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A NOVEL RECYCLING PROCESS OF TITANIUM METAL SCRAPS BY USING CHLORIDE WASTES

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Abstract

A novel process of recycling titanium metal scraps by utilizing chloride wastes (e.g., $FeCl_x$ and $AlCl_3$) that are obtained as by-products in the Kroll process or any other chlorination process has been investigated in this study. This is important from the viewpoint of the increase in titanium metal scraps and chloride wastes in the future. Thermodynamic analyses and some primary experiments have been carried out in previous studies. Based on these studies, a fundamental study was carried out: titanium granules were reacted with iron chloride ($FeCl_2$) in a sealed quartz tube under a reduced argon atmosphere over a temperature range of 900–1300 K. The analytical results of the obtained samples determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES), the potentiometric titration method, and X-ray diffraction (XRD) analyses reveal that the chlorine contained in the chloride wastes can be recovered by titanium granules as titanium chloride and the obtained titanium chloride can be easily separated from iron and other chlorides and then recovered. The recovered titanium chloride can be used as the feed material in titanium smelting processes.

Introduction

Currently, the titanium production process is referred to as the Kroll process [1–5], which basically involves the following three major chemical reaction steps: (1) carbo-chlorination of titanium oxide for producing titanium tetrachloride ($TiCl_4$), (2) purification of the obtained $TiCl_4$ by distillation, and (3) magnesiothermic reduction of the purified $TiCl_4$. Although this process can yield high-purity titanium, its production cost is high. This is partly because the reduction process is extremely slow and it involves an inefficient batch-type process. Furthermore, some amount of chloride wastes such as iron chlorides ($FeCl_x$, x = 2, 3) are generated from the chlorination process, as shown in Figure 1, because the titanium oxide feed contains impurities such as iron. At present, 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 wastes involves several problems such as the disposal cost and environmental issues, particularly in Japan. In addition, an additional amount of chlorine gas has to be purchased in order to compensate for 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 approximately 95% or more of titanium oxide is currently used as the raw material in the Kroll process. In the future, the amount of chloride wastes will increase as the production volume of titanium increases. It is projected that the quantity of titanium metal scraps will also increase in the future. These metal scraps are currently used for ferro-alloys, but it would be advantageous if they could be reused in the titanium smelting process for producing pure titanium.

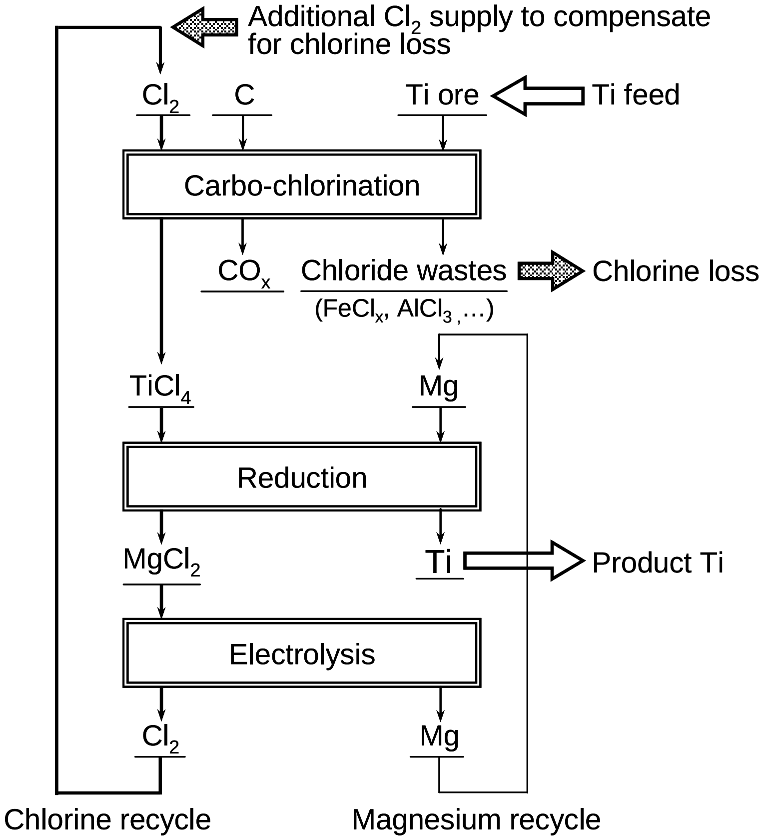

Figure 1 Chlorine cycle in the Kroll process.

