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

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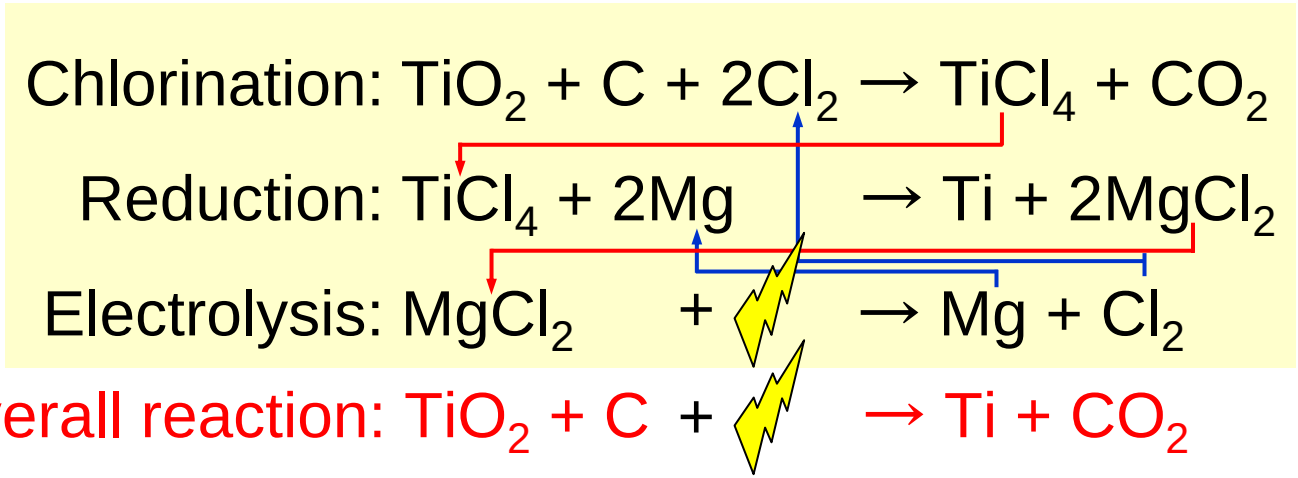
# The Kroll Process




- Huge exothermic reaction
- Reduction process is a batch type.

→The speed of reduction process is extremely slow, and 10 days are required to produce 10 tons of Ti.

A new process is urgently required in order to increase the applications of titanium metal.

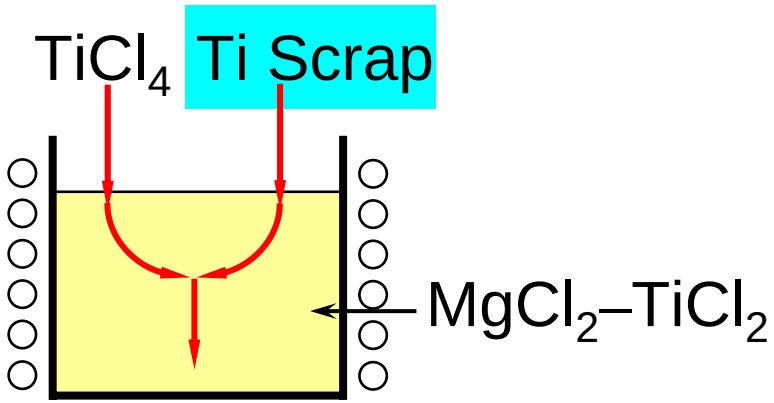
# Titanium Production Process by Disproportionation Reactions of $TiCl_2$

(1) $TiCl_2$ synthesis process: $TiCl_4\,(g)$ + Ti ($s$, scrap) → 2 $TiCl_2\,(s, l)$

