

## IRON REMOVAL FROM TITANIUM ORE USING SELECTIVE CHLORINATION AND EFFECTIVE UTILIZATION OF CHLORIDE WASTES

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### Abstract

Iron removal from titanium ore using selective chlorination and the effective utilization of chloride wastes generated from the titanium production process (Kroll process) were investigated in this study. The thermodynamic analyses of the chlorination reactions in the Ti-Fe-O-Cl system were carried out prior to the fundamental experimental work, and the conditions for the chlorination experiments were optimized. The iron in the titanium ore was selectively chlorinated by reacting low-grade titanium ore (ilmenite) and metal chloride ( $MCl_x$ ,  $M = Mg, Ca$ , etc.) at 1100 K under a nitrogen atmosphere, and low-iron titanium ore and iron chloride ( $FeCl_x$ ) were obtained. Chlorine in the  $FeCl_x$  produced by selective chlorination was recovered as  $TiCl_4$  by reacting  $FeCl_x$  and metallic titanium at 1100 K under an argon atmosphere. The recycling processes investigated in this study, which utilize low-grade ore or chloride wastes, are useful because the titanium scrap and chloride wastes are expected to increase in the future. This process, based on scrap combination, has the potential for developing a new environmentally sound technique of chloride metallurgy.

### Introduction

Titanium (Ti) is an extremely strong, lightweight, and high corrosion-resistant metal. It is therefore used in various fields such as aerospace, marine, chemical plant materials, and for the production of several consumer products (glasses, golf clubs, etc.). Currently, the annual world production of titanium is approximately 50 kt [1], and it is steadily increasing. However, this production volume of titanium is 1 / 16000 times less than that of iron (Fe) and 1 / 400 times less than that of aluminum (Al). As titanium is the 10th most abundant element in the earth's crust and its oxide ore is widely available as a natural resource, it has a potential to be a common metal in the future. One of the major reasons for this current low production volume despite the abundance of resources is the high production cost of titanium due to low productivity of the titanium reduction process.

Currently, titanium is produced commercially by the Kroll process [2-5], which involves three major steps. The first step is the chlorination of titanium ore using chlorine gas ( $Cl_2$ ) under a

carbon-saturated atmosphere, followed by the purification of titanium chloride ( $\text{TiCl}_4$ ) produced during the chlorination. The second step is the reduction of  $\text{TiCl}_4$  using a magnesium ( $\text{Mg}$ ) reductant; sponge titanium and magnesium chloride ( $\text{MgCl}_2$ ) are produced in this step. In the third step,  $\text{MgCl}_2$  is recovered and converted into  $\text{Mg}$  and  $\text{Cl}_2$  by molten salt electrolysis. These products are then returned to the chlorination and reduction processes, respectively. Efficient circulation of  $\text{Mg}$  and  $\text{Cl}_2$  is a feature of the Kroll process. However, a considerable amount of chloride wastes, such as iron chlorides ( $\text{FeCl}_x$ ,  $x = 2, 3$ ), are generated from the chlorination process. This is because titanium ore contains impurities such as iron ( $\text{Fe}$ ). The chloride scraps are discarded and cause several problems such as disposal cost and environmental issues, especially in Japan. Furthermore, an additional amount of chlorine gas has to be purchased to compensate for the chlorine loss caused by the generation of chloride wastes. These wastes also lead to environmental issues because an effective method to recycle them has not yet been established. Hence, upgraded ilmenite (UGI) that contains titanium oxide ( $\text{TiO}_x$ ) of approximately 95% purity is currently used as a raw material in the Kroll process in order to minimize the generation of chloride wastes. Although Japan completely relies on imports for its supply of titanium ore and labor costs are very high, it holds approximately 40% of the market share in sponge titanium production; further, a large amount of chloride wastes is treated by means of expensive procedures.

Due to the factors mentioned above, the authors are currently investigating two new processes, which are shown in Figure 1. One is iron removal from low-grade titanium ore, which is much cheaper than UGI, using selective chlorination (denoted as process number “1” in Figure 1). The other is the effective utilization of chloride wastes generated from the Kroll process (denoted as process number “2” in Figure 1). If the chlorine in the chloride wastes generated from titanium smelting and titanium scrap, which will increase in the future, can be effectively utilized and recovered, the problem of chloride waste disposal can be minimized and the loss of chlorine in the Kroll process can be decreased. In addition, low-grade titanium ore can be used in the Kroll process if an effective recovery process for chlorine is established. Hence, thermodynamic analyses of the reactions between  $\text{MCl}_x$  ( $M = \text{Fe}, \text{Ca}, \text{Mg}, \text{etc.}$ ) and titanium or its oxides ( $\text{TiO}_x$ ) have been carried out in this study. By means of analytical results, fundamental experimental work was conducted for demonstrating the feasibility of the process.

