Production of Titanium Dioxide Directly from Titanium Ore through Selective Chlorination Using Titanium Tetrachloride

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For the production of high-grade titanium dioxide (TiO₂) directly from titanium ore (Ti ore), a fundamental study on the development of a novel carbo-selective-chlorination method using titanium tetrachloride (TiCl₄) as a chlorinating agent was carried out. In order to selectively remove iron directly from low-grade Ti ore (mainly FeTiO₃), Ti ore and carbon powder were set in a gas-tight quartz tube that was then placed in a horizontal furnace to react with TiCl₄ at 1100 K. In the experiments, various types of Ti ores produced in different countries were reacted with TiCl₄ for durations from 4 to 6 h. Under certain conditions, the iron in the titanium ore was removed as iron chloride (FeCl₂), and 98% TiO₂ was obtained after the experiments. The effectiveness of TiCl₄ as a chlorinating agent for the carbo-selective-chlorination of iron oxide was verified in this study. Thus, it was demonstrated that the carbo-selective-chlorination is feasible for the selective removal of iron directly from low-grade titanium ore containing 51% TiO₂ to produce high-grade TiO₂ feed in a single step. [doi:10.2320/matertrans.M-M2013843]

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1. Introduction

Titanium (Ti) is produced by the Kroll process in current industrial manufacturing. The principal procedures of the Kroll process include (i) the chlorination of a high-grade TiO₂ feed by chlorine gas (Cl₂) in the presence of carbon to produce TiCl₄ (the chlorination process), (ii) the reduction of TiCl₄ by magnesium (Mg) to produce Ti metal, and (iii) the electrolysis of magnesium chloride (MgCl₂).^{1,2} There are several important issues involved in the effective operation of the Kroll process, such as increasing the efficiency of the electrolysis, controlling the heat produced by the reduction reaction, and reducing the amounts of chloride wastes produced.³ Among these issues, one of the most important issues is the grade (or purity) of the TiO₂ feed for the chlorination process.

Currently, high-grade TiO₂ with a purity above 95% is used for the Ti smelting process to decrease the chlorine loss, prevent pipe clogging, and prevent damage to the refractory materials in the chlorinator. However, the use of a high-grade TiO₂ feed has become more difficult nowadays, mainly because the price of high-grade TiO₂ feed has increased owing to the increase in consumption of TiO₂ feed in China and other developing countries.⁴ In this situation, Ti metal production companies in Japan have started to investigate the usage of lower grade feed, of about 90% TiO₂ feed, instead of the 95% TiO₂ feed.^{4,5}

However, this approach is still in limited use owing to certain unresolved technical problems in the current production process. For example, when low-grade TiO₂ feed is used in the chlorinator in the chlorination process, pipe clogging occurs as a consequence of the condensation of chlorides such as iron chlorides (FeCl_x, [$x = 2, 3$]).^{3,31} In addition, the generation of chloride wastes induces chlorine loss in the Kroll process, because Cl₂ is recycled and circulated in the Kroll process when producing not any chloride wastes.

Furthermore, if a low-grade TiO₂ feed containing certain amount of alkaline metals or alkaline earth metals is used as a feedstock, damage to the refractory materials inside the chlorinator occurs because such metal chlorides lead to a corrosive environment at high temperatures.

Currently, high-grade TiO₂ feed is produced by the Becher process,^{7,8} Benilite process,^{9–11} and slag process¹² with post-treatment (the UGS process). However, these processes have drawbacks such as multiple steps for removal of iron or the production of a large amount of acid aqueous waste solution.³ Some countries such as Japan have strict environmental regulations for the disposal and treatment of industrial wastes. Therefore, when the upgrading of low-grade Ti ore is considered in these countries, an environmentally sound process that does not produce a large amount of acid aqueous waste solution or that can recycle the wastes must be established.

