

FUNDAMENTAL STUDY
ON
MAGNESIOTHERMIC REDUCTION OF TITANIUM SUBCHLORIDES

O. Takeda ^a and T. H. Okabe ^{*}

Institute of Industrial Science, The University of Tokyo
4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

ABSTRACT

A fundamental study on the subhalide reduction process—based on the magnesiothermic reduction of titanium subchlorides (TiCl_x , $x = 2, 3$)—was carried out with the purpose of establishing a new (semi-)continuous/high-speed titanium production process. Titanium dichloride (TiCl_2) or titanium trichloride (TiCl_3) was synthesized beforehand by the reaction of titanium tetrachloride (TiCl_4) with titanium metal or other reductants (e.g., magnesium, aluminum). The TiCl_x feed material and magnesium reductant were set in a titanium reaction vessel, and the vessel was heated at a rate of 3.3 K/min. In all the experiments, the sample temperature rapidly increased above 973 K, and the magnesiothermic reduction of TiCl_x proceeded at a high speed. A two-step reaction was observed when TiCl_3 was reduced, whereas a one-step rise in the temperature was observed for the magnesiothermic reduction of TiCl_2 . Since the titanium reaction vessel was not damaged, it was shown that titanium metal can be used as a reactor material in the subhalide reduction process. Some results with regard to a novel TiCl_x synthetic process using molten salts as a reaction medium will also be shown.

Keywords: titanium, titanium subchloride, magnesiothermic reduction,
high-speed process, subhalide reduction process

^{*} Corresponding author: okabe@iis.u-tokyo.ac.jp

^a Present address: Research Associate, Department of Metallurgy, Graduate School of Engineering, Tohoku University, 6-6-2 Aramaki Aza Aoba, Aoba-ku, Sendai 980-8579, Japan

INTRODUCTION

In recent years, the rapid increase in the demand for titanium has resulted in a serious shortage of titanium in the market. However, an immediate increase in titanium production is difficult since the productivity of the current titanium production process—the Kroll process (1)—is low. In this process, titanium is produced by the magnesiothermic reduction of titanium tetrachloride (TiCl_4). Since the reduction of TiCl_4 is an extremely exothermic reaction, it is impossible to increase the speed of this reduction process. Even modern large-scale facilities require more than 10 days for the production of 10 tons of titanium by this process. Thus, the development of a new production process with a high productivity is an important requirement.

Recently, in order to overcome the disadvantages of the Kroll process, direct reduction processes of titanium dioxide (TiO_2) are actively being investigated all over the world (2–4). These new processes have the potential for producing low-cost titanium; however, several technical problems need to be resolved prior to establishing a large-scale commercial process.

Based on the abovementioned background, the authors are developing a new high-speed and (semi-)continuous titanium production process by the magnesiothermic reduction of titanium subchlorides—titanium dichloride (TiCl_2) and/or titanium trichloride (TiCl_3) (5–8). In this process, referred to as the subhalide reduction process, the TiCl_4 feed is converted into titanium subchlorides (TiCl_x , $x = 2, 3$) by reaction with magnesium (Mg) or titanium scraps. When these subchlorides are synthesized in the magnesium chloride (MgCl_2) medium, the TiCl_x generated is subsequently enriched in the MgCl_2 – TiCl_x molten salt. The TiCl_x feed (with MgCl_2) is then loaded into a titanium reaction vessel, and the TiCl_x is reduced by magnesium. After this reduction process, the MgCl_2 reaction product and excess magnesium are removed by draining and vacuum distillation.

The following are the advantages of utilizing subchlorides as feed materials for the reduction process. (a) A high-speed and (semi-)continuous process can be designed because the heat produced by the reduction of the subchlorides is substantially lower than that produced by the reduction of TiCl_4 . (b) The iron contamination of the titanium product can be avoided since metallic titanium can be utilized as a 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 crushing of the massive sponge can be avoided when the reactor size is reduced, and the titanium obtained can be melted and cast into an ingot directly after the vacuum distillation.

Thus far, the authors have carried out fundamental research with the aim of establishing the subhalide reduction process by employing the magnesiothermic reduction of TiCl_x (5–8) and have demonstrated its feasibility. A brief description of a

part of the results of the fundamental research for establishing the subhalide reduction process, including the experiment for the magnesiothermic reduction of TiCl_x , is provided below.