Due to the abovementioned factors, the authors are currently investigating a new process, as shown in Figure 2. The chlorine and titanium recovery process investigated in this study is a part of the new process that is shown as “2: Chlorine recovery” in Figure 2. In the process investigated in this study, titanium metal scraps are recycled 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 can the titanium metal scraps be recycled but it would also be possible to effectively recover the chlorine in the chloride wastes generated from titanium smelting or any other process. Another benefit of this process is that a low-grade titanium ore can be used in the Kroll process if chlorine can be efficiently recovered. In addition, this recycling process in which a combination of titanium metal scraps and chloride wastes is used can also be extended to other reactive metals such as rare earth metals and tantalum [6].

In order to establish this new environmentally sound recycling process, the thermodynamic analyses of the reactions between $FeCl_x$ and Ti and its oxides (TiO_x) and some preliminary experimental works were carried out in the previous study [7]. In that study, titanium powder was used as the initial material and it was reacted with $FeCl_2$ at 1100 K for 1 h. After the experiment, the concentrations of Ti and Fe in the obtained sample were 9.9% and 90.1%, respectively. It is demonstrated that it is feasible to recycle titanium metal scraps by utilizing chloride wastes as a chlorine resource. On the basis of the results of the previous studies, the experiments using titanium granules (particle size: 1–2 mm) as the starting material are conducted in this study, because it is more practical to use coarse titanium scraps as a starting material.

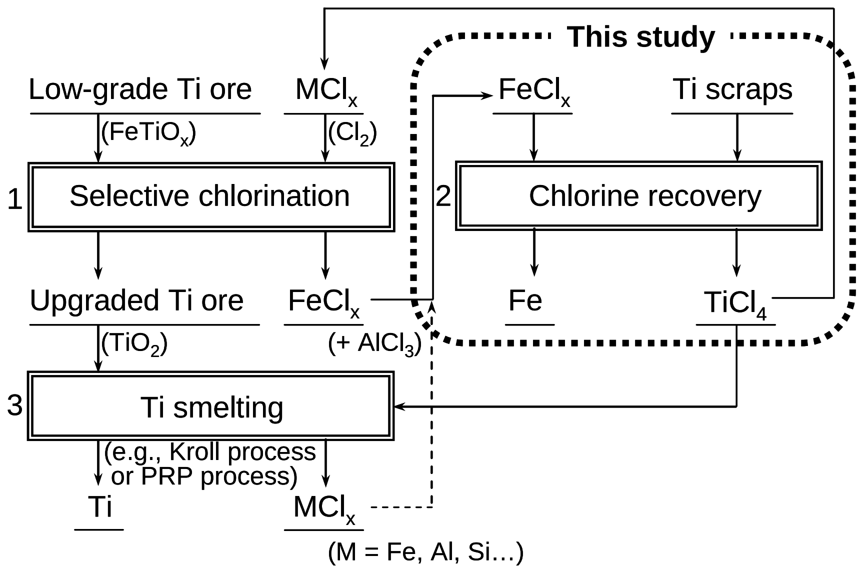

Figure 2 Flowchart of the new process discussed in this study.
1. Selective chlorination;
2. Chlorine and titanium scrap recovery;
3. Ti smelting, e.g. Kroll process and PRP process.