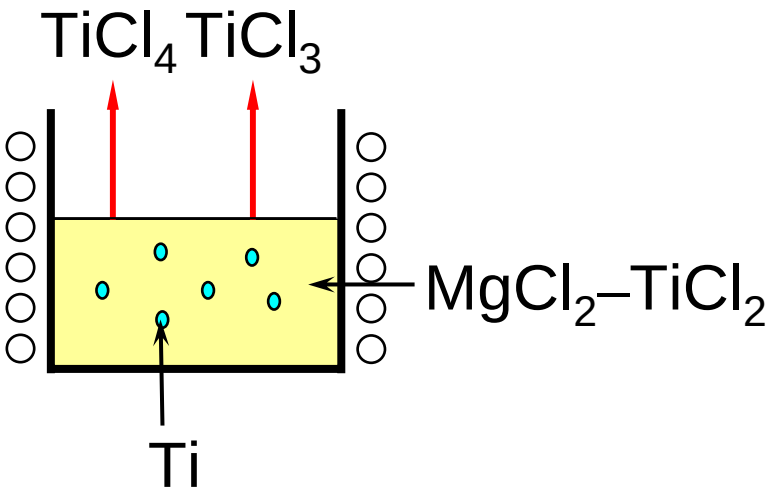
(2) Ti production process : 3 $TiCl_2\,(s, l)$ → Ti ($s$) + 2$TiCl_3\,(g)$

2 $TiCl_2\,(s, l)$ → Ti ($s$) + $TiCl_4\,(g)$

**Step (1)**:
High-efficient synthesis of $TiCl_2$ in $MgCl_2$ molten salt




**Step (2)**:
Titanium production by disproportionation reactions of $TiCl_2$ in $MgCl_2$ molten salt



# Features of This Process

◎Suitable for production of “high purity Ti”
→No use of reductants such as Mg
◎Disproportionation reaction can be applied to “titanium coating”
◎New application of efficient usage of “titanium scraps”

×Slow reaction speed in gas phase reaction
×Still no efficient synthesis method of high-purity $TiCl_2$

These problems can be solved
by utilizing condensed phase such as a molten salt.

# Purpose of This Study

Development of (1) a high-efficient $TiCl_2$ synthesis process and (2) Ti production process and/or Ti coating methods based on the disproportionation reactions of $TiCl_2$ in a molten salt.

# Titanium Production Process by Disproportionation Reactions of $TiCl_2$

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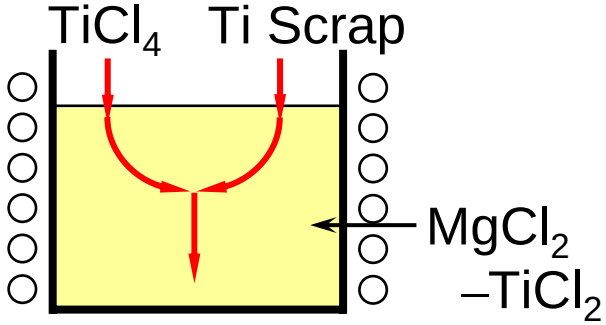
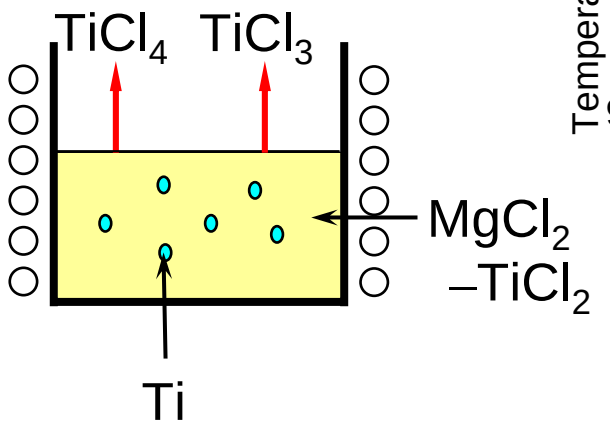
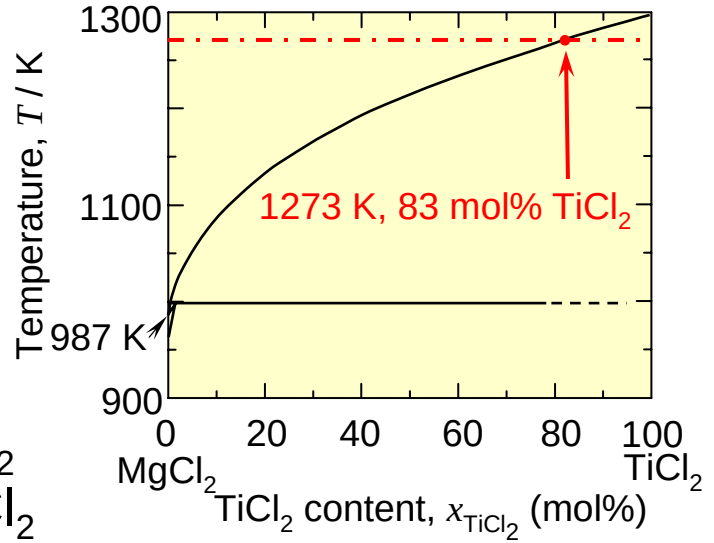



