Fundamental Study on Titanium Production Process by Disproportionation Reactions of $TiCl_2$ in $MgCl_2$ Molten Salt

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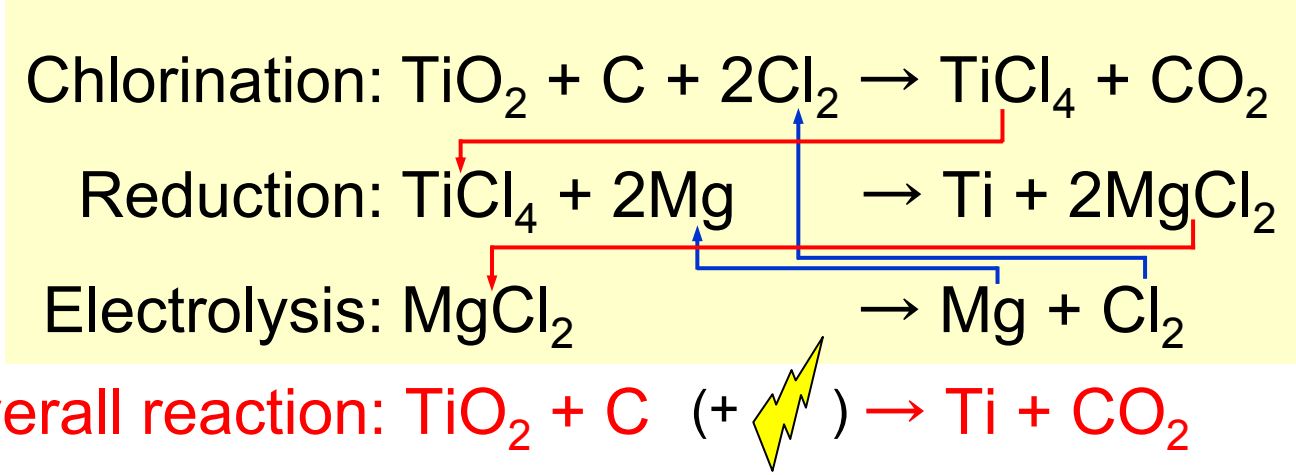
Titanium

Features of Titanium

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

Titanium is the 9th most abundant element in the earth's crust !!

The Kroll Process

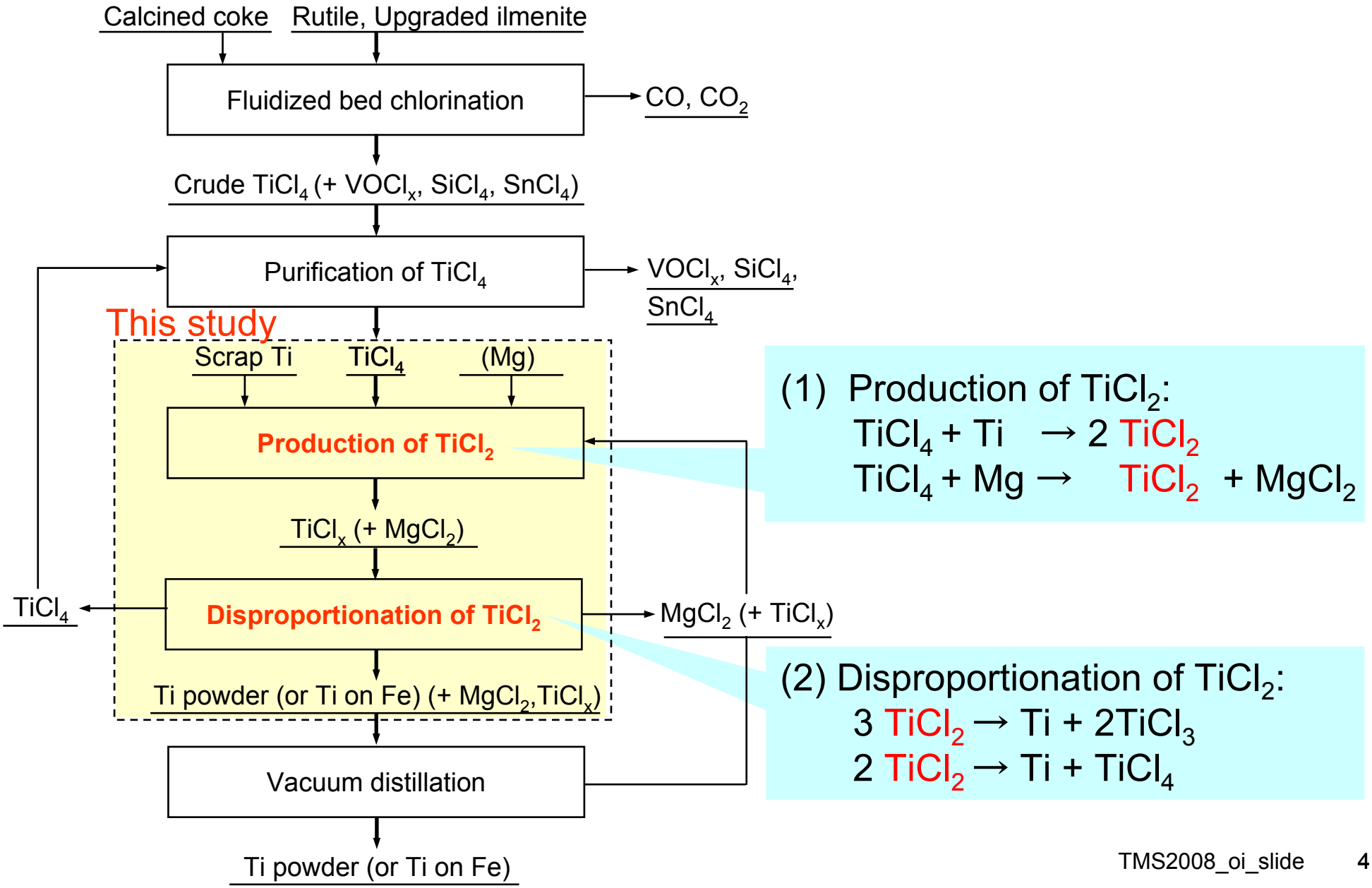


Overall reaction: $TiO_2 + C$ (+ ⚡) $\rightarrow Ti + CO_2$

- Huge exothermic reaction for the reduction
  → Reduction rate is extremely slow.
- Batch type process
  e.g.) 10 days are required for producing 10 ton of Ti.

