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A NEW HIGH SPEED TITANIUM PRODUCTION BY SUBHALIDE REDUCTION PROCESS

Osamu Takeda[1] and Toru H. Okabe[2]

[1]Graduate student, Graduate School of Engineering, The University of Tokyo; 7-3-1 Hongo Bunkyo-ku, Tokyo, 113-8656, Japan
[2]Institute of Industrial Science, The University of Tokyo; 4-6-1 Komaba Meguro-ku, Tokyo, 153-8505, Japan

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Abstract

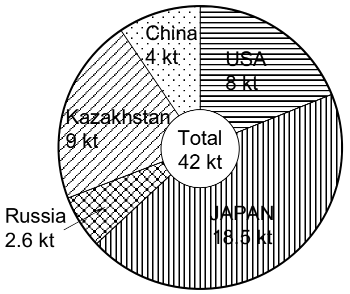
A new titanium production process using the magnesiothermic reduction of titanium subhalides employing a titanium reaction vessel was investigated. This study discusses the possibility of establishing a high-speed, semi-continuous process for the production of high-purity titanium. The titanium subhalide feed material, either titanium dichloride ($TiCl_2$) or titanium trichloride ($TiCl_3$), and the magnesium reductant were charged into a titanium reaction vessel, and the reaction vessel was heated in an argon gas atmosphere. The sample temperature rose monotonically to 973 K, after which it increased rapidly, implying that the magnesiothermic reduction of titanium subhalide proceeded at a high speed. After the reaction, excess magnesium and the reaction product, magnesium chloride ($MgCl_2$), were removed by leaching or draining and vacuum distillation. At this stage, titanium sponge with 99.8% purity was successfully obtained. The titanium reactor did not appear to be damaged and thus proved its suitability for the magnesiothermic reduction of titanium subhalides.

Introduction

Titanium is a promising material because of its excellent properties such as low density, high strength, corrosion resistance, and abundance. It is applied to the aerospace industry, chemical processing, marine applications, eyeglass frames, etc. Figure 1 (a) and (b) show the worldwide market share of titanium sponge production in 2003 and the transition of production volume of titanium mill products in Japan, respectively [1,2]. As depicted in this figure, titanium production is growing steadily; however, its total production volume globally is significantly smaller than that of common metals such as iron and aluminum. The principal reason for this is that the current titanium production process (the Kroll process) [3] is a batch-type process and the reduction process is lengthy. Due to these factors, the production cost of titanium metal is high. The production speed of titanium is lower than 1 t/day·batch despite using a 10 t batch reactor, which is currently the largest scale of operation. This productivity is extremely low compared to that of the other common metals. The demand for titanium is expected to increase in the future; however, the expansion of the production scale is limited so long as titanium is produced by the current production process.

Figure 2 is a schematic illustration of the titanium production process based on the Kroll process. In the Kroll process, either titanium feed ore (Rutile ore), which principally consists of titanium dioxide (TiO_2), or upgraded ore (UGI), which is an upgraded ilmenite ore ($FeTiO_3$), is converted to titanium tetrachloride ($TiCl_4$) by the reaction with chlorine (Cl_2) gas under a carbon-saturated atmosphere. The obtained $TiCl_4$ is purified by distillation, and iron and oxygen free feed is produced. The $TiCl_4$ feed material is dropped into a mild steel reactor in which molten magnesium (Mg) is charged. The feed material is then reduced by the magnesium at approximately 1100 K in an argon gas atmosphere. After the reaction, the by-product $MgCl_2$ and the excess magnesium are removed from the reactor both by tapping and by vacuum distillation. The recovered $MgCl_2$ is converted into magnesium reductant and chlorine gas by molten salt electrolysis, and the products are fed back to the reduction and chlorination process.

(a) Production of titanium sponge in the world (2003)



(b) Production of titanium mill products in Japan

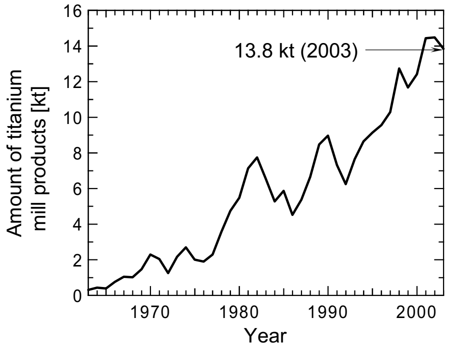


Figure 1. (a) Production of titanium sponge in the world, (b) production of titanium mill products in Japan [1,2].

