論 文 の 内 容 の 要 旨

論文題目　Fundamental Study on Removal of Iron Directly from Titanium Ore by Selective Chlorination
（選択塩化法によるチタン鉱石からの鉄の直接除去に関する基礎的研究）

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Titanium (Ti) has excellent physical and chemical properties such as a high specific strength and corrosion resistance. In addition, titanium is the ninth most abundant element in the Earth's crust. However, titanium is not as widely used as aluminum or iron because of its high production costs and low productivity. For example, the cost for processing titanium ore is 15 times higher than that of processing iron ore. For these reasons, the development of an efficient process for upgrading low-grade titanium ore ($FeTiO_3$, 30 – 65 % TiO_2) to high-grade titanium dioxide (TiO_2) feed with a purity of above 95 % is important. Therefore, in this thesis, a method for the selective chlorination of low-grade titanium ore using metal chlorides or hydrogen chloride (HCl) gas as a chlorinating agent was developed to produce high-grade TiO_2 feed by selectively removing iron directly from the Ti ore in a single step.

In chapter 1, the current statuses of titanium metal, titania pigment, titanium mineral concentrates, and the upgraded TiO_2 feed were briefly introduced. In addition, the industrial titanium smelting processes for converting the ore to metal and pigment were reviewed from various viewpoints. The use of high-grade TiO_2 as a feedstock for the production of titanium metal or titania pigment is very important. When low-grade titanium ore is used as a feedstock, many operating problems arise, such as clogging of the reactor pipes and chlorine loss in a chlorinator by the generation of a large amount of chloride waste, or the generation of waste containing heavy metals. Currently, high-grade TiO_2 feed is produced by the Becher, Benilite, and slag and UGS processes. However, these upgrading processes still have several disadvantages such as the generation of a large amount of acid waste solution containing heavy metals owing to the use of the highly concentrated acid and the need for multiple steps to remove iron from the ore.

In order to improve these disadvantages, the efficient and environmentally friendly selective chlorination method using metal chlorides or HCl gas was studied. The selective chlorination processes investigated in this thesis all have the following advantages in common. (i) A high-grade

TiO_2 feed can be obtained directly from the low-grade titanium ore in a single step. (ii) A highly concentrated acid or chlorine (Cl_2) gas is not used. (iii) Various types of low-grade titanium ores can be used as starting materials. In addition, selective chlorination using titanium tetrachloride ($TiCl_4$) has the following additional advantages. (iv) Recovery of chlorine from chloride waste is possible, because the waste is generated in a dry form. (v) Finally, the $TiCl_4$ is easy to obtain, because a large amount of $TiCl_4$ is circulated in the Kroll process.

In chapter 2, a thermodynamic study of the chlorination reactions of metals or oxides at elevated temperature was carried out in order to consider the feasibility of the iron removal directly from low-grade titanium ore through selective chlorination. In particular, various chlorination reactions were analyzed by utilizing the chemical potential diagrams of M-O-Cl systems (M = Fe, Ti, H, Ca, Mg), which were found to be applicable and useful for analyzing the selective chlorination of low-grade titanium ore. Furthermore, chlorination reactions with various types of chlorinating agents were discussed from various viewpoints. It was shown that the selective chlorination of iron from low-grade titanium ore by HCl, $CaCl_2$, $MgCl_2$, or $TiCl_4$ is thermodynamically feasible and efficient for the production of high-grade TiO_2 feed. These thermodynamic analysis results showed that a new upgrading process for the titanium ore using a dry method that does not discharge any aqueous waste solution could be developed.