Experimental

The study for recycling titanium metal scraps with chloride wastes is based on the following reaction with an excess amount of $FeCl_2$ [7, 8].

$$Ti\ (s) + 2\ FeCl_2\ (l) \rightarrow TiCl_4\ (g) + 2\ Fe\ (s) \qquad (1)$$
$$\Delta G^\circ = -205 \text{ kJ at } 1100 \text{ K}$$

The experimental work for obtaining titanium chloride was carried out by reacting metallic titanium and $FeCl_2$. Figure 3 shows a schematic illustration of the experimental apparatus used for the chlorination of metallic titanium. In a typical experiment, a graphite crucible (I.D. ϕ = 27 mm) was filled with a mixture of titanium powder (31 μm) and $FeCl_2$ powder, following which the crucible was placed in a quartz tube (I.D. ϕ = 41 mm and length = 450 mm). A NaOH gas trap sustained in a glass flange covered with SUS nets on both the ends was also installed in the quartz tube near the gas outlet port. In some experiments, titanium granules (1–2 mm) were used as the starting material instead of titanium powder. Prior to the experiment, the quartz tube, which was sealed with a silicone rubber plug, was evacuated and then filled with Ar gas; the pressure within the quartz tube was maintained at approximately 0.2 atm. The quartz tube containing the sample mixture and the NaOH gas trap was then introduced into an isothermal horizontal furnace and maintained at 1100 K for 3 h. After the experiment, the residue in the graphite crucible and the deposits both within the quartz tube and on the surface of NaOH were recovered and subsequently analyzed. The phases in the sample were identified by using X-ray diffraction analysis (XRD). Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used for determining the concentration of the metallic elements. The chlorine element in the sample was determined by using the potentiometric titration method.

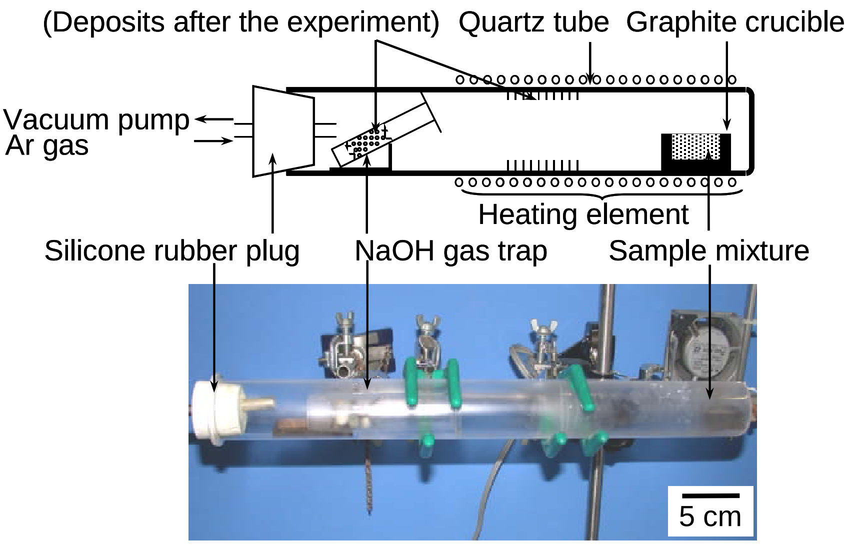

Figure 3 Experimental apparatus for the chlorination of titanium granules using $FeCl_2$.

Table I Initial materials used in this study.

Materials	Form	Purity (%)	Note / Supplier
Ti	Powder	98.0 up	Toho Titanium Co., Ltd.
Ti sponge	Granule	99.2*	Toho Titanium Co., Ltd.
$FeCl_2$	Powder	99.0	Kojyundo Chemical Laboratory Co., Ltd.

*: Determined by X-ray fluorescence analysis (XRF).

Results and discussion

Figure 4 (a) shows the assembled quartz tube after the experiment; the mixture of titanium granules and $FeCl_2$ was transferred to this tube and maintained at 1100 K for 3 h. During the experiments, the evolution of a white vapor, which was considered to be $TiCl_4$ or its related compounds, was observed. As shown in Figure 4, the major portion of this white vapor was deposited on the NaOH gas trap, whereas a small portion was deposited inside the quartz tube. After heating, brown flakes were deposited inside the quartz tube at a distance of 25 cm from the outlet of the quartz tube (Figure 4 (c)), and the residue (Figure 4 (d)) obtained in the graphite crucible was covered with a black powder.

