain *et al.*, 1997], 74 kJ·mol⁻¹ by Cl₂-CO for Nb₂O₅ [Allain *et al.*, 1997], 83 kJ·mol⁻¹ by Cl₂-CO for MoO₃ [Allain *et al.*, 1995a], 100 kJ·mol⁻¹ by Cl₂-CO for V₂O₅ [Allain *et al.*, 1995b]. Jena *et al.* (1999) described that dissociation of unstable intermediates produced by adsorption of chlorine atom on metal oxide as rate determining step could lead to relatively low activation energy.

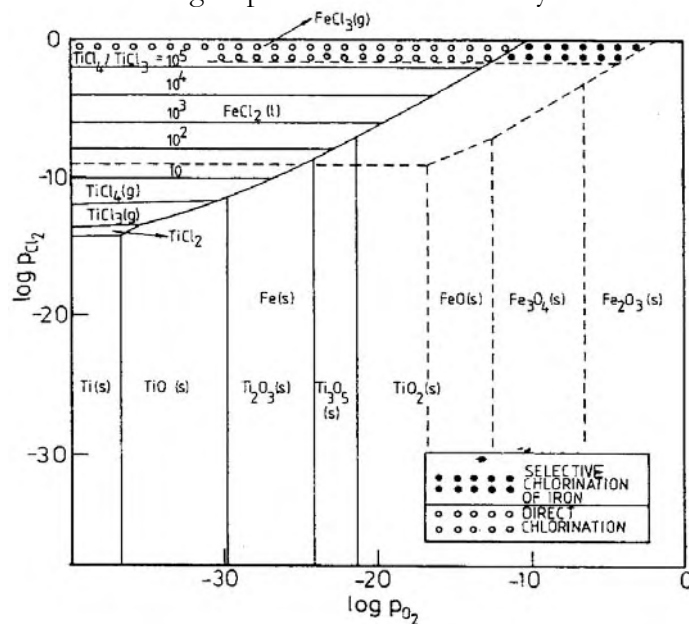


Figure 2.6. Predominance area diagram for the Ti-Fe-O-Cl system at 927 °C [Van Deventer, 1988]. The symbols ○ and ● indicate the condition for direct chlorination and selective chlorination of iron from ilmenite ores respectively.

The conditions for direct chlorination and selective chlorination of iron from ilmenite ores are shown on the predominance area diagram for the Ti-Fe-O-Cl system at 927 °C in **Figure 2.6**. Van Deventer (1988) experimentally investigated the kinetics of the selective carbochlorination of ilmenite using graphite in horizontal tube furnace in the range of 915 to 970 °C. He discovered that preferential iron chlorination could occur (**Figure 2.7**).

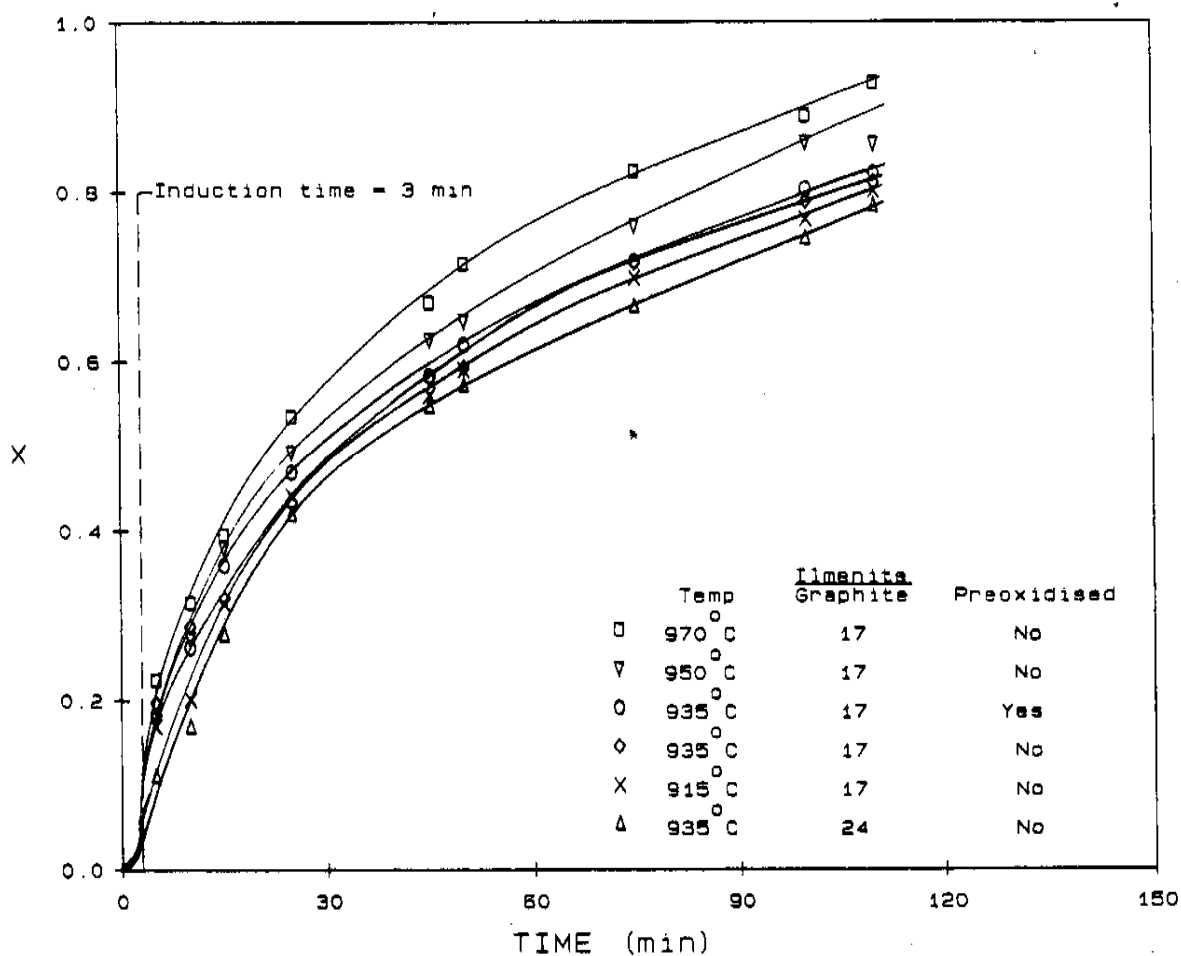
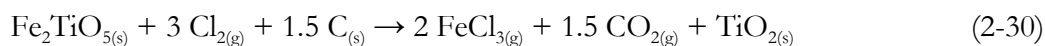


Figure 2.7. Kinetics of selective chlorination of ilmenite for different experimental conditions [Van Deventer, 1988]

Both direct and selective chlorination required relatively high chlorine partial pressure (approaching 1 atm) with very low oxygen partial pressure. A reductant such as carbon is required to obtain these conditions. At 927 °C and 1 atm pressure, Van Deventer (1988) suggested that chlorination of ilmenite in the presence of carbon should produce both iron and titanium chlorides. Selective chlorination of ilmenite will occur if the partial pressure of oxygen is greater than 10^{-12} atm. In the presence of carbon this is not theoretically possible,

but may occur by limiting the amount of carbon and by using carbon with low reactivity [Van Deventer, 1988].

Fuwa *et al.* (1978) also investigated the selective chlorination of iron oxide of pseudobrookite, Fe_2TiO_5 , in roasted or preoxidised ilmenite ore, using fluidised bed reactor. The reaction is described as:



It was found that preferential iron chlorination is dependent on roasted product morphology; nevertheless it is necessary to roast the raw ilmenite ore at 950 °C to convert ferrous iron to the ferric state [Fuwa *et al.*, 1978]. Ores that roasted below 900 °C were unsuitable for preferential chlorination especially in the case where hematite was precipitated as a roasted product. Fuwa *et al.* (1978) claimed that pre-oxidation of ilmenite to pseudobrookite leads to a better selective iron chlorination. Van Deventer (1988) and Misra and Bhatnagar (1968), on the other hand, found that preoxidation did not enhance selective iron carbochlorination significantly. Van Deventer (1988) roasted ilmenite in air at 1000 °C for 4 h followed by carbochlorination in a static bed. The roasting yielded little or no benefit at chlorination temperature of 935 °C (**Figure 2.7**). The differences in Fuwa *et al.* (1978) and Van Deventer (1988) observations on the effect of preoxidation could be from the dissimilarity of reactor type and the origins of ilmenite ores. Fuwa *et al.* (1978) employed fluidised bed to study Australian ilmenite while Van Deventer (1988) used fixed bed reactor to examine ilmenites ores from South Africa. In fluidised bed, Fuwa *et al.* (1978) achieved uniform particle mixing and temperature gradients within the bed. This however created distances between TiO_2 and carbon. The close packing of TiO_2 -C is crucial for mass transfer between solid particles (through the gas phase), which is shown on Section 2.3.1. Australian ilmenite ore used by Fuwa *et al.* (1978) had lower iron content compare to South African ilmenite ore, which was used by Van Deventer.

Van Deventer (1988) observed a significant change in composition of a grain of ilmenite after 5, 15, and 25 min of carbochlorination at 915 °C shown in **Figure 2.8**. He suggested that the conditions within the bed of ilmenite in the sample boat were not uniform. Grains on the surface were more accessible to chlorine and were converted to a greater extent than those below the surface.

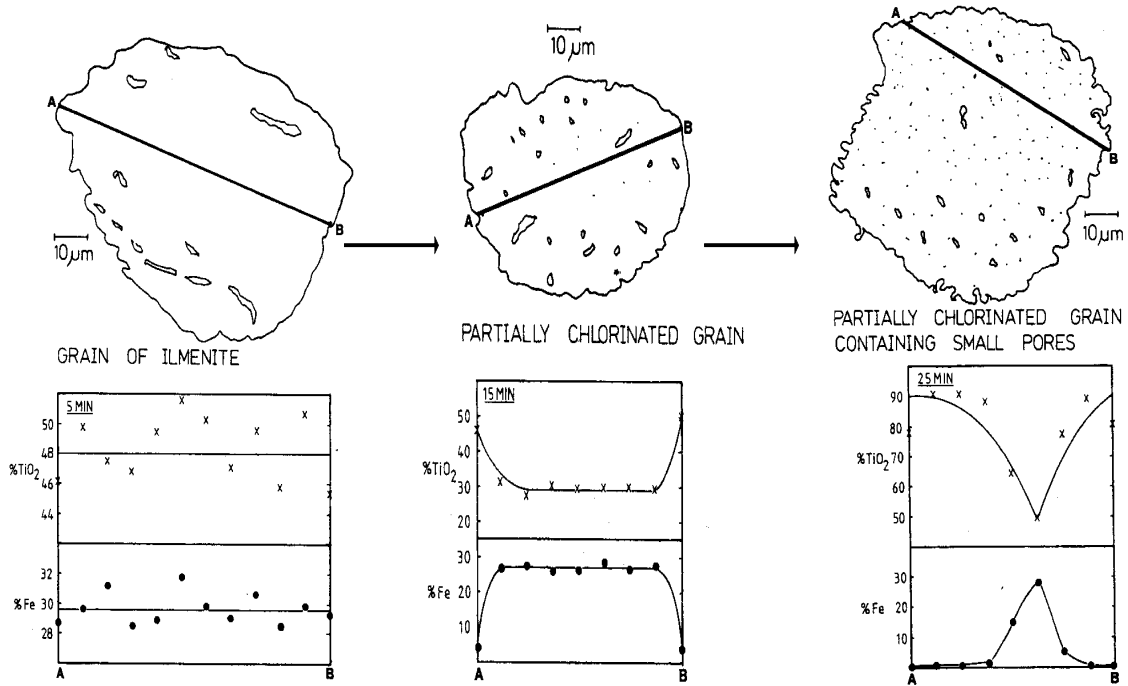


Figure 2.8. Composition of a grain ilmenite after carbochlorination at 915 °C for 5, 15, and 25 minutes [Van Deventer, 1988]

Based on these findings, Van Deventer (1988) concluded that carbochlorination of ilmenite at 915 °C can be described by shrinking core model. This conclusion is also in agreement with Fuwa *et al.* (1978).

Van Deventer (1988) found that the rate controlling step is diffusion of iron through a product layer of TiO_2 which formed on the particle surface. This finding was based on satisfactory fit of his experimental data to the spherical shrinking core model. The extent of chlorination X as a function of time for the diffusion through the reacted layer control is described by the equation:

$$\frac{t}{\tau} = f(X) = 1 - 3(1 - X)^{2/3} + 2(1 - X) \quad (2-31)$$

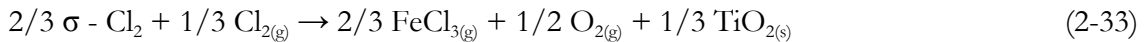
where τ is the total time required for full conversion $X = 1.0$

Van Deventer (1988) did not discuss in which form iron was diffusing. However, it can be concluded from his paper, that Van Deventer meant diffusion of gaseous FeCl_3 through TiO_2 shell. This was corroborated with Fuwa *et al.* (1978) findings, which also indicated that gaseous diffusion FeCl_3 through solid product layer TiO_2 was rate controlling.

Fuwa *et al.* (1978), suggested that selective carbochlorination of Fe_2TiO_5 is controlled by chemical reaction at the early stage when the outer product layer of TiO_2 is thin. Gradually, the reaction moves into the state where gaseous diffusion through the thickening product layer takes control. Fuwa *et al.* (1978) also suggested elementary reaction steps along the chlorination reaction which are shown below [Fuwa *et al.*, 1978]:



Elementary chemical reaction step:



where σ is the active site of the pseudobrookite on which chlorine is adsorbed and is being consumed by the chlorination, i.e., $\sigma = 1/2 (\text{Fe}_2\text{TiO}_5)$

Then, the overall reaction is given by:

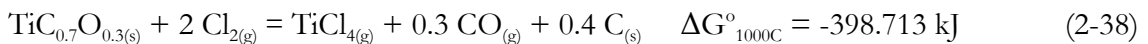
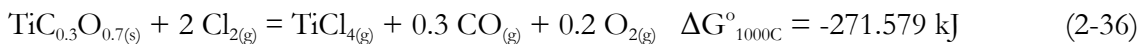
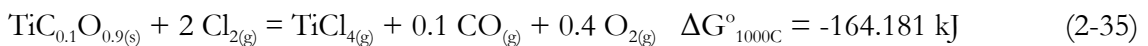
adsorption step + $3/2 \times$ (*elementary chemical reaction step*)

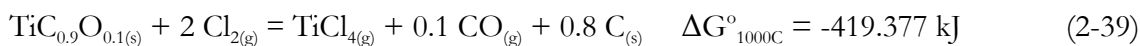


2.2.4. Chlorination of TiO, TiC, and TiN

The reduction of TiO_2 to TiC is difficult and some amount of oxygen always exists in the final product leaving solid solution of TiC-TiO [Zhang and Ostrovski, 2000]. Meerson *et al.* (1968), on the other hand suggested that complete reduction to TiC is not essential as the solid solution of TiC-TiO is quite suitable for chlorination.

Lower titanium oxides can be chlorinated without the addition of carbon [Vasyutinskii and Berezhko, 1967], what indicates that titanium sub-oxides chlorinate at lower temperatures compared to titania. Reactions (2-35) to (2-40) showed that the chlorination reaction thermodynamically is more favourable with decreasing the oxygen content in titanium oxide. This can be illustrated by the standard Gibbs free energy change for the following reactions at 1000 °C [Chase, 1998; Suzuki *et al.*, 1993]:





Chlorination of titanium oxycarbide ($\text{TiC}_{0.5}\text{O}_{0.5}$) produced no carbon residue as it is continuously removed in the form of CO. This could shift the reaction to the right by removal of TiCl_4 vapour and CO. Commercially this would be advantageous as there will be no downtime required for removal of unreacted product in the fluidised bed.

Chadwick and Rao (1988) calculated carbon and energy requirements for chlorination of titanium oxides in the systems $\text{Ti}_3\text{O}_{5(s)}\text{-Cl}_{2(g)}\text{-C}_{(s)}$, $\text{Ti}_2\text{O}_{3(s)}\text{-Cl}_{2(g)}\text{-C}_{(s)}$, $\text{TiO}_{(s)}\text{-Cl}_{2(g)}\text{-C}_{(s)}$ and found that less carbon was consumed in the chlorination of lower oxides. They concluded that this is due to smaller oxygen content in comparison with titania. Chadwick and Rao (1988) also computed the enthalpy changes that accompany the chlorination of these oxides. Chlorination of lower titanium oxides in the range of 827 to 1227 °C at 1 atm is exothermic.

The heat released in the chlorination process increases with the declining oxygen to titanium ratio of the oxide. Sponge titanium metal starts chlorinating at temperature as low as 120 °C, while the various titanium compounds such as TiN, TiCN, TiOC, or TiS_2 will react vigorously with chlorine at the temperature ranging from 250 to 400 °C; titania is carbochlorinated at 500 °C and achieves high chlorination rate at 700 °C [Rowe and Opie, 1955; Zverev and Barsukova, 1960].

Table 2.3. Enthalpy and Gibbs free energy of formation of various titanium compounds at 25 °C [Chase, 1998]

Compound	ΔH° , kJ	ΔG° , kJ
TiO_2	-944.747	-889.406
TiCl_4	-804.165	-737.219
TiO	-542.665	-513.278
TiN	-337.649	-308.929
TiC	-184.096	-180.438

Table 2.3 shows standard enthalpy and standard Gibbs free energy of formation of various titanium compounds at 25 °C [Chase, 1998]. Based on the standard Gibbs free energy of

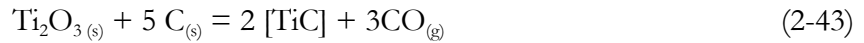
formation of various titanium compounds at 25 °C, Rowe and Opie (1955) suggested that TiO, TiN and TiC under standard conditions are less stable than TiCl₄ and therefore will chlorinate readily. The more stable titania can be chlorinated only in the presence of a reducing agent such as carbon or CO. It is apparent that TiO, TiN or TiC are by far the most efficient charge materials for chlorination than TiO₂ [Rowe and Opie, 1955].

Nieberlein (1957) investigated the process of low temperature chlorination of titanium carbide and suboxides produced by carbothermal reduction at 1500 °C. He found that temperature of 250 °C was sufficient to ignite the reaction; chlorination was performed at 400-500 °C. The ignition temperature means the temperature when the chlorination starts while chlorination temperature is the temperature at which the process proceeds with acceptable rate. Meerson *et al.* (1968) proposed a technology combining carburisation and low temperature chlorination for the production of titanium tetrachloride from titanium-iron concentrates and titanium slags. They found that carbothermal reduction at 1350-1450 °C and 150 - 200 mmHg pressure converted titania to titanium oxycarbide with 50-60 pct TiC and 50-40 pct TiO during 30 - 120 min. The chlorination rate of titanium oxycarbide at 600-700 °C was greater than that of titanium slag at 700-900 °C, but no detailed kinetic examination was reported. Zelikman and Leonova (1978) investigated the chlorination of titanium carbide in the form of compact briquettes at 600-900 °C. The reaction rate was controlled by the chlorine diffusion in the layer of carbon residue formed in the process of titanium chlorination.

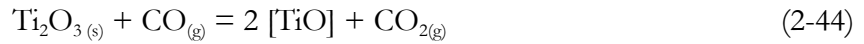
Hunter *et al.* (1975) developed technology for processing of calcium-containing titanium ores and slags. The materials reacted with solid carbon at high temperature between the melting points of CaC₂ and TiC (2160 °C to 3160 °C), and formed TiC distributed in the matrix of CaC₂. After cooling down, CaC₂ was removed by the reaction with water, and TiC was chlorinated at temperature above the boiling point of TiCl₄ and below chlorination temperature for impurities; high purity TiCl₄ was obtained without distillation. This technology was also applied to titaniferous ores [Elger *et al.*, 1980]. In general, CaC₂ is produced commercially by reaction of high purity quicklime and petroleum coke in an electric furnace at 2000 °C to 2200 °C and is formed in the liquid state [Cameron, 2001]. The technology developed by Hunter *et al.* (1975) is similar to the existing CaC₂ smelting production process that operates at temperature higher than CaC₂ boiling point (2300 °C).

2.2.5. Synthesis of Titanium Oxycarbide and Oxycarbonitride

In the synthesis of titanium oxycarbide by carbothermal reduction, TiO_2 is reduced through the Magnéli phases to Ti_3O_5 and Ti_2O_3 , and then a TiO-TiC solid solution is formed [Dewan *et. al*, 2009]. The carbothermal reduction reactions can be presented as follows [Dewan *et. al*, 2009]:



In argon and helium, Reactions (2-42) and (2-43) proceed through the following reactions [Dewan *et. al*, 2009]:



The CO_2 formed in Reactions (2-44) and (2-45) is then converted to CO by the Boudouard reaction [Dewan *et. al*, 2009]:



The standard Gibbs free energy for Reactions (2-41) to (2-46) was calculated using NIST-JANAF Thermochemical Tables in the temperature range of 1027-1527 °C [Chase, 1998; Dewan *et. al*, 2009]. The equilibrium partial pressure of CO for these reactions is presented in **Figure 2.9 (a)**. The reduction of TiO_2 to Ti_2O_3 thermodynamically is much easier than Ti_2O_3 further reduction to TiO and TiC.

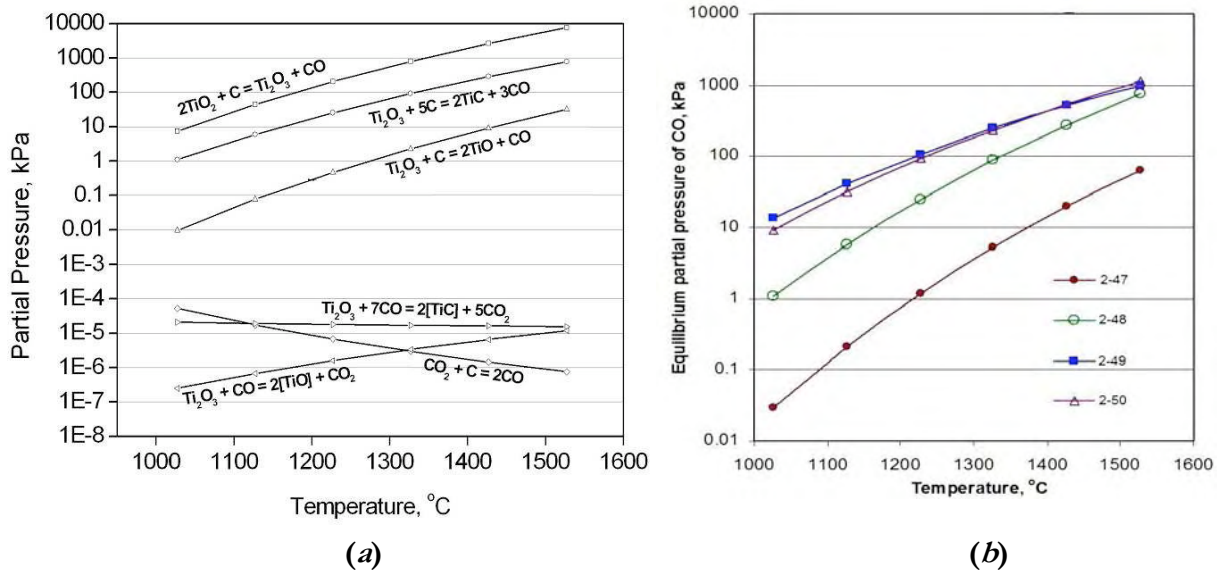
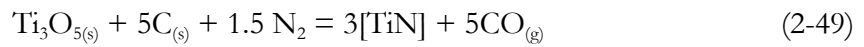
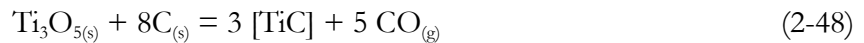
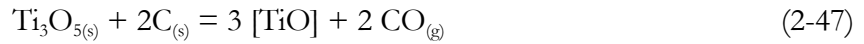
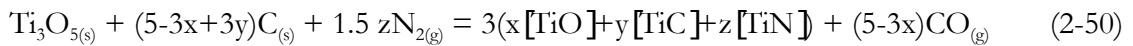


Figure 2.9. Equilibrium partial pressure of CO for: (a) Reactions 2-41 to 2-46 [Dewan *et al*, 2009], (b) Reactions 2-47 to 2-50 [Rezan *et al*, 2007]

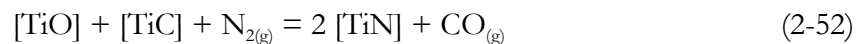
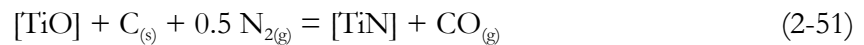
Dewan *et. al* (2009) reported that formation of titanium oxycarbide started at 1200°C in hydrogen, argon or helium atmosphere. The reduction in argon reached 90 to 95 pct after 300 min reduction at 1400-1500 °C [Dewan *et. al*, 2009]. In the process of formation of titanium oxycarbonitride, Ti_2O_3 is not detected by XRD [Berger and Gruener, 2002; White *et. al*, 1992; Rezan *et. al*, 2007]. The carbothermal reduction of TiO_2 to Ti_3O_5 can be presented by Reaction (2-41) [Rezan *et. al*, 2007]. Titanium oxycarbonitride (solid TiO-TiC-TiN solution) formation proceeds through Reactions (2-47) to (2-49) [Rezan *et. al*, 2007]:



The standard Gibbs free energy for Reactions (2-47) to (2-50) was calculated using NIST-JANAF Thermochemical Tables in the temperature range of 1027-1527 °C [Chase, 1998; Rezan *et. al*, 2007]. The equilibrium partial pressure of CO for these reactions is presented in **Figure 2.9 (b)**. The highest equilibrium pressure of CO is for reduction of TiO_2 to Ti_3O_5 (Reaction 2-47), followed by [TiN] formation from Ti_3O_5 (Reaction 2-49). This explains the reason of TiN became the main component in titanium oxycarbonitride. Formation of TiC by Reaction (2-48) is thermodynamically more favourable than formation of TiO by Reaction (2-47). Very low content of TiC in titanium oxycarbonitride can be explained by kinetic constraint of carbon transfer to the solid solution and consumption of carbon in removing oxygen from titanium oxides. Reactions (2-47)-(2-49) can be summarised as the following:



Rezan *et al.* (2007) suggest that formation of titanium oxycarbonitride is spontaneous when CO partial pressure is less than 10 kPa. In the final stage of reduction when titanium oxides are consumed, the reduction progresses slowly with conversion of TiO and TiC to TiN in the solid solution [Rezan *et. al*, 2007]:



Rezan *et. al* (2007) reported that complete conversion of titania to titanium oxycarbonitride in N_2-H_2 (50 vol. pct N_2) gas mixture was achieved in 180 min at 1150 °C, 90 min at 1200 °C, and 30 min at 1300 °C. **Figure 2.9** presents predominance area diagram for stable phases at 1300 °C in the Ti-O-C-N system [Jha and Yoon, 1999].

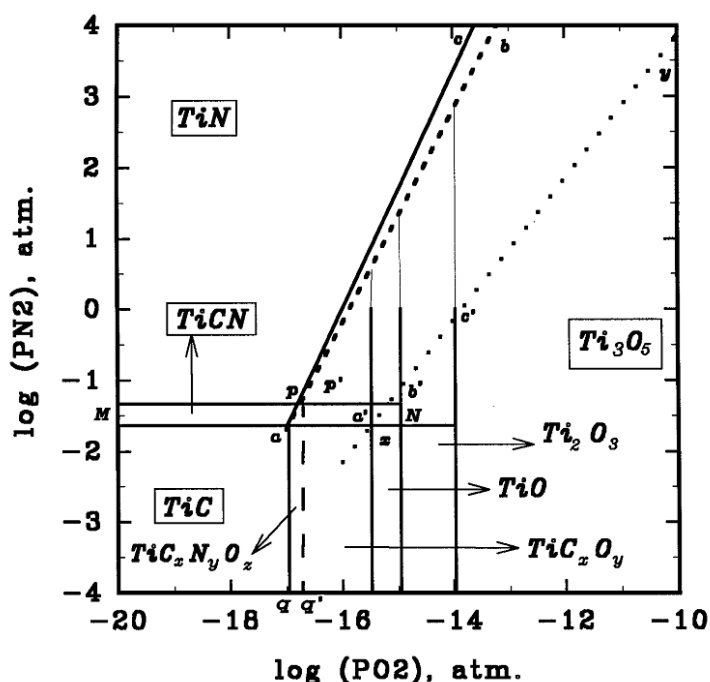


Figure 2.10. Predominance area diagram for stable phases at 1300 °C in the Ti-O-C-N system [Jha and Yoon, 1999]

2.3. Factors Influencing Chlorination of Rutile and Ilmenite

The rate and extent of rutile and ilmenite chlorination depend on reductant, duration of reaction and its temperature, particle size, ore composition, reactor type, and chlorinating agent.

2.3.1. Effect of Reductant

As mentioned previously, chlorination of TiO_2 requires low oxygen potential which can be achieved by the addition of carbon or CO as oxygen sink. Sulphur might also be used as reducing agent, although thermodynamically it is inferior to carbon and CO as shown by Patel and Jere (1960). By employing CO, carbochlorination proceeds at lower rates in comparison with solid carbon as reported by many authors [Barin and Schuler, 1980; Dunn, 1979; Chadwick and Rao, 1988; Bergholm, 1961; Takimoto and Hattori, 1955; Yang and Hlavacek, 1998]. Solid-solid contact has an effect on the initial stage of reaction. Solid-solid reactions proceed through the gas phase; actual reducing agent is CO which reacts with oxygen of oxide forming CO_2 . In the presence of graphite, CO_2 partial pressure is held low by the Boudouard reaction (Reaction 2-46). This makes solid carbon more efficient in titania chlorination than CO.

For solid-solid reactions Tamhankar and Doraiswamy (1979) has summarised the following reaction mechanisms:

- *Type 1*: Product layer diffusion control

A continuous product layer is formed during the initial stages of the reaction, and further reaction takes place by bulk diffusion of mobile reactant species through this product layer, which is the rate-controlling step.

- *Type 2*: Phase boundary reaction control

When the diffusion of the reactant species through the product layer is fast compared to reaction, the kinetics is controlled by phase boundary reactions.

- *Type 3*: Nuclei formation and growth control

Two steps are considered for the formation of the nuclei of the product phase at the active sites and the growth of these nuclei.

According to Yang and Hlavacek (1998) only type 2 (Phase boundary reaction control) is relevant to the carbochlorination of TiO_2 using carbon. These were in agreement with Yang and Hlavacek's thermodynamic analysis and the results from SEM analysis that showed that direct surface contact between two solid reactants remains until one solid reactant disappears [Yang and Hlavacek, 1998].

Carbochlorination of TiO_2 using CO can be summarised by the following steps [Yang and Hlavacek, 1998]:

- *Step 1*: Diffusion of gaseous reactants, Cl_2 and CO, from the bulk of the gas stream through the gas film to the surface of the TiO_2 solid particle. It assumed that each individual particle is nonporous.
- *Step 2*: Reaction of gaseous reactants (Cl_2 and CO) with the solid TiO_2 particle on the solid surface.
- *Step 3*: Diffusion of reaction products, TiCl_4 , and CO_2 , from the surface of the solid through the gas film back into the bulk of the gas stream.

Yang and Hlavacek (1998) studied carbochlorination kinetics of rutile and anatase with carbon and CO in a fixed bed reactor at temperatures ranging from 800 to 1000 °C. They observed that the activation energy with carbon was lower than with CO. Takimoto and Hattori (1955) found that the efficiency of carbochlorination of titania and ilmenite was reduced by nearly 30 pct when CO was used instead of carbon.

Barin and Schuler (1980) studied chlorination of rutile gravimetrically and found that the chlorination rate at temperature above 900 °C raised by a factor of 40 to 50 by employing solid carbon in comparison with chlorination without carbon. Van Deventer (1988) also reported that carbochlorination was more effective at higher graphite content especially in the range of 4 to 6 mass pct graphite.

Gennari *et al.* (1997) suggested that carbon affects carbochlorination of $\text{Fe}_2\text{O}_3\text{-TiO}_2$ in three ways:

1. It removes oxygen in direct chlorination through the formation of CO or CO_2 avoiding the reverse reaction.
2. Carbon forms the reaction intermediates in the gas phase which act as chlorinating agents for the oxides.
3. Chlorine interacts with carbon through a complex mechanism.

Bergholm (1961) investigated the chlorination of a pelletised rutile-coke mixture by $\text{Cl}_2\text{-Ar}$ in the temperature range of 680 to 860 °C and loose mixture of rutile and coke at 710 to 1020 °C. Chlorination rate of dense tablets of fine-grained rutile and coke at 700 °C was ten times higher than that of loose stationary mixtures of rutile and coke. However, at 850 °C the difference between those two was less pronounced. In tablet chlorination, the reaction rate was found to be proportional to the chlorine concentration and independent to the CO concentration in the furnace atmosphere [Bergholm, 1961]. Bergholm (1961) experiment could indicate that close packing between TiO_2 and C is crucial for mass transfer between solid-solid particles through the gas phase. This is justified by the experiments from Barin and Schuler (1980). They also reported that the influence of solid carbon on the chlorination rate decreases with increasing $\text{TiO}_2\text{-C}$ distance [Barin and Schuler, 1980]. This is shown in **Figure 2.11**, in which the chlorination rate of TiO_2 is plotted as a function of $\text{TiO}_2\text{-C}$ separation distance with different reactant gas mixtures.

The activation energy for chlorination of titania with $\text{Cl}_2\text{-Ar}$ and $\text{CO-CO}_2\text{-Cl}_2\text{-Ar}$ mixtures with carbon and in the absence of carbon at temperatures over 900 °C was calculated to be 80.8 and 146.4 $\text{kJ}\cdot\text{mol}^{-1}$ respectively [Barin and Schuler, 1980]. In the presence of carbon, lower activation energy was required due to dissociation of chlorine at the carbon surface [Barin and Schuler, 1980]. The investigations by Robson *et al.* (1968), Blackwood and Cullis (1970), and Kol'tsov *et al.* (1973) indicated that chlorine was chemisorbed at active sites of

the carbon surface mainly by forming C-Cl complexes. This according to Kol'tsov *et al.* (1973), were dissociated and desorbed in the gas phase at temperature above 400 °C.

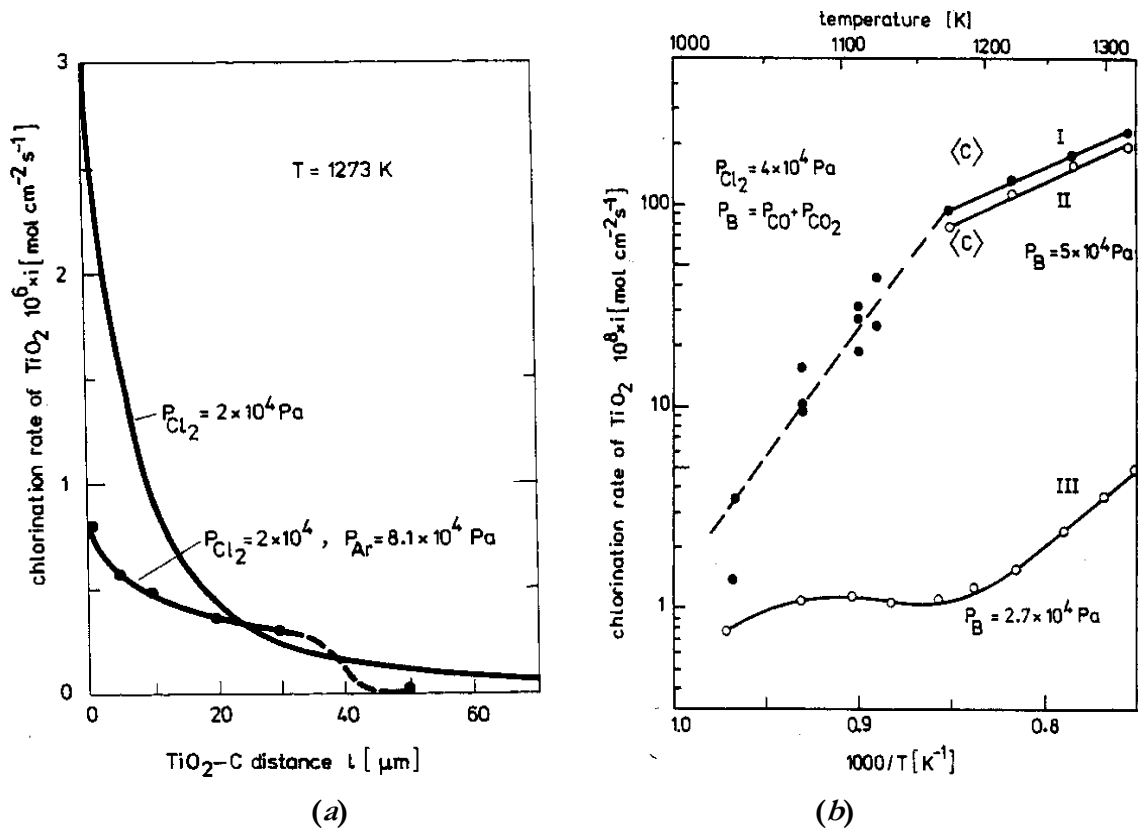


Figure 2.11. (a) Chlorination rate of TiO_2 as a function of TiO_2 -C separation, (b) rate of chlorination of TiO_2 with Cl_2 -Ar and CO - CO_2 - Cl_2 -Ar mixtures with carbon (I, II) and in the absence of carbon (III) [Barin and Schuler, 1980]

Kol'tsov *et al.* (1973) also suggested the formation of volatile C_xCl_y compound. On the other hand, Barin and Schuler (1980) found that there was no gravimetrically measurable reaction between chlorine and graphite at temperature in the range of 750 to 1050 °C provided no impurities were present. Barin and Schuler (1980) also observed that chlorination of titania was accelerated by carbon even when titania and carbon were separated by the gas phase. This indicated that activated chlorine species might be formed on the carbon surface and desorbed into the gas phase. **Figure 2.12** shows electron micrograph of titania surface before and after chlorination.

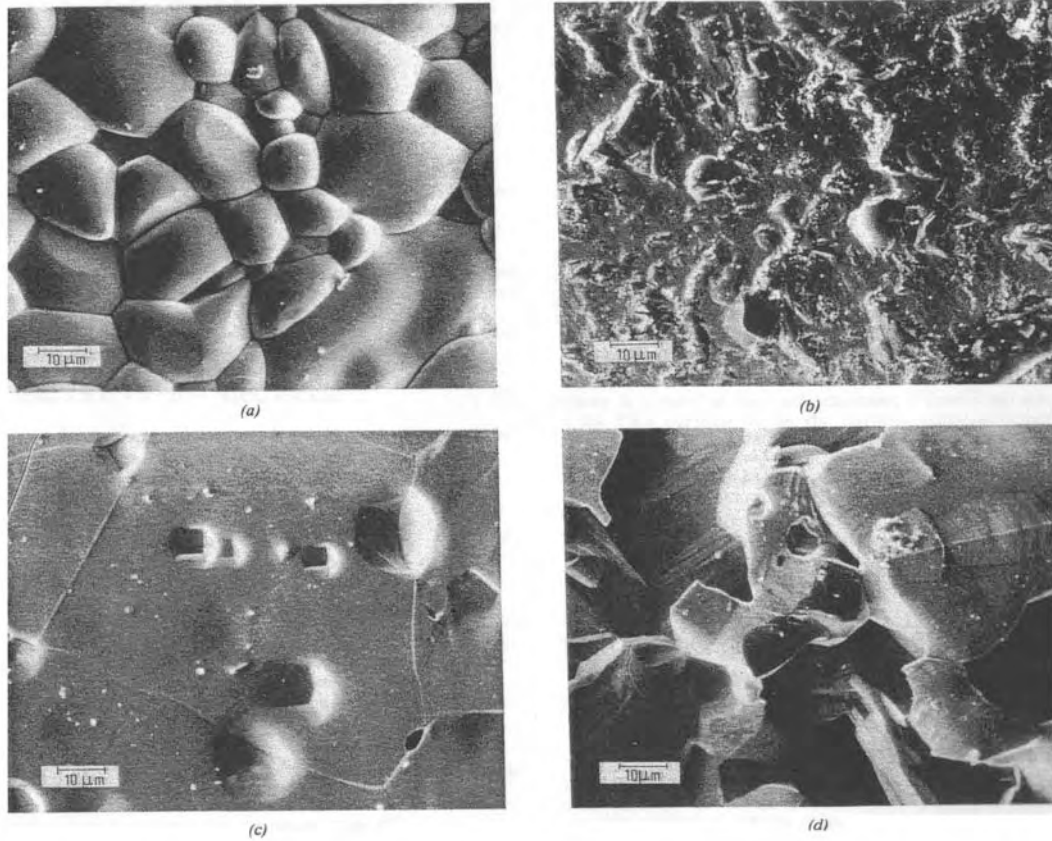
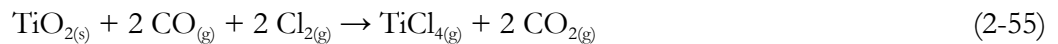
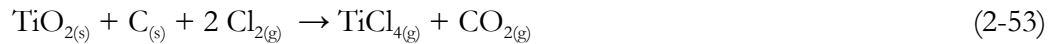


Figure 2.12. Electron micrographs of titania surface: (*a*) After sintering; (*b*) After grinding (before reaction); (*c*) After reaction at 1000 °C with P_{Cl_2} of 40 kPa for titania-carbon contact; (*d*) After reaction at 1000 °C with P_{Cl_2} of 40 kPa and total P_{CO} and P_{CO_2} of 27 kPa in the absence of solid carbon [Barin and Schuler, 1980]

The possible reactions for carbochlorination of titania using carbon at temperatures of 800-1000 °C were suggested by Yang and Hlavacek (1998) as the following:



Yang and Hlavacek (1998) investigated carbochlorination of rutile and anatase using carbon in fixed bed at temperature ranging from 800 to 1000 °C at 1 atm. **Figure 2.13** shows carbochlorination of TiO_2 conversion rate as a function of chlorine partial pressure and time at 800 °C and 1000 °C with carbon as reductant.

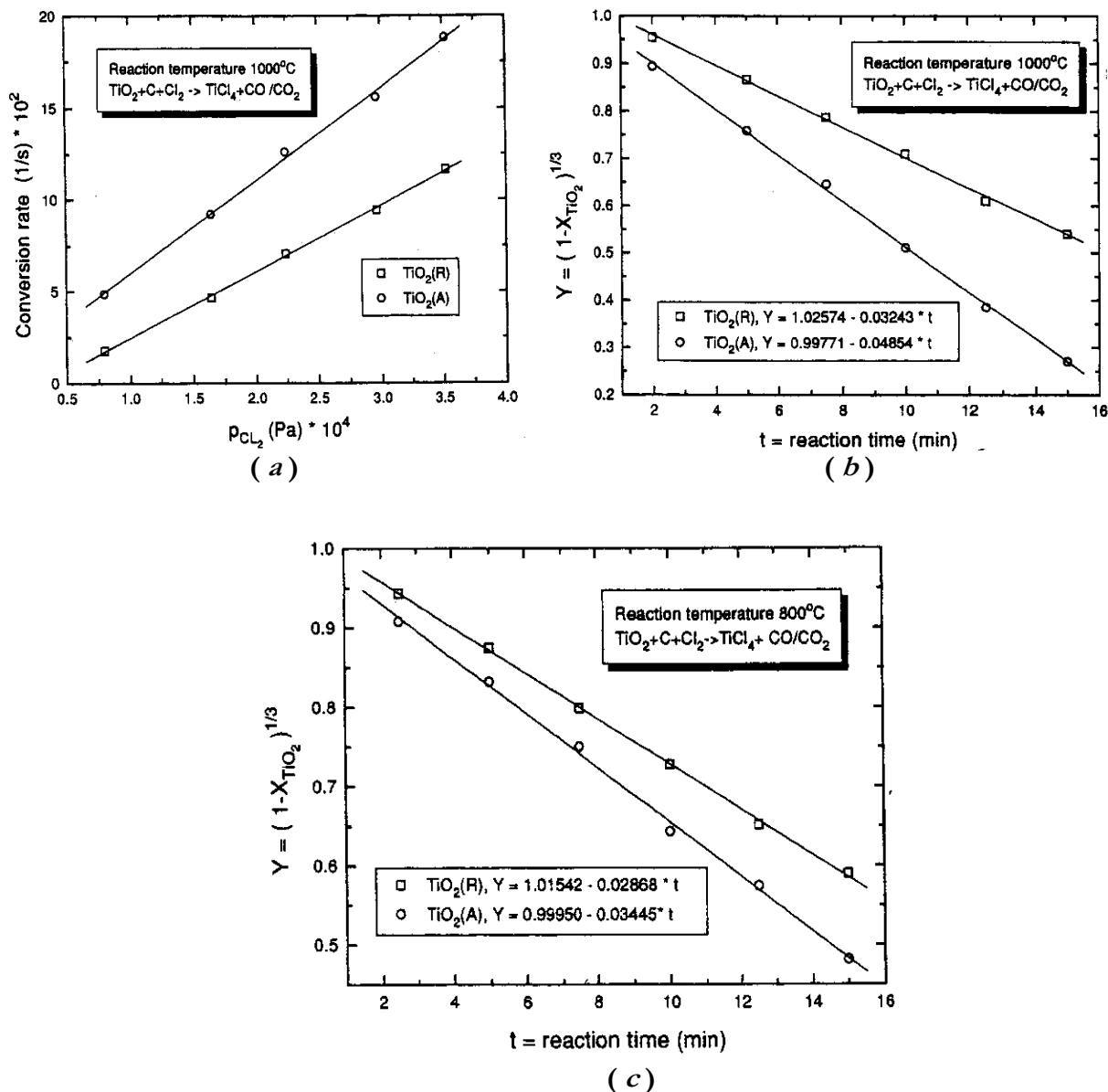


Figure 2.13. (a) Chlorine partial pressure vs TiO_2 conversion rate with carbon as reductant. TiO_2 conversion rate as a function of time at: (b) 800 °C; (c) 1000 °C [Yang and Hlavacek, 1998]

Figure 2.14 shows carbochlorination of TiO_2 conversion rate as a function of chlorine partial pressure and time at 800 °C to 1000 °C with CO as reductant.

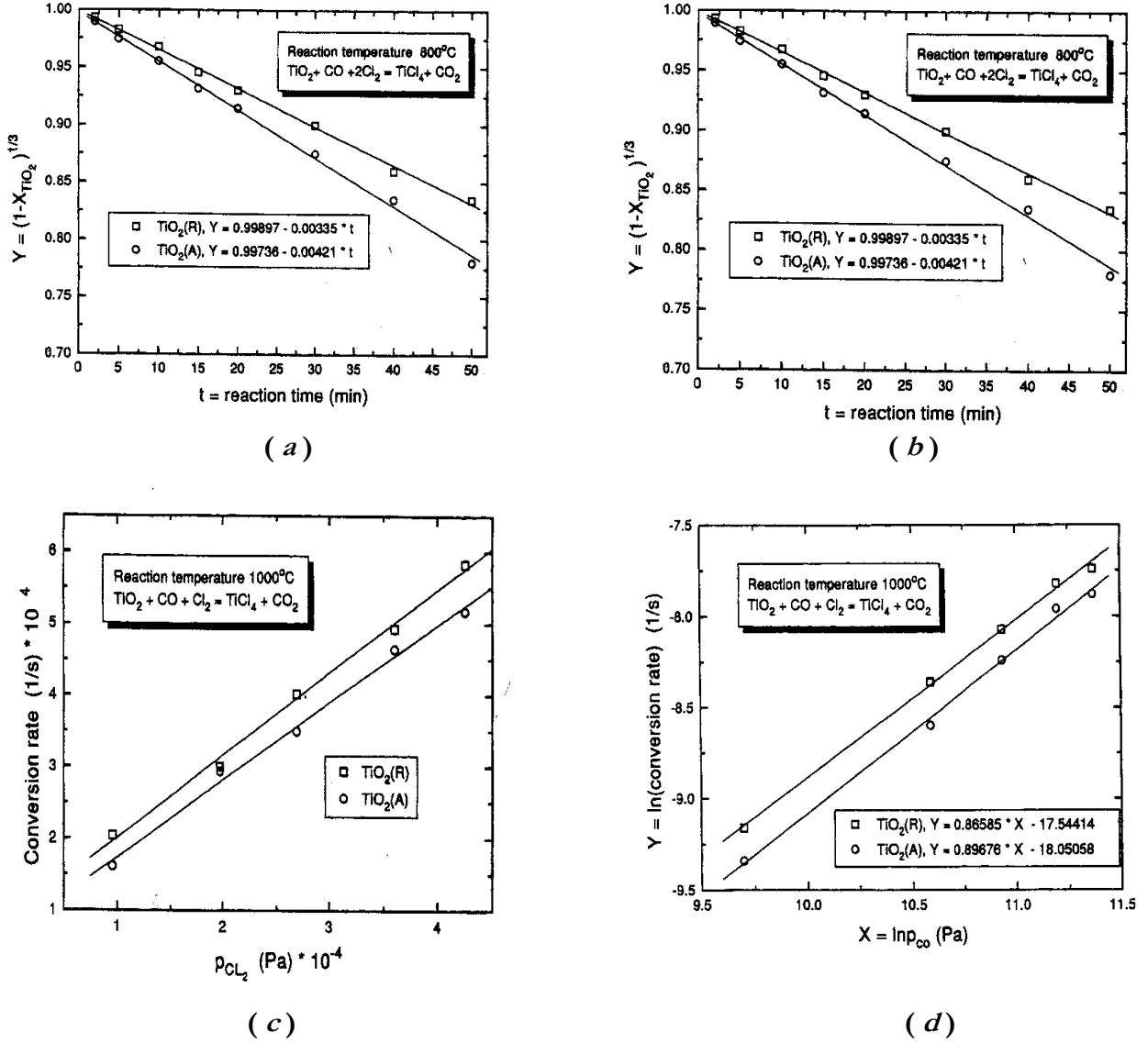


Figure 2.14. Carbochlorination of TiO_2 using CO as a function of time at (a) 800 °C; (b) 1000 °C; (c) effect of chlorine partial pressure on TiO_2 conversion rate with CO; (d) effect of CO partial pressure on TiO_2 conversion rate [Yang and Hlavacek, 1998]

Table 2.4 show the effect of carbon content on conversion for carbochlorination of titania. Tables 2.5 and 2.6 summarise Yang and Hlavacek (1998) results for kinetics of carbochlorination of titania using carbon and carbon monoxide, respectively.

Table 2.4. Effect of carbon content on conversion for carbochlorination of titania [Yang and Hlavacek, 1998]

TiO ₂ :C (Weight Ratio)	Conversion of TiO ₂ (R) (Pct)	TiO ₂ (R) (Reacted) C (Reacted)	Conversion of TiO ₂ (A) (Pct)	TiO ₂ (A) (Reacted) C (Reacted)
3:1	23.65	2.06:1	41.08	2.55:1
2:1	26.94	1.85:1	46.86	2.21:1
1:1	35.00	1.71:1	56.45	2.21:1

(R) and (A) indicates rutile and anatase respectively

Table 2.5. Summary of kinetic data for carbochlorination of titania [Yang and Hlavacek, 1998]

Symbols	Descriptions	Unit	Data of TiO ₂ (R)	Data of TiO ₂ (A)
$R_p (=r_0)$	effective particle radius of TiO ₂ from BET	cm	2.49×10^{-5}	7.87×10^{-6}
$\rho_{\text{TiO}_2}^{\text{BET}}$	density of solid TiO ₂	g/cm ³	4.23	3.90
p_{Cl_2}	partial pressure of Cl ₂	Pa	34,994	34,994
$K_{1000^\circ\text{C}}$	constant	min ⁻¹	0.0324	0.0485
$K_{800^\circ\text{C}}$	constant	min ⁻¹	0.0287	0.0345
$k_{1000^\circ\text{C}}$	constant	$\frac{\text{g}}{\text{cm}^2 \cdot \text{min}}$	3.42×10^{-6}	1.49×10^{-6}
$k_{800^\circ\text{C}}$	constant	$\frac{\text{g}}{\text{cm}^2 \cdot \text{min}}$	3.02×10^{-6}	1.06×10^{-6}
k^0	pseudofrequency factor	$\frac{\text{g}}{\text{cm}^2 \cdot \text{min} \cdot \text{Pa}}$	1.87×10^{-10}	2.65×10^{-10}
E_a	activation energy	J/mole	6.90×10^3	1.93×10^4

(R) and (A) indicates rutile and anatase respectively

Table 2.6. Summary of kinetic data for TiO₂ + Cl₂ + CO reaction system [Yang and Hlavacek, 1998]

Symbols	Descriptions	Unit	Data of TiO ₂ (R)	Data of TiO ₂ (A)
BET	surface area of oxides	cm ² /g	28,533	97,710
$R_p (=r_0)$	effective (initial) particle radius of TiO ₂ from BET	cm	2.49×10^{-5}	7.87×10^{-6}
ρ_{TiO_2}	molar density of solid TiO ₂	mole/cm ³	0.05294	0.04881
m	reaction order w.r.t. Cl ₂	—	1	1
n	reaction order w.r.t. CO	—	0.8659	0.8968
p_{Cl_2}	partial pressure of Cl ₂	Pa	37,595	37,595
p_{CO}	partial pressure of CO	Pa	64,505	64,505
$\tau_{1000^\circ\text{C}}$	time required for complete conversion at 1000 °C	min	82.37	91.32
$\tau_{800^\circ\text{C}}$	time required for complete conversion at 800 °C	min	298.51	237.53
$k_{5,1000^\circ\text{C}}$	rate constant at 1000 °C	$\frac{\text{cm}^2 \cdot \text{min} \cdot (P_a)^{n+1}}{\text{mole}}$	5.83×10^{-17}	1.09×10^{-17}
$k_{5,800^\circ\text{C}}$	rate constant at 800 °C	$\frac{\text{cm}^2 \cdot \text{min} \cdot (P_a)^{n+1}}{\text{mole}}$	1.60×10^{-17}	4.18×10^{-18}
k^0	frequency factor	$\frac{\text{g}}{\text{cm}^2 \cdot \text{min} \cdot (P_a)^{n+1}}$	6.01×10^{-14}	1.86×10^{-15}
E_a	activation energy	J/mol	7.34×10^4	5.44×10^4

(R) and (A) indicates rutile and anatase respectively

Yang and Hlavacek (1998) found that the activation energy for carbochlorination of rutile and anatase using carbon were 6.90 and 19.3 kJ·mole⁻¹ respectively at 800 °C to 1000 °C. Carbochlorination of rutile and anatase using carbon monoxide were 73.4 and 54.4 kJ·mole⁻¹, respectively at 800 °C to 1000 °C. Yang and Hlavacek (1998) argued that at high

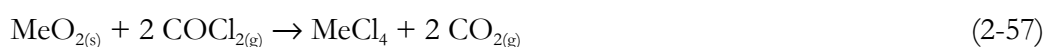
temperature, an activated C-TiO₂-Cl complex was formed on the TiO₂-C-Cl₂ interface, which was proportional to the surface area of TiO₂ particle and became the controlling step. This means that carbochlorination of rutile and anatase was controlled by phase boundary reaction. The activated complex which was responsible for high reactivity was then decomposed into CO and TiCl₄. In carbochlorination of rutile and anatase using carbon, TiO₂ particle was shrinking and no solid product layer exist and were in agreement with their thermodynamic and SEM analysis. However, chemical reaction control requires much higher activation energy (on the order of 160 to 320 kJ·mole⁻¹).

Activation energy for carbochlorination of rutile and anatase which was determined by Yang and Hlavacek (1998), was much lower than that found by Barin and Schuler (1980) (ie. 80.8 kJ.mol⁻¹). In Barin and Schuler's work, TiO₂ powder was pressed into tablets and sintered for three days at 1400 °C. They also pressed graphite powder into tablets. Carbochlorination of TiO₂ was investigated by Barin and Schuler by placing TiO₂ and carbon tablets closed together on silica clamp, while Yang and Hlavacek investigated carbochlorination of TiO₂ intimately mixed with graphite in a fixed bed reactor. The differences in experimental set-up between Yang and Hlavacek and Barin and Schuler led to different conditions for oxygen transfer from oxide to graphite and different activation energies. It can be expected, that chlorination of titania in experiments by Barin and Schuler proceeded under higher oxygen pressure than in work by Yang and Hlavacek.

With the increasing of reaction temperature, the rate should increase exponentially and diffusion limitations dominate the observed overall reaction kinetics. A low activation energy could indicate mixed control of mass transfer (diffusion of gaseous reactant and reaction products) and chemical reaction control for carbochlorination of rutile and anatase using carbon. For carbochlorination of rutile and anatase using carbon monoxide, Yang and Hlavacek (1998) argued that chemical reaction was the only rate limiting step as mass transfer limitations were eliminated by using high gas flow rate.

Bergholm (1961) indicated that the mechanisms of carbochlorination with carbon and CO are different. Barin (1980) suggested that for the TiO₂-C-Cl₂ system, the reaction occurs even though carbon and oxide particles are not intimately mixed together. Consequently several authors have argued that carbochlorination might involve the evolution of gaseous intermediates during reaction [Manukyan *et al.*, 2003; Gamboa *et al.*, 1999; Pasquevich *et al.*,

1992]. These are mainly phosgene [Stefanyuk and Morozov, 1965], chlorine atoms [Amorebieta and Colussi, 1985; Pasquevich and Amorebieta, 1992; Landsberg and Hoatson, 1972] and oxychlorides [Manukyan and Martirosyan, 2003; Dunn, 1979; Zelikman and Segarchanu, 1956; Medynski, 1976]. The formation of both phosgene and chlorine atoms may take place on the carbon surface [Gamboa *et al.*, 1999]. Phosgene perhaps formed by heterogeneous reaction of Cl_2 with CO, since CO is always initially adsorbed on carbon [Stefanyuk and Morozov, 1965]. This is shown by the following reactions [Stefanyuk and Morozov, 1965]:



Phosgene is generally found in the product gases at low temperatures [Zelikman and Segarchanu, 1956], however, phosgene completely dissociates at 700 °C; its presence was not detected at elevated temperatures. **Table 2.7** shows the degree of dissociation of phosgene at different temperatures.

Table 2.7. Degree of dissociation of phosgene [Morozov, 1966]

	Temperature, °C			
	300	400	500	800
Degree of dissociation of COCl_2 , pct	3.9	19.8	55.0	100.0

Chlorine atoms, on the other hand, could be formed by Cl_2 dissociation in the C- Cl_2 interaction, the oxygen is then replaced by chlorine [Gamboa *et al.*, 1999].



Consequently, either in phosgene formation or in chlorine atom generation, the carbon surface is involved. Gamboa *et al.* (1999) suggested that the overall reaction rate may be proportional to carbon content in the sample since the carbon area increases and the intermediate concentration in the gaseous phase is enhanced.

2.3.2. Effect of Chlorinating Agents

Neuschuetz *et al.* (1974) studied the rate of chlorination of titania with Cl_2 , HCl, COCl_2 , and mixtures of Cl_2 and CO. The COCl_2 actually decomposed at temperature higher than 430 °C. At 850 °C, they suggested that the COCl_2 behaved like a mixture of CO and Cl_2 .

The activation energies were calculated to be: $136.8 \text{ kJ}\cdot\text{mol}^{-1}$ for COCl_2 , $123 \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{CO} + \text{Cl}_2$, $29.3 \text{ kJ}\cdot\text{mol}^{-1}$ for HCl , and $184.1 \text{ kJ}\cdot\text{mol}^{-1}$ for Cl_2 [Neuschuetz *et al.*, 1974]. However employing CCl_4 or COCl_2 is costly and poses no marked advantages [Athavale and Altekhar, 1971].