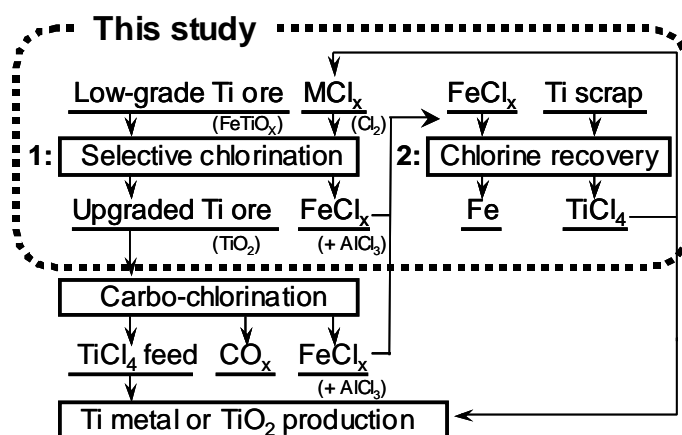
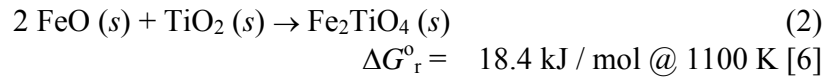
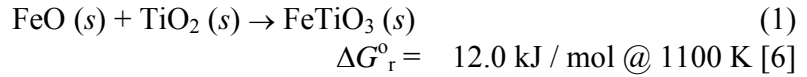


Figure 1. Flowchart of two processes discussed in this study.

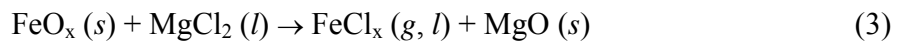
## Thermodynamic Analysis

### Iron Removal from Titanium Ore Using Selective Chlorination

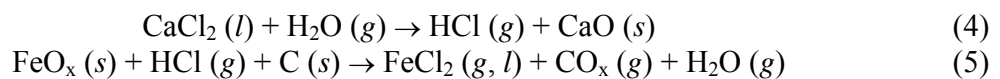
While discussing the thermodynamic properties of the Fe-Ti-O-Cl system at elevated temperatures, it is essential to consider the existence of  $\text{FeTi}_x\text{O}_y$  complex oxides. However, the Gibbs energy changes of the following reactions are not large compared to those of the redox reactions in the related systems.



Furthermore, when the activity of  $\text{FeO}_x$  decreases due to the formation of complex oxides, the activity of  $\text{TiO}_2$  decreases by almost the same magnitude. Titanium ore is therefore considered to be a mixture of  $\text{TiO}_x$  and  $\text{FeO}_x$  in order to facilitate a simple discussion. Figure 2 (a) and (b) show the isothermal chemical potential diagrams of the Fe-Cl-O and Ti-Cl-O systems, respectively, plotted as a function of chlorine partial pressure,  $p_{\text{Cl}_2}$ , and oxygen partial pressure,  $p_{\text{O}_2}$ , at 1100 K. The thermodynamically stable phases are shown in these figures. Furthermore, the oxygen partial pressure under the C / CO and CO / CO<sub>2</sub> equilibria is depicted for reference. Figure 3 shows the combined isothermal chemical potential diagram of the Fe-Cl-O (solid lines) and Ti-Cl-O (dotted lines) systems at 1100 K as a function of  $p_{\text{Cl}_2}$  and  $p_{\text{O}_2}$ . The oxygen partial pressure under the C / CO and CO / CO<sub>2</sub> equilibria as well as under the H<sub>2</sub> / H<sub>2</sub>O equilibrium is depicted in this figure. Furthermore, the equilibrium chemical potentials under the CaO / CaCl<sub>2</sub>, MgO / MgCl<sub>2</sub>, and H<sub>2</sub>O / HCl equilibria are depicted as dashed and chain slanting lines. The hatched region in Figure 3 is the chemical potential region in which  $\text{TiO}_x$  and  $\text{FeCl}_x$  are thermodynamically stable. In this potential region, the chlorination of  $\text{TiO}_x$  does not proceed whereas the chlorination of  $\text{FeO}_x$  proceeds. When the chemical potential is controlled in the hatched region, iron in the titanium ore is chlorinated to form  $\text{FeCl}_2$  or  $\text{FeCl}_3$  and iron free  $\text{TiO}_2$  can be obtained. Since the vapor pressure of  $\text{FeCl}_x$  is greater than 0.1 atm at 1100 K (see Figure 5 for reference), the iron in the ore can be selectively removed through the gas phase, and highly pure  $\text{TiO}_x$  can be obtained from a thermodynamic viewpoint. For example, when titanium ore containing iron is mixed with MgCl<sub>2</sub> and heat treated at 1100 K under the presence of carbon, the iron in the ore can be chlorinated by the following reaction.