Extensive studies have been carried out to improve the current processes for the effective production of high-grade TiO₂ feed at reduced costs, and selective chlorination using a pyrometallurgical method has been found to be promising for upgrading low-grade Ti ores.^{4,6,13–26} Comprehensive research was conducted on selective chlorination using a pyrometallurgical method. For example, selective chlorination of Ti ore by Cl₂ gas in the presence of carbon^{13–16} or under a CO/Cl₂ mixed atmosphere (carbo-chlorination) was conducted.^{17–19} Recently, selective chlorination using calcium chloride (CaCl₂) or MgCl₂ as a chlorinating agent has been investigated.^{20,21} In addition, the authors developed a new selective chlorination process using HCl gas produced in the presence of CaCl₂ or MgCl₂ as a chlorine source, and 97% TiO₂ was obtained from a low-grade Ti ore containing 51% TiO₂ under certain conditions.^{4,22} Although the effectiveness of selective chlorination using CaCl₂ or MgCl₂ was demonstrated, several technical problems regarding its practical application have remained unresolved. One such problem is the damage to the chlorinator used in the Kroll process by the condensed chlorides, such as CaCl₂ or MgCl₂,

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because they lead to a corrosive environment at high temperatures.

Meanwhile, among the researchers studying selective chlorination using metal chlorides in the past,^{23–26} Othmer extensively investigated chlorination processes using TiCl_4 .^{23–25} First, Othmer researched oxidation-chlorination, where the chlorination of Fe_2O_3 by TiCl_4 was claimed. Practically, this reaction is a replacement reaction of oxide(s) and chloride(s) in an oxidative atmosphere rather than an oxidation reaction. The second approach was reduction-chlorination. Generally, this process is called carbo-chlorination. Othmer claimed that Ti ore containing iron oxides could be chlorinated using Cl_2 gas in the presence of carbon to produce TiCl_4 . In addition, the chlorination of Ti ore containing FeO by TiCl_4 in the presence of carbon was also claimed. In this process, the exhaust gas stream containing TiCl_4 produced by carbo-chlorination in a reactor was directly used for chlorinating the Ti ore in another reactor that contains carbon. In any case, no systematic thermodynamic analysis considering the partial pressures of oxygen (p_{O_2}) and chlorine (p_{Cl_2}) was conducted.

Based on this background research, the authors conducted a fundamental study on a novel carbo-selective-chlorination method that used TiCl_4 as a chlorinating agent in the presence of carbon in order to selectively remove iron from Ti ores to produce high-grade TiO_2 . In addition, a systematic thermodynamic analysis utilizing chemical potential diagrams was carried out to verify the mechanism of this process, which had not been done in the past.

Figure 1 shows the flow diagram for the new Ti smelting process based on carbo-selective-chlorination investigated in this study. There are several advantages of this carbo-selective-chlorination using TiCl_4 when applied to a practical process. As shown in Fig. 1, first, because a large amount of TiCl_4 is circulated in the current Ti smelting process, the carbo-selective-chlorination process can easily be adapted into the Kroll process. Second, Cl_2 gas can be collected from the chloride wastes produced, because they are produced in a dry form not containing any water.²⁷ In addition, if this process is used for the pretreatment of low-grade TiO_2 feed, the problems with the chlorinator in the current chlorination process, such as chlorine loss and pipe clogging, can be decreased. Moreover, a large amount of acid aqueous waste solution is not generated, because no concentrated acid is necessary for removing iron from Ti ore. Furthermore, even though carbon powder is mixed with Ti ore as a feedstock for carbo-selective-chlorination, the mixture of the ore and carbon powder can be supplied directly to the current chlorination process. Finally, high-grade TiO_2 feed can be obtained directly from the low-grade Ti ore in a single step.

2. Thermodynamic Analysis of Carbo-selective-chlorination Using TiCl_4

Thermodynamically, the iron oxides and titanium oxides in the Ti ore can be considered to exist as a mixture of both oxides, because the Gibbs energy of formation of FeTiO_3 at 1100 K is a small negative value, as shown in eq. (1). Therefore, the thermodynamic analysis of the mechanism of

Fig. 1 Flow diagram for new titanium smelting adopting the selective chlorination process investigated in this study.

the chlorination of the Ti ore can be conducted by utilizing the chemical potential diagrams of the Fe–O–Cl and Ti–O–Cl systems at 1100 K.