2.3.3. Effect of a Reactor Type

Impurities in the ilmenite ore may cause problems in the chlorination process associated with fluxing or sintering in a static bed during chlorination and in condensation of the volatile chlorides [Van Deventer, 1988]. Athavale and Altekhar (1971) found that chlorination in the static bed using a briquetted charge have the usual difficulties of channelling, sintering, hanging, stratification, and poor temperature distribution which in the end might affect the process. In addition, the binding agent may consume a certain amount of chlorine, and the briquettes have a tendency to disintegrate in the reactor with the loss of binder.

These difficulties can be largely overcome by the application of a fluidised bed. Several advantages can be realised by the use of the fluidised solids process. The excellent heat transfer and lack of channelling permits a three to fourfold production rate per unit area. The feed and discharge can be made continuous, thus eliminating the frequent shutdowns required for discharging the static bed units.

However, Bergholm (1961) reported that the carbochlorination rate in the fluidised bed decreased in comparison to compact briquette composed of rutile and carbon. In the fluidised bed, carbon and rutile could not be intimately mixed together inside the reactor since specific particles sizes are required in order to make the bed fluidised. Noda (1955) suggested that the uniformity of mixing and the homogeneity and accuracy of the briquettes proved to be vital for improved chlorination.

The main problems encountered in design of a chlorinating unit were found in the condensing and collecting of the reaction products rather than in the formation of the chloride. These difficulties arise from [Rowe and Opie, 1955]:

1. Carry over of very fine dust and solid reaction products that can be only partially removed by cyclones.
2. Plugging of condenser lines with mixtures of dust, liquid tetrachloride, and titanium oxychloride.
3. Clogging of the off gas lines by hydrolysis of un-condensable tetrachloride fogs and mists which pass through the condensers.
4. Corrosion of the condensing system with Cl_2 and HCl .

The air leakage into the system, especially near the reaction zone, causes oxidation of TiCl_4 and FeCl_3 to produce very fine TiO_2 and Fe_2O_3 particles, while moisture leakage will produce solid titanium oxychloride. These effects can be minimised by thorough drying of the charge and by maintaining the system under a slight positive pressure [Rowe and Opie, 1955]. Handling the large amounts of FeCl_2 and FeCl_3 produced during the chlorination of ilmenite was notoriously difficult. Complete selective chlorination of either titanium or iron values is practically impossible, although FeCl_2 production can be minimised by proper control of the reaction conditions. The large difference between the boiling points of FeCl_3 (315 °C) and TiCl_4 (136 °C) should permit readily separation of the two phases. In practice, however, the separation is only partially effective, and considerable amounts of very fine FeCl_3 are carried along with the gas stream. When the two components condense together, a heavy mud is produced which is very difficult to handle. Furthermore, this condition could collapse the fluidised bed. In a continuous operation, the process is a slow cumulative one, with gradual build-up of FeCl_3 , at points in the system where wall friction causes a lowering of gas velocity. Air leaks can aggravate the problems by causing a deposition of Fe_2O_3 , along with FeCl_3 .

2.4. Summary and Project Objectives

In general, most of direct reduction processes to produce titanium metal require expensive high grade titania feed; they have difficulties in scaling up to large quantity production; contamination of electrolyte leads to low purity of titanium metal product, and low current efficiency. Therefore commercial titanium metal production solely relies on carbochlorination of rutile and reduction of titanium tetrachloride.

Introducing a reducing agent for chlorination of titania reduces oxygen partial pressure favouring chloride formation, prevents the reversal reaction, and reduces initiation reaction temperatures with less energy consumption. Carbon reductant may react with chlorine to form reaction intermediates that enhance reaction degree and rate. However, it may also assist chlorination of impurities.

The heat released in the chlorination process increases with the declining oxygen to titanium ratio of the oxide. Chlorination of reduced titanium oxide has higher rate in comparison with titania and it may undergo chlorination even without the addition of carbon. Titanium carbide and sub-oxides produced by carbothermal reduction at 1500 °C, can be chlorinated at as low temperature as 250 °C. Titanium carbonitride can also be chlorinated at low temperature of 350 °C. At these temperatures, only the reduced metal oxides such as titanium, iron, and vanadium were selectively chlorinated leaving residues of MgO, SiO₂ and Al₂O₃. The other oxides are not reactive and titanium tetrachloride product can be obtained. The optimal chlorination temperature was found between 200 to 500 °C.

In the low temperature chlorination, impurities chlorinate very slowly. This permits selective chlorination, decreases the chlorine consumption and waste generation, and smaller chlorinator reactor volumes. This makes the technology of ilmenite processing to be more efficient, sustainable, and environmentally friendly.

Currently no detailed investigation of kinetics and mechanisms of chlorination of Ti(O,C) or Ti(O,C,N) under different operational conditions was reported in literature. This project undertook a systematic study of chlorination of Ti(O,C) and Ti(O,C,N) with the aim to establish effect of operational parameters on their chlorination, optimal chlorination conditions and develop further understanding of chlorination reactions. The project investigated titania, ilmenite ores, and synthetic rutile reduced by carbon in argon and nitrogen and chlorinated at different temperatures, gas flow rates and compositions. Chlorination of titanium sub-oxides, iron and impurities in ilmenite was also examined.

CHAPTER 3. EXPERIMENTAL

This chapter presents chemicals and gases employed in the research project, characteristics of raw materials, description of the experimental set-up, methodologies, and the calculation of the extent of chlorination. Titania, ilmenite ores, and synthetic rutile were reduced by carbon in argon or nitrogen atmosphere and chlorinated at different temperatures, gas flow rates and compositions. Chlorination of titanium sub-oxides, iron and impurities in ilmenite was also studied.

3.1. Materials

3.1.1. Gases

The gases were provided by BOC and Linde Gases, Australia. Pure argon was employed in synthesis of titanium oxycarbide, while nitrogen was used in conversion of titanium oxides to titanium oxycarbonitride. **Table 3.1** displays gases, their grade and specific application.

Table 3.1. Gas specification

Gas	Specification	Application
Argon (Ar)	Ultra high purity, > 99.999 pct Linde Gases, Australia (CAS: 7440-37-1)	Inert gas for reduction of titania or ilmenite
Nitrogen (N ₂)	Ultra high purity, > 99.999 pct Linde Gases, Australia (CAS: 7727-37-9)	Reactant gas for reduction of titania or ilmenite
	High purity, > 99.99 pct Linde Gases, Australia (CAS: 7727-37-9)	Gas diluents for chlorination
Hydrogen (H ₂)	Ultra high purity, > 99.999 pct Linde Gases, Australia (CAS: 1333-74-0)	Reactant gas for reduction of titania or ilmenite
Chlorine (Cl ₂)	Ultra high purity, > 99.999 pct BOC Gases, Australia (CAS: 7782-50-5)	Reactant gas for chlorination

3.1.2. Chemicals

The chemicals are presented in **Table 3.2**; they were supplied by Sigma-Aldrich Chemicals Australia. Distilled water was generated by Labec Water Still, Australia. Ilmenite ores of three different grades identified as primary ilmenite, secondary ilmenite and HYTI 70 were supplied by ILUKA, Australia. Their chemical composition is shown in **Table 3.3**. The primary ilmenite was examined in the size range of 75 - 212 μm , while the size of secondary ilmenite and HYTI 70 was in the range 75 - 250 μm ; for the synthetic rutile it was 75 - 300 μm .

Table 3.2. Chemicals specification

Chemicals	Specification	Application
Synthetic graphite (C)	Powder size < 20 μm , purity > 99.9 pct (CAS 7782-42-5)	Reducing agent
Titania (TiO_2)	Powder size < 5 μm , purity > 99.9 pct (CAS 22422-7)	Reactant
Stearic acid ($\text{C}_{18}\text{H}_{36}\text{O}_2$)	NBS 372. Package No.: 2229 (CAS 57-11-4)	Sample binder
Carboxymethyl cellulose (CMC)	(CAS 9000-11-7)	Dispersant and emulsion stabiliser
Hydrochloric acid (HCl)	Concentration 32 wt pct (CAS 7647-01-0)	Titanium tetrachloride absorber
		Removal traces of metal iron
Sodium hydroxide (NaOH)	Concentration 10 wt pct (CAS 1310-73-2)	Chlorine absorber
Ammonium chloride (NH_4Cl)	Concentration of 0.1 M (CAS: 12125-02-9)	Catalyst to oxidise metallic iron
Drierite (CaSO_4)	Purity > 97pct (CAS: 7778-18-9)	Moisture absorber

3.2. Experimental Procedures and Setup

This section describes experimental procedures and setup for synthesis of titanium oxycarbide or oxycarbonitride, chlorination, and removal metallic iron from reduced ilmenite.

3.2.1. Synthesis of Ti(O,C) or Ti(O,C,N)

3.2.1.1. Procedures

Titanium oxycarbide or oxycarbonitride was produced by carbothermal reduction of pure titania or ilmenite ore. Titania or ilmenite ore were mixed with synthetic graphite powder. The mixture was ball milled with 0.3 pct of carboxymethyl cellulose and 40 pct water (based on solid weight) for 24 h and then dried in an oven at 150 °C for another 24 h. The dried mixture of rutile and graphite was then pressed uniaxially into cylindrical pellets of 3.2 g each with 15 mm in diameter and 10 mm in height. The pressing was carried out at a pressure of 141.5 MPa (25 kN) for 1 min. For ilmenite ores and synthetic rutile, the dried powder was pressed into cylindrical shape of 2.5 g each with 15 mm in diameter and 5 mm in height. The pressing was carried out at higher pressure of 226.4 MPa (40 kN) for 2 min.

The sample was heated to 1450 °C in horizontal electrical furnace equipped with alumina tube under argon or nitrogen atmosphere at 1 L·min⁻¹. Temperature was raised with ramping rate of 5 °C·min⁻¹ and held for 180 min. Finally, the sample was cooled down to room temperature also in the same gas atmosphere to prevent re-oxidation.

Analysis of the reduced samples proved that titanium oxycarbide or oxycarbonitride prepared by this manner was uniform and consistent which was crucial to the reliability of chlorination experiments. The variation in oxygen content of reduced samples with the same carbon to titania ratio produced in parallel reduction experiments was within the error of LECO analysis.

Table 3.3. Chemical compositions of ilmenite ores, wt pct

	Primary Ilmenite <i>MSR 1245</i>	Secondary Ilmenite <i>MSR 1246</i>	HYTI 70 <i>MSR 1247</i>	Synthetic Rutile <i>MSR 1248</i>
TiO ₂	53.9	58.20	66.57	92.46
Ti ₂ O ₃	-	-	-	12.1
Total Fe	30.5	25.89	18.75	2.75
MnO	1.63	1.15	0.86	0.86
FeO	18	11.22	2.38	-
SiO ₂	0.27	0.75	0.66	0.91
ZrO ₂	0.09	0.16	0.11	0.09
Fe ₂ O ₃	43.6	37.01	26.80	0.02
Al ₂ O ₃	0.4	0.51	1.1	0.97
P ₂ O ₅	0.01	0.033	0.045	1.57
S	0.004	0.01	0.09	0.63
Nb ₂ O ₃	-	-	-	0.23
Nb ₂ O ₅	0.1	0.14	0.23	-
Cr ₂ O ₃	0.047	0.05	0.084	0.072
CaO	<0.01	<0.01	0.006	0.02
CeO ₂	-	-	-	0.04
MgO	0.18	0.22	0.13	0.36
V ₂ O ₅	0.17	0.18	0.19	0.28
Fe/Ti	0.79	0.66	0.46	0.04

3.2.1.2. Reduction Equipment

The reduction experiments were conducted in a molybdenum disilicide horizontal furnace (Ceramic Engineering, Australia) with a re-crystallised alumina tube. The furnace had maximum operating temperature of 1700 °C. A schematic of experimental apparatus is shown in **Figure 3.1**. Mass flow controller (Brooks Instruments, Hatfield USA, model 5850E) was used to control the flow rate of gas. It was calibrated for argon, nitrogen, and hydrogen gas using bubble flow meter. A gas purifier was used to remove moisture from the gas. The calibration was performed under room temperature at 101.3 kPa. **Figure 3.2** shows calibration curves of the controllers for argon, nitrogen, and gas, respectively.

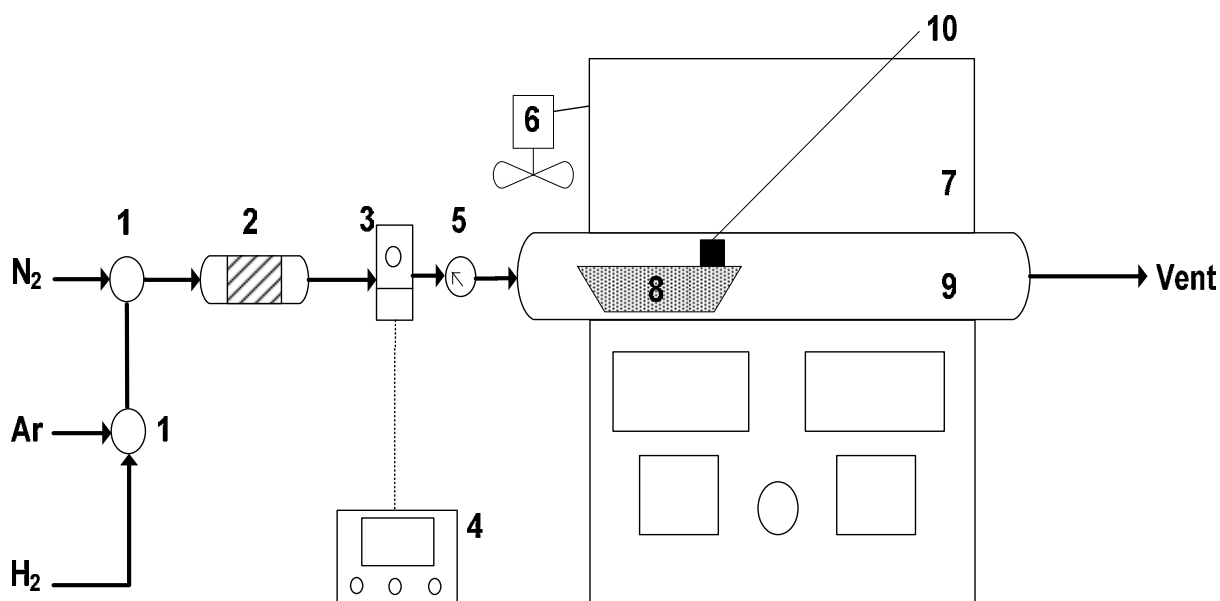


Figure 3.1. Schematic experimental setup for carbothermal reduction or nitridation. 1–2 way valve; 2–gas purifier; 3–mass flow; 4–mass flow controller; 5–pressure gauge; 6–cooling fan; 7–horizontal furnace; 8–alumina boat; 9–horizontal tube reactor; 10–sample

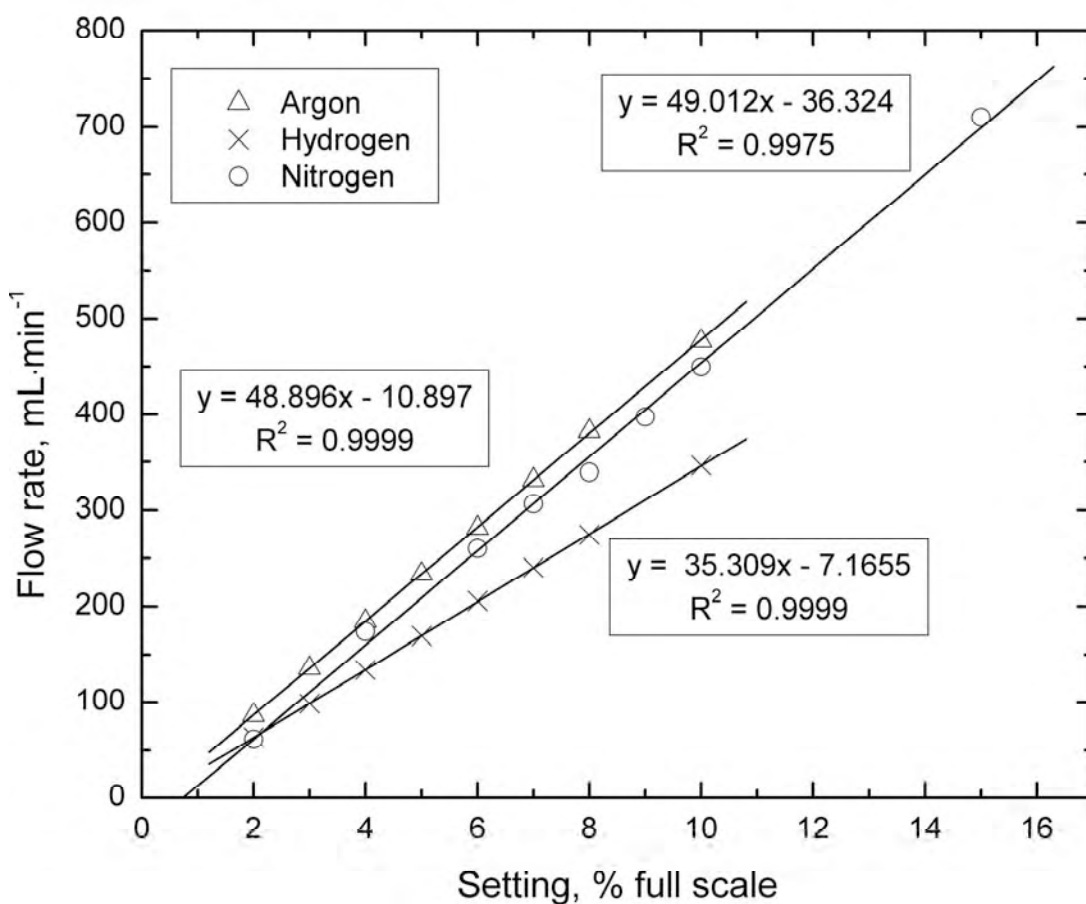


Figure 3.2. Calibration curves of the mass flow controller for reduction of titania

3.2.2. Chlorination of Ti(O,C) or Ti(O,C,N)

3.2.2.1. Procedures

The pellet of titanium oxycarbide or oxycarbonitride was attached to the tip of a type K thermocouple, which was inserted into the hot zone of the quartz tube. The location of the hot zone was determined by inserting thermocouple into quartz tube under constant flow rate of nitrogen at $1 \text{ L}\cdot\text{min}^{-1}$. The measurements were taken after 2 min for every 50 mm increments. **Figure 3.3** shows the temperature profiles across the reactor furnace.

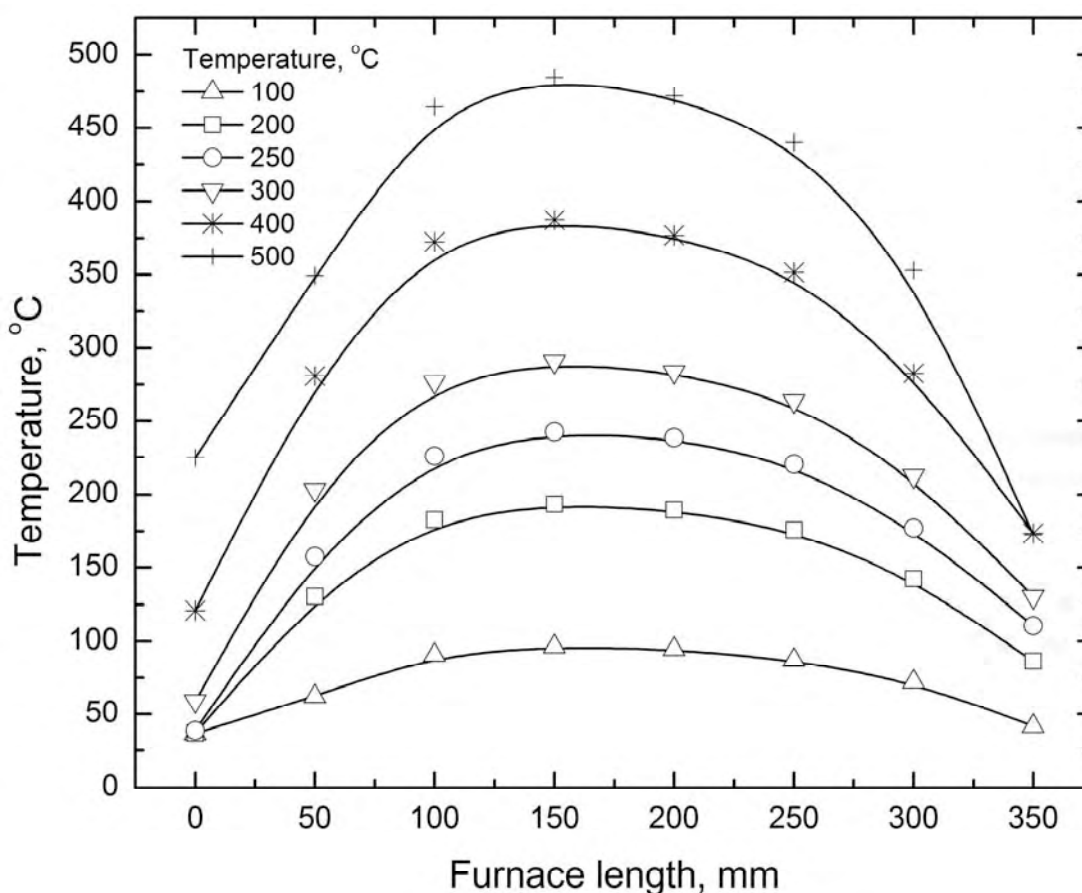


Figure 3.3. Temperature profiles across the reactor tube with flow rate nitrogen of $1 \text{ L}\cdot\text{min}^{-1}$

In experiments with particles of a small size, a sample was contained in an alumina boat in the furnace hot zone. Nitrogen gas was used for purging and in mixture with chlorine to control the chlorinating gas composition. Titanium tetrachloride vapour was absorbed in two scrubbers which contained 230 and 130 mL of 32 pct HCl, respectively. The third gas scrubber filled with 10 pct NaOH solution was used to absorb and remove un-reacted

chlorine from the off gas before it was vented. In order to prevent titanium tetrachloride vapour from condensing, a heat gun was used to heat up the connection between reactor tube outlet and scrubber. Temperature was raised above the boiling point of titanium tetrachloride.

In isothermal experiments, the furnace was heated to the experimental temperature. A sample was loaded as described above, and the reactor was purged with nitrogen at 500 mL·min⁻¹. After 10 min of purging, nitrogen was stopped and chlorine or its mixture with nitrogen was introduced into the reactor. 1.00 mL sample was taken from TiCl₄ scrubber every 10 min using syringe for titanium analysis. In some experiments, the venting gas was analysed by the CO-CO₂ infrared sensor.

In temperature programmed experiments, the furnace temperature was ramped from 100 to 400 °C at the rate of 3 °C·min⁻¹. After chlorination completed, chlorine was stopped and the reactor was purged by nitrogen to remove any remaining chlorine and titanium tetrachloride vapour. The purging was maintained until the furnace was cooled below 100 °C. Finally the sample was taken out, weighed and subjected to further analyses.

3.2.2.2. Chlorination Equipment

Isothermal and temperature programmed experiments were carried out in a transparent quartz tube of 22 mm internal diameter and 495 mm long placed in a horizontal electric furnace (Ceramic Engineering, Australia). The furnace had maximum operating temperature of 1000 °C. Eurotherm BTC 9090 programmable temperature controller was used to regulate the power to the heating element. The experimental setup is shown in **Figure 3.4**.

Teflon rotameters (Cole-Palmers, USA) were calibrated for nitrogen and chlorine gas at room temperature and ambient pressure. The calibration for chlorine gas was performed by Cole-Palmers. **Figure 3.5** shows calibration curves of the rotameters for chlorine and nitrogen gas, respectively.

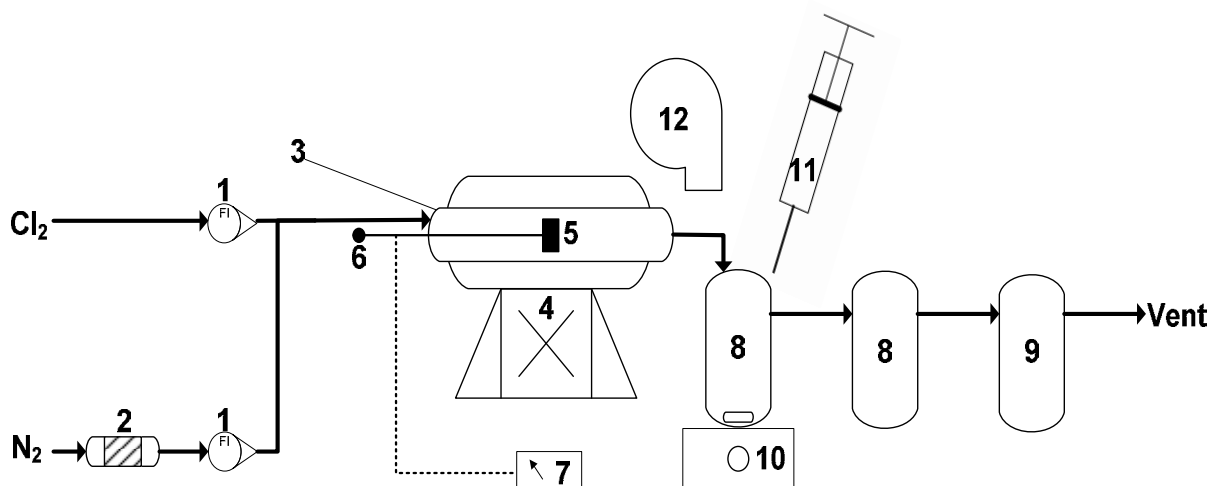


Figure 3.4. Schematic experimental setup for chlorination of titanium oxycarbide. 1-rotameters; 2-gas purifier; 3-quartz tube reactor; 4-horizontal tube furnace; 5-sample; 6-thermocouple; 7-temperature data logger; 8-TiCl₄ scrubbers; 9-Cl₂ scrubber; 10-magnetic stirrer; 11-sampling syringe; 12-heat gun

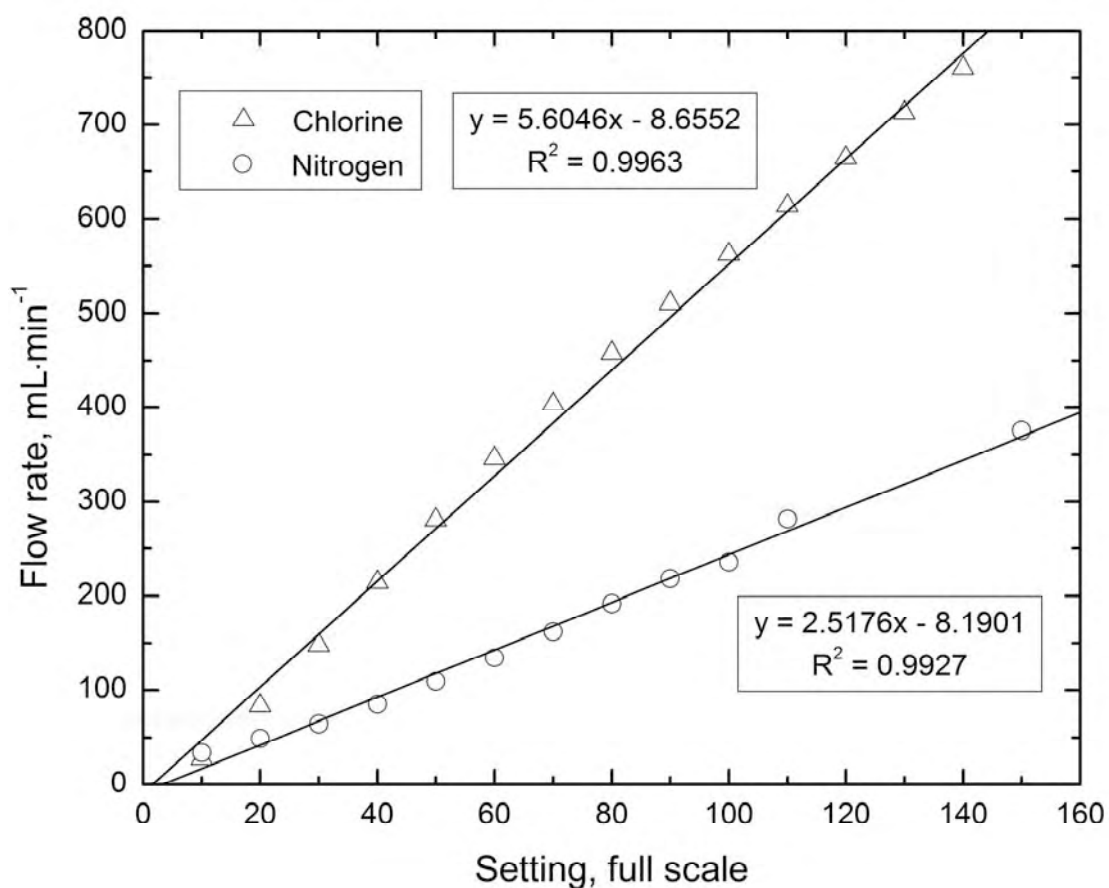


Figure 3.5. Calibration curves of the rotameters for chlorination experiment

Quartz tube reactor and glass scrubber flask were washed and rinsed thoroughly with distilled water after each run. They were then dried in the oven prior experiment to remove moisture which could cause blockage in chlorination experiments.

The sample temperature during chlorination was recorded with Comark Diligence EV N2014 data logger with a time interval of 1 sec. The temperature measured at the same conditions was reproduced with maximum standard deviation of 2.6 °C. **Figure 3.6** shows reproducibility of temperature measurements.

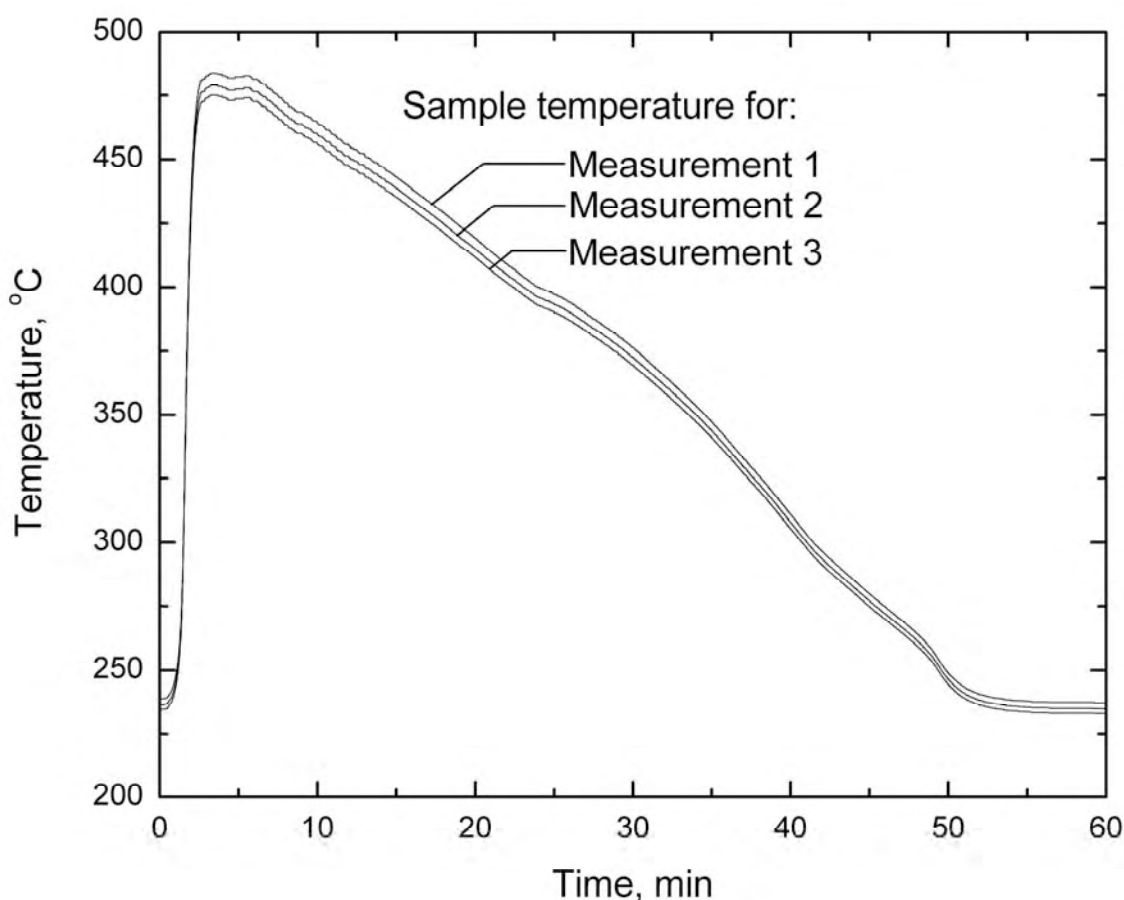


Figure 3.6. Sample temperature for reduced titania with molar ratio carbon to titania of 3.3 exposed to 50 mL.min⁻¹ chlorine with furnace temperature at 235 °C

3.2.3. Removal of Metallic Iron from Reduced Ilmenite

3.2.3.1. Procedures

A sample of reduced primary ilmenite with total weight of 22.5 g was crushed with rock mill into fine particles. Then it was transferred into a flask containing 0.372 M ammonium

chloride solution with the volume of 1000 mL and heated to 70 °C. The air was introduced into the slurry at flow rate of 2.5 L·min⁻¹. With the presence of ammonium chloride catalyst, the air facilitates removal of metallic iron from reduced ilmenite. The oxygen in the air caused metallic iron to oxidise and precipitate from titanium oxycarbide or oxycarbonitride in the form of iron oxide slime. The experiment was conducted for 5 h.

The slurry was then cooled and filtered. The filtrate was washed with distilled water and with 3.2 M of HCl to remove any traces of iron. The filtered cake was then dried in an oven at 150 °C for 24 h. The cake was then crushed into fine powder.

3.2.3.2. Aeration Equipment

The stirred aeration flask with volume of 2.0 L was used to facilitate removal of metallic iron from reduced ilmenite. Air for aerating the solution was generated by a compressor. The experimental setup is shown in **Figure 3.7**.

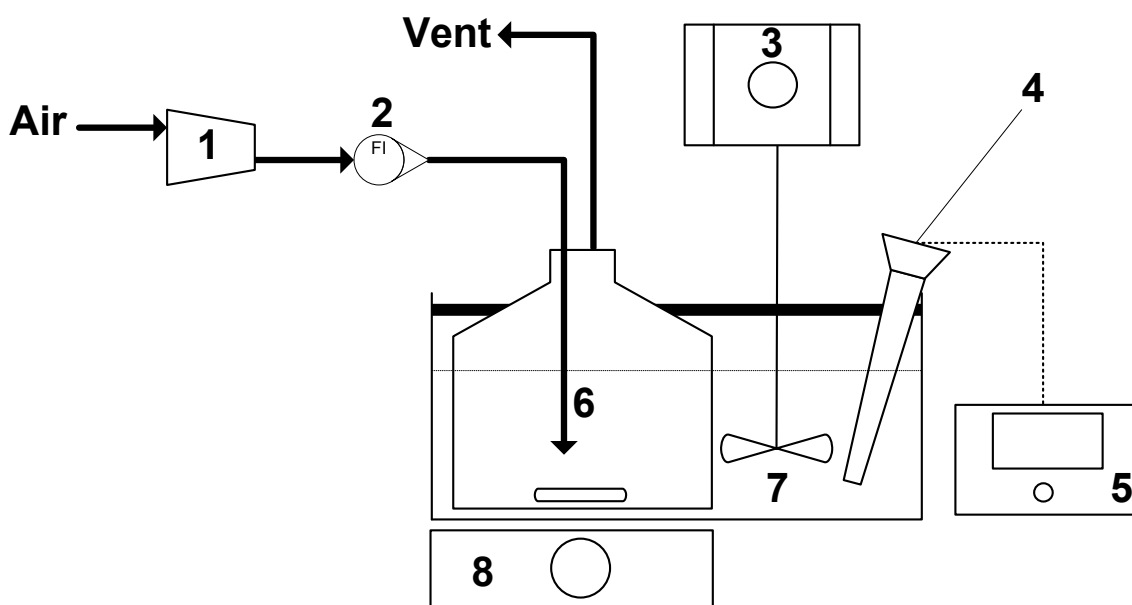


Figure 3.7. Schematic experimental setup for removal of metallic iron. 1–air compressor; 2–rotameter; 3–stirrer motor; 4–heating element; 5–temperature controller; 6–glass flask; 7–water bath; 8–magnetic stirrer

The rotameter was calibrated for air flow rate under ambient temperature and pressure.

Figure 3.8 shows the calibration curve of the rotameter.

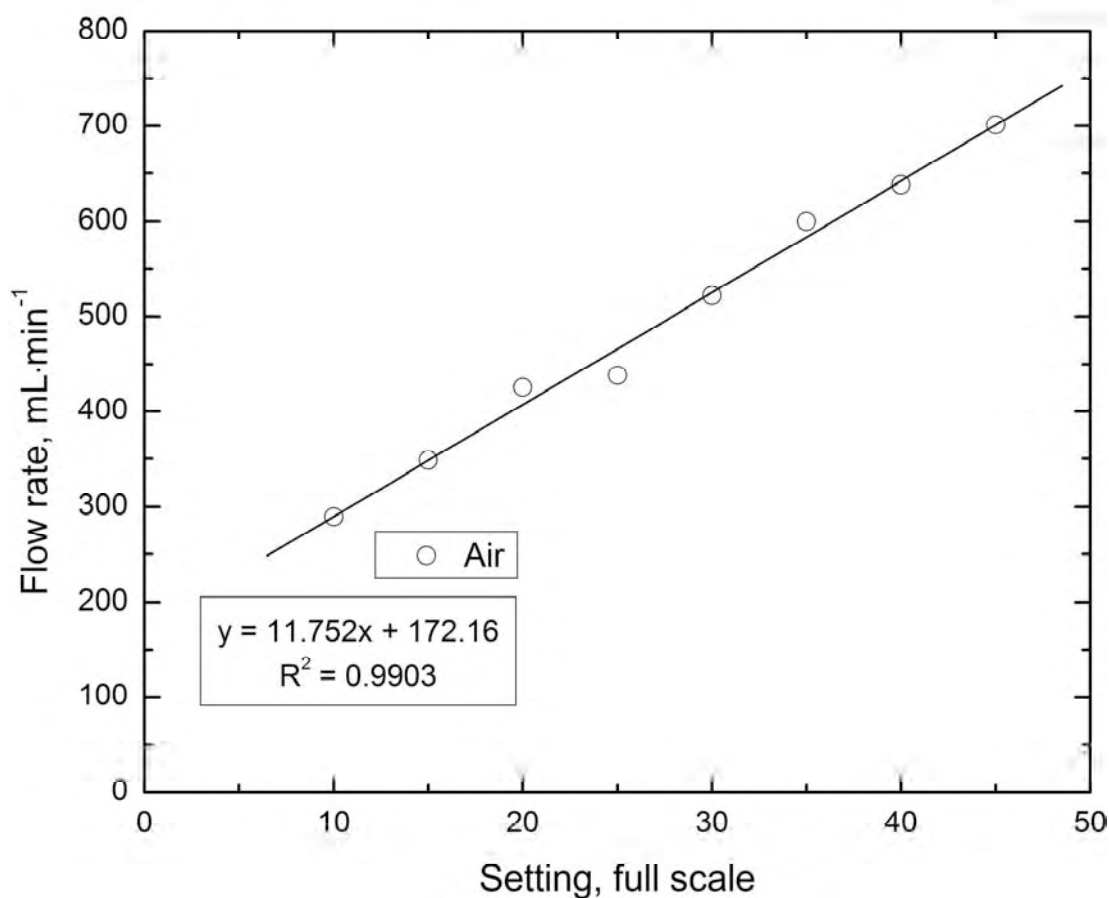


Figure 3.8. Calibration curves of the rotameter for removal of metallic iron from reduced ilmenite

3.3. Sample Characterisation

3.3.1. LECO Analysis

Oxygen and carbon contents in titanium oxycarbide or oxycarbonitride synthesised by reduction of titania or ilmenite were determined using LECO oxygen-nitrogen analyser (TC-436) and carbon-sulphur analyser (CS-444).

For carbon-sulphur analyser, a sample of 0.1 gram was weighed and placed into an alumina crucible with addition of a combustion catalyst. The sample was heated by induction furnace and was burnt with CO and CO₂ formation. This was then carried into infrared detector to measure the exact amounts of CO and CO₂ evolved from the combustion.

For oxygen analysis, a sample of 0.2 gram was loaded into a tin capsule, weighed, and placed into a nickel basket. The capsule and basket were loaded into a graphite crucible which was electrically heated as heating element. After purging the system with high purity helium, the crucible was preheated to remove the adsorbed oxygen on the sample and crucible. Then the crucible was heated to the combustion temperature. The oxygen in a sample combined with crucible carbon to form CO and CO₂ which were detected by thermal conduction detectors. The machine has the capacity to measure oxygen and nitrogen contents simultaneously.

3.3.2. X-Ray Diffraction Analysis

X-Ray Diffraction analysis is generally used for phase analysis of a multiphase crystalline material. By employing this analysis, the mean crystallite size ranging from 3-50 nm is estimated [Cullity, 1978].

In this study, phase composition of samples was measured by powder diffraction method and was carried out using XRD Siemens D5000 instrument. A sample was ground into small crystals (preferably of size less than 1 µm to 10 µm) to promote random orientation of the ground up crystals. This was then closely packed into 10 mm aperture of an amorphous plastic sample holder. The surface of the powder was pressed to ensure flat surface and close packing. The sample was then mounted into the instrument.

The X-Ray Diffractometer has a monochromators and a copper K α X-Ray source with wavelength, $\lambda = 1.541838 \text{ \AA}$. The voltage and current in the X-Ray emission tube were 30 KV and 30 mA, respectively. The scanning angle, 2θ , changed from 20 to 80°. The scanning rate was set at $0.6^\circ.\text{min}^{-1}$ with a step size of 0.01° . X'Pert HighScore Plus version 1.0 b by Philips Analytical B.V. was used to identify the peaks and the phases present in the sample. This phase identification is based on Bragg's law [Cullity, 1978]:

$$n\lambda = 2d \sin \theta \quad (3-1)$$

where, n is the order of reflection (integer); λ is the wavelength of X-Ray ($1.541838 \text{ \AA}$); d is interplanar distance of the crystal ($\text{\AA}$); and θ is the angle of incidence (degrees).

3.3.3. Surface Area Measurement

The specific surface area of the samples was measured with a single point Brunauer-Emmett-Teller (BET) technique using Micromeritics 2000 surface area analyser. Analysis was based on the adsorption of nitrogen at the boiling temperature of liquid nitrogen. The instrument utilised liquid nitrogen at the boiling temperature with 30.2 vol pct nitrogen in helium as adsorption agent. The principle of the specific surface area measurement is based on the physical adsorption of gaseous adsorbate by porous materials [Brunauer *et al.*, 1938]. The BET equation was derived by Brunauer *et al.* (1938) based on Langmuir's monomolecular model [Langmuir, 1916]. The following equation was used for the calculation of specific surface area [Brunauer *et al.*, 1938]:

$$\frac{P}{V(P^0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P^0} \quad (3-2)$$

where P and P^0 are the equilibrium pressure in the gas phase and saturation pressure of adsorbate, respectively. V and V_m are the adsorption volume of adsorbate at pressure P and that adsorbed for a complete single layer of adsorbate on sample surface. C is a model parameter related to the adsorption energy. The specific surface area was calculated according to the following equation:

$$S_g = \left(\frac{V_m N_0}{V_0} \right) a \quad (3-3)$$

Where $V_0 = 22400 \text{ ml} \cdot \text{mol}^{-1}$ is the volume of 1 mol gas at 1 atm and 0 °C

$N_0 = 6.032 \times 10^{23} \text{ mol}^{-1}$ is the Avogadro number;

$a = 15.8 \text{ \AA}^2$ is the area occupied by a single molecule of nitrogen.

3.3.4. ICP-OES Analysis

Inductive Coupled Plasma-Optical Emission Spectrometer, ICP-OES (also known as Inductive Coupled Plasma-Atomic Emission Spectrometer, ICP-AES) is used for the determination of trace concentrations of elements in samples. It uses plasma to evaporate any solids that were dissolved in the liquid. It then vaporised the liquid and atomised it into

atoms. These emit electromagnetic radiation at specific wavelengths which characterise a particular element. The intensity of its emission indicates concentration of specific element within the sample [Skoog, *et al.*, 1996].

3.3.4. Extent of Reaction

3.3.4.1. Titania Carbothermal Reduction

The extent of reduction of titania to titanium oxycarbide, $X_{(Ti,O,C)}$, defined as percentage of oxygen removed from titania in a sample, was calculated according to Zhang (2000). The initial sample (titania-graphite mixture) consists of three elements: titanium, oxygen and carbon. The weight fractions of titanium, oxygen, and carbon in a sample are:

$$f_{Ti}^0 = \frac{MW_{Ti}}{MW_{TiO_2}} = 47.9/79.9 = 0.5995$$

$$f_O^0 = \frac{2MW_O}{MW_{TiO_2}} = 32/79.9 = 0.4005$$

$$f_C^0 = \frac{3.3MW_C}{MW_{TiO_2}} = 39.6/79.9 = 0.4956$$

where MW_i is the molecular weight of component i (carbon, oxygen or titanium). The coefficient “3.3” for f_C^0 indicates the molar ratio of carbon to titania. The initial sample was made of TiO_2 and carbon with C/ TiO_2 molar ratio 3.3. The f_i^0 is the ratio of the mass of component i (carbon, oxygen or titanium) to the mass of titania in the titania-graphite sample. Therefore, $f_C^0 + f_{Ti}^0 + f_O^0 > 1$.

The weight fractions of oxygen and carbon in the reduced sample were measured by LECO analysis as f_O and f_C . The weight fraction of titanium was calculated as:

$$f_{Ti} = 1 - f_O - f_C \quad (3-4)$$

In the case of conversion of titania to titanium oxycarbonitride:

$$f_{Ti} = 1 - f_O - f_C - f_N \quad (3-5)$$

The initial mass of titania prior to reduction was W^0 ; after reduction it became W . According to the mass balance of titanium, the equations can be written as the following:

$$Wf_{Ti} = W^0 f_{Ti}^0$$

$$\frac{W}{W^0} = \frac{f_{Ti}^0}{f_{Ti}} \quad (3-6)$$

The extent of reduction is defined as the fraction of oxygen removed by the reduction reaction as:

$$X_{(Ti,O,C)} = 1 - \frac{Wf_o}{W^o f_o^o}$$

$$X_{(Ti,O,C)} = \left(1 - \frac{(1 - f_o^o - f_c^o)f_o}{(1 - f_o - f_c)f_o^o} \right) \times 100\% \quad (3-7)$$

where f_o^o and f_o are weight fractions of oxygen before and after reduction; f_c^o and f_c are weight fractions of carbon before and after reduction, respectively.

The extent of reduction for conversion of titania to titanium oxycarbonitride, $X_{(Ti,O,C,N)}$, was calculated using the following equation:

$$X_{(Ti,O,C,N)} = \left(1 - \frac{(1 - f_o^o - f_c^o)f_o}{(1 - f_o - f_c - f_N)f_o^o} \right) \times 100\% \quad (3-8)$$

where f_N is the weight fraction of nitrogen after reduction.

When titanium sub-oxides were not detected in a reduced sample by XRD analysis, all the oxygen was assigned to TiO, which allowed calculation of fractions of TiO and TiC in the TiC-TiO solid solution or fractions of TiO, TiC, and TiN in the TiC-TiO-TiN solid solution.

3.3.4.2. Ilmenite Carbothermal Reduction

The extent of reduction of ilmenite ores was calculated from the fraction of reducible oxygen removed according to Zhang (2000). The total fraction of oxygen in raw material is defined as $f_{O,T}^o$, while for the reducible part is $f_{O,R}^o$. The reducible oxygen ($f_{O,R}^o$) is associated from titanium, iron, and manganese oxides. The reducible oxygen is defined as oxygen in titanium, iron and manganese oxides which are reduced in the carbothermal reduction process. The fractions of carbon and oxygen obtained from LECO analysis after the reduction are defined as f_o and f_c . The mass balance for all the elements with the exception of oxygen and carbon is the following:

$$W(1 - f_o - f_c) = W^o(1 - f_{O,T}^o) \quad (3-9)$$

$$\frac{W}{W^0} = \frac{1 - f_{O,T}^0}{1 - f_O - f_C} \quad (3-10)$$

The reducible oxygen left in a sample was calculated by the following equation:

$$W_{O,R} = Wf_O - W^0(f_{O,T}^0 - f_{O,R}^0) \quad (3-11)$$

Based on the oxygen removed from initial mixture, the extent of reduction was calculated as the following:

$$X_{(Ti,O,C)} = 1 - \frac{(Wf_O - W^0(f_{O,T}^0 - f_{O,R}^0))}{W^0 f_{O,R}^0} \quad (3-12)$$

or

$$X_{(Ti,O,C)} = \frac{f_{O,T}^0}{f_{O,R}^0} - \frac{f_O(1 - f_{O,T}^0)}{f_{O,R}^0(1 - f_O - f_C)} \quad (3-13)$$

The extent of reduction conversion of titania in ilmenite to titanium oxycarbonitride was calculated using the following equation:

$$X_{(Ti,O,C,N)} = \frac{f_{O,T}^0}{f_{O,R}^0} - \frac{f_O(1 - f_{O,T}^0)}{f_{O,R}^0(1 - f_O - f_C - f_N)} \quad (3-14)$$

3.3.4.3. Chlorination Reaction

Liquid samples with extracted titanium which were taken from the gas scrubbers at different intervals were diluted and then analysed by ICP-OES (Perkin Elmer Optima 3000). Based on titanium content in the solution, the extent of chlorination was calculated as:

$$\alpha_{Ti} = \frac{m_{Ti}}{m_{Ti}^0} \times 100 \text{ pct} \quad (3-15)$$

where m_{Ti} and m_{Ti}^0 are the masses of titanium in $TiCl_4$ solution and in original titania-graphite pellet, respectively.

Based on iron content in the solution, the extent of its chlorination was calculated as:

$$\alpha_{Fe} = \frac{m_{Fe}}{m_{Fe}^0} \times 100 \text{ pct} \quad (3-16)$$

where m_{Fe} and m_{Fe}^0 are the masses of iron in $TiCl_4$ solution and in original ilmenites/synthetic rutile – graphite samples, respectively.

The accuracy of the ICP-OES analysis of titanium content in a solution (up to 100 ppm) was 1 ppm. Better precision can be obtained with the trade-offs in speed. The concentration of titanium in the solution was targeted in the range of 50-100 ppm, what was achieved by appropriate dilution. The overall error of the ICP-OES analysis was within 2 pct. The overall accuracy of calculated extent of chlorination was within 3 pct. Examination of reproducibility of chlorination experiments at the same conditions showed maximum standard deviation in the extent of chlorination of 1.2 pct. **Figure 3.9** show the reproducibility for the extent of chlorination.

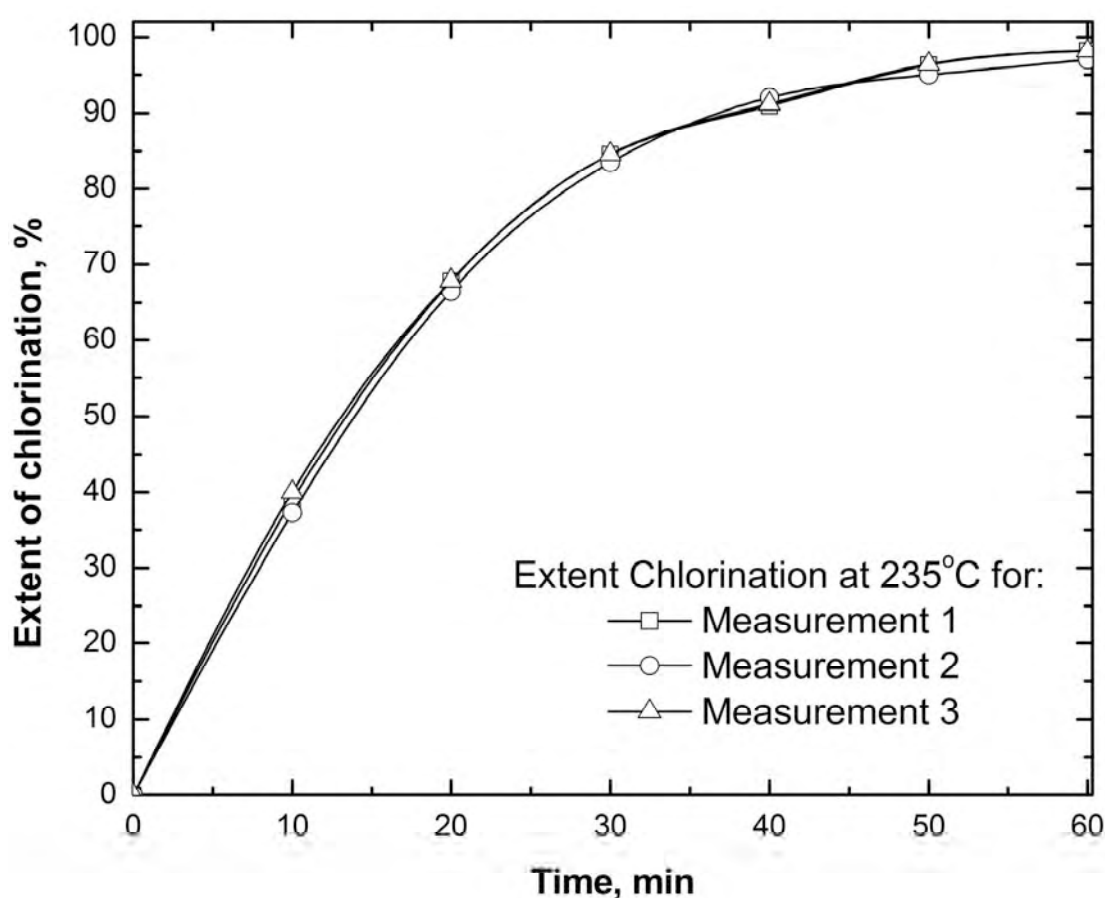


Figure 3.9. Extent of chlorination for reduced titania with molar carbon to titania ratio of 3.3 exposed to 50 mL.min⁻¹ chlorine with the furnace temperature at 235 °C

CHAPTER 4.

CHLORINATION OF TITANIUM OXYCARBIDE

This chapter presents results of study of chlorination of titanium oxycarbide. The effects of temperature, chlorine partial pressure, gas flow rate, particle size and suboxides on the rate of chlorination of titanium oxycarbide were examined. The experimental results of conversion of titania to titanium oxycarbide are also presented.

4.1. Reduction of Rutile

Mixtures of titania and graphite with different carbon to titania molar ratio were pressed into pellets and heated under argon atmosphere at 1450 °C (*see Chapter 3*). Composition of samples produced by carbothermal reduction of rutile with different carbon to rutile molar ratio is presented in **Table 4.1**. Their XRD spectra are shown in **Figure 4.1**. Samples A and B consisted of titanium oxycarbide and sub-oxides Ti_3O_5 and Ti_2O_3 , sample C was titanium oxycarbide, samples D and E included titanium oxycarbide and excess carbon, which amount was higher in sample E. The measurement of BET surface area for sample E was $6.38 \text{ m}^2\cdot\text{g}^{-1}$ with average porosity of 45.6 Å.

Table 4.1. Composition of reduced samples of rutile subjected to chlorination

Sample	A	B	C	D	E
Carbon content, wt pct	4.18	8.17	13.5	23.7	35.2
Oxygen content, wt pct	27.0	18.2	8.13	0.63	3.09
Extent of reduction, pct	41.4	60.0	84.5	98.8	92.5
Phase composition*	Ti_3O_5 , Ti_2O_3 , TiC_xO_y	Ti_3O_5 , Ti_2O_3 , TiC_xO_y	$TiC_{0.69}O_{0.31}$	$TiC_{0.98}O_{0.02}$, C (C/Ti = 0.43)	$TiC_{0.85}O_{0.15}$, C (C/Ti = 1.84)

* C/Ti represents free carbon to titanium molar ratio.

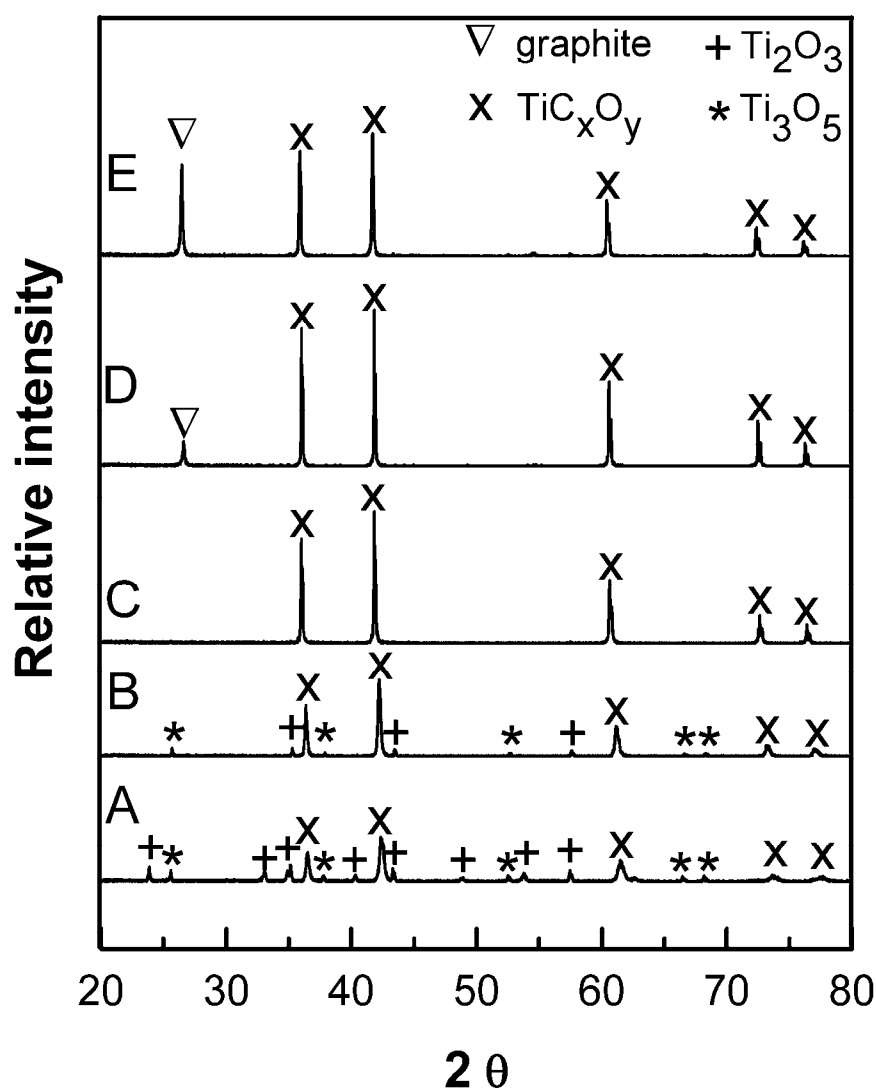


Figure 4.1. X-ray diffraction patterns of titanium oxycarbide for samples A to E

4.2. Effect of Temperature

The effect of furnace temperature on chlorination of titanium oxycarbide in samples A to E was studied in the temperature range of 235 to 400 °C at chlorine flow rates of 50 mL·min⁻¹ and 250 mL·min⁻¹. Chlorination curves for samples A to E at different temperatures with chlorine flow rate of 50 mL·min⁻¹ are presented in **Figure 4.2 (a) – (e)**. The rate and extent of chlorination tended to increase with increasing furnace temperature, however the effect was minor. The extent of chlorination of sample A was below 70 pct. This sample contained titanium suboxides (extent of titania reduction was 41.4 pct), of which chlorination was slow in comparison with titanium oxycarbide and incomplete.

