Producing Titanium by Reducing $TiCl_2$-$MgCl_2$ Mixed Salt with Magnesium in the Molten State

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In the Kroll process for titanium sponge metal production, $TiCl_4$ gas is introduced and reacted with molten magnesium metal via a gas-liquid reduction reaction. The magnesium reduction reaction of the mixed salt of $TiCl_2$-$MgCl_2$ via a liquid-liquid reaction has been investigated and the results are reported in this article. First, the molten mixed salt was synthesized through chlorination reaction of solid titanium sponge placed in molten $MgCl_2$ salt, while $TiCl_4$ gas was bubbled at around 1,173K. Then, the $TiCl_2$-$MgCl_2$ was reacted with molten magnesium at similar temperatures. This proposed magnesium reduction reaction of the $TiCl_2$-$MgCl_2$ in the molten state may be more efficient, easier to control, and suitable for realizing continuous titanium production.

INTRODUCTION

Presently, sponge titanium is produced via the Kroll process, invented by J.W. Kroll some 50 years ago.[1,2] The process is now operated in a semi-batch state where purified $TiCl_4$ is fed continuously in molten magnesium, producing and leaving sponge titanium product in the reactor and $MgCl_2$ salt that is tapped out from the reactor intermittently. Since its introduction, the Kroll process has been continuously improved, realizing higher productivity and energy efficiency.

However, the principles of the Kroll process chemistry remain the same and the same magnesiothermic, batch-type process involving many kinds of complex heterogeneous exothermic reactions and various gas, liquid, and solid phases is practiced. The Kroll reaction is considered to be an interfacial reaction where intensive evolution of heat of reaction is localized at some reactor area. This makes the process somewhat slow.

A number of intensive research efforts and process developments have been undertaken to overcome some of the crucial issues in the Kroll process. These initiatives are aimed at improving the titanium production and energy efficiency, and/or at developing a continuous production scheme to lower the titanium metal production cost.[3–8] The Fray-Farthing-Chen process is one such effort, which has been pursued for industrial process realization.[9,10]

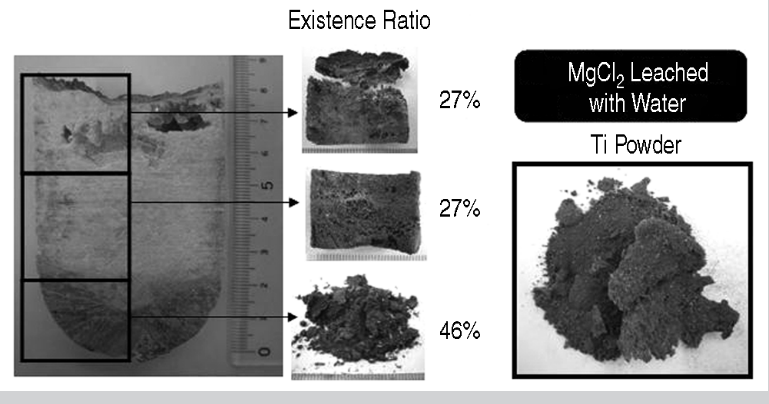

Figure 1. A macroscopic observation of titanium product, location, and shape. Shown are the cross section of the reactor, the location of titanium product and its existence ratio at top, middle, and bottom, and the titanium product after leaching out of $MgCl_2$ with water.

In a recent publication, a reaction mechanism of titanium sponge formation in the Kroll reduction reactor was discussed in detail.[11] In the discussion, it was argued that the complex heterogeneous reactions most probably involve the formation of lower-valence titanium chlorides, $TiCl_2$ and $TiCl_3$, as reaction intermediates.

This research presented in this article focused on the use of the mixed salt, $TiCl_2$-$MgCl_2$, in the titanium production process. In this newly proposed process scheme, titanium metal can be obtained by the magnesium reduction reaction of $TiCl_2$-$MgCl_2$ in the molten state. (Note: A somewhat similar processing scheme using $TiCl_2$-$MgCl_2$-KCl salt was proposed by G.R.B. Elliot,[12] which, however, was not accompanied by any experimental data or verification. This research summary is the first to verify the process feasibility and realization.)