A new production process is urgently required for further expansion of the applications of titanium metal.

Flow chart of the proposed new Ti production process



Titanium Production Process by Disproportionation Reactions of $TiCl_2$

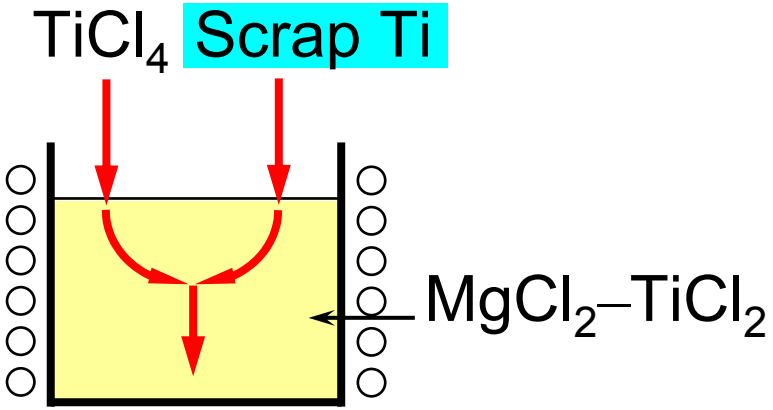
(1) $TiCl_2$ synthesis process: $TiCl_4\,(g) + Ti\,(s,\ \text{scrap}) \rightarrow 2\,TiCl_2\,(s,\ l)$

$TiCl_4\,(g) + Mg\,(l) \rightarrow TiCl_2\,(s,\ l) + MgCl_2\,(l)$

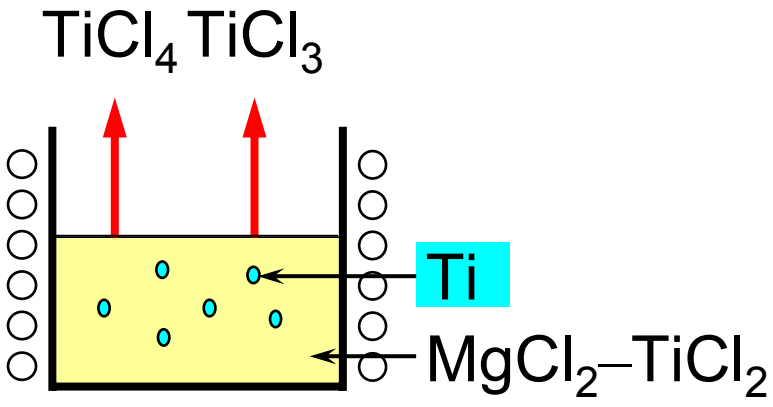
(2) Ti production process: $3\,TiCl_2\,(s,\ l) \rightarrow Ti\,(s) + 2TiCl_3\,(g)$

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

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



Step (2):
Ti production by disproportionation of $TiCl_2$ in $MgCl_2$ molten salt



Features of This Process

◎High purity Ti products with **low oxygen**
→ Chloride metallurgy
◎Applicable to titanium coating method
◎Utilizing titanium scrap for the feed

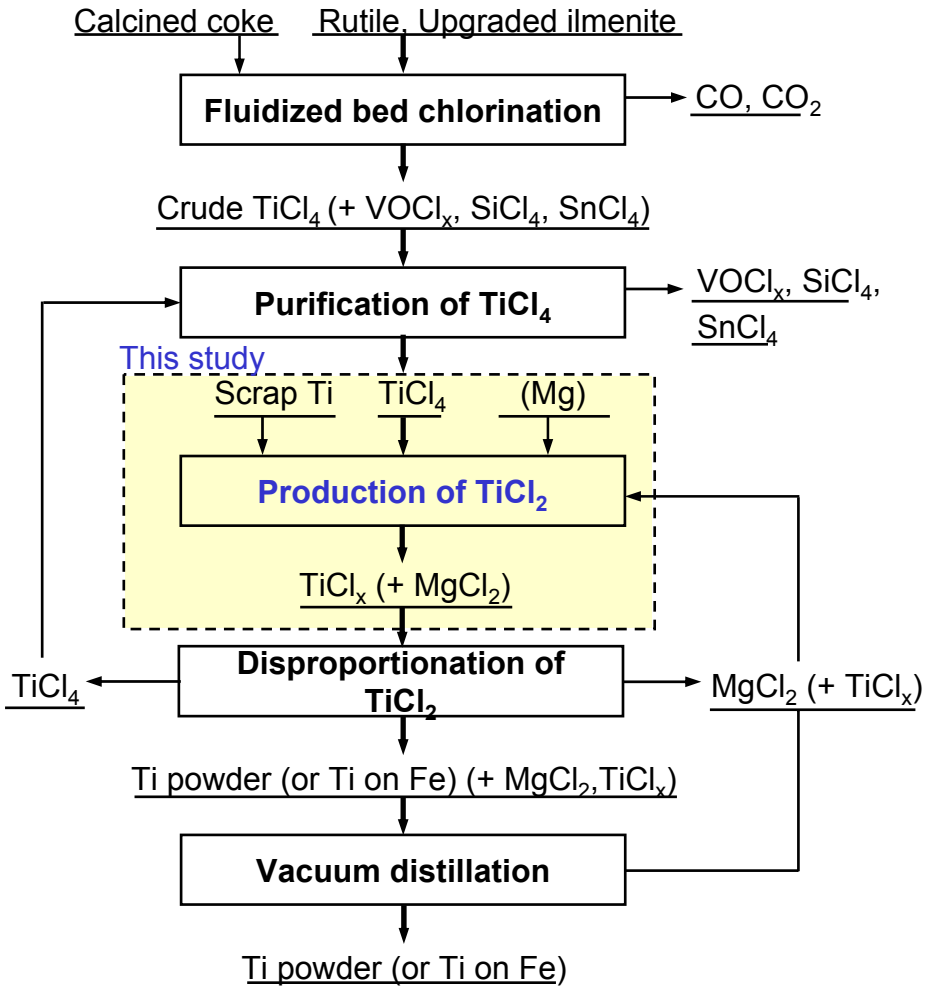
× Slow reaction speed in gas phase reaction
× Still no efficient synthesis method of high-purity $TiCl_2$