Figure 2 shows the combined chemical potential diagram of the Fe–O–Cl and Ti–O–Cl systems at 1100 K plotted with the logarithms of p_{Cl_2} and p_{O_2} as the abscissa and ordinate, respectively.²² By overlapping the two chemical potential diagrams, the potential region for the selective chlorination can be analyzed, and this potential region is indicated as a hatched region in Fig. 2. As shown in Fig. 2, the FeCl_x ($x = 2, 3$) and the TiO_2 are stable in the hatched region. Therefore, if p_{Cl_2} and p_{O_2} are located in that region, iron oxides in the Ti ore will be transformed to FeCl_x ($x = 2, 3$) and titanium oxides will remain as TiO_2 (s). In the case of FeCl_2 (l), although it is thermodynamically stable as a condensed phase at 1100 K, its vapor pressure at 1100 K is 0.09 atm, which is high enough for the FeCl_2 (l) to evaporate.²⁸ Therefore, if the chemical potentials of the oxygen and the chlorine are located in the selective chlorination region, the iron in the Ti ore can be selectively chlorinated as FeCl_x (l,g) ($x = 2, 3$), and TiO_2 (s) can be obtained.

Since an excess amount of TiCl_4 gas was used as a chlorinating agent in this study, the equilibrium line of the TiO_2 (s)/ TiCl_4 (g) eq. in Fig. 2 dominates the chlorination

**Fe-O-Cl system,
Ti-O-Cl system, $T = 1100$ K**

Fig. 2 Chemical potential diagrams of the Fe-O-Cl system (solid line) and the Ti-O-Cl system (dotted line) overlapped at 1100 K.²⁸⁾

reactions in the reaction system. This equilibrium line passes the borderline of the potential region for selective chlorination. In addition, the oxygen chemical potential in the reaction system is controlled by the C (s)/CO (g) eq. or the CO (g)/CO₂ (g) eq., because carbon was used in the reaction system. In this case, point d1 or d2 in Fig. 2 controls the chemical potentials of the reaction system. If the oxygen chemical potentials of the iron oxides in the Ti ore are considered, the p_{O_2} in the reaction system might be locally controlled by the FeO (s)/Fe₃O₄ (s) eq. (point e1 in Fig. 2) or Fe₃O₄ (s)/Fe₂O₃ (s) eq. (point e2 in Fig. 2). However, because the chlorination reaction was carried out in the presence of carbon, thermodynamically, the reaction system in this study is controlled by the conditions indicated by point d1 or d2 in Fig. 2.

Figure 3 shows equilibrium lines of the FeO_x (s)/FeCl_y (l,g) eq. and the TiO₂ (s)/TiCl₄ (g) eq. and the potential regions for several chlorination reactions at 1100 K. The potential region for the carbo-selective-chlorination investigated in this study is depicted as the cross-hatched region in Fig. 3. For reference, the potential regions for the oxidation-selective-chlorination investigated by Othmer²⁴⁾ and for the carbo-chlorination in the conventional chloride process are also shown in Fig. 3. It is worth noting that the carbo-chlorination process already has established applications in industry, whereas the carbo-selective-chlorination discussed here has not been applied in practical manufacturing so far.

Thermodynamically, if a large excess amount of TiCl₄ and carbon exist in the reaction system and the reaction system is in the equilibrium state, the chemical potential of the carbo-

Fig. 3 Comparison of potential regions for this study, carbo-chlorination, and oxidation chlorination using the modified chemical potential diagram of the Fe-O-Cl and the Ti-O-Cl systems at 1100 K.²⁸⁾

selective-chlorination is fixed at point d1 or d2 in Fig. 3. However, when the redox potential of solid FeO in Ti ore is considered, the carbo-selective-chlorination works in a wider oxygen chemical potential range. In this case, the oxygen chemical potential ranges from the log p_{O_2} value that is determined by the Fe (s)/FeO (s) eq. to point e1 in Fig. 3. Therefore, when the carbon in the system and the redox potential of solid FeO in Ti ore are considered, the oxygen chemical potential ranges from point d1 to point e1 in Fig. 3. Meanwhile, when the chlorination of a Ti ore particle is considered, the outermost boundary of the ore particle reacting with TiCl₄ is controlled by the TiO₂ (s)/TiCl₄ (g) eq., and the center of the ore particle not yet reacting with TiCl₄ is controlled by the FeO_x (s)/FeCl_y (l,g) eq. If the chemical potential gradient between the two equilibriums is considered, the chemical potential pair of p_{Cl_2} and p_{O_2} can be placed between the equilibrium lines of the FeO_x (s)/FeCl_y (l,g) eq. and the TiO₂ (s)/TiCl₄ (g) eq. can be identified as the potential region for the selective chlorination of iron in Ti ore. Thus, under these two conditions, the cross-hatched region shown in Fig. 3 becomes the potential region for the carbo-selective-chlorination in this study.