The CaO / CaCl<sub>2</sub> equilibrium line in Figure 3 does not pass through the hatched region; therefore, CaCl<sub>2</sub> itself is not a strong chlorinating agent. However, when H<sub>2</sub>O gas is introduced into the system under the presence of CaCl<sub>2</sub>, HCl gas is generated and the chlorination of iron in the ore using HCl gas can proceed according to the following reactions.



Furthermore, the formation of complex oxides (e.g. CaTiO<sub>x</sub>) may accelerate the chlorination reaction by CaCl<sub>2</sub> under the presence of H<sub>2</sub>O.

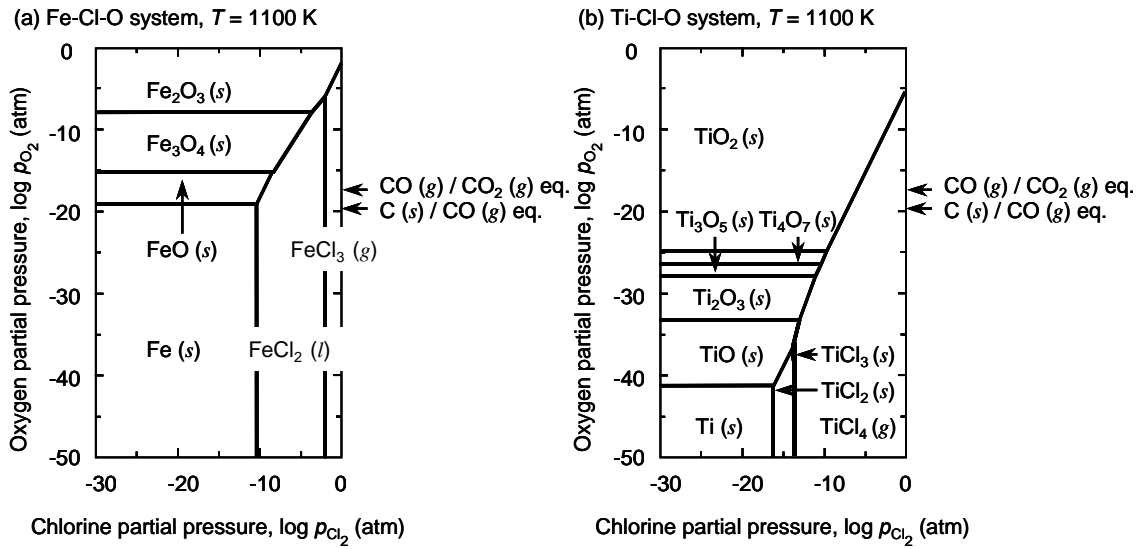


Figure 2. Chemical potential diagram of the Fe-Cl-O (a) and Ti-Cl-O (b) systems at 1100 K.

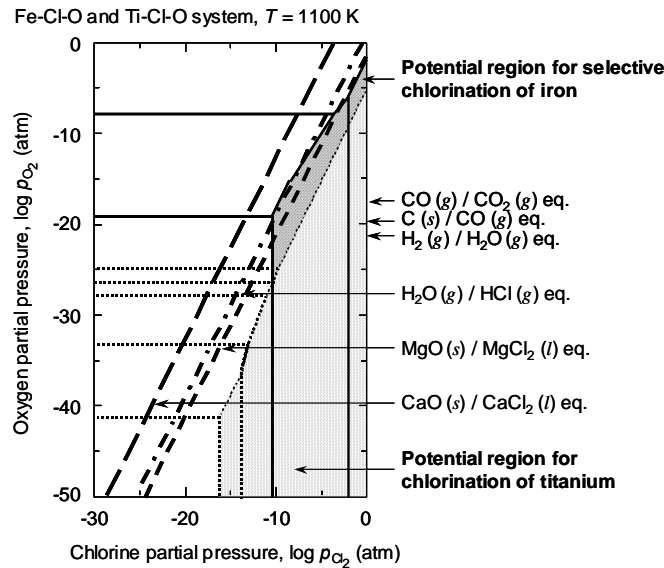
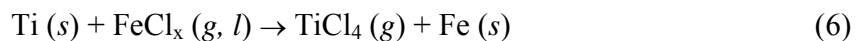