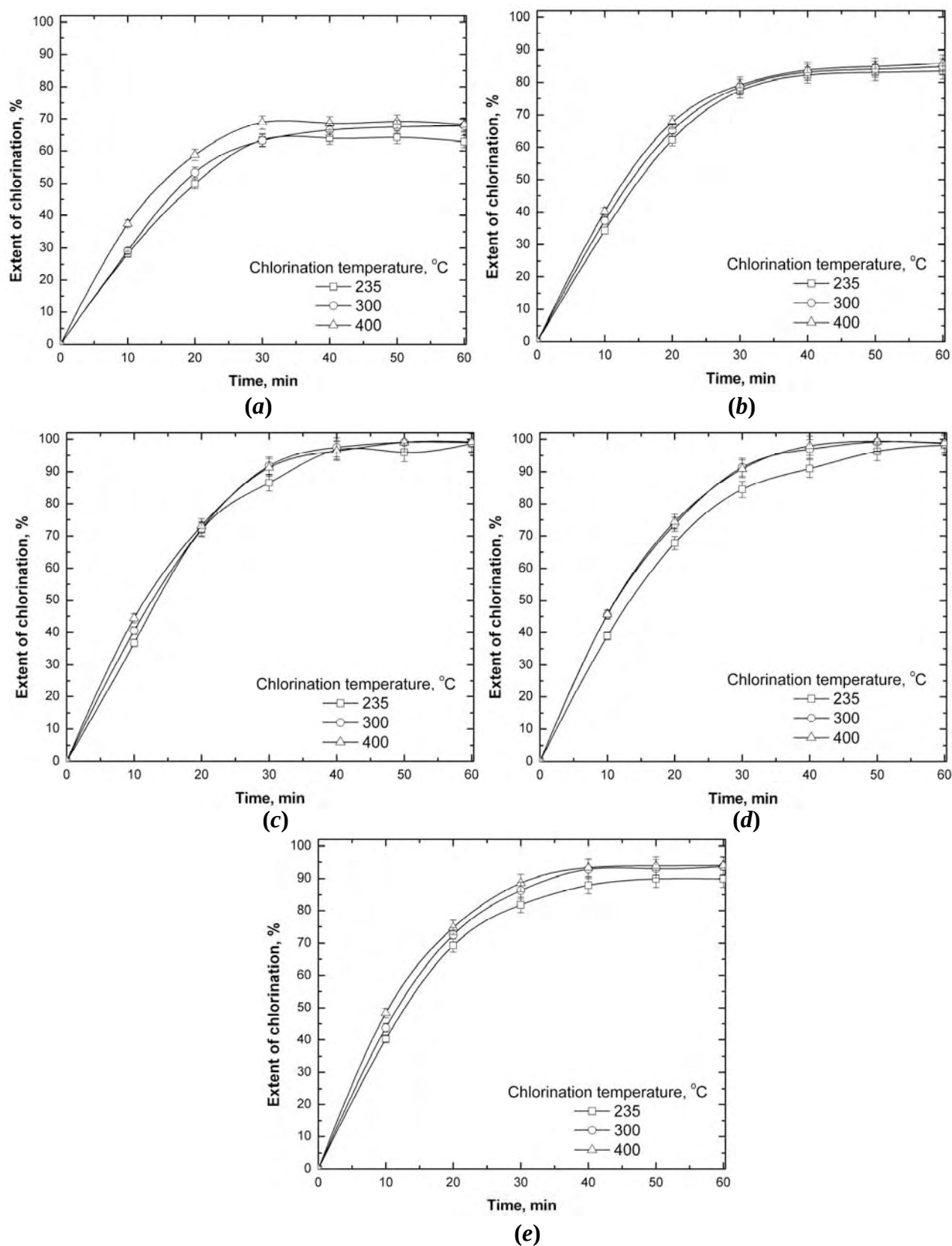


Figure 4.2. Extent of chlorination of titanium oxycarbide at temperatures from 235 to 400 °C with chlorine flow rate $50 \text{ mL} \cdot \text{min}^{-1}$ for sample: (a) A, (b) B, (c) C, (d) D, and (e) E

Sample B also contained titanium sub-oxides, but in much smaller amount than sample A. The extent of chlorination of this sample reached 85 pct. Extent of chlorination of sample C, which contained no other phases but titanium oxycarbide, was close to 100 pct. The extent of chlorination decreased with increasing carbon phase in a sample to below 95 pct for sample E. Most chlorination occurred during the first 30 min, and stopped after about 50 min.

Chlorination of titanium oxycarbide is highly exothermic. The change in sample temperature during chlorination of sample C at chlorine flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$ is presented in **Figure 4.3**. After a short period, generally less than 1 min, the sample temperature started to increase rapidly and reached maximum in about 5 min. Similar temperature change was observed for other samples.

The residues of chlorinated samples of titanium oxycarbide were examined by XRD analysis. **Figure 4.4** shows the XRD patterns of samples A to E after chlorination at 400°C for 60 min in pure chlorine with flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$. Similar XRD patterns were obtained for the residues after chlorination at 235°C and 300°C . Unconsumed graphite was observed in chlorinated samples D and E. Residual carbon was not detected by XRD for samples A to C, although the presence of free carbon in the residue was expected in sample C because of its higher content of TiC than TiO in titanium oxycarbide. In fact, up to 91.5 pct of carbon in a residue of sample C was detected by LECO carbon analysis. This carbon was amorphous and was not sensitive to XRD analysis (Avila-Brande *et al.*, 2006).

The mass balances of titanium, oxygen and carbon based on results of reduction and chlorination experiments showed that sub-oxides in samples A and B were partly chlorinated; degree of their chlorination was low relative to chlorination of titanium oxycarbide. In the residue of chlorination of samples A and B, strong peaks for Ti_2O_3 and Ti_3O_5 were detected. Weak XRD peaks for Ti_2O_3 and Ti_3O_5 were also observed in the residue of chlorination of samples D and E, indicating that formation of titanium oxycarbide by carbothermal reduction was incomplete, even when up to 50 pct extra carbon was used.

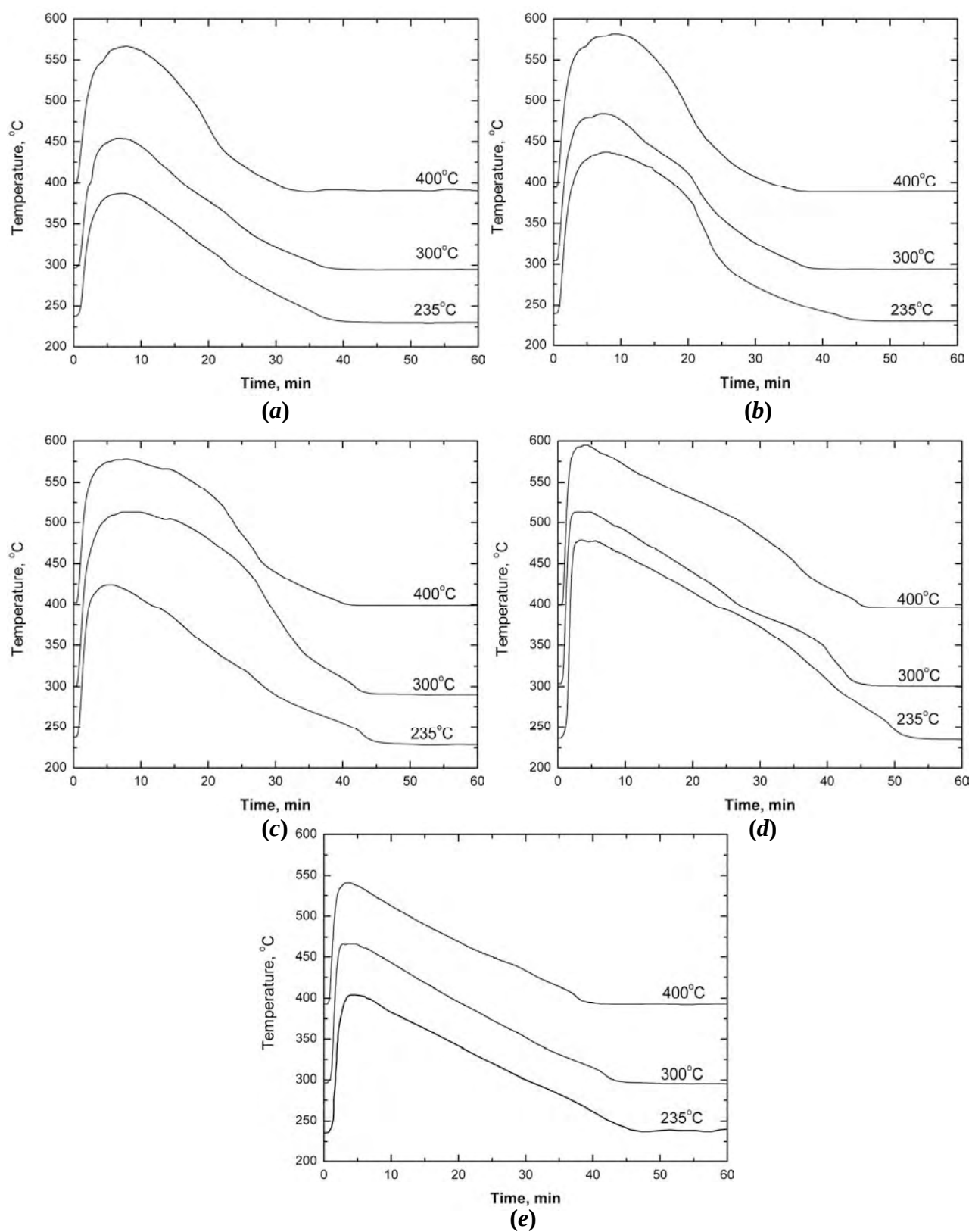


Figure 4.3. Change in sample temperature during chlorination of titanium oxycarbide with chlorine flow rate $50 \text{ mL} \cdot \text{min}^{-1}$ for sample: (a) A, (b) B, (c) C, (d) D, and (e) E

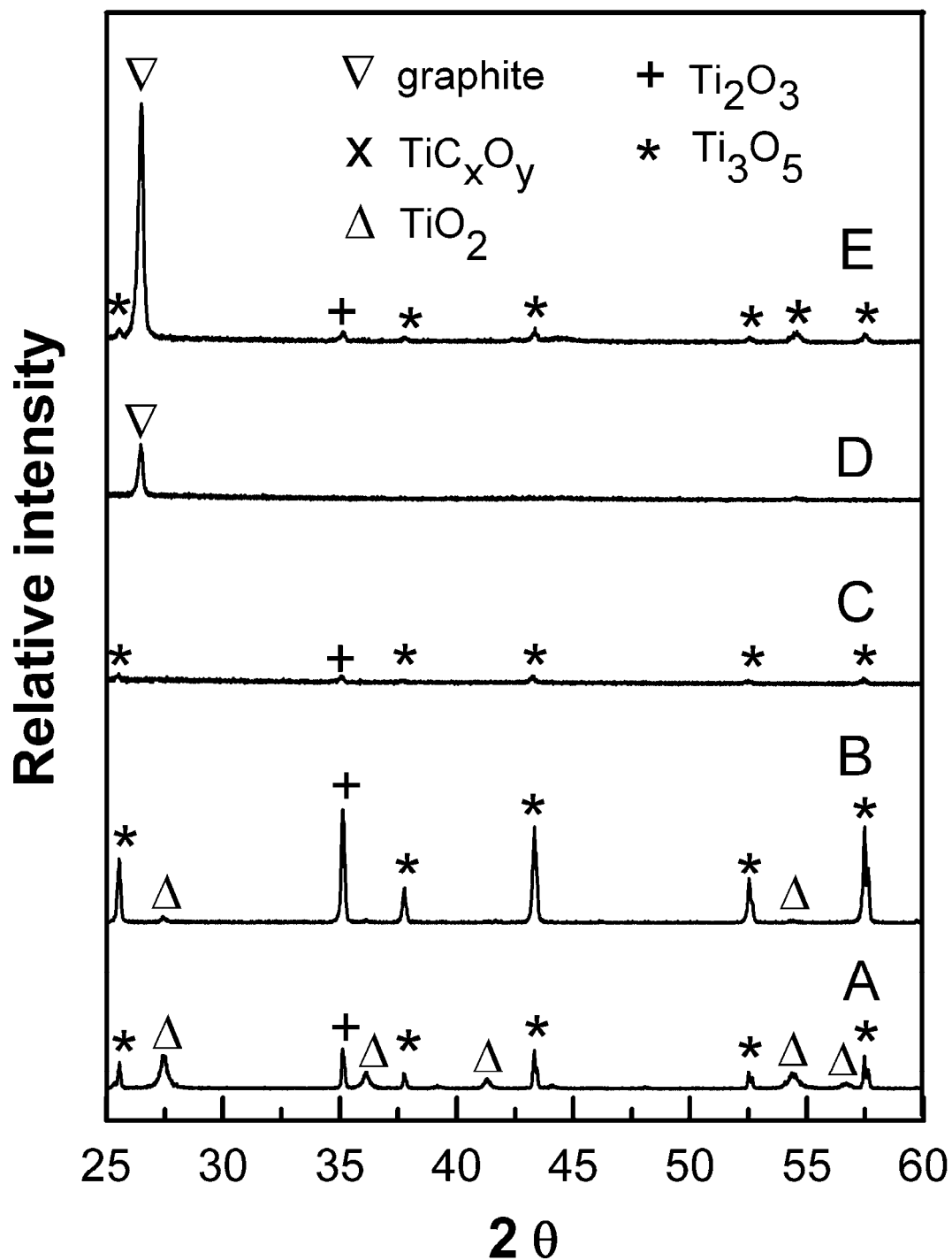


Figure 4.4. X-ray diffraction patterns of residues of titanium oxycarbide for samples A to E after chlorination with $50 \text{ ml}\cdot\text{min}^{-1}$ of chlorine at 400°C for 60 min

At higher chlorine flow rate, $250 \text{ mL}\cdot\text{min}^{-1}$, the effect of furnace temperature on chlorination of titanium oxycarbide was much stronger. This is seen in **Figure 4.5** which presents chlorination curves for sample C at 235, 300 and 400°C .

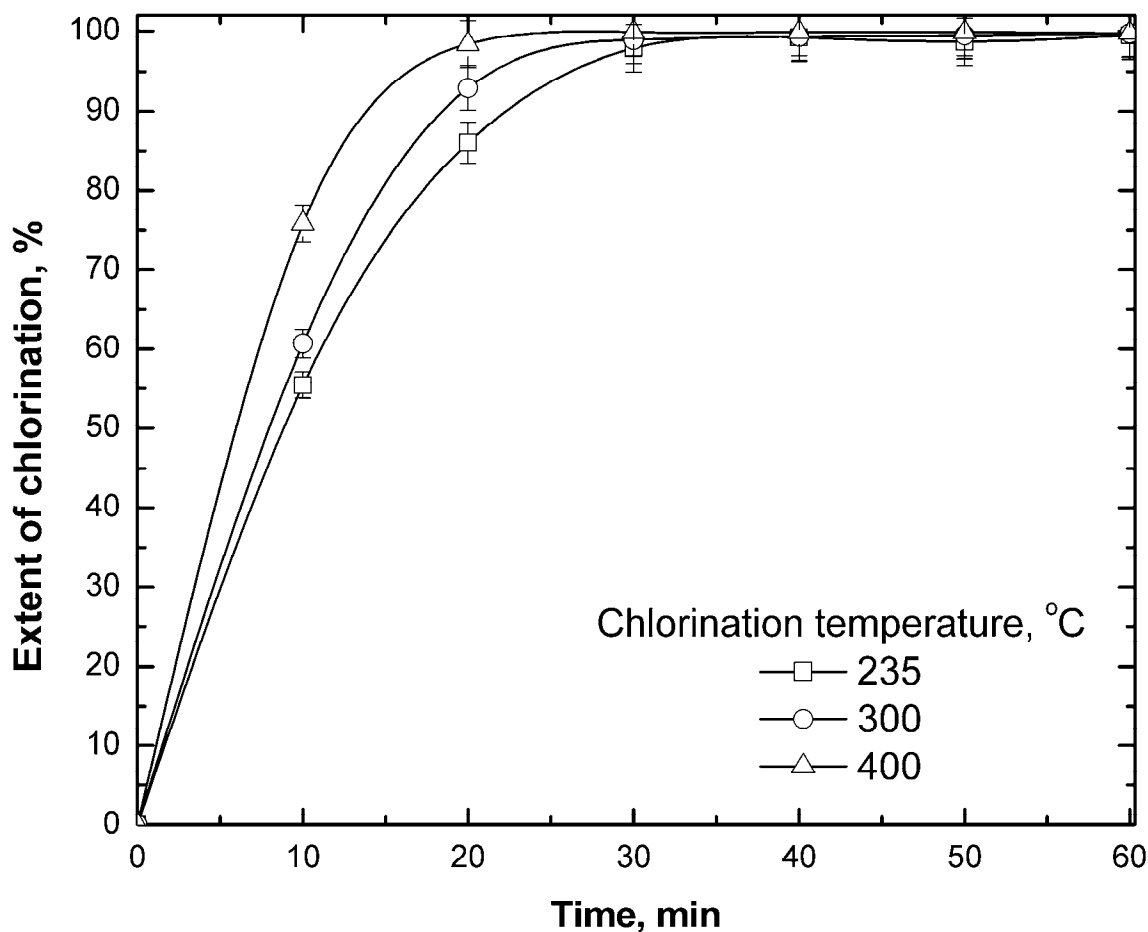


Figure 4.5. Extent of chlorination of sample C at temperatures from 235 to 400 °C with chlorine flow rate 250 mL·min⁻¹

The rate of chlorination increased with increasing temperature and was close to completion at 235 and 300 °C after 30 min and at 400 °C after 20 min. The chlorination was faster than that at chlorine flow rate of 50 mL·min⁻¹.

The ignition temperature was determined in non-isothermal experiments. **Figure 4.6** shows the change of the pellet's temperature for a sample A for chlorine gas flow rate in the range of 50 to 300 mL·min⁻¹. During the initial 25 to 30 min, the sample was heated up in line with the furnace temperature. Then, the rise of pellet's temperature started to speed up, indicating the ignition of the chlorination reaction. After achieving maximum temperature, the reaction slowly faded away and the sample temperature began to approach the furnace temperature. The ignition temperature was 150 °C for all three chlorine flow

rates; however, the maximum temperature was reached faster and was higher for the higher gas flow rate. The entire reaction period was also shorter.

Figure 4.7 compares the sample temperature for samples A to E in the temperature-programmed experiments with chlorine flow rate $300 \text{ mL}\cdot\text{min}^{-1}$. The chlorination of samples A to C was ignited at 150°C , while samples D and E had ignition temperatures higher than 200°C .

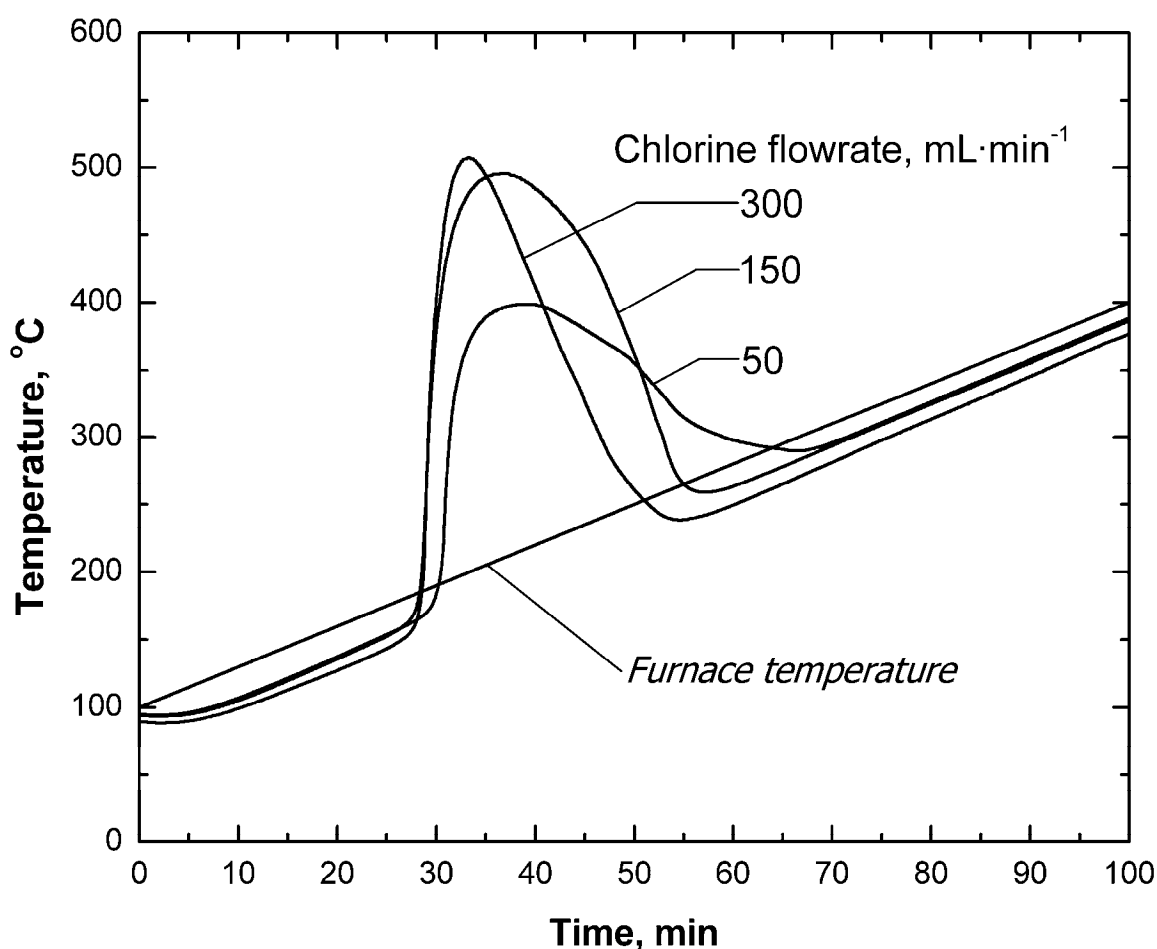


Figure 4.6. Change in the sample temperature during temperature programmed chlorination of titanium oxycarbide with ramping rate of $3^\circ\text{C}\cdot\text{min}^{-1}$ for sample A under chlorine flow rate from 50 to $300 \text{ mL}\cdot\text{min}^{-1}$

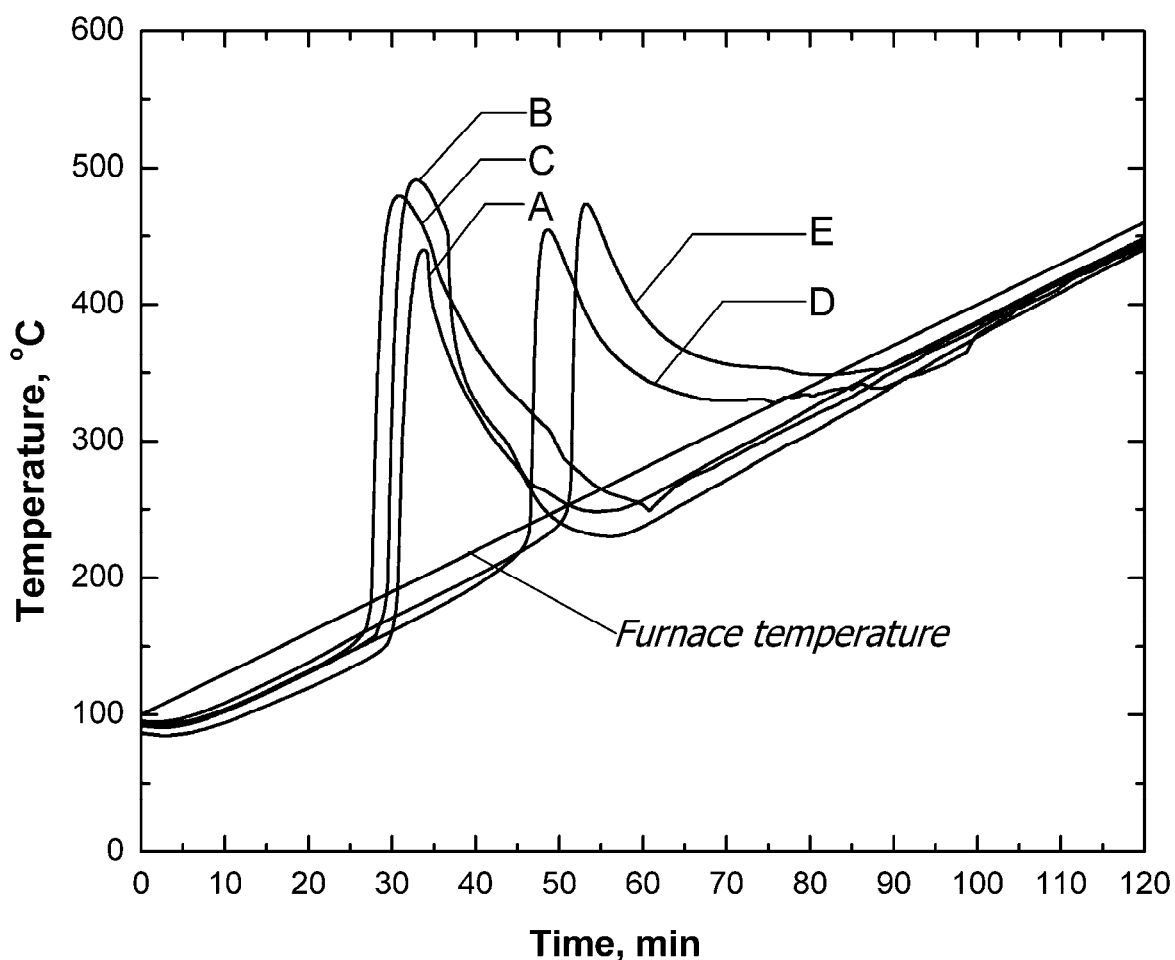
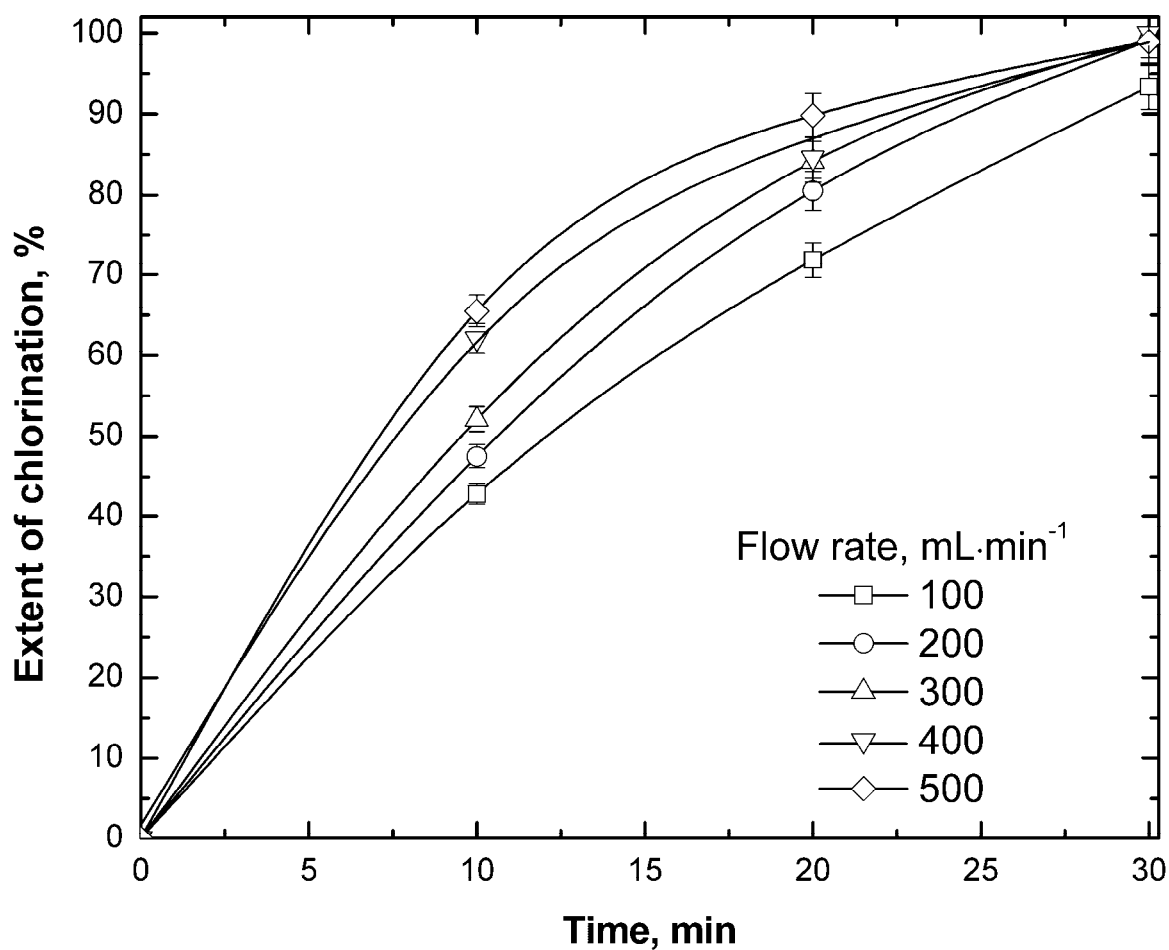


Figure 4.7. Change in the sample temperature during temperature programmed chlorination of titanium oxycarbide with ramping rate of $3\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ for samples A to E under chlorine flow rate of $300\text{ mL}\cdot\text{min}^{-1}$

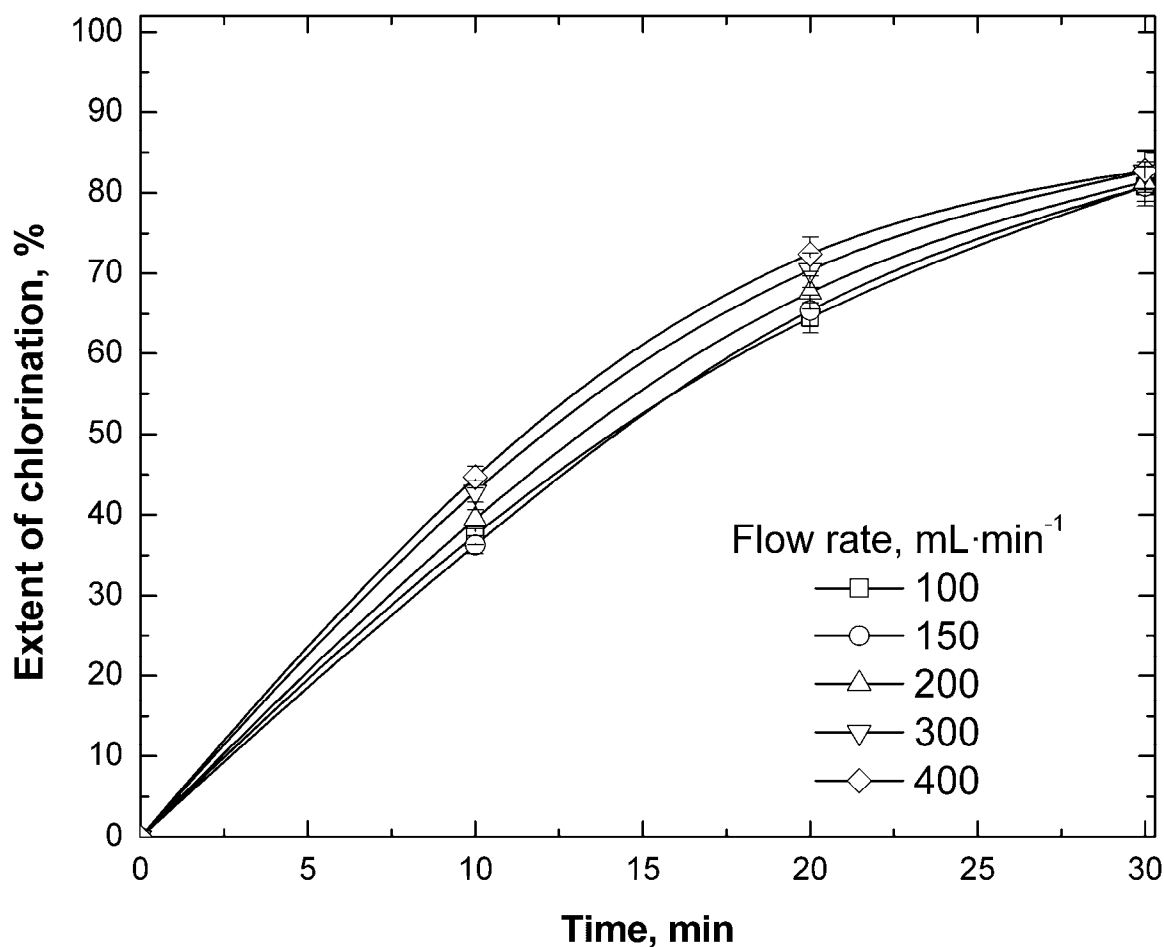
4.3. Effect of Gas Flow Rate

The effect of gas flow rate on chlorination was studied with samples C and D at $300\text{ }^{\circ}\text{C}$ using the $\text{Cl}_2\text{-N}_2$ gas mixture with constant chlorine partial pressure of 50 kPa . The flow rate of the gas mixture was in the range of 100 to $500\text{ mL}\cdot\text{min}^{-1}$. The progress of chlorination of samples C and D is shown in **Figures 4.8** and **4.9**, respectively. The chlorination rate increased with increasing gas flow rate. Its effect was more significant for sample C compared to sample D. The extent of chlorination of sample C was close to 100

pct after 30 min of reaction when the gas flow rate was $200 \text{ mL}\cdot\text{min}^{-1}$ and above. With $100 \text{ mL}\cdot\text{min}^{-1}$ gas flow, the extent of chlorination after 30 min was 93 pct. In comparison, the extent of chlorination achieved by sample D was in the range of 77 to 83 pct after 30 min of chlorination.



Figures 4.8. Effect of $\text{N}_2\text{-Cl}_2$ gas flow rate on the extent of chlorination at 300°C with 50 kPa chlorine partial pressure for sample C



Figures 4.9. Effect of $\text{N}_2\text{-Cl}_2$ gas flow rate on the extent of chlorination at 300 °C with 50 kPa chlorine partial pressure for sample D

The effect of gas flow rate on chlorination of sample C was also studied at 235 °C in pure chlorine. The gas flow rate was in the range from 30 to 300 $\text{mL}\cdot\text{min}^{-1}$. **Figure 4.10** shows that the chlorination rate increased with increasing chlorine flow rate until 200 $\text{mL}\cdot\text{min}^{-1}$, beyond which the effect of the gas flow rate was minor. The extent of chlorination of sample C was close to completion after 30 min of reaction when the gas flow rate was 150 $\text{mL}\cdot\text{min}^{-1}$ and above. With 300 $\text{mL}\cdot\text{min}^{-1}$ gas flow, the extent of chlorination was 98.4 pct after 60 min.

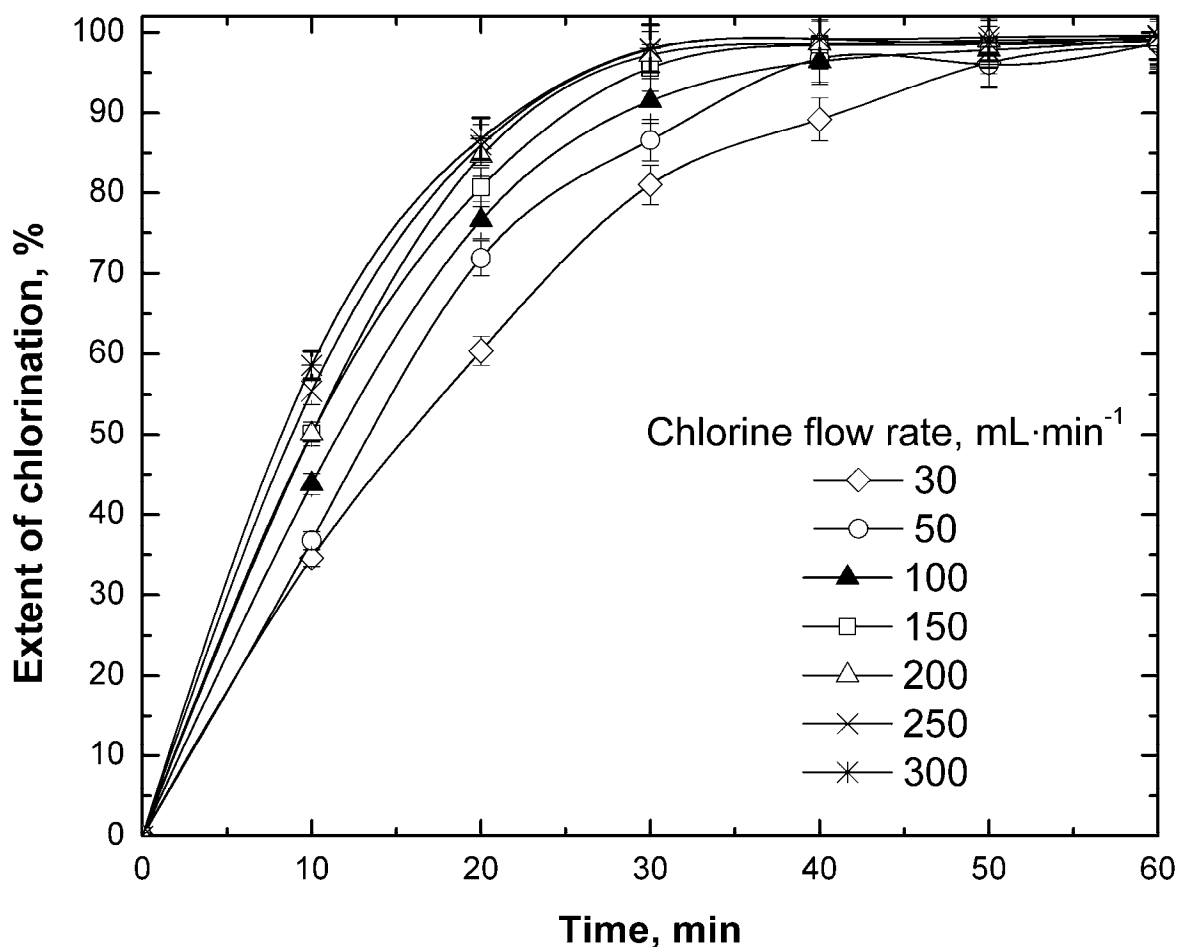


Figure 4.10. Effect of Cl_2 gas flow rate on the extent of chlorination of sample C at 235°C

The change in sample temperature during chlorination of titanium oxycarbide in the $\text{Cl}_2\text{-N}_2$ gas mixture (50 vol pct Cl_2) for samples C and D is presented in **Figures 4.11** and **4.12**. The change in the sample temperature during chlorination of sample C was notably higher than that of sample D. The change in temperature during chlorination of sample C in pure Cl_2 gas is presented in **Figure 4.13**. At chlorine flow rate of $200\text{ mL}\cdot\text{min}^{-1}$, a sample temperature raised rapidly to 600°C in 5 min and the thermocouple started to react with chlorine, elevating its recorded temperature to 770°C . Consequently, the samples were chlorinated in an alumina boat for flow rate of $200\text{ mL}\cdot\text{min}^{-1}$ and above. The change in the sample temperature with increasing flow rate of pure chlorine was more significant than in experiments with $\text{Cl}_2\text{-N}_2$ gas mixture.

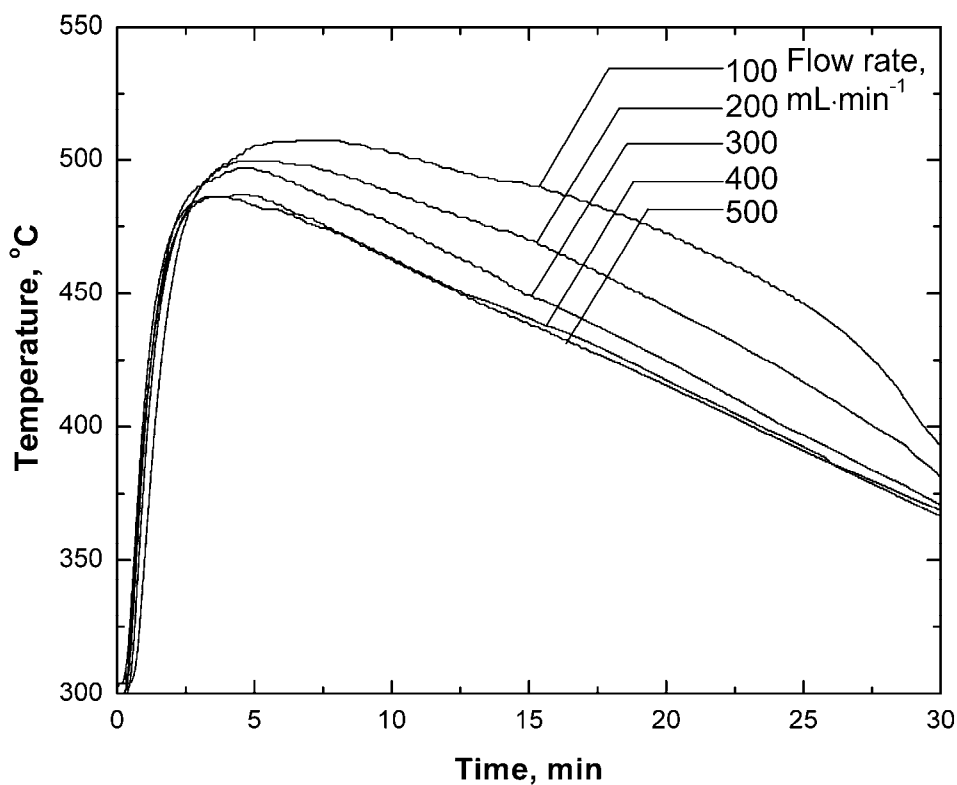


Figure 4.11. Change in sample temperature during chlorination of sample C in 50 pct N₂ - 50 pct Cl₂ mixture at 300 °C

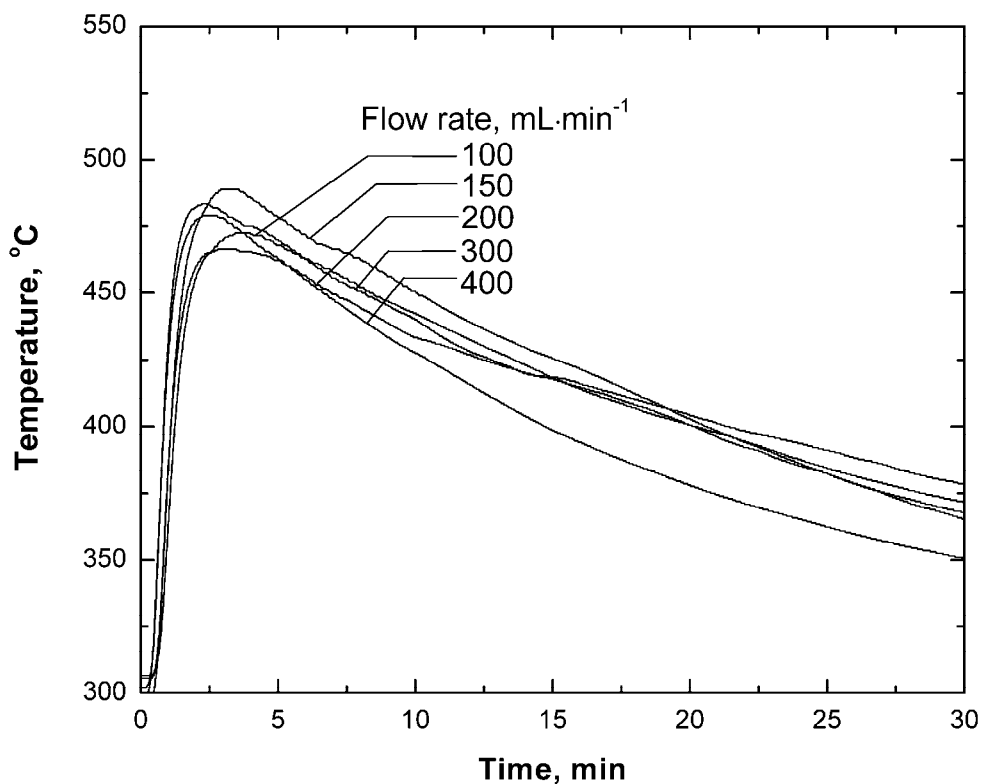


Figure 4.12. Change in sample temperature during chlorination of sample D in 50 pct N₂ - 50 pct Cl₂ mixture at 300 °C

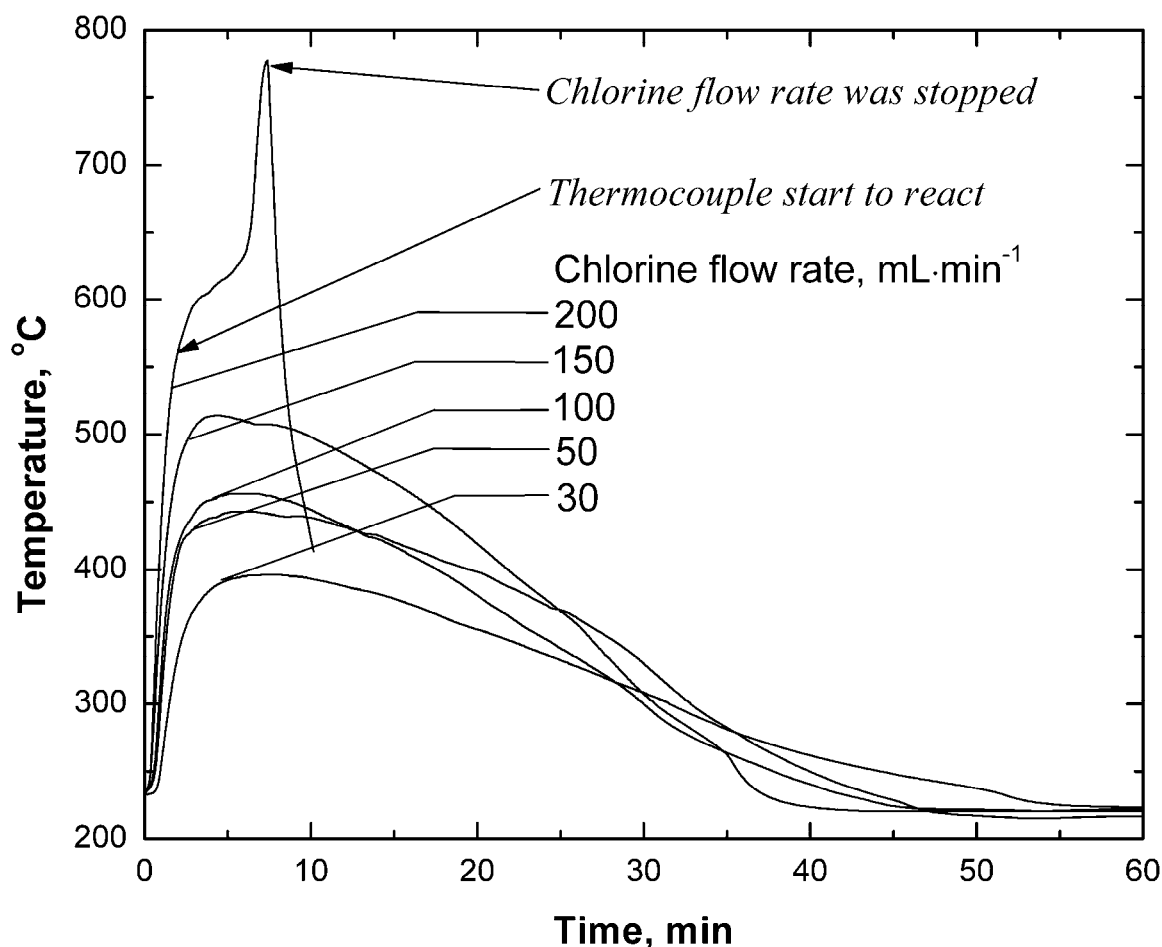


Figure 4.13. Change in sample temperature during chlorination of sample C in pure Cl_2 at 235 °C

4.4. Effect of Chlorine Partial Pressure

The effect of partial pressure of chlorine in the $\text{Cl}_2\text{-N}_2$ gas mixture on chlorination was examined using samples C and D at 300 °C. The partial pressure of chlorine was changed in the range of 20 to 100 kPa by adjusting the flow rate of chlorine and nitrogen. Total gas flow rate was maintained at 450 $\text{mL}\cdot\text{min}^{-1}$. As shown in **Figure 4.14**, the initial chlorination rate significantly increased with increasing chlorine partial pressure. Its effect was more significant for sample D (**Figure 4.15**) than for sample C (**Figure 4.14**). The final extent of chlorination of sample C was close to 100 pct even for P_{Cl_2} of 20 kPa, although the initial chlorination was slower. The extent of chlorination of sample D with P_{Cl_2} of 20 kPa was 92 pct; it approached 100 pct when P_{Cl_2} increased to 30 kPa.

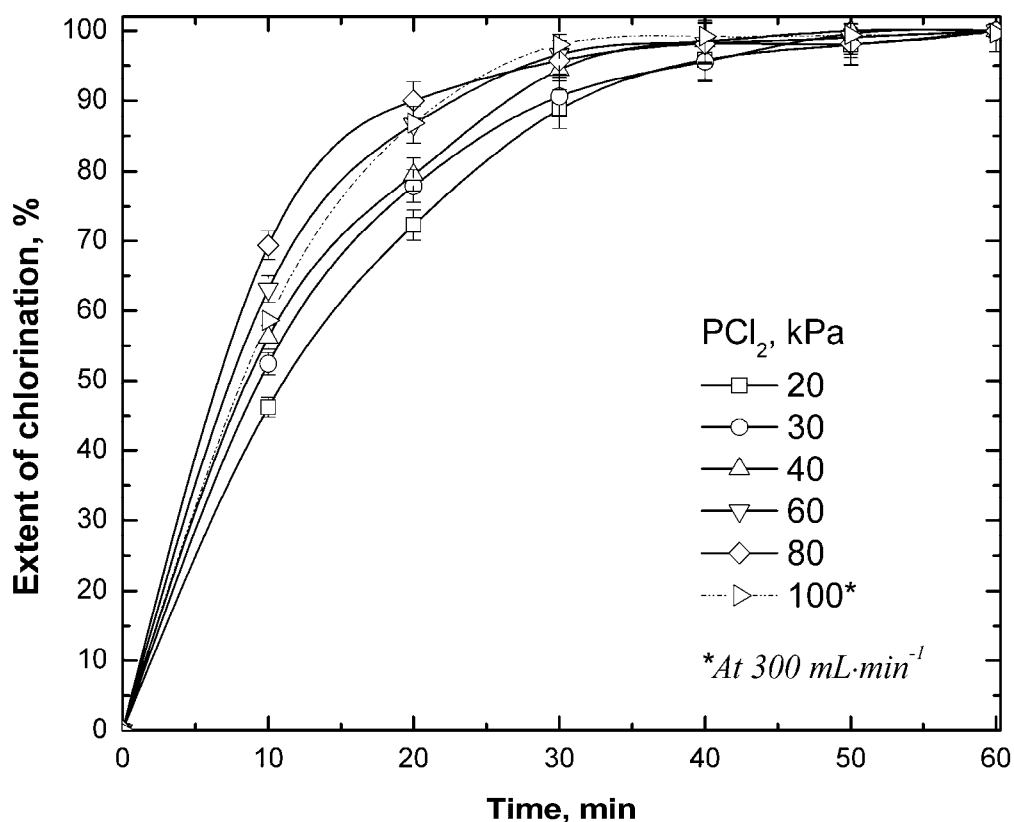


Figure 4.14. Effect of chlorine partial pressure on the extent of chlorination at 300 °C with $\text{Cl}_2 - \text{N}_2$ total flow rate $450 \text{ mL} \cdot \text{min}^{-1}$ for sample C

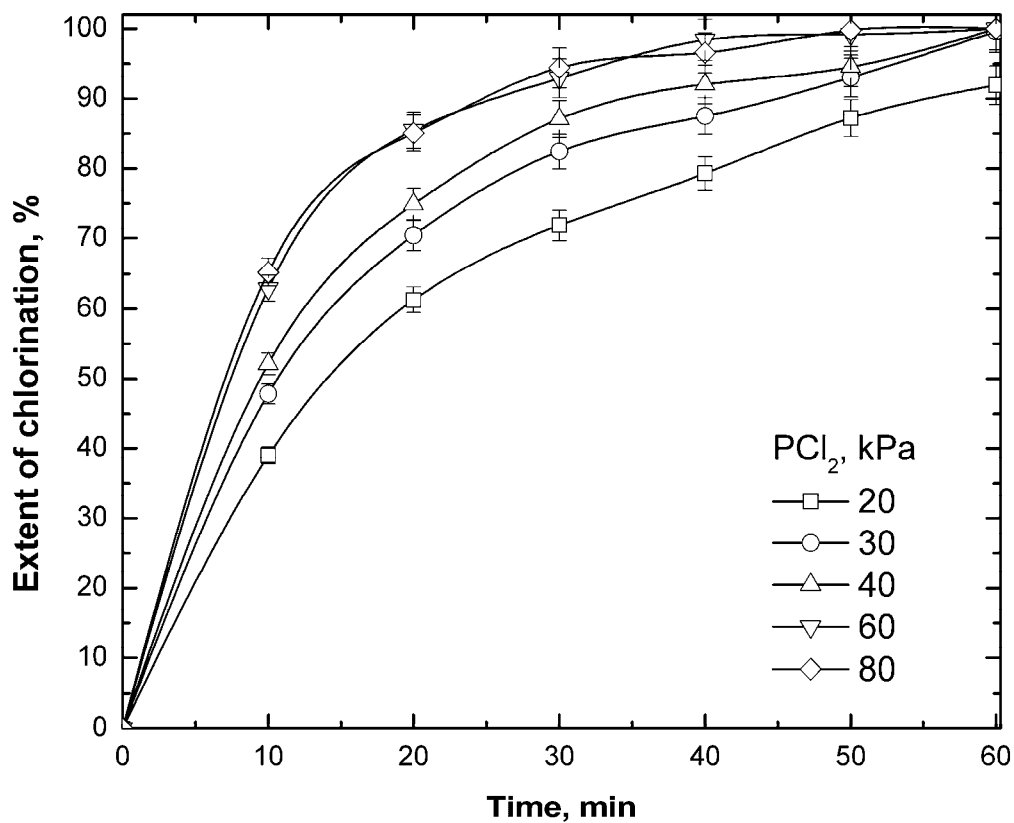


Figure 4.15. Effect of chlorine partial pressure on the extent of chlorination at 300 °C with $\text{Cl}_2 - \text{N}_2$ total flow rate $450 \text{ mL} \cdot \text{min}^{-1}$ for sample D

4.5. Effect of Particle Size

Samples C and D were crushed into different particle size ranges, placed in an alumina boat and chlorinated at 300 °C in the $\text{Cl}_2\text{-N}_2$ gas mixture with chlorine partial pressure of 40 kPa and total gas flow rate of 450 $\text{mL}\cdot\text{min}^{-1}$. The progress of the chlorination reaction is presented in **Figures 4.16** and **4.17**. Decreasing particle size increased the chlorination rate, but the effect was minor, especially for sample C.

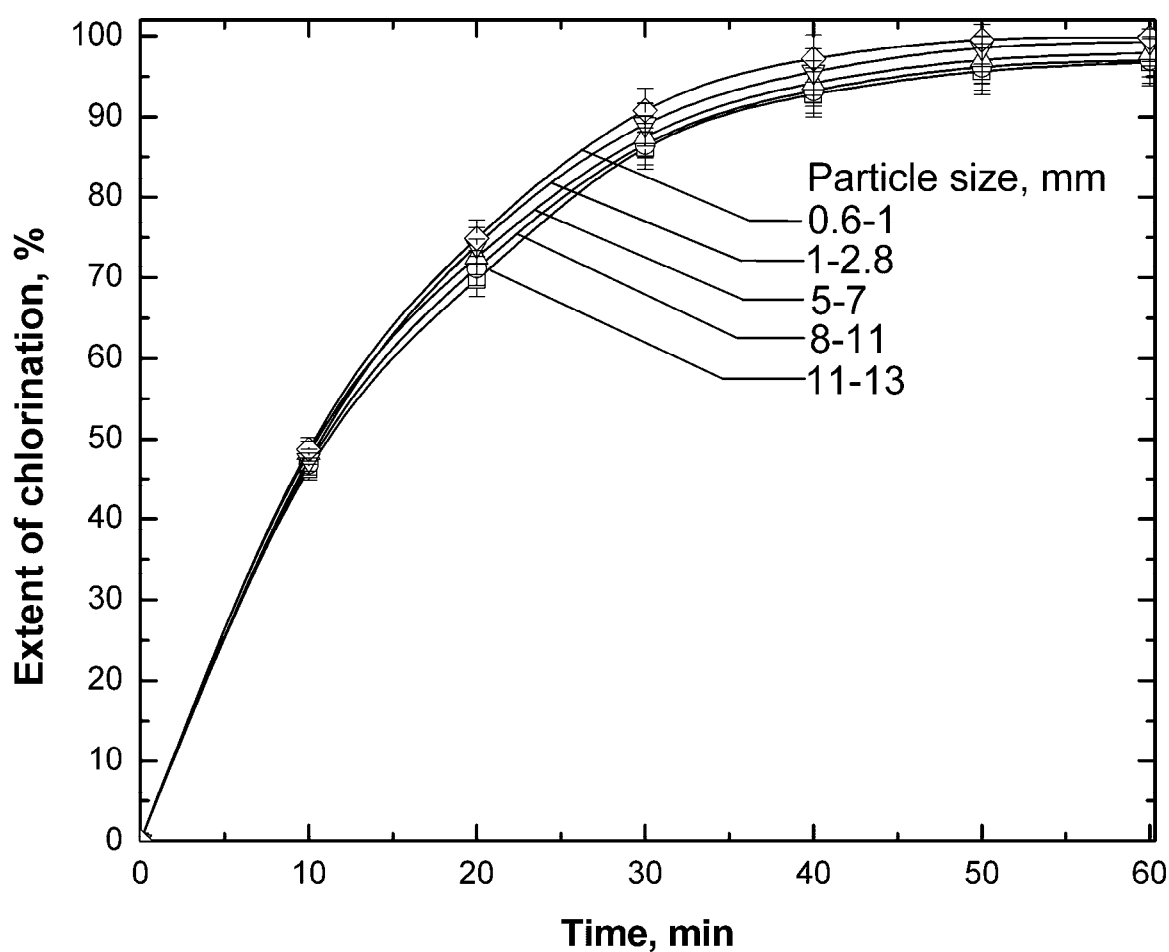


Figure 4.16. Effect of particle size on extent of chlorination at 300 °C for sample C with chlorine partial pressure 40 kPa and total gas flow rate 450 $\text{mL}\cdot\text{min}^{-1}$

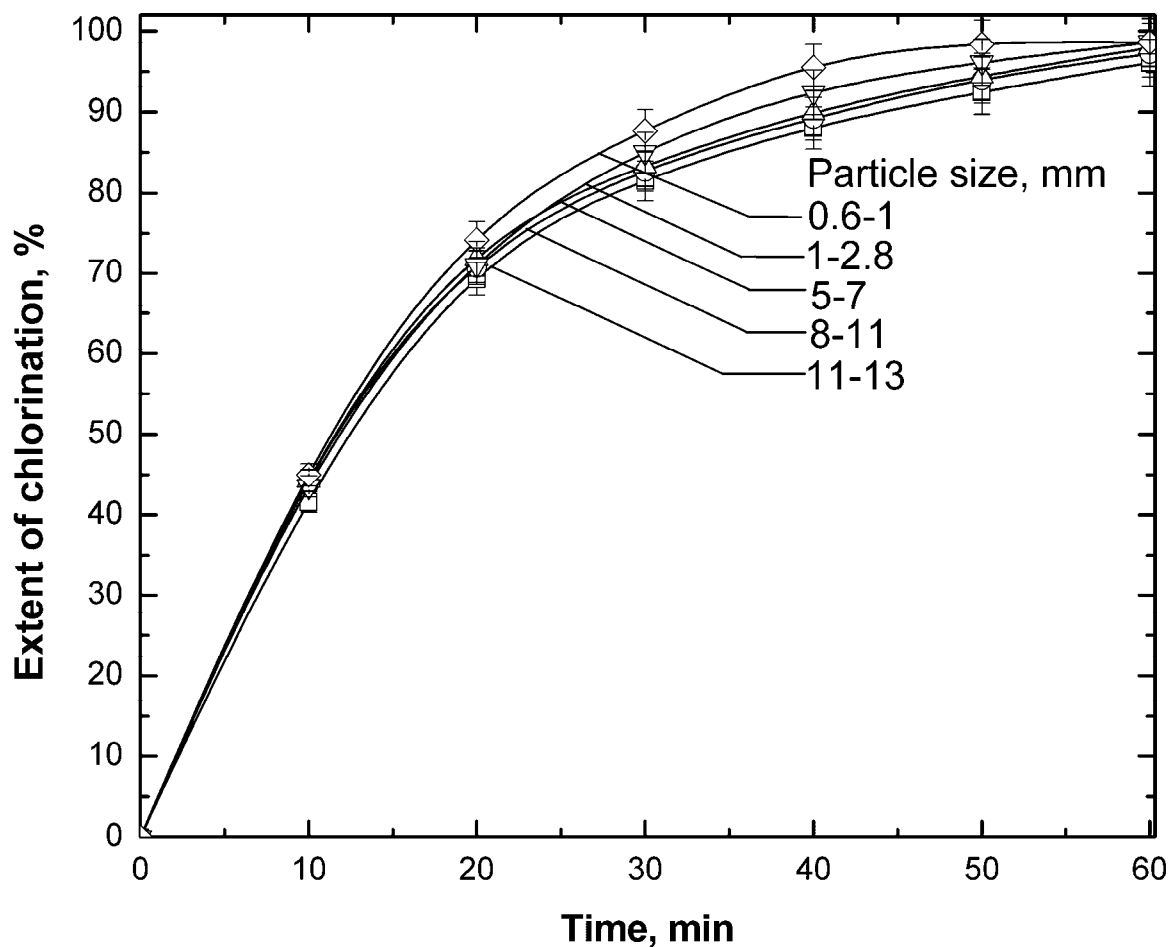


Figure 4.17. Effect of particle size on extent of chlorination at 300 °C for sample D with chlorine partial pressure 40 kPa and total gas flow rate 450 mL·min⁻¹.