These problems can be solved
by utilizing condensed phase like molten salt
as a reaction medium.

Purpose of This Study

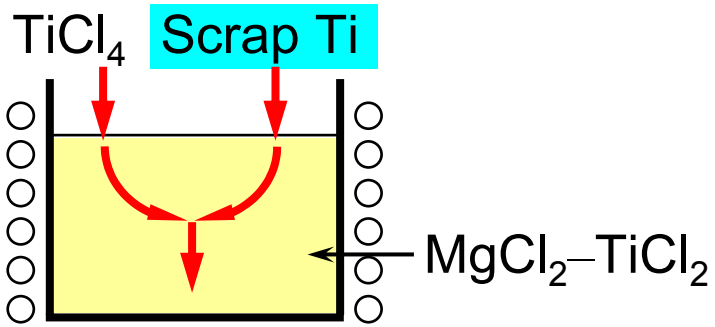
Development of
(1) high-efficient $TiCl_2$ synthesis process
(2) Ti production process and/or Ti plating method
based on disproportionation of $TiCl_2$ in molten salt.

(1) $TiCl_2$ synthesis by reaction of $TiCl_4$ with Ti in Molten Salt



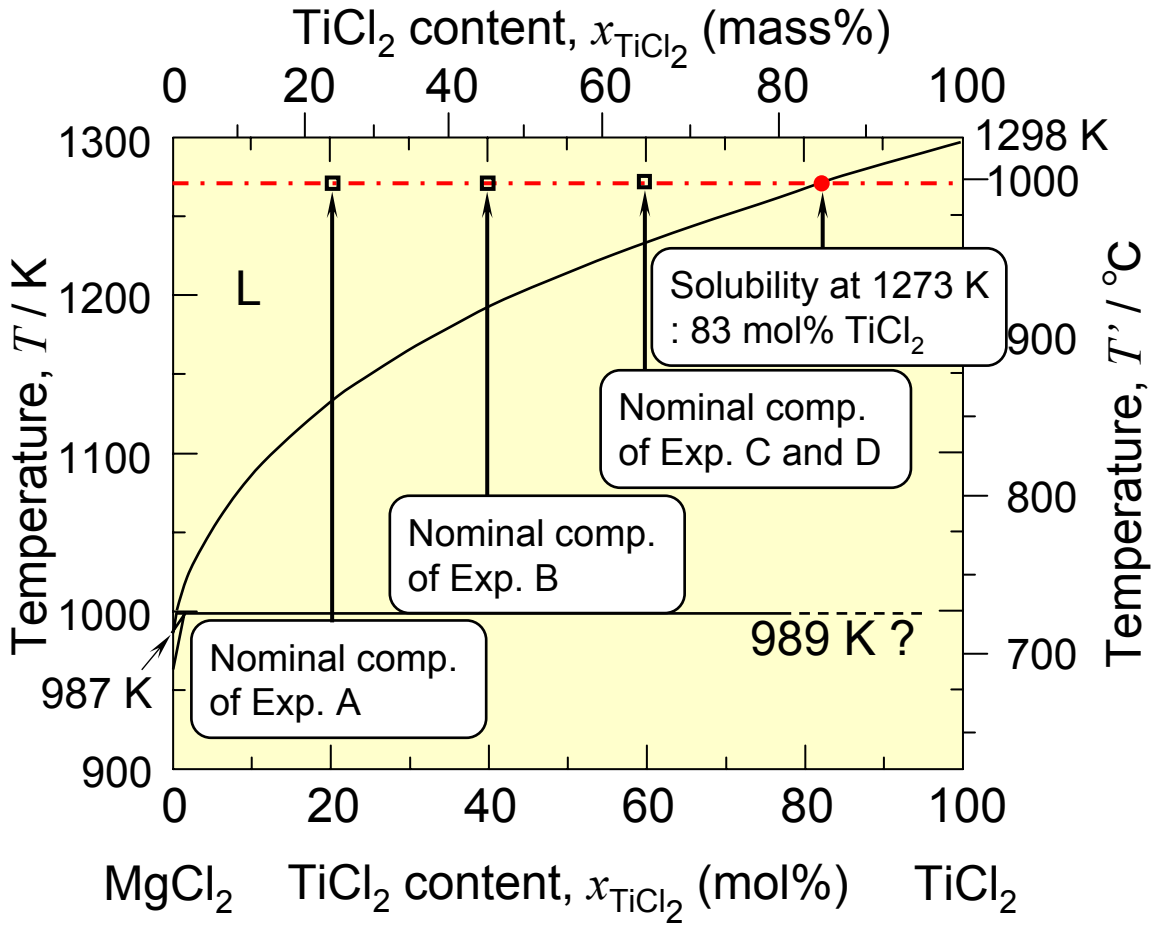
(1) Production of $TiCl_2$:

