

Effect of Impurities in the Chlorination Process of TiO₂

Seok Hong Min, Tae Kwon Ha

Abstract—With the increasing interest on Ti alloys, the extraction process of Ti from its typical ore, TiO₂, has long been and will be important issue. As an intermediate product for the production of pigment or titanium metal sponge, tetrachloride (TiCl₄) is produced by fluidized bed using high TiO₂ feedstock. The purity of TiCl₄ after chlorination is subjected to the quality of the titanium feedstock. Since the impurities in the TiCl₄ product are reported to final products, the purification process of the crude TiCl₄ is required. The purification process includes fractional distillation and chemical treatment, which depends on the nature of the impurities present and the required quality of the final product. In this study, thermodynamic analysis on the impurity effect in the chlorination process, which is the first step of extraction of Ti from TiO₂, has been conducted. All thermodynamic calculations were performed using the FactSage thermodynamical software.

Keywords—Rutile, titanium, chlorination process, impurities, thermodynamic calculation, FactSage.

I. INTRODUCTION

TETRACHLORIDE (TiCl₄) is produced by two different processes: A fluidized bed process and a molten salt process. A fluidized bed process uses high TiO₂ feedstock and is primarily used by the US, Japanese, Chinese producers. On the other hand, a molten salt process uses lower TiO₂ feedstock and is primarily used by Commonwealth of Independent States (CIS) countries and some of Chinese producers [1].

Ilmenite and rutile are the two most important titanium-bearing resources. Chloride ilmenite is heavily weathered ilmenite and includes leucosene. Sulfate slag (TiO₂ equivalent 80-83%) is obtained by smelting ilmenite with relatively low content of TiO₂, which forms solid solution with hematite or magnetite. A chloride slag fine is also treated as sulfate slag due to its size. Chloride slag (TiO₂ equivalent 85-92%) is obtained by smelting ore with relatively high TiO₂ content. Upgraded slag, known as UGS of QIT (TiO₂ ~95%), is also treated as chloride slag [2]. There are two types of rutile: synthetic and natural. Synthetic rutile is produced mainly by solid-state reduction of ilmenite ore. Ilmenite accounts for 90% of TiO₂ units produced for pigment and titanium-sponge manufacture. TiO₂ feedstock is mainly produced by Australia, South Africa, Canada, and China in order, which accounts for 67% collectively. Australia is the largest producer of feedstock [3]. The pigment industry consumes about 93% of the produced

TiO₂ units, and greatly influences the economics of titanium feedstock production [4]. Chloride process accounts for 56% of the pigment production. Titanium sponge/metal industry consumes nearly 4%, and the production of fluxes consumes the remainder. Therefore, 56% of the produced TiO₂ is transformed into the intermediate product titanium TiCl₄ before the final products, either pigment or titanium sponge/metal [2].

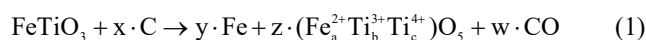
The TiCl₄ product is transported in its liquid form by rails in cars. Due to its high affinity to water, stringent handling procedures must be employed for safety even at ambient level of humidity [5]. The objectives of the present study are to do benchmarking the production of titanium TiCl₄. Methods of TiCl₄ productions were reviewed. Especially, the fluidized bed process was extensively studied. In addition, the market study and the safety issue regarding TiCl₄ were overviewed.

II. PRODUCTION OF TITANIUM TiCl₄

Generally speaking, the production of TiCl₄ includes 4 process units: Chlorination, purification of TiCl₄, gas treatment, and waste treatment. Fig. 1 shows a generic flowsheet of production of TiCl₄ with the fluidized bed process. The present report concentrates on chlorination and purification of TiCl₄ [6].

Production of TiCl₄ is carried out by two different processes: Molten salt process and fluidized bed process. The choice of process depends on the content of TiO₂ in the feed. Generally speaking, the molten salt process is for the feed with relatively low content of TiO₂ in the feed.

