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Effect of Impurities in the Chlorination Process of TiO_2

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Abstract**—**With the increasing interest on Ti alloys, the extraction process of Ti from its typical ore, TiO_2, has long been and will be important issue. As an intermediate product for the production of pigment or titanium metal sponge, tetrachloride ($TiCl_4$) is produced by fluidized bed using high TiO_2 feedstock. The purity of $TiCl_4$ after chlorination is subjected to the quality of the titanium feedstock. Since the impurities in the $TiCl_4$ product are reported to final products, the purification process of the crude $TiCl_4$ 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 TiO_2, 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 ($TiCl_4$) is produced by two different processes: A fluidized bed process and a molten salt process. A fluidized bed process uses high TiO_2 feedstock and is primarily used by the US, Japanese, Chinese producers. On the other hand, a molten salt process uses lower TiO_2 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 leucoxene. Sulfate slag (TiO_2 equivalent 80-83%) is obtained by smelting ilmenite with relatively low content of TiO_2, which forms solid solution with hematite or magnetite. A chloride slag fine is also treated as sulfate slag due to its size. Chloride slag (TiO_2 equivalent 85-92%) is obtained by smelting ore with relatively high TiO_2 content. Upgraded slag, known as UGS of QIT (TiO_2 ~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 TiO_2 units produced for pigment and titanium-sponge manufacture. TiO_2 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 TiO_2 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 TiO_2 is transformed into the intermediate product titanium $TiCl_4$ before the final products, either pigment or titanium sponge/metal [2].

The $TiCl_4$ 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 $TiCl_4$. Methods of $TiCl_4$ productions were reviewed. Especially, the fluidized bed process was extensively studied. In addition, the market study and the safety issue regarding $TiCl_4$ were overviewed.

II. PRODUCTION OF TITANIUM $TiCl_4$

Generally speaking, the production of $TiCl_4$ includes 4 process units: Chlorination, purification of $TiCl_4$, gas treatment, and waste treatment. Fig. 1 shows a generic flowsheet of production of $TiCl_4$ with the fluidized bed process. The present report concentrates on chlorination and purification of $TiCl_4$ [6].

Production of $TiCl_4$ is carried out by two different processes: Molten salt process and fluidized bed process. The choice of process depends on the content of TiO_2 in the feed. Generally speaking, the molten salt process is for the feed with relatively low content of TiO_2 in the feed.

Titanium sponge producers in CIS countries use molten salt process in order to produce $TiCl_4$. 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):

$$FeTiO_3 + x \cdot C \rightarrow y \cdot Fe + z \cdot (Fe^{2+}_{a}Ti^{3+}_{b}Ti^{4+}_{c})O_5 + w \cdot CO \qquad (1)$$

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 $TiCl_4$ 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 $TiCl_4$ 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].