$TiCl_4\,(g) + Ti\,(s) \rightarrow 2\ TiCl_2\,(l)$ in $MgCl_2\,(l)$



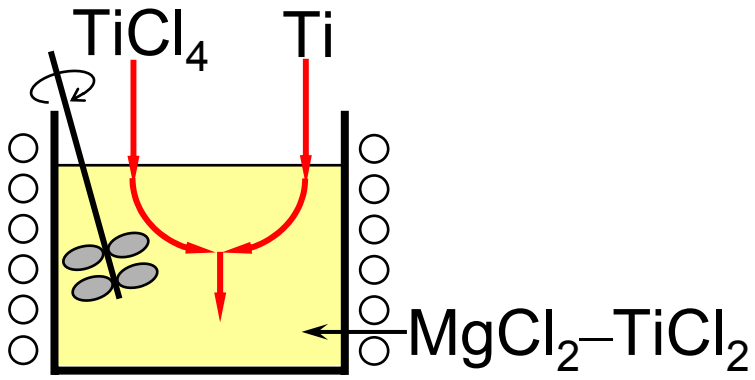
Experimental Procedure

Quasi-binary phase diagram for the $MgCl_2$–$TiCl_2$ system



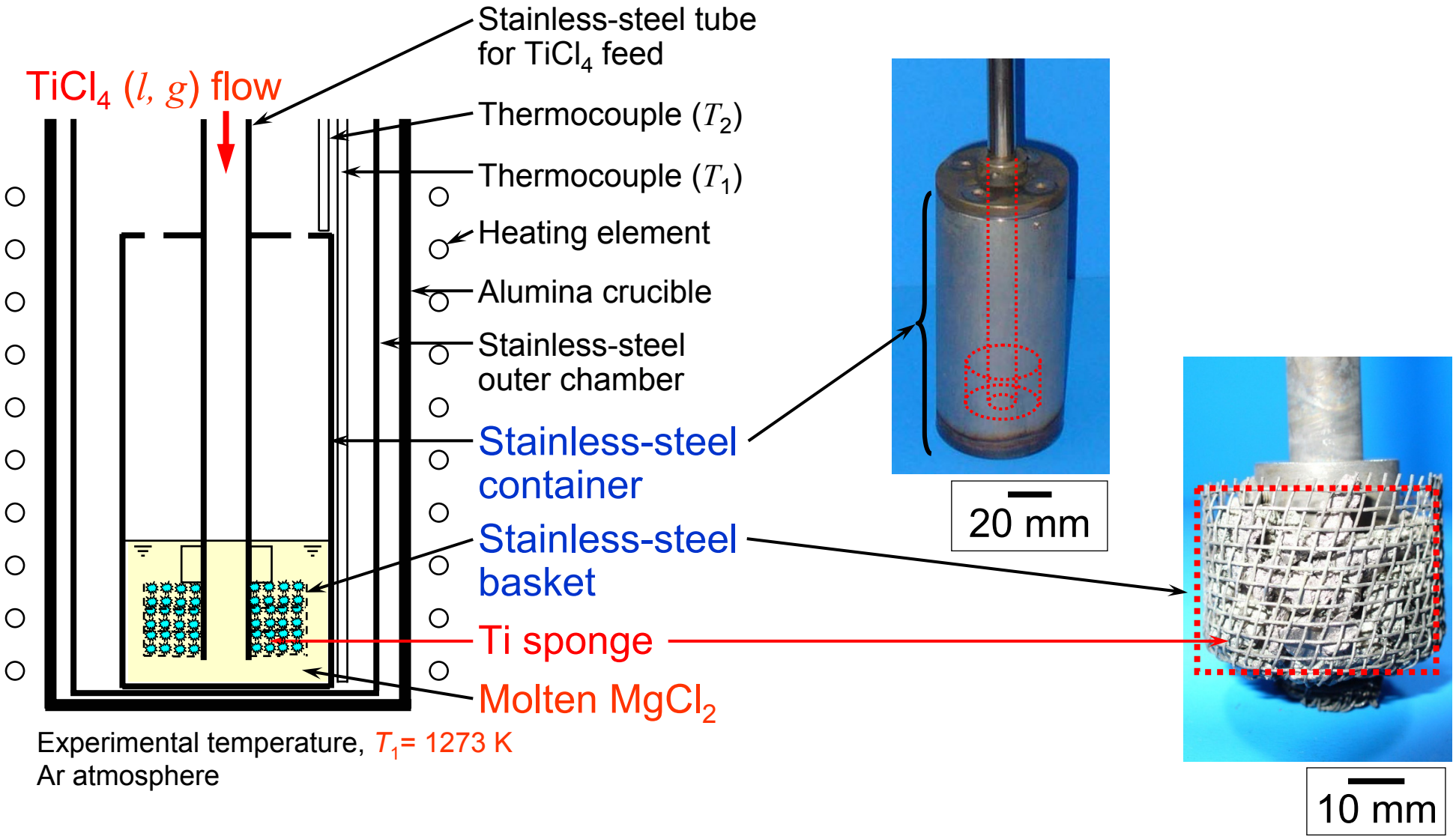
[Komarek and P. Herasymenko: J. Electrochem. Soc. 105 (1958) p 210.]

