

**SELECTIVE CHLORINATION OF TITANIUM ORE
AND
PRODUCTION OF TITANIUM POWDER BY PREFORM REDUCTION PROCESS (PRP)**

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ABSTRACT

A fundamental study was performed on the removal of iron from titanium ore by selective chlorination using metal chlorides (MCl_x , $M = Mg, Ca$, etc.) and the production of titanium powder directly from titanium ore. The objective of this study was to achieve reduction in the production cost of titanium. In order to remove iron from the ore, the titanium ore (ilmenite) was reacted with metal chlorides (and water vapor) in a graphite crucible at 1023 - 1293 K. After the iron removal experiment by selective chlorination, a titanium ore with low iron content was obtained, and the by-product—iron chloride gas ($FeCl_x$)—was recovered by condensation. In order to obtain titanium powder directly from the abovementioned titanium ore, the preform reduction process (PRP) based on the calciothermic reduction of titanium oxide contained in the feed preform was applied. When the preform containing titanium ore was reduced by calcium vapor at 1273 K, metallic titanium powder with a purity exceeding 99% was obtained.

Keywords: titanium ore, iron removal, selective chlorination, metal chloride, titanium powder, calciothermic reduction, preform reduction process (PRP)

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INTRODUCTION

Titanium (Ti) is used in various fields because of its high strength, light weight, high-temperature performance, excellent flexibility, extraordinary corrosion resistance, and biocompatibility characteristics. Furthermore, titanium is the ninth most abundant element in the earth's crust in addition to its mineral resources. Currently, titanium finds extensive applications in aerospace, marine, chemical plant materials, medical equipments, buildings, and several consumer products (glasses, golf clubs, etc.), thereby increasingly gaining importance. Therefore, titanium possesses the potential to become a common and prosperous material in the future.

The current production process of titanium, referred to as the Kroll process [1], is based on the magnisiothermic reduction of titanium tetrachloride. Although this process can produce high purity titanium, its production cost is high. This is partly because the reduction process is extremely slow and involves an inefficient batch-type process. With the objective of producing low-cost titanium, numerous researches on titanium smelting processes such as the FFC [2], OS [3], EMR [4], ESR [5], and PRP [6] processes have been carried out. The first four of the abovementioned processes are based on the direct reduction of titanium oxide by the electrochemical method in a molten salt. Although it is anticipated that the electrochemical method has the potential to replace the current Kroll process, it is still difficult to control the impurity content in the obtained titanium; furthermore, several technical problems need to be resolved before a large-scale commercial process can be established.

Due to the abovementioned factors, a new process for reducing the production cost of titanium and minimizing its environmental burden was investigated. The main technical points of this process are listed as follows: the removal of iron from titanium ore by selective chlorination using metal chlorides (MCl_x , $M = Mg, Ca$, etc.), recycling of chloride wastes (e.g., $FeCl_x$ and $AlCl_3$) using titanium scraps, and the production of titanium powder directly from the titanium ore or the de-ironized ore. This study focuses on the removal of iron from low-grade titanium ore by selective chlorination using metal chlorides and the production of titanium powder directly from natural titanium ore by using the preform reduction process (PRP).

EXPERIMENTAL

Selective Chlorination of Titanium Ore

A representative schematic illustration of the experimental apparatus used for the selective chlorination of titanium ore is shown in Figure 1. Approximately 3.03 g of ilmenite ore, containing 53.7 mass% of iron, was mixed with 1.98 g of $CaCl_2$ and reacted at 1073 K for 6 h in a graphite crucible under a $N_2 + H_2O$ ($p_{H_2O} = 0.04$ atm) atmosphere.

After the experiment, the solid sample obtained in the graphite crucible was analyzed by X-ray fluorescence (XRF) analysis.

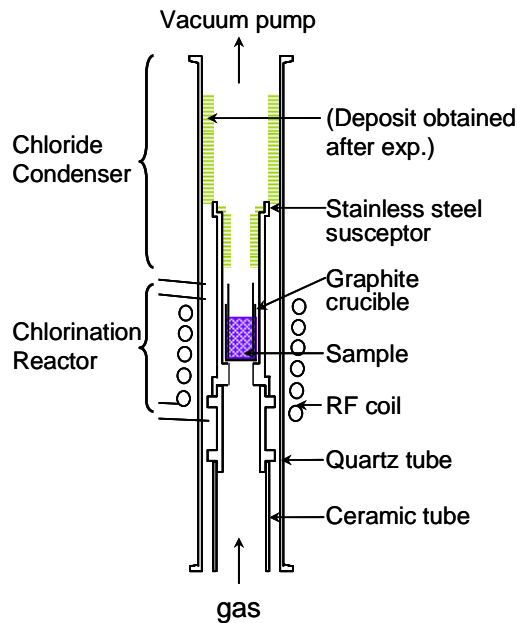
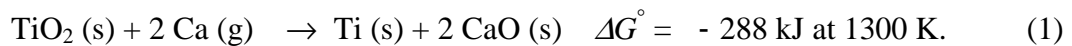


Figure 1 - Experimental apparatus for the selective chlorination of titanium ore using radio frequency (RF) furnace.

Titanium Powder Production by PRP

The preform reduction process (PRP) based on the calciothermic reduction of titanium ore (TiO_2) was investigated [6]. The overall reaction of the reduction process is expressed as the following reaction [7]:



PRP involves four major steps: (1) preform fabrication by a mixture of natural rutile ore, calcium chloride (CaCl_2) as the flux, and collodion as the binder at room temperature; (2) calcination of the preform at an elevated temperature; (3) reduction by Ca vapor at an elevated temperature; and (4) leaching at room temperature. In this study, carbon powder was introduced into the feed preform; this is a new method employed in this process for achieving efficient iron removal from the feed preform.