4.6. Chlorination of Titanium Suboxides

Chlorination of titanium suboxides was studied in additional experiments. Ti_2O_3 was prepared by reducing titania powder in hydrogen at 1400 °C for 180 min. XRD analysis confirmed that Ti_2O_3 was the major phase, although a small amount of Ti_3O_5 was also detected.

In some experiments, a sample was chlorinated without graphite; in others titanium suboxide was mixed with graphite with C/ Ti_2O_3 molar ratio of 2.25. 60 min-exposure of a sample without graphite at 400 °C to pure chlorine with flow rate of 50 mL·min⁻¹, produced no reaction. 4.2 pct chlorination was detected in the experiment with Ti_2O_3 –graphite

powder mixture. Chlorination was observed only during the initial of 10 min. A higher extent of chlorination was achieved in experiments with titanium suboxides–graphite pellets. These results show the importance of carbon-suboxide contacts. Further experiments were carried out with titania-graphite pellets.

The pellets with carbon to titania molar ratio of 1.5 were heated at 1250 °C. XRD analysis shown in **Figure 4.18** indicated that the reduced sample contained titanium suboxides Ti_2O_3 and Ti_3O_5 , while titanium oxycarbide was undetectable. The reduced sample was chlorinated at 400 °C in pure chlorine with the flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$ for 60 min. The chlorination was mainly occurred in the initial of 25 min, with a final extent of chlorination of 18 pct. Another sample with carbon to titania molar ratio of 4.5 was produced by the reduction at 1200 °C, and chlorinated under the same conditions. Although the extent of titania reduction was less than in the previous case, the degree of chlorination increased to 32 pct. This increase was attributed to improved contact between titanium suboxides and carbon powder. Further chlorination was also observed when the residual pellets of partially reduced samples were crushed and then pressed into new pellets to improve contacts between carbon and titanium suboxide phases.

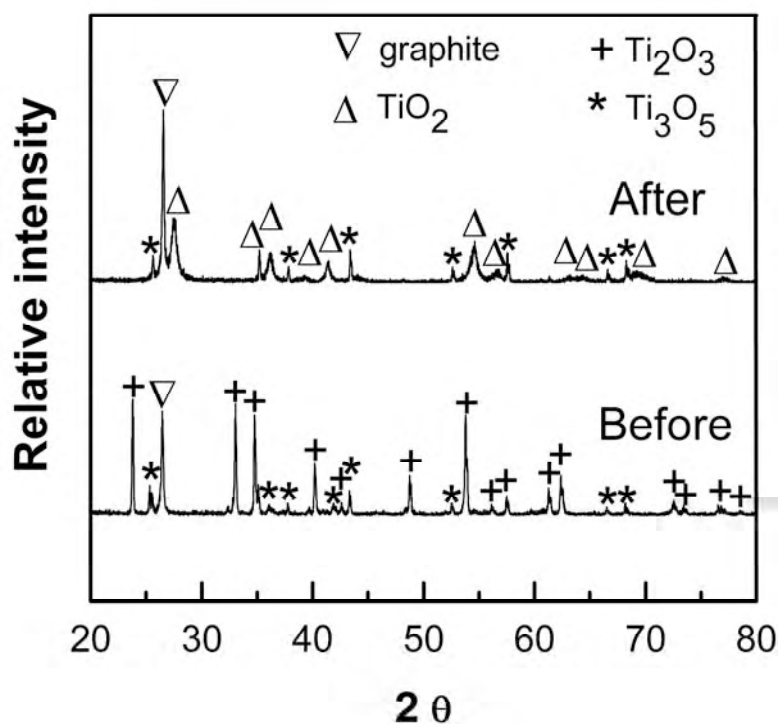


Figure 4.18. X-ray diffraction patterns of titanium suboxide sample before and after chlorination. The sample was prepared with carbon to titania molar ratio 1.5 and was chlorinated at 400 °C for 60 min, with chlorine flow at $50 \text{ mL}\cdot\text{min}^{-1}$

The XRD spectra in **Figure 4.4** indicate the presence of rutile in the residue of samples A and B, although it was not observed before chlorination. Rutile was also detected in the residue of samples of titanium suboxides after chlorination (**Figure 4.18**).

In the process of chlorination, titanium suboxides in the reduced sample could be reoxidised to titania by CO formed by the chlorination reaction. This was studied using a sample of titanium suboxide obtained by reduction of titania in hydrogen. This sample was exposed to a 10 vol pct CO–90 vol pct Ar gas mixture with a flow rate of $1 \text{ L}\cdot\text{min}^{-1}$ at 380°C for 60 min. **Figure 4.19** presents the XRD spectra of the titanium suboxide (Ti_2O_3 , Ti_3O_5) before and after the exposure. Before exposure the sample contained mainly Ti_2O_3 with a small amount of Ti_3O_5 . Both suboxides were converted into titania after exposure to the gas mixture, with appearance of a strong graphite peak. Although in the chlorination experiment, the CO content in the gas was much smaller than 10 vol pct, these experiments support suggested interpretation of experimental observations in chlorination of suboxides (*see Discussion*).

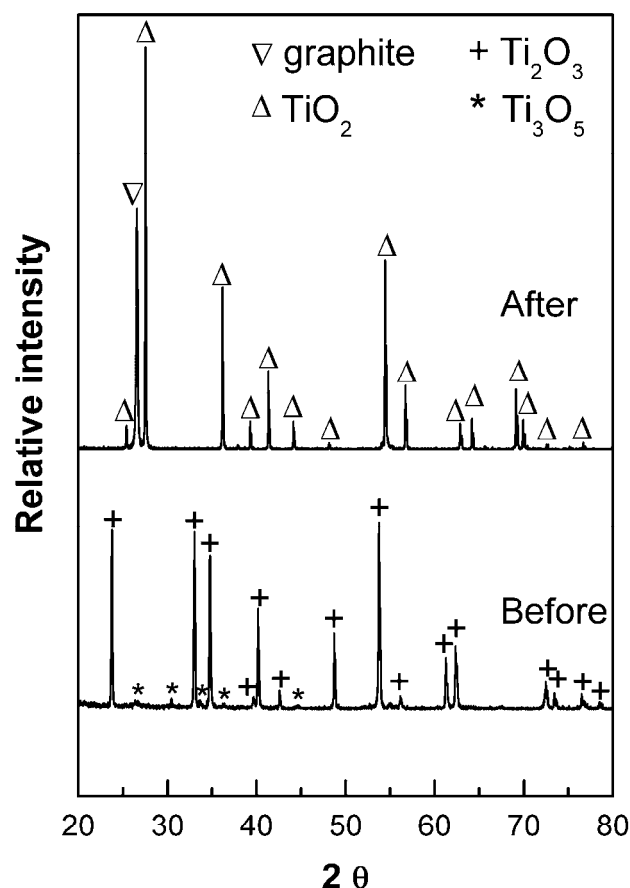
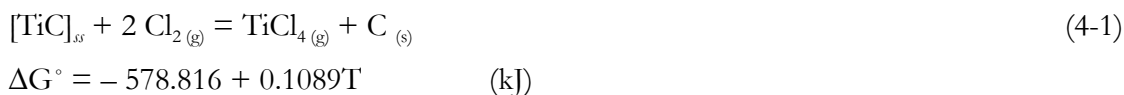


Figure 4.19. X-ray diffraction patterns of titanium suboxide before and after exposed to a 10 vol pct CO–90 vol pct Ar gas mixture at 380°C for 60 min

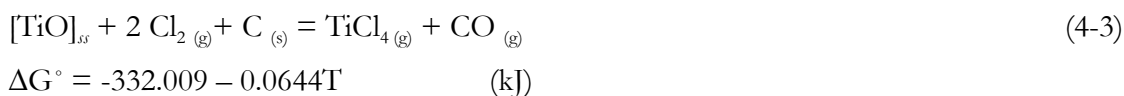
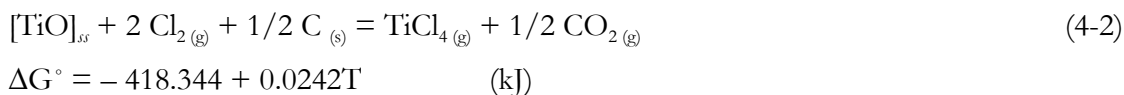
4.7. Discussion

4.7.1. Thermodynamic Analysis and Mechanisms of Chlorination Ti(O,C)

Titanium oxycarbide Ti(O,C) prepared by carbothermal reduction of rutile, is a solid solution of TiC and TiO. Chlorination of TiC proceeds by Reaction (4-1), where *ss* indicates that the chemical in the square bracket is in the solid solution:



Chlorination of TiO may occur by Reactions (4-2) or (4-3):



The standard Gibbs free energy change for Reactions (4-1) to (4-3) calculated using NIST JANAF Thermochemical Tables [Chase, 1998] is shown in **Figure 4.20**. All three chlorination reactions have very high equilibrium constants; equilibrium partial pressure is in the order of 10^{101} to 10^{43} kPa for CO_2 (Reaction 4-2) and 10^{89} to 10^{43} kPa for CO (Reaction 4-3) in the temperature range 150 to 700 °C.

The analysis of the venting gas by the CO – CO_2 infrared sensor indicated that the chlorination of TiO followed Reaction (4-3). The detected CO_2 concentration in the venting gas was less than 3 pct of that of CO. Furthermore, it was determined by a titration method that the amount of CO_2 dissolved in the NaOH solution in the chlorine scrubber was negligible. Equilibrium CO/ CO_2 partial pressure ratio in the presence of carbon is defined by the Boudouard reaction [See Section 2.25; Reaction (2-46)]. Equilibrium constant for this reaction for the sample temperature in the range 400 - 600°C it changes from 7.35×10^{-5} to 8.58×10^{-2} . Therefore, equilibrium CO_2/CO partial pressure ratio in this temperature range is expected to be $(13605 - 12)P_{\text{CO}}$. CO partial pressure measured by IR

sensor was 1.97 vol pct, while CO_2 was 0.047 vol pct. This explains a low CO_2 partial pressure observed in the chlorination experiments. Obviously, chlorination proceeded under non-equilibrium conditions, the gas-carbon equilibrium was not achieved and the Boudouard reaction was very slow.

At temperature below 800 °C, carbon could catalyse the formation of phosgene gas, COCl_2 which also acts as chlorinating agent [Stefanyuk and Morozov, 1965]. However at temperature above 200 °C, phosgene starts to revert to carbon monoxide and chlorine [Bodenstein, 1924]. Chlorination of titanium oxycarbide and oxycarbonitride was performed above 200 °C, at temperatures at which phosgene is unstable.

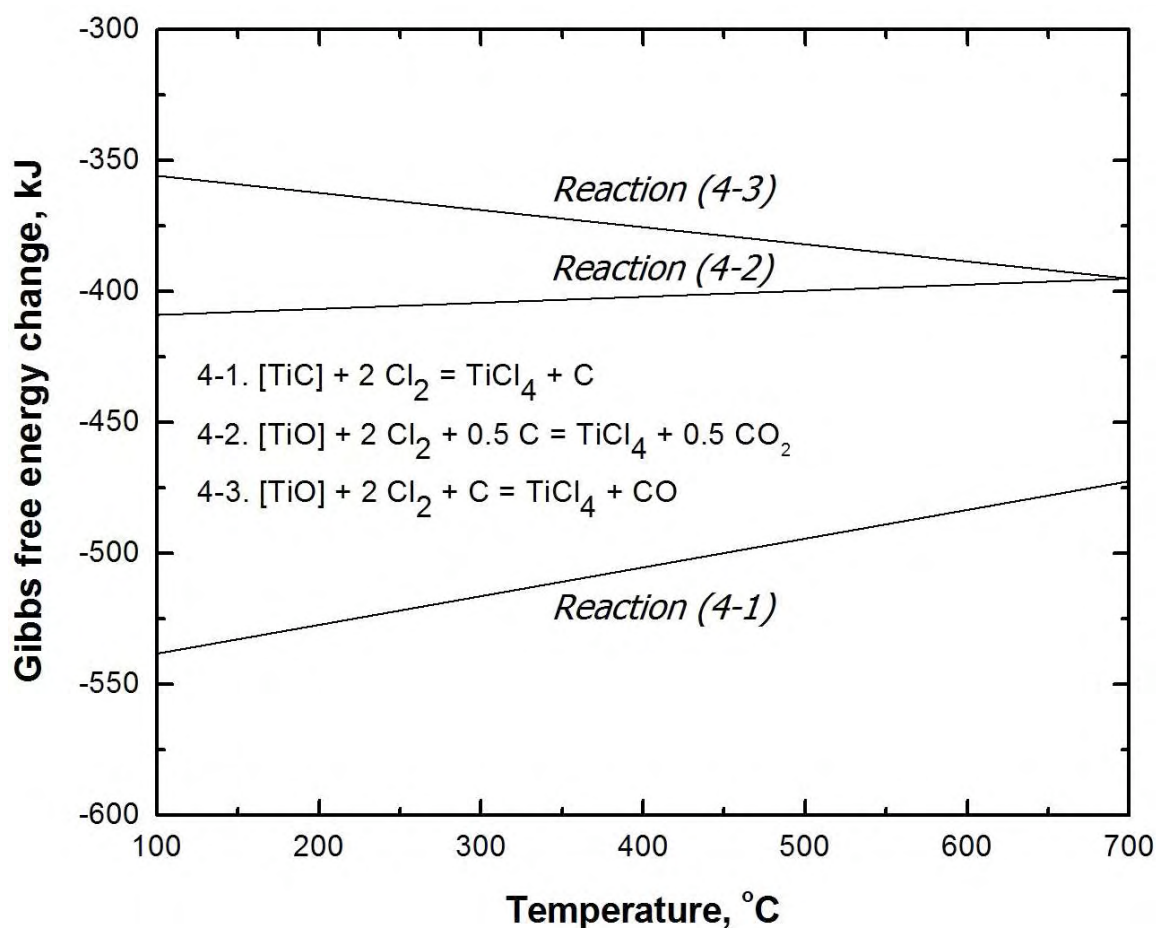


Figure 4.20. Standard Gibbs free energy changes of Reactions (4-1) to (4-3) in the temperature range from 100 to 700°C [Chase, 1998]

4.7.2. Effect of Temperature and Gas Flow Rate

Chlorination for reactions (4-1) and (4-3) are highly exothermic and the actual samples temperature was appreciably higher than the furnace temperature. It is an essential characteristic of an exothermic reaction that the heat released in the reaction increased the samples temperature and amplified the chlorination rate. At the maximal samples temperature, the heat generated from the chlorination reaction was balanced by the heat dissipation to the gas phase. $Ti(O,C)$ was gradually consumed and the reaction rate altogether with its samples temperature was slowly reduced. Finally, when the reaction was close to completion, the chlorination became slow and the samples cooled down to the furnace temperature.

In chlorination experiments with chlorine flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$, the furnace temperature had a minor effect on the reaction rate as shown in **Figures 4.2 (a) - (e)**. This could be attributed to starvation of reactant chlorine. This was also supported by experiments with varied chlorine flow rate. Increasing chlorine flow rate to $200 \text{ mL}\cdot\text{min}^{-1}$ increased the chlorination rate, while further increase in the flow rate to $300 \text{ mL}\cdot\text{min}^{-1}$ had a relatively minor effect. It can be concluded that at the chlorine flow rate $200 \text{ mL}\cdot\text{min}^{-1}$ and below, the reaction was chlorine starved and controlled by chlorine supply.

At the flow rate of $250 \text{ mL}\cdot\text{min}^{-1}$, the chlorination rate was clearly affected by the furnace temperature. In experiments with pure chlorine, maximum sample temperature raised considerably with increasing flow rate. At chlorine gas flow rate of $200 \text{ mL}\cdot\text{min}^{-1}$, the sample temperature reached 600°C when the furnace temperature was only at 235°C shown in **Figure 4.11** and **4.12**.

The ignition temperature for the chlorination reaction was determined in temperature programmed chlorination experiments, in which the furnace temperature ramped from 100 to 400°C at $3^\circ\text{C}\cdot\text{min}^{-1}$ (**Figure 4.7**). During the initial 25 to 30 min, the sample was heated up in line with the furnace temperature. Afterwards the rise of pellet's temperature started to speed up, indicating the ignition of the chlorination reaction. After achieving maximum temperature, the reaction slowly faded away and the sample temperature began to approach the furnace temperature. The ignition temperature was 150°C for all three chlorine flow

rates; however, the maximum temperature was reached faster and was higher for the higher gas flow rate. The entire reaction period was also shorter.

Figure 4.12 compares the sample temperature for samples A to E in the temperature programmed experiments with chlorine flow rate of $300 \text{ mL}\cdot\text{min}^{-1}$. The chlorination of samples A to C was ignited at 150°C , while samples D and E had ignition temperatures higher than 200°C . The change in ignition temperature is related to the residual carbon in samples D and E, which could deprive the heat build-up needed for igniting the reaction. Carbon was not chlorinated and this was proved by chlorinating graphite powder in alumina boat at a furnace temperature 235°C . There was no weight change observed. This is in agreement with Bergholm (1961) who also concluded that carbon is not chlorinated at low temperatures.

It should be noted that the temperature change in chlorination experiments did not always follow the trend in the reaction rate. This is demonstrated by temperature curves obtained in experiments with varied flow rate of $\text{Cl}_2\text{-N}_2$ gas mixture (**Figure 4.11**) in comparison with chlorination curves (**Figure 4.8**). Although the rate of chlorination increased along with increase in gas flow rate, the maximal sample temperature changed in the opposite direction. This can be explained by the heat balance; increasing heat removal with increasing gas flow rate prevails over the increasing rate of heat generation.

In a number of experiments, chlorination residues were combusted in air in order to burn off carbon and to oxidise the residual titanium to TiO_2 . Chemical analysis of products of combustion detected rutile which confirmed incomplete chlorination of titanium in samples A to E. Extension of the duration of reaction to 120 min unable to yield a visible increase in the extent of chlorination; titanium suboxides were still detected in the residues by XRD analysis.

Chlorination of titanium suboxides Ti_2O_3 and Ti_3O_5 which were present in reduced samples was slow even at the furnace temperature of 400°C . This contradicts to Nieberlein (1957) who argued that titanium suboxides can be chlorinated at low temperatures. This discrepancy could arise from different raw materials used by Nieberlein (1957), which contained Fe, Al, SiO_2 , and Nb.

XRD spectra indicate the presence of rutile in the residue of samples even though it was not observed before chlorination. It was also detected in the residue of samples of titanium suboxides subsequent to chlorination. Chlorination of Ti_2O_3 and Ti_3O_5 by Reactions (4-4) and (4-5) is thermodynamically feasible under experimental conditions and proceeds as the following:



$$\Delta G^\circ = -567.802 + 0.1206T \quad (\text{kJ})$$



$$\Delta G^\circ = -576.546 + 0.1162T \quad (\text{kJ})$$

Chlorination of suboxides Ti_2O_3 and Ti_3O_5 was not observed in chlorination experiments with titanium suboxides without carbon. In the presence of carbon this reaction can proceed through Reactions (4-6) and (4-7):



$$\Delta G^\circ = -345.839 - 0.2988T \quad (\text{kJ})$$



$$\Delta G^\circ = -391.503 - 0.5403T \quad (\text{kJ})$$

The appearance of TiO_2 in the chlorination residues could be attributed to the oxidation of titanium suboxides by CO:



$$\Delta G^\circ = -263.255 + 0.1800T \quad (\text{kJ})$$



$$\Delta G^\circ = -267.627 + 0.1778T \quad (\text{kJ})$$

At a temperature below 800 °C, the equilibrium CO partial pressure for Reactions (4-8) and (4-9) is below 2.03×10^{-3} kPa. Thermodynamically, these reactions are feasible and were confirmed by the experiments described above. Before exposure to CO, the samples

contained mainly Ti_2O_3 , with small amount of Ti_3O_5 . Both suboxides were partly converted into titania by reacting with CO, released in chlorination of titanium oxycarbide with appearance of a graphite peak. The standard Gibbs free energy change for Reactions (4-4) to (4-9) calculated using NIST-JANAF Thermochemical Tables [Chase, 1998] is presented in **Figure 4.21**.

According to Reactions (4-1) and (4-3), the ideal titanium oxycarbide of which complete chlorination theoretically can be achieved with no residue carbon is $\text{TiC}_{0.5}\text{O}_{0.5}$. In the experiments, titanium oxycarbide produced with molar ratio of carbon to titania of 2.5, did not contain titanium suboxides and had minimum titanium carbide content in titanium oxycarbide, 69 pct (with 31 pct TiO). Under the conditions investigated in this project, a carbon to titania molar ratio of 2.5 is considered to be the optimal for production of titanium oxycarbide for chlorination.

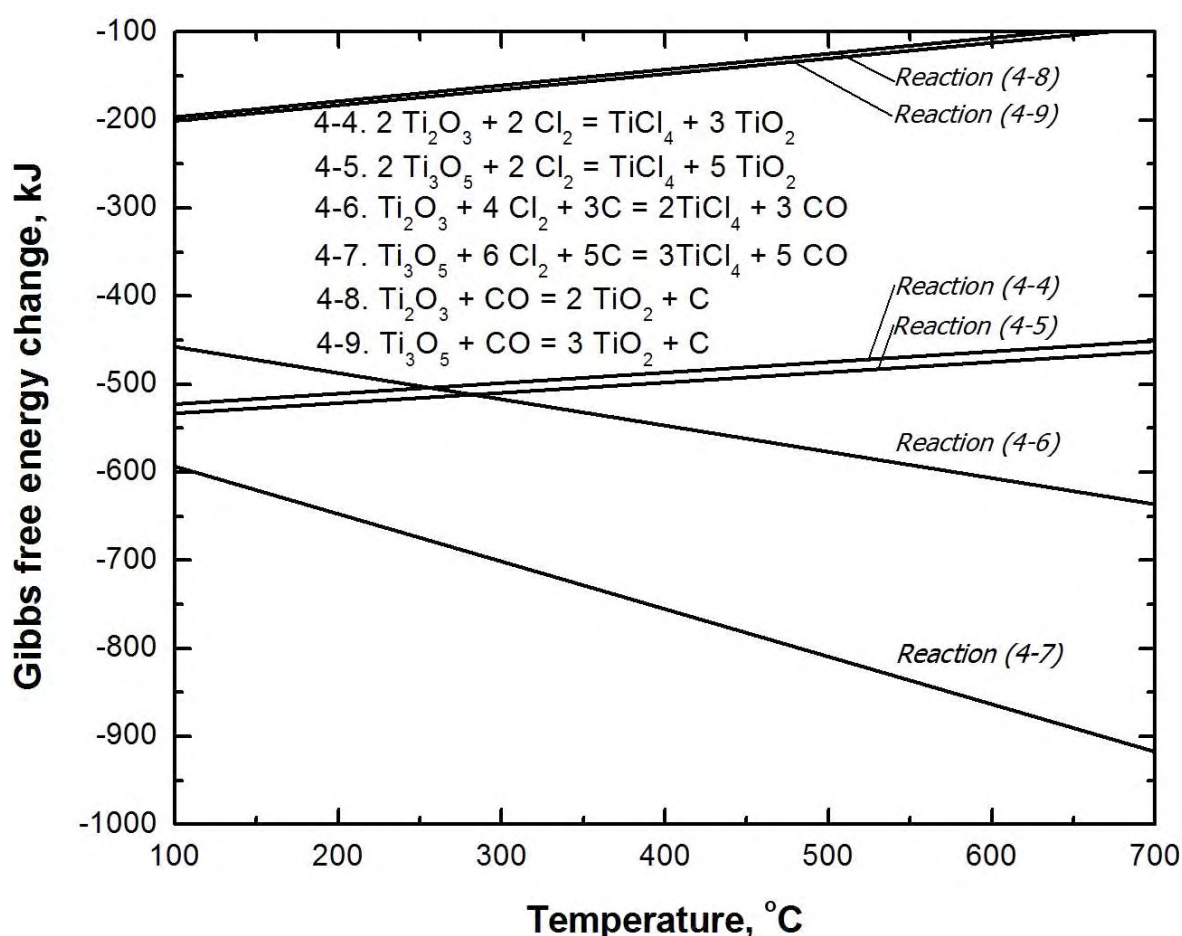


Figure 4.21. Standard Gibbs free energy changes of Reactions (4-4) to (4-9) in the temperature range from 100 °C to 700 °C [Chase, 1998]

4.8. Summary

Titanium oxycarbide prepared by carbothermal reduction was chlorinated in the temperature range of 235 to 400 °C. Due to strong exothermic reaction, the sample temperature during chlorination was up to 200 °C higher than the furnace temperature. The chlorination was ignited at 150 to 200 °C. The effect of furnace temperature on chlorination in isothermal experiments with chlorine flow rate of 50 mL·min⁻¹ was not observed due to gas reactant starvation. Above the chlorine flow rate of 200 mL·min⁻¹, the effect of furnace temperature was significant; chlorination at 235 to 400 °C was close to completion in 30 min. Sample composition had a significant effect on the extent of chlorination. The best results were obtained for sample C which was produced with carbon to titania molar ratio of 2.5 and contained no detectable excess carbon or unreduced titanium suboxides. Chlorination of this sample was close to 100 pct. When carbon to titania ratio was low, the reduced samples contained titanium suboxides of which chlorination was slow (samples A and B). Chlorination of samples E and D was affected by the excess carbon in the samples. Increasing gas flow rate and chlorine partial pressure enhanced the reaction rate. The effect of particle size was insignificant. Titanium suboxides were chlorinated at low temperatures only when they were well mixed with graphite and pressed into pellets. The rate and extent of their chlorination were low.

CHAPTER 5.

CHLORINATION OF TITANIUM OXYCARBONITRIDE

This chapter presents results of conversion of titania to titanium oxycarbonitride and its chlorination. Effects of temperature, chlorine partial pressure, gas flow rate, particle size on the rate of chlorination of titanium oxycarbonitride were examined. Chlorination of titanium oxycarbonitride was compared with chlorination of titanium oxycarbide and pure chemicals of titanium carbide, nitride, and carbonitride.

5.1. Reduction and Nitridation of Rutile

Mixtures of titania and graphite with different carbon to titania molar ratio were pressed into pellets and heated under nitrogen atmosphere at 1450 °C (see Chapter 3). The composition of samples produced by carbothermal nitridation of rutile with different carbon to rutile molar ratio is presented in **Table 5.1**. Their XRD spectra are shown in **Figure 5.1**. Samples A and B consisted of titanium oxycarbonitride and suboxides (Ti_3O_5 and Ti_2O_3); sample C was titanium oxycarbonitride with small amount of free carbon; samples D and E included titanium oxycarbonitride and excess carbon, which amount was higher in sample E. The measurement of BET surface area for sample E was $8.31 \text{ m}^2\cdot\text{g}^{-1}$ with average porosity of 51.2 Å.

Table 5.1. Composition of nitrided samples of rutile subjected to chlorination

Sample	A	B	C	D	E	F
Carbon content, wt pct	0.54	1.19	6.44	20.40	31.31	13.5
Oxygen content, wt pct	22.90	7.76	2.02	0.91	1.51	8.13
Nitrogen content, wt pct	10.12	10.64	16.69	15.79	14.03	-
Extent of Reduction, pct	48.44	85.56	95.96	97.84	95.75	84.5
Phase composition*	Ti_3O_5 , Ti_2O_3 , $\text{TiC}_x\text{O}_y\text{N}_z$	Ti_3O_5 , Ti_2O_3 , $\text{TiC}_x\text{O}_y\text{N}_z$	$\text{TiC}_{0.16}\text{O}_{0.08}\text{N}_{0.76}$, C (C/Ti: 0.29)	$\text{TiC}_{0.10}\text{O}_{0.04}\text{N}_{0.86}$, C (C/Ti: 1.57)	$\text{TiC}_{0.013}\text{O}_{0.09}\text{N}_{0.90}$, C (C/Ti: 2.59)	$\text{TiC}_{0.69}\text{O}_{0.31}$

* C/Ti represents free carbon to titanium molar ratio. Free carbon in samples A, B and F was negligible.

Sample F prepared by carbothermal reduction of titania in argon under otherwise the same conditions as sample C, is also presented in **Table 5.1**. The only phase in sample F identified by XRD analysis was titanium oxycarbide. This sample was chlorinated for comparison purpose.

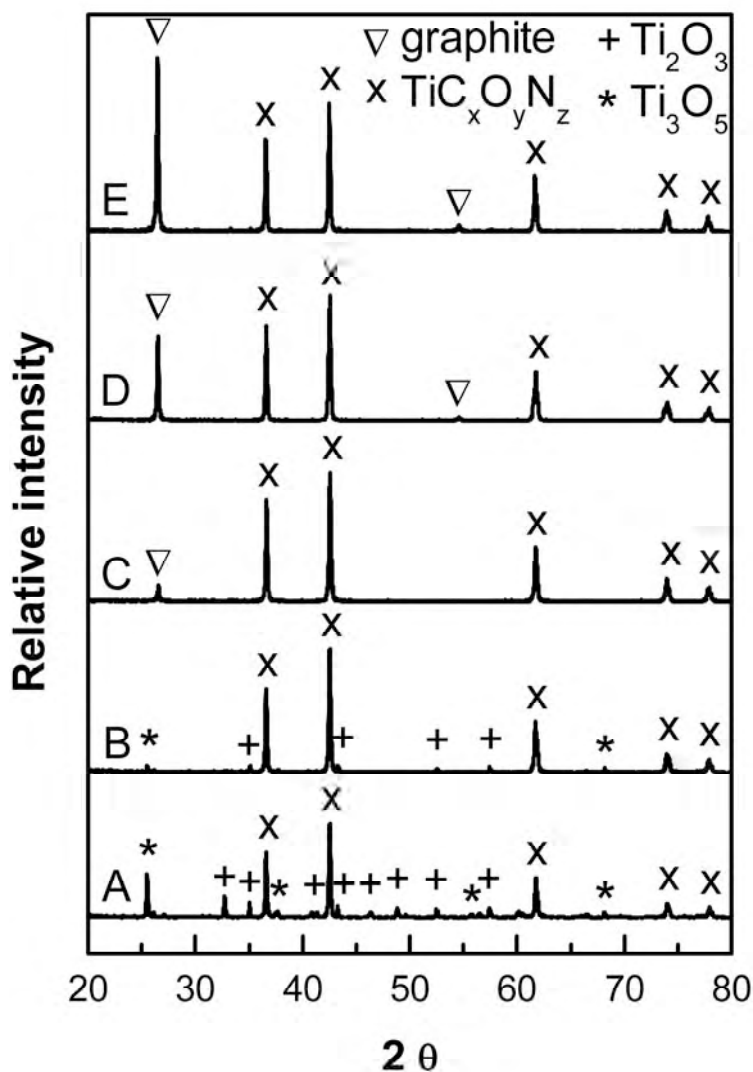


Figure 5.1. X-ray diffraction patterns of titanium oxycarbonitride for samples A to E

5.2. Effect of Temperature.

The effect of furnace temperature on chlorination of samples A to E was studied in the temperature range of 235 to 400 °C at chlorine flow rates of 50 mL·min⁻¹ and 250 mL·min⁻¹; it was also studied in the Cl₂-N₂ gas mixture with gas flow rate 450 mL·min⁻¹ and chlorine partial pressure of 20 kPa. Chlorination curves for samples A-E at different temperatures with chlorine flow rate of 50 mL·min⁻¹ are presented in **Figure 5.2 (a) – (e)**.

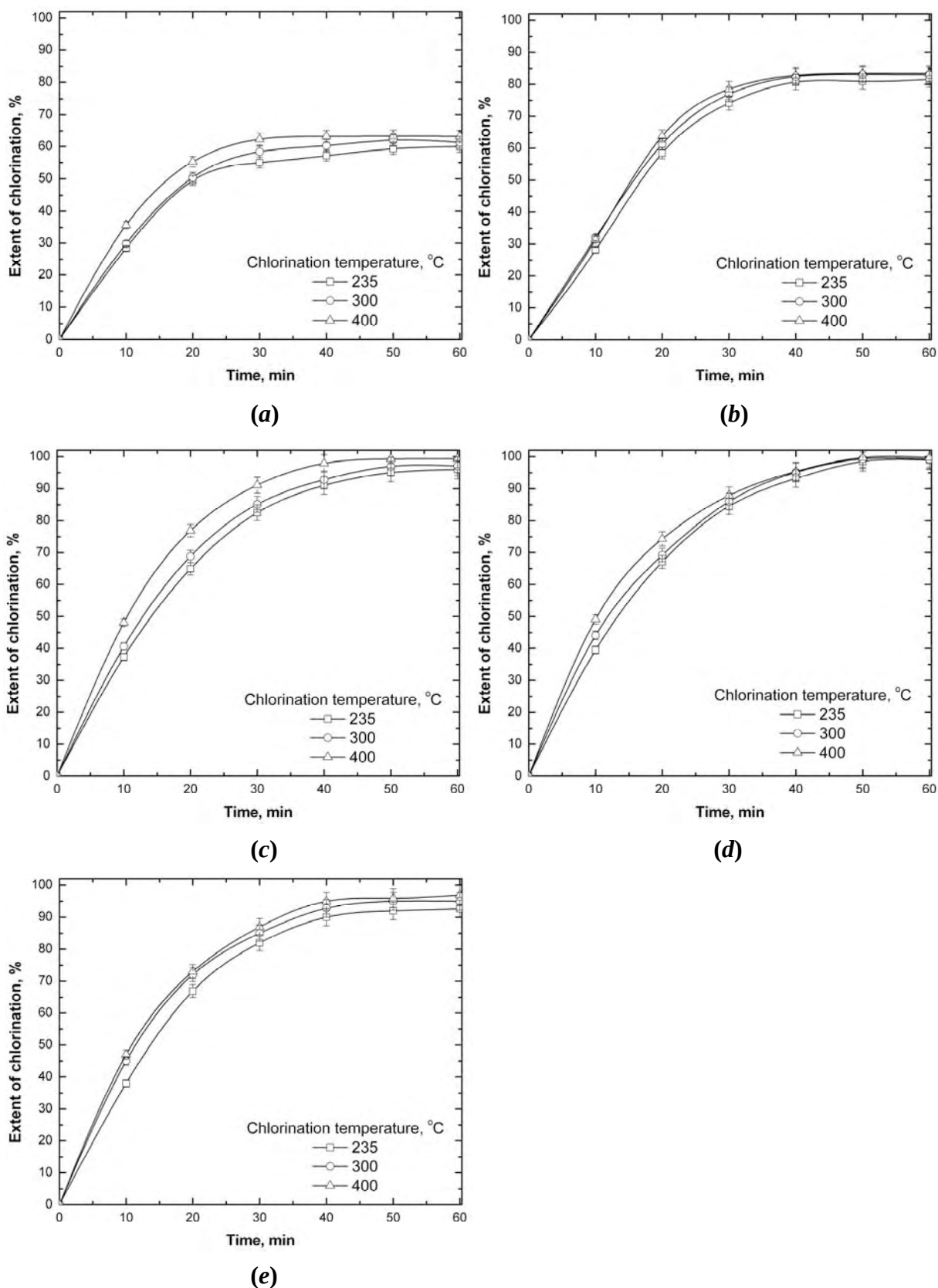


Figure 5.2. Extent of chlorination of titanium oxycarbonitride at temperatures from 235 °C to 400 °C with chlorine flow rate at 50 mL min⁻¹ for samples (a) A, (b) B, (c) C, (d) D, and (e) E

The rate and extent of chlorination increased with increasing furnace temperature, but the effect was minor. The extent of chlorination of sample A was below 70 pct. This sample contained titanium suboxides of which chlorination was slow in comparison with titanium oxycarbonitride and incomplete. Similar results were obtained in chlorination of samples of titanium oxycarbide with titanium suboxides as described in *Section § 4.6*. Sample B also contained titanium suboxides, but in a much less amount than sample A. The extent of chlorination of this sample reached 83 pct. Extent of chlorination of samples C and D, which contained no other phases but titanium oxycarbonitride and carbon, was above 95 pct.

The extent of chlorination slightly decreased with increasing content of excess carbon in sample E. Most chlorination occurred during the first 40 min, and stopped after about 50 min. Chlorination of titanium oxycarbonitride is highly exothermic. The change in sample temperature during chlorination of samples A through E at chlorine flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$ is presented in **Figure 5.3**. After a short period, generally less than 1 min, the sample temperature started to increase rapidly and reached maximum in about 5 min. After completion of chlorination reaction the sample temperature was close to the furnace temperature. The change of temperature for samples A through D reached 550°C and above, whilst sample E only reached maximum temperature of 520°C . With higher carbon content, the increase of sample temperature was slightly less and at shorter period before its temperature went back to furnace temperature.

The residues of chlorinated samples of titanium oxycarbonitride were examined by XRD analysis. **Figure 5.4** shows the XRD patterns of samples A to E after chlorination at 400°C for 60 min in pure chlorine with flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$. Similar XRD patterns were obtained for the residues after chlorination at 235°C and 300°C . Unconsumed graphite was observed in chlorinated residues for samples C, D and E.

Samples A and B contained titanium suboxides, which were also observed in the residues of these samples. XRD analysis of samples C, D and E before chlorination did not detect any titanium suboxides. However, weak XRD peaks for Ti_2O_3 and Ti_3O_5 were observed in the residues of chlorination of these samples, indicating that conversion of titania to titanium oxycarbonitride was incomplete.

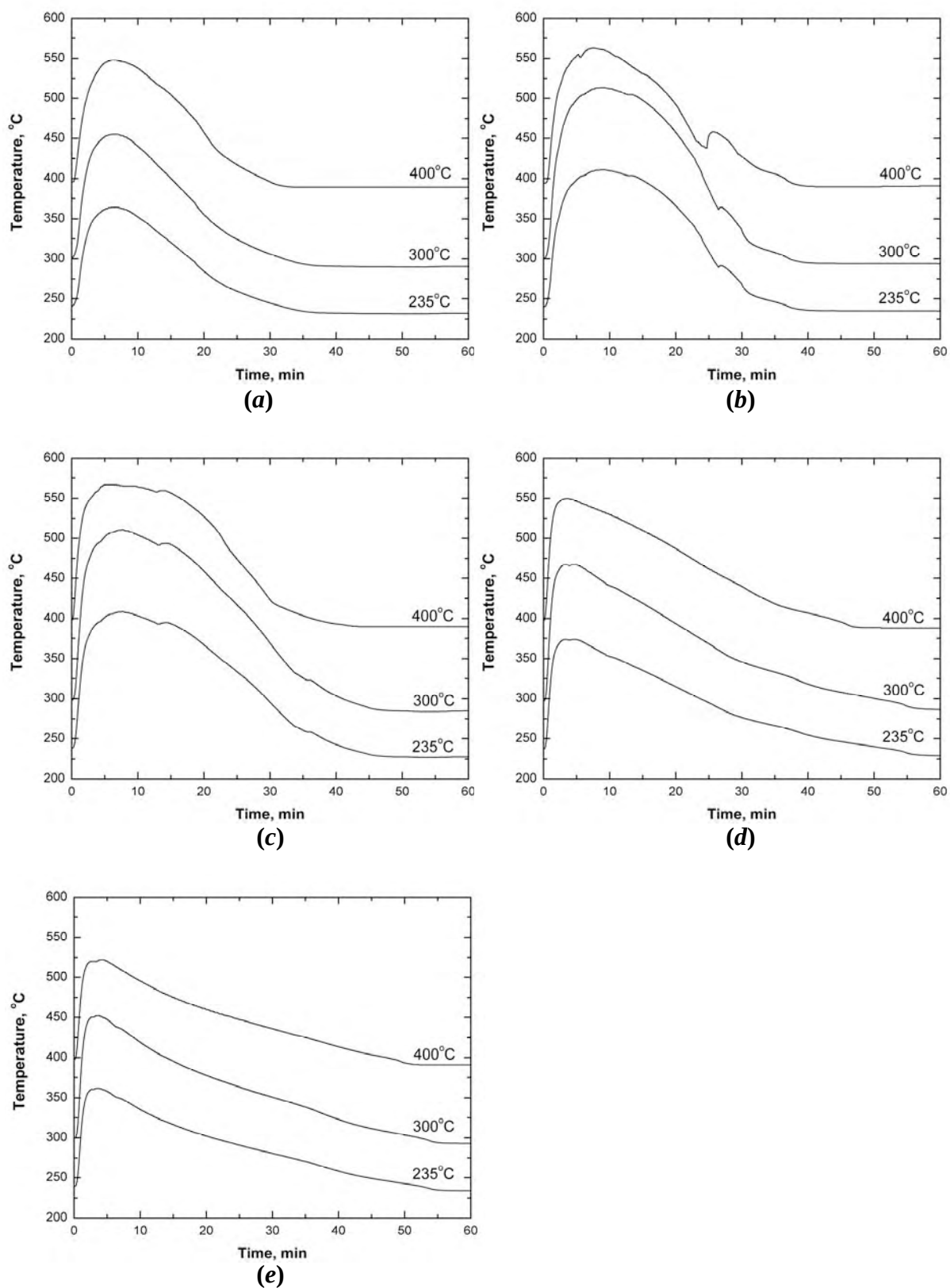


Figure 5.3. Change in sample temperature during chlorination of titanium oxycarbonitride with chlorine flow rate at $50 \text{ mL} \cdot \text{min}^{-1}$ for samples (a) A, (b) B, (c) C, (d) D, and (e) E

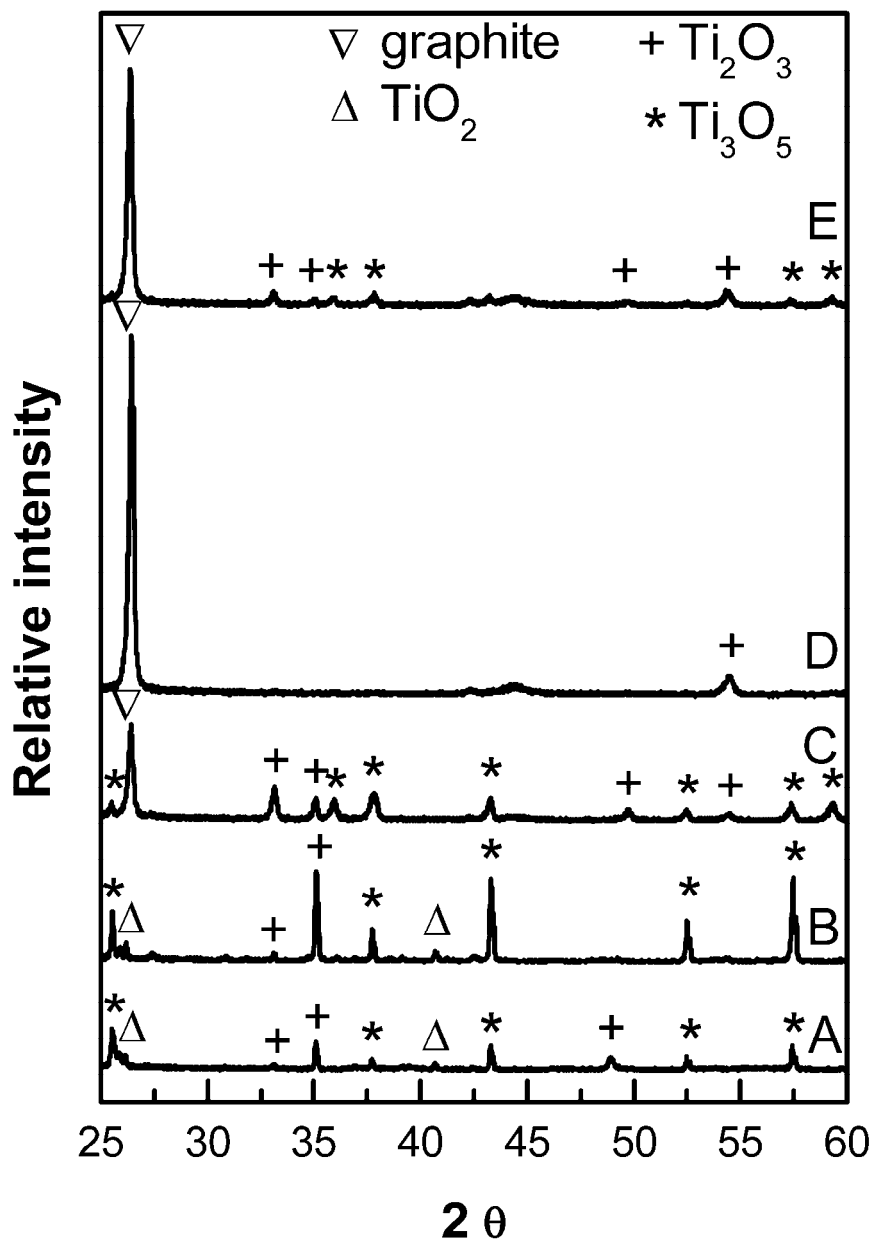


Figure 5.4. X-ray diffraction patterns of residues of titanium oxycarbonitride for samples A to E after chlorination with $50 \text{ ml} \cdot \text{min}^{-1}$ of chlorine at 400°C for 60 min

Previous study on chlorination of titanium suboxides and titanium oxycarbide (Section § 4.6) showed that suboxides Ti_2O_3 and Ti_3O_5 were partly chlorinated. Their extent of chlorination was relatively low in comparison to titanium oxycarbonitride. In a chlorination experiment at 400°C , the suboxides were still present even after 180 min.

Some of chlorinated residues for samples A to E were combusted in air at 1000°C for 720 min in order to burn off carbon and to oxidise the residual titanium to TiO_2 . XRD analysis

of the combustion residues detected rutile, which confirmed incomplete chlorination of titanium in samples A to E.

At higher chlorine flow rate, $250 \text{ mL}\cdot\text{min}^{-1}$, the effect of furnace temperature on chlorination of titanium oxycarbonitride was stronger. This is seen in **Figure 5.5** which presents chlorination curves for sample C at 235°C , 300°C and 400°C . The rate of chlorination increased with increasing temperature and was close to completion after 30 min at 235°C , 25 min at 300°C and 20 min at 400°C . The chlorination was faster than that at chlorine flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$.

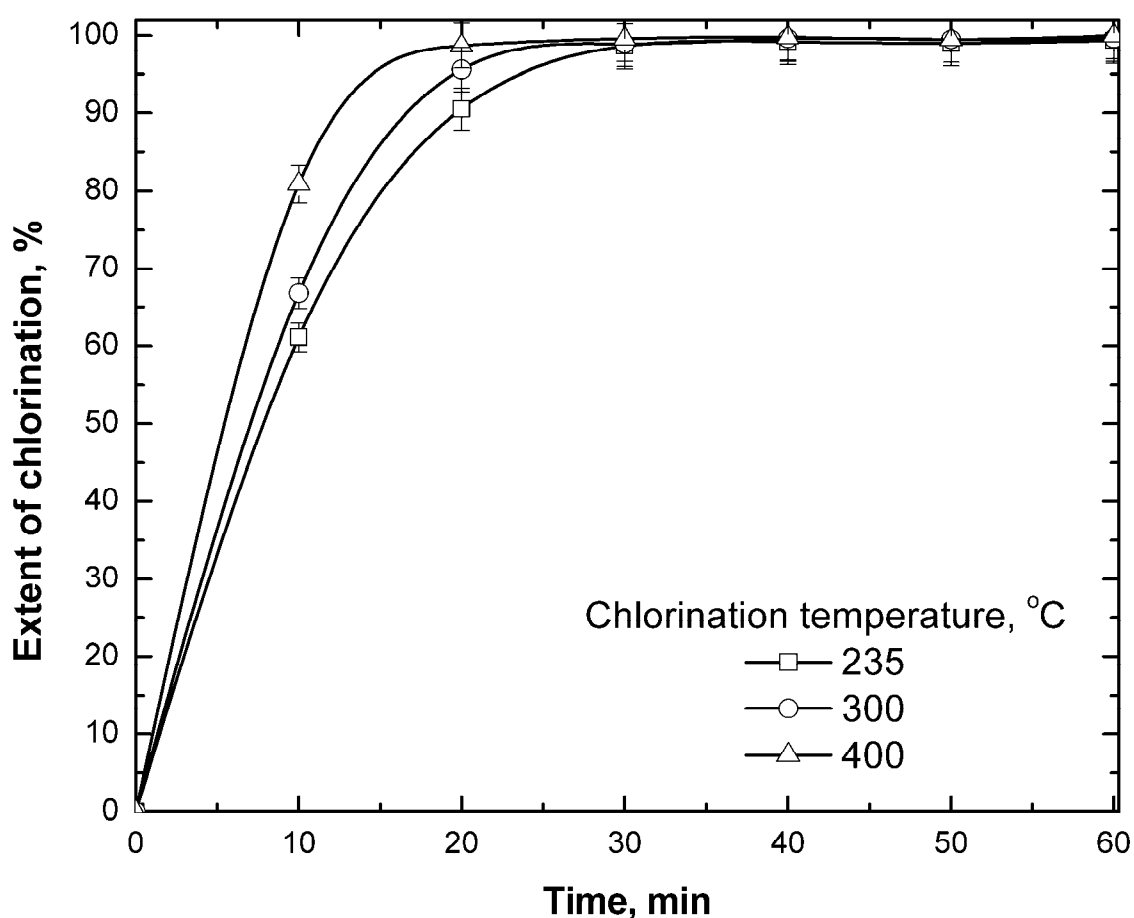


Figure 5.5. Extent of chlorination of sample C at different temperatures with pure chlorine at a flow rate of $250 \text{ mL}\cdot\text{min}^{-1}$

The effect of furnace temperature on chlorination of titanium oxycarbonitride was also observed in experiments with $\text{Cl}_2\text{-N}_2$ gas mixture with total flow rate of $450 \text{ mL}\cdot\text{min}^{-1}$ and chlorine partial pressure of 20 kPa. This is presented in **Figure 5.6** which shows the extent

of chlorination for sample C at 250, 300, 350, 450 and 550 °C. The rate of chlorination increased with increasing temperature and reached 90 pct at 250 °C and 350 °C after 60 min. The maximum extent of chlorination reached at 450 °C and 550 °C was 95 pct.

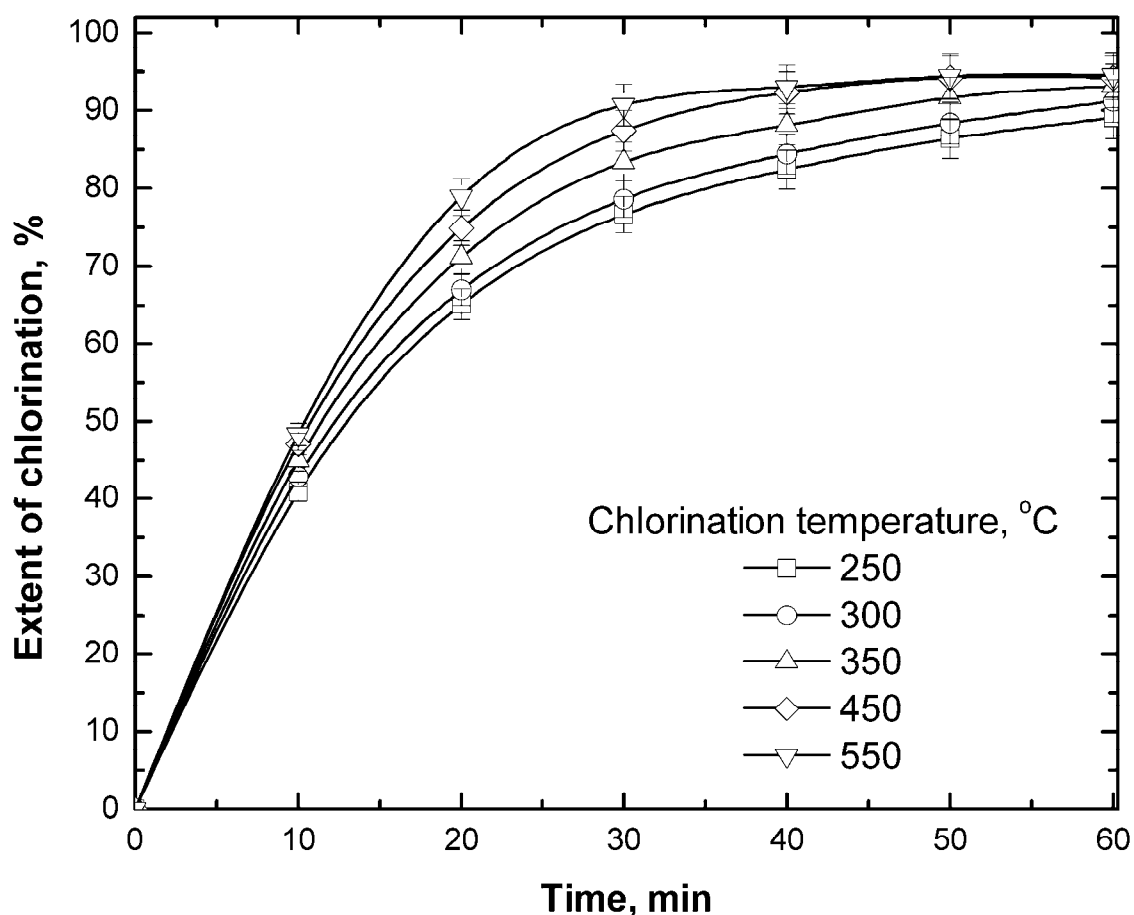


Figure 5.6. Extent of chlorination of sample C at different temperatures with $\text{Cl}_2\text{-N}_2$ gas mixture with chlorine partial pressure of 20 kPa and total flow rate of 450 $\text{mL}\cdot\text{min}^{-1}$

The ignition temperature was determined in non-isothermal experiments. Figure 5.7 compares the sample temperature for samples A to E in the temperature-programmed experiments with chlorine flow rate 300 $\text{mL}\cdot\text{min}^{-1}$. The chlorination of samples A to C was ignited at 150 °C, while samples D and E had ignition temperatures higher than 200 °C.

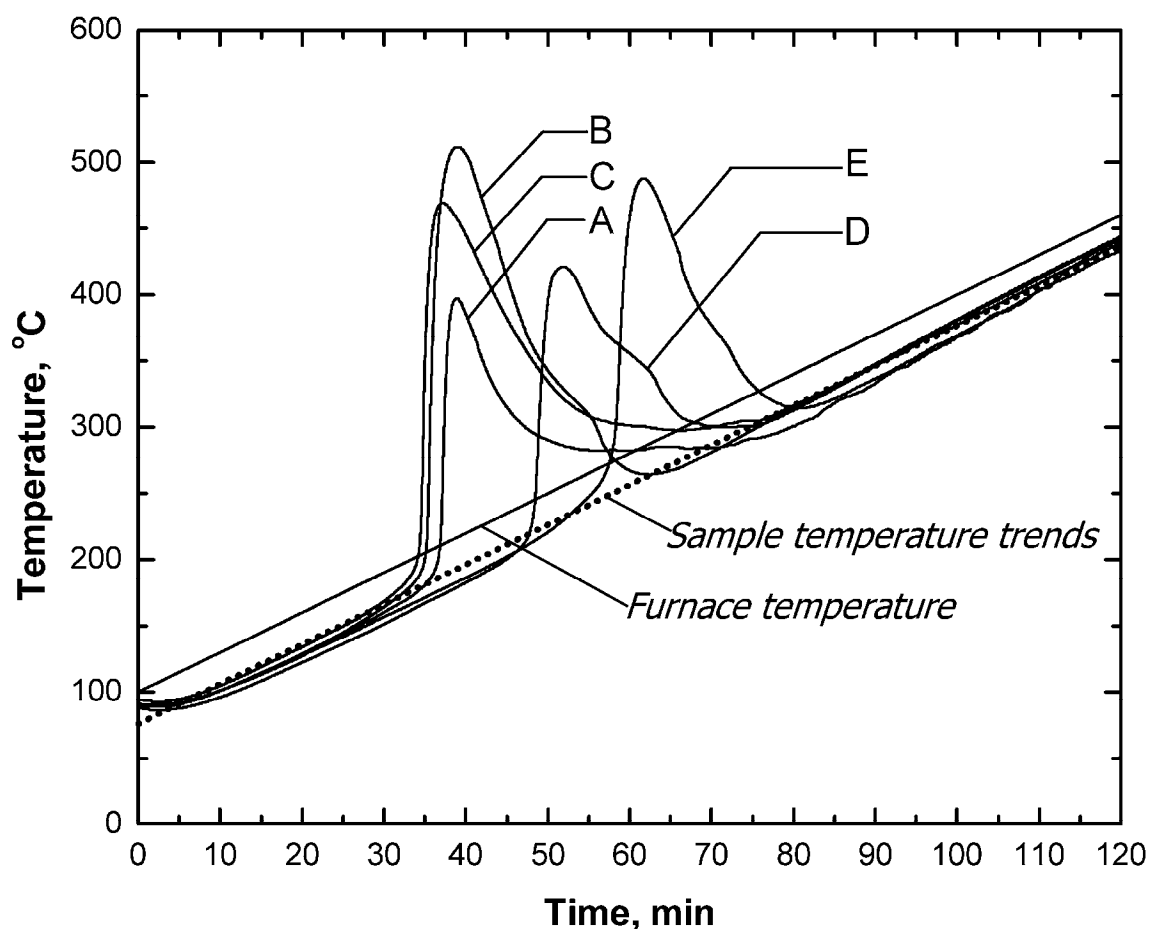


Figure 5.7. Change in the sample temperature during temperature programmed chlorination of titanium oxycarbonitride with a ramping rate of $3\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ for samples A to E with chlorine flow rate at $300\text{ mL}\cdot\text{min}^{-1}$

5.3. Effect of Gas Flow Rate

The effect of pure chlorine gas flow rate on chlorination of sample C was studied at $235\text{ }^{\circ}\text{C}$. The gas flow rate was changed in the range from 30 to $300\text{ mL}\cdot\text{min}^{-1}$. The progress of the chlorination is presented in **Figure 5.8**. It is shown that the chlorination rate significantly increased with increasing chlorine flow rate until $100\text{ mL}\cdot\text{min}^{-1}$. Beyond that, the effect of the gas flow rate was minor. The extent of chlorination of sample C was close to completion after 40 min of reaction when the gas flow rate was $100\text{ mL}\cdot\text{min}^{-1}$ and above.