Chlorination: $TiO_2 + C + 2Cl_2 \rightarrow TiCl_4 + CO_2$

Reduction: $TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$

Electrolysis: $MgCl_2 \rightarrow Mg + Cl_2$

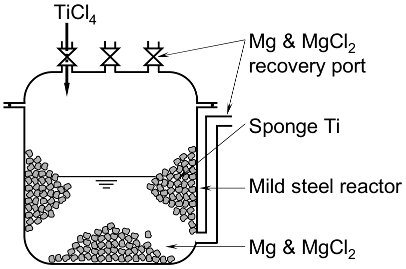


Figure 2. Schematic illustration of the reduction process for titanium production in the Kroll process.

Table I. Features of various reduction processes

Process	Advantages	Disadvantages
Kroll process	◎High-purity titanium obtainable ◎Easy metal/salt separation ○Established chlorine circulation ○Utilizes efficient Mg electrolysis ○Reduction and electrolysis operation can be independently carried out	×Complicated process ×Slow production speed ×Batch-type process
FFC process	◎Simple process ○Semi-continuous process	×Difficult metal/salt separation ×Reduction and electrolysis have to be simultaneously carried out △Sensitive to carbon and iron contamination △Low current efficiency
OS process	◎Simple process ○Semi-continuous process	×Difficult metal/salt separation △Sensitive to carbon and iron contamination △Low current efficiency
EMR/MSE process	◎Resistant to iron and carbon contamination ○Semi-continuous process ○Reduction and electrolysis operation can be independently carried out	×Difficult metal/salt separation when oxide system is used ×Complicated cell structure △Complicated process
PRP	◎Effective control of purity and morphology ◎Flexible scalability ◎Resistant to contamination ○Small amount of fluxes required	×Difficult recovery of reductant ×Environmental burden caused by leaching
This study	◎High-speed reduction process ○Semi-continuous process ○Effectively uses titanium scraps ○Facilities of the Kroll process can be utilized	×Difficulty in $TiCl_2$ handling △Multiple reduction process

The obtained sponge titanium deposit is then mechanically crushed into small pieces, and melted and cast into an ingot. The Kroll process has several beneficial features, e.g., the magnesium and chlorine cycles are established and high-purity titanium is obtained.

However, as mentioned previously, the reduction process is a batch-type process and its production speed is extremely low. The low productivity of the reduction process is one of the major factors leading to the increase in the cost of titanium production, thereby preventing the expansion of titanium application in the market.

A new process termed as the FFC Cambridge process [4], recently developed by Fray *et al.*, has stimulated titanium research activity. As a result, several processes that enable titanium production directly from titanium oxide, such as the OS process developed by Ono and Suzuki [5], the EMR/MSE process [6], and the preform reduction process (PRP) developed by Okabe *et al.* [7], are currently being actively investigated in Japan. The features of these processes are summarized in Table I. In the FFC process, the sintered TiO_2 electrode is immersed in molten calcium chloride ($CaCl_2$) salt and is polarized cathodically to remove the oxygen from the feed electrode. Metallic titanium is directly obtained through this electrochemical process. In the OS process, reductant calcium is produced by the electrolysis of molten $CaCl_2$ salt. Further, TiO_2 powder is supplied to the molten $CaCl_2$ salt, and TiO_2 is reduced by calcium. The EMR/MSE process utilizes an electronically mediated reaction (EMR) in the metallothermic reduction to effectively prevent impurity contamination. The overall reaction of the FFC, OS, and EMR/MSE processes are identical and they use large amounts of molten salts. However, these processes possess several advantages as well as drawbacks (See Table I). The PRP differs from the abovementioned processes. In this process, the fabricated feed preform containing TiO_2 is reduced by calcium metal vapor. This process is essentially resistant to contamination and has flexible scalability since it is based on the metallothermic reduction using metal vapor. In these processes,

