



Recycling titanium metal scraps by utilizing chloride wastes

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Abstract

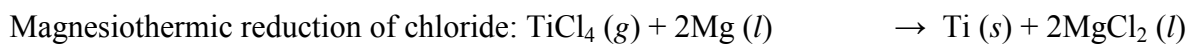
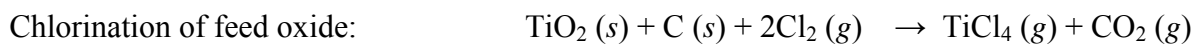
A novel process for recycling titanium metal scraps by utilizing the chloride wastes that is generated from the Kroll process or any other processes was investigated. Iron chlorides (e.g., FeCl_2 , FeCl_3) and metallic titanium (Ti) were reacted at temperatures ranging between 700 and 1300 K, and the chlorine in the iron chlorides was extracted in the form of TiCl_4 gas. It was found that the iron chloride wastes can be utilized as a source of chlorine for the production of TiCl_4 , and this process is demonstrated to be suitable for application to the treatment of titanium scraps. The behavior of chloride in the Fe-Ti-Cl-O system at 1100 K was thermodynamically analyzed. The investigation of the recycling process of the chloride wastes may be useful because it has the potential to improve the chlorine cycle in the Kroll process. If chlorine from the chloride wastes generated from titanium smelting can be efficiently recovered, the problem concerning the disposal of chloride wastes will be minimized and the loss of chlorine in the process will also decrease. The technique to recover chlorine from chloride wastes is also important, particularly when treating low-grade titanium ore, which will be an essential resource for the titanium industry in the future. This recycling process, which utilizes chloride wastes, can also be extended to other reactive metals such as rare earth metals and tantalum.



1 Introduction

Titanium (Ti) is used in various fields such as aerospace, marine, and automobiles; further, it is used for chemical plant materials, medical equipments, buildings, and several consumer products (glasses, golf clubs, etc.). Ti has such diverse uses because of its high strength, light weight, high-temperature performance, excellent flexibility, extraordinary corrosion-resistance, and biocompatibility characteristics. Ti has abundant mineral resources and is the 10th most abundant element and the 4th most common structural metal in the Earth's crust. It therefore possesses the potential to become a common and prosperous material in the future. However, the annual world production of metallic titanium, produced commercially by the currently used Ti production process, which is referred to as the Kroll process [1-5], has been approximately 66 kt in 2003 [6], and this production volume is substantially smaller than that of other common metals such as iron (Fe) and aluminum (Al) despite its abundant mineral resources. The reason for this low production volume is the high production cost resulting from the slow batch-type reduction process and the multi-step processing in the Kroll process.

The current production process of Ti involves three major chemical reactions that are listed as follows:



In the chlorination process, the titanium ore is reacted with chlorine gas (Cl_2) in a fluid bed reactor at approximately 1300 K under a carbon-saturated atmosphere [2], and the produced titanium tetrachloride (TiCl_4) gas is condensed by cooling. The major product obtained from this carbochlorination process is liquid TiCl_4 with impurities, which is then purified by distillation. The impurities in the TiCl_4 are removed and discarded as chloride wastes. The second step involves the magnesiothermic reduction of purified TiCl_4 using a magnesium (Mg) reductant at approximately 1100 K. This reduction process generates sponge-like solid Ti, which usually is referred to as sponge Ti, and liquid magnesium chloride (MgCl_2). The by-product MgCl_2 is extracted from sponge Ti either by tapping or by vacuum distillation. The recovered MgCl_2 is then converted into Mg and Cl_2 by molten salt electrolysis. These electrolysis products are then returned to the reduction and chlorination processes, respectively. One of the features of the Kroll process is that it efficiently facilitates the circulation of Mg and Cl_2 .

As shown in Figure 1, some amount of chloride wastes, such as iron chlorides (FeCl_x , $x = 2, 3$), are generated from the chlorination process because titanium oxide feed (TiO_2) contains impurities such as iron. Currently, there is no process that efficiently recycles or treats the chloride wastes that are generated from the Kroll process; therefore, they are discarded after chemical treatment. The treatment of chloride waste involves several problems such as disposal cost and environmental



issues, particularly in Japan. Furthermore, an additional amount of chlorine gas has to be purchased in order to compensate the chlorine loss caused during the generation of chloride wastes. In order to minimize the generation of chloride wastes, rutile ore or upgraded ilmenite (UGI) comprising of approximately 95% or more of titanium oxide is currently used as a raw material in the Kroll process. In the future, the amount of chloride wastes will increase as the production volume of titanium increases.