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



- $MgCl_2$ is expected to work as a medium that removes $TiCl_2$ film formed on the surface of metallic Ti by dissolving it.
- $MgCl_2$ accumulates $TiCl_2$ in its interior.

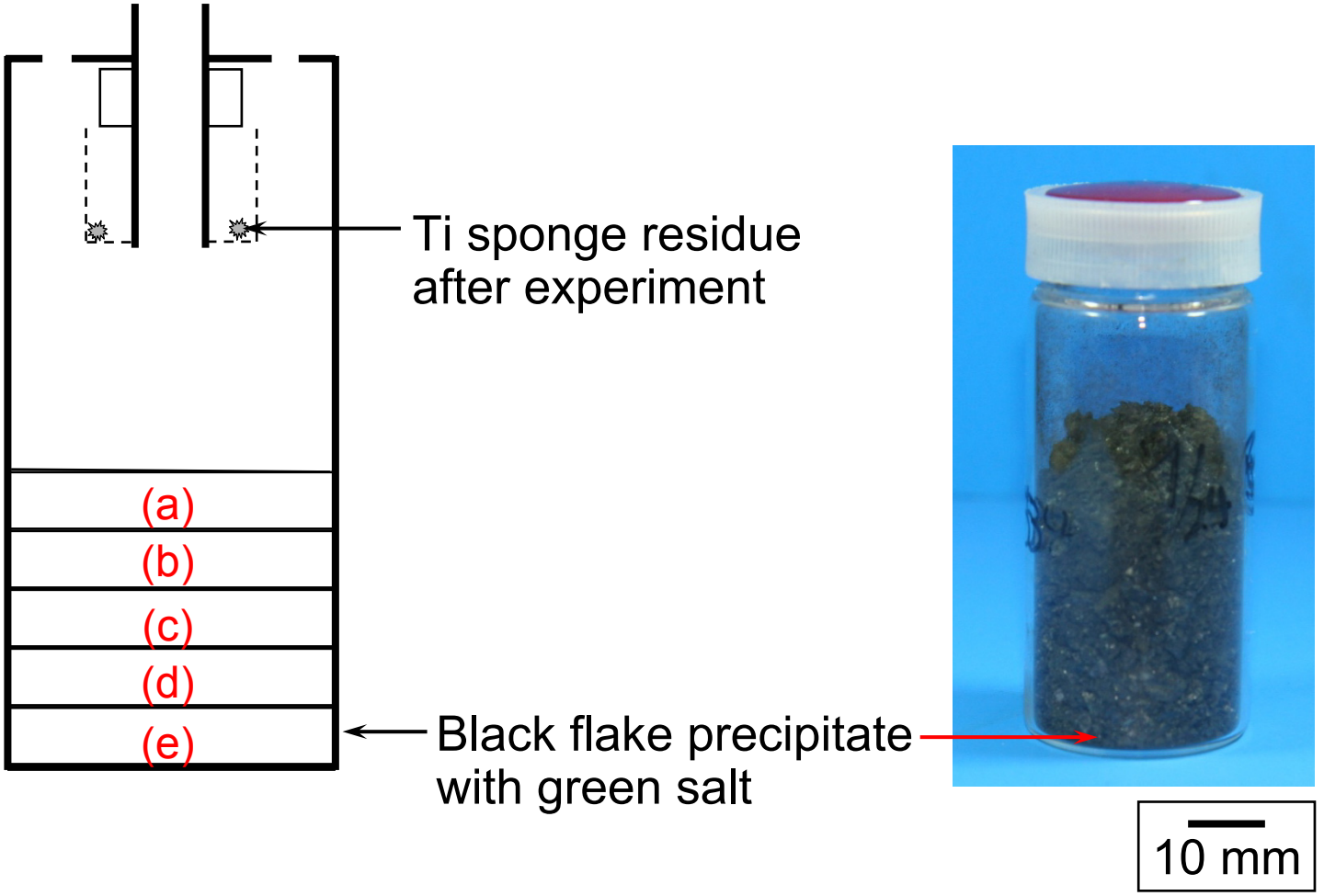
$TiCl_2$ Synthesis: Experimental



Experimental temperature, T_1= 1273 K
Ar atmosphere

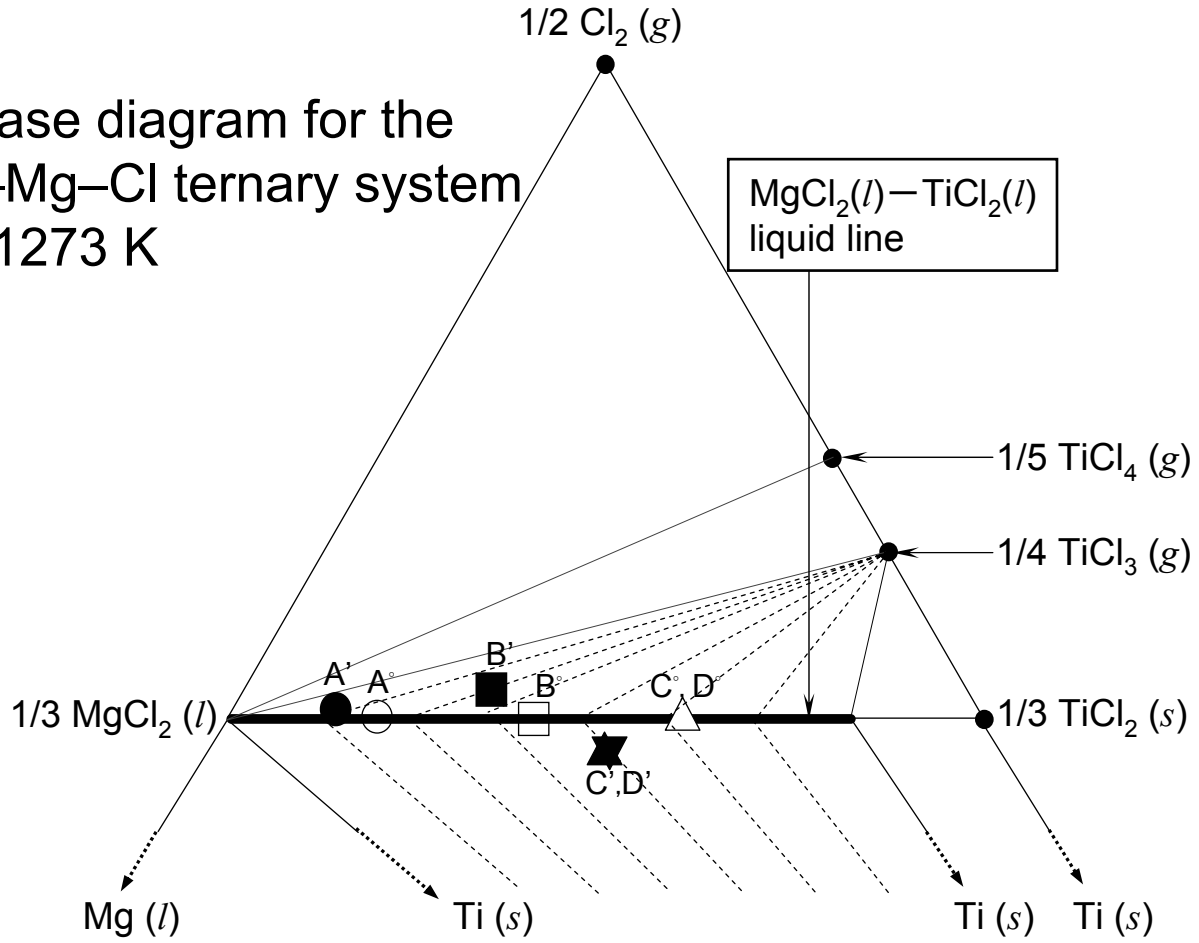
$TiCl_2$ Synthesis: Experimental Results (1)

Solidification of the salt



$TiCl_2$ Synthesis: Experimental Results (2)

Phase diagram for the Ti–Mg–Cl ternary system at 1273 K