The potential region for the carbo-selective-chlorination is located within the stability region of FeCl₂ (l), and the vapor pressure of FeCl₂ (l) at 1100 K is high enough to allow for evaporation, as mentioned before. Therefore, when TiCl₄ is used as a chlorinating agent for the carbo-selective-chlorination at 1100 K, the iron oxide in the Ti ore is removed as FeCl₂ (l,g) and the TiO₂ remains, according to the following overall chemical reaction.

Table 1 Experimental conditions used in this study.

Exp. no.* ¹	Source country for Ti ore	Reaction time, t_r /h	Weight of carbon, w_c /g	TiCl ₄ feed* ⁵		
				Rate, f_{TiCl_4} /g·min ⁻¹	Feeding pattern	Feeding time, t_{TiCl_4} /ks
130626* ²	Vietnam	5	—	0.185	1	10.5
130703* ³	Vietnam	6	0.50	0.164	2	9.12
130704* ³	Australia	6	0.50	0.163	2	9.18
130708* ³	China	6	0.50	0.167	2	9.00
130730* ⁴	Vietnam	4	0.50	0.192	2	7.80

*¹Experimental conditions;

Reaction temperature, $T = 1100$ K.

Weight of Ti ore, $w_{\text{ore}} = 2.00$ g.

Size of Ti ore used, $d_{\text{ore}} = 74\text{--}149$ μm .

*²Ar flow rate for entire reaction time with fan, $f_{\text{Ar}} = 500$ sccm.

*³Ar flow rate for 5 h (from 0 to 5 h) with fan, $f_{\text{Ar}} = 500$ sccm.

Ar flow rate for 1 h (from 5 to 6 h) without fan, $f_{\text{Ar}} = 1000$ sccm.

*⁴Ar flow rate for entire reaction time with fan, $f_{\text{Ar}} = 500$ sccm.

Time for evacuation before taking out the quartz tube from furnace = 10 min, and when evacuation was performed, exhaust gas was captured in the glass bottle cooled by liquid nitrogen.

Titanium ore was mixed with carbon.

*⁵Amount of TiCl₄ used, $w_{\text{TiCl}_4} = 25$ g.

TiCl₄ feeding pattern 1: feeding for 30 min and break of feeding for 10 min.

TiCl₄ feeding pattern 2: continuous feeding without break.

Feeding time of feeding pattern 1 includes periodic breaks.

3. Experimental

Figure 4 shows a schematic diagram of the experimental apparatus used in this study and a photograph of the quartz reaction tube taken before the experiment. In addition, detailed experimental conditions for this study are summarized in Table 1.

Prior to the experiments, Ti ore (see Table 2) and carbon powder (Kojundo Chemical Lab. Co., Ltd., purity $\geq 99.9\%$) were placed in separate quartz crucibles (crucible for carbon: $\phi = 26$ mm, I.D.; $d = 24$ mm, depth; crucible for Ti ore: $\phi = 25$ mm, I.D.; $d = 120$ mm, depth), which were subsequently positioned in the quartz tube ($\phi = 44.5$ mm, I.D.; $l = 820$ mm, length), as shown in Fig. 4. As exceptional cases, in Exp. no. 130626, carbon was not used in the experiments in order to increase the p_{O_2} in the system, and in Exp. no. 130730, a mixture of Ti ore and carbon was used. After the samples were placed in the quartz tube, the tube was plugged by a Viton rubber plug. Afterward, liquid TiCl₄ (Wako Pure Chemical Industries Ltd., purity $\geq 99.0\%$) was transferred from the reagent bottle to a glass bottle filled with argon gas (Ar, purity $\geq 99.9995\%$) in a glove bag purged with nitrogen gas (N₂, purity $\geq 99.999\%$) to prevent the reaction between TiCl₄ and the H₂O present in air as much as possible.

