Fundamental Study on Titanium Production Process by the Disproportionation Reactions of Titanium Subchlorides

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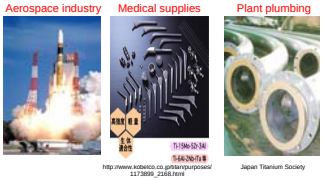
Introduction

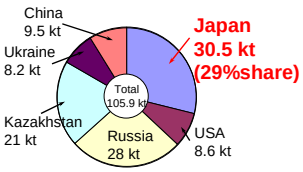
Features of Titanium
1. Light and high-strength
2. Corrosion resistance
3. Biocompatibility
4. Some titanium alloys:
   shape memory
   super elasticity

Aerospace industry | Medical supplies | Plant plumbing



http://www.kobelco.co.jp/titan/purposes/1173899_2168.html | Japan Titanium Society

● Production of Ti sponge in the world (2005)

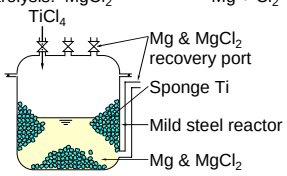


● The Kroll process

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

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

Electrolysis: $MgCl_2 \rightarrow Mg + Cl_2$



Features:
- ◎High-purity Ti can be obtained.
- ◎Metal/salt separation is easy.
- ○Chlorine circulation is established.
- ○Efficient Mg electrolysis has been utilized.
- ○Reduction and electrolysis operation have been carried out independently.
- ×Process is complicated.
- **×Reduction process is batch type.**
- **×Large facilities are required for electrolysis.**

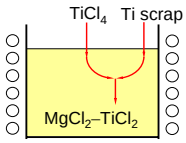
Production speed of Ti is less than 1 t/day·batch.

High cost

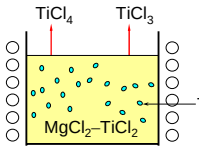
● Titanium production process by disproportionation reacitons of $TiCl_2$

Step 1: $TiCl_4\,(g) + Ti\,(s,\ scrap) \rightarrow 2\,TiCl_2\,(s)$

Step 2: $3\,TiCl_2(s) \rightarrow Ti\,(s) + 2\,TiCl_3\,(g)$
: $2\,TiCl_2(s) \rightarrow Ti\,(s) + TiCl_4\,(g)$



Step 1: High-efficient synthesis of $TiCl_2$



Step 2: Titanium production by disproportionation reactions of $TiCl_2$

● Features of this process

- ◎Suitable for producing "high purity Ti"
  →No use of reductants such as Mg
- ◎Disproportionation reaction can be applied to "titanium coating" on substrates like steel.
- ◎New application of efficient usage of "titanium scraps"
- ○Large-scale facilities are not required

- ×Titanium production speed is critically slow in the case of using gas phase.
- ×An efficient method for synthesizing high-purity $TiCl_2$ has not been established until now.

These problems can be solved by utilizing condensed phase like molten salt.

● Purpose of this study:

Development of a high-efficient $TiCl_2$ synthesis process and Ti production process and/or Ti coating methods based on the disproportionation reactions of $TiCl_2$ in molten salt.

Experimental works

● **Part I**: $TiCl_x$ synthesis by reaction of titanium metal with $TiCl_4$

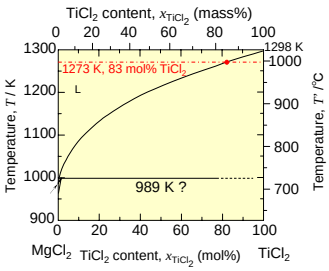


Fig. Phase diagram for the $MgCl_2$–$TiCl_2$ system

$MgCl_2$ is expected to work as a medium that removes $TiCl_2$ film formed on the surface of titanium metal by dissolving, and accumulates $TiCl_2$ in its interior.

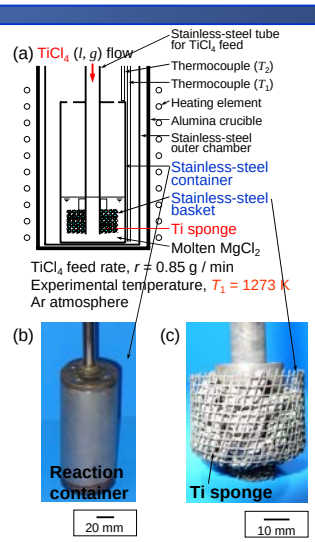


Fig. The experimental apparatus for the $TiCl_2$ synthesis by reaction of Ti metal with $TiCl_4$ in molten $MgCl_2$.

