Production of Titanium Subchloride by Employing Molten Salts as Reaction Medium

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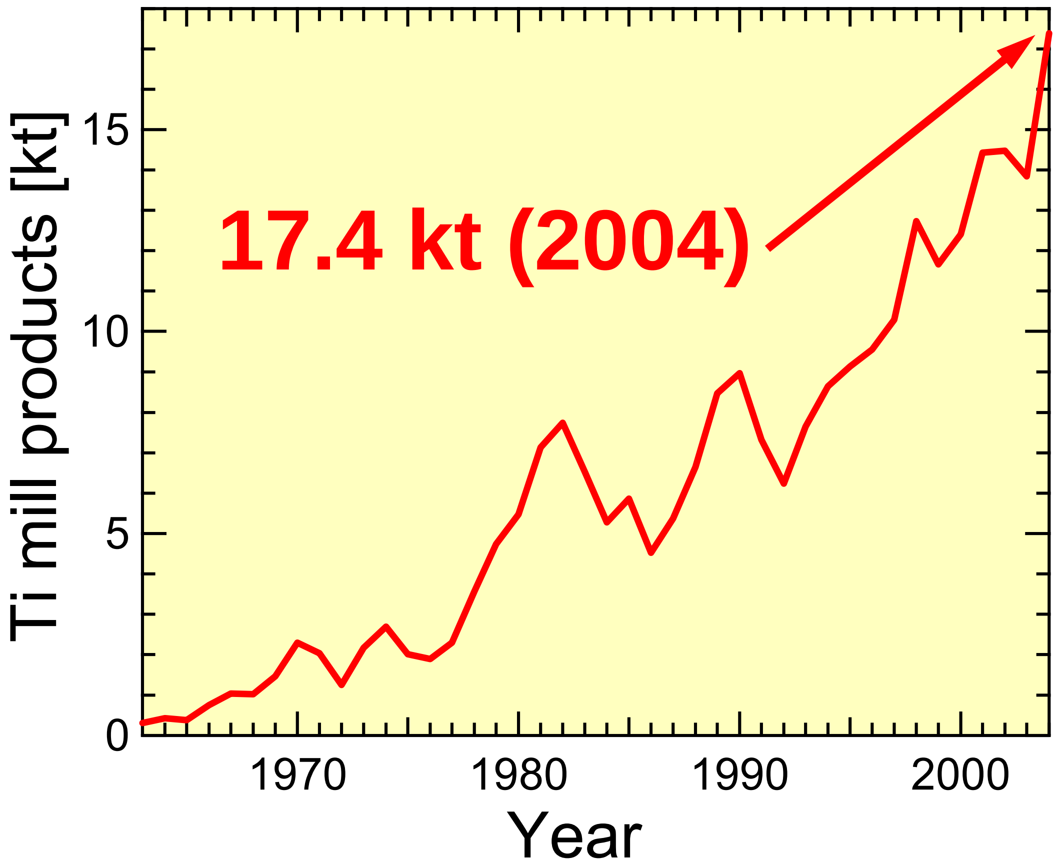
Current Status of Titanium Production

Production of Ti mill products in Japan



- Demand for Ti is rapidly increasing.
- Limited supply of Ti caused serious shortage of Ti in the market.

- A new production process with high productivity is urgently required.

[S. Nakamura: Industrial Rare Metals, (Tokyo, Japan: Arumu Publish co., 2004), pp. 52–55.]

Purpose of this Study

The Kroll process
Feed: $TiCl_4$

- Huge exothermic reaction

→Reduction speed is extremely slow, and 10 days are required for producing 10 ton of Ti.
→Vacuum distillation and cooling process are also "time consuming".

⬇

Development of a continuous and high-speed Ti production process based on the magnesiothermic reduction of Ti subchlorides (Subhalide reduction process)

Physical and Chemical Properties of Titanium Chlorides

	$TiCl_4$	$TiCl_3$	$TiCl_2$
Appearance			
Color	Clear	Red	Black
Molecular weight (g/mol)	189.7	154.2	118.8
Density (g/cm^3)	1.70	No data	3.13
Melting point (°C)	–24.1	–	–
Boiling point (°C)	136.5	–	–
Sublimation point (°C)	–	830	1307
ΔG°_{f} at 800°C (kJ/mol Cl_2)	–317	–327	–344
$\Delta G'^{\circ}_{f}$ at 800°C (kJ/mol Ti)	–637	–491	–344
Vapor pressure at 800°C (atm)	–	0.74	1.2×10^{-4}