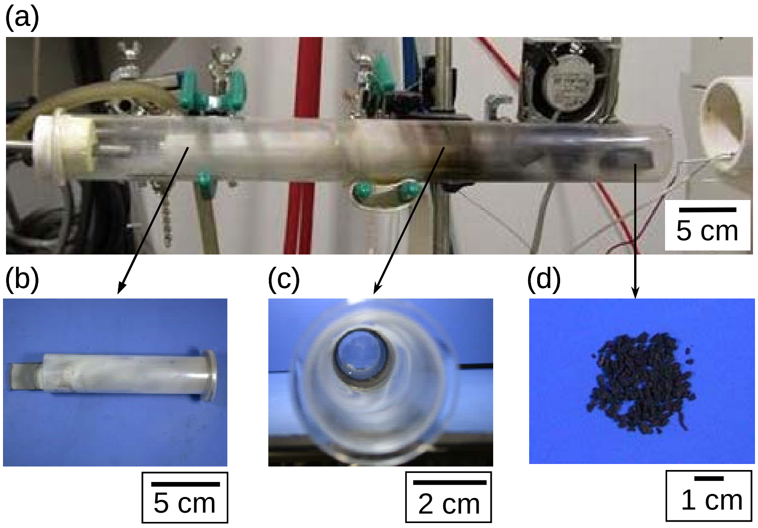

Figure 4 (a) Assembled quartz tube after experiment;
(b) Deposit on the surface of the NaOH gas trap;
(c) Deposit inside the quartz tube;
(d) Residue in the graphite crucible.

Figure 5 shows the XRD patterns of the residues obtained after heating with titanium powder and titanium granules as the starting material. The XRD patterns indicate that α-Fe was obtained in the sample after heating. However, when titanium granules were used as the starting material, the amount of unreacted Ti increased after heating. This indicates that the efficiency of the recovery of titanium scraps and chlorine was effected by the morphology of the titanium scraps. As compared to the results obtained in the previous study [7], the speed of chlorine formation was slow, and the reaction speed decreased when titanium granules were used.

The results of the element analysis, as determined by ICP-AES and potentiometric titration, are listed in Table II. The black powder on the surface of the obtained sample was considered to be Fe powder according to the analytical results shown in Table II, the XRD analysis, magnetic properties, and color of the powder. As shown in Table II, the flakes that were deposited at a distance of 25 cm from the outlet of the quartz tube were $FeCl_2$, which was transferred from the graphite crucible as vapor and was condensed and deposited inside the quartz tube. The vapor pressure of $FeCl_2$ at the reaction temperature (1100 K) is approximately 0.093 atm, and the temperature at which deposition occurs (at a distance of 25 cm from the outlet of the quartz tube) is approximately 990 K and the vapor pressure of $FeCl_2$ at this temperature is approximately 0.02 atm.

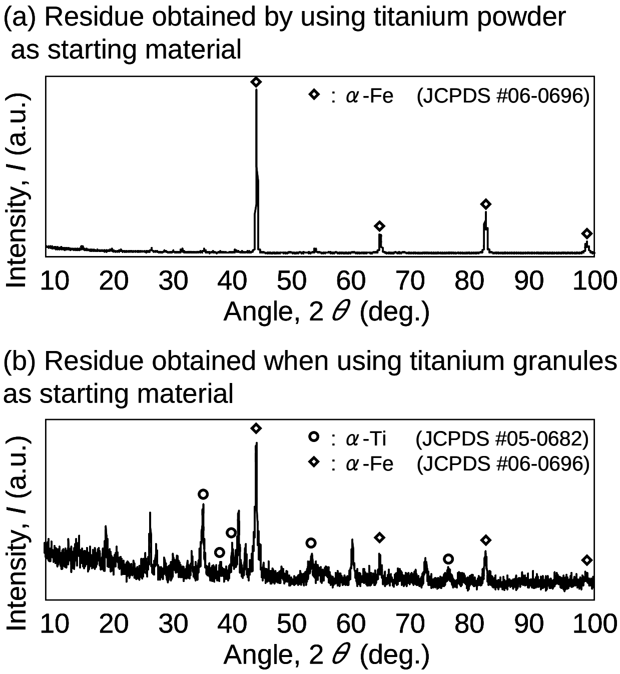

Figure 5 Comparison of the XRD patterns of the residue obtained after heating the sample mixed with either titanium powder [7] or titanium granules