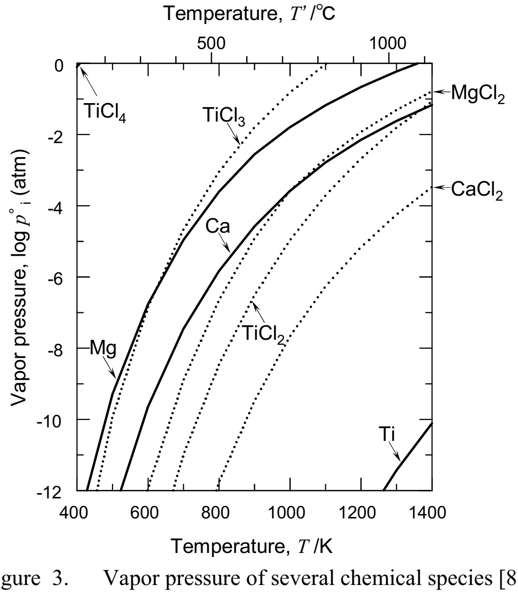


Figure 3. Vapor pressure of several chemical species [8].

the titanium production process can be simplified by utilizing the oxide feed, and a semi-continuous process can be designed. However, these direct reduction processes of titanium oxide have several problems: purity control of the titanium deposit is difficult, production speed is not high, and vacuum distillation cannot be utilized for the removal of $CaCl_2$ from the titanium product because the vapor pressure of $CaCl_2$ is low (See Figure 3 for reference [8]). As a result, the leaching process using an acid solution has to be employed, but this leads to difficulties in the metal/salt separation and in the establishment of calcium and chlorine recycling. The direct reduction process of TiO_2 is simple but it is essential to establish an efficient process for the production of high-purity TiO_2 from ore by the removal of impurities such as iron, aluminum, and silicon. At this stage, several technical problems have to be solved before a large-scale commercial process for the production of high-purity titanium directly from TiO_2 can be established.

The Kroll process is unsuitable for the development of a continuous reduction process; further, this reduction process is lengthy. However, the Kroll process has several beneficial features as follows: (1) the feed $TiCl_4$, which is produced by chlorinating titanium feed ore containing TiO_2, is in the liquid state at ambient temperature, and it can be purified by distillation due to its high vapor pressure. As a result, not only oxygen but also metal impurities such as iron and aluminum are efficiently removed through the chlorination and distillation processes; (2) the magnesium and chlorine cycles are established and they are repeatedly recycled; (3) the by-product $MgCl_2$ has a high vapor pressure and can be removed by evaporation without leaching. Subsequently, high-purity titanium is obtained. The titanium production process based on chloride metallurgy, as represented by the Kroll process, essentially has the advantage of producing high-quality titanium, because this process is based on an oxygen-free system. Therefore, it is reasonable and practical to develop a new reduction process that utilizes the advantages of the magnesiothermic reduction of chlorides.

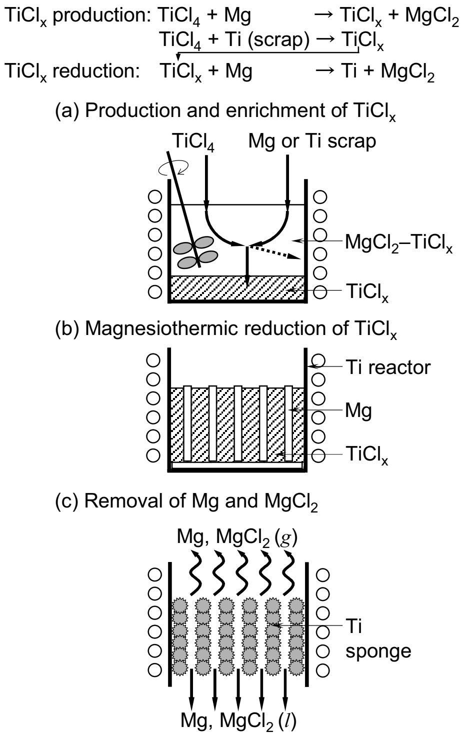


Figure 4. Schematic representation of the steps involved in the new titanium production process: (a) production and enrichment of $TiCl_x$ in $MgCl_2$ bath, (b) magnesiothermic reduction of $TiCl_x$ in titanium reactor, (c) removal of excess Mg and by-product $MgCl_2$ by draining and vacuum distillation.