After the samples and liquid TiCl₄ were prepared, the quartz tube was evacuated thrice for 5 min each, and the tube was filled with Ar gas between the evacuations until the internal pressure reached 1 atm. After the final filling

Fig. 4 (a) Schematic diagram of the experimental apparatus and (b) photograph taken before the experiments showing some of the samples placed in the quartz tube.

with Ar gas, Ar gas was flowed through the quartz tube at a controlled rate using a mass flow controller (MFC) while the internal pressure of the tube was maintained at 1 atm. In all the procedures, Ar gas was supplied into the quartz tube through magnesium perchlorate (Mg(ClO₄)₂, Kanto Chemical Co., Inc., purity $\geq 75\%$) to remove the H₂O in the Ar gas.

Table 2 Analytical results for the feedstock used and residues obtained after experiments.

Exp. no.	Source country for Ti ore	Concentration of element <i>i</i> , <i>C_i</i> (mass%)* ¹				
		Ti	Fe	Mn	Si	Al
Feedstock* ² (Initial)	Vietnam	45.0	49.7	3.47	0.57	0.33
	Australia	48.5	46.7	1.69	1.00	1.02
	China	47.2	45.4	2.79	1.65	1.41
130626	Vietnam	98.0	0.69	0.05	0.36	N.D
130703	Vietnam	97.7	0.39	0.05	0.96	N.D
130704	Australia	97.6	0.39	0.04	0.63	N.D
130708	China	94.8	2.28	0.15	0.83	N.D
130730	Vietnam	97.6	0.50	0.11	0.71	N.D

*¹Determined by XRF analysis (excluding oxygen and other gaseous element).

N.D Not Detected. Below the detection limit of the XRF (<0.01 mass%),

Values are determined by average of analytical results of five samples.

*²Particle size of Ti ore used, $d_{\text{ore}} = 74\text{--}149\ \mu\text{m}$.

After these atmosphere control procedures, the quartz tube was placed in a horizontal furnace preheated up to 1100 K for 30 min. The reaction temperature of 1100 K was chosen by considering the reduction of energy consumption and reaction kinetics for the production of TiO_2 (s). The quartz tube was placed at an angle of 1.7° relative to the horizontal axis of the horizontal furnace, and the front part of the quartz tube outside the furnace was cooled by a fan to promote effective TiCl_4 circulation inside the quartz tube. After the quartz tube was heated for 30 min in the furnace, liquid TiCl_4 (boiling temperature: 408 K) was fed into the tube by a peristaltic pump (Cole-Parmer Instrument Co., MasterFlex L/S Digital Drive, 7523-70; PTFE Tubing Pump, 77390-00) at a flow rate of 0.163–0.192 g/min. A continuous flow of liquid TiCl_4 into the quartz tube was used, except for in Exp. no. 130626. A TiCl_4 feeding pattern including periodic breaks was examined in order to decrease the amount of TiCl_4 discharged from the quartz tube without participating in the chlorination reaction.²⁹⁾

In most cases, the quartz tube was instantly removed from the furnace after the reaction at a preset time and cooled down at room temperature. However, for Exp. no. 130730, evacuation using a diaphragm pump (As One Co., MAS-1) was performed 10 min prior to the removal of the quartz tube from the furnace until the quartz tube was cooled down. The aim of this step was to remove the exhaust gas remaining in the quartz tube. Afterward, the quartz tube was filled with Ar gas until the internal pressure reached 1 atm, and Ar gas was flowed at room temperature while the internal pressure of the tube was maintained at 1 atm.

Three methods were applied to collect the residues from the quartz tube after the experiments. In Exp. no. 130704, the quartz tube was placed in a furnace preheated up to 500 K for 4 h under a N_2 gas atmosphere before the tube was taken out. Then, the quartz tube was filled with Ar gas until the internal pressure of the tube reached 1 atm, and subsequently Ar gas was flowed through the tube at room temperature until the TiCl_4 inside the tube was dried. The vapor pressure of TiCl_4 (*l*) at 300 K is 0.02 atm, which is sufficient for evaporation.²⁸⁾

Fig. 5 Results of XRD analysis of the (a) Vietnamese, (b) Australian, and (c) Chinese Ti ores used in this study.

Therefore, the TiCl_4 in the quartz tube could be dried by supplying Ar gas. In Exp. no. 130730, the Ar gas was flowed through the quartz tube at room temperature until the TiCl_4 inside the tube was dried. For all the other experiments, a small amount of acetone was injected into the quartz tube through the outlet pipe while the Ar gas flow was maintained to remove TiCl_4 from the front part of the tube.³⁰⁾ After the residues were taken out of the quartz tube, they were dissolved in deionized water and sonicated for over one hour at room temperature.