	Nominal comp. before exp.	Overall comp. after exp.
A	○	●
B	□	■
C	△	▲
D	△	▼

Overall compositions of all the experiments were close to $MgCl_2$-$TiCl_2(l)$ liquid line !

$TiCl_2$ Synthesis: Experimental Results (3)

Table Yield of $TiCl_x$ and Ti consumption rate.

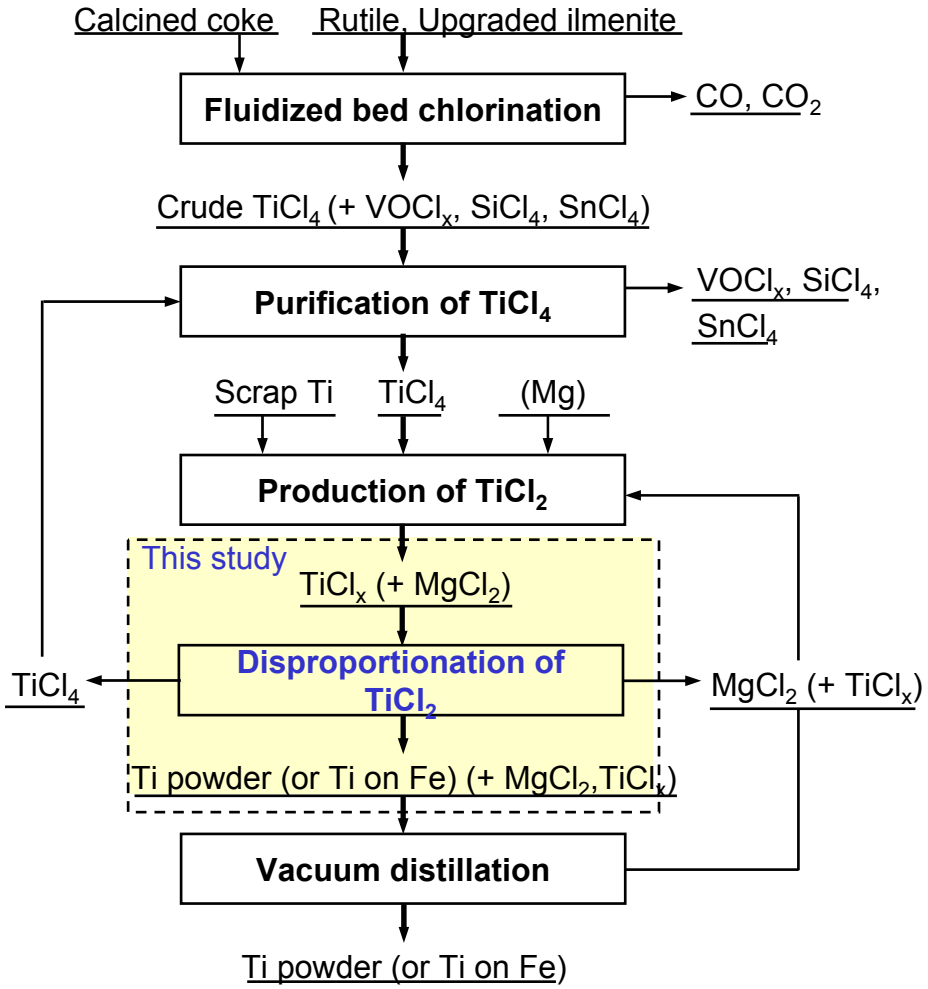
Exp. No.	$TiCl_4$ feed rate, r / g min^{-1}	Yield of $TiCl_x$, R_{TiCl_x} (%)	Ti consumption ratio, R_{Ti}' (%)
A	0.13	49	84
B	0.65	60	75
C	0.85	50	84
D	1.64	42	94

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).