In this process, the overall reaction is described as

$$TiCl_2\text{-}MgCl_2\,(l) + Mg(l) = Ti(s) + 2\,MgCl_2(l) \qquad (1)$$

First, the molten $TiCl_2$-$MgCl_2$, which is a reaction intermediate in this process, is synthesized by reacting solid sponge titanium seed, which is placed in molten $MgCl_2$, with incoming $TiCl_4$ gas. This synthesis reaction may be described as

$$Ti(s) + MgCl_2(l) + TiCl_4(g) = TiCl_2\text{-}MgCl_2(l) \qquad (2)$$

Next, titanium metal is obtained by the magnesium reduction of the mixed salt in the molten state, following Reaction 1. The salient feature of this reaction scheme is that the reduction is a simpler liquid-liquid reaction compared with the

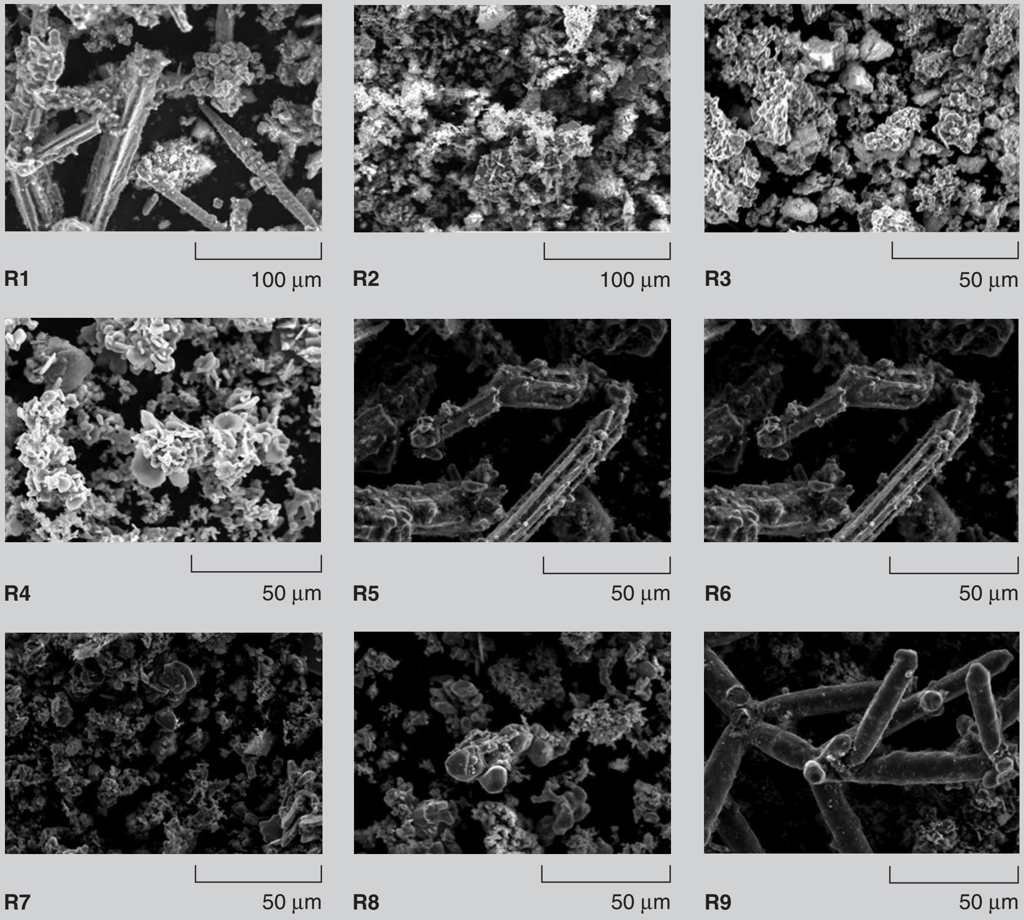

Figure 2. An SEM observation of titanium product in the various experiments.

complex Kroll process. In this process, the reduction reaction takes place in a bulk region, incorporating larger reaction regions and space with a fast and controllable reaction, homogeneous heat evolution, less localized heat burden, etc. This new process scheme has a potential to become a continuous process whereby efficient liquid-liquid reaction takes place with enhanced reaction control.