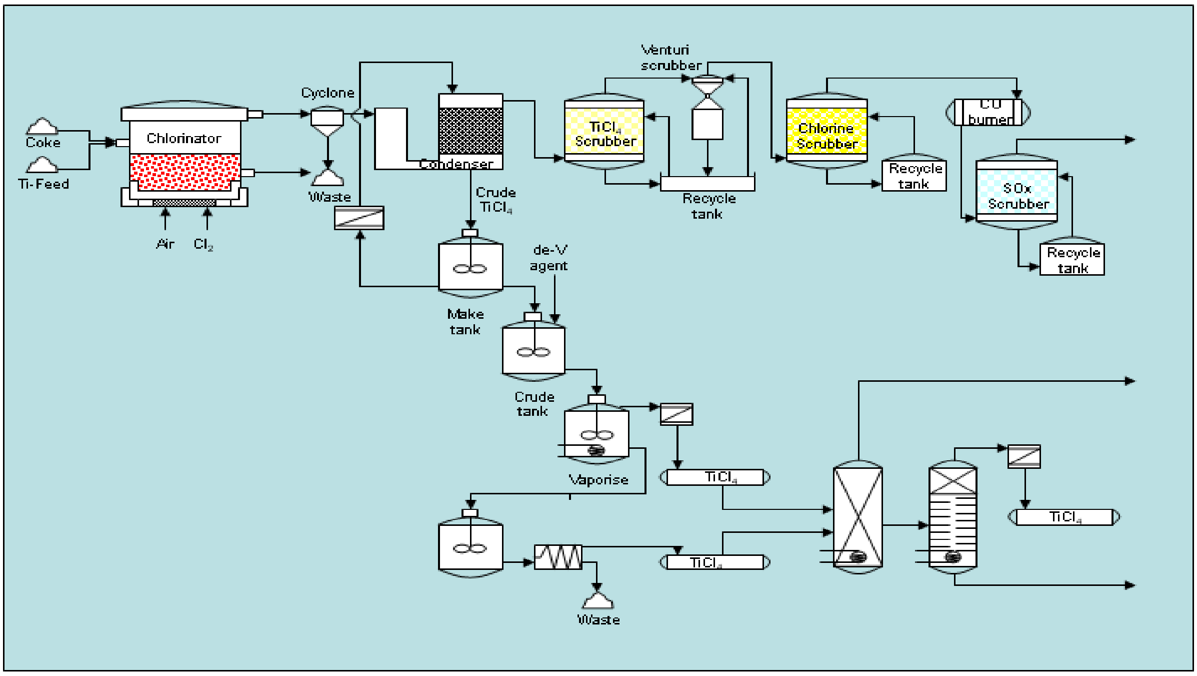

Fig. 1 Production of $TiCl_4$ by fluidized bed technology [8]

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 ~40 °C, and condensed to -10 – 0 °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 ~70 °C for removal of $SiCl_4(l)$. Then, it is further heated up to 140 °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 drossing.

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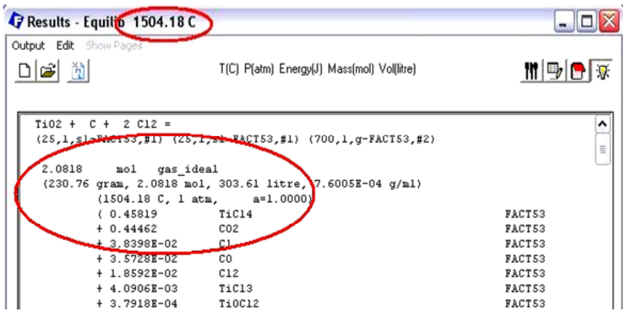
III. SIMULATION OF CHLORINATION PROCESS

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 °C as shown in Fig. 2, appropriate cooling is therefore required. This is why the temperature of chlorination process should be maintained at 1000 °C.

In Fig. 3, simulation result of chlorination reaction at various temperatures from 50 to 1000 °C was illustrated, in which $TiCl_4$ appeared to form from the temperature of 110 °C and at 1000 °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 °C. Interestingly, only solid $FeCl_2$ phase is expected to exist below 520 °C as shown in Fig. 4 (b).



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 TiO2 +  C +  2 Cl2 =
 (25,1,s1-FACT53,#1) (25,1,s1-FACT53,#1) (700,1,g-FACT53,#2)

  2.0818     mol   gas_ideal
  (230.76 gram, 2.0818 mol, 303.61 litre, 7.6005E-04 g/ml)
          (1504.18 C, 1 atm,     a=1.0000)
          ( 0.45819       TiCl4                          FACT53
          + 0.44462       CO2                            FACT53
          + 3.8398E-02    Cl                             FACT53
          + 3.5728E-02    CO                             FACT53
          + 1.8592E-02    Cl2                            FACT53
          + 4.0906E-03    TiCl3                          FACT53
          + 3.7918E-04    TiOCl2                         FACT53
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Fig. 2 Result of energy balance calculation of chlorination process showing maximum temperature increases up to 1504.18 °C