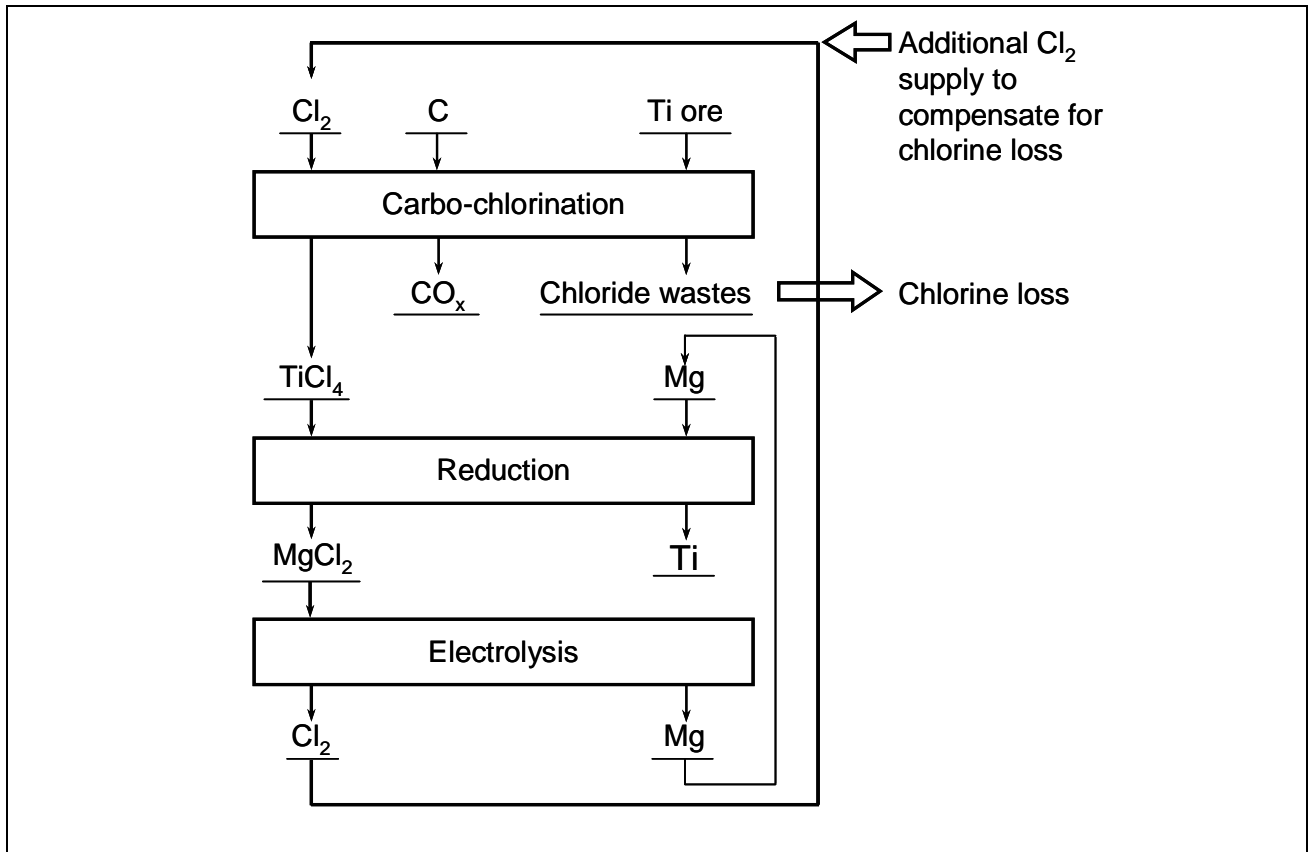


Figure 1: Chlorine cycle in the current titanium smelting process (Kroll process).

It is projected that titanium metal scraps will also increase in the future. These metal scraps are currently used for ferro-alloys, but it would be advantageous if this can be reused in the titanium smelting process for producing pure titanium.