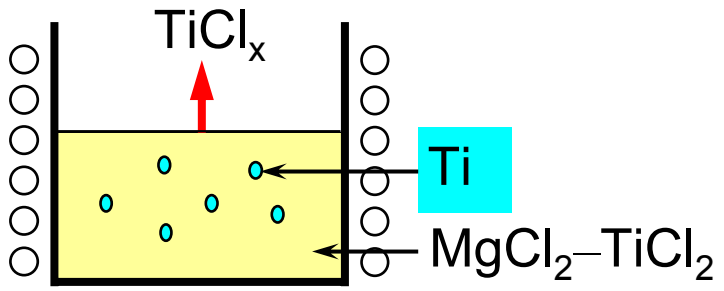
(2) Ti production by disproportionation of $TiCl_2$ in $MgCl_2$ molten salt



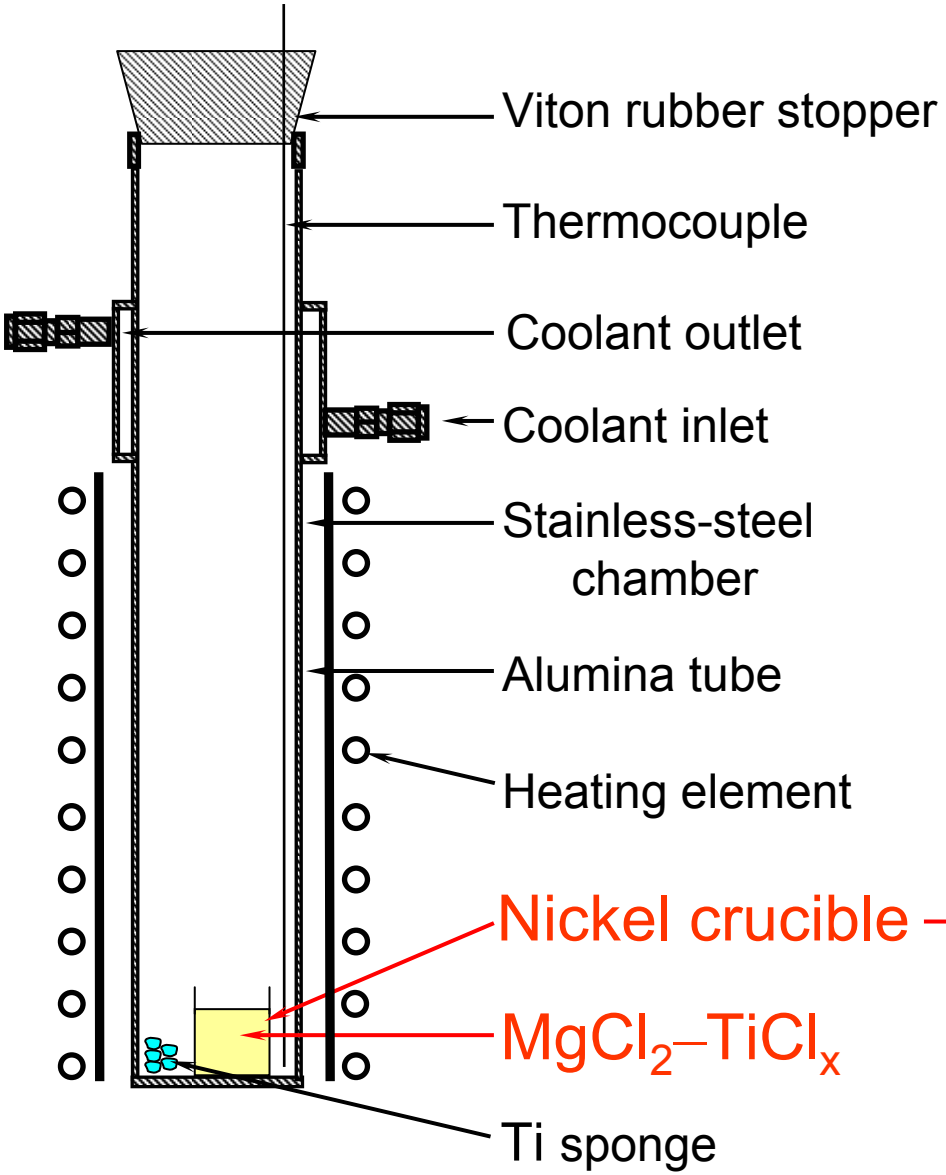
(2) Disproportionation of $TiCl_2$:

$3\ TiCl_2 \rightarrow Ti\ (s) + 2TiCl_3\ (g)$

$2\ TiCl_2 \rightarrow Ti\ (s) + TiCl_4\ (g)$



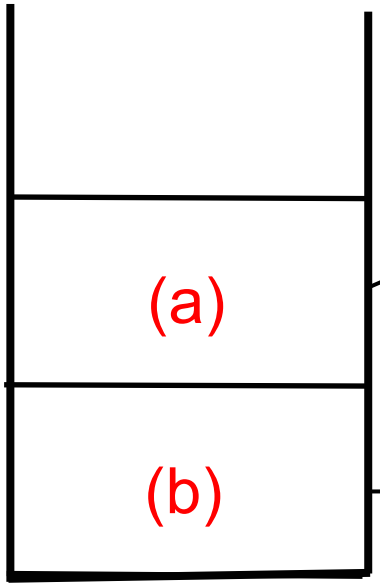
Disproportionation: Experimental



Experimental temperature, T = 1273 K
Reaction time, t = 3 or 6 h
Ar atmosphere

Disproportionation: Experimental Results (1)