**Step (2)**:
Titanium production by disproportionation reactions of $TiCl_2$ in $MgCl_2$ molten salt

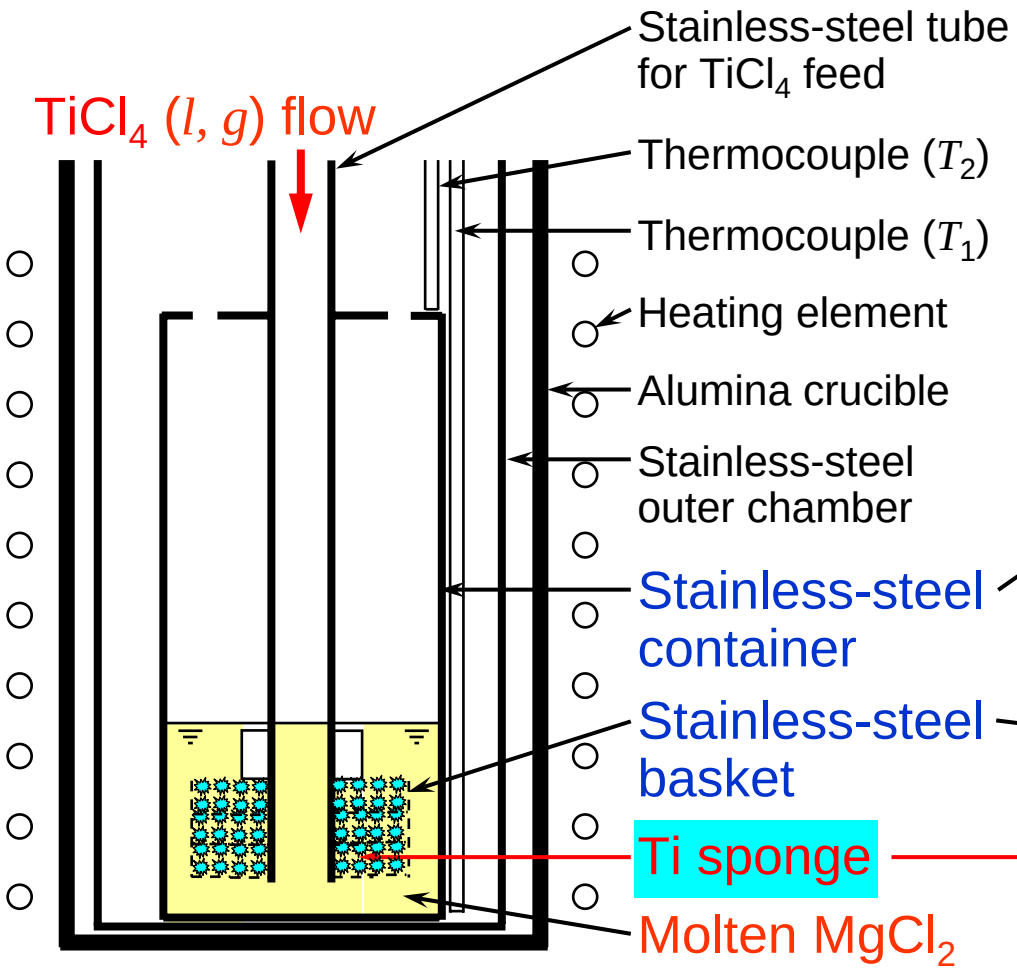


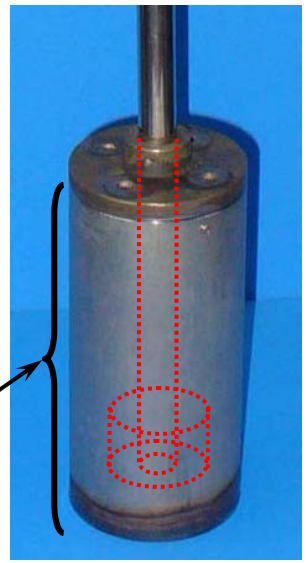

Phase diagram for the $MgCl_2$–$TiCl_2$ system

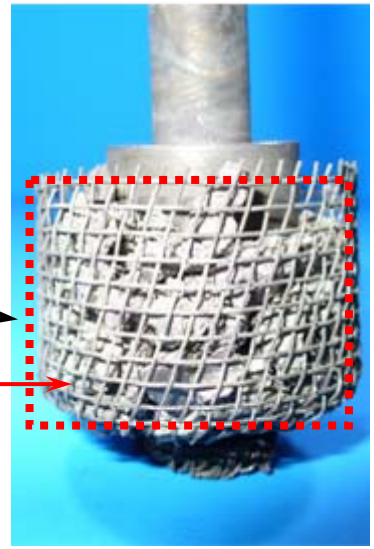


# Titanium Dichloride Synthesis By the Reaction of $TiCl_4$ with Ti in $MgCl_2$ Molten Salt

# $TiCl_2$ Synthesis: Experimental



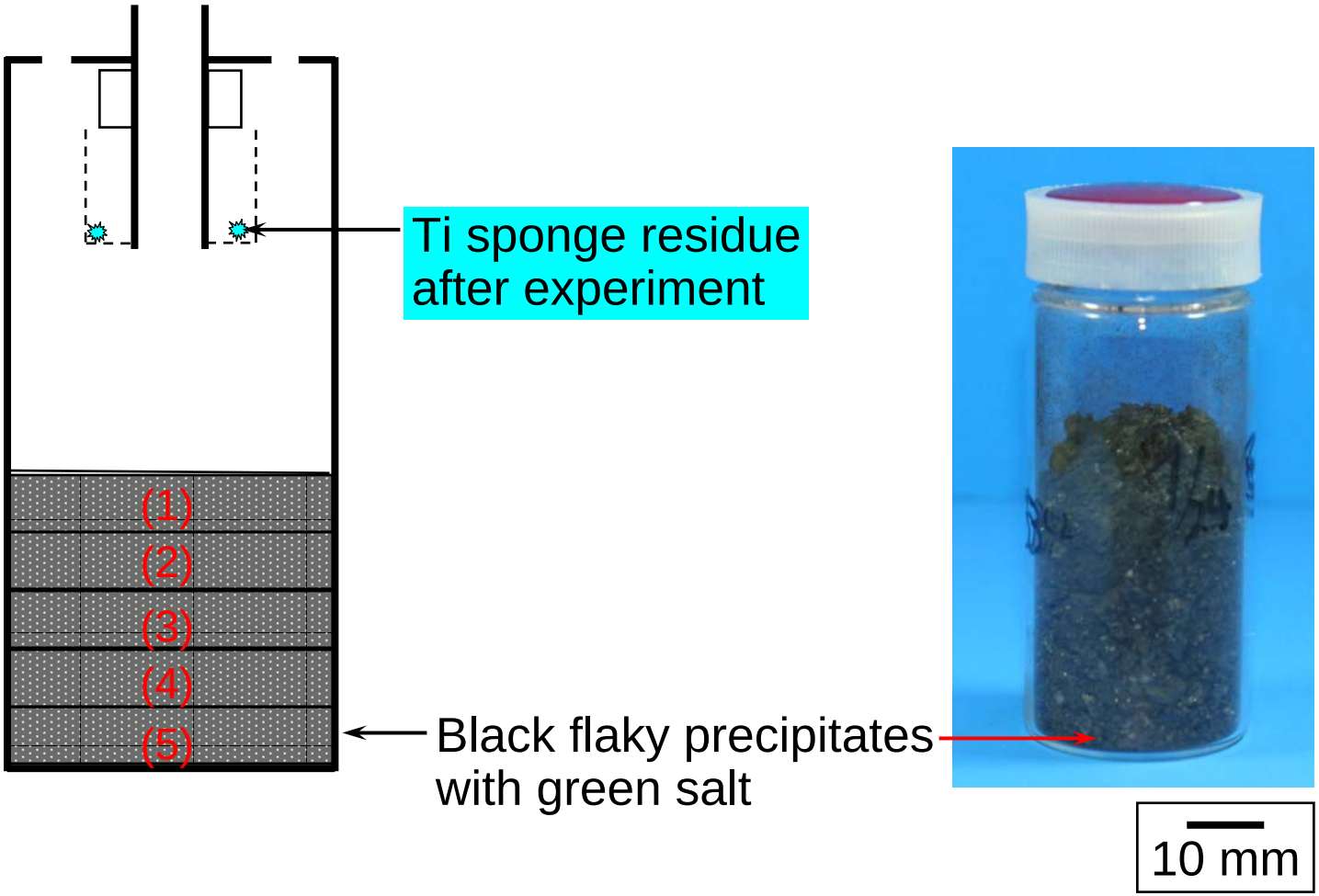