Titanium sponge producers in CIS countries use molten salt process in order to produce TiCl₄. Firstly, ilmenite feed is reduced by carbothermic reaction in an electric arc furnace, by which titania slag is produced as well as high purity iron as co-product. The main chemical reaction in the arc furnace can be represented by (1):



where $a + b + c \cong 3$.

The slag contains relatively high levels of impurities since most of impurities in the feed and the coal report to the titania slag rather than to the liquid iron. Unlike in the fluidized bed process, the impurities in the slag have little effect on the production of TiCl₄ in the molten slag process. The slag is then subjected to cooling and crushing processes before it is fed into a bath of molten salt, where the crude TiCl₄ is produced. Compared to the fluidized bed process, the molten salt process has significantly high loss of Ti element (~12%).

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The producers of $TiCl_4$ in US, Japan, and China use fluidized bed process. The high TiO_2 feed with a specific size range and the calcined petroleum coke are fed into a fluid bed reactor where Cl_2 in the preheated gas is provided for chlorination. The

ratio of coke-to-feed is between 0.2 and 0.4, depending depends on the TiO_2 feed quality. The size of the feed is carefully monitored for the optimum fluid bed process [7].

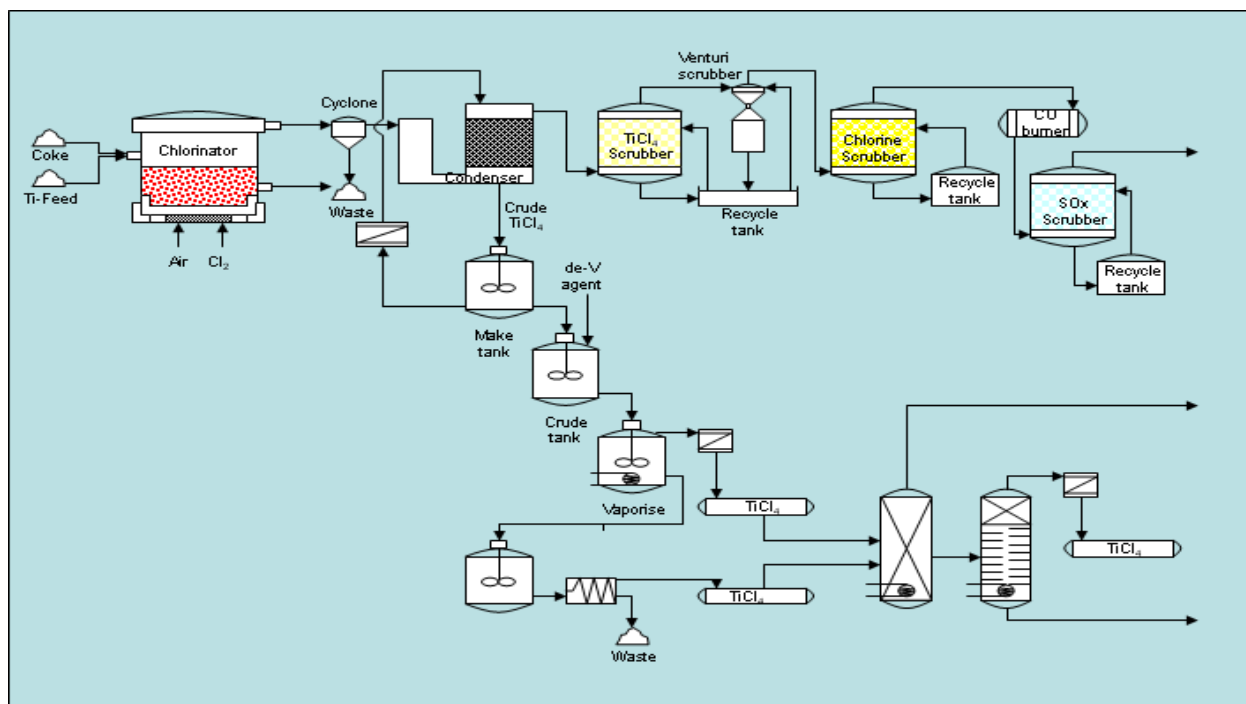


Fig. 1 Production of $TiCl_4$ by fluidized bed technology [8]

The feed for the fluidized bed process includes synthetic/natural rutile, UGS (Up-Graded Slag), and chloride slag. Chloride slag is the product of ilmenite smelting and contains the equivalent TiO_2 (all Ti is expressed as TiO_2) more than 85 wt. %. Unlike rutile and UGS (Up-Graded Slag), chloride slag contains Ti^{3+} (as in Ti_2O_3), which releases a certain energy when it is chlorinated.