In chapter 3, a fundamental investigation of the selective chlorination of low-grade titanium ore using $CaCl_2$ to produce high-grade TiO_2 feed was carried out. The experimental results showed that iron in the low-grade titanium ore was selectively removed as $FeCl_x$ (*l*, *g*) (x = 2, 3) by HCl gas produced directly from the mixture of $CaCl_2$/titanium ore and $CaCl_2$ at 1100 K. When the HCl reacted with various types of low-grade titanium ores, 97 % TiO_2 feed with a porous microstructure was produced in a single step under certain conditions. In addition, when $CaCl_2$ directly reacted with low-grade titanium ore, the concentration of iron in the titanium ore decreased from about 50 % to 18 %, and $CaTiO_3$ was mainly produced. In some cases, iron was insufficiently removed from the titanium ore because the $CaTiO_3$ produced in the outmost parts of the titanium ore particles by the reaction between titanium ore and $CaCl_2$ hindered the removal of iron from the center of the titanium ore particles. On the other hand, the production of $CaTiO_3$ helped to generate the HCl from $CaCl_2$ by lowering the activity of CaO in $CaCl_2$.

Chapter 4 describes a fundamental study on increasing the amount of iron removed from low-grade titanium ore by reaction with $CaCl_2$ through physical contact. In the experiment, iron was selectively removed as $FeCl_2$ (*l*, *g*) from various types of titanium ores, and high-grade $CaTiO_3$ was produced. When the selective chlorination was conducted using ≤ 74 μm titanium ore particles at 1240 K for at least 8 hours, the concentration of iron in the titanium ore decreased from about 50 % to 1.8 %. It was found that the amount of iron removed from a titanium ore increased when the reaction temperature or time were increased or particle size of titanium ore was decreased. In addition, the feasibility of the scale up of the selective chlorination using $CaCl_2$ was demonstrated.

In chapter 5, a method for the selective chlorination of low-grade titanium ore using $MgCl_2$ was developed for the production of high-grade TiO_2 feed. Iron was selectively removed from the low-grade titanium ore as $FeCl_2$ (*l*, *g*) directly by HCl gas generated from the $MgCl_2$/titanium ore mixture and $MgCl_2$ at 1000 K. When HCl reacted with various types of low-grade titanium ores, 97 % TiO_2 feed with a porous microstructure was produced in a single step under certain conditions. In addition, it was shown that the time required for the completion of the removal of iron from the titanium ore was decreased when the experiments were conducted in the presence of H_2O gas because of the accelerated production of HCl gas from the $MgCl_2$. When $MgCl_2$ directly reacted with low-grade titanium ore, the iron concentration in the titanium ore was decreased from about 50 % to 18 %. It was found that the formation of the $MgTiO_3$ at the outer part of the titanium ore particles physically hindered further reaction between $MgCl_2$ and iron in the central portions of the titanium ore particles.

In chapter 6, in order to selectively remove iron directly from low-grade titanium ore by $TiCl_4$ under a low oxygen chemical potential (p_{O_2}), thermodynamic analysis considering the chemical potentials of oxygen and chlorine was conducted. Then, the suitable chemical potential region for the selective chlorination of iron in the titanium ore using $TiCl_4$ under low p_{O_2} was investigated to produce high-grade TiO_2 feed. When the experiments were conducted under a reducing atmosphere, which was maintained by the presence of carbon, at 1100 K, the iron in the various types of titanium ores was selectively removed in the form of $FeCl_2$ (*l*, *g*). As a result, 98 % TiO_2 feed with a porous microstructure was produced directly from low-grade titanium ore containing 51 % TiO_2 in a single step under certain conditions. In addition, the $FeCl_2$ was produced in a dry form, because H_2O did not participate in the reactions, which makes it possible to recover the chlorine from chloride waste.