EXPERIMENTAL

Figure 1 shows the representative experimental apparatus used in this study. The TiCl_2 or TiCl_3 feed material (5.97~102 g) and magnesium reductant (99.9%, 1.47~22.5 g) were set in a titanium reaction container. In some experiments, a stainless-steel cell with a stainless-steel foil lining was used as the reaction container instead of the titanium reaction container. The container was heated to 1073 K at a rate of 3.3 K/min in an argon atmosphere, and the change in the sample temperature by the magnesiothermic reduction of TiCl_x was monitored at the center (T_1) and outside the vessel (T_2).

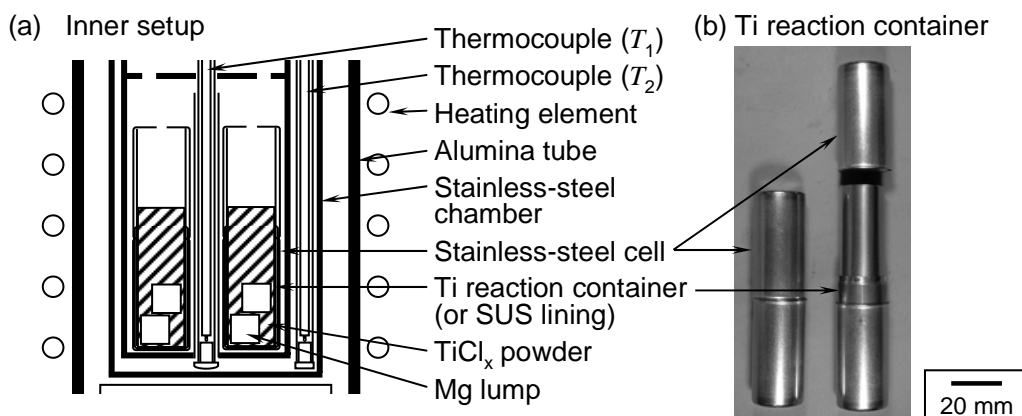
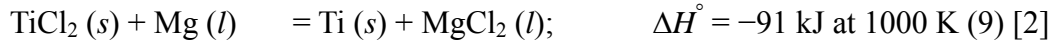


Figure 1 – Schematic illustration and image of the experimental apparatus for the magnesiothermic reduction of TiCl_x (one end closed type): (a) The inner setup of reaction vessel. (b) Titanium reaction container.

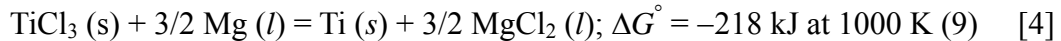
RESULTS AND DISCUSSION

In all the experiments, the sample temperature T_1 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 the temperature was observed for the magnesiothermic reduction of TiCl_3 , whereas a one-step rise in temperature was observed for the magnesiothermic reduction of TiCl_2 . These results indicate that the reduction process of TiCl_3 proceeded by the following two-step reaction:



When a large amount of TiCl_3 was charged, the two-step temperature change was not observed. 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 authors are currently conducting a detailed analysis of the reduction pathways during the metallothermic reduction of titanium subchlorides.

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. According to the reaction in Eq. [3], TiCl_3 may damage 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 given by Eq. [3] is slower than that given by Eq. [4] under the conditions employed in this study. This result shows that the titanium container can be used in the magnesiothermic reduction of TiCl_x .



By the subhalide reduction process, a titanium sponge with a purity of 99.8% was successfully obtained by using a titanium reaction container. When a stainless-steel reaction container was used, the titanium product was heavily contaminated by iron, chromium, and nickel. As shown in Figure 2, these impurities diffused from the reaction container, and the purity of the titanium product was below 96 mass%. The authors continue to develop some key technologies, e.g., an enrichment process for TiCl_x in molten salts, for establishing a new titanium production method based on the subhalide reduction process.

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 subhalides. The experiment for the magnesiothermic reduction of the titanium subchloride TiCl_3 or TiCl_2 was carried out, and it was found that the magnesiothermic reduction of TiCl_x proceeded at a high speed. It was also shown that 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 demonstrated that the titanium reaction container could be used for the magnesiothermic reduction of titanium subchlorides, and titanium with 99.8% purity could be obtained.