$TiCl_4$ feed rate, $r$ = 0.85 g / min
Experimental temperature, $T_1$ = 1273 K
Ar atmosphere

# $TiCl_2$ Synthesis: Experimental Results (1)

## Solidification of the salt



# $TiCl_2$ Synthesis: Experimental Results (2)

Table Analytical results of the obtained salt samples.

| Exp. No. (Position) | Concentration of element $i$, $C_i$ (mass%) | | | | | | x value in $TiCl_x$ |
|---|---|---|---|---|---|---|---|
| | Ti [a] | Cl [b] | Mg [a] | Fe [a] | Ni [a] | Cr [a] | |
| 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).

The main product was $TiCl_2$.

# $TiCl_2$ Synthesis: Experimental Results (3)

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%

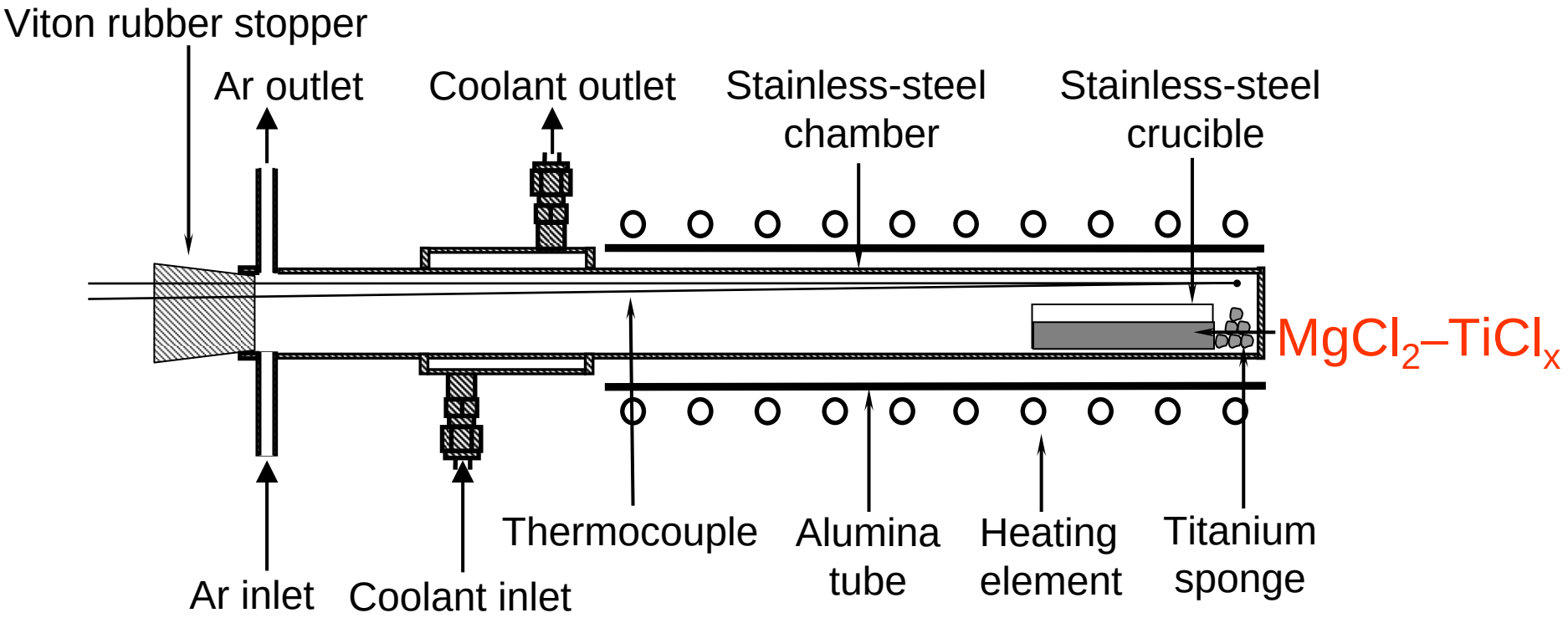
The efficiency of $TiCl_x$ formation was improved by using molten $MgCl_2$ as a reaction medium.