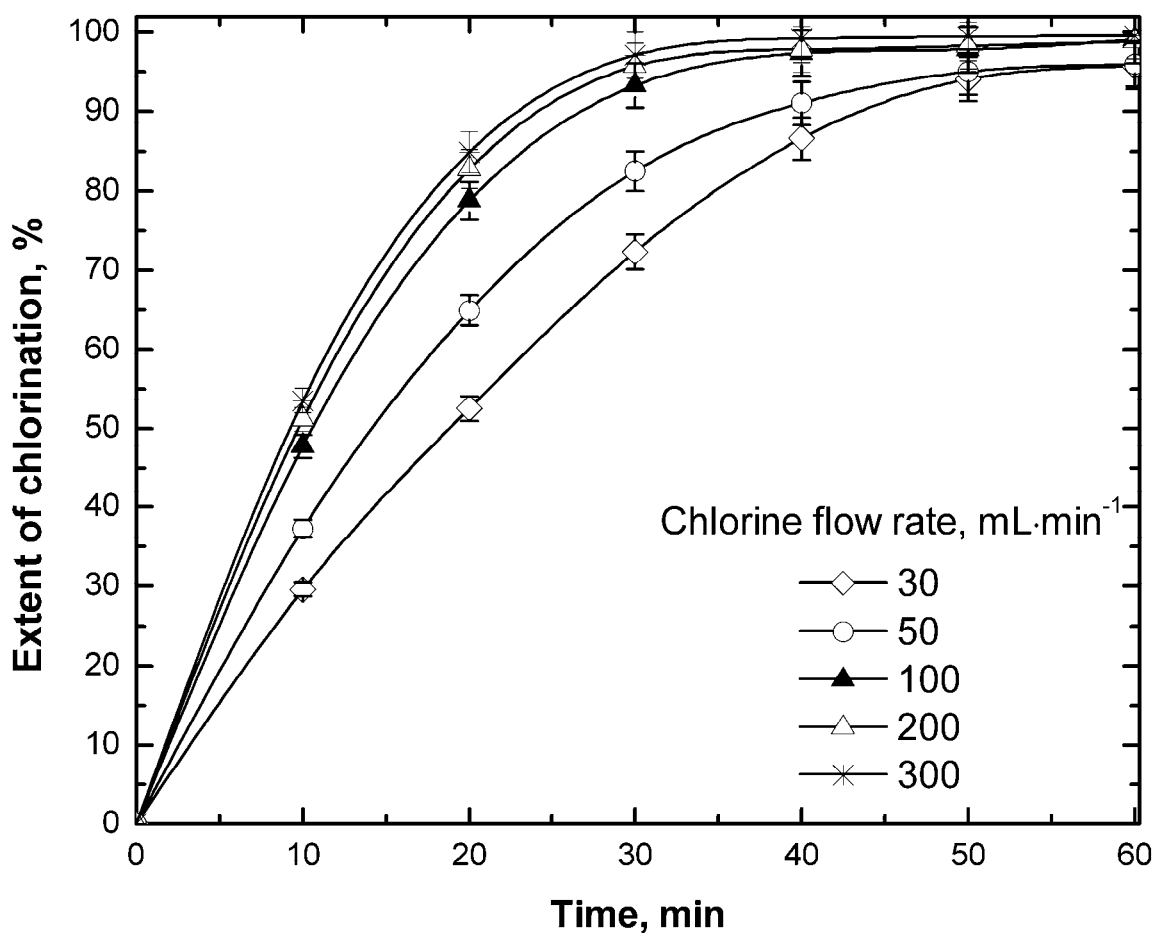


Figure 5.8. Effect of Cl_2 gas flow rate on the extent of chlorination at 235 °C for sample C

The effect of gas flow rate on chlorination was further studied with sample C at 300 °C using Cl_2 - N_2 gas mixture with constant chlorine partial pressure of 50 kPa. The flow rate of the gas mixture was changed in the range of 100 to 500 $\text{mL}\cdot\text{min}^{-1}$. The progress of the chlorination of sample C is shown in **Figure 5.9**. The chlorination rate increased with increasing gas flow rate. However, this increase became less significant at higher gas flow rate. With 100 $\text{mL}\cdot\text{min}^{-1}$ gas flow rate, the extent of chlorination after 30 min was 85 pct. It increased to 95 pct when the gas flow rate was increased to 300 $\text{mL}\cdot\text{min}^{-1}$ and practically did not change with further increase in the gas flow rate to 500 $\text{mL}\cdot\text{min}^{-1}$.

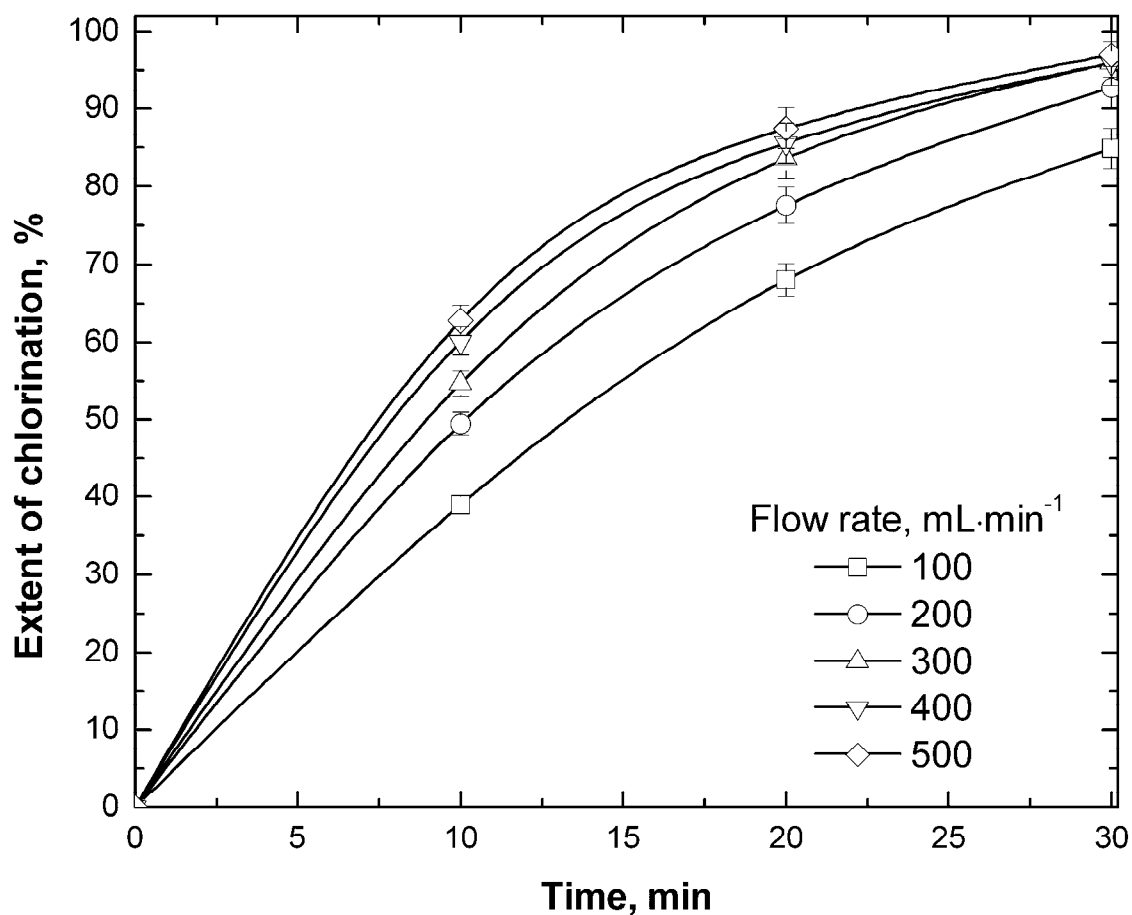


Figure 5.9. Effect of $\text{N}_2\text{-Cl}_2$ gas flow rate on the extent of chlorination at 300 °C with 50 kPa chlorine partial pressure for sample C

The change in the sample temperature during chlorination of titanium oxycarbonitride in sample C in pure Cl_2 gas as presented in **Figure 5.8** is shown in **Figure 5.10**, while that in the $\text{Cl}_2\text{-N}_2$ gas mixture (**Figure 5.9**) is shown in **Figure 5.11**.

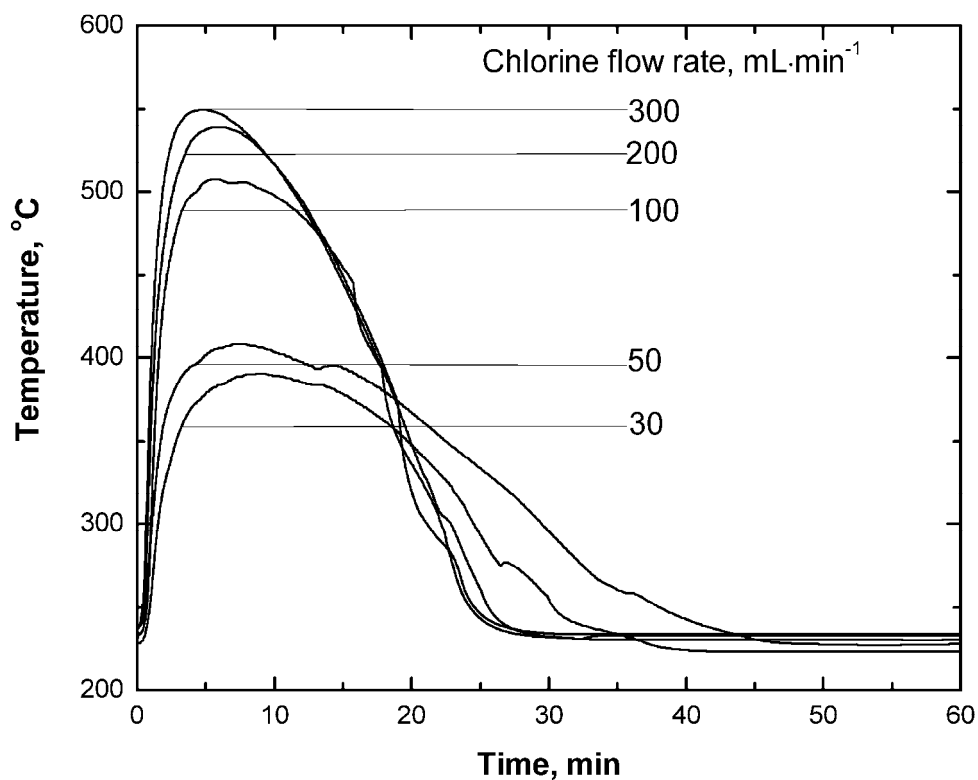


Figure 5.10. Change in sample temperature during chlorination of sample C in pure chlorine at furnace temperature of 300 °C

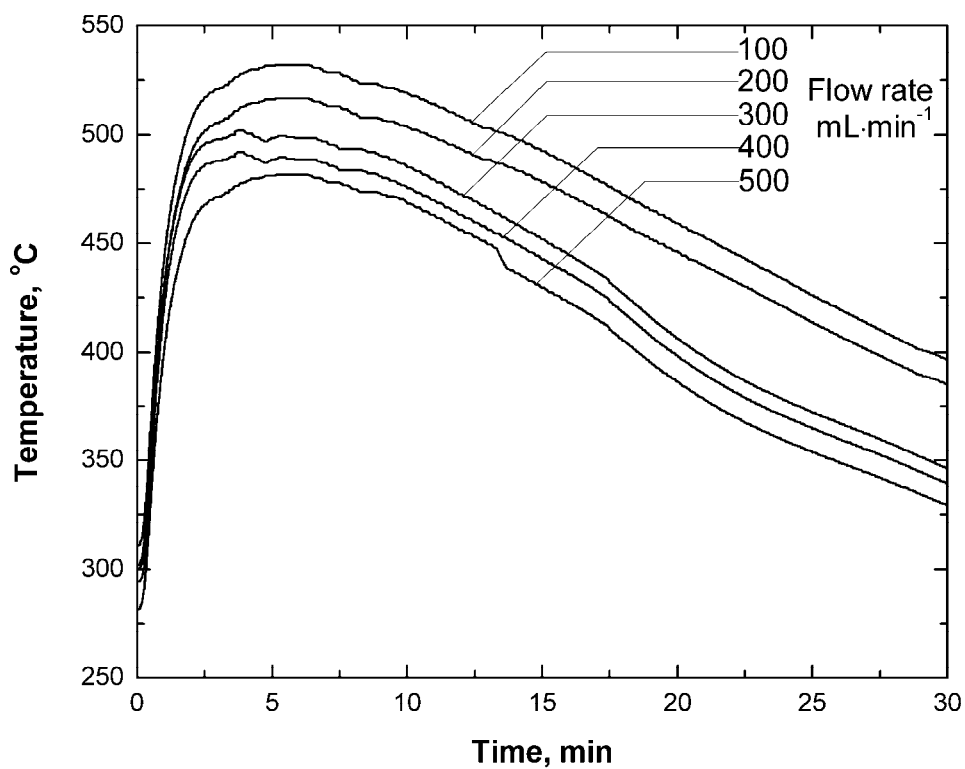


Figure 5.11. Change in sample temperature during chlorination of sample C in 50 pct N₂ – 50 pct Cl₂ mixture at furnace temperature of 300 °C

As shown in **Figure 5.10**, along with increase in the flow rate of pure chlorine, the sample temperature increased more rapidly and reached higher maximum temperature. At 30 mL·min⁻¹ the sample temperature increased to 390 °C in 10 min. At chlorine flow rate of 300 mL·min⁻¹, the sample temperature rose rapidly to a maximum of 550 °C in 4 min. However, the increased temperature was maintained for only 30 min when the chlorine flow rate was 100 mL·min⁻¹ and above. After this period, the sample temperature went back to the furnace temperature because the chlorination reaction had become insignificant due to depletion of titanium oxycarbonitride.

According to **Figure 5.11**, the maximum sample temperature reached during chlorination with 50 pct N₂-50 pct Cl₂ mixture at 300 °C actually decreased with increasing gas flow rate, which is opposite to the case of pure chlorine. It was 532 °C with 100 mL·min⁻¹ and 460 °C with 500 mL·min⁻¹ gas flow rate. Also different from the case of pure chlorine, the maximum temperature was reached in about 5 min for all the gas flow rates when the gas mixture was used.

5.4. Effect of Chlorine Partial Pressure

The effect of partial pressure of chlorine in the Cl₂-N₂ gas mixture on chlorination was examined using samples C and D at 300 °C. The partial pressure of chlorine was changed in the range of 20 to 60 kPa by adjusting the flow rate of chlorine and nitrogen while the total gas mixture flow rate was maintained at 450 mL·min⁻¹.

As shown in **Figure 5.12**, the initial chlorination rate significantly increased with increasing chlorine partial pressure. The extent of chlorination with P_{Cl₂} 20 kPa and 30 kPa was 91 pct and 94 pct respectively; it approached 100 pct when P_{Cl₂} increased to 40 kPa and above.

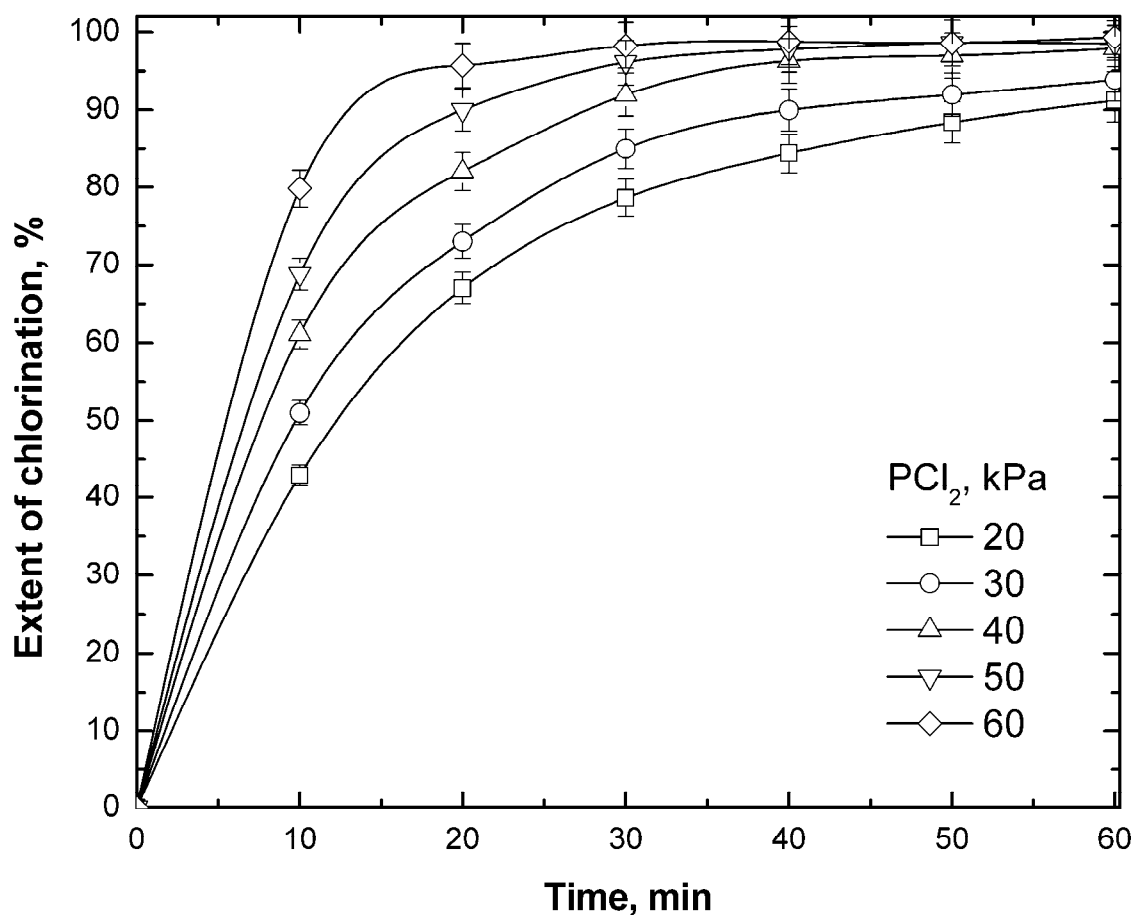


Figure 5.12. Effect of chlorine partial pressure on the extent of chlorination at 300 °C with $\text{Cl}_2 - \text{N}_2$ total flow rate $450 \text{ mL} \cdot \text{min}^{-1}$ for sample C

Figure 5.13 presents the temperature change of pellets during chlorination experiments with the changing chlorine partial pressure. The maximum temperature was reached in 4 min after chlorination reaction started. This maximum temperature also increased with increasing chlorine partial pressure: at higher chlorine partial pressure, 60 kPa, the sample temperature reached 533 °C; at lower chlorine partial pressure, 20 kPa, it was 421 °C.

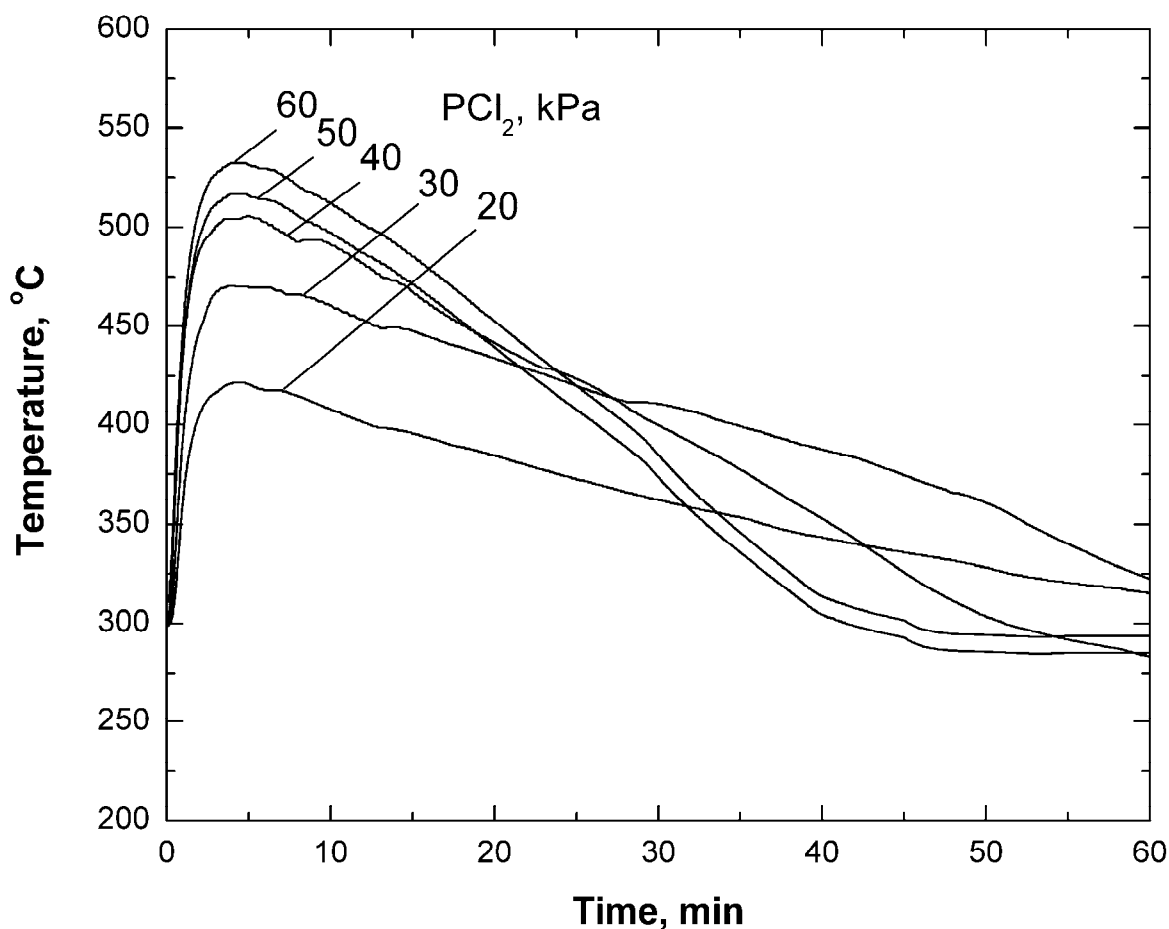


Figure 5.13. Change in sample temperature during chlorination of sample C at furnace temperature of 300 °C with $\text{Cl}_2\text{-N}_2$ total flow rate of $450 \text{ mL}\cdot\text{min}^{-1}$

5.5. Effect of Particle Size

Samples C were crushed into different particle size ranges, placed in an alumina boat and chlorinated at 300 °C in the $\text{Cl}_2\text{-N}_2$ gas mixture with chlorine partial pressure of 40 kPa and total gas flow rate of $450 \text{ mL}\cdot\text{min}^{-1}$. The progress of the chlorination reaction is presented in **Figure 5.14**. Decreasing particle size increased the chlorination rate, but the effect was not as significant as the effect of chlorine partial pressure and gas flow rate.

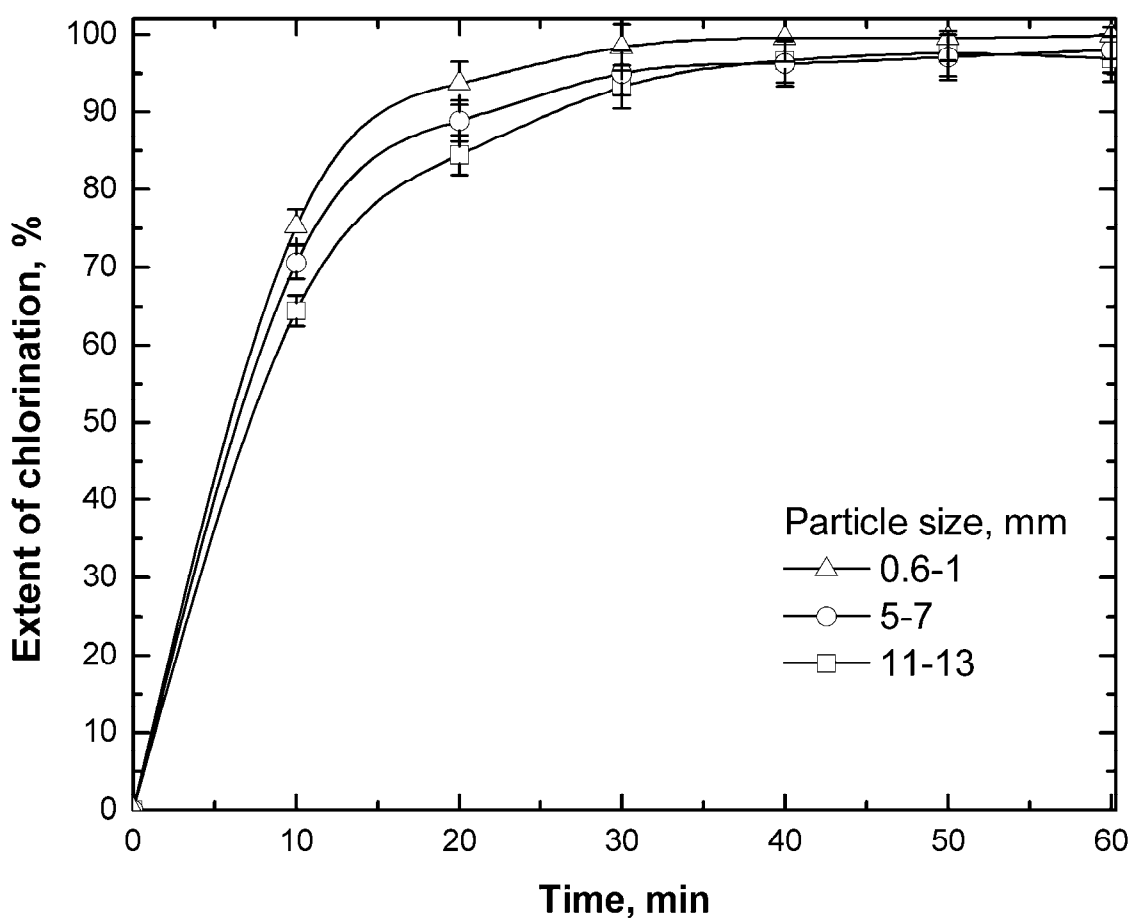


Figure 5.14. Effect of particle size on extent of chlorination of sample C at 300 °C with chlorine partial pressure 40 kPa and total gas flow rate 450 mL·min⁻¹

5.6. Chlorination of Ti(O,C), Ti(O,C,N), TiC, and TiN

The comparison of chlorination of sample C (titanium oxycarbonitride), sample F (titanium oxycarbide), and pure chemicals titanium carbide TiC, nitride TiN, and carbonitride TiC_{0.5}N_{0.5} is shown in **Figure 5.15**. LECO analysis showed that oxygen content in the chemicals was below 0.1 wt pct. The chlorination was carried out at 235 °C in the Cl₂-N₂ gas mixture with flow rate 450 mL·min⁻¹ and chlorine partial pressure 20 kPa.

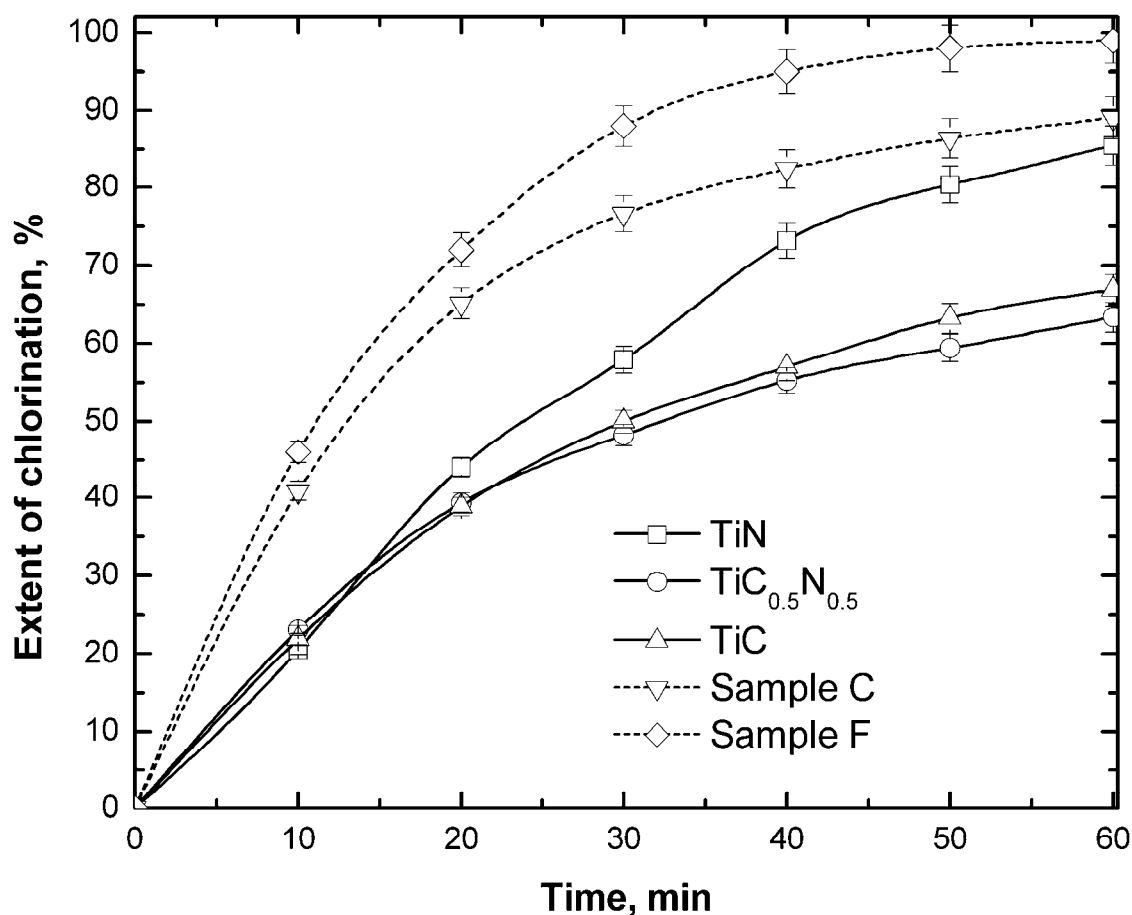


Figure 5.15. Extent of chlorination of titanium oxycarbide, oxycarbonitride, titanium nitride, carbide, and carbonitride at 235 °C with total flow rate of 450 $\text{mL}\cdot\text{min}^{-1}$ and P_{Cl_2} of 20 kPa

As shown in **Figure 5.15**, chlorination of titanium oxycarbide ($\text{TiC}_{0.5}\text{O}_{0.5}$) was the fastest and close to completion in 60 min. The rate of chlorination of titanium oxycarbonitride was close to that of oxycarbide in the first 20 min, although the final extent of chlorination was slightly lower and reached 89 pct. Pure samples of titanium nitride, carbonitride, and carbide chlorinated significantly slower. The extent of chlorination after 60 min reaction reached 86, 67 and 63 pct for titanium nitride, carbide and carbonitride, respectively.

The rate of chlorination of TiN in the first 10 min of reaction was slightly lower in comparison with TiC and $\text{TiC}_{0.5}\text{N}_{0.5}$, however, the degree of chlorination of TiN after 60 min was higher than that of TiC and $\text{TiC}_{0.5}\text{N}_{0.5}$. Such chlorination behaviour was reflected in the sample temperature curves in **Figure 5.16**; at the beginning of chlorination of titanium nitride, the sample temperature reached maximum of 375 °C in 10 min, and

decreased slowly afterwards. Although the chlorination curves for titanium carbide and carbonitride were close, the temperature of titanium carbide reached maximum of 395 °C in 5 min, while a maximum temperature of titanium carbonitride of 336 °C was reached in 7 min. This difference can be explained by different enthalpies of chlorination reactions, which is higher for TiC than for TiN and $\text{TiC}_{0.5}\text{N}_{0.5}$. High chlorination rate of TiN was maintained for longer time in comparison with TiC and $\text{TiC}_{0.5}\text{N}_{0.5}$. This elucidates position of the temperature curve in chlorination of TiN.

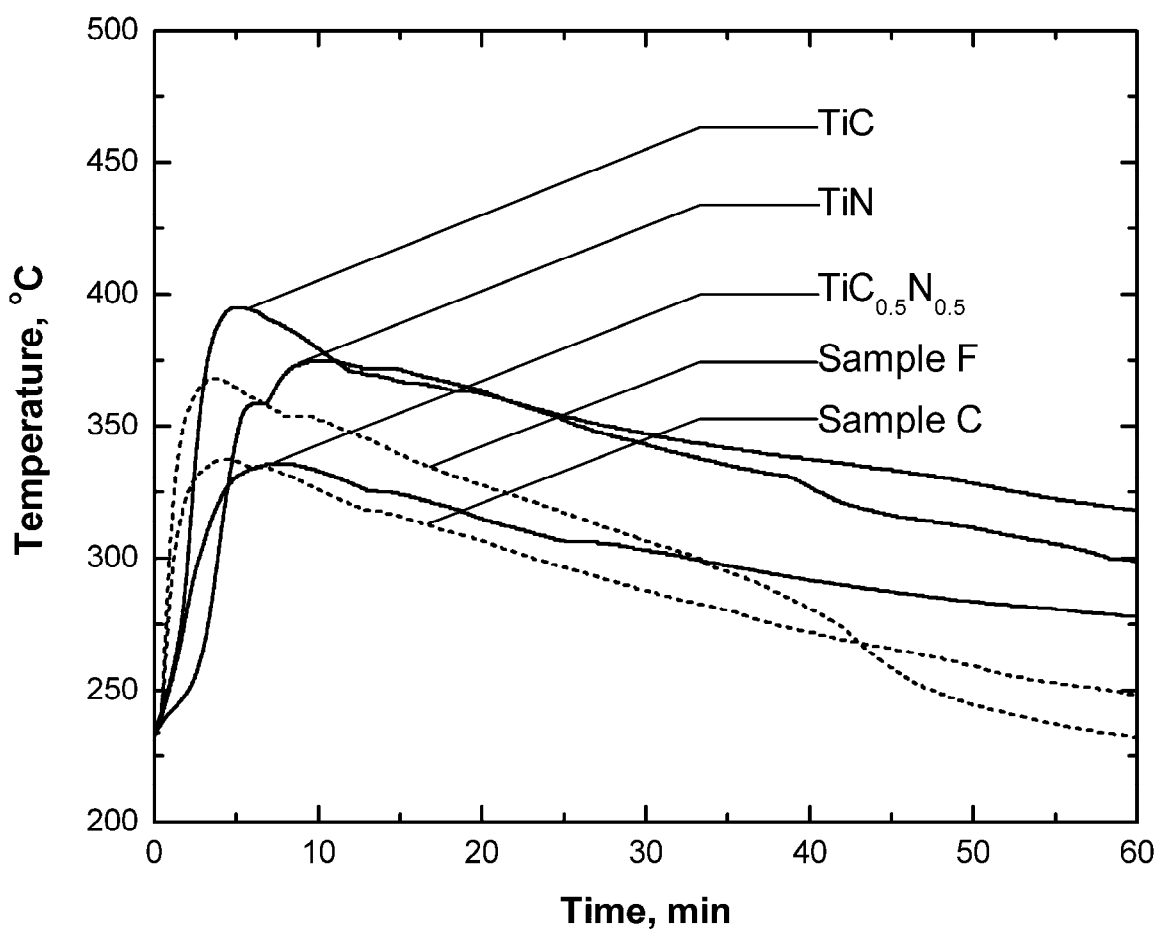
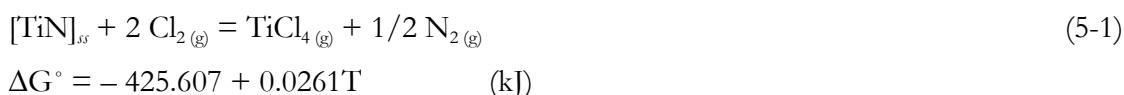


Figure 5.16. Change in sample temperature during chlorination of titanium oxycarbide, oxycarbonitride, titanium nitride, carbide, and carbonitride at furnace temperature of 235 °C with total flow rate of 450 mL·min⁻¹ and P_{Cl_2} of 20 kPa

5.7. Discussion

5.7.1. Thermodynamic Analysis of Chlorination of Ti(O,C,N)

Titanium oxycarbonitride, Ti(O,C,N) prepared by carbothermal reduction of titania under nitrogen atmosphere, is a solid solution of TiC, TiO and TiN. Chlorination proceeds by Reactions (4-1), (4-2) (*See Section 4.7.1*) and (5-1):



The standard Gibbs free energy change for reaction (5-1) is calculated using NIST JANAF Thermochemical Tables [Chase, 1998]. Thermodynamically, reaction (5-1) proceeds in preference to chlorination of titania (Reaction (2-1), *Section § 2.2*) and TiO (Reaction (4-3), *Section § 4.7.1*). In terms of standard Gibbs free energy change, the stability decreases from TiO, to TiN, and TiC. Chlorination of Ti(O,C,N) has very high equilibrium constants; the equilibrium partial pressure is in the order of 10^{210} to 10^{150} for N_2 (reaction (5-1)) in the temperature range of 150 to 700 °C.

5.7.2. Effect of Temperature and Gas Flow Rate

Chlorination by reaction (5-1) is highly exothermic and the actual samples temperature was appreciably higher than the furnace temperature which is similar to the conditions observed in chlorination of Ti(O,C).

In general, the effect of temperature on the chlorination of titanium oxycarbonitride in the experiments with chlorine flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$ was minor. It was more prominent in experiments with chlorine flow rate of $250 \text{ mL}\cdot\text{min}^{-1}$ and with $\text{Cl}_2 - \text{N}_2$ gas mixture at gas flow rate of $450 \text{ mL}\cdot\text{min}^{-1}$. It follows from **Figure 5.2** that at flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$ pure chlorine, in the initial stage of chlorination when the rate of reaction was fast, up to 75 pct of chlorine supplied to the reactor was consumed. Considering that the cross-section area of the sample pellet occupied less than 50 pct of the reactor tube cross-section area, it can be suggested that the chlorine partial pressure in the $\text{Cl}_2\text{--TiCl}_4\text{--CO}$ gas mixture at the pellet

surface and interior was low at all temperatures and was insufficient for adequate chlorination. This was confirmed by experiments with varied chlorine flow rate. Increasing chlorine flow rate to $100 \text{ mL}\cdot\text{min}^{-1}$ increased the chlorination rate, while further increase to $300 \text{ mL}\cdot\text{min}^{-1}$ had a relatively minor effect. It can be concluded that at the chlorine flow rate of $100 \text{ mL}\cdot\text{min}^{-1}$ and below, the reaction was chlorine-starved and controlled by chlorine supply.

Comparing chlorination curves for sample C at 300°C , it can be noticed that chlorination with flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$ pure chlorine (**Figure 5.2 (c)**) had a higher rate than that with $450 \text{ mL}\cdot\text{min}^{-1}$ $\text{Cl}_2\text{-N}_2$ gas flow rate and 20 kPa chlorine partial pressure (**Figure 5.6**), although the actual chlorine supply rate was higher in the latter case. In chlorination experiments with $\text{Cl}_2\text{-N}_2$ gas mixture, the diffusion of Cl_2 in the gas phase could offer additional mass transfer resistance which resulted in lower chlorination rate. This is consistent with the results shown in **Figure 5.12**. The diffusion of chlorine in nitrogen at 235°C , $D_{\text{Cl}_2\text{-N}_2}$ was calculated to be $3.219 \times 10^{-5} \text{ m}^2\cdot\text{s}^{-1}$. (See *Appendix B*).

The ignition temperature for the chlorination reaction was determined in temperature programmed chlorination experiments, in which the furnace temperature ramped from 100 to 400°C at the rate of $3^\circ\text{C}\cdot\text{min}^{-1}$ (**Figure 5.7**). In the course of initial heating prior to chlorination stage, the sample was heated up in line with the furnace temperature. A significant increase in the sample temperature corresponded to the beginning of the chlorination reaction. After achieving maximum temperature, the reaction rate gradually decreased and the sample temperature decreased correspondingly (**Figure 5.7**). The chlorination of samples A to C was ignited at 150°C , whereas samples D and E had ignition temperatures higher than 200°C . This difference is attributed to the residual carbon in samples D and E, which could decrease the rate of heat generation and increase the heat dissipation; as a result the ignition temperature was increased.

Chlorination is strongly exothermic and the rate of heat generation is proportional to the rate of reaction. The maximum sample temperature was determined by the balance of heat generation and its dissipation by the gas stream. There is a different effect of gas flow rate on the maximum sample temperature as shown in **Figures 5.10** and **5.11**. In experiments with pure chlorine (**Figure 5.10**), increasing heat generation prevailed over increasing heat dissipation with increasing chlorine flow rate. The maximum sample temperature increased

and chlorination time decreased with increasing chlorine flow rate. In contrast, in the experiments with 50 vol pct Cl_2 -50 vol pct N_2 presented in **Figure 5.11**, increasing heat dissipation due to increasing heat transfer coefficient with increasing gas mixture flow rate had a more profound effect than increasing heat generation. In this case, increasing flow rate of chlorine-nitrogen gas mixture decreased maximum sample temperature, although the chlorination rate increased. As a result, sample's temperature profile in experiments with 50 vol pct Cl_2 -50 vol pct N_2 gas mixture (**Figure 5.11**) is different from that in experiments with pure chlorine (**Figure 5.10**).

Titanium nitride thermodynamically is more stable than titanium carbide. Conversion of titanium nitride to titanium tetrachloride requires more energy than chlorination of titanium carbide. However, chlorination of titanium nitride did not generate a residual carbon layer which formed resistance to the diffusion of chlorine. Chlorination of titanium carbide and carbonitride had higher initial rate (**Figure 5.15**), however the carbon residue formed in the process of chlorination had a negative effect on the rate and extent of reaction. Both initial chlorination rate and final extent of chlorination of titanium oxycarbide (sample F) were higher than those of titanium oxycarbonitride (sample C). It should be mentioned that sample F contained no free carbon, while sample C was composed of titanium oxycarbonitride and free carbon. Although carbon content in titanium oxycarbide was much higher than in titanium oxycarbonitride, free carbon present in sample C could offer more significant resistance in the mass transfer of gaseous reactant and products than residual carbon formed in the chlorination process. Chlorination of pure chemicals was incomplete after 60 min of reaction, and slower in comparison with titanium oxycarbide and oxycarbonitride. This can be explained by low porosity of samples of TiC , TiN , and $\text{TiC}_{0.5}\text{N}_{0.5}$. Samples C and F prepared by carbothermal reduction of titania under nitrogen and argon atmosphere, respectively, contained pores that were developed throughout the reduction process. Samples of titanium carbide, nitride and carbonitride were directly pressed from powders of chemicals to produce pellet, and had less porosity in comparison to samples C and F.

5.8. Summary

Chlorination of titanium oxycarbonitride prepared by carbothermal nitridation of rutile was investigated in a laboratory horizontal furnace. The exothermic chlorination reaction raised the sample temperature significantly higher than the furnace temperature. Temperature programmed chlorination experiments showed that chlorination of oxycarbonitride was ignited at low temperature between 150 °C to 200 °C, depending on the sample composition. With chlorine flow rate at 50 mL·min⁻¹, changing furnace temperature from 235 to 400 °C caused insignificant effect on the progress of chlorination due to gas reactant starvation. Above 100 mL·min⁻¹ of chlorine, the effect of furnace temperature became significant.

Sample C, which was prepared from rutile-graphite mixture with carbon to titania ratio of 2.5, had titanium suboxides and excess carbon below the detectable by XRD level. This sample was optimum for chlorination. The reaction of sample C was completed in 30 min with chlorine flow rate at 250 mL·min⁻¹. Samples A and B had low final extent of chlorination due to incomplete reduction and containing significant amount of titanium suboxides.

Increasing chlorine partial pressure, gas flow rate and decreasing particle size had a positive effect on the extent of chlorination, the latter effect was not as significant as chlorine partial pressure and gas flow rate.

The rate of chlorination of titanium oxycarbonitride was comparable to that of titanium oxycarbide, both being faster than that of pellets of titanium nitride, carbide and carbonitride.

CHAPTER 6.

CHLORINATION OF REDUCED ILMENITE ORES AND SYNTHETIC RUTILE

This chapter presents results of examination of chlorination of titanium oxycarbide and oxycarbonitride produced by carbothermal reduction of ilmenite ores in argon or nitrogen atmosphere. This also includes a study of chlorination of titanium oxycarbide produced by leaching of iron from reduced ilmenite, and the behaviour of impurities in the process of chlorination.

6.1. Reduction of Ilmenite Ores and Synthetic Rutile

The project studied reduction and chlorination of primary, secondary, and HYTI 70 grade ilmenites and synthetic rutile, all supplied by Iluka Resources Limited. Their chemical composition is presented in **Table 3.3** (*See Experimental Section § 3.2.1.1*). **Figure 6.1** shows the XRD spectra for ilmenite ores and synthetic rutile.

XRD analysis of unreduced ores indicates that primary and secondary ilmenites consisted predominantly of pseudorutile, $\text{Fe}_2\text{Ti}_3\text{O}_9$, and ilmenite, FeTiO_3 . HYTI 70 ilmenite had higher titanium content, which existed in the form of pseudorutile, ilmenite, and rutile (**Figure 6.1**). Impurities in ilmenites were present in relatively small amount, below the detectable level by XRD analysis. Synthetic rutile was produced by Iluka Resources Limited from ilmenites by reduction and iron removal. XRD analysis indicates that synthetic rutile consisted of titania and suboxides (Ti_2O_3 , Ti_3O_5 , Ti_4O_7) (**Figure 6.1**). Iron oxides or metallic iron were not detected by XRD, however analysis by XRF indicated 2.8 pct of iron in synthetic rutile.

Primary grade ilmenite ore containing 53.9 pct of titania was mixed with graphite with carbon to TiO_2 (C/TiO_2) molar ratio of 3.3 to 4.5. **Figure 6.2** shows the XRD spectra for reduced primary ilmenite in argon atmosphere with C/TiO_2 molar ratio of 3.3 to 4.5. The XRD spectra indicated that primary ilmenite with C/TiO_2 molar ratio of 3.3 was reduced in argon atmosphere to $\text{Ti}(\text{O,C})$ and metallic iron with traces of suboxides (Ti_2O_3 , Ti_3O_5) (**Figure 6.1**). Suboxide peaks receded with increasing C/TiO_2 molar ratio. Ti_2O_3 peak was

still observed in samples with C/TiO₂ molar ratio of 4.5 which suggests that the reduction was incomplete. The reduced samples with higher molar C/TiO₂ ratio were observed to be harder and sintered.

Primary, secondary, HYTI 70 ilmenite and synthetic rutile mixed with graphite with C/TiO₂ molar ratio of 4.5 had molar ratio of carbon to reducible oxygen 2.94, 3.14, 3.46, and 4.04 respectively. Samples of ilmenite – carbon mixtures were pressed uniaxially and exposed to argon or nitrogen atmosphere at 1450 °C (See *Experimental Section § 3.2.1*).

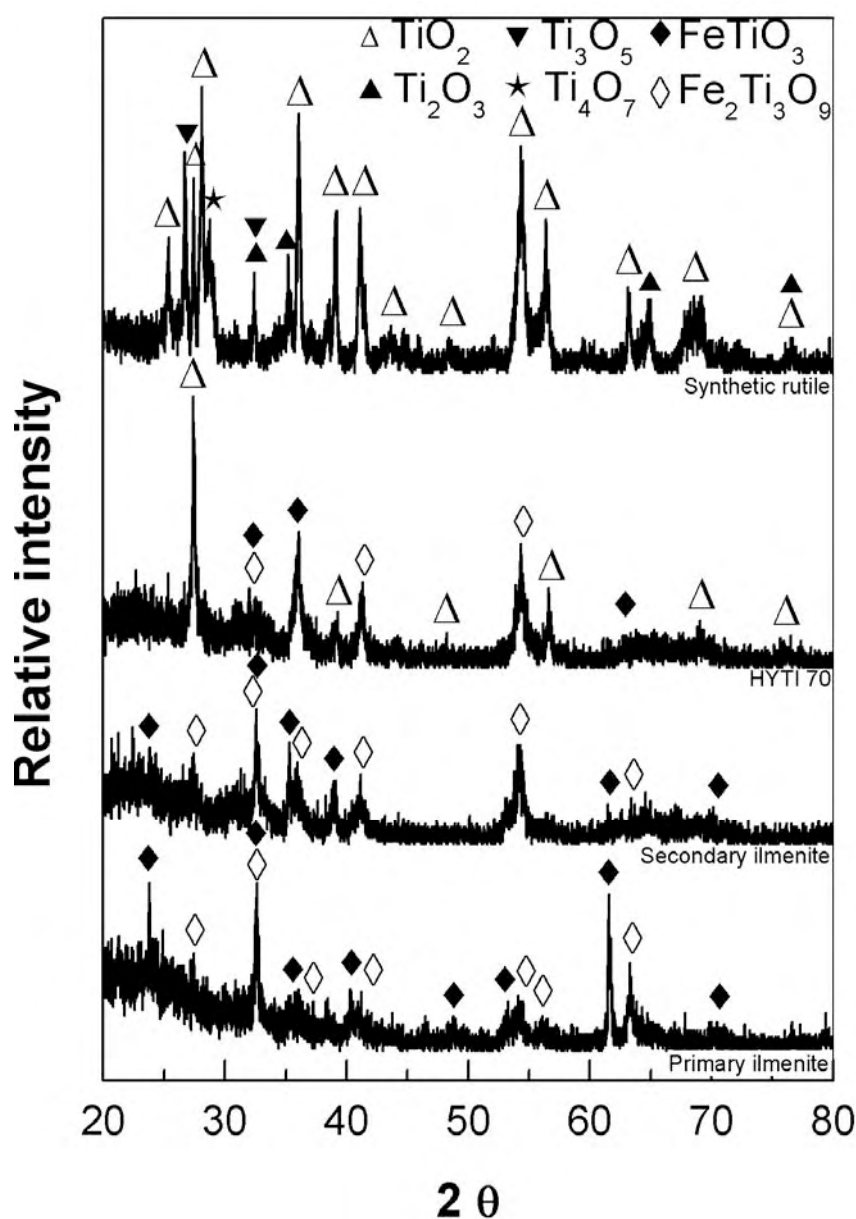


Figure 6.1. X-ray diffraction patterns of primary, secondary, HYTI 70 ilmenite ores and synthetic rutile

The composition of samples produced by carbothermal reduction of ilmenite in argon and nitrogen with C/TiO₂ molar ratio of 4.5, are presented in **Tables 6.1** and **6.2** respectively. **Figures 6.3** and **6.4** show the XRD spectra for reduced ilmenites and synthetic rutile with C/TiO₂ molar ratio of 4.5 in argon and nitrogen atmosphere, respectively.

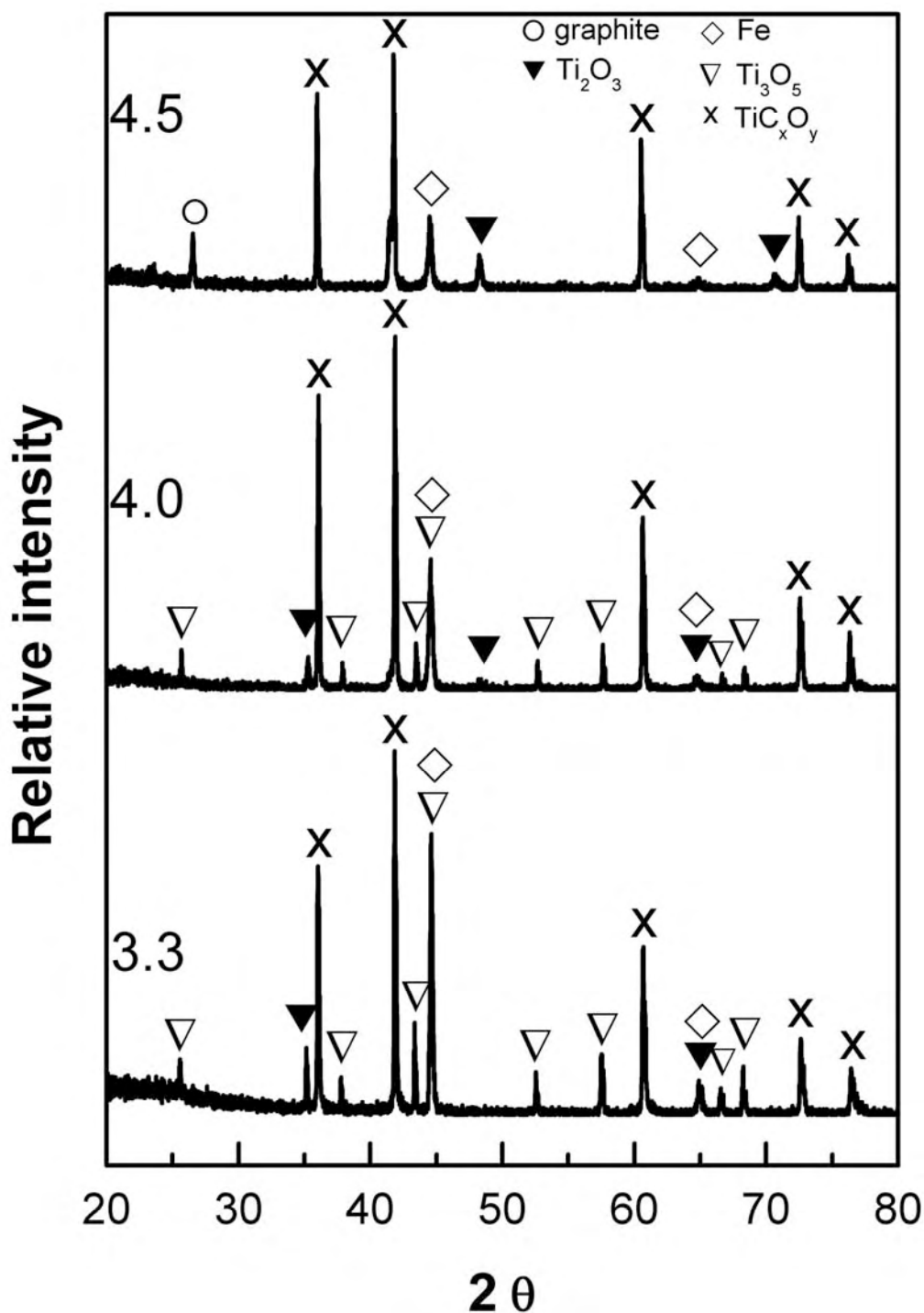


Figure 6.2. X-ray diffraction patterns of primary ilmenite reduced at 1450 °C in argon atmosphere with molar carbon to TiO₂ ratio of: (A) 3.3, (B) 4.0, and (C) 4.5

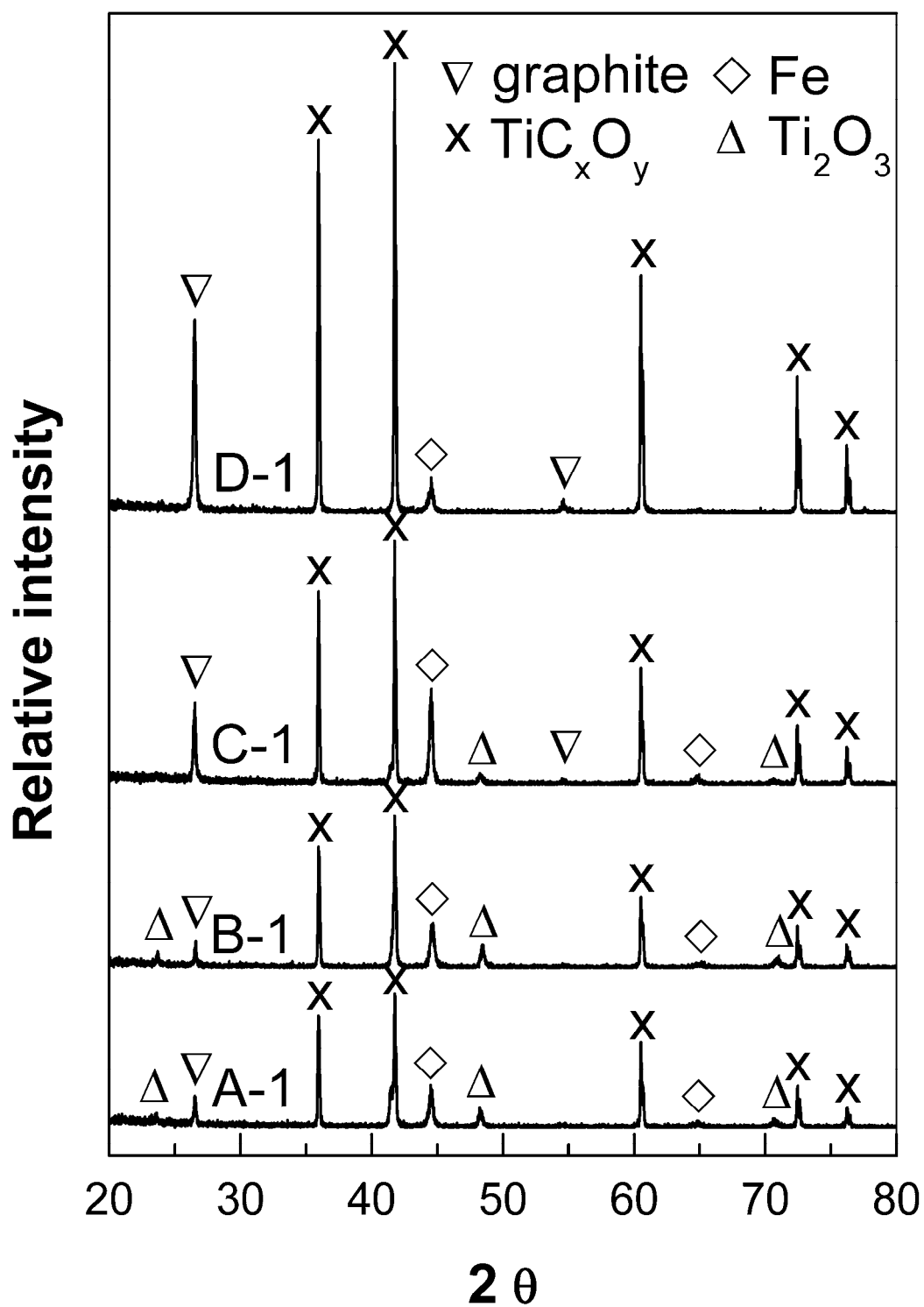


Figure 6.3. X-ray diffraction patterns of (A) primary, (B) secondary, (C) HYTI 70 ilmenite, and (D) synthetic rutile reduced with molar carbon to TiO_2 ratio of 4.5 at 1450 °C under argon atmosphere

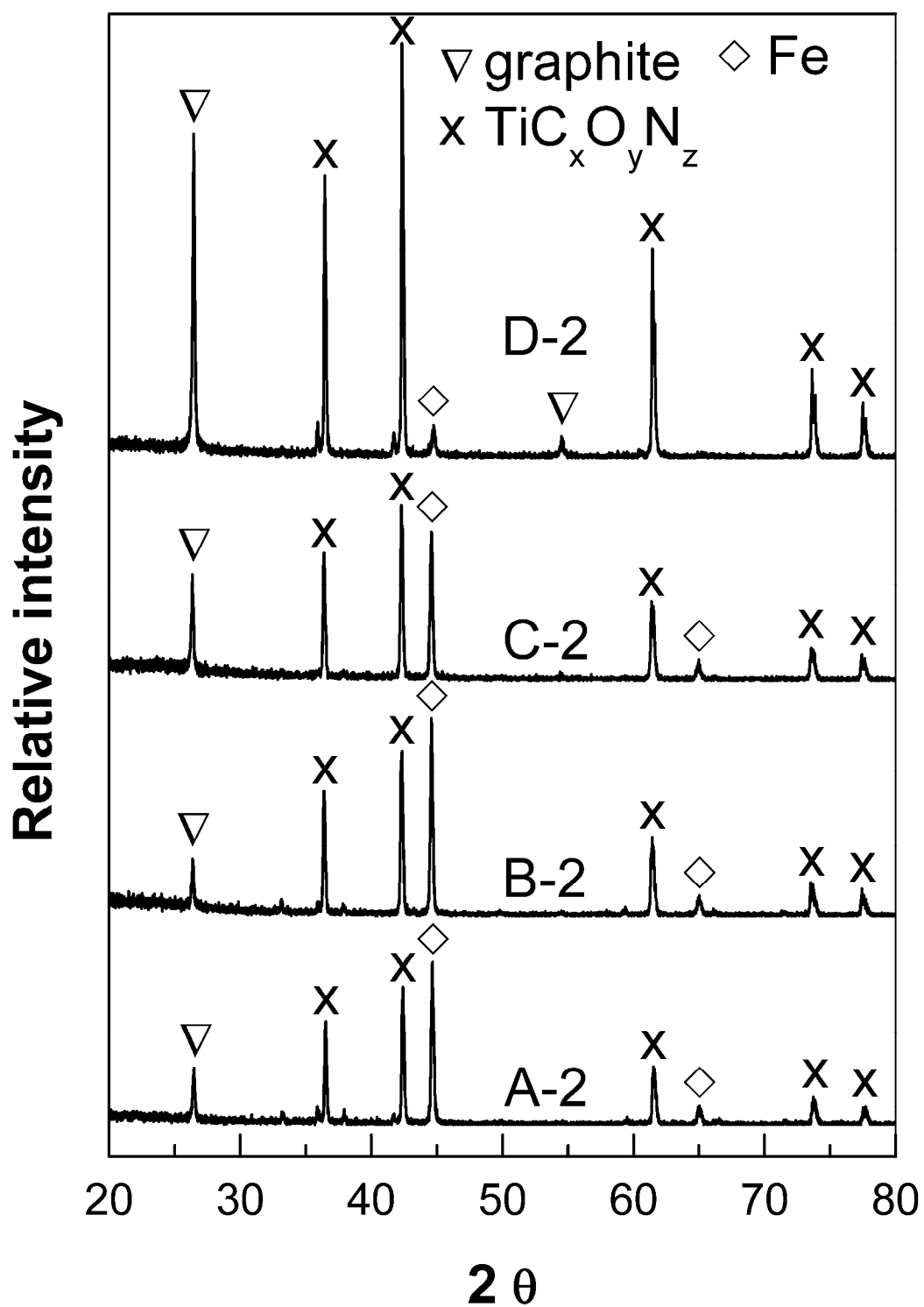


Figure 6.4. X-ray diffraction patterns of (A) primary, (B) secondary, (C) HYTI 70 ilmenite, and (D) synthetic rutile reduced with molar carbon to TiO_2 ratio of 4.5 at 1450 °C under nitrogen atmosphere

Table 6.1. Composition of reduced ilmenites and synthetic rutile in argon atmosphere at 1450 °C for 3 h

	A-1	B-1	C-1	D-1
Type	Primary Ilmenite	Secondary Ilmenite	HYTI 70	Synthetic Rutile
Carbon content, wt pct	12.73	16.15	24.85	37.51
Oxygen content, wt pct	4.32	3.87	3.56	3.27
Extent of Reduction, pct	83.39	85.6	87.45	90.20
Phase Composition	C, Fe, TiC_xO_y , Ti_3O_5 , Ti_2O_3	C, Fe, TiC_xO_y , Ti_3O_5 , Ti_2O_3	C, Fe, TiC_xO_y , Ti_2O_3	C, Fe, $\text{TiC}_{0.84}\text{O}_{0.16}$
Molar ratio C/O _{reducible}	2.94	3.14	3.46	4.04

Table 6.2. Composition of reduced ilmenites and synthetic rutile in nitrogen atmosphere at 1450 °C for 3 h

	A-2	B-2	C-2	D-2
Type	Primary Ilmenite	Secondary Ilmenite	HYTI 70	Synthetic Rutile
Carbon content, wt. pct	12.00	15.20	20.70	32.20
Oxygen content, wt. pct	0.80	0.70	0.70	0.98
Nitrogen content, wt. pct	10.41	11.23	10.88	12.03
Extent of Reduction, pct	97.59	98.26	98.89	99.81
Phase Composition	C, Fe, $\text{TiC}_{0.50}\text{O}_{0.031}\text{N}_{0.46}$	C, Fe, $\text{TiC}_{0.45}\text{O}_{0.029}\text{N}_{0.53}$	C, Fe, $\text{TiC}_{0.42}\text{O}_{0.031}\text{N}_{0.55}$	C, Fe, $\text{TiC}_{0.20}\text{O}_{0.054}\text{N}_{0.75}$
Molar ratio C/O _{reducible}	2.94	3.14	3.46	4.04

The BET surface area of sample A-1 was $0.14 \text{ m}^2\cdot\text{g}^{-1}$ with average porosity of $35.7 \text{ \AA}$ while BET surface area for sample A-2 was $0.45 \text{ m}^2\cdot\text{g}^{-1}$ with apparent porosity of $43.2 \text{ \AA}$. Carbothermal reduction of ilmenites in nitrogen with the formation of $\text{Ti}(\text{O,C,N})$ showed higher extent of reduction in comparison with its reduction in argon when $\text{Ti}(\text{O,C})$ was formed. No titanium suboxides (Ti_2O_3 , Ti_3O_5) were detected in the samples reduced in nitrogen (**Figure 6.4**). These suboxides were present in the ilmenite ores reduced in argon atmosphere even with C/TiO_2 molar ratio of 4.5 but have not been seen in the reduced rutile (**Figure 6.3**). Graphite peak in samples reduced in nitrogen was stronger; the reduced samples were not sintered. The samples reduced either in argon or nitrogen atmosphere were observed to exhibit magnetic properties as a result of formation of metallic iron.