The crude $TiCl_4$, produced by either the molten salt process or the fluidized bed process, contains impurities that are stripped during the purification process. Fe and V, the major impurities in the crude $TiCl_4$, are removed by selective condensation and distillation. Compared to the production of pigment, the production of titanium sponge employs extra stages of purification process with taller fractional distillation towers with increased numbers of plates, with which impurities such as Ni, Cr, As and Sb can be but inefficiently reduced to very low levels. The purification of the crude $TiCl_4(g)$ is carried out in two stages. First, it is cooled down to $\sim 40^\circ C$, and condensed to $-10 - 0^\circ C$ to separate CO , CO_2 , $HCl(g)$, unreacted Cl_2 , etc. The crude condensed $TiCl_4(l)$ is split into two streams. One stream is recirculated to the chlorinator for cooling the off-gas, while the other stream is subjected to further distillation in order to eliminate the entrained impurities

$TiCl_4$ for the purification is heated up to $\sim 70^\circ C$ for removal of $SiCl_4(l)$. Then, it is further heated up to $140^\circ C$ so that it completely evaporates. At the same time, a mineral oil is added in order to precipitate and separate $VOCl_2(s)$ from the distilled $TiCl_4(g)$. The rate of mineral oil to the crude $TiCl_4(l)$ is

normally considerably higher than the stoichiometric requirements for the precipitation of vanadium. In the molten salt process, vanadium is removed using metallic dressing. The producers of $TiCl_4$ in US, Japan, and China use fluidized bed process. The high TiO_2 feed with a specific size range and the calcined petroleum coke are fed into a fluid bed reactor where Cl_2 in the preheated gas is provided for chlorination. The ratio of coke-to-feed is between 0.2 and 0.4, depending depends on the TiO_2 feed quality. The size of the feed is carefully monitored for the optimum fluid bed process.

III. SIMULATION OF CHLORINATION PROCESS

Equilibrium module and databases such as FTsalt, FACT53 and FToxid were used in this study. Considering energy balance of the chlorination reaction, it has been found that the temperature increases up to $1504.18^\circ C$ as shown in Fig. 2, appropriate cooling is therefore required. This is why the temperature of chlorination process should be maintained at $1000^\circ C$.

In Fig. 3, simulation result of chlorination reaction at various temperatures from 50 to $1000^\circ C$ was illustrated, in which $TiCl_4$ appeared to form from the temperature of $110^\circ C$ and at $1000^\circ C$ mixed gas of CO_2 and $TiCl_4$ can be formed. The effect of impurity on the chlorination process was simulated and the result was given in Fig. 4 for the FeO , in which gaseous $FeCl_2$ and $FeCl_3$ phases could form above $700^\circ C$. Interestingly, only

solid FeCl_2 phase is expected to exist below 520°C as shown in Fig. 4 (b).

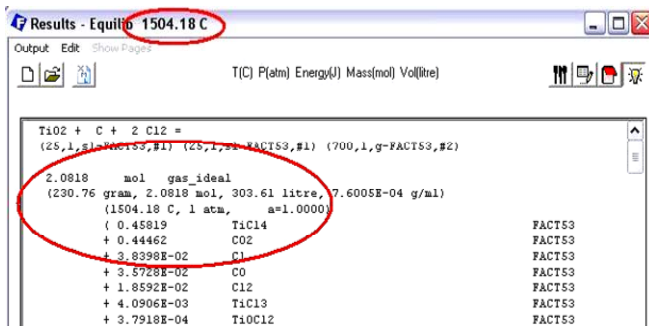


Fig. 2 Result of energy balance calculation of chlorination process showing maximum temperature increases up to 1504.18°C

