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Titanium Production Process by Utilizing Titanium Subchlorides

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This study discusses the possibility of a new high-speed (semi-)continuous titanium production process that utilizes titanium subchlorides ($TiCl_x$, x = 2, 3). This titanium production process is based on the magnesiothermic reduction of subchlorides referred to as the "subhalide reduction process". Titanium dichloride ($TiC1_2$) or titanium trichloride ($TiCl_3$) is synthesized in advance by the reaction of titanium tetrachloride ($TiC1_4$) with titanium metal or other reductants (e.g., magnesium and aluminum), and the obtained $TiCl_x$ is reduced by magnesium in a titanium reaction container. The following points are the main findings of this study: (1) The rate of formation of the titanium deposit by the magnesiothermic reduction of $TiCl_x$ is significantly higher than that by the magnesiothermic reduction of $TiCl_4$ (the Kroll process). (2) The titanium reaction container was shown to be applicable not only for the $TiC1_2$ reduction but also for the $TiCl_3$ reduction, and a titanium product with high purity (e.g., 99.8 mass%) can be obtained. (3) The reaction product ($MgC1_2$) formed after the magnesiothermic reduction of $TiCl_x$ can be efficiently removed by a newly developed separation process combining draining and/or vacuum distillation. From a series of research and development activities, the feasibility of the subhalide reduction process was demonstrated.

Keywords: Titanium, Subchloride, High-speed reduction process, Titanium Smelting, subhalide reduction process

1. Introduction

In the recent field of research on titanium smelting, new reduction processes as replacements for the Kroll process [1)] are actively being investigated all over the world [2)]. The direct reduction processes of titanium oxide by the electrochemical method [3,4)] or by calciothermic reduction [5,6)] in particular are spotlighted. These new processes have the potential for producing low-cost titanium by simplifying the titanium production process. However, several technical problems, such as low reduction speed and the difficulty in the recycling of the calcium reductant, need to be resolved prior to establishing a large-scale commercial process. Meanwhile, new titanium reduction processes based on chloride metallurgy are also being investigated [7,8)] because chloride metallurgy can surely produce high-quality titanium by carrying out the reduction process in an oxygen-free system.

From the abovementioned background, the authors are developing a new high-speed and (semi-)continuous titanium production process based on the magnesiothermic reduction of titanium subchlorides ($TiCl_x$, x = 2, 3) referred to as the subhalide reduction process [9-12)]. As shown in Figure 1, titanium subchlorides are synthesized by the reaction of titanium tetrachloride ($TiC1_4$) with magnesium (Mg) or titanium scraps. When the subchlorides are synthesized in a molten magnesium chloride ($MgCl_2$) medium, they are subsequently enriched in the $MgCl_2$—$TiCl_x$ molten salt. The $TiCl_x$ feed (with $MgCl_2$) is then loaded into a titanium reaction container, where $TiCl_x$ is reduced by magnesium. After the reduction process, the $MgCl_2$ reaction product and excess magnesium are removed by draining and/or vacuum distillation.

The following are the advantages of utilizing subchlorides as the feed materials for the reduction process: (a) A high-speed and (semi-)continuous process can be designed using conventional techniques because the heat produced by the reduction of subchlorides is substantially lower than that produced by the reduction of $TiC1_4$. In addition, the density of the reaction field and the rate of heat extraction from the reaction container increase drastically by employing the reduction process in the condensed phase. The feed subchlorides are stable as a condensed phase (sublimation point, $TiC1_3$: 1103 K, $TiC1_2$: 1580 K [13)]) and have low vapor pressure even at elevated temperatures. (b) The iron contamination of the titanium products from the reaction container can be avoided since

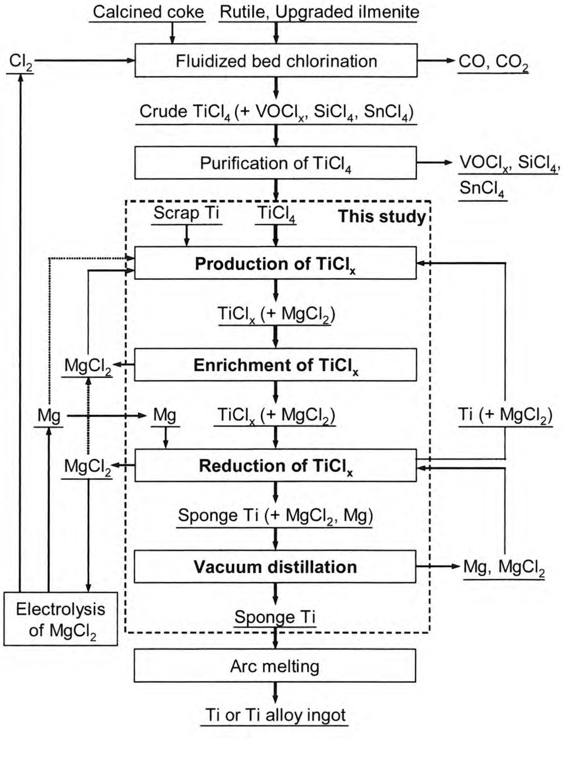

Figure 1. Flowchart of the new titanium production process based on the subhalide reduction process.