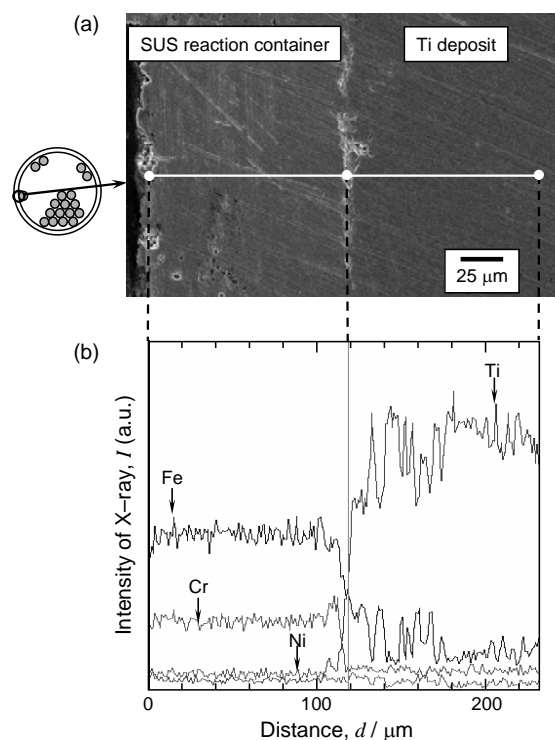


Figure 2 – (a) Scanning electron micrograph of the sectioned stainless-steel reaction container after the experiment for the magnesiothermic reduction of TiCl_3 . (b) Element concentration profile across the boundary between inner wall of reaction container and titanium deposit.

ACKNOWLEDGEMENTS

The authors are grateful to Professors Masafumi Maeda and Yoshitaka Mitsuda of the University of Tokyo and Professor Tetsuya Uda of Kyoto University for their valuable discussions throughout this project. The authors also thank Mr. Susumu Kosemura, Mr. Masanori Yamaguchi, and Mr. Yuichi Ono of Toho Titanium Co., Ltd. for their valuable discussions and for providing the samples. This work was financially supported by a Grant-in-Aid for Scientific Research (A) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT, Project ID. #15686031). A part of this research includes the result of the program “Development of Electrochemical Reduction Process for Oxide Nuclear Fuel” conducted by the Central Research Institute of the Electric Power Industry, which is financially supported by MEXT. One of the authors O. Takeda is grateful for the financial support provided by a Grant for the 21st Century COE Program “Human-friendly Materials based on Chemistry” from MEXT and the financial support provided by the Research Fellowships of the Japan Society for the Promotion of Science (JSPS) for Young Scientists.

REFERENCES

1. W. Kroll, "The Production of Ductile Titanium", Transactions of Electrochemical Society, Vol. 78, 1940, 35–47.
2. Z. Chen, D.J. Fray, and T.W. Farthing, "Direct Electrochemical Reduction of Titanium Dioxide to Titanium in Molten Calcium Chloride", Nature, Vol. 407, 2000, 361–364.
3. K. Ono and R.O. Suzuki, "A New Concept for Producing Ti Sponge: Calciothermic Reduction", JOM (Journal of Metals), Vol. 54, February, 2002, 59–61.
4. T. Abiko, I. Park, and T.H. Okabe, "Reduction of Titanium Oxide in Molten Salt Medium", Proceedings of 10th World Conference on Titanium, G. Lutjering and J. Albecht Eds., Deutsche Gesellschaft fur Materialkunde e. V., Hamburg, Germany, 2003, 253–260.
5. O. Takeda and T.H. Okabe, "High Speed Reduction Process of Titanium Using Subhalide", Abstracts of the Mining and Materials Processing Institute of Japan (MMIJ) 2004 Autumn Meeting II, Morioka, Japan, 2004, 329–330.
6. O. Takeda and T.H. Okabe, "A New High Speed Titanium Production by Subhalide Reduction Process", Proceedings of the 2005 TMS Annual Meeting, Light Metals 2005, H. Kvande Ed., TMS, San Francisco, USA, 2005, 1139–1144.
7. O. Takeda and T.H. Okabe, "High-speed Titanium Production by Magnesiothermic Reduction of Titanium Trichloride", Materials Transactions, Vol. 47, No. 4, 2006, 1145–1154.
8. O. Takeda and T.H. Okabe, "Fundamental Study on Magnesiothermic Reduction of Titanium Dichloride", Metallurgical and Materials Transactions B, in print.
9. I. Barin, Thermochemical Data of Pure Substances, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1989.