Owing to the factors mentioned above, the authors are currently investigating a new process, as shown in Figure 2. The process investigated in this study recycles titanium metal scraps by utilizing the chloride wastes generated from the upgrading process of low-grade titanium ore or from the Kroll process. If this new process is feasible, not only titanium metal scraps can be recycled but also the chlorine in the chloride wastes generated from titanium smelting or any other process can be effectively recovered. Another benefit of this process is that low-grade titanium ore can be used in the Kroll process if chlorine can be efficiently recovered. In addition, this recycling process by the combination of titanium metal scraps and chloride wastes can also be extended to other reactive



metals such as rare earth metals and tantalum [7]. In order to establish this new environmentally-sound recycling process, thermodynamic analyses of the reactions between FeCl_x and Ti and its oxides (TiO_x) have been carried out in this study. Based on the results of the thermodynamic analysis, fundamental experiments were conducted in order to test the feasibility of this process.

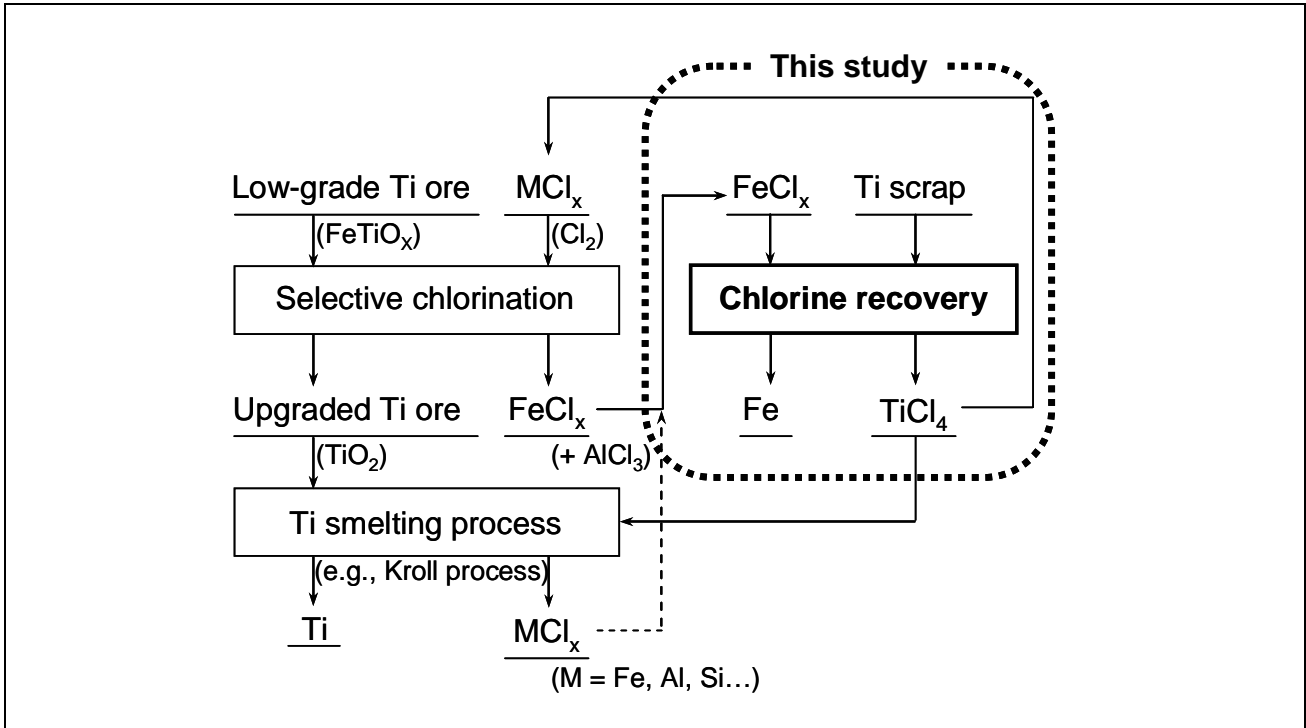


Figure 2: Flowchart of the new process discussed in this study.



2 Thermodynamic analysis of chlorination reactions

In this section, the reactions between FeCl_x and Ti and its oxides (TiO_x), which are essential for the new recycling process, are discussed using the thermodynamic information obtained from the literature reference [8].