The chemical compositions of the residues obtained after the experiments were analyzed using X-ray fluorescence spectroscopy (XRF: JEOL, JSX-3100RII). The crystalline phases were identified by X-ray diffraction (XRD: RIGAKU, RINT 2500, $\text{Cu-K}\alpha$ radiation), and the microstructures and compositions were analyzed by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS: JEOL, JSM-6510LV).

4. Results and Discussion

Figure 5 shows the results of XRD analysis of the Vietnamese, Australian, and Chinese Ti ores used in this study. As shown in Fig. 5, the main crystalline phase in the Ti ores was FeTiO_3 . In addition, TiO_2 was also identified depending on the types of Ti ores.

Figure 6 shows representative photographs of the low-temperature part of the quartz reaction tube during and after the experiment. TiCl_4 has a high vapor pressure even at room temperature, as mentioned before. Therefore, a certain amount of TiCl_4 that did not react with Ti ore was discharged from the quartz tube during the experiments and then condensed in a liquid form in the middle of the outlet line. To minimize the loss of unreacted TiCl_4 , several methods were used to facilitate TiCl_4 circulation in the quartz tube, such as the use of a cooling fan or setting the quartz tube at a small tilting angle. As a result, as shown in Fig. 6(a),

Fig. 6 Representative photographs of low-temperature part of the quartz tube (a) during the experiment (Exp. no. 130626) and (b) after the experiment (Exp. no. 130704).

Fig. 7 Results of XRD analysis of the powders condensed in the low-temperature part of the quartz tube (Exp. no. 130704): (a) yellow part before the quartz tube was dried and (b) yellow part changed from brown after the quartz tube was dried.

a certain amount of unreacted TiCl_4 discharged from the reaction zone was cooled and condensed into a liquid in the cooling zone, and this liquid flowed back towards the reaction zone during the experiment because the horizontal quartz tube was slightly tilted.

After the experiments, yellow (and white) and brown deposits were generated inside the quartz tube, as shown in Fig. 6(b). The brown deposits became yellow after the quartz tube was dried. Therefore, it is supposed that the TiCl_4 remaining in the low-temperature part of the quartz tube was evaporated and removed when Ar gas was flowed through the tube. Figure 7 shows the results of XRD analysis of the two different yellow deposits obtained after drying brown or yellow deposits in the quartz tube. As shown in Fig. 7, FeCl_2 and $\text{FeCl}_2 \cdot 2(\text{H}_2\text{O})$ were identified by the XRD analysis. Regarding the H_2O in the $\text{FeCl}_2 \cdot 2(\text{H}_2\text{O})$, it seems H_2O in air had attached to FeCl_2 when the Viton rubber plug was removed from the quartz tube in order to obtain the residues.

Figure 8 shows SEM images of the surface of a Ti ore particle obtained before and after the carbo-selective-

Fig. 8 SEM images of the surface of a Vietnamese Ti ore particle (a) before the experiment and (b) after the selective chlorination experiment (Exp. no. 130703).

chlorination experiment. As shown in Fig. 8, small pores were formed on the surfaces of the residues obtained after experiment. It is expected that the majority of the pores were formed by the evaporation of iron chloride. This is because the vapor pressure of FeCl_2 generated by the reaction at 1100 K is high enough for the FeCl_2 to evaporate, and the evaporated FeCl_2 was condensed at the low-temperature part of the quartz tube. Therefore, the authors concluded that the iron in the Ti ore was removed as FeCl_2 (*l.g*) by TiCl_4 at 1100 K as expected from the thermodynamic analysis.

Table 2 summarizes the analytical results for the feedstock used and the residues obtained after the experiments. In addition, Fig. 9 shows the results of XRD analysis of the residues obtained after experiments when the Vietnamese Ti ore (Exp. no. 130703), Australian Ti ore (Exp. no. 130704), and Chinese Ti ore (Exp. no. 130708) were used as feedstock. As shown in Table 2 and Fig. 9, when the Vietnamese and Australian Ti ores were used as feedstock, the concentrations of Ti increased from 45 to 98 mass% and from 49 to 98 mass%, respectively, after the selective removal of iron from the Ti ore. As a result, 98% TiO_2 was obtained in both cases. The purity of TiO_2 was calculated by converting all the elements measured by XRF to their nominal simple oxides. In addition, when the Chinese Ti ore was used as feedstock, 95% TiO_2 was obtained after the experiment.