Figure 3. Combined chemical potential diagram of the Fe-Cl-O (solid line) and Ti-Cl-O (dotted line) systems at 1100 K. It is a combination of Figures 2 (a) and (b).

### Chlorine Recovery from Chloride Wastes

In order to recover chlorine from the chloride wastes, the extraction of chlorine from  $\text{FeCl}_x$  using metallic titanium is considered from a thermodynamic viewpoint. Figure 4 shows the 3-D chemical potential diagram of the Fe-Ti-Cl system at 1100 K. The most stable phases are shown as a plane in the 3-D space. In the figure, point A shows the chemical potential of  $\text{FeCl}_2(l)$  in equilibrium with the  $\text{FeCl}_3$ - $\text{TiCl}_4$  gas mixture. This figure also shows that  $\text{Ti}(s)$  does not co-exist with  $\text{FeCl}_x$  at 1100 K. Therefore,  $\text{TiCl}_4(g)$  can be generated by the following reaction by reacting  $\text{FeCl}_x(g, l)$  and  $\text{Ti}(s)$ .



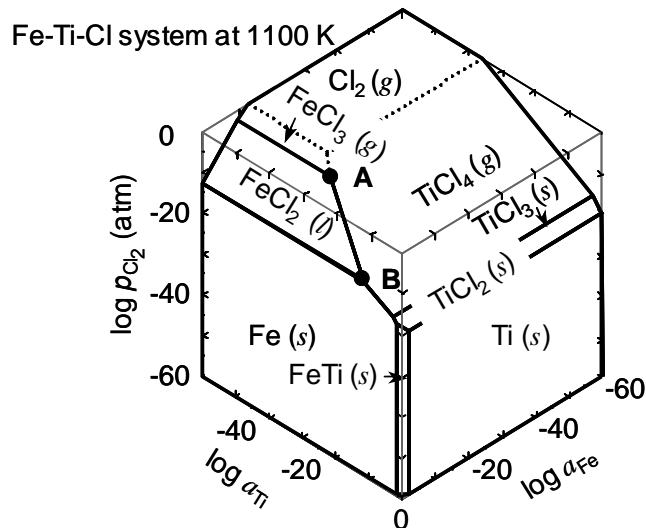


Figure 4. Chemical potential diagram of the Fe-Ti-Cl system at 1100 K.

According to Figure 4, an intermetallic compound, such as  $\text{FeTi} (s)$ , may be formed during the chlorination reaction of titanium under certain conditions. However, all titanium are expected to be chlorinated by the addition of a large amount of  $\text{FeCl}_x$  into the system at a low  $p_{\text{O}_2}$ . The figure shows that chlorine in iron chlorides can be extracted by metallic titanium, and  $\text{TiCl}_4$  gas is obtained as far as  $\text{FeCl}_x$  exists in the system.

The  $\text{TiCl}_4$  gas obtained from the chlorination reaction can be transferred through the gas phase and recovered at lower temperatures by condensation. Figure 5 shows the vapor pressure of titanium and iron chlorides as a function of reciprocal temperature. Since the vapor pressure of  $\text{TiCl}_4$  is very high and different from that of  $\text{FeCl}_x$  [6], it is easy to separate  $\text{TiCl}_4$  from iron chlorides. The obtained highly pure  $\text{TiCl}_4$  can be returned to the titanium smelting process, and this reduces both the chlorine loss and the amount of chloride wastes (see Figure 1).