Solidification of the salt



Black chip
with white powder

Black sintered object
coated by gold colored
membrane

b-1 from top side

b-2 from bottom side

Disproportionation: Experimental Results (2)

XRD pattern of the sample obtained after leaching

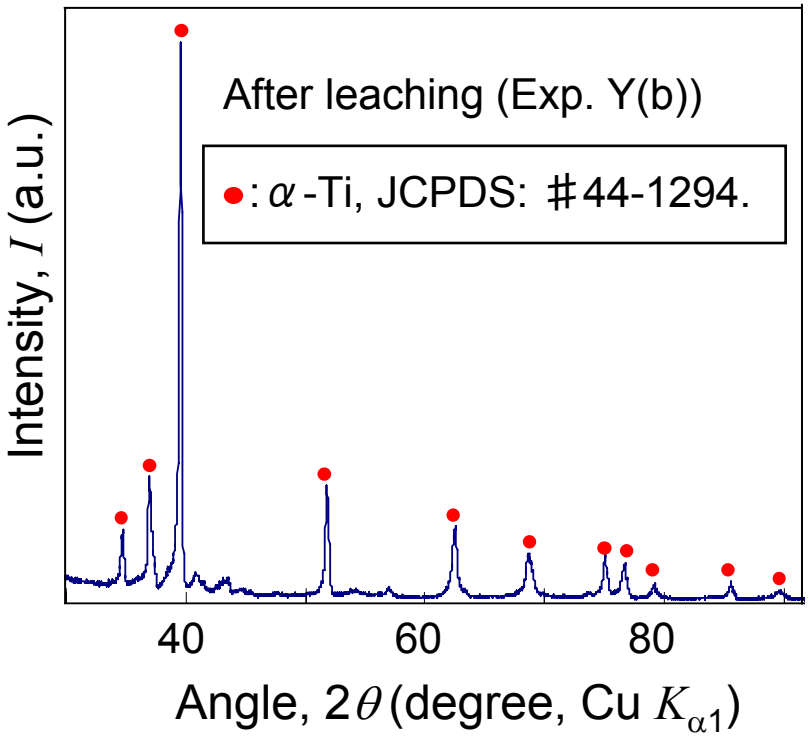


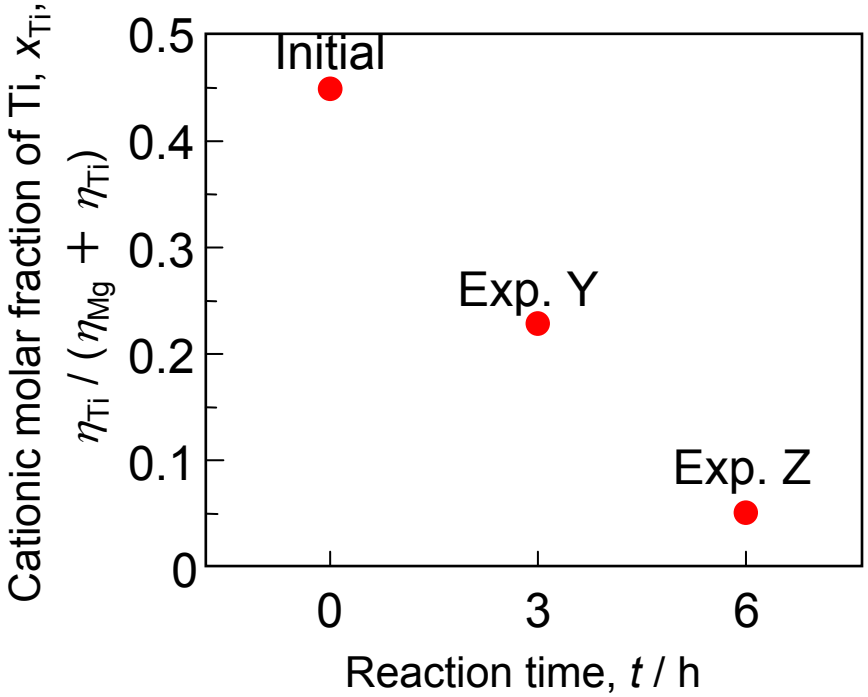
Table Analytical results of the obtained samples after leaching.

Exp.No. (position)	Time, *t* / h	Concentration of element *i* in obtained Ti sample, C_i (mass%)[a]				
		Ti	Mg	Fe	Ni	Cr
Y(a)	3	99.1	0.01	0.71	0.09	0.13
Y(b)	3	99.2	<0.01	0.53	0.09	0.15
Z(a)	6	96.7	<0.01	1.59	1.24	0.43
Z(b)	6	97.3	0.01	1.36	1.00	0.30

a: Determined by X-ray fluorescence analysis (XRF); the value excludes carbon and gaseous elements.

Titanium powder with a purity of over 99% was successfully obtained.

Disproportionation: Experimental Results (3)



Cationic molar fraction of titanium in the $MgCl_2$-$TiCl_2$ salt was evaluated;

$$R = \left(1 - \frac{x_{Ti}\,(\text{after experiment})}{x_{Ti}\,(\text{initial})}\right) \times 100$$

R = 49% (Exp. Y, 3 h)
= 87% (Exp. Z, 6 h)

Disproportionation of $TiCl_2$ in $MgCl_2$ molten salt almost finished by the reaction time of 6 h.

Conclusions

A high-efficient synthesis process for $TiCl_2$
and a production process for titanium metal
were investigated by using reactions in 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 disproportionation of $TiCl_2$ in molten $MgCl_2$ was confirmed.