This article reports on the experimental procedures and results of the $TiCl_2$-$MgCl_2$ mixed salt synthesis and magnesium reduction reactions. In particular, the influence and/or effect on location and morphology of the obtained titanium metal product are discussed. The experiments were conducted according to the following conditions: the crucible material was either electrically conductive (stainless steel basket and container) or non-conductive, such as Al_2O_3; a mixing process was employed where liquid magnesium metal is added to the molten mixed salt or the liquid mixed salt is added to liquid magnesium; $TiCl_2$ concentration was controlled in the $TiCl_2$-$MgCl_2$; and reaction temperature was controlled.

See the sidebar for experimental procedures.

RESULTS AND DISCUSSION

In all the experimental measurements, titanium metal product formed in the bulk body of the reactor and conformed itself to the reactor shape. Titanium metal product is very fragile and loses its shape easily when it is handled. Figure 1 shows a typical example of titanium metal location, existence ratio, and shape. Titanium metal forms along the reactor shape and is powdery in appearance and nature.

Scanning-electron microscopy (SEM) observations of titanium products from various experiments are shown in Figure 2. Two kinds of titanium product microstructures appear—columnar-shaped

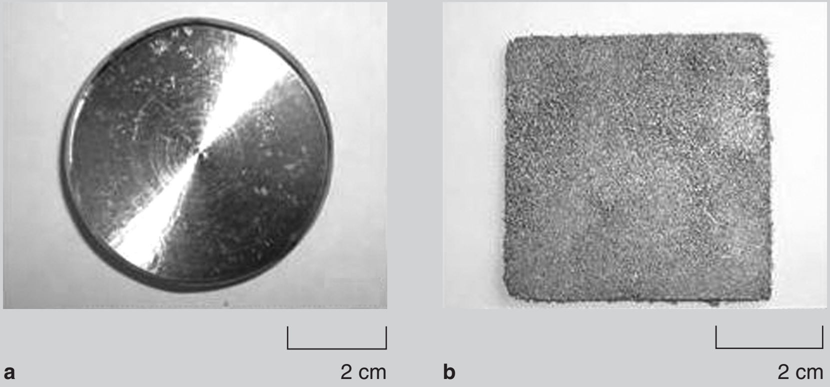

Figure 3. A titanium specimen: (a) button-melted and (b) green compact. The green compact is easily made from the titanium powder obtained from the reaction product leaching out of $MgCl_2$.

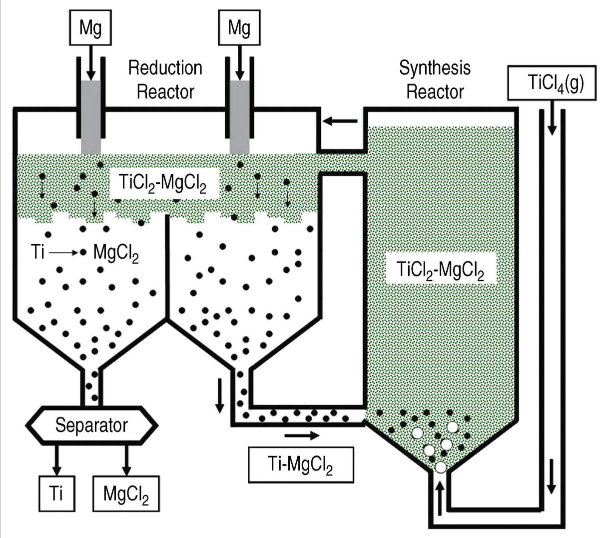

Figure 4. A schematic drawing of a continuous titanium production plan. The apparatus is composed of synthesis reactor, magnesium reduction reactor, and separator of $MgCl_2$ and titanium product. The reduction reactor is divided into two halves, one for regeneration of the mixed salt and the other for titanium product recovery.

microstructures of 40–100 µm in length and grain-aggregates 6–30 µm in diameter. Experimental conditions influencing the titanium product shape, location, and morphology are reactor material, mixing mode, and $TiCl_2$ concentration.