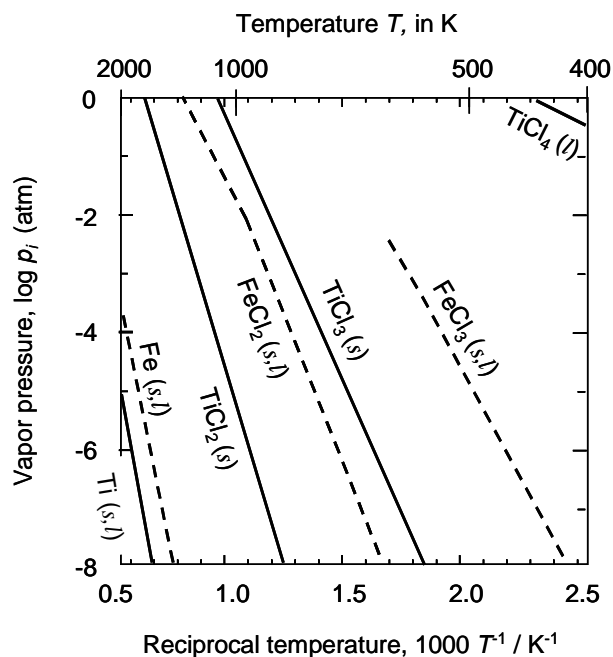


Figure 5. Vapor pressure of chlorides as a function of reciprocal temperature.

## Experiments and Results

### Iron Removal from Titanium Ore Using Selective Chlorination

On the basis of the thermodynamic analysis mentioned above, the authors are currently conducting experimental work for selective chlorination by reacting titanium ore and  $\text{MgCl}_2$  or  $\text{CaCl}_2 + \text{H}_2\text{O}$ . Figure 6 shows the schematic illustration of the experimental apparatus for the selective chlorination of titanium ore. Approximately 4.0 g of upgraded ilmenite (UGI), containing 2.3 mass% of iron, and 2.0 g of  $\text{MgCl}_2$  were mixed and filled in a graphite crucible installed in a furnace, as shown in Figure 6. The mixture was heated at 1100 K for 1 h under a nitrogen atmosphere. In another experiments, approximately 3.0 g of ilmenite ore, containing 44.5 mass% of iron, was mixed with 2.0 g of  $\text{CaCl}_2$  and reacted at 1100 K for 6 h and at 1300 K for 2 h in the graphite crucible under a  $\text{N}_2 + \text{H}_2\text{O}$  ( $p_{\text{H}_2\text{O}} = 0.04$  atm) atmosphere. After the experiment using  $\text{MgCl}_2$ , the solid sample obtained in the graphite crucible and the deposit in the condenser were analyzed.

The obtained samples were analyzed by X-ray fluorescence spectroscopy (XRF), and the results are listed in Table I. These results show that the iron concentration of the titanium ore decreased to 0.43 mass% and iron removal from titanium ore was successfully carried out. Figure 7 shows the X-ray diffraction (XRD) pattern of the deposit in condenser after heating. This pattern indicates that  $\text{FeCl}_2$  was generated and deposited in the quartz tube. The above-mentioned results indicate that the following reaction occurred, and they are in good agreement with the thermodynamic analysis.

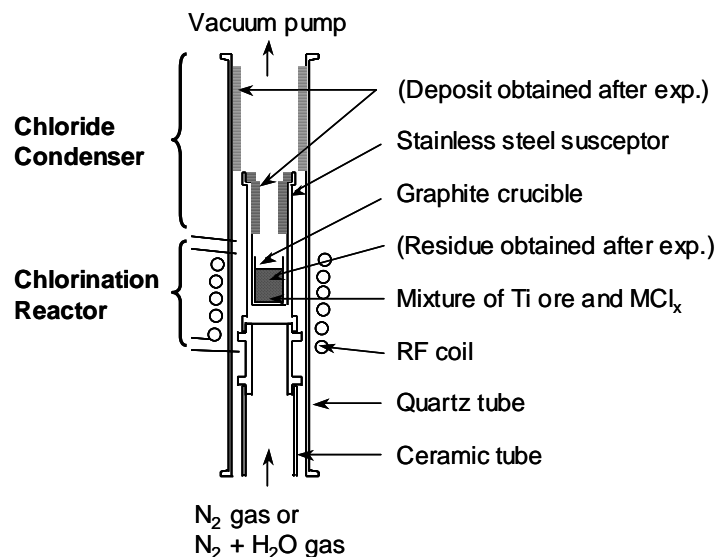
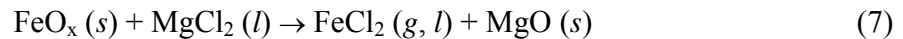


Figure 6. Experimental apparatus for the selective chlorination of titanium ore using  $\text{MgCl}_2$  or  $\text{CaCl}_2 + \text{H}_2\text{O}$  as a chlorine source.