The feed preform was fabricated from a slurry that was prepared by mixing approximately 7.55 g of natural rutile ore (Major impurities: Fe 1.75 mass %), 2.45 g of CaCl_2 as the flux, and collodion as the binder. The prepared preform was then heated at 1273 K for 1 h in order to remove the binder and water present in the preform. A schematic illustration of the experimental apparatus used for the reduction is shown in Figure 2. In this reduction step, multiple pieces of sintered preform (15~30 g in total) and calcium shots (~60 g) were set in a stainless steel reaction vessel. The reaction vessel was then heated at 1273 K for 6 h in order to reduce the titanium ore by Ca vapor. After the

reduction, the reaction vessel was removed from the furnace and quenched in water. The preform in the reaction vessel was mechanically recovered at room temperature and subjected to the following leaching process. In the leaching step, the sample obtained from the reduction process was reacted with a 50% acetic acid solution for 48 h and 20% hydrochloric acid for 24 h to remove the by-product (CaO) and excess reductant (Ca) present in the sample. Further, it was rinsed thrice with distilled water, twice with isopropanol, and once with acetone at room temperature. Finally, the obtained powder was dried in a vacuum dryer.

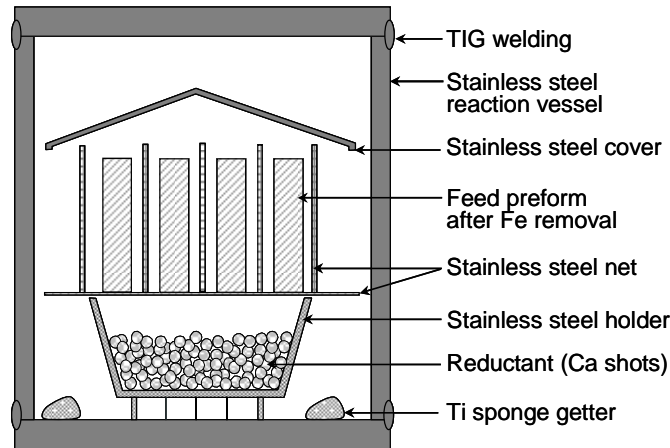


Figure 2 - Schematic illustration of the experimental apparatus for reduction of de-ironized titanium ore by preform reduction process (PRP).

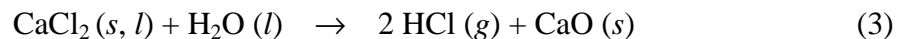
RESULTS AND DISCUSSION

Selective Chlorination of Titanium Ore

The iron concentration of the titanium ore, as determined by X-ray fluorescence (XRF) analysis, decreased from 53.7 to 16.3 mass% after the experiment, and it was demonstrated that iron was successfully removed from the titanium ore. The mechanism of the selective chlorination can be explained by the following reactions:



or



Titanium Powder Production by PRP

Figure 3(a) shows the X-ray diffraction (XRD) pattern of the sample obtained after leaching. Only the α -Ti phase was detected in the sample. Figure 3(b) shows the scanning electron microscopic (SEM) image of the sample obtained after leaching. Titanium powder in the form of sponge with a primary particle size of 2–5 μm was obtained successfully. The sample obtained after leaching was also analyzed by energy dispersive spectroscopy (EDS); the analytical result indicates that metallic titanium powder with a purity of 99.2% was obtained.

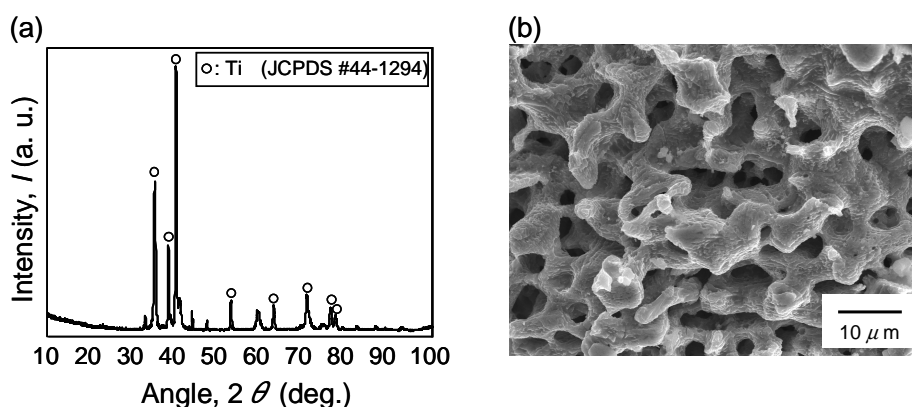


Figure 3 - X-ray diffraction (XRD) pattern (a) and scanning electron microscopic (SEM) image (b) of titanium powder obtained by preform reduction process (PRP). (Exp. #PE)

CONCLUSIONS AND REMARKS

Iron was removed from low-grade titanium ore (ilmenite) by selective chlorination using metal chlorides. Metallic titanium powder with a purity exceeding 99% was obtained directly from titanium ore (Rutile) by the preform reduction process.

In the future, the mass balance and detailed mechanism of the selective chlorination reactions will be investigated. In addition, a more effective method for removing iron from titanium ore by the selective chlorination method will be investigated for developing a low-cost innovative process for producing high purity titanium powder.

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