Reactor Material

The container material has critical significance if the titanium reduction reaction takes place via the electrically mediated reduction (EMR) mechanism in the electro-conductive reactor. If EMR occurs, titanium metal may be produced on and/or grows from the conductive metal wall. Therefore, in this research two kinds of reactor materials were investigated: an electro-conductive crucible made of stainless steel and a non-conductive Al_2O_3 container. The results in R2 and R3 shown in Figure 2 indicate that there are no distinct differences in titanium product location and shape, and no titanium product adhered to the reactor wall. This is perhaps the proof that no EMR mechanism is occurring to any appreciable extent.

Mixing Mode

The mixing scheme (i.e., magnesium metal addition to the $TiCl_2$-$MgCl_2$ or $TiCl_2$-$MgCl_2$ addition to magnesium) has an effect on the titanium product shape and morphology. In the former case, the $TiCl_2$ concentration in the mixed salt decreases continuously with magnesium addition, while in the latter case, it remains the same and the added mixed salt reacts with molten magnesium during its descent in the reactor. The difference in $TiCl_2$ concentration in the reduction reaction may have some influence on titanium produced. This was examined through the titanium product evaluation, which revealed that the temperature attained during the reduction was different depending on the mixing mode due to the latent heat required for melting magnesium droplets. However, the mixing mode did not appear to influence the titanium shape or morphology to a great extent, as shown in R3 and R4, and in R6 and R7 in Figure 2.

$TiCl_2$ Concentration in the Mixed Salt

The temperature reached during the reduction reaction is higher due to the higher heat of reaction when the $TiCl_2$ content in the mixed salt is increased, as seen in R1 and R4 in Figure 2. This increase in reaction temperature affected titanium morphology.

Reduction Products

The titanium products at higher reduction-reaction temperatures (i.e.,

EXPERIMENTAL PROCEDURES

Synthesis of $TiCl_2$-$MgCl_2$ Mixed Salt

The experimental apparatus used is shown in Figure A, where a certain amount of seed sponge titanium has been placed in a basket in a stainless-steel container and $TiCl_4$ is pipe-fed through the seed sponge titanium. After placing a known amount of $MgCl_2$ in the container and raising the reactor to the experimental temperature of either 1,123K or 1,173K, a fixed amount of $TiCl_4$ gas, along with inert argon gas, was introduced through the feed pipe and reacted with feed sponge titanium immersed in molten $MgCl_2$. The $TiCl_4$ feed amount was selected such that a predetermined concentration of $TiCl_2$ in the mixed-salt $TiCl_2$-$MgCl_2$ was obtained. The resultant mixed salt was analyzed for its constituents by chemical analysis and for its phase relationship by thermal analysis. Table A shows the experimental conditions and results obtained in this investigation. The $TiCl_2$-$MgCl_2$ is generally green in color. While the 2.8 mole percent $TiCl_2$-$MgCl_2$ (M1 specimen) is emerald green, the 24 mole percent $TiCl_2$-$MgCl_2$ is dark green. The

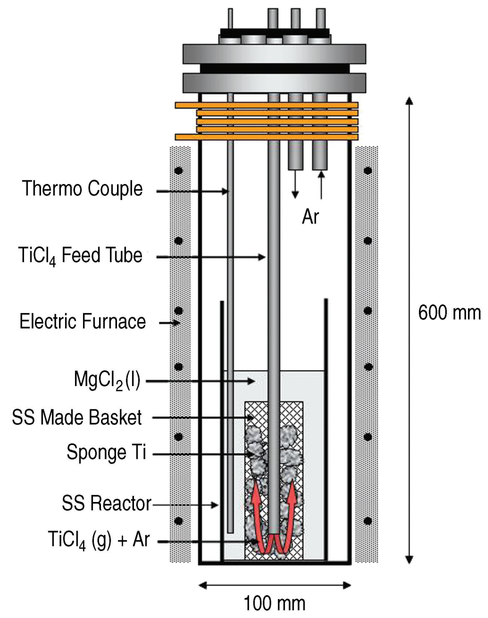

Figure A. A schematic illustration of experimental apparatus used for synthesis of $TiCl_2$-$MgCl_2$. The mixed salt is synthesized by the chlorination reaction of sponge titanium in $MgCl_2$ with incoming $TiCl_4$ reactant gas introduced through the feed pipe.