The representative results for the selective chlorination of ilmenite using  $\text{CaCl}_2 + \text{H}_2\text{O}$  are listed in Table II. These results show that the iron concentration of ilmenite decreased to 8.52 mass% and the iron removal from titanium ore was successfully carried out. The XRD pattern of the deposit after heating is shown in the same pattern of Figure 7. This XRD pattern indicates that  $\text{FeCl}_2$  was obtained after heating and deposited in the quartz tube. These results indicate that the selective chlorination of iron (e.g. equations (4) and (5)) occurred during the experiment but the iron content in the sample after the experiment was substantially higher than the estimated value. The authors are currently investigating the detailed mechanism of the chlorination reaction and are optimizing the conditions for selective chlorination.

Table I. Analytical results of titanium ore and the residue obtained by the selective chlorination of titanium ore.

	Concentration of element $i$ , $C_i$ (mass%) <sup>a</sup>				
	Ti	Fe	Si	Al	V
Ti ore <sup>b</sup>	95.10	2.29	0.41	0.12	0.75
After experiment	96.45	0.43	0.44	0.37	1.50

a: Value determined by XRF analysis.

b: Upgraded ilmenite (UGI) produced in India.

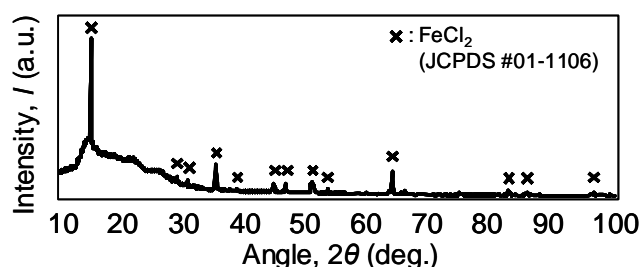


Figure 7. XRD pattern of the deposit in the chloride condenser. The sample powder was sealed with Kapton film before analysis.

Table II. Analytical results of titanium ore and the residue obtained by the selective chlorination of titanium ore.

	Concentration of element $i$ , $C_i$ (mass%) <sup>a</sup>				
	Ti	Fe	Si	Al	V
Ti ore <sup>b</sup>	44.56	47.70	2.24	0.96	0.61
After experiment	86.84	8.52	0.28	n.d.	0.88

a: Value determined by XRF analysis.

b: Ilmenite from Vietnam.

## Chlorine Recovery from Chloride Wastes

On the basis of the thermodynamic analysis mentioned above, the authors are currently conducting experimental work for obtaining titanium chloride by reacting metallic titanium and FeCl<sub>2</sub>. Figure 8 shows the schematic illustration of the experimental apparatus for the chlorination of metallic titanium. Approximately 0.3 g of titanium powder and 2.0 g of FeCl<sub>2</sub> powder were reacted at 1100 K for 6 h in the graphite crucible under an argon atmosphere. After the experiment, the obtained solid sample in the graphite crucible and the deposits in the quartz tube and on the silicone rubber plug were analyzed.

The deposited samples (deposited on the rubber plug and quartz tube) were analyzed by XRF and the results are listed in Table III. These results show that Fe-free TiCl<sub>x</sub> and FeCl<sub>2</sub> were successfully obtained on the rubber plug and in the quartz tube, respectively. The results indicate that the following reaction occurred in the system, which is in good agreement with the thermodynamic analysis.



Figures 9 (a) and (b) show the XRD patterns of the powder before heating and the obtained solid after heating. These XRD patterns indicate that the α-Ti phase disappeared and that α-Fe and FeCl<sub>2</sub>·2H<sub>2</sub>O were obtained after heating. In this study, it was demonstrated that the chlorination of titanium by FeCl<sub>x</sub> is feasible, and Fe-free TiCl<sub>x</sub> was obtained. The authors are currently investigating the mass balance of the chlorination reaction and the behavior of chlorine during the reaction.