6.2. Chlorination of Ilmenite Ores and Synthetic Rutile Reduced in Argon

Titanium in the ilmenites and synthetic rutile reduced in argon was predominantly in the form of oxycarbide. In chlorination of reduced ilmenites and synthetic rutile, both $\text{Ti}(\text{O,C})$ and metallic iron were chlorinated. Extents of chlorination of $\text{Ti}(\text{O,C})$ and iron in reduced primary ilmenite with C/TiO_2 molar ratio of 3.3 to 4.5 are presented in **Figure 6.5**. Chlorination was studied at 235°C under the flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$ of pure chlorine. As described in the previous section, the reduced ilmenites contained a small amount of titanium suboxides (Ti_2O_3 , Ti_3O_5) which decreased with increasing C/TiO_2 molar ratio.

The rate and extent of chlorination of titanium increased with increasing C/TiO_2 molar ratio as the amount of suboxides in the sample decreased. Carbon to TiO_2 ratio also affected the rate of chlorination of iron; the final extent of chlorination of iron increased slightly with increasing C/TiO_2 ratio from 3.3 to 4.5. In the course of chlorination of samples with C/TiO_2 molar ratio of 3.3, the rate of chlorination of metallic iron was comparable with $\text{Ti}(\text{O,C})$ (**Figure 6.5 (a)**). After 60 min of reaction, the extent of chlorination of iron reached 87 pct, while $\text{Ti}(\text{O,C})$ chlorinated only to 81 pct. The extent of chlorination of $\text{Ti}(\text{O,C})$ in ilmenites, reduced with C/TiO_2 molar ratio of 4.0 and 4.5, increased to 82 and 85 pct after 60 min of reaction, respectively; chlorination of iron in these samples reached 91 to 92 pct.

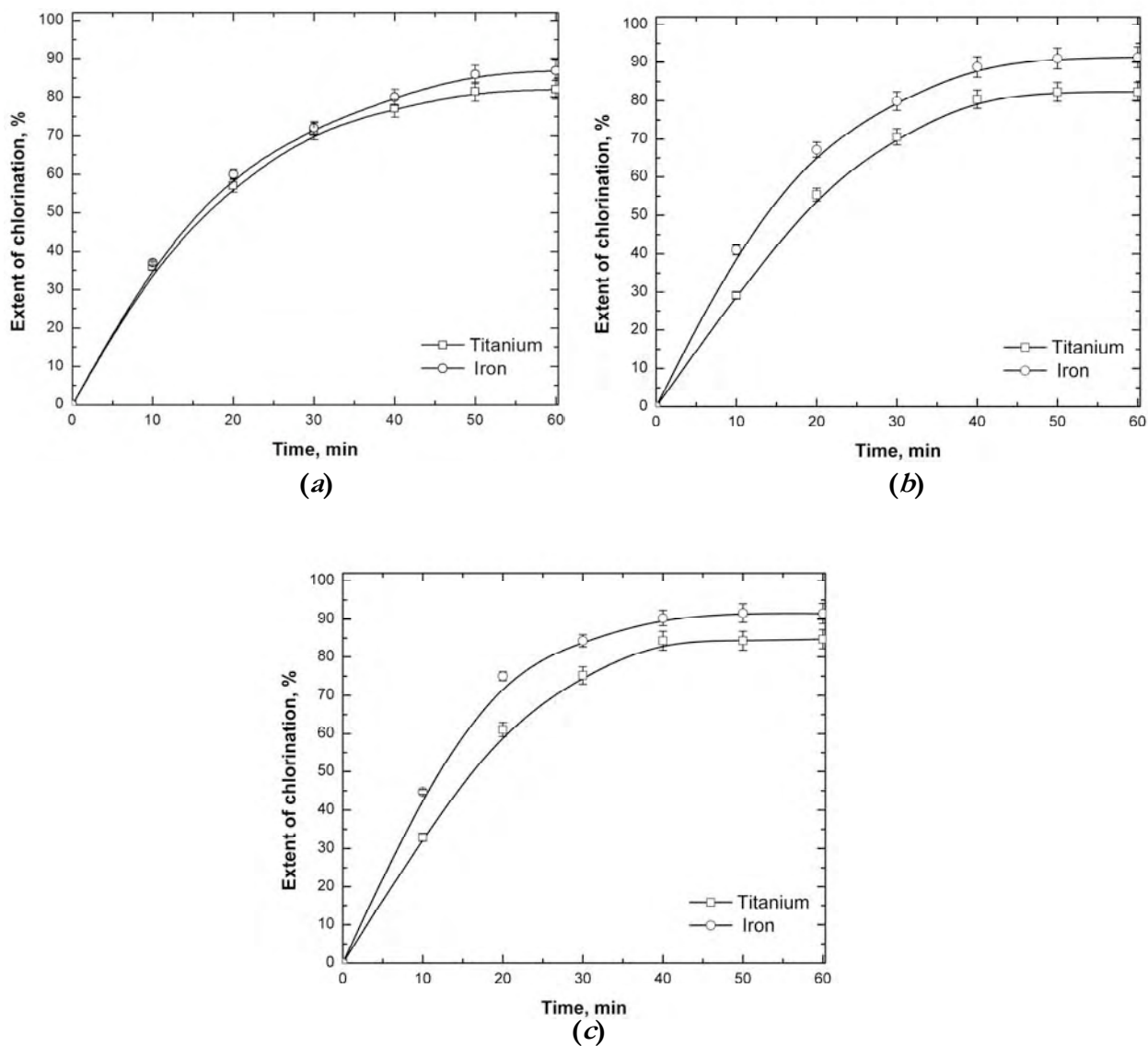


Figure 6.5. Extents of chlorination of reduced primary ilmenite at 235 °C at flow rate of 50 mL·min⁻¹ chlorine. Molar carbon to TiO_2 ratio in the graphite - ilmenite mixture: (a) 3.3, (b) 4.0, and (c) 4.5

The change in sample's temperature in the process of chlorination of reduced primary ilmenite with C/TiO₂ molar ratio of 3.3 to 4.5 is presented in **Figure 6.6**. Chlorination of samples with higher carbon content reached higher temperature and remained high at longer period before it slowly cooled down to the furnace temperature of 235 °C. The sample temperature increased very rapidly; it reached 446 °C after 6.5 min of reaction for a sample with C/TiO₂ molar ratio of 3.3. Temperature of samples produced with C/TiO₂ molar ratio 4.0 and 4.5 reached 456 and 470 °C, respectively, after only 4 min of reaction.

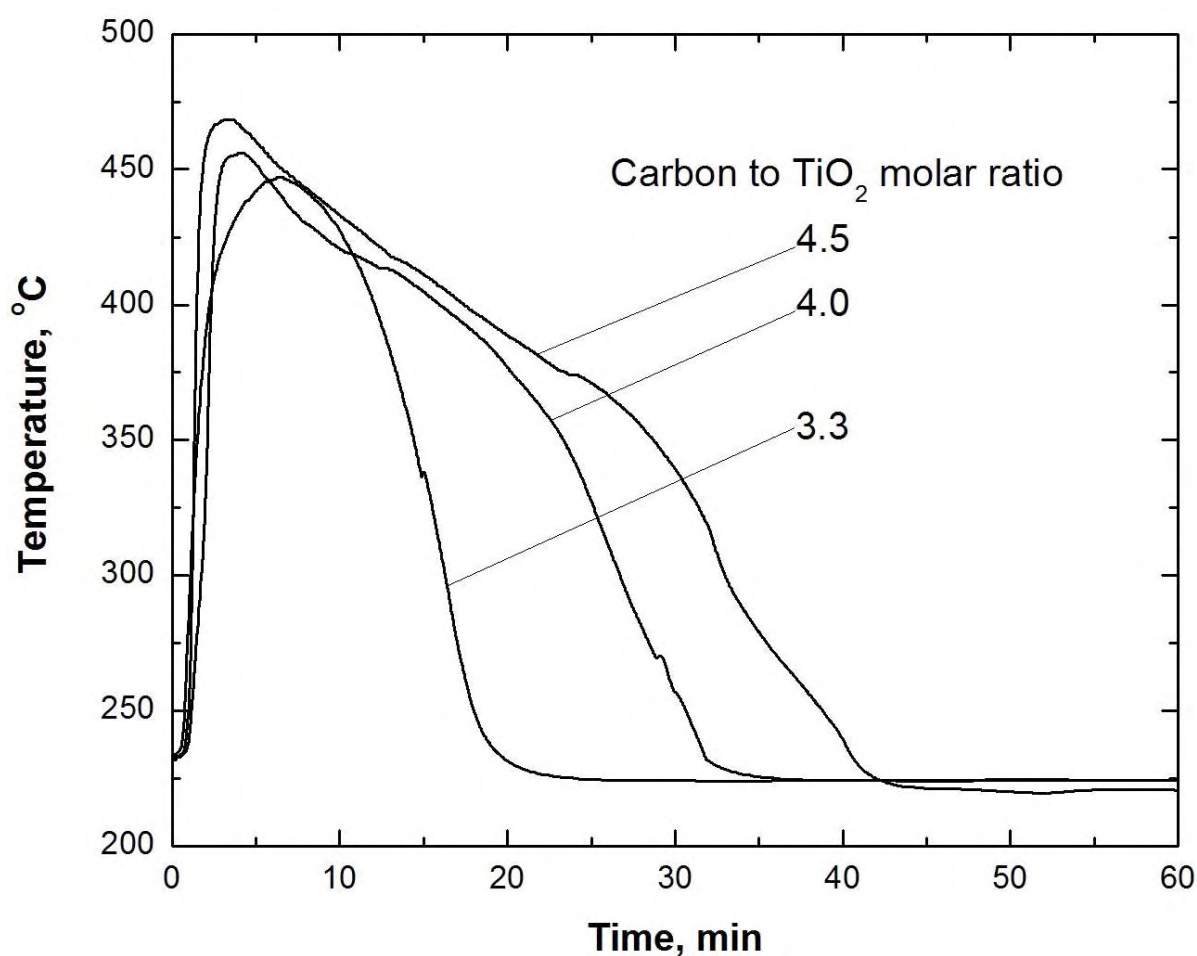


Figure 6.6. Change in sample temperature during chlorination of reduced primary ilmenite at chlorine flow rate 50 mL·min⁻¹; Carbon to TiO₂ molar ratio changed from 3.3 to 4.5

XRD spectra of residues after chlorination are shown in **Figure 6.7**. $\text{Ti}(\text{O,C})$, Ti_2O_3 , and metallic iron were chlorinated leaving residues mainly composed of TiO_2 , Ti_3O_5 , Ti_4O_7 for primary ilmenite reduced with C/ TiO_2 molar ratio of 3.3. For C/ TiO_2 ratio of 4.0, Ti_3O_5 and TiO_2 were detected. Excess graphite and Al_2O_3 were detected in the residues of chlorinated primary ilmenite reduced with C/ TiO_2 molar ratio of 3.3.

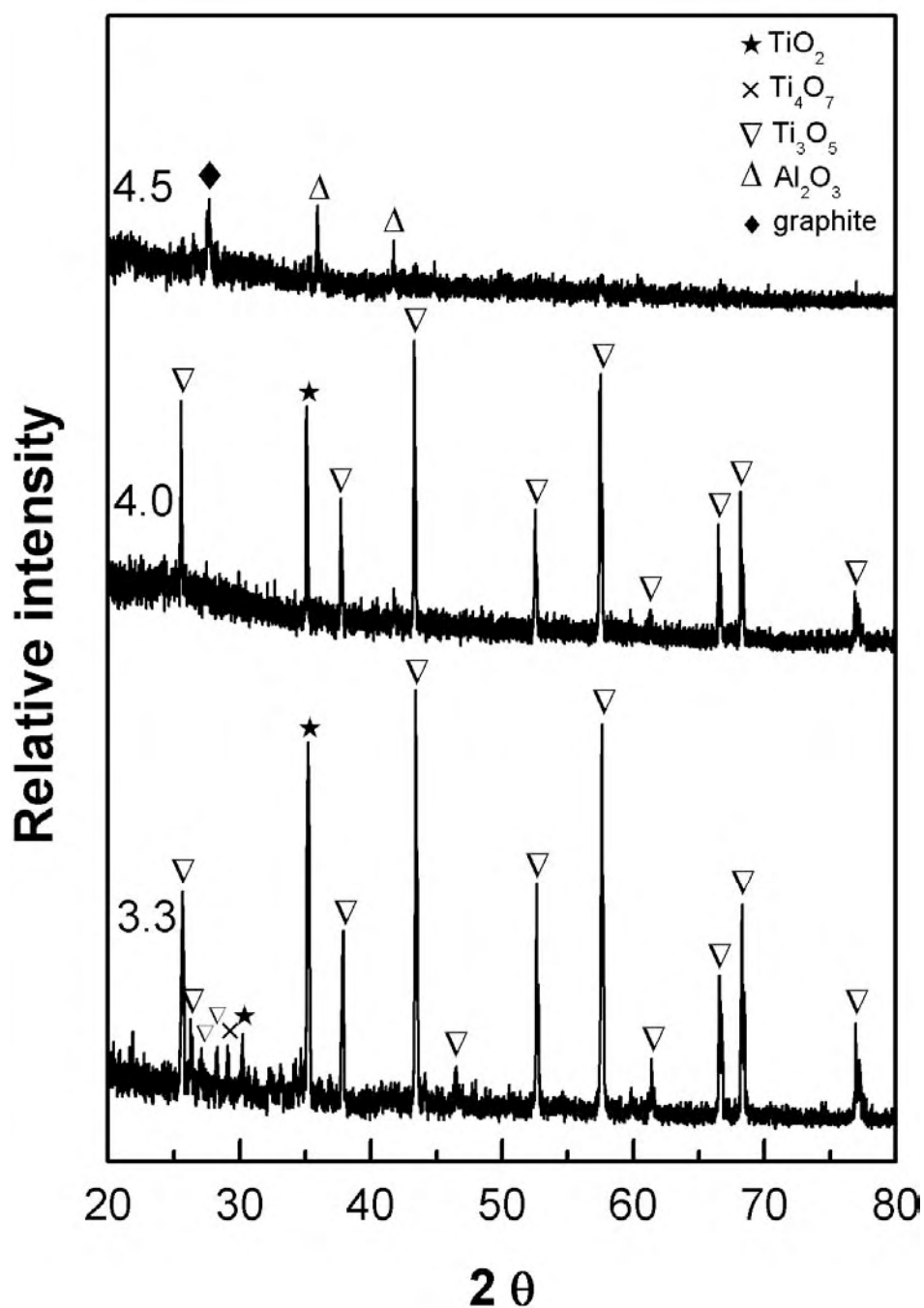


Figure 6.7. X-ray diffraction patterns of residues of chlorination of reduced primary ilmenite carbon to TiO_2 molar ratio of 3.3 to 4.5

The extent of chlorination of $\text{Ti}(\text{O,C})$ in ilmenites, and synthetic rutile reduced with C/TiO_2 molar ratio of 4.5 is presented in **Figure 6.8 (a) to (d)** with corresponding change in the samples temperature shown in **Figure 6.9**.

In these experiments, chlorine flow rate was higher, $100 \text{ mL}\cdot\text{min}^{-1}$. Both rate and extent of chlorination gradually increased from primary, to secondary, HYTI 70 ilmenite, and finally synthetic rutile. The change of the sample temperature followed a similar trend (**Figure 6.9**). With higher grade of ores, the rate and extent of chlorination of $\text{Ti}(\text{O,C})$ increased as fraction of titanium oxycarbide in the reduced samples increased; also chlorine consumption decreased with decreasing amount of metallic iron in the higher grade ores.

The XRD spectra of chlorinated residues of ilmenites and synthetic rutile with C/TiO_2 molar ratio of 4.5 are shown in **Figure 6.10**. Chlorination was performed at 235°C under flow rate of $100 \text{ mL}\cdot\text{min}^{-1}$ of pure chlorine. $\text{Ti}(\text{O,C})$, Ti_2O_3 , and metallic iron in the samples were chlorinated. XRD spectra of chlorinated residues (**Figure 6.10**) include peaks for unconsumed graphite and Al_2O_3 .

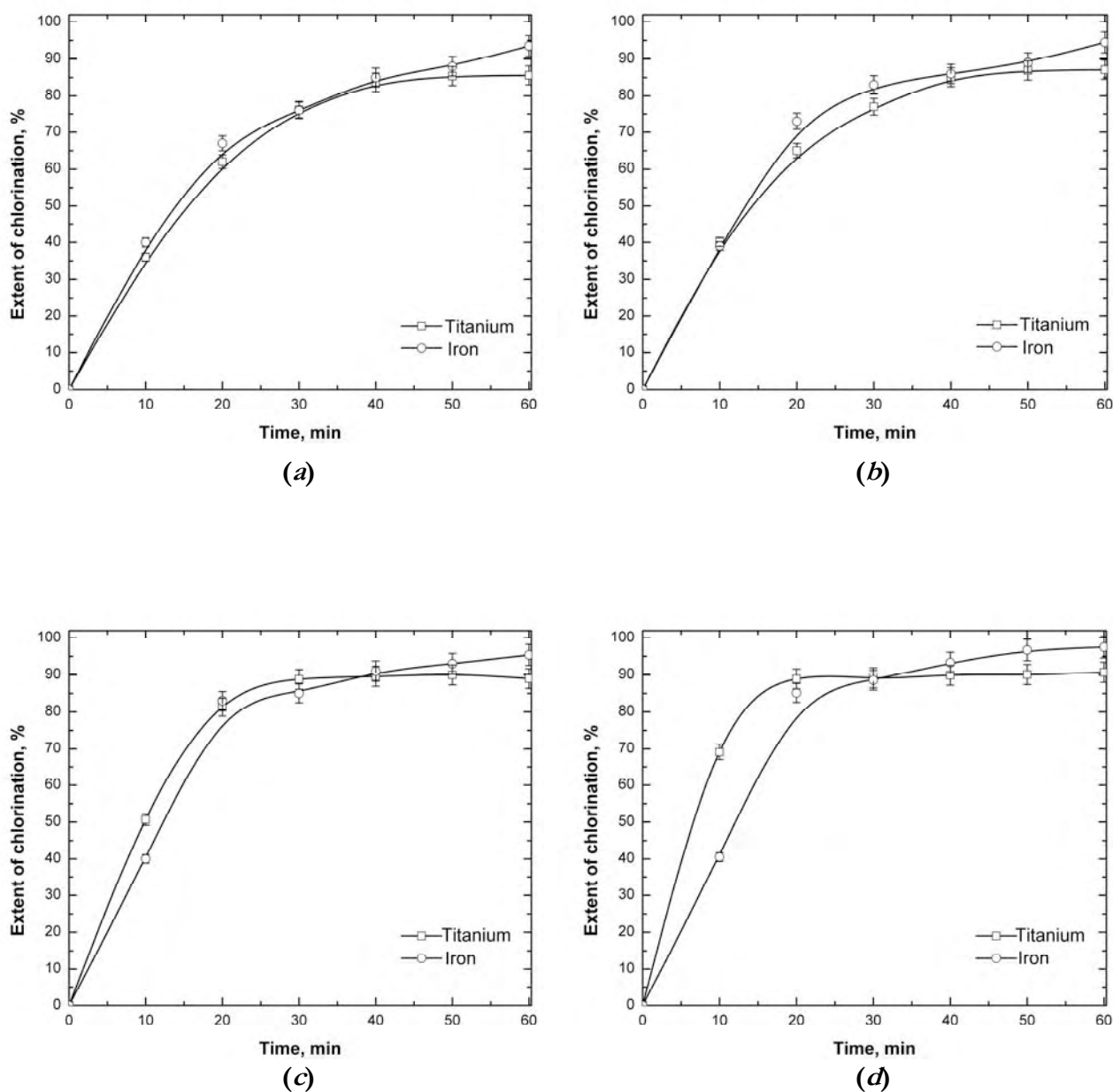


Figure 6.8. Extents of chlorination of (a) primary ilmenite, (b) secondary ilmenite, (c) HYTI 70, and (d) synthetic rutile. Chlorination was carried out at 235 °C for 60 min with pure chlorine flow rate of 100 mL·min⁻¹. Molar carbon to TiO₂ ratio was 4.5 in the graphite-ilmenite ore mixtures

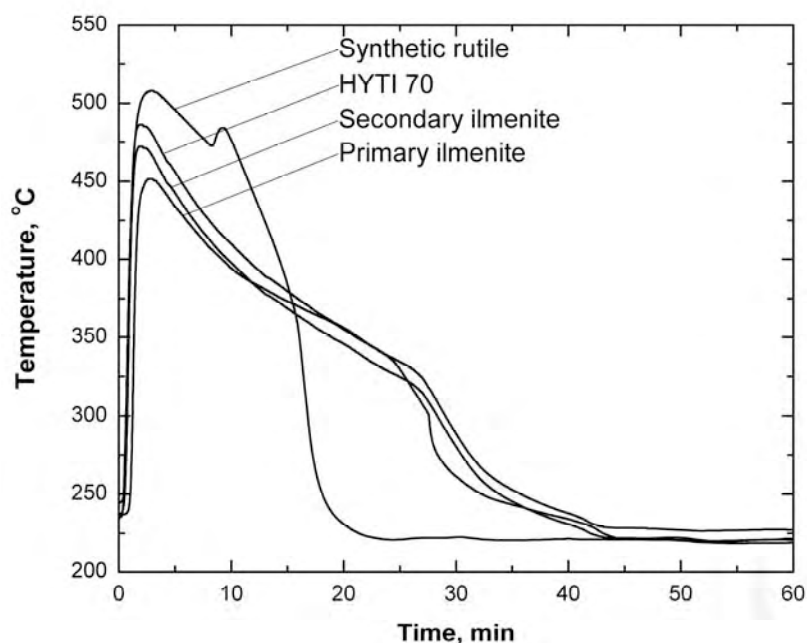


Figure 6.9. Change in sample temperature during chlorination of reduced primary, secondary, HYTI 70 ilmenite, and synthetic rutile at pure chlorine flow rate of 100 mL·min⁻¹

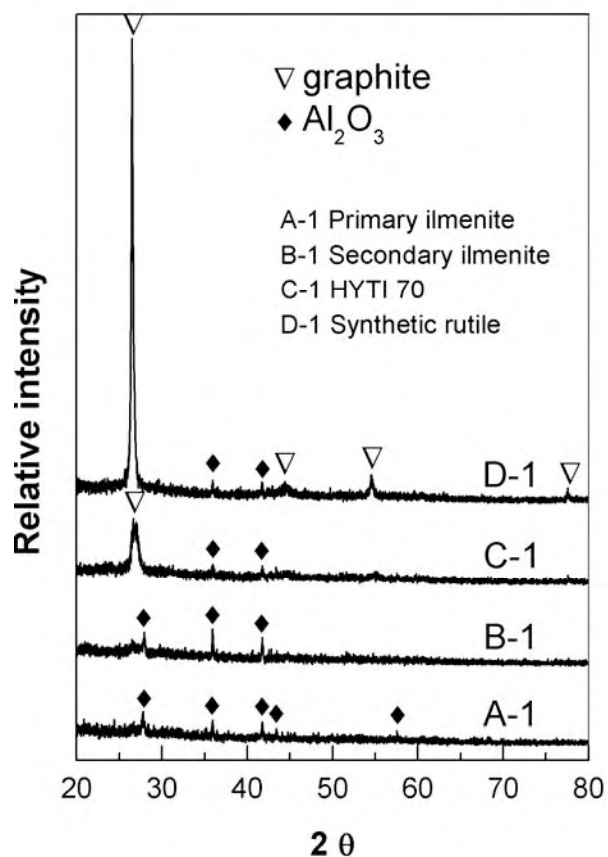


Figure. 6.10. X-ray diffraction patterns of residues of samples of reduced primary, secondary, HYTI 70 ilmenite, and synthetic rutile chlorinated at 235 °C with pure chlorine flow rate of 100 mL·min⁻¹

6.3. Chlorination of Ilmenite Ores and Synthetic Rutile Reduced in Nitrogen

Titanium in the ilmenites and synthetic rutile reduced in nitrogen atmosphere was predominantly in the form of $\text{Ti}(\text{O,C,N})$. Chlorination experiments were performed at 235 °C for 60 min with $100 \text{ mL} \cdot \text{min}^{-1}$ of pure chlorine. Carbothermal reduction of ilmenite ores and synthetic rutile in nitrogen atmosphere produced fragile samples, which caused difficulty in attaching a pellet to the tip of a thermocouple. As a result, chlorination experiments were only performed in alumina boat.

In chlorination of reduced ilmenites and synthetic rutile, both $\text{Ti}(\text{O,C,N})$ and metallic iron were rapidly chlorinated. The extents of chlorination of $\text{Ti}(\text{O,C,N})$ and iron in ilmenites and synthetic rutile reduced with C/TiO_2 molar ratio of 4.5 are presented in **Figure 6.11**. The figure suggests that the rates and extents of chlorination gradually increased from primary, to secondary, HYTI 70 ilmenite, and finally synthetic rutile. The extent of chlorination of $\text{Ti}(\text{O,C,N})$ increased from 95 to 98 pct from primary ilmenite to synthetic rutile, while for iron it was from 95 to 99 pct.

Chlorination of $\text{Ti}(\text{O,C,N})$ from reduced primary and secondary ilmenites was close to completion after 50 min, while its chlorination from reduced HYTI 70 and synthetic rutile occurred at much faster rate and was close to completion after 30 min. The rate of chlorination of iron from nitrified ilmenite ores and synthetic rutile was significantly higher than that of titanium: it was close to completion after 30 min for primary and secondary ilmenite ores and in 15 min for HYTI 70 and synthetic rutile. The extent chlorination of iron from ilmenite ores reduced in nitrogen was higher than that of samples reduced in argon.

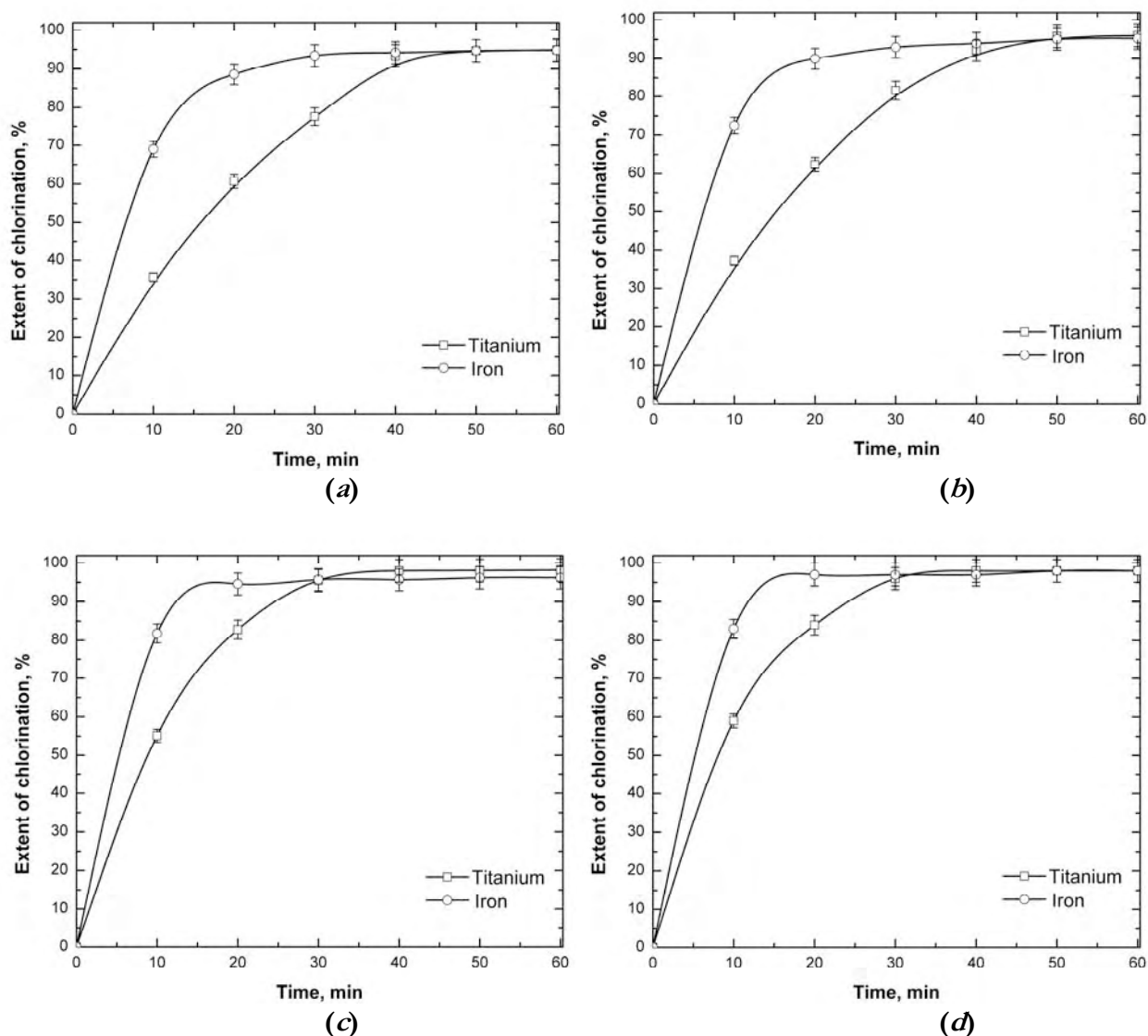


Figure 6.11. Extents of chlorination of titanium oxycarbonitride and iron from reduced: (a) primary, (b) secondary, (c) HYTI 70 ilmenite, and (d) synthetic rutile. Chlorination was carried out at 235 °C for 60 min with pure chlorine flow rate of 100 mL·min⁻¹. Molar carbon to TiO₂ ratio was 4.5 in the graphite-ilmenite ore mixtures

The XRD spectra of chlorinated residues Ti(O,C,N) prepared from reduction of ilmenites and synthetic rutile with C/TiO₂ molar ratio of 4.5 in nitrogen are shown in **Figure 6.12**. The intensity of graphite peak increased from chlorinated residues of reduced primary ilmenite to synthetic rutile. SiO₂ and Al₂O₃ were also detected in chlorinated residues of nitrated ilmenites and synthetic rutile.

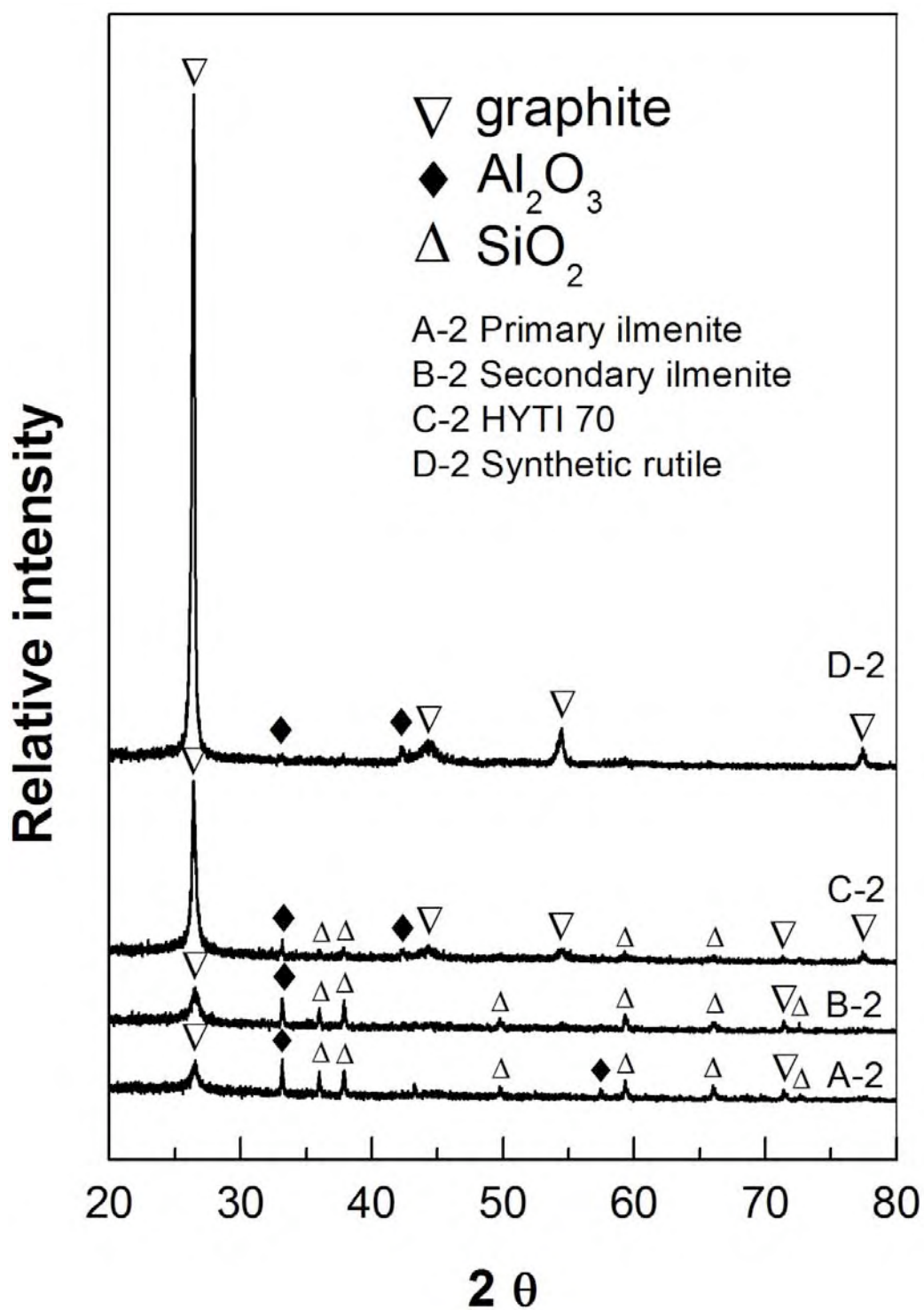


Figure. 6.12. X-ray diffraction patterns of residues of samples of reduced primary, secondary, HYTI 70 ilmenite, and synthetic rutile after chlorination at 235 °C with pure chlorine flow rate of 100 mL·min⁻¹

6.4. Chlorination of Titanium Oxycarbide and Oxycarbonitride after Removal of Iron by Aeration and Leaching

The project studied chlorination of titanium oxycarbide and oxycarbonitride in reduced ilmenite ores and synthetic rutile after removal of iron. The reduction of ilmenite ores either in argon or in nitrogen atmosphere produced $\text{Ti}(\text{O,C})$ or $\text{Ti}(\text{O,C,N})$ together with metallic iron at 1450 °C. Chlorination was not selective, *i.e.* the metallic iron chlorinated together with $\text{Ti}(\text{O,C})$ and $\text{Ti}(\text{O,C,N})$, which necessitates the removal of iron before chlorination stage.

The XRD spectra of reduced primary ilmenite ore treated under different conditions to remove iron are shown in **Figure 6.13**. All samples were washed and dried at 150 °C for 24 h prior to XRD analysis. The following conditions were tested in experiments with the reduced primary ilmenite ore:

- (1) The reduced primary ilmenite ore was leached in hydrochloric solution with concentration of 0.1 and 3.2 M for 5 and 12 h at room temperature. This however, did not effectively remove iron.
- (2) The reduced ilmenite ore was aerated with 0.1 M of NH_4Cl bath solution at 40 °C with flow rate $1 \text{ L}\cdot\text{min}^{-1}$ of air for 3 h. After the treatment, iron was still detected even after using higher bath temperature of 70 °C.
- (3) Aeration of reduced primary ilmenite with 0.372 M of NH_4Cl bath solution and flow rate $2.5 \text{ L}\cdot\text{min}^{-1}$ of air at 70 °C for 5 h.

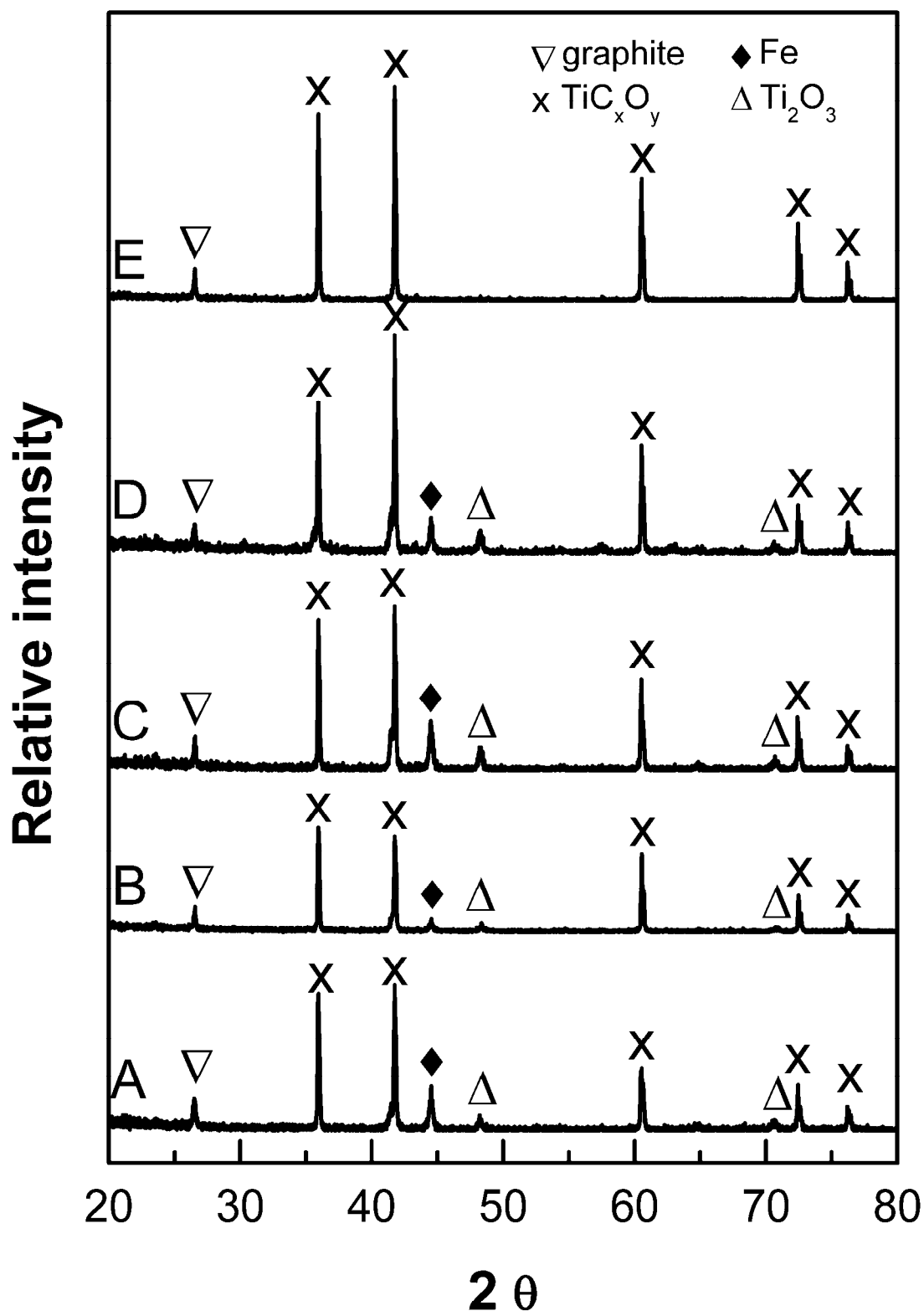


Figure 6.13. X-ray diffraction patterns of reduced primary ilmenite treated with: (A) 0.1 M of HCl at room temperature for 5 h, (B) 3.2 M of HCl at room temperature for 12 h, (C) 0.1 M of NH_4Cl at 40 °C with air flow rate of 1 $\text{L}\cdot\text{min}^{-1}$ for 3 h, (D) 0.1 M of NH_4Cl at 70 °C with air flow rate of 1 $\text{L}\cdot\text{min}^{-1}$ for 3 h, and (E) 0.372 M of NH_4Cl at 70 °C with air flow rate of 2.5 $\text{L}\cdot\text{min}^{-1}$ for 5 h

After treatment following procedure (3), iron in the sample was undetected by XRD analysis. As a result of iron removal, the samples lost its magnetic property. XRD analysis of primary, secondary, HYTI 70 ilmenites and synthetic rutile subjected to aeration and leaching under these conditions (**Figure 6.14**) detected only titanium oxycarbide. However, XRF analysis still detected iron content in the range of 0.88 to 1.71 pct.

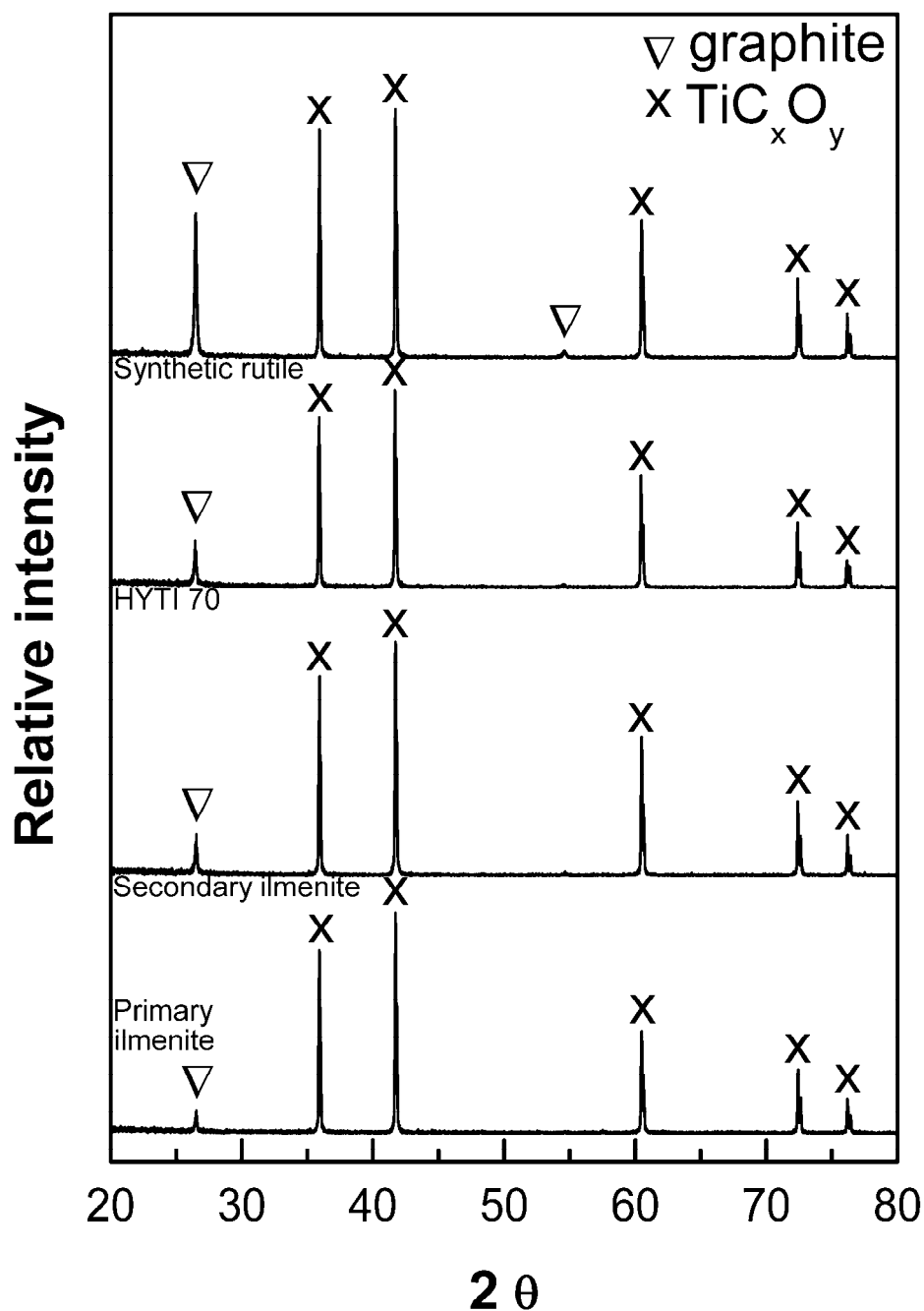


Figure 6.14. X-ray diffraction patterns of reduced ilmenite ores and synthetic rutile with C/TiO₂ molar ratio of 4.5 subsequent to aeration with 0.372 M of NH₄Cl at 70 °C with air flow rate of 2.5 L·min⁻¹ for 5 h

The extent of chlorination of titanium oxycarbide and residual iron from reduced ilmenite ores after leaching is presented in **Figure 6.15 (a) – (c)**. Extents of chlorination of titanium oxycarbonitride and residual iron from primary ilmenite ore after leaching is presented in **Figure 6.16**. These ores were reduced with C/TiO₂ molar ratio of 4.5; reduced samples were chlorinated at 235 °C with pure chlorine flow rate of 100 mL·min⁻¹.

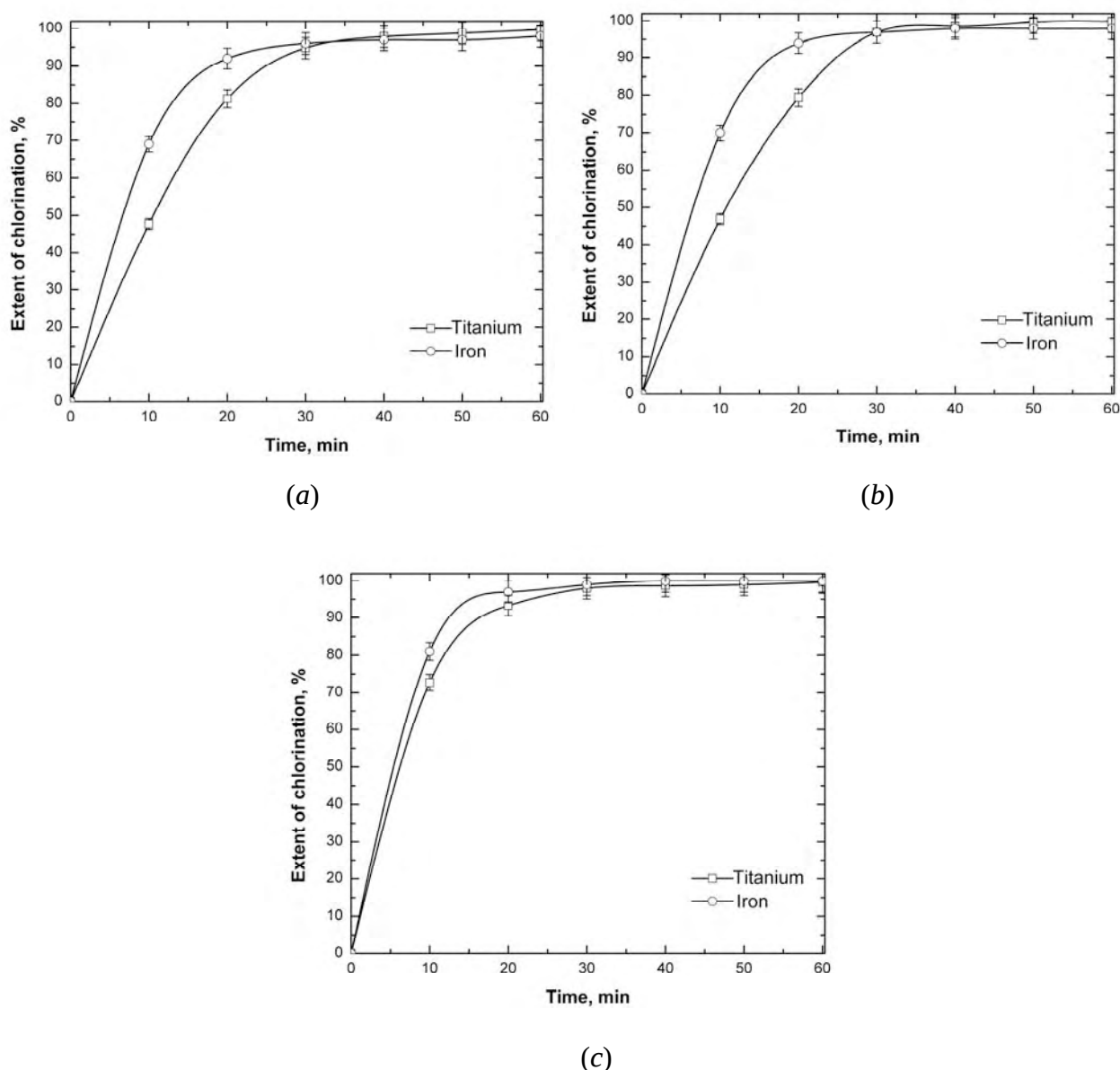


Figure 6.15. Extent of chlorination of titanium oxycarbide from reduced (a) primary, (b) secondary, and (c) HYTI 70 ilmenite after iron leaching. Chlorination was performed at 235 °C with pure chlorine flow rate of 100 mL·min⁻¹

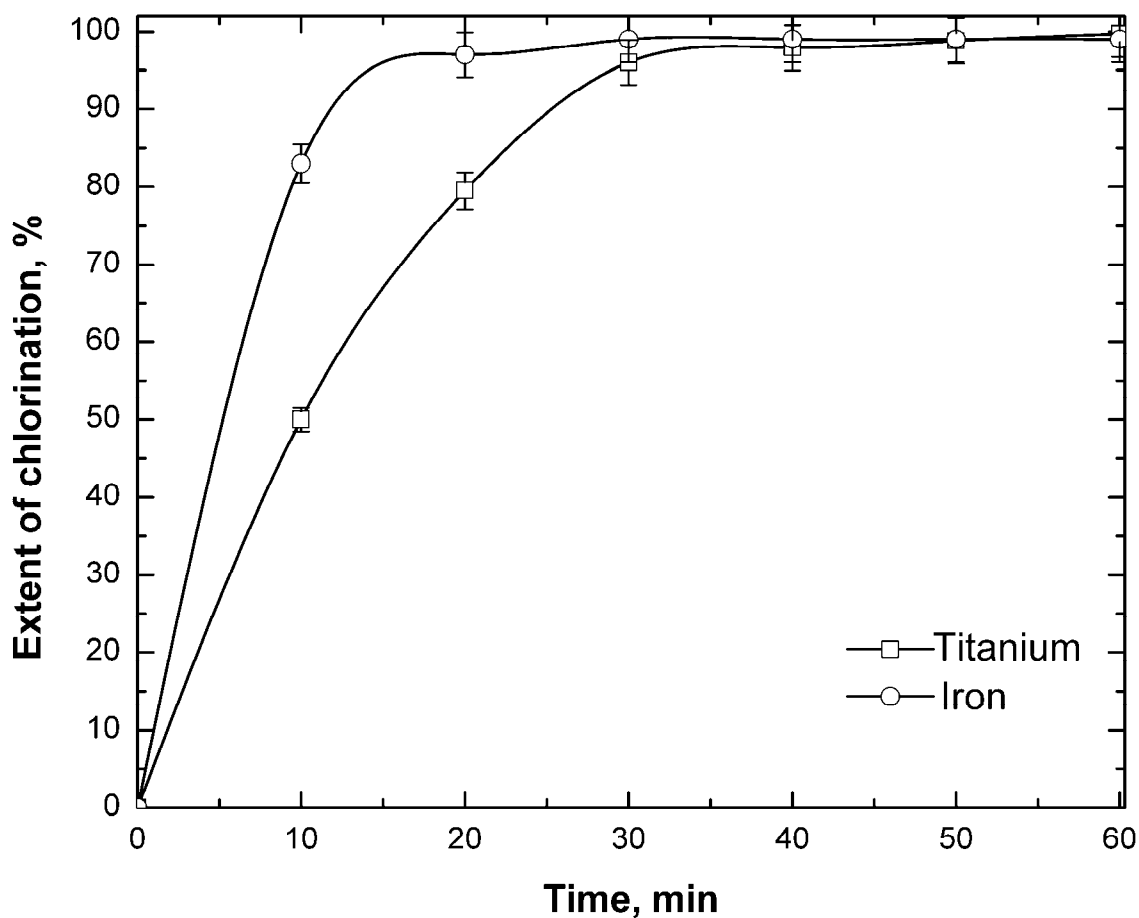


Figure 6.16. Extent of chlorination of titanium oxycarbonitride from reduced primary ilmenite after iron leaching. Chlorination was performed at 235 °C with pure chlorine flow rate of 100 mL·min⁻¹

The XRD spectra of residues of chlorinated samples are shown in **Figure 6.17**. Higher rate and extent of chlorination of Ti(O,C) were observed subsequent to iron removal. The chlorination was completed after 30 min of reaction.