Reduction Heat

Titanium subchlorides • Low reduction heat

At 1073 K

① $TiCl_4(g) + Mg(l) \rightarrow TiCl_2(s) + MgCl_2(l)$

$\Delta H^\circ = -339$ kJ, $\Delta G^\circ = -185$kJ

This is suitable for developing high speed process

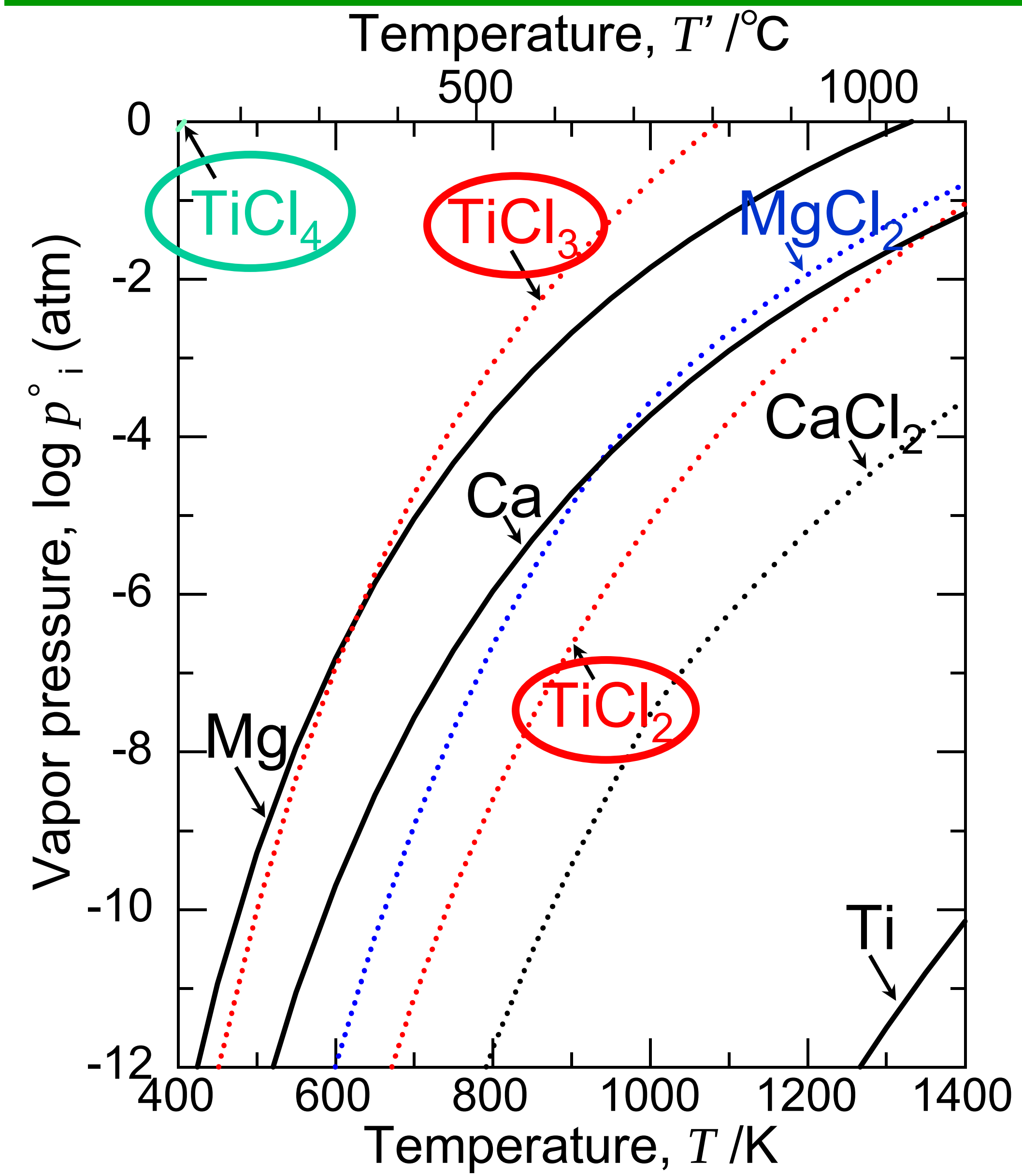
② $TiCl_2(s) + Mg(l) \rightarrow Ti(s) + MgCl_2(l)$

$\Delta H^\circ = -91$ kJ, $\Delta G^\circ = -130$ kJ

③ $TiCl_4(g) + 2\,Mg(l) \rightarrow Ti(s) + 2\,MgCl_2(l)$

(=①+②) $\Delta H^\circ = -430$ kJ, $\Delta G^\circ = -315$ kJ

Vapor Pressure



Titanium subchlorides

- Low vapor pressure
- Stable as a condensed phase

[I. Barin, Thermochemical Data of Pure Substances, VCH Verlagsgesellschaft, Weinheim, (1989).]