metallic titanium can be utilized as the reactor material under $Ti/TiCl_2$ equilibrium. (c) The $MgCl_2$ reaction product can be easily removed by vacuum distillation, and high-purity titanium with a low oxygen content can be obtained. (d) The titanium sponge obtained can be melted directly together with the reactor because the reactor is made of titanium metal. Therefore, the crushing of the massive titanium sponge can be avoided, and the obtained titanium sponge after vacuum distillation can be melted and cast directly into an ingot.

The authors have thus far carried out fundamental research with the aim of establishing the new titanium production process by utilizing titanium subchlorides [9-12) and have demonstrated the feasibility of this process. The representative results of the fundamental research are briefly introduced below.

2. Experimental

2.1 Synthesis and Enrichment of Titanium Subchlorides

In order to develop an efficient synthetic process for titanium subchlorides, the reaction of $TiCl_4$ gas with titanium metal was investigated by a laboratory scale experiment [12). Titanium sponge (99.7%, ca. half inch in size) or titanium powder (99. 4%, average particle diameter d_{50} is 25 μm) placed on molybdenum trays or stainless steel trays was reacted with $TiC1_4$ (99%) gas supplied at rates of 0.12-0.64 g/min at 1073-1273 K in an argon atmosphere. In some experiments, the titanium sponge placed in a stainless steel basket was immersed in a molten $MgC1_2$ bath, where the titanium sponge was reacted with $TiC1_4$ gas bubbles blown into the bath. The $MgCl_2$—$TiCl_x$ mixture salt obtained by the synthesis was then filled into a tubular stainless steel capsule, where $TiCl_x$ was enriched by utilizing the difference in the solubility of $TiCl_x$ in $MgC1_2$ at different temperatures. After the experiments, the samples were recovered in a dry nitrogen atmosphere and were subjected to analysis. The phases in the samples were identified by X-ray diffraction (XRD) analysis, and the composition of the samples was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and the potentiometric titration method.

2.2 Magnesiothermic Reduction of Titanium Subchlorides

The fundamental study for titanium production by the magnesiothermic reduction of titanium dichloride ($TiCl_2$) or titanium trichloride ($TiCl_3$) by employing a titanium reaction container was experimentally carried out [9-11). The $TiC1_2$ feed powder used in this study was synthesized by the reaction of $TiC1_3$ powder with titanium metal powder in advance. $TiCl_x$ feed powder and magnesium reductant lump (99.9%) were set in the titanium reaction container. The samples were heated to 1073 K at a rate of 3.3 K/min in an argon atmosphere, and the change in temperature by the magnesiothermic reduction of $TiCl_x$ was monitored. After the reduction experiment, the samples were slowly cooled in an electric furnace and mechanically recovered. The $MgCl_2$ reaction product and the excess magnesium reductant mixed with the obtained titanium metal were removed by acid leaching. In some experiments, the reaction system holding the samples was subsequently evacuated at 1273 K after the reduction, and the $MgC1_2$ reaction product and excess magnesium reductant were removed by vacuum distillation. Furthermore, the separation process for the $MgC1_2$ reaction product and excess magnesium reductant by the combination of both draining and vacuum distillation was also studied. The phases in the obtained titanium product were identified by 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).

3. Results and Discussion

3.1 Synthesis and Enrichment of Titanium Subchlorides

The representative experimental results of the $TiCl_x$ synthesis are summarized in Table 1. As shown in the table, the efficiency of the $TiCl_x$ synthesis (titanium consumption ratio, R_{Ti}') by the direct reaction of $TiCl_4$ gas with titanium metal was low. This is probably because the $TiC1_2$ thin film formed on the surface of the titanium metal feed (sponge and powder) hindered the chlorination reaction. Furthermore, the $TiCl_2$ solid was converted into $TiCl_3$ gas by the reaction with the $TiC1_4$ gas during the synthesis. Therefore, for improving the efficiency of the $TiCl_x$ synthesis, the $TiCl_2$ solid film formed has to be removed from the surface and stored in a stable form.

In order to remove the $TiCl_2$ solid from the surface, molten $MgCl_2$ was utilized as a reaction medium that dissolves and accumulates $TiC1_2$ in the medium. This is because the solubility of $TiC1_2$ in $MgCl_2$ at 1273 K is reported to be high (~83 mol%). As shown in Table 1, the efficiency of the $TiCl_x$ synthesis (R_{Ti}') was drastically improved by employing molten $MgCl_2$, and it was found that $MgCl_2$ can be used as the reaction medium for the synthesis of the $TiCl_x$ feed for the subchloride reduction process.