Table II. Comparison of the Kroll process and new process

	Kroll process	This study
Process type	Batch-type, limited speed	(Semi-)continuous, high speed
Feed material	$TiCl_4$ (*l*, *g*)	$TiCl_2$ or $TiCl_3$ (*s*, *l*)
Heat of reduction, ($\Delta H°$/kJ mol Ti)	High (−434)	Low (−94∼−191)
Reactor material	Mild steel (Iron contamination unavoidable)	Titanium (No iron contamination)
Reactor size	Large (Crush and melt)	Small (No crush and direct melt)
Flux, sealant	Not used	$MgCl_2$, Ti
Common features	Magnesiothermic reduction of chloride Removal of $MgCl_2$ and Mg from Ti sponge by draining and vacuum distillation High-purity Ti with low oxygen content can be produced	

The authors are currently developing a new titanium production process that enables the establishment of a continuous and high-speed reduction process based on the magnesiothermic reduction of titanium chlorides. In the current titanium production process, the reduction of $TiCl_4$ is a highly exothermic reaction, and the reduction process has to be operated slowly so that the reaction temperature can be controlled. Further, the reaction vessel requires several days to cool down. Considering that titanium subchlorides ($TiCl_x$, x = 2,3) are stable in a condensed phase even at high temperatures, the authors are currently studying a new process that is not based on the direct reduction of $TiCl_4$. Figure 4 shows the flow of the new process. As shown in Figure 4, the $TiCl_4$ feed is converted to titanium subchloride, either titanium dichloride ($TiCl_2$) or titanium trichloride ($TiCl_3$), by the reaction with magnesium or titanium scraps. The generated subchloride is subsequently enriched in molten $MgCl_2$. The mixture of $MgCl_2$ and titanium subchloride is then loaded into a titanium reactor and the subchloride is reduced by magnesium. A titanium reactor cannot be utilized in the Kroll process because $TiCl_4$ easily reacts with metallic titanium, and components made of titanium are corroded by $TiCl_4$. In the new process, however, it is possible to utilize titanium metal as a material for the reactor chamber because $TiCl_2$ equilibrates with metallic titanium. After the reaction, the by-product $MgCl_2$ and the excess magnesium are removed and recovered by draining and vacuum distillation. The obtained titanium can be directly melted without crushing and can be cast into an ingot because the product is, in principle, oxygen and iron free titanium.

Table II summarizes the comparison between the Kroll process and the new process. The Kroll process is a batch-type, slow process, whereas the proposed process is a semi-continuous, high-speed process. This is because the heat produced by the reduction of subchloride is substantially lower than that produced by the reduction of $TiCl_4$, and the heat extraction ratio can be dramatically increased since the reduction process can be conducted in the condensed phase excluding the gas phase. The iron contamination of titanium can be avoided since it is possible to use metallic titanium as the reaction container. This process is suitable for a small-scale semi-continuous process, and the crushing of massive sponge is unnecessary when the reactor size is reduced. The obtained titanium can be melted and cast into the ingot directly after the vacuum distillation. Both processes share common features such as the magnesiothermic reduction of chlorides, the removal of $MgCl_2$ and magnesium by vacuum distillation, and the production of low oxygen content titanium. Furthermore, the new process can utilize the facilities of the Kroll process, and it can be constructed as an environmentally sound process by effectively using the titanium scraps.

The authors have thus far carried out a fundamental research with the aim of establishing the new process, and have demonstrated the feasibility of this process that uses the magnesiothermic reduction of $TiCl_3$ [9,10]. A part of the results of the systematic study for the establishment of the new process, including the experiment for $TiCl_2$ synthesis by reaction of $TiCl_3$ with metallic titanium and the experiment for magnesiothermic reduction of $TiCl_2$, is briefly described below.

Experimental

The phase diagram for the Ti–Mg–Cl system at 1073 K is shown in Figure 5 [11]. As shown in this figure, there are several reaction pathways for obtaining metallic titanium from $TiCl_4$ using subchlorides. We have conducted two types of experiments for titanium production by magnesiothermic reduction: Route A using $TiCl_3$ and Route B using $TiCl_2$, depicted as the dashed line in Figure 5. In this study, the $TiCl_2$ feed was produced by the reaction of $TiCl_3$ with metallic titanium.