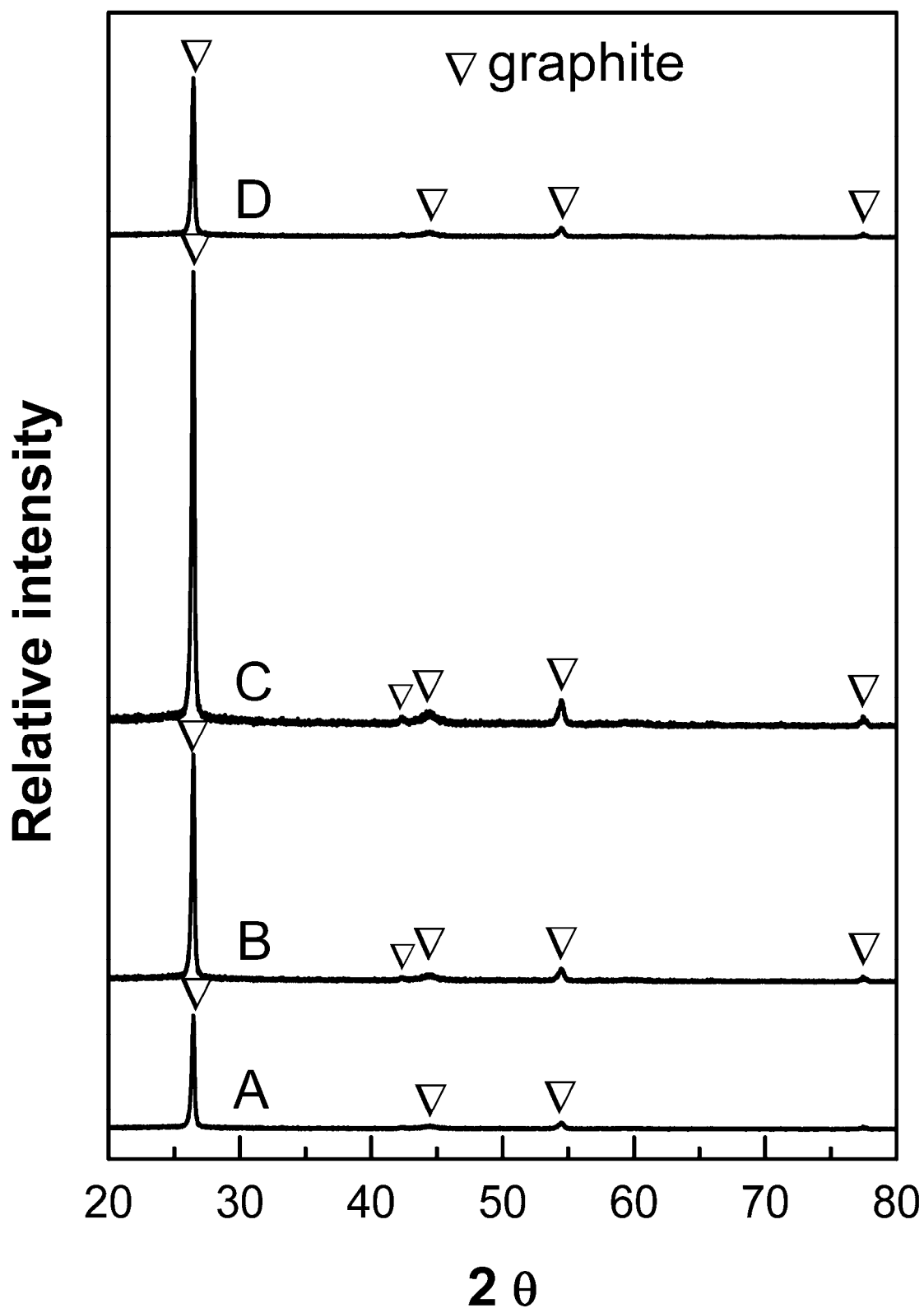


Figure 6.17. X-ray diffraction patterns of residues of chlorination of: titanium oxycarbide from reduced primary (A), secondary ilmenite (B), HYTI 70 (C) and titanium oxycarbonitride from reduced primary ilmenite (D) at 235 °C with pure chlorine flow rate of 100 mL·min⁻¹

6.5. Chlorination of Reduced MgTiO_3 and CaTiO_3

Chlorination of magnesium and calcium oxides as impurities in the conventional chlorination technology for titanium oxide TiO_2 at high temperatures 800-1000 °C is a concern as it can cause a collapse of the fluidised bed (*See Section §2.4.4*). The project studied chlorination of these oxides at low temperatures suitable for chlorination of titanium oxycarbide and oxycarbonitride.

MgTiO_3 – graphite mixture was prepared with carbon to MgTiO_3 molar ratio of 5.0, using technique described in the *Section § 3.3.1*. Carbon to CaTiO_3 molar ratio in the CaTiO_3 – graphite mixture was 5.6. Samples were then reduced under flow rate of $1 \text{ L} \cdot \text{min}^{-1}$ of argon at 1450 °C for 3 h. XRD spectra of reduced MgTiO_3 is shown in **Figure 6.18**.

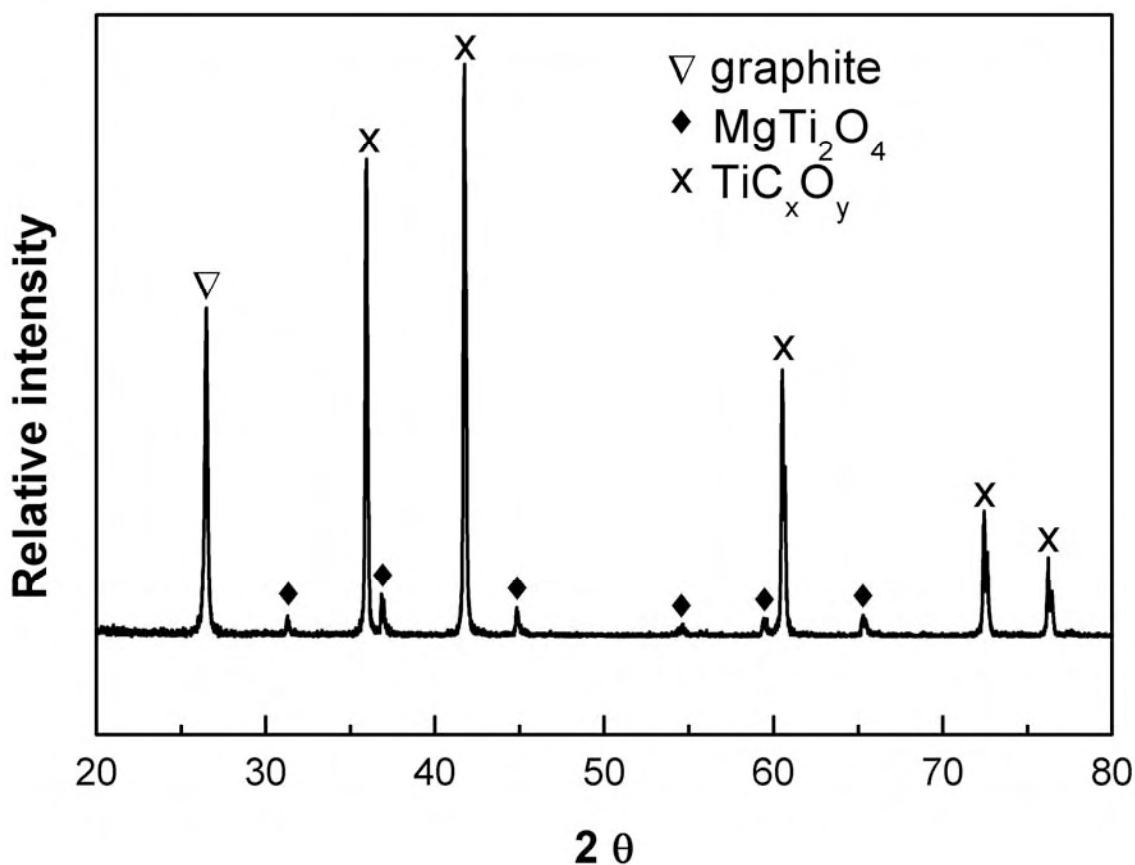


Figure 6.18. X-ray diffraction patterns of MgTiO_3 reduced at 1450 °C in argon atmosphere with carbon to MgTiO_3 molar ratio of 5.0

The phases identified by XRD in reduced MgTiO_3 were excess graphite, Ti(O,C) , and MgTi_2O_4 (**Figure 6.18**). Chlorination of reduced MgTiO_3 was studied with chlorine flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$. Chlorination curves at 235°C and 300°C for reduced MgTiO_3 are presented in **Figure 6.19**.

Magnesium, titanium, and iron oxides in the ilmenite ore can be present in the form of $(\text{Fe,Mg,Ti})\text{O}_3$. Iron oxide was reduced to the metallic state in the reduction process. TiO_2 of MgTiO_3 was reduced to Ti_2O_3 ; these reactions transformed $(\text{Fe,Mg,Ti})\text{O}_3$ to MgTi_2O_4 . Ti(O,C) and titanium in MgTi_2O_4 were chlorinated with the extent increasing with increasing furnace temperature. Magnesium oxide was not chlorinated under experimental conditions used in this work; MgO started to chlorinate at temperature above 640°C as indicated by Ishii *et al.* (1974). Magnesium was not chlorinated; MgO started to chlorinate at temperature above 640°C as indicated by Ishii *et al.* (1974). Chlorination of MgTi_2O_4 has not been reported in literature.

Chlorination of Ti(O,C) was fast during the first 20 min, and reached 86 and 95 pct after 30 min of reaction at furnace temperature of 200°C and 300°C , respectively (**Figure 6.19**). The boiling temperature of MgCl_2 is high (1412°C), making it not volatilised at experimental conditions in this project. ICP-OES analysis did not detect traces of chlorinated magnesium in the TiCl_4 scrubber.

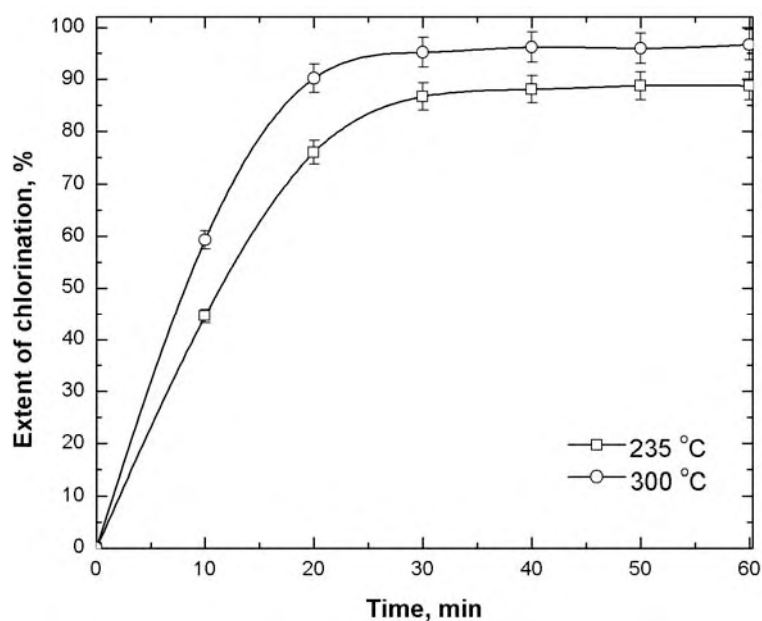


Figure 6.19. Extent of chlorination of reduced MgTiO_3 at 235°C and 300°C at flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$ chlorine

Figures 6.20 show XRD spectra of residues of chlorination at 235 and 300 °C. All of Ti(O,C) was chlorinated; Ti_2O_3 of MgTi_2O_4 was also chlorinated following to Reaction (4-4) (*Chapter 4*) what transformed TiO_2 of MgTiO_3 . Excess carbon and MgTiO_3 were present in the residues. There were no residues of MgCl_2 detected by XRD. The extent chlorination of reduced MgTiO_3 was higher than the extent of Ti_2O_3 alone. This is because chlorination of Ti(O,C) in reduced MgTiO_3 .

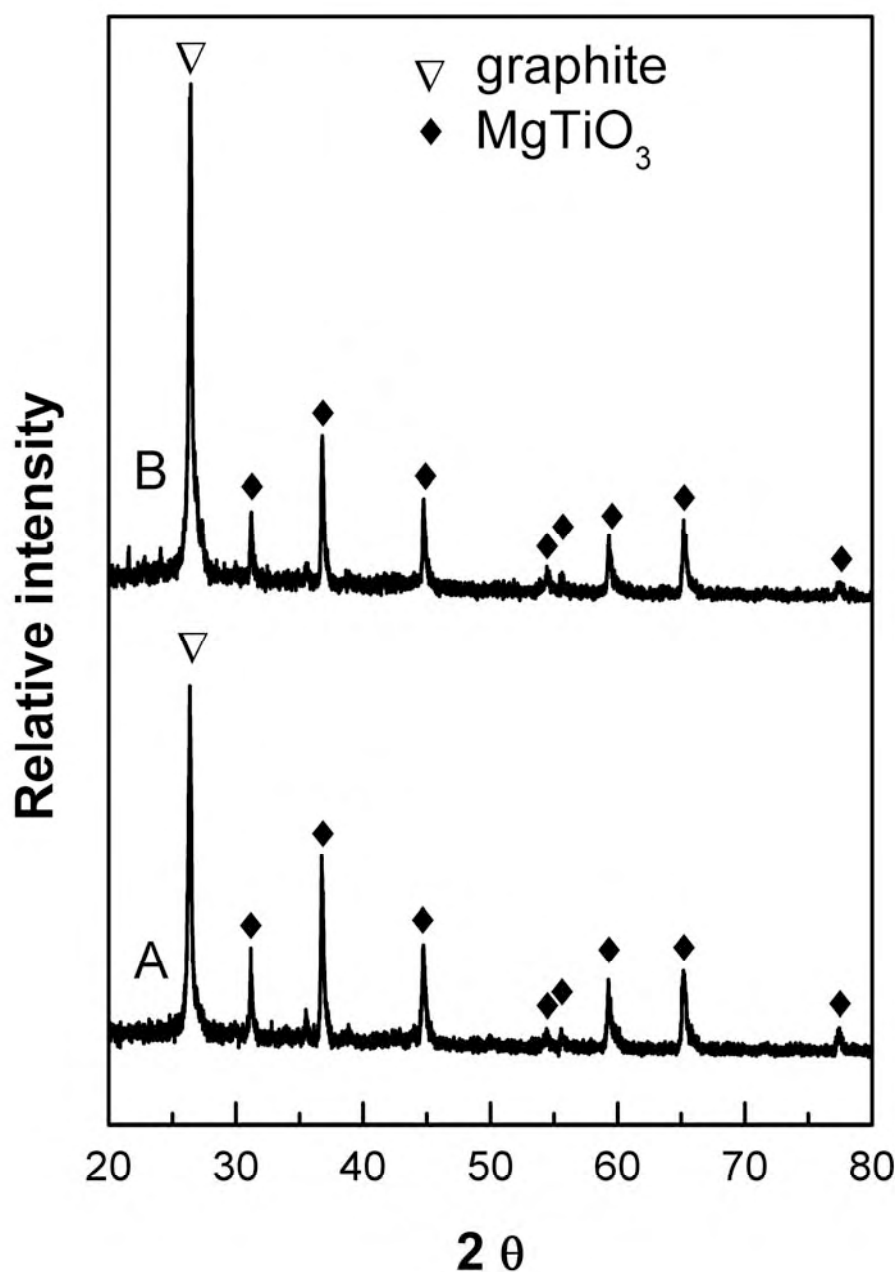


Figure. 6.20. X-ray diffraction patterns of residues of samples of reduced MgTiO_3 after chlorination at (A) 235 °C and (B) 300 °C with pure chlorine flow rate of $50 \text{ mL} \cdot \text{min}^{-1}$

Carbothermal reduction of CaTiO_3 was incomplete as seen from XRD spectra shown in **Figure 6.21**. The reduced sample contained Ti(O,C) , CaO , graphite, and CaTiO_3 . Even with undetected CaC_2 in reduced samples, acetylene scent was emanated which indicated its reaction with moisture in the air.

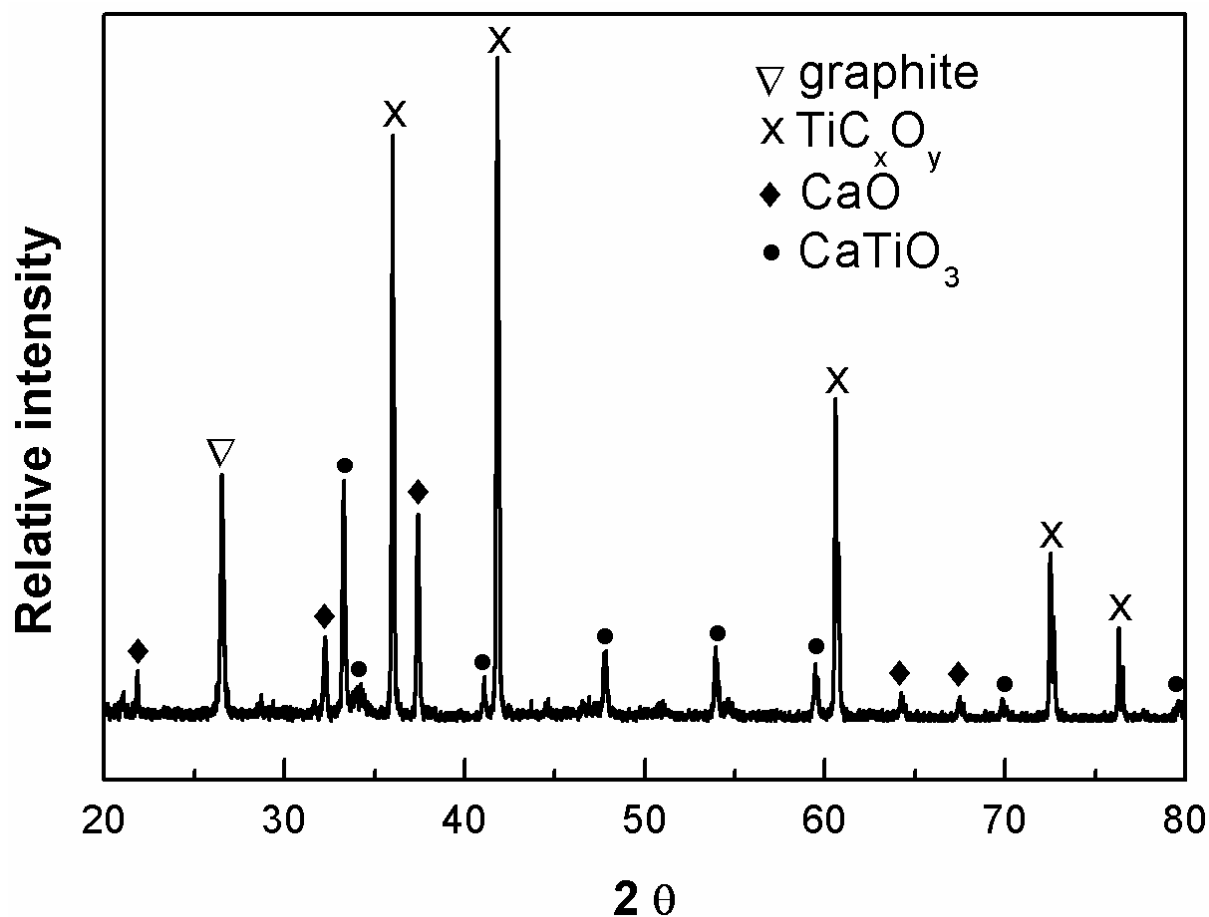


Figure 6.21. X-ray diffraction patterns of reduced CaTiO_3 at 1450 °C in argon atmosphere with carbon to CaTiO_3 molar ratio of 5.6

The extent of chlorination of reduced CaTiO_3 was studied in the temperature range of 235 °C to 500 °C at chlorine flow rate of 50 $\text{mL}\cdot\text{min}^{-1}$. Chlorination curves for reduced CaTiO_3 at different temperatures are presented in **Figure 6.22**. The rate and extent of chlorination Ti(O,C) increased with increasing furnace temperature. Chlorination of titanium reached 21, 30, and 39 pct after 25 min of reaction at temperature of 235, 300, and 500 °C, respectively.

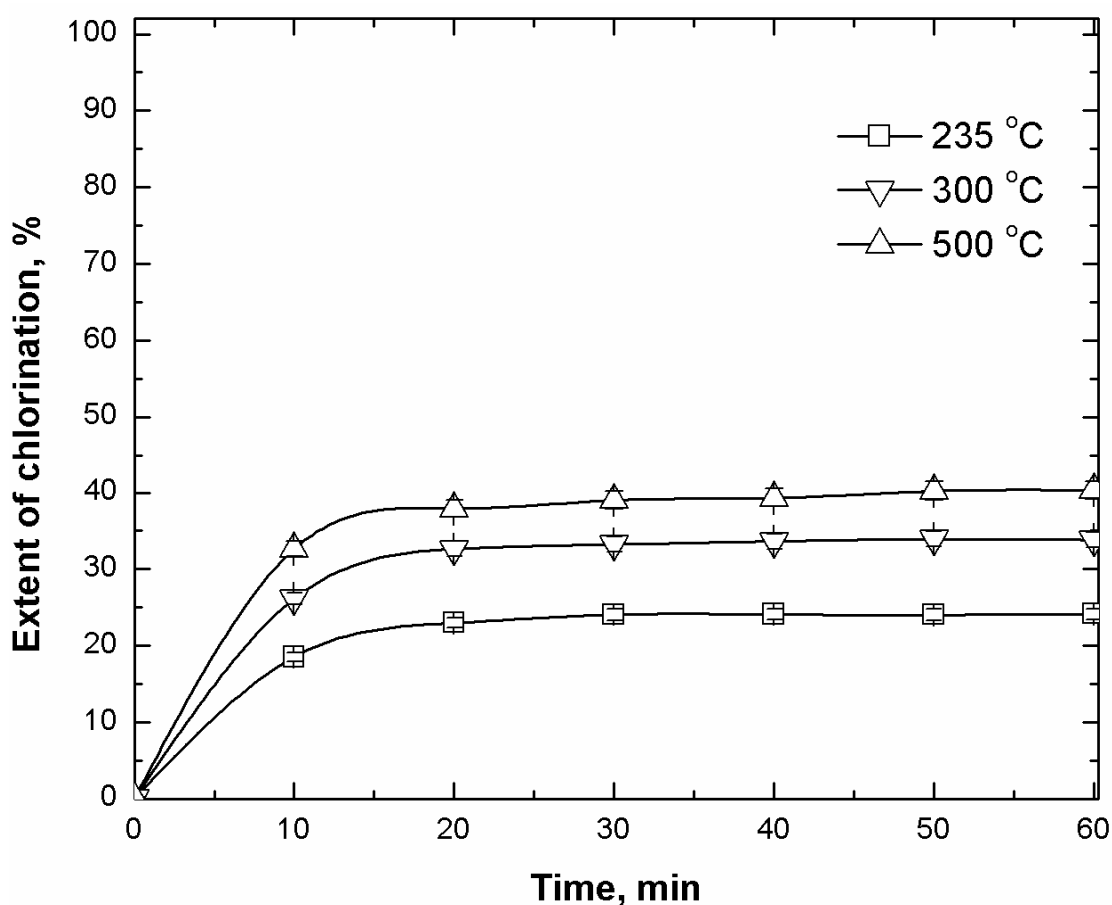


Figure 6.22. Extent of chlorination of reduced CaTiO_3 at 235 to 500 °C at flow rate of $50 \text{ mL} \cdot \text{min}^{-1}$ chlorine

Figure 6.23 shows residues of chlorination at 235 °C. Chlorination of $\text{Ti}(\text{O,C})$ was not complete and its peaks were still present in the XRD spectra of residues. Carbon, CaO , $\text{Ca}(\text{OH})_2$, CaCl_2 and CaTiO_3 were also detected in the residues. Only traces of CaTiO_3 remained in the residues what evidences that titanium in CaTiO_3 was partially chlorinated together with $\text{Ti}(\text{O,C})$.

Chlorination of $\text{Ti}(\text{O,C})$ produced by reduction of calcium titanate was incomplete. Calcium oxide can be chlorinated at 333 °C [Yake and Ulrichson, 1981], its partial chlorination was observed experimentally. The extent of chlorination was affected by the formation of CaCl_2 which covered the surface of a pellet that increased the resistance to transfer of reactant gas penetrating the samples. The final weight gain and droplets of CaCl_2 were also observed.

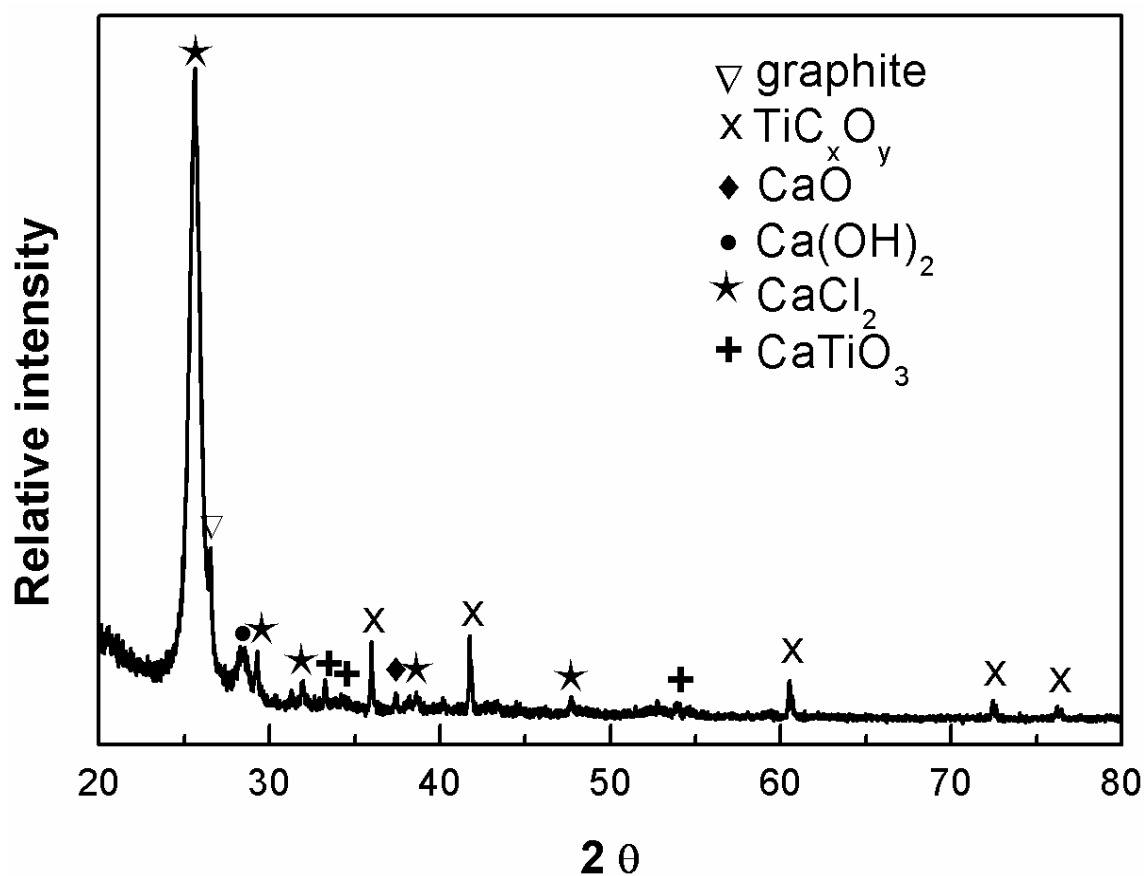


Figure. 6.23. X-ray diffraction patterns of residues of samples of reduced CaTiO_3 after chlorination at 235 °C with pure chlorine flow rate of 50 $\text{mL}\cdot\text{min}^{-1}$

6.6. Chlorination of Impurities

The effect of impurities was studied by adding oxides of aluminium, chromium, magnesium, manganese, silicon, and vanadium to the titania-graphite mixture with molar carbon to titania ratio 3.3, as presented in **Table 6.3** The mixture was prepared using technique described in the *Section § 3.3.1*.

Table 6.3. Addition of oxides to the titania-carbon mixture

Impurities	Quantity, wt. pct
MnO	2.2
MgO	2.2
Al_2O_3	2.4
V_2O_5	2.2
Cr_2O_3	2.3
SiO_2	2.3

The premixed samples were reduced under argon atmosphere at 1450 °C for 3 h. After the reduction, samples were too fragile and therefore were chlorinated in alumina boat. XRD spectra of reduced samples are presented in **Figure 6.24**. $\text{Ti}(\text{O,C})$, graphite, and Al_2O_3 were detected, however the amounts of other oxides in a sample after reduction was too small to be identified by XRD analysis.

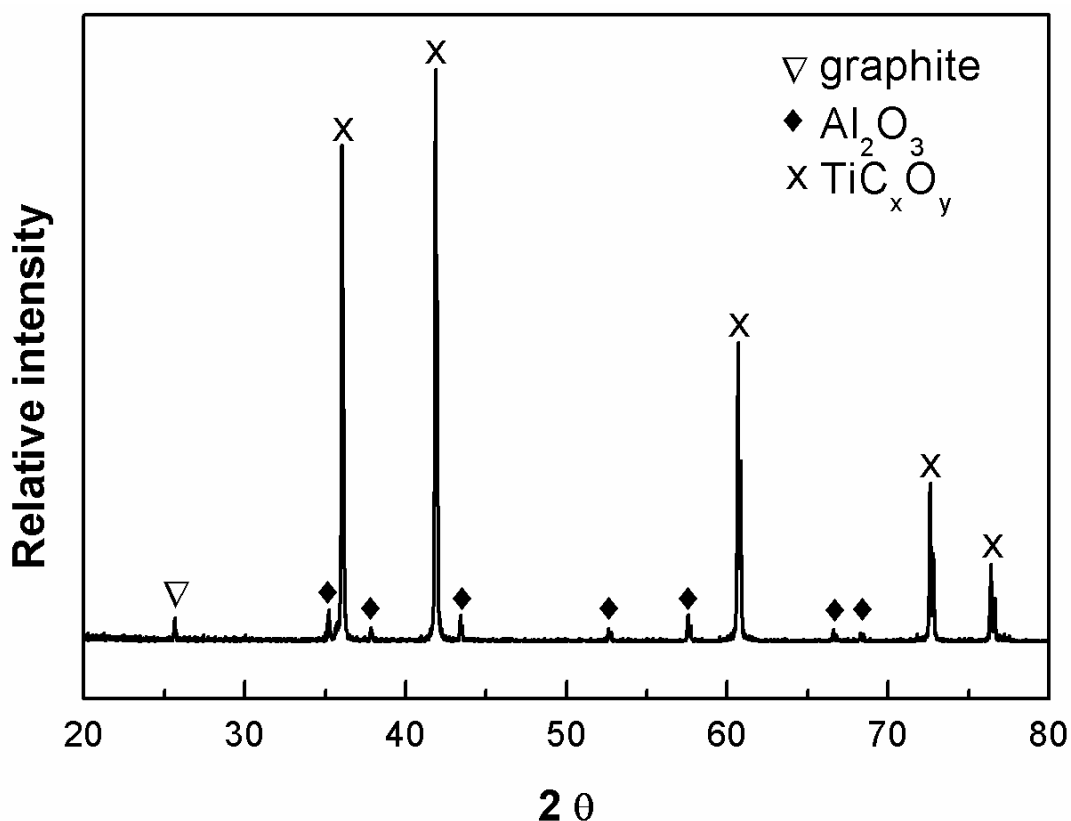


Figure 6.24. X-ray diffraction patterns of titania with added metal oxides reduced at 1450 °C for 3 h in argon atmosphere

The chlorination was investigated at 250 to 400 °C by using pure chlorine at 50 mL·min⁻¹ flow rate for two hours. **Figures 6.25 (a) – (c)** present the extent of chlorination of chromium, titanium, and vanadium at 250 °C to 400 °C. All the other elements such as manganese, magnesium, aluminium, and silicon were undetected in TiCl_4 scrubbers even at higher furnace temperature.

The rates and extents of chlorination of chromium, titanium, and vanadium increased with increasing furnace temperature, with chromium chlorinated at the highest rate followed by titanium and vanadium. The extent of chlorination of titanium was only 91 pct after 70 min

at 250 °C. The rate of chlorination of titanium was also lower with the addition of impurities.

At 250 °C, the extent of chlorination of chromium and vanadium reached 98.3 and 97.3 pct, respectively after 120 min of reaction. Chromium carbide could be chlorinated and it formed chromyl chloride CrO_2Cl_2 in the presence of CO. The boiling point of CrO_2Cl_2 is 117 °C and its vapour was absorbed in TiCl_4 scrubber.

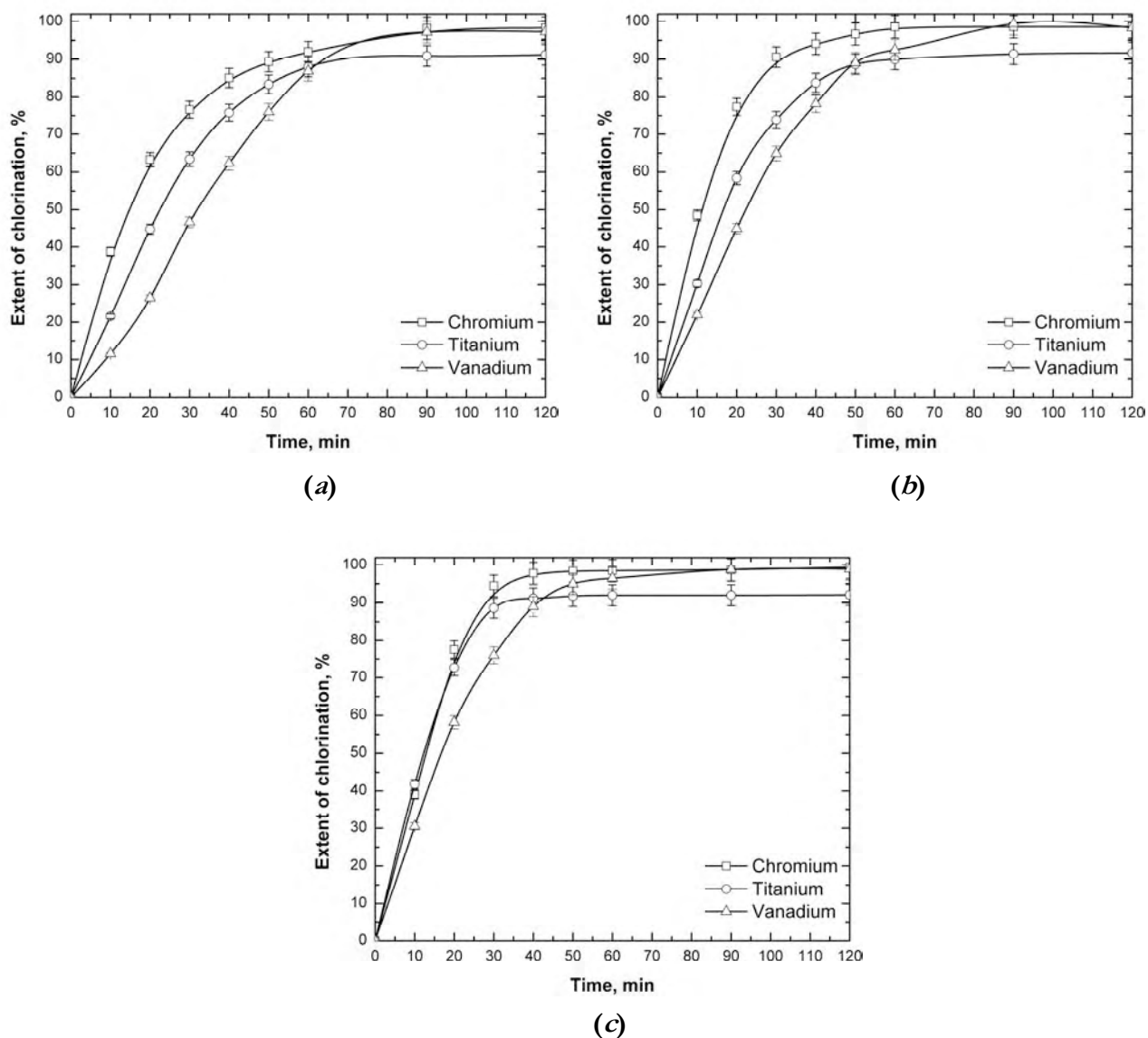


Figure 6.25. Extent of chlorination of chromium, titanium, and vanadium from titania-graphite-metal oxides mixture with $50 \text{ mL} \cdot \text{min}^{-1}$ of Cl_2 at: (a) 250 °C, (b) 300 °C, and (c) 400 °C

Figure 6.26 presents the XRD pattern of residue after chlorination reaction at 250 °C. Al_2O_3 and SiO_2 were not chlorinated and were present in the residue.

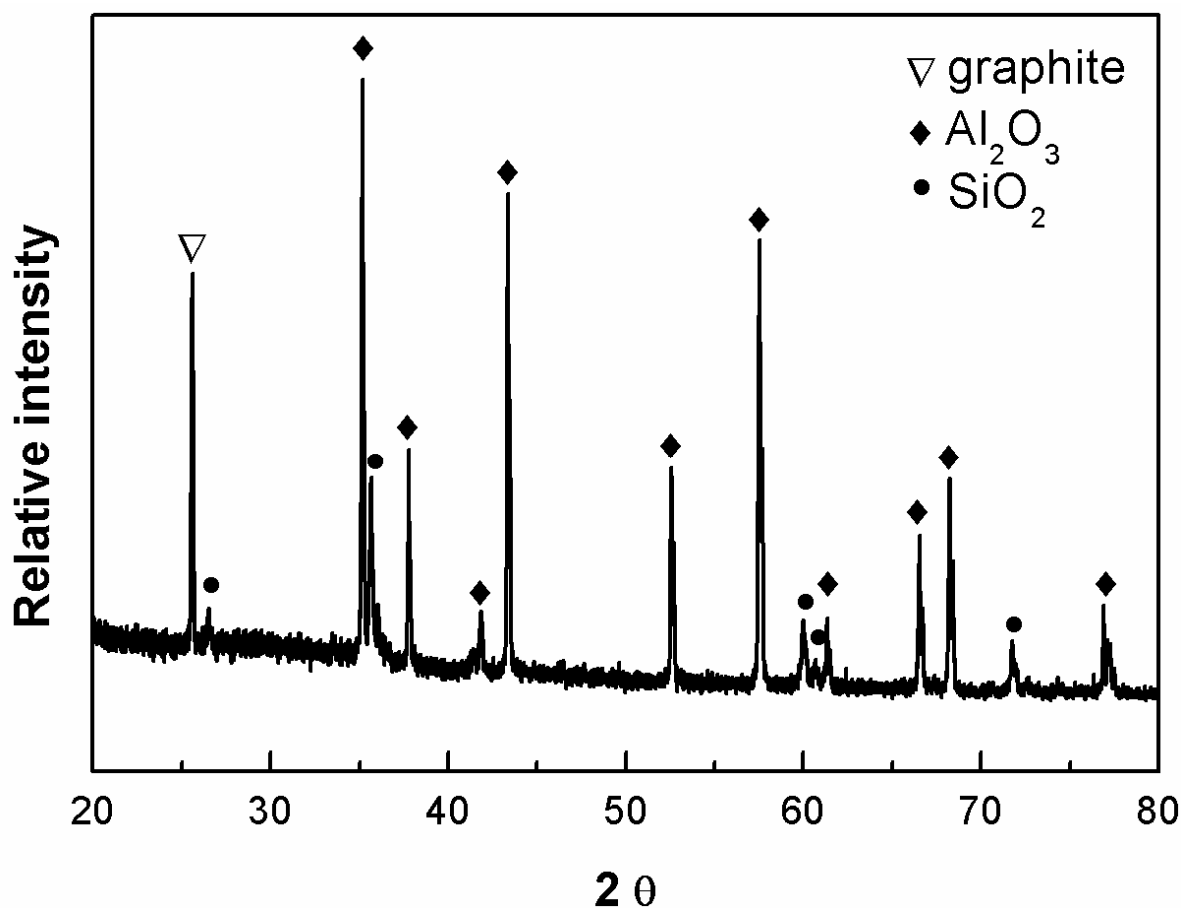


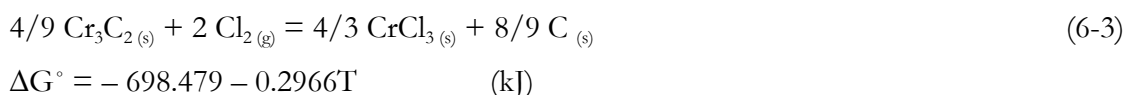
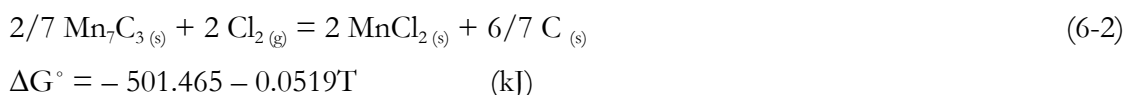
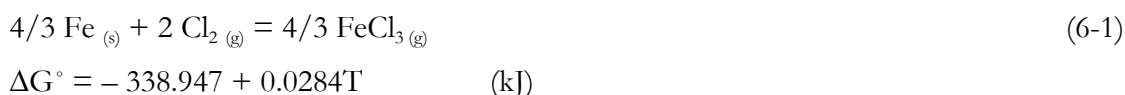
Figure 6.26. X-ray diffraction patterns of residues of chlorinated samples with oxides addition. Chlorination temperature was 235 °C; flow rate of pure chlorine was 50 mL·min⁻¹

6.7. Discussion

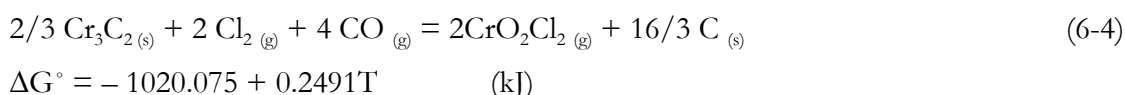
In ilmenite ores, FeO, Fe_2O_3 , SiO_2 , Al_2O_3 , Cr_2O_3 , MgO and MnO are present as the main impurities. From these, only FeO, Fe_2O_3 , Cr_2O_3 , and MnO are reduced at temperature of 1450 °C used for synthesis of $\text{Ti}(\text{O},\text{C})$ or $\text{Ti}(\text{O},\text{C},\text{N})$. Carbothermal reduction of MnO to Mn_7C_3 under standard conditions started at 1340 °C [Anacleto *et al.*, 2004], reduction of Cr_2O_3 to Cr_3C_2 at 1113 °C [Anacleto and Ostrovski, 2004], while reduction of Fe_2O_3 to metallic iron at 567 °C. Cementite Fe_3C is thermodynamically unstable and is not formed in carbothermal reduction. It can be formed in the reduction of iron oxide by methane or CO containing gas with high carbon activity [Longbottom *et al.*, 2007]. The reduction of iron, chromium, manganese and vanadium oxides to metal/carbide facilitates their chlorination.

The more rapid chlorination of metallic iron in the oxycarbonitride relative to the oxycarbide in reduced primary ilmenite samples was observed. This effect was due to high porosity of oxycarbonitride in relative to oxycarbide samples.

Chlorination of iron proceeds by the formation of FeCl_2 [Fouga *et al.*, 2007] which reacts with continuously supplied chlorine converting to FeCl_3 . Reactions (6-1) to (6-3) describe chlorination of Fe, Mn_7C_3 , and Cr_3C_2 :



CO which was produced in chlorination of $\text{Ti}(\text{O,C})$ can also be involved in chlorination of impurities. This is described by Reaction (6-4) for chlorination of chromium carbide:

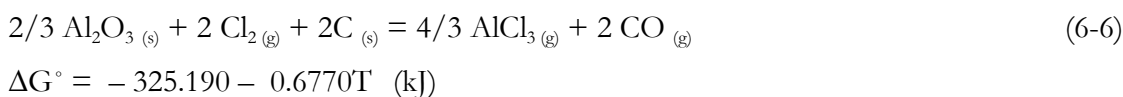
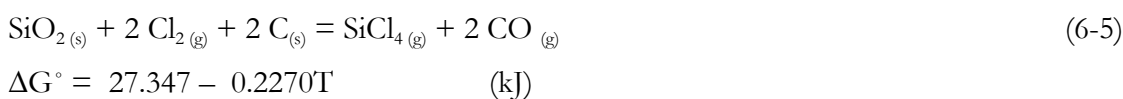


Thermodynamically, Reaction (6-4) could occur in preference to Reaction (6-3). Chromic chloride, CrCl_3 has a boiling point of 1300 °C, while chromyl chloride CrO_2Cl_2 is boiled at only 117 °C. In the low temperature chlorination below 500 °C, only CrO_2Cl_2 is volatile and can be removed from reactor by continuous of gas stream. The presence of chromium in the scrubber confirms that chlorination proceeded through Reaction (6-4). In addition, there was no evidence of solid CrCl_3 in chlorinated residues.

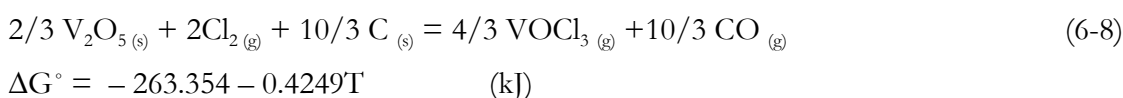
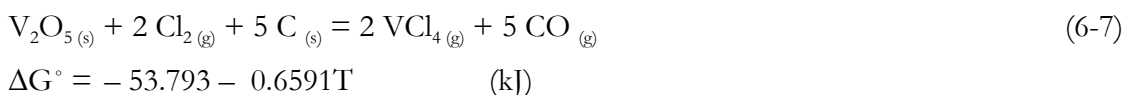
Ferric chloride, FeCl_3 has a boiling point of 315 °C; it undergoes partial decomposition to FeCl_2 (melting point 677 °C) with liberation of Cl_2 . Only with continuous supply of chlorine, FeCl_3 is stabilised. Throughout chlorination of ilmenites especially at furnace temperature 235 °C, there was clear visibility of brown precipitate of FeCl_3 in the outlet of

the reactor tube. By heating it using heat gun to temperature of 350 °C, the precipitate started to melt and vaporise. The vapour was then absorbed by TiCl₄ scrubber in the first column.

In order to reduce stable metal oxides such as SiO₂ and Al₂O₃, higher temperature and strongly reducing conditions are required. Nevertheless, both of these oxides can be carbochlorinated directly without the reduction step. Thermodynamically, SiO₂ can be chlorinated at room temperature (Reaction (6-5)). Many authors indicated that the chlorination reaction proceeds at much higher temperature. Thermodynamic does not give an indication for the reaction rate, as thermodynamic is strongly dependent on the kinetic factors. Carbochlorination of Al₂O₃ (Reaction (6-6)) was reported to start at temperature of 800 °C while SiO₂ at 1200 °C [Zverev and Barsukova, 1960; Titi-Manyaka and Iwasaki, 1973]. In this case, kinetic reaction control prevails over thermodynamic feasibility of the chlorination reaction.



Thermodynamically, carbochlorination of vanadium pentaoxide, V₂O₅ (Reaction (6-7)) can occur at low temperature. Gaballah *et al.* (1995) reported carbochlorination of V₂O₅ using CO at 400 °C. When V₂O₅ was well mixed with carbon, chlorination proceeded at 200 to 400 °C; in this case reaction started by the formation of VOCl₃ gas [Gaballah *et al.*, 1995]. The boiling point of VCl₄ is 154 °C, while VOCl₃ is at 126.7 °C.



Chlorination of metallic iron and reduced metal oxides such as Cr_3C_2 and Mn_7C_3 by TiCl_4 is not feasible thermodynamically. However, TiCl_4 vapour can chlorinate metal oxides [Nowak, 1969]. This depends on the relative affinity of titanium and a metal, which oxide is considered, for chlorine and oxygen. Thus, TiCl_4 can chlorinate Fe_2O_3 forming FeCl_2 and TiO_2 . The standard Gibbs free energy change for Reactions (6-1) to (6-8) calculated using NIST-JANAF Thermochemical Tables [Chase, 1998] is presented in **Figure 6.27**.

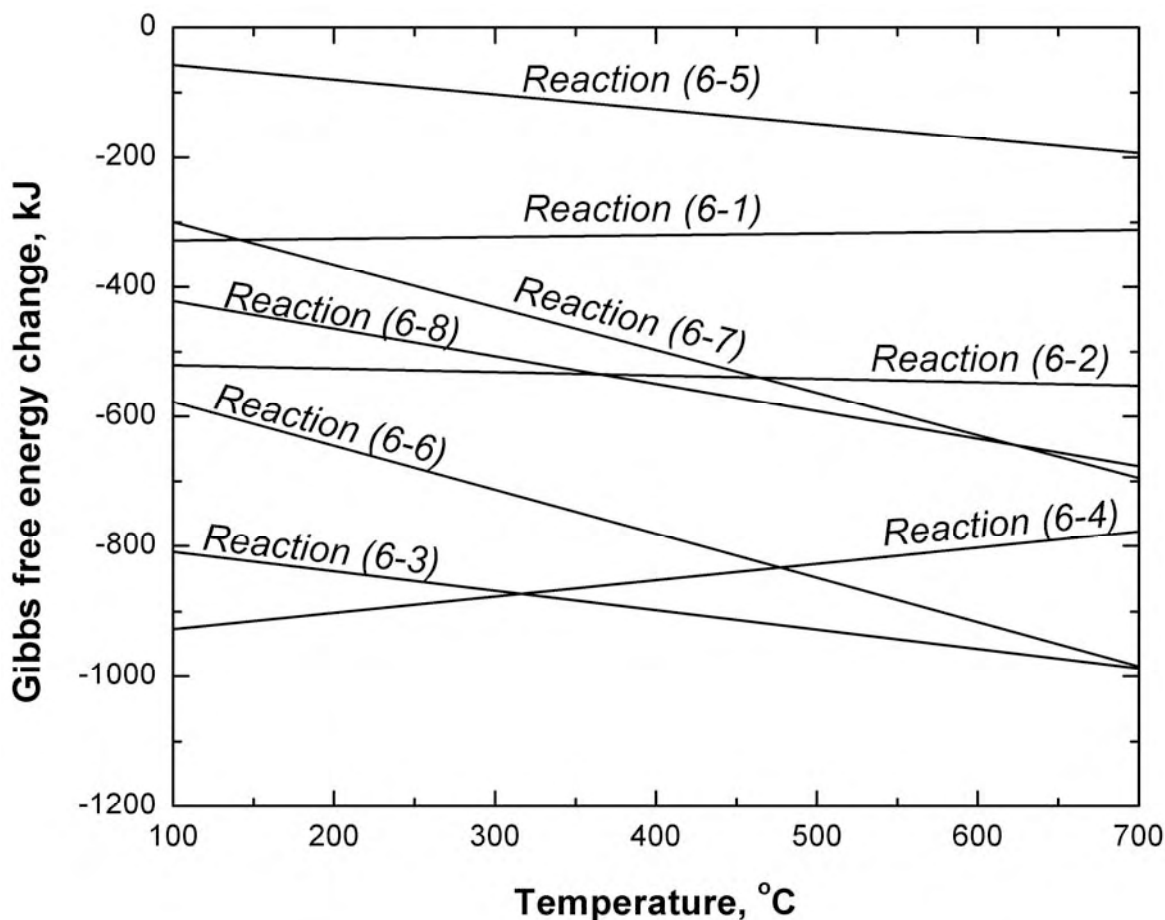


Figure 6.27. Standard Gibbs free energy changes of Reactions (6-1) to (6-8) in the temperature range from 100 °C to 700 °C [Chase, 1998]

6.8. Summary

The main phases of primary and secondary ilmenites were $\text{Fe}_2\text{Ti}_3\text{O}_9$ and FeTiO_3 ; HYTI 70 grade also contained TiO_2 ; synthetic rutile consisted of titania with traces of metallic iron and suboxides (Ti_2O_3 , Ti_3O_5 , Ti_4O_7). Carbothermal reduction of ilmenites at 1450 °C produced $\text{Ti}(\text{O,C})$ or $\text{Ti}(\text{O,C,N})$ in argon or nitrogen, respectively. Iron oxides were

reduced to metallic iron. In chlorination, $\text{Ti}(\text{O,C})$ or $\text{Ti}(\text{O,C,N})$, metallic iron, and Ti_2O_3 were chlorinated. The rate and extent of chlorination of titanium increased with increasing C/TiO_2 molar ratio. Chlorination of Ti_2O_3 was slow relative to $\text{Ti}(\text{O,C})$ or $\text{Ti}(\text{O,C,N})$ and iron. Chlorination of impurity oxides such as silica, magnesia, and alumina was not observed.

Chlorination of reduced ilmenites and synthetic rutile was not selective, metallic iron was chlorinated together with $\text{Ti}(\text{O,C})$ and $\text{Ti}(\text{O,C,N})$. This necessitates the removal of iron prior to chlorination stage. Aeration of reduced samples in 0.372 M NH_4Cl bath solution with $2.5 \text{ L}\cdot\text{min}^{-1}$ of air at 70°C was proven to be effective in removing iron from reduced primary ilmenite. XRD analysis indicated $\text{Ti}(\text{O,C})$ without the presence of titanium suboxides and iron. XRF analysis, however still detected iron content in the range of 0.88 to 1.71 pct. Higher rate and extent of chlorination of $\text{Ti}(\text{O,C})$ were observed subsequent to iron removal. Chlorination was completed after 30 min of reaction.

The rate and extent of chlorination of titanium from reduced MgTiO_3 and CaTiO_3 increased with increasing furnace temperature. Magnesium was not chlorinated as chlorination of magnesium oxide requires temperature above 640°C . Chlorination of titanium oxycarbide produced by reduction of calcium titanate was incomplete. Calcium oxide can be chlorinated at 333°C , its partial chlorination to CaCl_2 was observed experimentally. The extent of chlorination of reduced CaTiO_3 was affected due to formation of a CaCl_2 layer which covered the surface of pellet and impeded gas-solid contact.

The effect of impurities was studied by adding oxides of aluminium, chromium, magnesium, manganese, silicon, and vanadium to titania graphite mixture which was reduced in argon at 1450°C . Chlorination of manganese, magnesium, aluminium, and silicon was undetected by ICP-OES in the temperature range studied. The rates and extents of chlorination of chromium, titanium, and vanadium increased with increasing furnace temperature with chromium chlorinated with the highest rate followed by titanium and vanadium. The extent of chlorination of titanium was only 91 pct after 70 min at 250°C . At 250°C , extent of chlorination of chromium and vanadium reached 98.3 and 97.3 pct, respectively after 120 min of reaction. Chromium carbide was carbochlorinated with CO and formed CrO_2Cl_2 (boiling point 117°C).

CHAPTER 7.

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

7.1. Conclusions

Commercial Kroll and Hunter processes and the new direct reduction processes which are under development, in the course of production titanium metal require high grade titania feed. Titanium metal or titania pigment production solely relies on carbochlorination of rutile at 800 °C to 1100 °C and the reduction of titanium tetrachloride.

At 800 to 1100 °C the impurities are also chlorinated, however at low temperature impurities do not chlorinate or chlorinate slowly. Chlorination of titanium oxycarbide $\text{Ti}(\text{O},\text{C})$ or oxycarbonitride $\text{Ti}(\text{O},\text{C},\text{N})$ can be implemented at much lower temperature in the range of 200 °C to 400 °C. Low temperature chlorination has a higher selectivity than conventional chlorination at 800-1100°C. This decreases chlorine consumption and waste generation, and makes the whole technology of ilmenite processing more efficient and environmentally friendly than conventional chlorination process. Chlorination of $\text{Ti}(\text{O},\text{C})$ or $\text{Ti}(\text{O},\text{C},\text{N})$ is a viable alternative technology in processing titanium minerals.

This project has been greatly devoted to systematic study of chlorination of titanium oxycarbide and oxycarbonitride with the objective to develop further understanding of kinetics and mechanisms of chlorination process. The project studied titania, ilmenite ores, and synthetic rutile reduced by carbon in argon and nitrogen and chlorinated at different temperatures, gas flow rates and compositions. Chlorination of titanium sub-oxides, iron and impurities in ilmenite was also examined. Experimental facilities were designed and developed for carbothermal reduction, chlorination, and removal of metallic iron in the School of Materials Science and Engineering (UNSW).

Major project outcomes are summarised as follows.

Chlorination of Ti(O,C) Produced by Carbothermal Reduction of Rutile

Titanium oxycarbide prepared by carbothermal reduction of rutile was chlorinated in the temperature range of 235 °C to 400 °C. Due to strong exothermic reaction, the sample temperature during chlorination was up to 200 °C higher than the furnace temperature. The chlorination was ignited at 150 °C to 200 °C. Chlorination experiments with chlorine flow rate of 50 mL·min⁻¹, were conducted with gas reactant starvation. Effect of furnace temperature in these experiments was insignificant. Chlorine gas starvation was avoided by increasing the chlorine flow rate to 200 mL·min⁻¹. Increase in the furnace temperature in experiments with the chlorine flow rate above 200 mL·min⁻¹ increased the chlorination rate. Chlorination of titanium oxycarbide at 235 °C to 400 °C was close to completion in 30 min.

Sample composition had a significant effect on the extent of chlorination. The best results were obtained for TiC_{0.69}O_{0.31} which was produced with carbon to titania molar ratio of 2.5 and contained no detectable excess carbon or unreduced titanium suboxides. Chlorination of this sample was close to 100 pct. When carbon to titania ratio was low, the reduced samples contained titanium suboxides of which chlorination was slow. This was observed in chlorination of samples that were prepared from rutile – graphite mixture with carbon to titania ratio below 2.5. Chlorination of TiC_{0.98}O_{0.02} and TiC_{0.85}O_{0.15} which were prepared with molar carbon to titania ratio of 3.3 to 4.5 was affected by excess carbon in the samples.

Increasing gas flow rate and chlorine partial pressure enhanced the reaction rate. The effect of particle size was insignificant. Titanium suboxides were chlorinated at low temperatures only when they were well mixed with graphite and pressed into pellets. The rate and extent of their chlorination were low.

Chlorination of Ti(O,C,N) Produced by Carbothermal Nitridation of Rutile

Titanium oxycarbonitride prepared by carbothermal nitridation of rutile was chlorinated in the temperature range of 235 °C to 400 °C. The exothermic chlorination reaction raised the sample temperature significantly higher than the furnace temperature similar as chlorination of titanium oxycarbide. Temperature programmed chlorination experiments showed that chlorination of oxycarbonitride was ignited at low temperature between 150

°C to 200 °C, depending on the sample composition. With chlorine flow rate at 50 mL·min⁻¹, changing furnace temperature from 235 °C to 400 °C had no visible effect on chlorination due to gas reactant starvation. In experiments with chlorine flow rate above 100 mL·min⁻¹, the effect of furnace temperature became significant.

TiC_{0.16}O_{0.08}N_{0.76}, which was prepared from rutile – graphite mixture with carbon to titania molar ratio of 2.5, was optimum for chlorination. The chlorination reaction with this sample was completed in 30 min with chlorine flow rate at 250 mL·min⁻¹. Samples that were prepared from rutile – graphite mixture with carbon to titania ratio below 2.5 had low final extent of chlorination due to significant amount of titanium suboxides of Ti₃O₅ and Ti₂O₃.

Increasing chlorine partial pressure, gas flow rate and decreasing particle size had a positive effect on the extent of chlorination. The effect of particle size was not as significant as chlorine partial pressure and gas flow rate.

Chlorination of titanium oxycarbonitride was compared with chlorination of titanium oxycarbide, titanium nitride, carbide and carbonitride. The rate of chlorination of titanium nitride in the first 10 min of reaction was slightly lower in comparison with titanium carbide and oxycarbide (TiC_{0.5}N_{0.5}), however the degree of chlorination of titanium nitride after 60 min was higher than that of titanium carbide and oxycarbide.