Since the concentration of $TiCl_x$ synthesized in the molten salt was low, $TiCl_x$ has to be enriched in order to improve the efficiency of the subsequent reduction process. In the representative experiment for the enrichment process

Table 1. Representative yield of $TiCl_x$ and Ti consumption ratio in the experiment for $TiCl_x$ synthesis [12)

Exp. No.	$TiCl_4$ feed rate, r / g·min^{-1}	Yield of $TiCl_x$, R_{TiCl_x} (%)	Ti consumption ratio,
$TiCl_x$ synthesis by direct reaction of $TiCl_4$ gas with solid titanium			
A	0.64	26	43
B	0.17	32	44
C	0.17	23	42
D	0.12	35	45
$TiCl_x$ synthesis in molten salt			
E	0.56	64	80
F	0.16	46	93
G	0.13	49	84
H	0.65	60	75

of $TiCl_x$, the titanium concentration in the molten value (8. 9mass%) to a higher value (17 mass%), and $MgCl_2$—$TiCl_x$ salt successfully increased from its initial feasibility of the enrichment process was demonstrated.

3.2 Magnesiothermic Reduction of Titanium Subchlorides

In all the reduction experiments, the sample temperature increased monotonically up to 973 K, beyond which it increased rapidly and then decreased. From a series of experiments, it was found that the exothermic magnesiothermic reduction of $TiCl_x$ proceeded at a high speed within 200 s. A two-step rise in temperature was observed in the magnesiothermic reduction of $TiCl_3$, whereas a one-step rise in temperature was observed in the magnesiothermic reduction of $TiCl_2$. These results indicate that the reduction process of $TiCl_3$ proceeded by the two-step reaction. When a large amount of $TiCl_3$ was charged, the two-step temperature change was not observed.

Since the method for supplying feed material into the reaction container in the Kroll process differs entirely from that in the subhalide reduction process discussed in this study, a comparison of the rate of formation of the titanium deposits in these methods is difficult. However, it is important and worth trying to compare the nominal reduction speed. A comparison in the rates of formation of the titanium deposit in the reduction process between the Kroll process and the subhalide reduction process is summarized in Table 2 11). As shown in the table, the rates in the subhalide reduction process are extremely high in comparison with that obtained in the Kroll process, and the subhalide reduction process is probably suitable for high-speed reduction.

After the reduction experiment, the titanium reaction container was recovered and its condition was investigated in detail. It is noteworthy that the titanium reaction container was not damaged not only in the experiments employing $TiCl_2$ but also in those employing $TiCl_3$ as the feed material. From the viewpoint of thermodynamics, $TiCl_3$ damages the titanium container by reacting with metallic titanium to form $TiCl_2$. The experimental results, however, showed no damage to the titanium container. This is probably due to the fact that the reaction of $TiCl_3$ with titanium metal is slower than the magnesiothermic reduction of $TiCl_3$ under the conditions employed in this study. This result shows that the titanium container can be used in the magnesiothermic reduction of $TiCl_x$.

In some experiments, $TiCl_2$ was observed on the porous metallic titanium after the reduction experiment. This incomplete reduction is probably due to the blockage of the supply pathway for magnesium reductant. The titanium deposit generated in the middle of the container may hinder the reductant flow from the bottom to the top of the container. From this result, it was also found that the diffusion pathway of the magnesium reductant to the $TiCl_x$ feed must be appropriately controlled in order to efficiently proceed with the reduction.

The representative analytical results of the titanium metal samples obtained by the magnesiothermic reduction of $TiCl_2$ and $TiCl_3$ are summarized in Tables 3 and 4, respectively. As shown in Table 3, titanium metal with more than 99.7% purity was successfully obtained by the magnesiothermic reduction of $TiCl_2$ using the titanium reaction container followed by vacuum distillation, and the yield of the titanium metal was 89%~99%. When a

Table 2. Comparison in rate of formation of titanium deposit in reduction process between the Kroll process and the subhalide reduction process 11).