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

# Titanium Production by the Disproportionation Reactions of $TiCl_2$ in $MgCl_2$ Molten Salt

# Disproportionation: Experimental

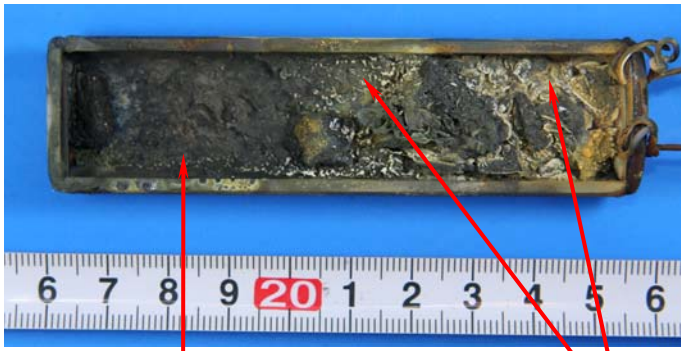
## Reaction container




Experimental temperature, $T$ = 1300 or 1373 K
Reaction time, $t$ = 3 or 6 h
Ar atmosphere

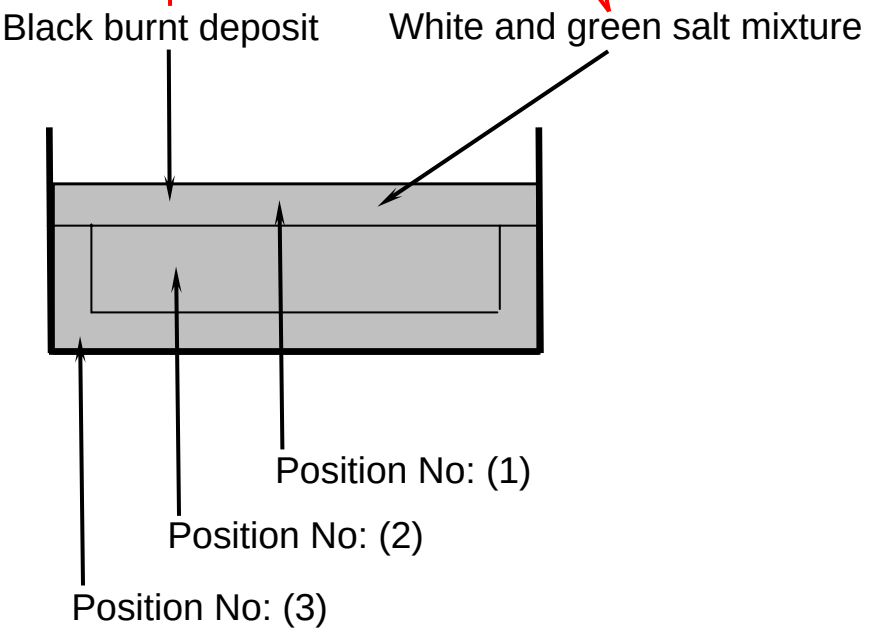
# Disproportionation: Experimental Results (1)