In chapter 7, the selective removal of iron from the titanium ore using $TiCl_4$ under high p_{O_2} was investigated, in order to produce high-grade TiO_2 feed directly from low-grade titanium ore in a single step. The appropriate chemical potential region for selective chlorination under high p_{O_2} was studied by utilizing the chemical potential diagram considering chlorine chemical potential (p_{Cl_2}) and p_{O_2}. When the selective chlorination of various types of titanium ore particles with sizes of 74 – 149 μm was conducted at 1200 K under high p_{O_2} (1 ppm, 1 %, or 10 % O_2), the iron in the titanium ore was directly removed as $FeCl_x$ (*l*, *g*) (x = 2, 3) in a dry form, and 98 % TiO_2 feed with a porous microstructure was obtained in a single step under certain conditions. In addition, when the selective chlorination using titanium ore particles with sizes of 74 – 297 μm was conducted at 1200 K under an Ar + 1 ppm O_2 atmosphere, TiO_2 feed with more than 95 % purity was obtained. However, when the titanium ore particle size was larger than 297 μm, the concentration of iron in the titanium ore decreased from about 50 % to 11 %, because unreacted iron remained in the central portions of the titanium particles owing to the insufficient reaction time.

In chapter 8, the application of the selective chlorination using $TiCl_4$ under low p_{O_2} was investigated with the purpose of upgrading titania slag to produce the high-grade TiO_2 feed directly. Generally, titania slag with a purity of 75 – 86 % TiO_2 is further upgraded before use by the UGS process using highly concentrated acid to produce high-grade TiO_2 feed. As a result of the upgrading process, a large amount of acid waste solution containing heavy metals is generated. In the experiments, various types of titania slags, as-received titania slag, the oxidized titania slag, the reduced titania slag after oxidation, and the upgraded slag, were reacted with $TiCl_4$ in the presence of carbon at 1100 K. The iron in the titania slag feedstocks was selectively removed as $FeCl_2$ (*l*, *g*) in a dry form, and TiO_2 feed with more than 94 % purity was directly obtained. These results show that the selective chlorination using $TiCl_4$ could be used instead of the UGS process for upgrading titania slag.

In chapter 9, the problems of the current titanium ore upgrading processes were briefly reviewed again. Thereafter, a novel environmentally friendly titanium ore upgrading process that does not discharge waste solution or chloride waste was proposed, and the features of the new process were characterized in detail. In particular, establishment of a novel selective chlorination process through pyrometallurgical method (high-temperature process) for the production of the high-grade TiO_2 feed for titanium metal and titania pigment production was proposed. When this selective chlorination process is used, it is also possible to decrease the chlorine loss in the chlorination process, because the chlorine can be recovered using a pyrometallurgical method such as the oxidation reaction. Thus, the environmental burden can be decreased, because the iron in the titanium ore is discharged from the system as pig iron or iron oxide (Fe_2O_3) in the new titanium smelting process.

In this thesis, thermodynamic analysis considering the chemical potentials of oxygen and chlorine was conducted in order to remove iron selectively and directly from low-grade titanium ore. Then, the suitable chemical potential region for the selective chlorination using HCl, $CaCl_2$, $MgCl_2$, or $TiCl_4$ as the chlorinating agent for the production of high-grade TiO_2 feed was investigated by utilizing the chemical potential diagrams. The experimental results showed that iron was selectively removed from low-grade titanium ore as iron chlorides by these chlorides, and 97 – 98 % TiO_2 feed was produced directly from titanium ore containing 51 % TiO_2 in a single step under certain conditions.

When the reaction rate, environment of a reactor during operation, recycling of chlorides waste, reduction in chlorine loss of chlorinating agent, and ease of obtaining chlorinating agent are considered, the selective chlorination process will be one of the most efficient methods for the production of the high-grade TiO_2 feed in the future. Especially, the selective chlorination process using $TiCl_4$ is an environmentally friendly method, because any acid waste solution is not discharged and recovery of chlorine from chlorides waste is possible.

In recent years, interest in a method that allows inexpensive low-grade titanium ore to be used in the titanium smelting industry has increased along with the rising price of titanium ore. Therefore, it is expected that the selective chlorination method investigated in this thesis will be used as a novel environmentally friendly process for the production of high-grade TiO_2 feedstock for titanium metal and titania pigment production.