Figure 3 (a) shows a chemical potential diagram for the Ti-Cl-O system that is calculated under a constant chlorine partial pressure ($p_{\text{Cl}_2} = 0.1$ atm) and plotted with oxygen partial pressure (p_{O_2}) as a function of temperature. The dotted lines plotted in the figure represents the equilibrium oxygen partial pressure under $\text{C (s)}/\text{CO (g)}$, $\text{CO (g)}/\text{CO}_2 (\text{g})$, and $\text{C (s)}/\text{CO}_2 (\text{g})$ equilibria. This figure shows that TiCl_4 is generated by the chlorination of TiO_2 when carbon or CO is introduced into the system under a high p_{Cl_2} atmosphere (e.g., $p_{\text{Cl}_2} = 0.1$ atm). When p_{O_2} is high, TiO_2 is thermodynamically stable and TiCl_4 cannot be obtained even under a high p_{Cl_2} atmosphere.

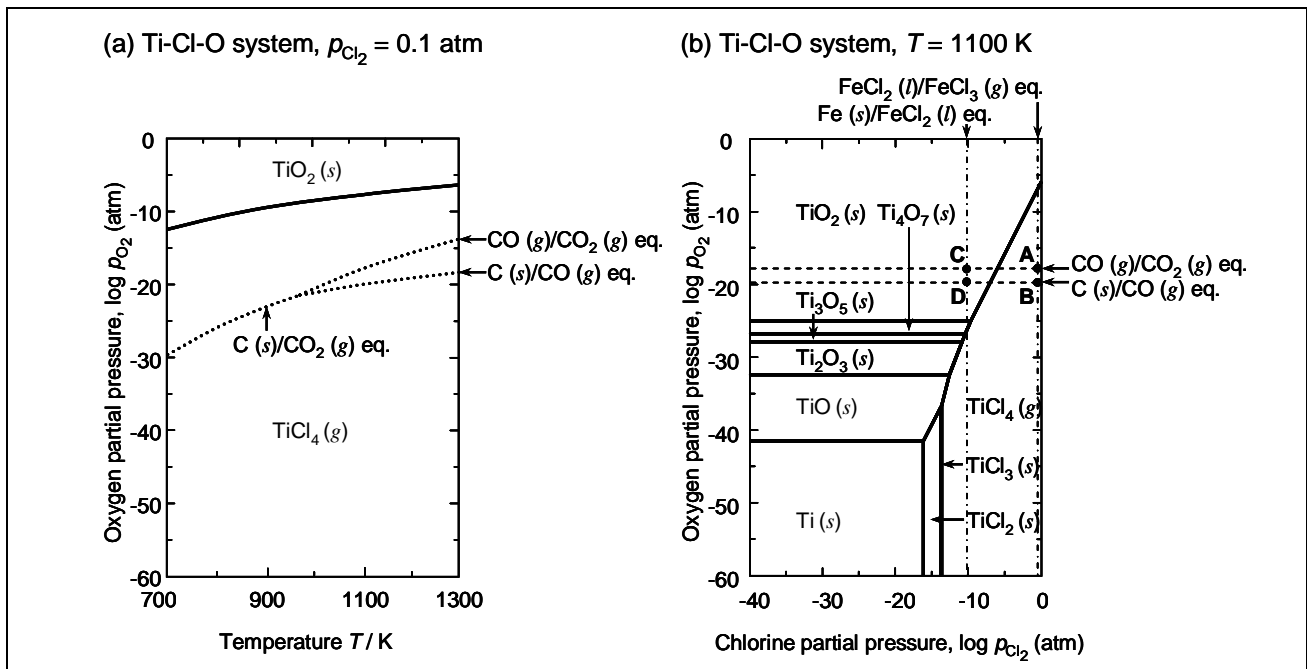


Figure 3: Chemical potential diagrams for the Ti-Cl-O system.

Figure 3 (b) shows the isothermal chemical potential diagram for the Ti-Cl-O system at 1100 K, plotted with p_{Cl_2} , as the abscissa and p_{O_2} , as the ordinate. In this figure, equilibrium oxygen partial pressure under $\text{C (s)}/\text{CO (g)}$ and $\text{CO (g)}/\text{CO}_2 (\text{g})$ equilibria and equilibrium chlorine partial pressure under $\text{FeCl}_2 (\text{l})/\text{FeCl}_3 (\text{g})$ and $\text{Fe (s)}/\text{FeCl}_2 (\text{l})$ equilibria are depicted as dashed lines and chain lines, respectively. The intersections of these lines are labeled as points A, B, C, and D. As shown in this figure, TiCl_4 is stable at points A and B ($\text{FeCl}_2 (\text{l})/\text{FeCl}_3 (\text{g})$ equilibrium, $p_{\text{Cl}_2} = 0.1$ atm) and the chlorination of TiO_2 proceeds when FeCl_3 is reacted with TiO_2 in the presence of carbon (s) or CO (g). TiO_2 is stable at points C and D ($\text{Fe (s)}/\text{FeCl}_2 (\text{l})$ equilibrium, $p_{\text{Cl}_2} = 8.0 \times 10^{-11}$ atm); therefore,