Table II Analytical results of the obtained residue in the graphite crucible, the deposits obtained inside the quartz tube and on the surface of NaOH gas trap after heating.

Exp. # CD	Concentration of element i, C_i (mass%)		
	Ti	Fe	Cl
Residue in the graphite crucible	62.8[a]	37.2[a]	-[a]
Deposit inside the quartz tube	0.1[a]	49.7[a]	50.2[b]
Deposit on the surface of NaOH gas trap	0.2[a]	0.4[a]	99.4[b]

a: Determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).
b: Determined by the potentiometric titration method.

The abovementioned results demonstrated that the recovery of chlorine in $FeCl_2$ by using titanium granules is feasible. However, the efficiency of the recovery of titanium and chlorine from the mixture of titanium scraps and $FeCl_x$ is still low, and the efficiency needs to be improved for practical applications. Furthermore, the reaction speed was lower than that using titanium powder as the starting material [8]. Currently, the authors are investigating the mass balance of the chlorination reaction (Equation 2) and studying a new method for enhancing the efficiency of recovery and the reaction speed. Some recycling processes of other reactive metal scraps by using chloride wastes are also under investigation.

$$\mathrm{Ti}\ (s) + m\ \mathrm{FeCl_x}\ (l, g) \rightarrow \mathrm{TiCl_y}\ (g) + n\ \mathrm{Fe}\ (s) \qquad (2)$$

Conclusions and remarks

Some fundamental experiments on recycling chlorine present in chloride wastes by utilizing titanium metal scraps were carried out. It was demonstrated that the chlorine contained in the chloride wastes can be recovered by using titanium granules at 1100 K. The efficiency of titanium and chlorine recovery and the reaction speed were lower when titanium granules were used as the starting material as compared to the case in which titanium powder was used as the starting material. For enhancing the recovery efficiency and the reaction speed, the mass balance of the chlorination reaction of titanium metal scraps is under investigation.

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References

1. W. Kroll, “The Production of Ductile Titanium,” *Tr. Electrochem. Soc.*, 78 (1940), 35–47.

2. T. Fukuyama et al., “Production of Titanium Sponge and Ingot at Toho Titanium Co. Ltd.,” *Journal of the Mining and Materials Processing Institute of Japan,* 109 (1993), 1157–1163.

3. A. Moriya and A. Kanai, “Production of Titanium at Sumitomo Sitix Corporation,” *Journal of the Mining and Materials Processing Institute of Japan*, 109 (1993), 1164–1169.

4. F. Habashi, *Handbook of Extractive Metallurgy*, (Weinheim, Federal Republic of Germany: VCH Verlagsgesellschaft mbH, 1997), 1129–1180.

5. The Japan Titanium Society ed., “Titanium is now taking off from the cradle to the growing age” (Commemorative Publication of 50th Anniversary of JTS), (Tokyo, Japan: The Japan Titanium Society, 2002), 47.

6. K. Mineta and T.H. Okabe, “Development of Recycling Process for Tantalum from Capacitor Scraps,” *Journal of Physics and Chemistry of Solids*, 66 (2005), 318–321.

7. H. Zheng, R. Matsuoka, and T.H. Okabe, “Recycling Titanium Metal Scraps by Utilizing Chloride Wastes,” *Proc. European Metallurgical Conference 2005, EMC2005* [Dresden, Germany, September 18–21, 2005], 1509–1518.

8. I. Barin, *Thermochemical Data of Pure Substances, 3rd ed*., (Weinheim, Federal Republic of Germany: VCH Verlagsgesellschaft mbH, 1997).