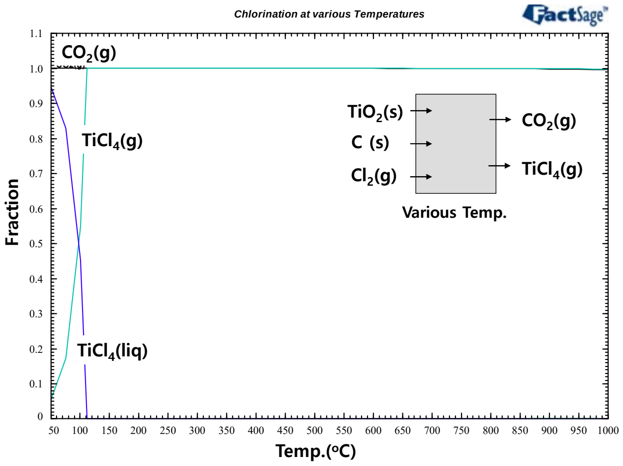

Fig. 3 Chlorination result simulated at various temperatures

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. $TiCl_4$ is supplied in drums and is transported by rail in cars, similar to those specified for liquid chlorine transportation. Due to its handing 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.

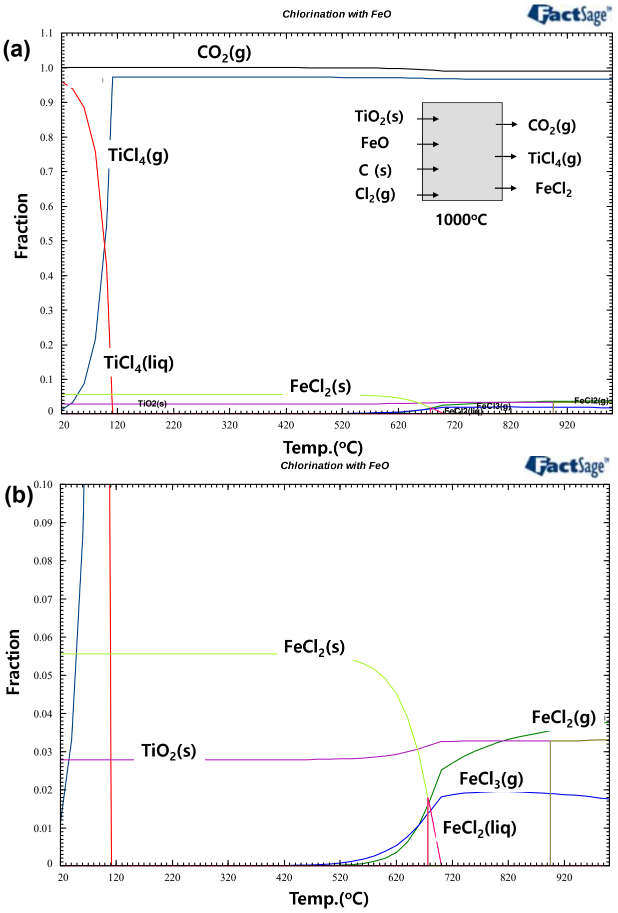

Fig. 4 Chlorination result simulated with impurity of FeO in the ore (a) and enlarged illustration of within the fraction of 0.1 (b)

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.