higher the concentration of $TiCl_2$, the denser is the green color. The remaining, un-reacted sponge titanium was brittle and fragile and was easily reduced to powder. The mixed salt is essentially composed of $TiCl_2$ and $MgCl_2$ with a minute amount of $TiCl_3$ at the lower synthetic temperature. The mixed salt is considered a binary $TiCl_2$-$MgCl_2$ salt. The result also shows that the mixed salt with a certain desired $TiCl_2$ concentration can be synthesized at the higher temperature of 1,173K than at the lower 1,123K temperature. This is due to the fact that synthesis reaction between sponge titanium and $TiCl_4$ is more favored at higher temperatures as faster reaction kinetics are achieved. The impurities from the container and basket material are found to be minor. The thermal analysis result is shown in the $TiCl_2$-$MgCl_2$ binary phase diagram in Figure B, where dots are experimental values and the solid line is from the previous study of the phase diagram.[13]

Production of Titanium by Mg Reduction of $TiCl_2$-$MgCl_2$

The experimental apparatus used is shown in Figure C. The titanium metal product shape, morphology, and distribution are well characterized and found to depend on the

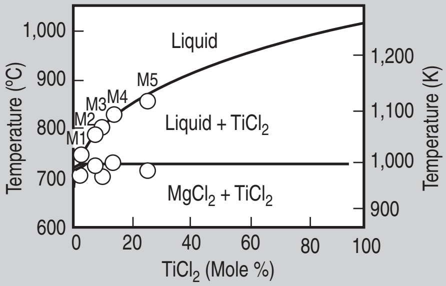

Figure B. The phase diagram of the $MgCl_2$-$TiCl_2$ binary system, along with experimental results of thermal analysis of the mixed salts. The solid line is from the previous phase diagram study and dots are from this research, showing good match between them.

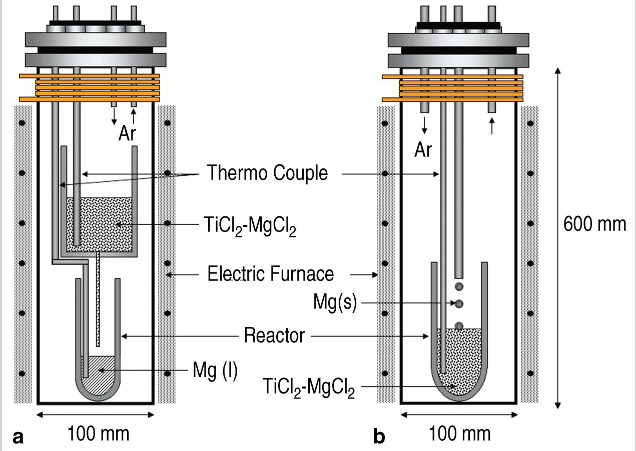

Figure C. A schematic illustration of experimental apparatus for magnesium reduction of the mixed salt $TiCl_2$-$MgCl_2$: (a) $TiCl_2$-$MgCl_2$ is added to molten magnesium and (b) magnesium droplets are added to the $TiCl_2$-$MgCl_2$. The reactor material used is either conductive stainless steel or non-conductive Al_2O_3 for EMR verification in the reduction reaction.