the chlorination of TiO_2 by FeCl_2 is difficult even at oxygen partial pressure under $\text{C (s)}/\text{CO (g)}$ equilibrium.

The chlorination of metallic titanium by FeCl_x at 1100 K can be analyzed by using a 3D chemical potential diagram of the Fe-Ti-Cl system, as shown in Figure 4. The most stable phases are shown as planes in the 3D space diagram. Figure 4 shows that Ti (s) does not coexist with FeCl_x at 1100 K. Point A in the figure is a three-component-equilibrium point for Fe (s) , $\text{FeCl}_2 (l)$, and $\text{TiCl}_4 (g)$. When Ti (s) is reacted with $\text{FeCl}_2 (l)$, $\text{TiCl}_4 (g)$ can be generated and the chlorination reaction of titanium terminates at the potential point A.



As shown in Figure 4, an intermetallic compound such as FeTi (s) might be generated during the chlorination process of titanium under a certain condition. However, if a large amount of FeCl_3 is introduced in the system, all the titanium is expected to be chlorinated to form TiCl_4 gas, as shown in the equation below.



It is worth noting that metallic titanium is a strong de-chlorination (chlorine extraction) agent at elevated temperatures in a system involving chloride, and it can be used as an agent for the recovery of chlorine from chloride waste.

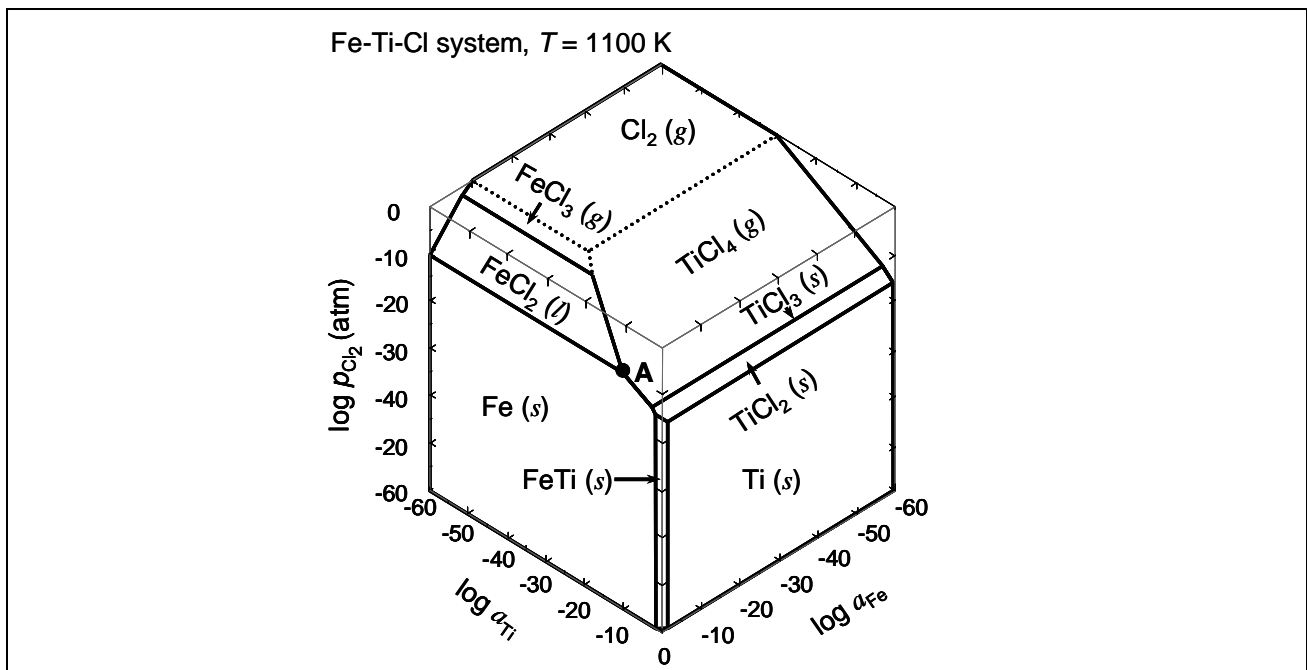


Figure 4: Chemical potential diagram for the Fe-Ti-Cl system at 1100 K.