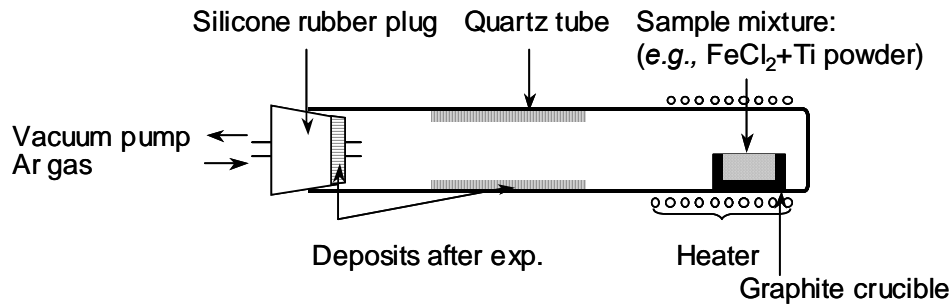


Figure 8. Experimental apparatus for the chlorination of titanium using FeCl<sub>2</sub> as a chlorine source.

Table III. Analytical results of the samples before and after heating and the samples deposited in the quartz tube and on the rubber plug.

	Concentration of element <i>i</i> , <i>C<sub>i</sub></i> (mass%) <sup>a</sup>		
	Ti	Fe	Cl
Sample before heating	18.4	45.3	36.2
Residue after heating	9.8	80.1	9.0
Deposit in quartz tube after heating	3.5	50.4	46.1
Deposit on rubber after heating	64.9	0.9	34.1

a: Value determined by XRF analysis.



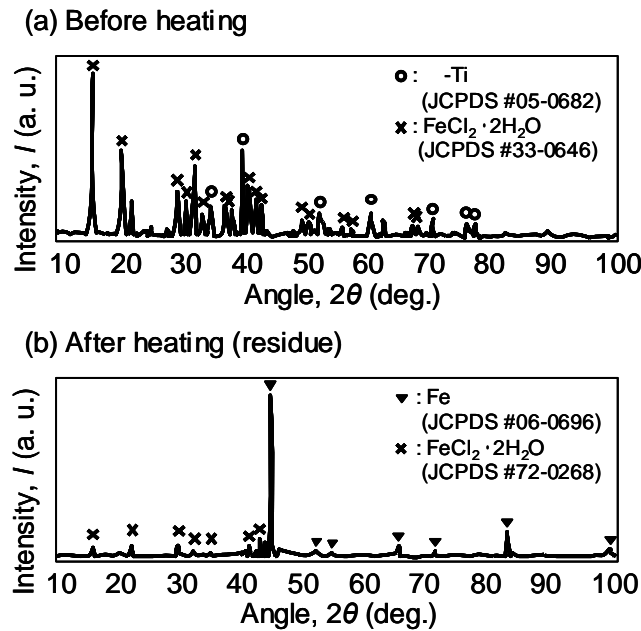


Figure 9. XRD patterns of the sample before heating (a) and the residue after heating (b).

### Conclusions and Future Remarks

The feasibility of the new chlorination processes for iron removal from titanium ore (UGI or ilmenite) using selective chlorination and the effective utilization of chloride wastes generated from the Kroll process are discussed from a thermodynamic viewpoint. For the purpose of minimizing chlorine loss, recovery of chlorine from the chloride wastes generated from titanium smelting is also discussed.

Iron removal from titanium ore using selective chlorination proceeds when iron containing titanium ore is reacted with  $\text{MgCl}_2$  or  $\text{CaCl}_2 + \text{H}_2\text{O}$ . In the chlorine recovery experiments, it was demonstrated that chlorine in  $\text{FeCl}_2$  can be extracted using metallic titanium, and Fe-free  $\text{TiCl}_x$  was obtained from this process. These experimental results were consistent with those of the thermodynamic analysis.

At present, the iron content in the sample obtained after selective chlorination is high compared to that of the thermodynamic analysis. The detailed mechanism of chlorination is under investigation. Furthermore, selective chlorination of titanium ore using various chlorine sources (e.g.,  $\text{CCl}_4 + \text{H}_2\text{O}$ ,  $\text{TiCl}_4$ ) will be studied for the purpose of developing an efficient process for producing Fe-free titanium ore. The behavior of chlorine and the mass balance of the chlorination reaction of titanium scrap will also be investigated to establish a new environmentally sound process for the recovery of chlorine from chloride wastes.

If chlorine can be effectively recovered from chloride wastes generated from titanium smelting, the chloride waste disposal problem can be minimized, and the loss of chlorine in the Kroll process can also be decreased. In addition, in the future if an effective chlorine recovery process is established, a new environmentally sound technique of chloride metallurgy using low-cost low-grade ore can be developed.

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