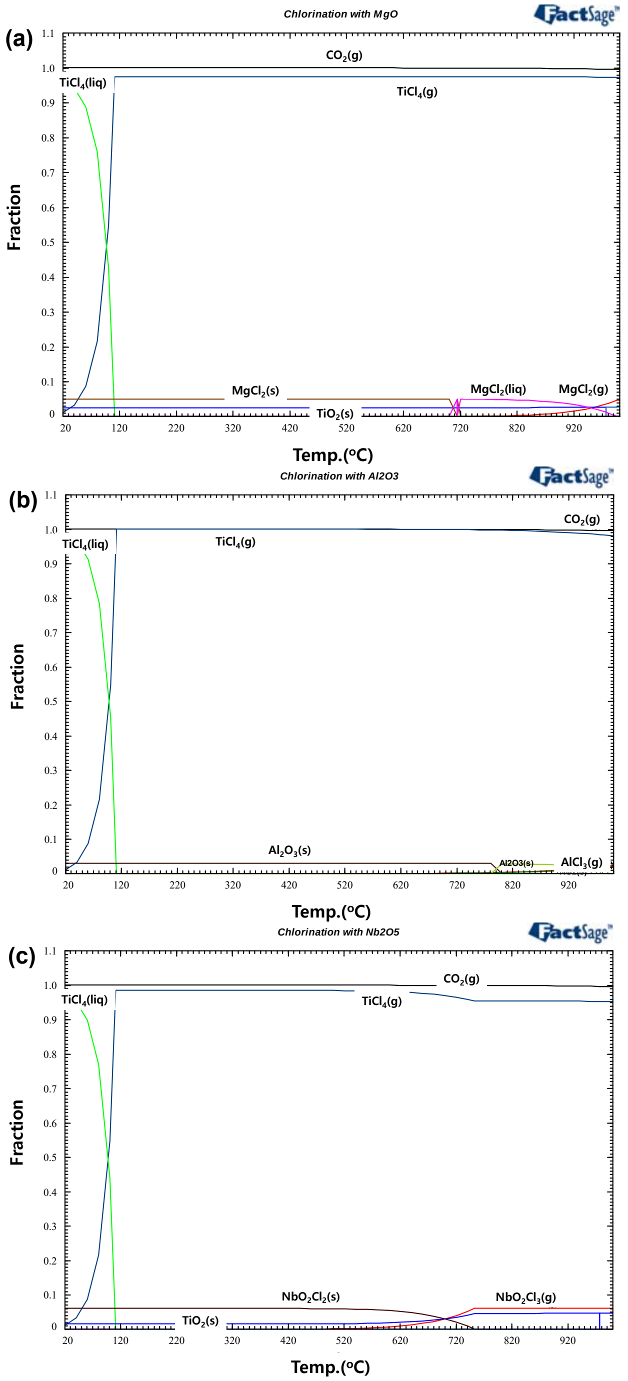

Fig. 5 Chlorination result simulated with impurities of MgO (a), Al_2O_3 (b) and Nb_2O_5 (c) in the ore

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REFERENCES

[1] S. Kosemura, E. Fukasawa, S. Ampo, T. Shiraki, and T.Sannohe, Nippon Steel Tech. Rep. No. 85, p. 31, 2002.

[2] H. Burger, D. Bessinger, and S. Moodley, The 7th International Heavy Minerals Conference, The Southern African Institute of Mining and Metallurgy, p. 187, 2009.

[3] C. O. Robichaud, A. E. Uyar, M. R. Darby, L. G.Zuker, and M. R. Wiesner, Evironn. Sci. Tech., vol. 43, p. 4227, 2008.

[4] A. J. Morris, and R. F. Jensen, Metall. Trans. B, vol. 7, p. 89, 1976.

[5] H. Judd, US Patent 3,112,178, 1963.

[6] W. E. Dunn, Metall. Trans. B, vol. 10, p. 271, 1979.

[7] P. D. Hoed, M. J. Freeman, A. Luckos, and J. Nell, Proceeding of the South African Chem. Eng. Congress, p. 1, September, 2003.

[8] P. C. Pistorius, and J. T. Ferdus Le Roux, Can. J. Metall. Mater. Sci., vol. 41, p. 289, 2002.

[9] P. K. Jena, E. A. Brocchi, and R. I. Garcia, Metall. Trans. B, vol. 28, p. 39, 1997.

[10] J. Kang, and T. H. Okabe, Mater. Trans., vol. 54, p. 1444, 2013.