Figure 5 shows the vapor pressure of titanium and iron chlorides as a function of reciprocal temperature. The vapor pressure of TiCl_4 is very high and different from that of FeCl_x ; therefore, it is easy to separate TiCl_4 from iron chlorides. The obtained Fe-free TiCl_4 can be returned to the titanium smelting process; thus, reducing both the chlorine loss and the amount of generated chloride wastes (Figure 1 and 2).

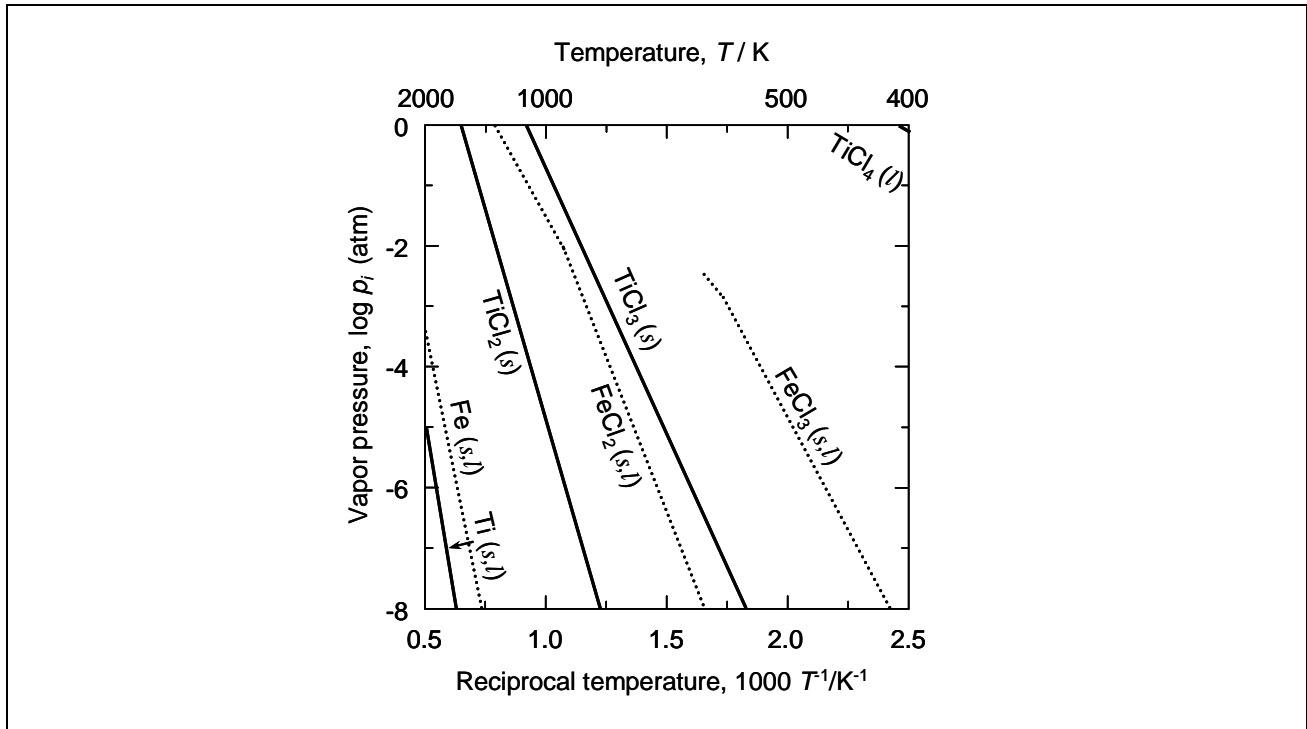


Figure 5: Vapor pressure of certain chlorides as a function of reciprocal temperature.