Fig. 9 Results of XRD analysis of the residues obtained after experiments when the (a) Vietnamese (Exp. no. 130703), (b) Australian (Exp. no. 130704), and (c) Chinese (Exp. no. 130708) Ti ores were used as feedstock.

Therefore, it can be claimed that various types of Ti ores can be upgraded to the TiO_2 with a purity of above 95% by selectively removing iron directly from the ores in a single step through carbo-selective-chlorination.

As mentioned before, to increase the circulation of TiCl_4 inside the quartz tube, two types of TiCl_4 feeding patterns were examined: continuous feeding of TiCl_4 and feeding of TiCl_4 with periodic breaks. However, in the results from Exp. no. 130626 and Exp. no. 130703 shown in Table 2, even though different feeding patterns of TiCl_4 were adopted, no significant difference in the TiO_2 purity (98% in both cases) was observed under the experimental conditions applied in this study.

As discussed regarding the thermodynamic analysis of the carbo-selective-chlorination method (see Fig. 3), the potential region of this study is considered to be the cross-hatched region in which the oxygen chemical potential ranges from point d1 ($\text{C (s)}/\text{CO (g)}$ eq.) to point e1 ($\text{FeO (s)}/\text{Fe}_3\text{O}_4 \text{ (s)}$ eq.) in Fig. 3. When carbon and TiCl_4 exist in the reaction system, the potential of the system is located in the oxygen chemical potential ranges from point d1 to point d2 in the cross-hatched region in Fig. 3. The experimental conditions for Exp. no. 130626 and Exp. no. 130703 can be considered examples of two conditions: one in which the p_{O_2} is located in the range from the $\log p_{\text{O}_2}$ value determined by the $\text{Fe (s)}/\text{FeO (s)}$ eq. to point e1, and another in which the p_{O_2} value is located in the range from point d1 to point d2. In both cases, the iron in the Ti ore was selectively removed, and 98% TiO_2 was obtained. Therefore, the authors claim that if the chemical potentials of oxygen and chlorine are located in the potential region for carbo-selective-chlorination shown in Fig. 3, iron can be selectively removed from Ti ore and a high-grade TiO_2 can be obtained.

Ti ore contains several impurities besides iron, such as manganese (Mn), aluminum (Al), or silicon (Si). Among

these impurities, it was found that manganese oxide (MnO) was also removed from Ti ore by the carbo-selective-chlorination, as shown in Table 2. The chemical reaction between MnO and TiCl_4 is shown in eq. (3).

$$\Delta G^\circ_r = -98.9 \text{ kJ at } 1100 \text{ K}^{(28)}$$

The analytical results showed decreased concentrations of aluminum in the residues after experiments. However, in the case of aluminum, from a thermodynamic point of view, Al_2O_3 is difficult to remove with TiCl_4 , as shown in eq. (4). Therefore, further study is required to investigate the behavior of aluminum and other impurities in the Ti ore during the carbo-selective-chlorination process.

$$\Delta G^\circ_r = 102.4 \text{ kJ at } 1100 \text{ K}^{(28)}$$

5. Conclusions

In order to selectively remove iron directly from low-grade titanium ore (e.g., FeTiO_3), thermodynamic analysis considering the chemical potentials of oxygen and chlorine was conducted. Then, the suitable chemical potential region for carbo-selective-chlorination using TiCl_4 as a chlorinating agent was investigated for the selective removal of iron from Ti ore to produce high-grade TiO_2 . When the selective chlorination experiments were conducted under Ar or Ar + C atmospheres at 1100 K using low-grade Ti ores produced from Vietnam, Australia, and China as feedstock, the iron in the ores was selectively removed in the form of iron chloride (FeCl_2). As a result, 98% TiO_2 was produced directly from low-grade Ti ore containing 51% TiO_2 in a single step under certain conditions. Thus, the carbo-selective-chlorination investigated in this study is demonstrated to be a feasible process for upgrading low-grade titanium ore for the production of high-grade titanium dioxide.

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