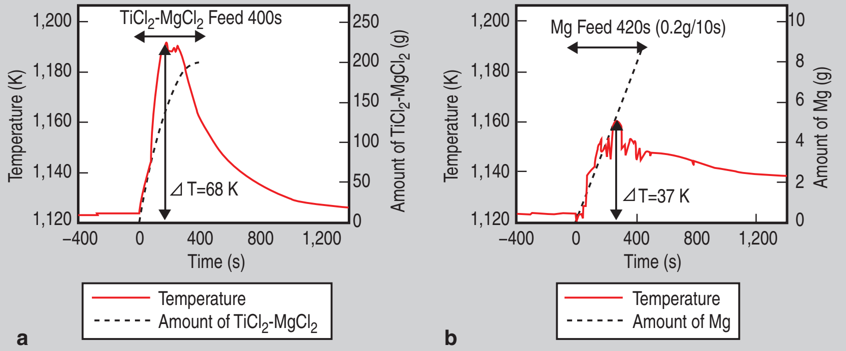

Figure D. The results of temperature profile during the reduction reaction: (a) the $TiCl_2$-$MgCl_2$ is added to molten magnesium and (b) magnesium droplets are added to the $TiCl_2$-$MgCl_2$. The time for adding reactant of either the mixed salt or magnesium is around 400 s. Here, the temperature rise is smaller in the magnesium addition case due to the latent heat required for melting magnesium droplets and probable slower mixing and reaction rate.

more than 1,260K) have the mixed microstructure of columns and grain aggregates while those at lower temperatures have mostly grain aggregates as exemplified in the results of R8 andR9 in Figure 2. The key factor controlling the microstructure is most likely the reduction temperature, where the higher temperature brings about columnar microstructure indicating the titanium crystalline growth and partial sintering of grain aggregates during magnesium reduction of the mixed salt in the molten state. It also appears that the filtering (i.e., separation) of $MgCl_2$ salt from the titanium product will be easier than the Kroll process, although this aspect was not examined in this research.

Titanium Metal Quality

Titanium metal thus obtained was then button-melted in an arc furnace. The resultant specimen and titanium powder green compact are shown in Figure 3. The impurity constituents in the button-melted specimen are, in weight percent, O-0.22 N-0.34 Fe-0.104 Ni-0.145 Cr-0.048 Ti-99.4. It appears that the titanium metal product thus obtained is suitable for its powder as well as melted product applications.

THE FUTURE PROSPECT

The magnesium reduction of $TiCl_2$-$MgCl_2$ offers several advantages. The chemistry in the process is simple and well known from the thermodynamic point of view, and the processing facilities are mostly established. Thus, there is less chance of failure in realizing a commercial scheme based on this concept. The process can be well suited for scrap titanium metal reprocessing due to its energy efficiency.

This may be developed into a continuous process, recognizing that the process feeds are liquids (magnesium and the $TiCl_2$-$MgCl_2$) and the products are liquid (molten $MgCl_2$) and solid (titanium metal powder). A preliminary plan of a continuous process is sketched in Figure 4, where the mixed salt is continuously synthesized by reacting, in one part, titanium metal with $TiCl_2$, and circulating it to the magnesium reduction step. In the other part, titanium metal product is continuously separated from $MgCl_2$. Further research, of course, should be conducted for commercial development of this process that will evaluate the filtering system (i.e., separation of $MgCl_2$ from titanium product) and the control of titanium product morphology in terms of reduction temperature.

CONCLUSION

The magnesium reduction reaction of $TiCl_2$-$MgCl_2$ has been shown to produce titanium metal where the $TiCl_2$-$MgCl_2$ was synthesized through the reaction of seed titanium in molten $MgCl_2$ and $TiCl_4$ gas. The macroscopic shape of the titanium product and its microscopic morphology depend on reduction temperature. The titanium metal obtained in this process appears to be suitable for metal powder product application and melted product application.

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process conditions of reactor material, mixing process, $TiCl_2$ concentration, and the reaction temperature. The container material issue is such that when the electrically mediated reduction (EMR) process[14] occurs, titanium metal is produced on the conductive metal wall. The location of titanium in the container is, thus, a confirmation of the EMR process. Two kinds of mixing procedures were conducted: adding $TiCl_2$-$MgCl_2$ to molten magnesium using the experimental apparatus shown in Figure Ca, and adding magnesium droplets to molten mixed salt as shown in Figure Cb. The experimental conditions employed in this research are shown in Table B.