3 Chlorination experiments and results

Experimental work was carried out for obtaining titanium chloride by reacting metallic titanium and FeCl_2 . Figure 6 shows a schematic illustration of the experimental apparatus used for the chlorination of metallic titanium. A mixture of titanium powder (99.8%, 0.3 g) and FeCl_2 powder (99%, 2.0 g) was filled in a graphite crucible (I.D. = 27 mm) and then set in a quartz tube (I.D. = 41 mm, length = 450 mm). A NaOH gas trap sustained in a glass flange covered with SUS nets at both ends was also installed in the quartz tube near the gas outlet port. Before the experiment, the quartz tube, which was sealed with a silicone plug, was evacuated and then filled with Ar gas; the pressure within the quartz tube was maintained at approximately 0.1 atm. The quartz tube with the sample mixture and the NaOH gas trap is then introduced into an isothermal horizontal furnace and maintained at 1100 K. After the experiment, the residue in the graphite crucible, and the deposits within the quartz tube and on the surface of NaOH were recovered and then analyzed.

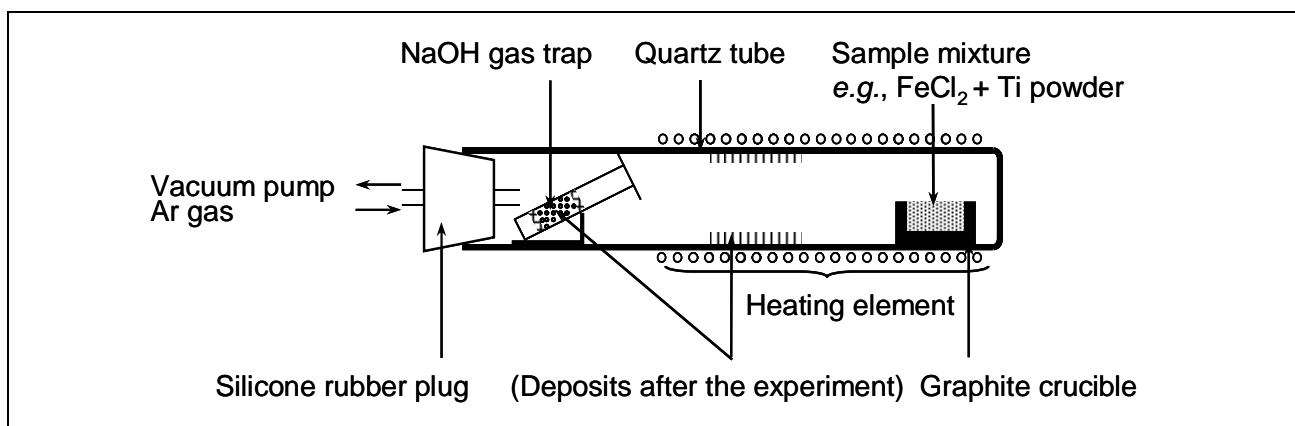


Figure 6: Experimental apparatus for the chlorination of titanium using FeCl_2 as the source of chlorine.

The residue obtained in the graphite crucible after heating as well as the deposits within the quartz tube and on the surface of NaOH were analyzed by X-ray fluorescence analysis (XRF); the results thus obtained are listed in Table 1. As shown in the table, TiCl_4 was formed and trapped on the NaOH gas trap, and the unreacted FeCl_2 was condensed and deposited within the quartz tube in the form of flakes. Figure 7 (a) and (b) show the X-ray diffraction analysis (XRD) patterns of the sample mixture before heating and of the residue obtained after heating. These XRD patterns indicate that the α -Ti phase disappeared and that α -Fe was obtained after heating. All the results are in good agreement with the thermodynamic analysis. This study demonstrated that the recovery of chlorine in FeCl_2 by Ti and the production of TiCl_4 are feasible. The authors are currently investigating the mechanism of chlorination in detail. They are also investigating the efficiency and mass balance of the following chlorination reaction:



Table 1: Analytical results of the samples before and after heating, and the deposits obtained within the quartz tube and on the surface of the NaOH gas trap after heating.

| Exp. # 050104 | Concentration of element i , C_i (mass%) ^a | | |
|--|---|------|------|
| | Ti | Fe | Cl |
| Initial sample in the graphite crucible before heating | 23.0 | 49.5 | 27.5 |
| Residue in the graphite crucible after heating | 9.9 | 90.1 | n.d. |
| Deposit inside the quartz tube | 2.7 | 54.6 | 42.7 |
| Deposit on the surface of the NaOH gas trap (white) | 43.3 | 3.3 | 53.4 |

a: Determined by XRF analysis, n.d. = not detected (below 0.1%).