Synthesis of $TiCl_2$

A titanium reaction container fabricated from titanium foil (99.9%, 0.2 mm thickness) was used for the experiment of $TiCl_2$ synthesis. $TiCl_3$ powder was mixed with titanium powder (99.7%) in a glove box, and the mixture placed in the titanium reaction container was loaded into a stainless steel vessel. Subsequently, the stainless steel vessel was placed in a gas-tight stainless steel chamber and heated to 1073 K in an argon atmosphere. After the experiment, the sample was recovered from the titanium reaction container in the glove box and was subjected to analysis. Phases in the sample were identified using X-ray diffraction (XRD) analysis, and the composition of the sample was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and the potentiometric titration method.

$$\begin{array}{lll} \text{Route A:} & 2\,TiCl_3 + 3\,Mg & \rightarrow 2\,Ti + 3\,MgCl_2 \\ \text{Route B:} & 2\,TiCl_3 + Ti & \rightarrow 3\,TiCl_2 \\ & TiCl_2 + Mg & \rightarrow Ti + MgCl_2 \end{array}$$

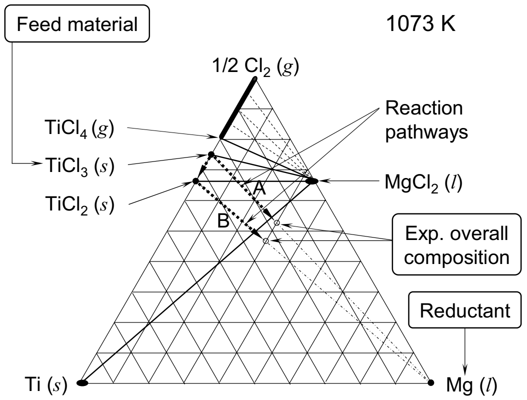


Figure 5. Phase diagram for the Ti–Mg–Cl system at 1073 K. Experimental reaction pathways for titanium production are also shown [11].

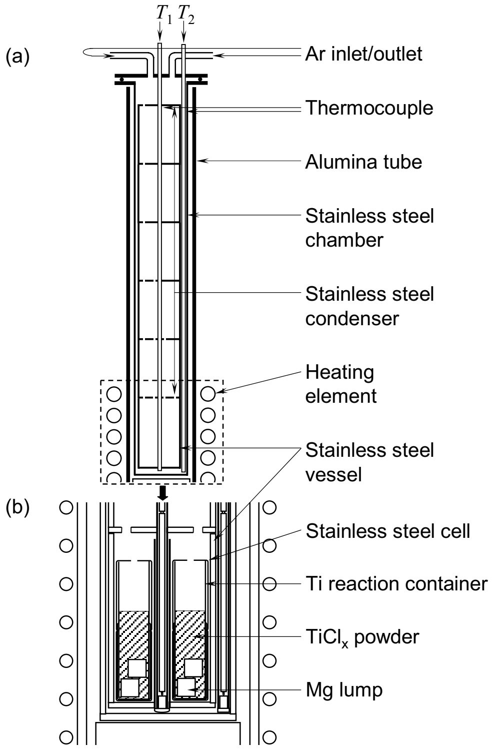


Figure 6. Schematic illustrations of the experimental apparatus for the magnesiothermic reduction of $TiCl_x$: (a) arrangement of the reduction chamber, (b) magnified picture of the reaction vessel at the bottom of the reduction chamber.

Magnesiothermic reduction of $TiCl_x$

Figure 6 shows a representative arrangement of the experimental apparatus used for titanium production by the magnesiothermic reduction of $TiCl_x$. A titanium reaction container fabricated from titanium foil (99.9%, 0.1~0.2 mm thickness) and/or a titanium tube (99.9%, 1 mm thickness) was used. $TiCl_x$ powder (5.97~102 g) was loaded in the reaction container with the magnesium lump (99.9%, 1.47~22.5 g) in a glove box (O_2 and H_2O level is maintained below 1 ppm), and 1~4 sets of the container were set in a stainless steel vessel. Subsequently, the stainless steel vessel was placed in a gas-tight stainless steel chamber that was connected to a stainless steel condenser. Thermocouples were placed in the center of (inside temperature, T_1) and outside (outside temperature, T_2) the reaction container, and the transition of temperature during the experiment was monitored. The sample was heated to 1073 K and was maintained at this temperature for 10 min in an argon atmosphere. In some experiments, following the reduction experiment, the reaction container was cooled down to ambient temperature, and the sample in the container was mechanically recovered. The by-product $MgCl_2$ and the excess magnesium in the sample were removed by leaching, and the obtained titanium deposit was subjected to analysis. In another series of experiments, the stainless steel chamber was evacuated following the reduction experiment and the sample was heated to 1273 K to remove the by-product $MgCl_2$ and excess magnesium. After the sample temperature reached 1273 K, the vacuum distillation process was terminated and the sample was cooled to ambient temperature in an argon atmosphere. The sample was then mechanically recovered and subjected to analysis. The phases in the sample were identified using XRD analysis, and the composition of the sample was determined by X-ray fluorescence analysis (XRF). The morphology of the sample was observed by scanning electron microscopy (SEM).