Process	Dimensions of reaction region in reactor: cross-sectional area, S/m^2	Dimensions of reaction region in reactor: volume, V/m^3	Nominal rate of formation of titanium deposit: per unit area, $r_a/\mathrm{kg\cdot m^{-2}\cdot s^{-1}}$	Nominal rate of formation of titanium deposit: per unit volume, $r_V/\mathrm{kg\cdot m^{-3}\cdot s^{-1}}$	Ref.
Kroll (Shimosaki and Kuramoto) [a]	3.3×10^{-3}	(3.3×10^{-4}) [b]	0.006	(0.060) [c]	[14]
Kroll (Noda) [d]	9.9×10^{-1}	(1.0) [b]	0.009	(0.009) [c]	[15]
Subhalide ($TiCl_2$, Fuwa and Takaya)	3.9×10^{-3} [e]	1.2×10^{-3} [e]	Not analyzed	Not analyzed	[8]
Subhalide ($TiCl_3$, Takeda and Okabe)	2.8×10^{-3}	2.3×10^{-4}	(0.043) [c]	0.54	[10]
Subhalide ($TiCl_2$, Takeda and Okabe)	3.1×10^{-4}	2.5×10^{-5}	(0.061) [c]	0.76	[11]

a: Reaction temperature: 1000 K.
b: Assumed value.
c: Calculated reference value.
d: Reaction temperature was not provided.
e: Representative value (private communication).

Table 3. Representative analytical results of the titanium samples obtained by the magnesiothermic reduction of $TiCl_2$ 11).

Exp. No.	Concentration of element i, C_i (mass%)[a]: Ti	Fe	Ni	Cr	Mg	Al	Yield (%)	Removal method of reaction product
A	99.7	0.16	0.04	<0.01	0.06	0.03	99	Leaching
B	99.2	0.10	<0.01	0.04	0.50	0.16	≥89[b]	Leaching
C	99.8	0.22	<0.01	0.03	<0.01	<0.01	98	Vacuum distillation
D	99.7	0.16	<0.01	<0.01	<0.01	0.10	99	Vacuum distillation

a: Determined by X-ray fluorescence analysis (XRF); the value excludes carbon and gaseous elements.
b: This value includes the uncertainty due to mechanical separation.

Table 4. Representative analytical results of the titanium sample obtained by the magnesiothermic reduction of $TiCl_3$ [10].

Exp.	Concentration of element i in obtained Ti sample, C_i (mass%) [a]						Yield	Removal method of
No.	Ti	Fe	Ni	Cr	Mg	Al	(%)	reaction product
A	96.4	0.13	<0.01	0.03	0.02	3.47	81	Leaching
B	99.4	0.16	<0.01	0.02	0.16	0.44	99	Vacuum distillation
C [b]	95.8	1.74	0.33	0.36	<0.01	1.77	80	Vacuum distillation
D	99.3 [c]	0.29 [c]	<0.01 [c]	<0.01 [c]	0.10 [c]	0.36 [c]	66	Leaching
E	99.5 [c]	0.12 [c]	<0.01 [c]	<0.01 [c]	0.11 [c]	0.24 [c]	91	Leaching
F	99.0 [c]	0.18 [c]	0.02 [c]	0.02 [c]	0.09 [c]	0.65 [c]	82	Draining and Vacuum distillation
G	99.2 [c]	0.50 [c]	<0.01 [c]	0.01 [c]	0.09 [c]	0.21 [c]	87	

a: Determined by X-ray fluorescence analysis (XRF), and the value excludes carbon and gaseous elements.
b: Stainless steel reaction container was used.
c: Average of top part and bottom part in the obtained titanium sample.

stainless-steel reaction container was used for the magnesiothermic reduction of $TiCl_3$, the titanium product was heavily contaminated by iron, chromium,and nickel (cf. Table 4, Exp. No. C).

In some experiments, the $MgCl_2$ reaction product and excess magnesium reductant were removed by the combination of both draining and vacuum distillation after the reduction (cf. Table 4, Exp. Nos. F and G). The removal rate by the newly developed separation process reached more than 5 times as compared with that by only vacuum distillation, and titanium metal was efficiently obtained.

From these results, it was demonstrated that the magnesiothermic reduction of $TiCl_2$ and $TiCl_3$ using the titanium reaction container followed by vacuum distillation is effective in producing pure metallic titanium.

4. Conclusions

Fundamental research was conducted in order to develop a new high-speed and (semi-)continuous titanium production process based on the magnesiothermic reduction of titanium subhalides. The experiment for the synthesis of titanium subchlorides by the reaction of $TiCl_4$ gas with titanium metal was carried out, and it was found that the efficiency of the $TiCl_x$ synthesis was drastically improved by employing molten $MgCl_2$ as the reaction medium. The feasibility of the enrichment process for $TiCl_x$ in molten $MgCl_2$—$TiCl_x$ was also demonstrated. The magnesiothermic reduction of the titanium subchloride—$TiCl_3$ and $TiCl_2$—was carried out, and it was found that the magnesiothermic reduction of $TiCl_x$ proceeded at a high speed. For producing low chlorine titanium, the diffusion pathway of the magnesium reductant to the $TiCl_x$ feed must be appropriately controlled in order to efficiently proceed with the reaction. It was also demonstrated that a titanium reaction container could be used for the magnesiothermic reduction of titanium subchlorides, and titanium with 99.8% purity could be obtained.

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