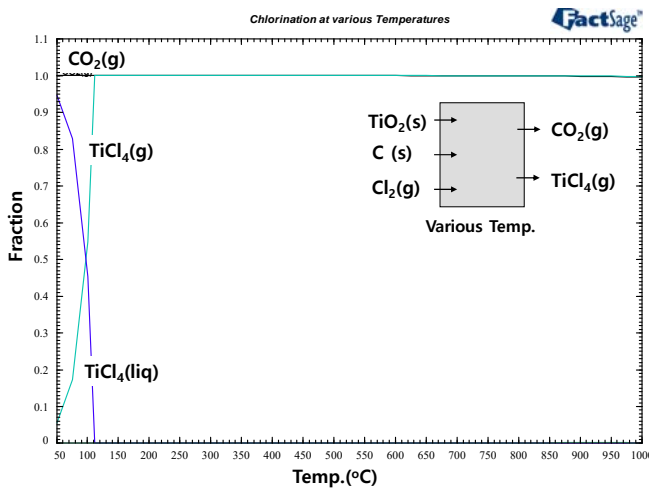


Fig. 3 Chlorination result simulated at various temperatures

Fig. 5 shows the effect of various impurities such as Al_2O_3 , MgO and Nb_2O_5 , showing various metal chlorides could be formed [9]. These chlorides should be eliminated by the distillation or selective chlorination process to obtain high quality TiCl_4 [10]. Meanwhile, TiCl_4 is beginning to be traded more widely. A special care is required for the handling of TiCl_4 because it violently reacts with water even with moisture in the atmosphere, thereby generating hydrochloric acid mist. It is categorized as potentially fatal if inhaled. Therefore, it is vital to take all necessary precautions to prevent loss of containment of TiCl_4 . Containment and transportation requirements for TiCl_4 are similar to those for TiCl_4 . TiCl_4 is supplied in drums and is transported by rail in cars, similar to those specified for liquid chlorine transportation. Due to its handling with extreme caution, the international trade of TiCl_4 is extremely rare, and is only performed in small volumes practically not enough for titanium sponge production.