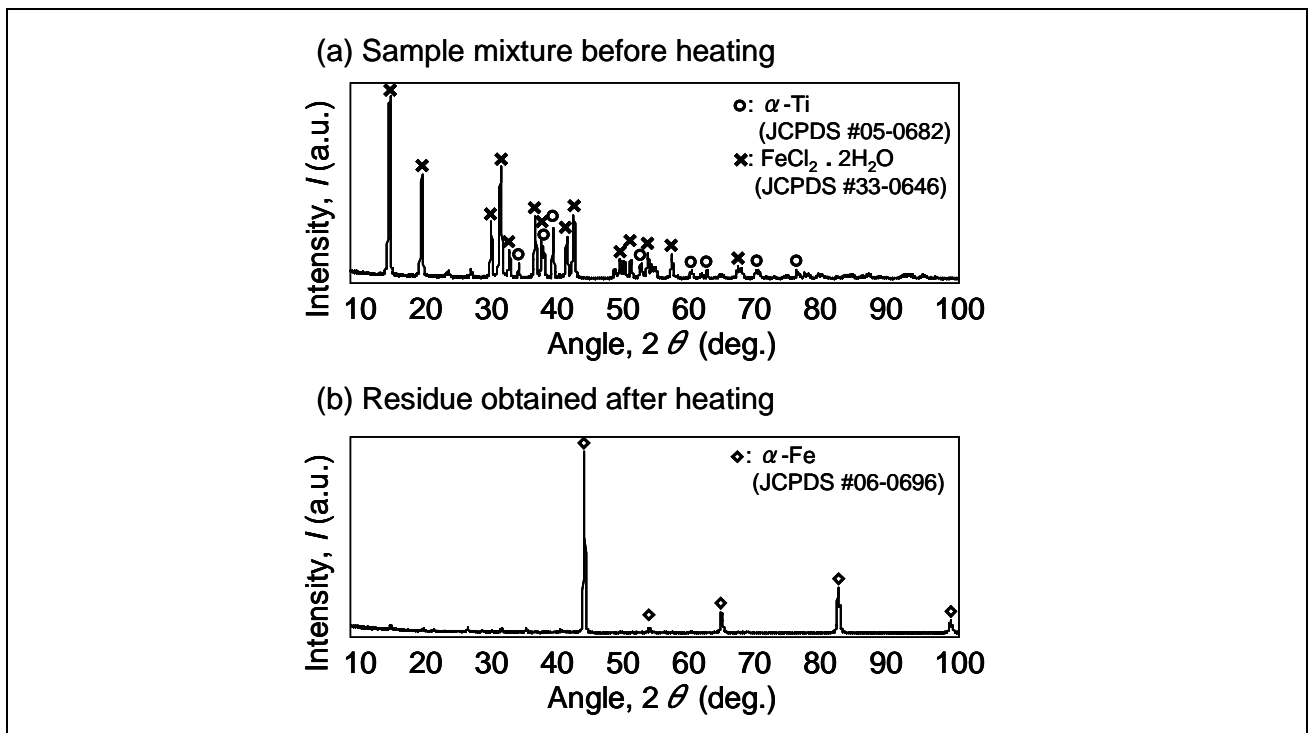


Figure 7: XRD patterns of the sample before heating (a) and of the residue after heating (b) (Exp. # 050104).

4 Conclusions and remarks

The feasibility of the new recycling process of chlorine in the chloride wastes by titanium metal scraps is discussed from a thermodynamic viewpoint, and some fundamental experiments were carried out. It was demonstrated that metallic titanium can be used for the recovery of chlorine from chloride wastes, such as FeCl_2 , and TiCl_4 can also be obtained using this process. The experimental results that were obtained are consistent with those of the thermodynamic analysis.

Currently, the detailed mechanism of chlorination, the mass balance of the chlorination reaction of titanium metal scraps, and the recycling process of other reactive metal scraps by chloride wastes are under investigation. The development of a new environmentally-sound process for the recycling of reactive metal scraps by utilizing the chloride wastes is an important issue for an environmentally sustainable society.



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