In the first mixing and reduction experiment, a predetermined amount of the mixed salt was placed in the stainless-steel container with a small plug-hole, and magnesium was contained in the reactor (either electro-conductive stainless steel or non-conductive Al_2O_3). After reaching the experimental temperature, the mixed salt was added into molten magnesium through the hole by pulling the plug and the reduction reaction was started. The time of completion for adding the mixed salt was estimated by its gravity-feeding rate through the hole.

In the second mixing scheme, solid magnesium droplets were added slowly and manually through the opening hole into the lower reactor (either electro-conductive stainless steel or non-conductive Al_2O_3) containing the molten mixed salt held at the reduction temperature. In both reduction experiments, the amount of magnesium used in the reduction reaction was the 95 mole percent of stoichiometric requirement to reduce $TiCl_2$ in the mixed salt. During the reduction experiment, reaction temperature was monitored by a thermocouple. The maximum temperature reached in respective experiments is shown in Table B. Figure Da and Db shows the temperature profiles in these respective mixing schemes of R4 and R3 in Table B, respectively.

In the former scheme, where the mixed salt was added to molten magnesium, reaction temperature started to rise as the mixed salt was added, indicating that the mixing and exothermic reduction reactions are very rapid. The process reached its peak temperature of 1,191K on the way to completion. In the latter scheme, magnesium droplets at room temperature were added manually, and reaction temperature was lowered slightly due to the addition of cold magnesium droplets before melting the magnesium. After the melting of magnesium droplets, an exothermic reduction reaction started. The temperature started to rise and it reached a peak of 1,160K very rapidly as the reduction reaction approached completion. Following the completion of mixing, the reactor was held at experimental temperature for 30 min. and cooled in the furnace. The products, titanium metal and $MgCl_2$, were examined for titanium product shape and location by macroscopic evaluation. After water-leaching treatment for removal of $MgCl_2$, titanium metal was examined by scanning-electron microscopy to determine its microscopic morphology. Finally, the titanium metal was melted and analyzed for impurity ingredients.

Table A. Synthesis of $TiCl_2$-$MgCl_2$

	Synthesis Experimental Conditions		Constituents Analysis				
No.	Temperature (K)	Targeted $TiCl_2$ Concentration (mol.%)	$TiCl_2$ (mol.%)	$TiCl_3$ (mol.%)	Fe (wt.%)	Cr (wt.%)	Ni (wt.%)
M1	1,123	5	2.8	0.1	0.016	0.004	—
M2	1,123	10	9.2	0.1	0.035	0.020	0.001
M3	1,123	15	12.2	0.5	0.085	0.043	0.001
M4	1,173	7	6.9	—	0.23	0.019	0.001
M5	1,173	24	24.1	—	0.26	0.047	0.002

Table B. Mg Reduction of $TiCl_2$-$MgCl_2$

	Experimental Conditions				Result	
No.	Initial Temperature (K)	$TiCl_2$ Concentration (mol.%)	Reactor Materials	Reactant Added	Maximum Temperature Reached (K)	Titanium Microscopic Morphology
R1	1,143	24.1	Al_2O_3	MS*	1,273	Columnar (50–100 µm) and granular (5–30 µm)
R2	1,123	18.2	Al_2O_3	Mg	1,169	Granular (5–10 µm)
R3	1,123	18.2	SS**	Mg	1,160	Granular (5–30 µm)
R4	1,123	18.2	SS	MS	1,191	Granular (5–30 µm)
R5	1,123	20.1	Al_2O_3	Mg	1,250	Columnar (30–80 µm) and granular (5–20 µm)
R6	1,123	20.1	SS	Mg	1,161	Granular (5–20 µm)
R7	1,123	20.1	SS	MS	1,182	Granular (5–20 µm)
R8	1,173	20.1	Al_2O_3	Mg	1,208	Granular (5–30 µm)
R9	1,223	20.1	Al_2O_3	Mg	1,279	Columnar (40–70 µm) and granular (5–20 µm)

* MS = mixed salt; ** SS = stainless steel.