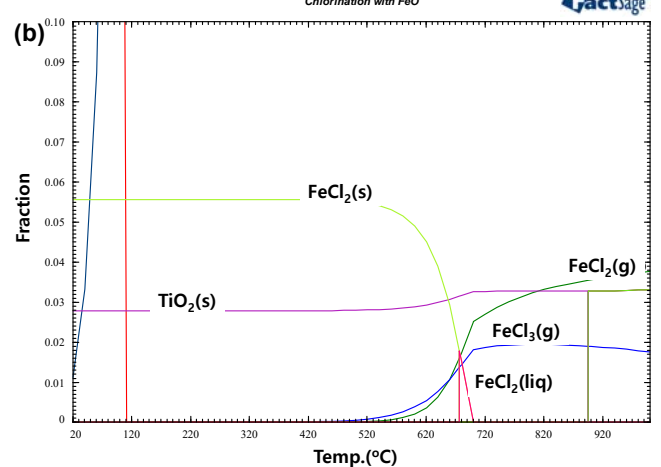
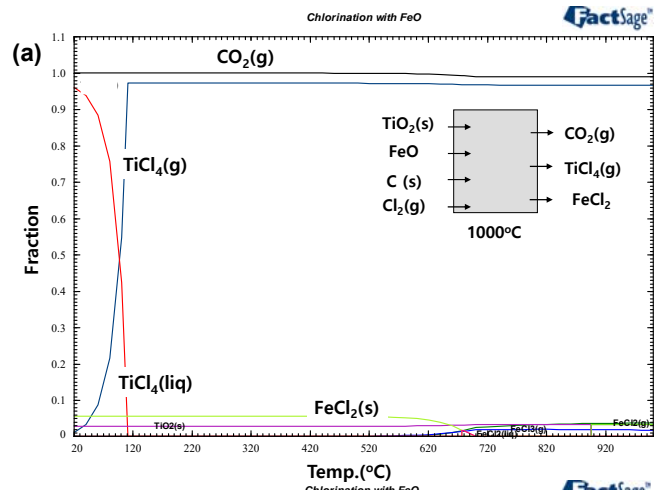
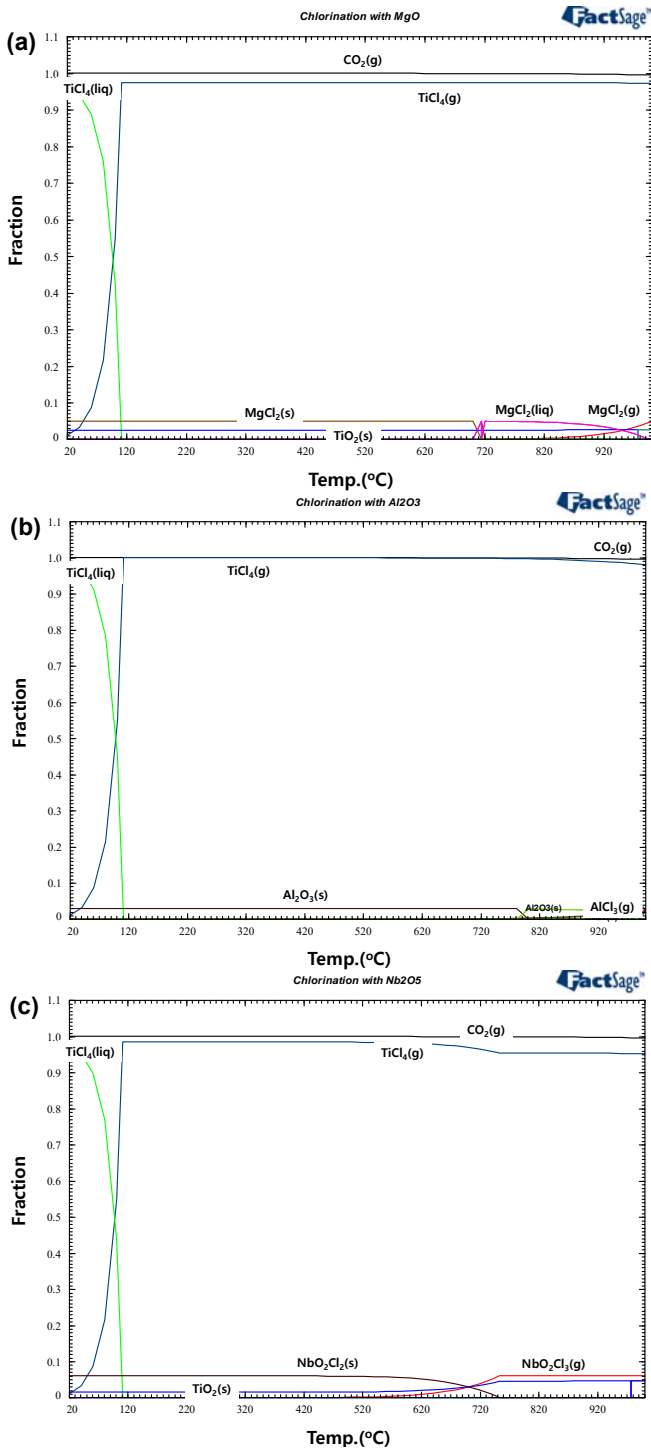


Fig. 4 Chlorination result simulated with impurity of FeO in the ore (a) and enlarged illustration of within the fraction of 0.1 (b)

IV. CONCLUSIONS

In the present study, production of TiCl_4 was summarized and the process was thermodynamically simulated with special focus on the impurity effect in the ore. With impurities such as FeO , MgO , Al_2O_3 and Nb_2O_5 in TiO_2 ore, corresponding metal chlorides such as FeCl_2 , MgCl_2 , AlCl_3 and NbCl_3 were expected and should be eliminated by distillation process.



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Fig. 5 Chlorination result simulated with impurities of MgO (a), Al_2O_3 (b) and Nb_2O_5 (c) in the ore

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