Results and discussion

Synthesis of $TiCl_2$

Using XRD, the black powder obtained after the $TiCl_2$ synthesis experiment was identified as $TiCl_2$ (JCPDS: 10-0315 and 73-0751). The composition of chlorine in $TiCl_2$ was determined to be x = 2.00~2.28 ($TiCl_x$) using the potentiometric titration method. It is worth noting that the titanium reaction container was not damaged and its original shape was preserved.

Magnesiothermic reduction of $TiCl_x$

The sample temperature (T_1) monotonically rose in all the experiments until it reached 973 K. Figure 7 (a) shows the representative result of the transition of the sample temperature after it reached 973 K during magnesiothermic reduction of $TiCl_3$, while Figure 7 (b) shows that of $TiCl_2$. As shown in Figure 7 (a) and (b), temperature T_1 rapidly rose after 973 K and then lowered, indicating that the exothermic magnesiothermic reduction of $TiCl_x$ proceeded at a high speed within 200 s. There was a two-step rise in the temperature on the magnesiothermic reduction of $TiCl_3$, whereas there was a one-step rise in the temperature on the magnesiothermic reduction of $TiCl_2$. These results indicate that the reduction process of $TiCl_3$ proceeded by the following two-step reaction;

$$2\,TiCl_3 + Mg \rightarrow 2\,TiCl_2 + MgCl_2 \qquad (1)$$

$$TiCl_2 + Mg \rightarrow Ti + MgCl_2 \qquad (2)$$

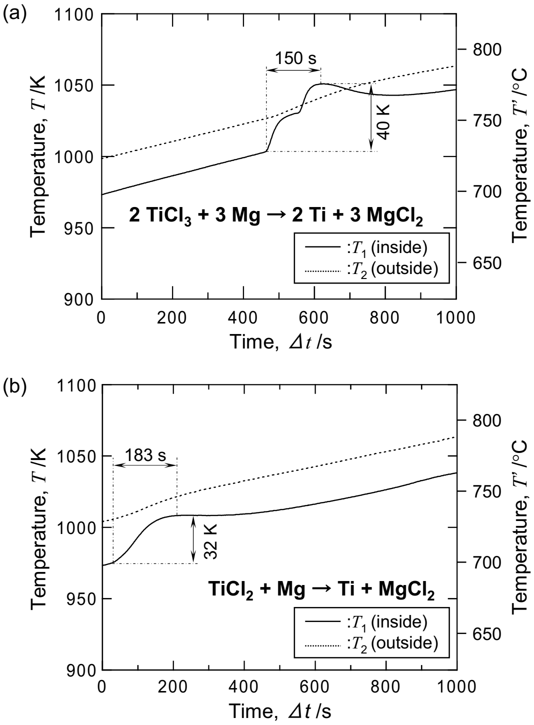
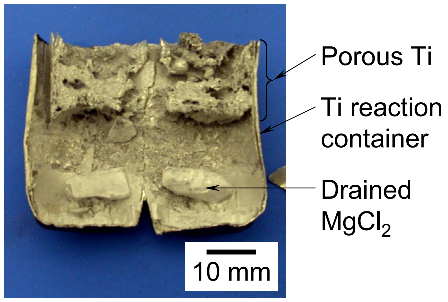


Figure 7. Representative result of the transition of sample temperature during the magnesiothermic reduction of (a) $TiCl_3$, (b) $TiCl_2$.