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

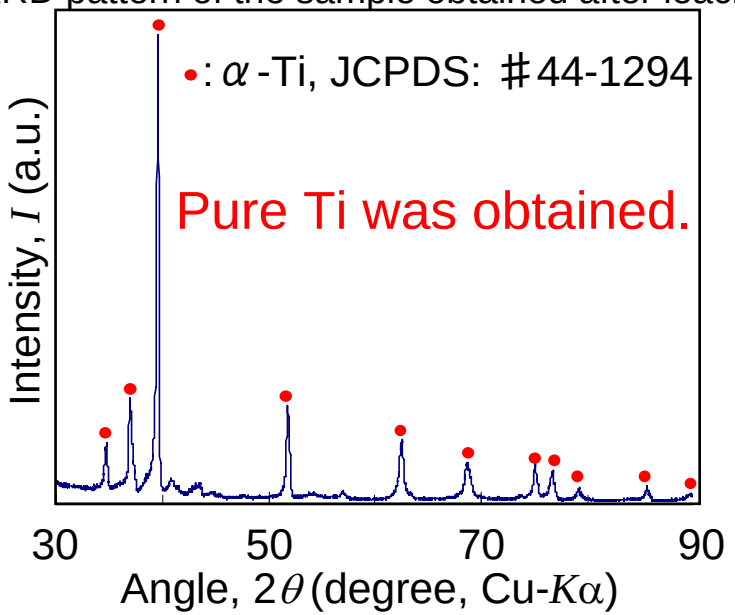


Leaching

Sample obtained after leaching




XRD pattern of the sample obtained after leaching



# Disproportionation: Experimental Results (2)

Table Analytical results of the obtained salt samples.

| Exp.No. (position) | Temperature, $T$ / K | Time, $t$ / h | Concentration of element $i$ in obtained Ti sample, $C_i$ (mass%)[a] | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Ti | Cl | Mg | Fe | Ni | Cr |
| X | 1373 | 3 | 92.2 | 0.19 | 0.11 | 4.65 | 0.92 | 1.95 |
| Y(1) | 1373 | 6 | 96.1 | 0.09 | 0.22 | 2.41 | 0.01 | 1.16 |
| Y(2) | 1373 | 6 | 96.2 | 0.23 | 0.09 | 2.31 | 0.05 | 1.15 |
| Y(3) | 1373 | 6 | 96.3 | 0.02 | 0.01 | 1.56 | 0.03 | 2.09 |
| Z(1) | 1300 | 6 | 97.6 | <0.01 | <0.01 | 1.35 | 0.05 | 1.01 |
| Z(2) | 1300 | 6 | 98.9 | 0.01 | 0.07 | 0.18 | 0.06 | 0.82 |
| Z(3) | 1300 | 6 | 95.9 | <0.01 | 0.02 | 1.76 | 0.05 | 2.24 |

a: Determined by X-ray fluorescence analysis (XRF)

Titanium powder with a purity of over 90% was successfully obtained.

# Conclusions

In order to develop 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 reactions of $TiCl_2$ in a molten salt.

- The efficiency of $TiCl_2$ synthesis was improved when using molten $MgCl_2$ as a reaction medium.

- The feasibility of the titanium production process by the disproportionation reactions of $TiCl_2$ in molten $MgCl_2$ was confirmed.

# Future Works

- More efficient production process of $TiCl_2$ from $TiCl_4$
- Clarification of detailed reaction mechanism for producing Ti from $TiCl_2$
- Investigation of titanium coating methods by using disproportionation reactions of $TiCl_2$
- Development of high-purity Ti production process due to effective utilization of titanium scraps