● Experimental results 1

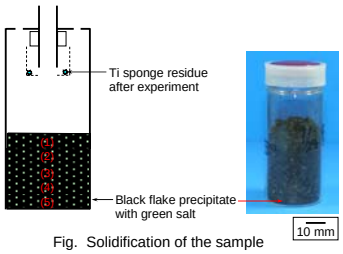


Fig. Solidification of the sample after the $TiCl_2$ synthesis experiment

Table Analytical results of the samples obtained after the $TiCl_x$ synthesis.

Exp. No. (Position)	Concentration of element i, C_i (mass%) Ti [a]	Cl [b]	Mg [a]	Fe [a]	Ni [a]	Cr [a]	x value in $TiCl_x$
A(1)	21.0	67.4	11.5	<0.01	<0.01	0.01	2.18
A(2)	18.0	68.0	14.0	<0.01	<0.01	0.01	2.04
A(3)	19.3	69.3	11.4	0.01	<0.01	0.01	2.53
A(4)	25.1	64.0	10.9	0.01	<0.01	0.01	1.74
A(5)	29.5	60.2	10.2	0.04	<0.01	0.02	1.39

a: Determined by ICP-AES.
b: Determined by potentiometric titration method.

- Value of x in $MgCl_2$–$TiCl_x$ was calculated to be 2.04~2.53 (upper part).
- Main product was $TiCl_2$.

● Experimental results 2

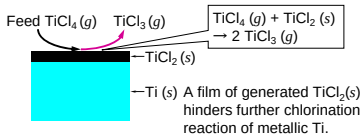
Table Yield of $TiCl_x$ and Ti consumption rate.

Exp. No.	$TiCl_4$ feed rate, r / g min^{-1}	Yield of $TiCl_x$, R_{TiCl_x} (%)	Ti consumption ratio, R_{Ti}' (%)
A	0.85	50	84

Direct reaction of $TiCl_4$ with Ti*
Yield of $TiCl_x$: 23~35%
Consumption ratio of feed Ti :42~45%

* Takeda et al., The 1st Workshop on Reactive Metal Processing (2006).

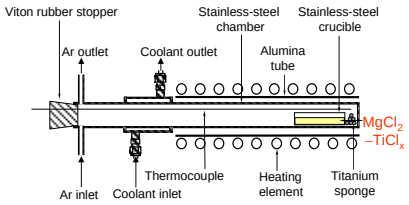
The efficiency of $TiCl_x$ formation was improved by using molten $MgCl_2$ as a reaction medium.



Generated $TiCl_2$ was successfully removed from the reaction interface.

● **Part II**: Disproportionation reactions of $TiCl_2$

$MgCl_2$-$TiCl_x$ salt synthesized in the previous experiment was used in this study.
(Titanium concentration :18.0~19.3 mass%)

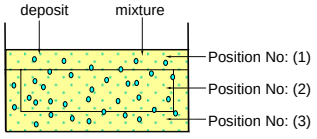


Experimental temperature, T = 1300 K
Reaction time, t = 21.6 ks
Ar atmosphere

Fig. The experimental apparatus for the titanium production by disproportionation reactions of $TiCl_2$

● Experimental results 1

Solidification of the salt
(Exp. Z(2)) (1300 K, 21.6 ks)



The salt was recovered from the three locations in the crucible.

Fig. Photograph of the sample after the experiment.

● Experimental results 2

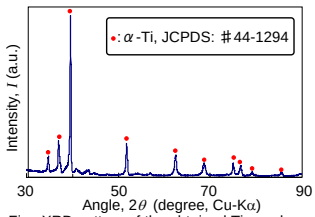


Fig. XRD pattern of the obtained Ti powder after leaching

Table Analytical results of the obtained Ti powder after disproportionation reaction of $TiCl_2$.

Exp.No. (position)	Concentration of element i, C_i (mass%) Ti	Cl	Mg	Fe	Ni	Cr
Z(1)	97.6	<0.01	<0.01	1.35	0.05	1.01
Z(2)	98.9	0.01	0.07	0.18	0.06	0.82
Z(3)	95.9	<0.01	0.02	1.76	0.05	2.24

a: Determined by X-ray fluorescence analysis.

Titanium powder with a purity of over 95% was successfully obtained from molten salt.

Conclusion

In order to establish a new titanium production process and/or titanium coating methods, a high-efficient synthesis process for $TiCl_2$ and a production process for titanium metal were investigated by using reaction of $TiCl_2$ in molten salt.

- **A new synthesis process of $TiCl_2$ from titanium metal and $TiCl_4$ in $MgCl_2$ molten salt was investigated, and the efficiency of $TiCl_x$ formation was improved by using $MgCl_2$ molten salt as a reaction medium.**
- **Ti production by disproportionation reactions of $TiCl_2$ was carried out, and the feasibility of titanium production was confirmed.**

Future works

- **More efficient production process of $TiCl_2$ from $TiCl_4$**
- **Development of high-purity Ti production process due to effective utilization of titanium scraps**