This chlorination behaviour was also reflected in the sample temperature curves; at the beginning of chlorination of titanium nitride, the sample temperature reached maximum of 375 °C in 10 min, and decreased slowly afterwards. Although the chlorination curves for titanium carbide and carbonitride were close, the temperature of titanium carbide reached maximum of 395 °C in 5 min, while a maximum temperature of titanium carbonitride of 336 °C was reached in 7 min. This difference can be explained by different enthalpies of chlorination reactions, which is higher for titanium carbide than for nitride and oxycarbide. High chlorination rate of titanium nitride was maintained for longer period in comparison with titanium carbide and oxycarbide. This elucidates position of the temperature curve in chlorination of titanium nitride.

Chlorination of Reduced Ilmenite Ores and Synthetic Rutile

The main phases of ilmenites were $\text{Fe}_2\text{Ti}_3\text{O}_9$, FeTiO_3 , TiO_2 ; synthetic rutile consisted of titania with traces of elemental iron and suboxides (Ti_2O_3 , Ti_3O_5 , Ti_4O_7). Carbothermal reduction of ilmenites at 1450 °C produced titanium oxycarbide or oxycarbonitride in argon or nitrogen, respectively. Iron oxides were reduced to metallic iron. In chlorination, titanium oxycarbide or oxycarbonitride, metallic iron, and Ti_2O_3 were chlorinated. The rate and extent of chlorination of titanium increased with increasing carbon to TiO_2 molar ratio. Chlorination of Ti_2O_3 was slow relative to titanium oxycarbide or oxycarbonitride and iron. Chlorination of impurity oxides such as silica, magnesia, and alumina was not observed.

Chlorination of reduced ilmenites and synthetic rutile was not selective, metallic iron was chlorinated together with titanium oxycarbide and oxycarbonitride. This necessitates the removal of iron prior to chlorination stage. Aeration of reduced samples in 0.372 M NH_4Cl bath solution with 2.5 $\text{L}\cdot\text{min}^{-1}$ of air at 70 °C was proven to be effective in removing iron from reduced primary ilmenite. XRD analysis indicated titanium oxycarbide without the presence of suboxides and iron. XRF analysis however, detected iron content in the range of 0.88 to 1.71 pct. Higher rate and extent of chlorination of titanium oxycarbide were observed subsequent to iron removal. Chlorination was completed after 30 min of reaction.

Chlorination of magnesium and calcium oxides as impurities in conventional chlorination technology for titanium oxide at high temperatures is a concern as it can cause a collapse of the fluidised bed. Chlorination of reduced magnesium and calcium titanate was studied with 50 $\text{mL}\cdot\text{min}^{-1}$ flow rate of chlorine. The rate and extent of chlorination of titanium from reduced calcium and magnesium titanate increased with increasing furnace temperature. Magnesium was not chlorinated as chlorination of magnesium oxide requires temperature above 640 °C. Chlorination of titanium oxycarbide produced by reduction of calcium titanate was incomplete. The reduced CaTiO_3 can be chlorinated at 235 °C; its partial chlorination was observed experimentally. Extent of chlorination of titanium was affected by the formation of CaCl_2 , which covered the surface of pellet and impeded mass transfer of chlorine to titanium oxycarbide.

The effect of impurities was studied by adding oxides of aluminium, chromium, magnesium, manganese, silicon, and vanadium to titania graphite mixture which was reduced in argon at 1450 °C. Extent of chlorination was investigated at 250 to 400 °C with

chlorine flow rate at 50 mL·min⁻¹. Chlorination of manganese, magnesium, aluminium, and silicon was undetected by ICP-OES in the temperature range studied. The rates and extents of chlorination of chromium, titanium, and vanadium increased with increasing furnace temperature with chromium chlorinated with highest rate followed by titanium and vanadium. Extent of chlorination of titanium was 91 pct after 70 min at 250 °C. At 250 °C, extent of chlorination of chromium and vanadium reached 98.3 and 97.3 pct, respectively after 120 min of reaction. Chromium carbide was carbochlorinated with CO and formed CrO₂Cl₂ (boiling point 117 °C).

7.2. Recommendations for Further Research

This project focused on chlorination of titanium oxycarbide and oxycarbonitride produced by carbothermal reduction of rutile. Although chlorination of reduced ilmenite was also studied, detailed examination of behaviour of impurities in ilmenite ores was beyond the scope of this project and requires further study.

Ilmenite in the deposits of Murray Basin, Australia presented processing challenges due to high content of chrome spinels or chromite, FeCr₂O₄. Chrome spinels found in the Murray Basin deposit make these mineral sands unique from those found in Western Australia. This requires different approach for processing these ores. As chrome spinels' physical properties are very similar to those of ilmenite grains, they cannot be separated through conventional mineral sands separation procedures, which involve reduction of iron oxide followed by magnetic separation or leaching of iron. The reduction and chlorination of Murray Basin ilmenites can be recommended for further study. Carbothermal reduction and nitridation followed by low temperature chlorination can be a viable approach to process these ilmenites.

The application of the present results could contribute to the current production process of titanium metal and pigment industry. This can be achieved by the additional carbothermal reduction stage prior to chlorination step. Chlorination of Ti(O,C) and Ti(O,C,N) can proceed at 200 °C to 400 °C and has lower chlorine consumption, waste generation than conventional chlorination process. Project's research findings showed that titanium, iron and chromium in ilmenites could be extracted and chlorinated at low temperature. Crude products of volatile halides such as FeCl₃ (boiling point 315 °C), TiCl₄ (boiling point 136 °C), and CrO₂Cl₂ (boiling point 117 °C) can be refined by distillation. TiCl₄ produced from

low temperature chlorination can be employed in a novel process based on the continuous reduction of TiCl_4 with magnesium producing a titanium powder developed by the Light Metals Flagship of CSIRO, Australia.

BIBLIOGRAPHY

- Abiko T., Park I., Okabe T. H. (2003), Reduction of titanium oxide in molten salt medium, *Proceedings of the 10th World Conference on Titanium Hamburg Germany*, 253-260.
- Allain E., Djona M., Gaballah I. (1997), Kinetics of chlorination and carbochlorination of pure tantalum and niobium pentoxide, *Metall. Trans. B*, 28B(2), 223-233.
- Amorebieta V.T., Colussi A.J. (1985), Direct study of the catalytic decomposition of chlorine and chloromethanes over carbon films, *Int. J. Chem. Kinet.*, 17, 849-58.
- Anacleto N., Ostrovski O. (2004), Solid-state reduction of chromium oxide by methane-containing gas, *Metall. Trans. B*, 35B(4), 609-615.
- Anacleto N., Ostrovski O., Ganguly S. (2004), Reduction of manganese ores by methane-containing gas, *ISIJ Int.*, 44(10), 1615-1622.
- Anon. (1993), Pigment process adds value to mine. *Australian Mining*, 85(4), 30-31, 1993.
- Anon. (1975), Energy Use Patterns in Metallurgical and Nonmetallic Mineral Processing, *Report No. PB-246 357 Battelle Columbus Laboratories U.S. Department of Commerce*.
- Athavale A.S., Altekar V.A. (1971), Kinetics of selective chlorination of ilmenite using HCl in a fluidized bed, *Ind. Eng. Chem. Process Des. Develop.*, 10(4), 523-530.
- Athavale A.S., Altekar V.A. (1971), Kinetics of selective chlorination of ilmenite using hydrogen chloride in a fluidized bed, *Ind. Eng. Chem. Process Des. Develop.*, 10(4), 523-531.
- Avila-Brande D., Katcho N. A., Urones-Garrote E., Gomez-Herrero A., Landa-Canovas A. R., Otero-Diaz L. C. (2006), Nano-structured carbon obtained by chlorination of NbC, *Carbon*, vol. 44(4), 753-761.
- Aylward G., Findlay T. (1998), *SI chemical data 4th edition*, John Wiley & Sons, Singapore, 16-82.
- Barin I., Schuler W. (1980), On the kinetics of the chlorination of titanium dioxide in the presence of solid carbon, *Metall. Trans. B*, 11B, 199-207.
- Barksdale J. (1949), *Titanium its occurrence chemistry and technology*, The Ronald Press Company, New York, 49-88.

- Becher R. G., Canning R. G., Goodheart B. A., Uusna S. (1965), A new process for upgrading ilmenitic mineral sands, *Proceedings of the Australian institute of mining and metallurgy*, 214, 21-44.
- Bergholm A. (1961), Chlorination of rutile, *Trans. Metall. Soc. AIME*, 221, 1121-1128.
- Brunauer S., Emmett, P.H. and Teller, E. (1938), Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.*, 60, 309-319.
- BHP Biliton (2005), Titanium 2005, *21st Annual Conference Scottsdale USA*.
- Blackwood J.D., Cullis B.D. (1970), Kinetics of the direct chlorination of carbon, *Aust J. Chem.* 23, 725-735.
- Bodenstein M., Plaut H. (1924), Die Metall Chemie, *Z. Phys. Chem.*, 110, 399.
- Bonsack J.P., Schneider F.E. (2001), Entrained flow chlorination of titaniferous slag to produce TiCl_4 , *Metall. Mater. Trans. B*, 32B, 389-393.
- Brandstatter H.G. (1985), Recovery of titanium values. *U.S. Patent US 4 521 385*, 5pp.
- Brooks G., Cooksey, M., Wellwood, G., Goodes, C. (2007), Challenges in light metals production. *Trans. Inst. Min. Metall. C*, 116(1), 25-33.
- Cameron W. L (2001), *Calcium Carbide in Kirk Othmer encyclopaedia of chemical technology Volume 4*, John Wiley & Sons, Singapore.
- Chadwick B.K., Rao Y.K.(1988), Carbon and energy requirements of chlorination of TiO_2 -an equilibrium analysis, *Trans. Inst. Min. Metall. C*, 97C, 143-49.
- Chase M. W. Jr. (1998), *NIST-JANAF Thermochemical Tables 4th ed.*, American Chemical Society, Washington DC.
- Cullity B.D. (1978), *Elements of X-ray diffraction*, Addison-Wesley Pub. Co., Singapore.
- Chen G. Z., Fray D. J., Farthing T. W. (2000), Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride, *Nature*, 407, 361-364.
- Department of Industry, Science and Resources, Australia Leading the Light Metals Age, Canberra, (2001), Australia. (Also can be retrieved from Light Metals Action Agenda website <http://www.isr.gov.au/agenda/sectors/LightMetals>).
- Djona M., Allain E., Gaballah I. (1995), Kinetics of chlorination and carbochlorination of molybdenum trioxide, *Metall. Trans. B*, 26B(4), 703-710.
- Donachie M. J. (1988), *Titanium a technical guide*, ASM International.
- Dooley III G.J. (1975), Titanium production ilmenite vs rutile, *Journal of Metals*, 8-16.
- Dunn W.E. Jr. (1960), High temperature chlorination of TiO_2 bearing minerals, *Trans. Metall. AIME*, 218, 6-12.

-
- Dunn W.E. Jr. (1979), High temperature chlorination of titanium bearing minerals: part II, *Metall Trans. B*, 10B, 271-277.
- EHK Technolgies. (2004), Summary of emerging titanium cost reduction technologies, *US Dept. of Energy Oak Ridge National Laboratory*.
- Elger G.W., Hunter W.L. and Mauser J.E. (1980), Preparation and chlorination of titanium carbide from domestic titaniferous ores. *Report of Investigations 8497 United States Department of the Interior Bureau of Mines*.
- Fine H.A., Geiger G.H. (1979), *Handbook on material and energy balance calculations in metallurgical processes*, AIME, New York.
- Fouga G.G., Pasquevich D.M., Bohe A.E. (2007), The kinetics and mechanism of selective iron chlorination of an ilmenite ore, *Trans. Inst. Min. Metall. C*, 116(4), 230-238.
- Freemantle M. (2000), Titanium extracted directly from TiO_2 , *Chem. Eng. News*, 78, 12–13.
- Froes F.H. (2001), *Titanium and titanium alloys in Kirk Othmer encyclopaedia of chemical technology Volume 24*, John Wiley & Sons, Singapore.
- Fruehan R. J. (1972), The rate of chlorination of metals and oxides: Part I. Fe, Ni, and Sn in chlorine, *Metallurgical Transactions*, 3 (10), 2585-2592.
- Fruehan R. J., Martonik L. J. (1973), The rate of chlorination of metals and oxides: Rate of chlorination of iron(III) oxide and nickel(II) oxide in chlorine and hydrogen chloride. *Metallurgical Transactions*, 4(12), 2793-2797.
- Fuwa A., Kimura E., Fukushima S., Kinetics of iron chlorination in roasted ilmenite ore Fe_2TiO_5 in a fluidized-bed reactor, *Metall. Trans. B*, 9B, p643-52, (1978).
- Gaballah I., Djona M., Allain E. (1995), Kinetics of chlorination and carbochlorination of vanadium pentoxide, *Metall. Trans. B*, 26B(4), 711-718.
- Gamboa J.A., Bohé A.E., Pasquevich D.M. (1999), Carbochlorination of TiO_2 , *Thermochimica Acta*, 334, 131-139.
- Gambogi J. (2008), *Titanium minerals concentrates*, US Department of Interior, Bureau of Mines, Washington.
- Gennari F.C., Bohe A.E., Pasquevich D.M. (1997), Effect of reaction temperature on the chlorination of a Fe_2O_3 - TiO_2 -C mixture, *Thermochimica Acta*, 302, 53-61.
- Gilchrist J.D. (1980), *Extraction metallurgy 2nd edition*, Pergamon Press, England.
- Gonzalez J. A., Quiroga O. D., Ruiz M. (2005), Kinetic study of the chlorination of gallium oxide, *Metall. Trans. B*, 36B(4), 445-452.
- Gorski C.H. (1951), Preparation of titanium tetrachloride from rutile, *Trans. AIME*, 191, 131-133.

- Graham G. A. (1974), The production of titanium metal, B.Eng Thesis UNSW Australia.
- Gupta K.C. (2003), *Chemical Metallurgy Principles and Practice*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
- Habashi F. (1986), *Principles of Extractive Metallurgy. Volume 3: Pyrometallurgy*, Gordon & Breach; 1st edition, Singapore.
- Haddeland G. E. and Morikawa S.(1978), *Titanium Dioxide Pigment*, Process Economics Program Report No. 117 Stanford Research Institute International, Menlo Park, California.
- Hitching K.D. and Kelly E.G. (1982), Carburization/chlorination process for production of titanium tetrachloride from titaniferous slag. *Trans. Instn Min. Metall. (sec.C: Mineral Process. Extr. Metall.)*, 91C, 97-99.
- Hunter W.L., White J.C., Stickney W.A. (1975), Highly pure titanium tetrachloride from Ilmenite slag. *US Patent 3899569*, 7pp.
- Ikeshima T. (1984), *Proceedings of the 5th International Conference on Titanium Science and Technology*, Munich, Germany, 3.
- Jena P.K., Brocchi E.A., Gameiro D.H. (1998), Kinetics of chlorination of TiO₂ by Cl₂ in the presence of graphite powder, *Trans. Instn Min. Metall. (Sect. C: Mineral Process. Extr. Metall.)*, 107, 139-145.
- Jena P.K., Brocchi E.A., Reis M.L.D. (1999), Kinetics of chlorination of zirconia in mixture with petroleum coke by chlorine gas, *Metall. Trans. B*, 30B(3), 375-381.
- Jena P.K., Gameiro D.M., Brocchi E.A., (1991), Kinetics of chlorination of briquetted anatase by carbon tetrachloride, *Trans. Instn Min. Metall. (Sect.C: Mineral Process. Extr. Metall.)*, 100, 65-67.
- Jena P.K., Brocchi, E.A., Garcia, R.I. (1997), Kinetics of chlorination of niobium pentoxide by carbon tetrachloride, *Metall. Trans. B*, 28B(1), 39-45.
- Kanari N., Gaballah I. (1999), Chlorination and carbochlorination of magnesium oxide, *Metall. Trans. B*, 30B, 383-391.
- Kanari N., Gaballah I. and Allain E. (1999), A study of chromite carbochlorination kinetics, *Metall. Mater. Trans. B*, 30B, 577-587.
- Kelley K., Todd, S. S, King, E. G. (1954), Heat and free-energy data for titanates of iron and the alkaline earth metals. *US Bureau of Mines Rept. Invest. No. 5059*, 37pp.
- Kubaschewski O., *Metallurgical Thermochemistry 6th ed.*, Pergamon, Oxford.
- Kol'tsov S.I, Smirnov E.P, Aleskovskii V.B. (1973), Interaction of chlorine with microcrystalline carbon, *Zh. Obshch. Khim.*, 43, 1657-1661.

-
- Landsberg A., Hoatson C.L., Block F.E. (1972), The chlorination kinetics of zirconium dioxide in the presence of carbon and carbon monoxide, *Metall. Trans. B*, 3B, 517-523.
- Lavecchia R., Piga L., Pochetti F., Chacon L. (1993), Production of $TiCl_4$ by chlorination of ilmenite with CCl_4 , *Trans. Instn Min. Metall. (Sect.C: Mineral Process. Extr. Metall)*, 102, p174-178.
- Langmuir, I. (1916), The constitution of fundamental properties of solids and liquids: Part I. Solids, *J. Am. Chem. Soc.*, 38, 2221-2295.
- Levenspiel, O. (1972), *Chemical Reaction Engineering 2nd ed.*, Wiley, New York.
- Lin, C.I., Chiu, T.Y. (1988), Kinetic Study on the Chlorination of Rutile-Carbon Pellet. *Journal of the Chin. I. Ch.E.*, Vol.19, No. 4, 215-224.
- Longbottom R.J., Ostrovski O., Zhang J., Young D.(2007), Stability of cementite formed from hematite and titanomagnetite ore. *Metall. Trans. B*, 38B(2), 175-184.
- Lyday T. Q., *The mineral industry of Australia-1997*, Minerals Council of Australia, Retrieved August 2007, from http://www.minerals.org.au/pages/page3_42.asp.
- Manukyan N.V., Martirosyan V.H. (2003), Investigation of the chlorination mechanism of metal oxides by chlorine, *Journal of Materials Processing Technology*, 142, 145-151.
- Matsuura H., Tsukihashi, F. (2006), Chlorination kinetics of ZnO with $Ar-Cl_2-O_2$ gas and the effect of oxychloride formation, *Metall. Trans. B*, 37B, 413-420.
- Medynski M., (1976), Kinetics and mechanism of mineral oxide chlorination, Ph.D. Thesis, University of Sydney, Australia.
- Meerson G.A., Olesov Yu.G., Pampushko N.A. (1968), Reduction carburization of iron-titanium concentrate and titanium slag in vacuo. *Tsvet. Metall.*, 41 (4), 68-71.
- Minkler W. W. and Baroch E. F. (1981), *The Production of Titanium, Zirconium and Hafnium*, 1981. In: Tien T.K. and Elliott J. F. (1981), *Metallurgical Treatises*, The Metallurgical Society (AIME), Warrendale, Pennsylvania, 171-189.
- Misra, R. N., Sankaran, C., Bhatnagar, P. P. (1968), Selective chlorination of iron from ilmenite with hydrochloric acid gas. *Advan. Extr. Met., Proc. Symp. London*, 480-500.
- Morozov I.S. (1966), *Use of Chlorine in the Metallurgy of Rare and Non-ferrous Metals*, Nauka Moscow, 253.
- Morris A.J., Jensen R.F. (1976), Fluidized bed chlorination rates of Australian rutile, *Metall. Trans. B*, 7B, 89-93.

- Mostert G.J, Rohrmann B.R., Wedlake R.J. and Baxter R.C. (1992), Titanium Recovery from Ores and Slags by Nitriding and Chlorinating, *Brit. UK Pat. Appl. GB 2246345*, 12pp.
- Nanjo M., Mimura K., Sato N. (1988), Refining of titanium ore and separation of its metal contents. *Jpn. Kokai Tokyo Kobo JP 63014826*, 9pp.
- Neuschuetz D., Lodh K.S., Knacke O. (1974), Mechanism chlorination of TiO_2 , *Erzmetall*, 27, 371-378.
- Nieberlein V.A. (1957), Low temperature chlorination of Columbium bearing titanium minerals, *Report of Investigations 5349 US Bureau of Mines*.
- Nieberlein V.A. (1960), Separation of chloride vapors during ilmenite Chlorination, *Report of Investigations 5602 US Bureau of Mines*.
- Noda T. (1965), Titanium from slag in Japan, *J. Metals*, 17,25-32.
- Nowak R. (1969), Process for the production of metallic chlorides from substances containing metallic oxides, *US Patent 3,446,169*.
- Okabe T. H., Oda T., Mitsuda Y. (2003), Titanium powder production by preform reduction process, *10th World Conference on Titanium, Hamburg Germany*.
- Okahara Y., Iwasaki I. (1970), Chlorination of manganiferous iron ores, *Trans. Soc. Mining Eng. AIME*, 247, 73-80.
- Pasquevich D.M., Gamboa J.A., Caneiro A. (1992), On the role of carbon in the carbochlorination of refractory oxides, *Thermochimica Acta*, 209, 209-222.
- Pasquevich, D. M., Amorebieta V. T. (1992), Mass spectrometric study of volatile products during the carbochlorination of zirconia, *Ber. Bunsengens Phys. Chem.*, 96, 534-537.
- Patel C.C., Jere G.V. (1960), Some thermodynamical considerations in the chlorination of ilmenite, *Trans. Metall. Soc. AIME*, 218, 219-25.
- Perkins E.C., Dolezal H., Lang R.S. (1961), Chlorination of an Idaho ilmenite, *Report of Investigations 5763 US Bureau of Mines*, 1-15.
- Rhee, K.I., Sohn, H.Y. (1990a), The selective chlorination of iron from ilmenite ore by CO-Cl_2 mixtures. I. Intrinsic kinetics, *Metall. Trans. B*, 21B, 321.
- Rhee, K.I., Sohn, H.Y. (1990b), The selective chlorination of iron from ilmenite ore by CO-Cl_2 mixtures. II. Mathematical modelling of the fluidized bed process, *Metall. Trans B*, 21B, 331.
- Rhee, K.I., Sohn, H.Y. (1990c), The selective carbochlorination of iron from titaniferous magnetite ore in a fluidized bed, *Metall. Trans. B*, 21B, 341.

-
- Robson D., Harker H., Lord Wynne-Jones. (1968), The effect of halogens on the electron spin resonance of carbon, *Surf. Sci.*, 9, 246-256.
- Rowe L.W., Opie W.R. (1955), Production and purification TiCl_4 , *J. Metals*, 7, 1189-1193.
- Schomate C.H., Naylor B.F., Boericke F.S. (1946), Thermodynamic properties of ilmenite and selective reduction of iron in ilmenite, *US Bureau of Mines Rept., Invest. No. 3864*, 19 pp.
- Slatnick J. A. (1994), Availability of Titanium in Market Economy Countries, *Bureau of Mines Information Circular IC No. 9413*, 28.
- Smillie L. D., Heydenrych M. (1997), Low temperature TiO_2 production process, *Titanium Extraction and Processing*, B. Mishra, G.J Kipouros, Eds. TMS, Indiana, USA, 129.
- Sohn H.Y., Zhou L. (1999), The chlorination kinetics of beneficiated ilmenite particles by $\text{CO}+\text{Cl}_2$ mixtures, *Chemical Engineering Journal*, 72, 37-42.
- Skoog D.A., West D.M., Holler J. (2000), *Analytical Chemistry: An Introduction (Hardcover)*, Thomson Brooks-Cole, Singapore.
- Stefanyuk S.L., Morozov I.S. (1965), Kinetics and mechanism of chlorination of minerals-Loparite Pyrochlore Zircon and Euxenite, *Zh. Prikl. Khim.*, 38(4), 737-742.
- Suzuki K., Koyama K., Hashimoto T. (1993), A consideration about standard Gibbs free energy of formation of TiC_xO_y in equilibrium with carbon, *Reports of the Faculty of Engineering Himeji Institute of Technology*, 46, 55-59.
- Suzuki R. O., Inoue H. (2003), Calciothermic reduction of titanium oxide in molten CaCl_2 , *Metall. Mater. Trans. B*, 34B, 277-285.
- Svoboda O. and Wilson B. M. (1985), Commodity profiles for selected metals. *MINTEK, Report No. M221*.
- Stwertka, A. (1998). *Titanium Guide to the Elements (Revised ed.)*. Oxford University Press. 81-82.
- Takeda O, Okabe T.H. (2005), A new high speed titanium production by subhalide reduction process, *TMS Light Metals 2005 Edited by Halvor Kvande*, 1139-1144.
- Tamhankar S.S., Doraiswamy L.K. (1979), Analysis of solid-solid reactions: a review, *AIChE J.*, 25, 561-82.
- Titi-Manyaka R. (1973), Chlorination behaviors of some metal sulfides as investigated by thermogravimetric analysis, *Trans. Metall. Soc. AIME*, 254, 37-42.
- Titi-Manyaka, R., Iwasaki I., (1972), Thermogravimetric investigation of the chlorination behaviors of some common metals and their oxides, *Trans. Metall. Soc. AIME*, 252, 307-314.

- Takimoto Y., Hattori H. (1955), Chlorination of ilmenite, *J. Chem. Soc. Jpn. Ind. Chem. Soc.*, 58, 654-656.
- Town J.W., Sanders C.W. (1961), Laboratory concentration of seven titanium bearing ores of the Pacific Northwest, *Report of Investigations 5771 US Bureau of Mines*, 1-12.
- TZ Mineral International. (2009), 'TiO₂ Congress 2009 - Asia in Focus, *Proceedings of the 32nd Annual TZMI Congress Singapore 21st - 23rd October*.
- Van Deventer J.S.J. (1988), Kinetics of the selective chlorination of ilmenite, *Thermochimica Acta*, 124, 205-215.
- Vasyutinskii N.A., Berezhko A.V. (1967), Changes of titanium slag on heating in oxygen and chlorine, *Zh. Prikl. Khim.*, 40(12), 2646.
- Verhulst D., Sabacky B., Spitler T., Duyvesteyn W. (2002), The Altair TiO₂ pigment process, *Proceedings of the 32nd Annual Hydrometallurgical Meeting and International Conference on the Practice and Theory of Chloride/Metal Interaction*, 417-432.
- Van Vuuren D. S., Stone A. K. (2006), Selective recovery of titanium dioxide from low grade sources. (http://researchspace.csir.co.za/dspace/bitstream/10204/937/1/van%20Vuuren_2006_D1.pdf (accessed June 1, 2008)).
- Walker B.V. (1967), Titanium dioxide from New Zealand titaniferous materials, *N.Z. J/ Sci.*, 10 (1), 3-25.
- Walpole E. A., Winter J. D. (2002), *The Austpac ERMS and EARS Processes for the Manufacture of High-grade Synthetic Rutile by the Hydrochloric Acid Leaching of Ilmenite*, Austpac Resources N.L., Australia.
- Withers J. C., Loutfy R. O. (2003), A new novel electrolytic process to produce titanium, *The 19th Annual Titanium Conference of the International Titanium Association*, Monterey.
- Weast R. C. (1982), *CRC Handbook of Chemistry 62nd ed.*, CRC Press, Inc., Boca Raton.
- Yake D. E., Ulrichson D. L. (1981), Kinetics of calcium oxide chlorination and pore closure models, *Chem. Eng. Commun.*, 12, 97-120.
- Yang F., Hlavacek V. (1998), Carbochlorination kinetics of TiO₂ with C and CO as reductant, *Metall. Mater. Trans. B*, 29B, 1297-1307.
- Yang F., Hlavacek V. (1998), Carbochlorination kinetics of titanium dioxide with carbon and carbon monoxide as reductant, *Metall. Trans. B*, 29B, 1297-1307.
- Zelikman A.N., Segerchanu T., (1956), Studies of chlorination reactions of titanium oxide. *Zhur. Obsheei Khim.*, 26, 625-629.
- Zelikman A.N. and Leonova L.M. (1978), Chlorination of the Carbide Constituents of Hard Alloys. *Non-Ferrous Metals*, 5, 56-58.

-
- Zverev, L. V., Barsukova, Z.S. (1960), Chlorination of rare-metal silicates in a melt of alkali-metal chlorides, *Doklady Akad. Nauk. USSR*, 130, 593-595.
- Zhang G., Ostrovski, O. (2000), Reduction of titania by Methane-Hydrogen-Argon gas mixtures, *Metall. Trans. B*, 31 (2), 129-139.
- Zhang G., Ostrovski, O. (2001), Kinetic modeling of Titania reduction by a Methane-Hydrogen-Argon gas mixture, *Metall. Trans. B*, 32 (3), 465-473.
- Zhang J., Ostrovski, O. (2001), Cementite formation in $\text{CH}_4\text{-H}_2\text{-Ar}$ gas mixture and cementite stability, *ISIJ International*, 41(4), 333-339.

APPENDIX A

The Appendix A presents the development of experimental set-up for examination of carbothermal reduction, chlorination and iron leaching.

A.1. Carbothermal Reduction Experiments

The main objective of establishment of reduction experiments was to find reliable methods for producing consistent and uniform samples, which will be examined further in chlorination experiments. Initially titania was dry mixed with synthetic graphite powder with carbon to TiO_2 molar ratio of 3.3. The mixing was performed in SPEX Sample Prep Mixer/Mills for 70 min. Samples mixture were then pressed into pellets of 2 g each with 15 mm diameter. The pressing was carried out at a pressure of 85 MPa (15 kN) for 5 min. Samples were heated to 1200 °C in a horizontal electrical furnace at flow rate of 1 L·min⁻¹ of hydrogen. Temperature was raised with ramping rate of 5 °C·min⁻¹; samples were held at 1200°C for 180 min. Then samples were cooled down to room temperature also in hydrogen. XRD analysis indicated that reduced samples contained Ti(O,C) and still had suboxides (Ti_2O_3 , Ti_3O_5). The reduction in hydrogen at elevated temperature (1300 °C) produced Ti(O,C) without the presence of suboxides. However, excess graphite was consumed by the reaction with hydrogen, and samples were reduced in size especially those parts which were directly exposed to hydrogen gas. Based on these preliminary results it was decided to run reduction experiments in argon at flow rate of 1 L·min⁻¹ at higher furnace temperature (1450 °C), as carbothermal reduction in argon is much slower than in hydrogen. Samples mixing was also improved by using carboxymethyl cellulose as dispersant and using wet ball mixing. These improvements provided consistent results.

The reduction was controlled by monitoring the weight change in the reduction process and using XRD analysis. Samples were weighed before and after reduction. Sample weight change was calculated as:

$$\text{Sample weight change, pct} = \frac{W^{final} - W^{initial}}{W^{initial}} \times 100 \text{ pct} \quad (\text{A-1})$$

where W^{final} and $W^{initial}$ are sample weights after and prior to carbothermal reduction. Tables A.1 and A.2 show samples average weight changes for titania, ilmenites, and synthetic rutile in argon or nitrogen atmosphere. **Figure A.1** shows horizontal furnace for carbothermal reduction or nitridation experiments.

Table A.1. Samples average weight changes for carbothermal reduction of titania in argon and nitrogen atmosphere.

C/TiO ₂ molar ratio	Average weight change, pct	
	Argon	Nitrogen
1.5	- 28.10	- 26.76
2.0	- 36.55	- 36.24
2.5	- 43.58	- 40.20
3.3	- 46.95	- 37.09
4.5	- 41.68	- 33.82

Table A.2. Samples average weight changes for carbothermal reduction of ilmenites and synthetic rutile with C/TiO₂ 4.5 in argon or nitrogen atmosphere.

Type of Samples	Average weight change, pct	
	Argon	Nitrogen
Primary ilmenite	- 45.69	- 40.50
Secondary ilmenite	- 47.45	- 41.42
HYTI 70	- 46.58	- 41.23
Synthetic rutile	- 44.87	- 37.69



Figure A.1. Horizontal furnace for carbothermal reduction or nitridation experiments

A.2. Chlorination Experiments

Titanium tetrachloride produced in chlorination experiments is easy to be hydrolysed, forming corrosive HCl. This corrosive environments requires special measures for equipment design and experimental procedure. It was important to absorb TiCl_4 in liquid solvents, avoiding its hydrolysis. Initially distilled water was used, however formation of titanium oxides and oxychloride quickly blocked the outlet line. Chloroform CHCl_3 , sulphuric acid H_2SO_4 , nitric acid HNO_3 were also failed to absorb TiCl_4 . Finally complete absorption of TiCl_4 was achieved by using highly concentrated 32 pct of HCl.

Due to the hazardous nature of chlorine, the experiments were strictly conducted under the fume cupboard. A special custom made box was used to store and lock chlorine cylinder.

Figure A.2 shows experimental set up for chlorination experiments.



Figure A.2. Experimental set up for chlorination experiments

The presence of moisture could affect chlorination of Ti(O,C) as some chlorine is consumed by reaction (A-2).



Samples of Ti(O,C) with molar ratio carbon to titania of 2.5 were left in open air for 30 days. There was noticeable samples weight change; it gained about 6 pct from its initial weight. **Figures A.3 (a) and (b)** compare the extent of chlorination and temperature in the chlorination process of freshly prepared sample with a sample which contained moisture. Both Ti(O,C) samples were prepared with molar carbon to titania ratio of 2.5 and were reduced under the same conditions. The rate of chlorination of a sample with moisture was slow in comparison to freshly prepared sample and the final extent of chlorination was dropped to 75 pct (**Figure A.3 (a)**). There was a 5-min delay in the reaction ignition, although samples were heated for 10 min under nitrogen prior to chlorination (**Figure A.3 (b)**). The sample temperature was also lower in comparison to the fresh one.

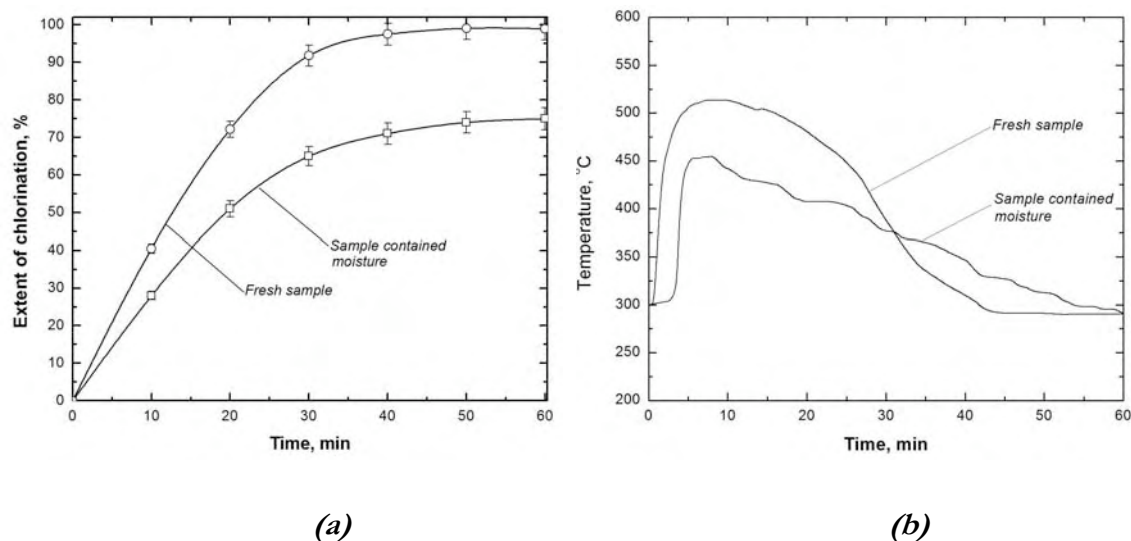


Figure A.3. Chlorination of titanium oxycarbide at 300 °C with pure chlorine flow rate of 50 mL·min⁻¹. (a) Extent of chlorination; (b) associated sample temperature change

It was essential for chlorination experiments to avoid moisture in the sample, which was achieved by working with freshly reduced samples.

A.3. Removal of Iron by Aeration and Leaching

The reduction of ilmenites either in argon or in nitrogen atmosphere produced Ti(O,C) or Ti(O,C,N) together with metallic iron. Metallic iron was chlorinated together with Ti(O,C) and Ti(O,C,N) , which necessitates the removal of iron before chlorination stage. **Figure A.4** show experimental set up for the removal of iron by aeration. It was established that aeration of reduced primary ilmenite with 0.372 M of NH_4Cl bath solution and flow rate $2.5 \text{ L}\cdot\text{min}^{-1}$ of air at 70°C for 5 h was effective for iron removal.

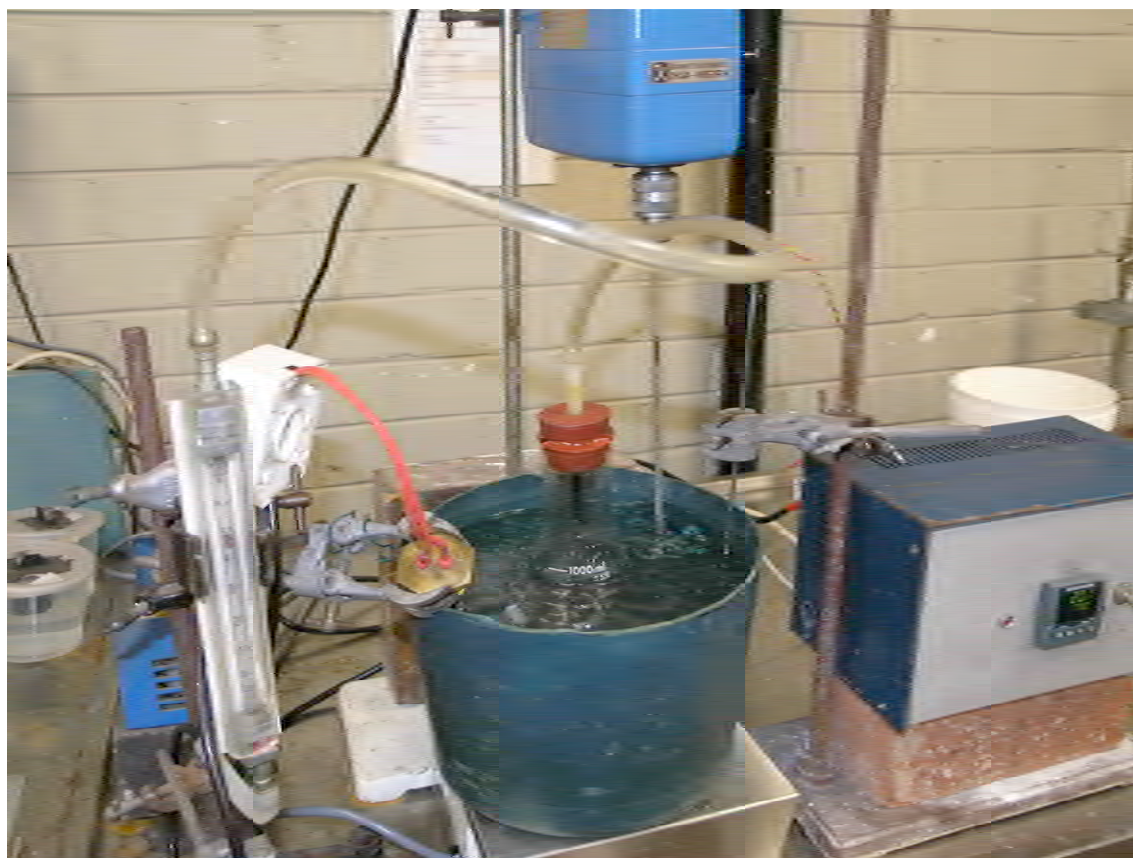


Figure A.4. Experimental set up for removal iron by aeration

APPENDIX B.

KINETIC MODELLING OF CHLORINATION OF TITANIUM OXYCARBIDE

Kinetic modelling of chlorination of titanium oxycarbide and oxycarbonitride is of importance for understanding further reaction mechanism and kinetics. This information can be used to predict chlorination behaviour at different operating conditions. Only the model's framework has been developed as the kinetic modelling was beyond the scope of this project.

Titanium oxycarbide was presented as a solution of titanium carbide, TiC and titanium monoxide, TiO, which react with chlorine to produce titanium tetrachloride, TiCl₄, carbon, C, and carbon monoxide, CO according to the reactions (4-1) and (4-3) (*Chapter 4*). Reaction rate $\mathfrak{R}_s$, is defined as moles of TiCl₄ formed on unit surface area per unit time and can be described by equations (B-1) and (B-2), respectively:

$$\mathfrak{R}_s = k_o \exp\left(\frac{-E_a}{RT}\right) (P_{Cl_2})^n \quad (B-1)$$

$$\mathfrak{R}_s = -\rho_s \frac{dr_c}{dt} \quad (B-2)$$

The extent of chlorination for reactions (4-1) and (4-3) are related to the location of reaction front, r_c , and can be expressed by equation (B-3):

$$x = 1 - \left(\frac{r_c}{r_g}\right)^3 \quad (B-3)$$

where r_c / r_g is dimensionless locations of reaction fronts; r_g is the average radius of a grain.

The overall extent of chlorination, X , can be calculated by:

$$X = \frac{\int_0^{r_p} x r^2 dr}{\int_0^{r_p} r^2 dr} \quad (B-4)$$

where r_p is the radius of a pellet.

The relationship between $\mathfrak{R}_s$ and $\mathfrak{R}_v$ where $\mathfrak{R}_v$ is defined as moles of TiCl_4 formed within the unit volume of pellet per unit time:

$$\mathfrak{R}_v = \mathfrak{R}_s \frac{3\varepsilon_p r_c^3}{r_g^3} \quad (\text{B-5})$$

where ε_p is the initial volumetric fraction of titanium oxycarbide in the pellet.

B.1. Mass Balances Within a Sphere Pellet

Consider a spherical layer of pellet with radii z and $z + dz$. Due to relatively low density of gas phase; the amount of gas accumulated because of change in concentration can be neglected. The pressure change within a pellet is also negligible due to relatively small pellet size.

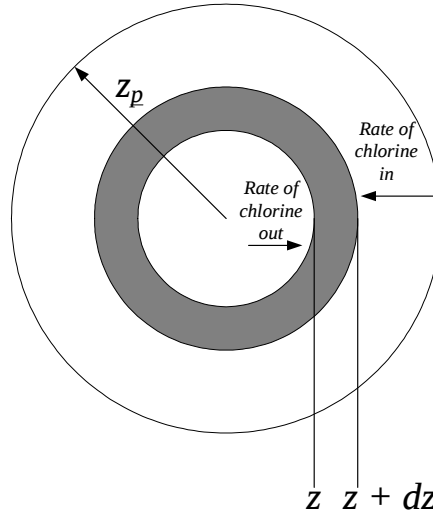


Figure B.1. Shell balance within spherical pellet of titanium oxycarbide

The diffusion problem is solved by making mass balances for chlorine over a thin shell of titanium oxycarbide. The shell mass balance for spherical pellet can be written as:

$$(\text{Rate of chlorine in}) = (\text{Rate of chlorine out}) + (\text{Rate of chlorine consumed}) \quad (\text{B-6})$$

where:

Rate of chlorine in at $(z + dz)$:

$$(W_{\text{Cl}_2}) \left(4\pi z^2 \Big|_{z+dz} \right) + (C_{\text{Cl}_2}) \left(M_{\text{Cl}_2} \Big|_{z+dz} \right) \quad (\text{B-7})$$

Rate of chlorine out at z :

$$(W_{Cl_2})\left(4\pi z^2 \Big|_z\right) + (C_{Cl_2})\left(M_{Cl_2} \Big|_z\right) \quad (B-8)$$

Rate of chlorine consumed within the shell, dz :

$$2\left(4\pi z^2 dz\right)(\Re v) \quad (B-9)$$

Therefore the equation (B-8) can be written as:

$$4\pi\left(W_{Cl_2} z^2 \Big|_{z+dz} - W_{Cl_2} z^2 \Big|_z\right) + \left(C_{Cl_2} M_{Cl_2} \Big|_{z+dz} - C_{Cl_2} M_{Cl_2} \Big|_z\right) = (\Re v) 8\pi z^2 dz \quad (B-10)$$

Division by dz on both side and taking the limit as dz approaches zero gives:

$$4\pi \frac{d}{dz} (W_{Cl_2} z^2) + \frac{d}{dz} (C_{Cl_2} M_{Cl_2}) = (\Re v) 8\pi z^2 \quad (B-11)$$

where the molar flux of chlorine at radius z , is defined by Fick's law of diffusion as:

$$W_{Cl_2} = -D_{eff} \frac{dC_{Cl_2}}{dz} \quad (B-12)$$

Volumetric flow rate of chlorine due to its consumption is defined as:

$$M_{Cl_2} = \left(\int_0^z 4\pi z^2 \Re v dz \right) \frac{RT}{P} \quad (B-13)$$

Substituting Equations (B-12) and (B-13) to (B-11) and differentiating gives:

$$4\pi \left(-D_{eff} \right) \frac{d}{dz} \left(z^2 \frac{dC_{Cl_2}}{dz} \right) + \left(M_{Cl_2} \frac{dC_{Cl_2}}{dz} + 4\pi z^2 \Re v C_{Cl_2} \frac{RT}{P} \right) = (\Re v) 8\pi z^2 \quad (B-14)$$

Division by 4π on both side and rearranging of the equation gives mass balances equation:

$$\left(-D_{eff} \right) \frac{d}{dz} \left(z^2 \frac{dC_{Cl_2}}{dz} \right) + \left(\frac{M_{Cl_2}}{4\pi} \frac{dC_{Cl_2}}{dz} \right) = \left(2 - C_{Cl_2} \frac{RT}{P} \right) z^2 \Re v \quad (B-15)$$

The initial conditions for mass balances equation are:

$$\text{at } t = 0; C_{Cl_2} = 0 \text{ for } z = 0 \text{ to } z_p \quad (B-16)$$

The boundary conditions for mass balance equation are:

$$\text{at } z = 0; \frac{dC_{Cl_2}}{dz} = 0 \quad \{\text{Symmetric condition at the center of pellet}\} \quad (B-17)$$

$$\text{at } z = z_p; \frac{M_{Cl_2}}{2\pi z_p^2} = h_D \left(C_{Cl_2,b} - \epsilon_{Cl_2,s} \right) \frac{CM_{Cl_2}}{4\pi z_p^2} \quad \{\text{Mass flux}\} \quad (B-18)$$

MATLAB pdepe.m solver program can be implemented by using the following format:

$$c \left(x, t, u, \frac{\partial u}{\partial x} \right) \frac{\partial u}{\partial t} = x^{-m} \frac{\partial}{\partial x} \left(x^m f \left(x, t, u, \frac{\partial u}{\partial x} \right) \right) + s \left(x, t, u, \frac{\partial u}{\partial x} \right) \quad (B-19)$$

The mass balance in Equation (B-15) was rearranged to yield similar format with MATLAB pdepe.m in Equation (B-19):

$$z^{-2} \frac{\partial}{\partial z} \left(z^2 \frac{\partial C_{Cl_2}}{\partial z} \right) + \left(\frac{-M_{Cl_2}}{4\pi D_{eff} z_p^2} \right) \frac{\partial C_{Cl_2}}{\partial z} + \left(2 - \frac{RT C_{Cl_2}}{P} \right) \frac{Rv}{D_{eff}} = 0 \quad (B-20)$$

MATLAB parameters pdepe for mass balance equation is the following:

$$c = 0 \quad (B-21)$$

$$f = \frac{\partial C_{Cl_2}}{\partial z} \quad (B-22)$$

$$s = \left(\frac{-M_{Cl_2}}{4\pi D_{eff} z_p^2} \right) \frac{\partial C_{Cl_2}}{\partial z} + \left(2 - \frac{RT C_{Cl_2}}{P} \right) \frac{Rv}{D_{eff}} \quad (B-23)$$

For boundary conditions, MATLAB employs the following format:

$$p(x, t, u) + q(x, t, u) f \left(x, t, u, \frac{\partial u}{\partial x} \right) = 0 \quad (B-24)$$

MATLAB parameters for boundary conditions as the following:

For boundary condition for the center of the particle (ie. $z_c = 0$):

$$p_l = 0 \quad (B-25)$$

$$q_l = 1 \quad (B-26)$$

For boundary condition for the surface of the particle (ie. $z = z_p$):

$$p_r = \left(2 - C_{Cl_2}\right) \left(\frac{M_{Cl_2}}{4\pi z_p^2} \right) - h_t (C_{bulk} - C_{surface}) \quad (B-27)$$

$$q_r = 0 \quad (B-28)$$

B.2. Heat Balances Within a Sphere Pellet

The shell heat balance for spherical pellet can be written as:

$$\begin{aligned} & (\text{Rate of heat in}) - (\text{Rate of heat out}) + (\text{Rate of heat generated}) \\ & - (\text{Rate of heat consumed}) = 0 \end{aligned} \quad (B-29)$$

where:

Rate of chlorine in at z :

$$\left(-4\pi z^2 \lambda \frac{\partial T}{\partial z} \Big|_z \right) \quad (B-30)$$

Rate of heat out at $(z + dz)$:

$$\left(-4\pi z^2 \lambda \frac{\partial T}{\partial z} \Big|_{z+dz} \right) \quad (B-31)$$

Rate of heat generation within the shell, dz :

$$(4\pi z^2 \mathfrak{R}_v) (-\Delta H) dz \quad (B-32)$$

Rate of heat absorbed by increasing solid temperature:

$$4\pi z^2 C_{ps} \frac{\partial T}{\partial t} \Big|_z dz \quad (B-33)$$

where C_s is the overall heat capacity of solid material within unit volume of pellet.

Rate of heat absorbed by chlorine within the pellet:

$$-2 \left(M_{Cl_2} \frac{P}{VRT} \right) C_{p,Cl_2} \frac{\partial T}{\partial z} dz \quad (B-34)$$

where C_{p,Cl_2} is the heat capacity of chlorine; V is the volume of the gas.

Rate of heat released by titanium tetrachloride from the pellet:

$$- \left(M_{Cl_2} \frac{P}{VRT} \right) C_{p,TiCl_4} \frac{\partial T}{\partial z} dz \quad (B-35)$$

where $C_{p,TiCl_4}$ is the heat capacity of titanium tetrachloride.

Heat balances can be written as the following:

$$\begin{aligned} -4\pi\lambda \left(z^2 \frac{\partial T}{\partial z} \Big|_z - z^2 \frac{\partial T}{\partial z} \Big|_{z+dz} \right) + (4\pi z^2 \Re_v) (-\Delta H) dz - 4\pi z^2 C_{ps} \frac{\partial T}{\partial t} \Big|_z dz \\ + (2C_{p,Cl_2} - \epsilon_{p,TiCl_4}) \left(M_{Cl_2} \frac{P}{VRT} \right) \frac{\partial T}{\partial z} dz = 0 \end{aligned}$$

$$\left(\frac{C_{ps}}{\lambda} \right) \frac{\partial T}{\partial t} = z^{-2} \frac{\partial}{\partial z} \left(z^2 \frac{\partial T}{\partial z} \right) + \left(\frac{(2C_{p,Cl_2} - C_{p,TiCl_4}) M_{Cl_2} P}{4\pi R T \lambda z^2} \right) \frac{\partial T}{\partial z} + \frac{\Re_v (-\Delta H)}{\lambda} \quad (B-36)$$

The initial conditions for heat balances equation are:

$$\text{at } t = 0; T = T_{furnace} \text{ for } z = 0 \text{ to } z_p \quad (B-37)$$

The boundary conditions for heat balances equation are:

$$\text{at } z = 0; \frac{\partial T}{\partial z} = 0 \quad \{ \text{Symmetric condition at the center of pellet} \} \quad (B-38)$$

$$\text{at } z = z_p; h_c (T_s - T_{furnace}) = -\lambda \frac{\partial T}{\partial z} \Big|_{z=z_p} \quad \{ \text{Heat flux} \} \quad (B-39)$$

MATLAB parameters pdepe for heat balance is the following:

$$c = \frac{C_{ps}}{\lambda} \quad (B-40)$$

$$f = \frac{\partial T}{\partial z} \quad (B-41)$$

$$s = \left(\frac{(2C_{p,Cl_2} - C_{p,TiCl_4}) M_{Cl_2} P}{4\pi R T \lambda z^2} \right) \frac{\partial T}{\partial z} + \frac{\Re v(-\Delta H)}{\lambda} \quad (B-42)$$

MATLAB parameters for boundary conditions as the following:

For boundary condition for the center of the particle (ie. $z_c = 0$):

$$p_l = 0 \quad (B-43)$$

$$q_l = 1 \quad (B-44)$$

For boundary condition for the surface of the particle (ie. $z_c = z_p$):

$$p_r = h_t (T_{\text{surface}} - T_{\text{fluid}}) \quad (B-45)$$

$$q_r = \lambda \quad (B-46)$$

B.3. MATLAB Output

Calculation of parameters lead to the following results:

Diffusion coefficient for Cl₂-TiCl₄ (Deff), m²/s:

9.3439e-06

Heat transfer coefficient (ht), W/(m².K):

3.8335e+00

Mass transfer coefficient (hd), m²/s:

2.9332e-05

MCl₂=

1.0531e-11

Rv=

1.5349e-04

Rs=

6.2397e-16

B.4. MATLAB Program Listing

From the files “*Allprogram.m*”

```
%-----  
% Clearing memory and declaration of variables  
clc; clear all; format short e;  
global R T Ts P Deff m zp Rs ep rg rc Ea ko n rhos Rv PCl2 MCl2 lambda  
global DH CpCl2 CpTiCl4 Cps ht hd  
%-----  
  
%-----  
% Data inputs  
R=8.314*10^-3;      %Gas constant, kPa.m3/(mol.K)  
T=200+273.15;      %Initial temperature of the furnace, K  
P=101.325;          %Pressure, kPa  
m=2;                %Sphere shape factor  
ep=0.5;             %Value of porosity  
zp=.5*15E-3;        %Radius of pellet, m  
rg=7*10^-6;         %Average diameter of grains, m  
rc=zp;  
Ea=165;              %INITIAL GUESS VALUE of Activation energy, J/mol  
ko=0.1;              %INITIAL GUESS VALUE of frequency factor  
n=2;                 %INITIAL GUESS VALUE of the reaction  
CpCl2=34;            %J/K.mol  
CpTiCl4=37;          %J/K.mol  
Cps=(.7*34)+(.3*31); %Cp TiC 34 31 J/K.mol; Cp TiO = 31 J/K.mol  
PCl2=P;              %Partial pressure of chlorine, kPa  
dtube=0.022;         %Diameter of silica tube, m  
mucl2=14.1E-6;       %Viscosity of chlorine gas, Pa.s or kg/m.s  
lambdacl2=0.0093;    %Thermal conductivity of chlorine gas, W/m.K  
rhoTiC=4.910;        %Density of titanium carbide, g/cm3  
rhoTiO=4.888;        %Density of titanium monoxide, g/cm3  
%-----
```

```
%-----
%Calculations of parameters
rhocl2=((P*70.9/101.325)/(82.05783*T))*1000;      %Density of chlorine at Tfurnace
and 1 atm, kg/m3
lambda=(.7*21)+(.3*3);                          %Thermal conductivity of titanium
oxycarbide, W/m.K
DH=(0.3*(-414.186-0.006662*T)+0.7*(-326.366-0.009157*T))*1000;      %Enthalpy of
reactions, J
rhos=((.7*rhoTiC)+(.3*rhoTiO))*1e3;              %Density of (TiC-TiO)ss, kg/m3
Rs=ko*exp(-Ea/R/T)*(PCl2^n);                     %Reaction rate on unit surface area
per unit time
Rv=(Rs*3*ep*rc^2)/(rg^3);                        %Reaction rate on unit pellet
volume per unit time
%-----

%-----
%Calculation for diffusion coefficient for Cl2-TiCl4 (Deff), m2/s
Deff=((1.858E-27*T^1.5)*((70.99^-1)+(189.70^-1))^0.5)/(1.1326*1*(5.014E-10)^2);
disp('Diffusion coefficient for Cl2-TiCl (Deff), m2/s:')
disp(Deff)
disp('-----')
%-----

%-----
%Calculation for heat transfer coefficient (ht), W/(m2.K)
FCl2=(5E-5)*573.15/298.15;
velocity=(FCl2/60)*4/pi/dtube^2;
Prandtl=(CpCl2*1000/70.9)*mucl2/lambdacl2;      %Prandtl number
Reynold=(zp*velocity*rhocl2)/mucl2;             %Reynold number
Nusselt= 2 + (0.6*(Reynold^0.5)*(Prandtl^(1/3))); %Nusselt number
ht=Nusselt*lambdacl2/zp;
disp('Heat transfer coefficient (ht), W/(m2.K):')
```

```
disp(ht)
disp('-----')
%-----

%-----

%Calculation for mass transfer coefficient (hd), m2/s
Schmidt=mucl2/(rhocl2*Deff); %Schmidt number
Sherwood= 2 + (0.6*(Reynold^0.5)*(Schmidt^(1/3))); %Sherwood number
hd=Sherwood*Deff;
disp('Mass transfer coefficient (hd), m2/s:')
disp(hd)
disp('-----')
%-----

%-----

%Calculation of MCl2
F=@(z) (4*pi*z.^2);
MCl2=(quadl(F,0,zp))*Rv*R*T/P;
disp('MCl2=');disp(MCl2)
disp('Rv=');disp(Rv)
disp('Rs=');disp(Rs)
disp('-----')
%-----

ALLHEATMASS %Recalling heat and mass program solver

From the files “Allheatmass.m”

%-----

% Solving heat and mass balance equation
function heatbalance
global m zp
```

```
%Constructing Figure
z = linspace(0,zp,100);
t = linspace(0,60,100);

hb = pdepe(m,@pdexhb,@pdexhbic,@pdexhbhc,z,t);

% Extract the first solution component as temperature (Temp).
Temp = hb(:,1);
C = hb(:,2);

% A surface plot construction.
figure;
surf(z,t,Temp);
title('Numerical solution heat balance for spherical pellet');
xlabel('Radius, z');
ylabel('Time, t');
zlabel('Temperature, K');
figure;

subplot(1,2,1),plot(z,Temp);
title('Temperature profile for spherical pellet');
xlabel('Radius, z');
ylabel('Sample Temperature, K');

subplot(1,2,2),plot(t,Temp);
title('Temperature profile with increasing time');
xlabel('Time, min');
ylabel('Sample Temperature, K');

% A surface plot construction.
figure;
surf(z,t,C);
```

```
title('Numerical solution mass balance for spherical pellet');
xlabel('Radius z, m');
ylabel('Time t, min');

figure;
plot(z,C);
title('Concentration profile for spherical pellet');
xlabel('Radius, z');
ylabel('Concentration of chlorine');

%Heat balance Partial Differential Equation
function [c,f,s] = pdexhb(z,t,u,DuDx)
global R T P Rv MCl2 lambda DH CpCl2 CpTiCl4 Cps rhos
global Deff MCl2 R T P Rv ep rc rg

Temp=u(1);
C=u(2);
DTDz=DuDx(1);
DCDz=DuDx(2);

c=[Cps/lambda;0];
f=[DTDz;DCDz];
s=[(((2*CpCl2-CpTiCl4)*MCl2*P*DTDz) / (4*pi*lambda*R*T*z^2)) + (Rv*-
DH/lambda);(-MCl2*DCDz/(4*pi*Deff*z^2)) + ((2-(R*T*C/P)) * Rv/Deff)];

%Initial Condition
function T0 = pdexhbic(z)
global T
C=0;
T0=[T; C];

%Boundary Conditions
```

```
function [pl,ql,pr,qr] = pdexhbbc(xl,ul,xr,ur,t)
global ht lambda T Temp
global zp Deff MCl2 R T P hd C

Cbulk=ul(2);
Csurface=ur(2);
Tf=ul(1);
Ts=ur(1);

pl = [0;0];
ql = [1;1];

pr = [(Ts-Tf)*ht;((2-Csurface)*MCl2 / (4*pi*zp^2)) - (hd*(Cbulk-Csurface))];
qr = [lambda;0];
%-----
```