(a) Sectioned reaction container after reduction (without leaching)



(b) Initial setup of (a)

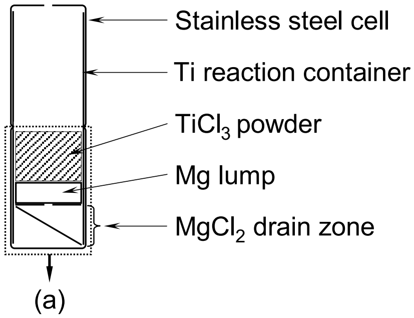


Figure 8. Sectioned titanium reaction vessel after the experiment for the magnesiothermic reduction of $TiCl_3$: (a) photograph of obtained sample, (b) initial setup of the reaction vessel.

When a large amount of $TiCl_3$ was charged, a two-step temperature change was not observed. The authors are currently analyzing the reduction pathways during the metallothermic reduction of titanium subhalides.

Figure 8 (a) is a representation of the sectioned container after the reduction experiment (prior to leaching). As shown in Figure 8, porous titanium metal was formed in the upper part of the container in the experiments. It is worth noting that the titanium reaction container was not damaged. This result shows the titanium container can be applicable to the magnesiothermic reduction of $TiCl_x$. In the experiment shown in Figure 8, $MgCl_2$ and magnesium were drained into the bottom of the container, and were separated from the titanium product. The authors are currently employing a method to establish a more efficient separation process by the combination of both draining and vacuum distillation. At this stage, titanium sponge with 99.8% purity was successfully obtained.

Figure 9 shows the SEM image of the obtained titanium sample after the by-product was removed by leaching. In the experiment for the magnesiothermic reduction of $TiCl_3$, titanium metal with a coral-like structure, shown in Figure 9 (a),

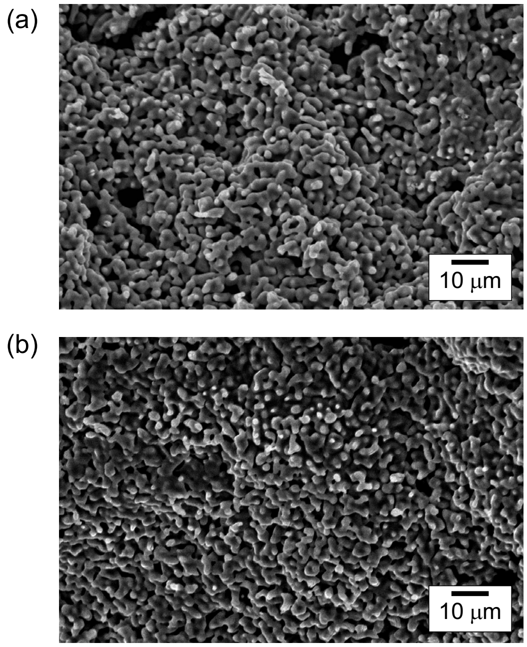


Figure 9. Scanning electron micrograph of the obtained titanium on experiment for magnesiothermic reduction of: (a) $TiCl_3$, (b) $TiCl_2$.

consisting of tightly combined primary particles with diameters of 1~5 μm, was obtained. Figure 9 (b) shows the SEM image of the obtained titanium sample after the magnesiothermic reduction of $TiCl_2$. No significant difference was observed between the titanium samples obtained from the magnesiothermic reduction of $TiCl_3$ and $TiCl_2$, and in both cases, deposits with coral-like structures were obtained. In case of titanium sample after the removal of the by-product by vacuum distillation, the neck of each primary particle in the titanium sample grew. Platy structure made of primary particles, which had lost their round shape, and jagged primary particles were also observed in some experiments. This result shows that the sintering of the primary particle proceeded in the dry separation process. The mechanism of neck formation of primary particle is currently under investigation.

Conclusions

Fundamental research was conducted in order to develop a new high-speed, semi-continuous titanium production process by subhalide reduction to obtain high-purity titanium, and the feasibility of the process was also demonstrated. $TiCl_2$ was synthesized by the reaction of $TiCl_3$ with metallic titanium. The experiment for the magnesiothermic reduction of titanium subhalide, either $TiCl_3$ or $TiCl_2$, was carried out, and titanium with 99.8% purity was successfully obtained. The reaction container made of titanium was demonstrated to be applicable to the magnesiothermic reduction of titanium subhalide, and the by-product was shown to be efficiently removed by combining both draining and vacuum distillation. The authors are currently developing a process for the production of $TiCl_x$ from $TiCl_4$ and the enrichment process of $TiCl_x$ with the aim of establishing a high-speed semi-continuous titanium production process.

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