New Titanium Production Process Using Titanium Subhalides

① $TiCl_4(l, g) + Mg(l, g) \rightarrow TiCl_x(s, l) + MgCl_2(l)$

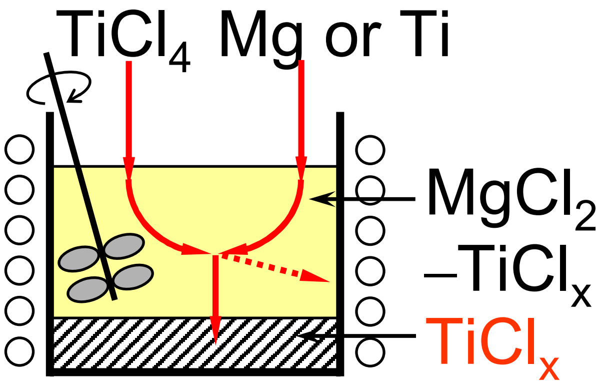
$TiCl_4(l, g) + Ti(s, \text{scrap}) \rightarrow TiCl_x(s, l)$

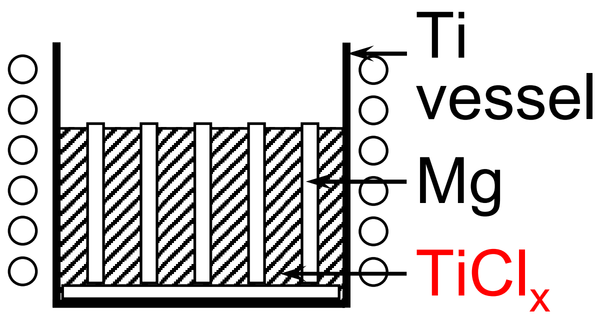
② $TiCl_x(s, l) + Mg\ (l, g) \rightarrow Ti\ (s) + MgCl_2\ (l, g)$

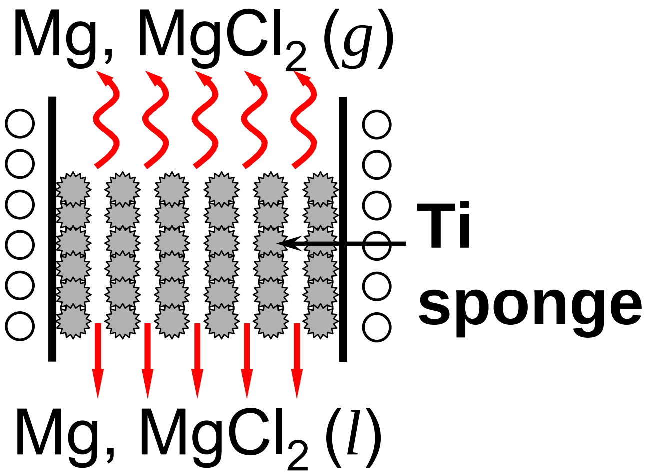
Step 1:
High-speed production of Ti subchlorides and enrichment of $TiCl_x$

Step 2:
High-speed magnesiothermic reduction of $TiCl_x$

Step 3:
High-speed removal of Mg and $MgCl_2$ from Ti sponge by draining and vacuum distillation







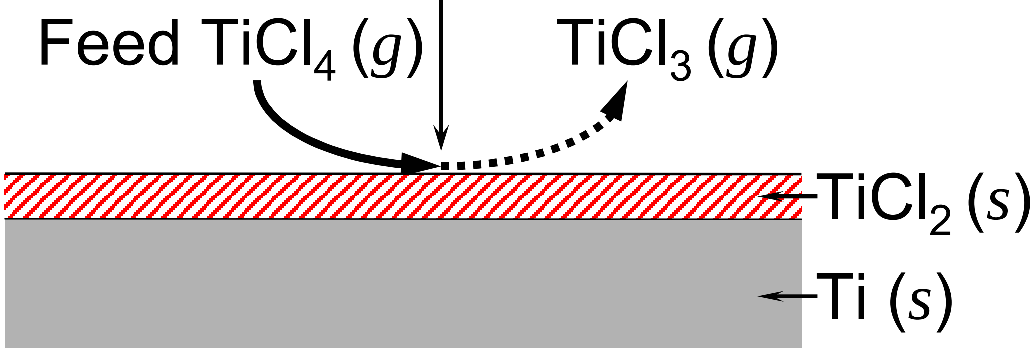
Features of the New Process

Table Comparison of the Kroll process and new process

	Kroll process	New process
Process type	Batch-type, limited speed	(Semi-)Continuous, high speed
Feed material	$TiCl_4$ (*l*, *g*)	$TiCl_2$ or $TiCl_3$ (*s*, *l*)
Heat of reduction, ΔH° / kJ mol Ti	High (–434)	Low (–94 ~ –191)
Reactor material	Mild steel (Fe contamination unavoidable)	Ti (No Fe contamination)
Reactor size	Large (Crush and melt)	Small (No crush and direct melt)
Flux, sealant	Not used	$MgCl_2$, Ti
Common features	• Magnesiothermic reduction of chloride • Removal of $MgCl_2$ and Mg from Ti sponge by draining and vacuum distillation • Production of high-purity Ti with low oxygen content	

Problem on the Previous Study

$TiCl_4\ (g) + TiCl_2\ (s) \rightarrow 2\ TiCl_3\ (g)$



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

Reason for low efficiency of $TiCl_x$ formation

1. $TiCl_3$ formed, evaporated, and dissipated.
2. $TiCl_2$ solid film formed on surface of metallic Ti hindered chlorination reaction of metallic Ti.
3. $TiCl_2$ was converted to $TiCl_3$ by reaction with $TiCl_4$.

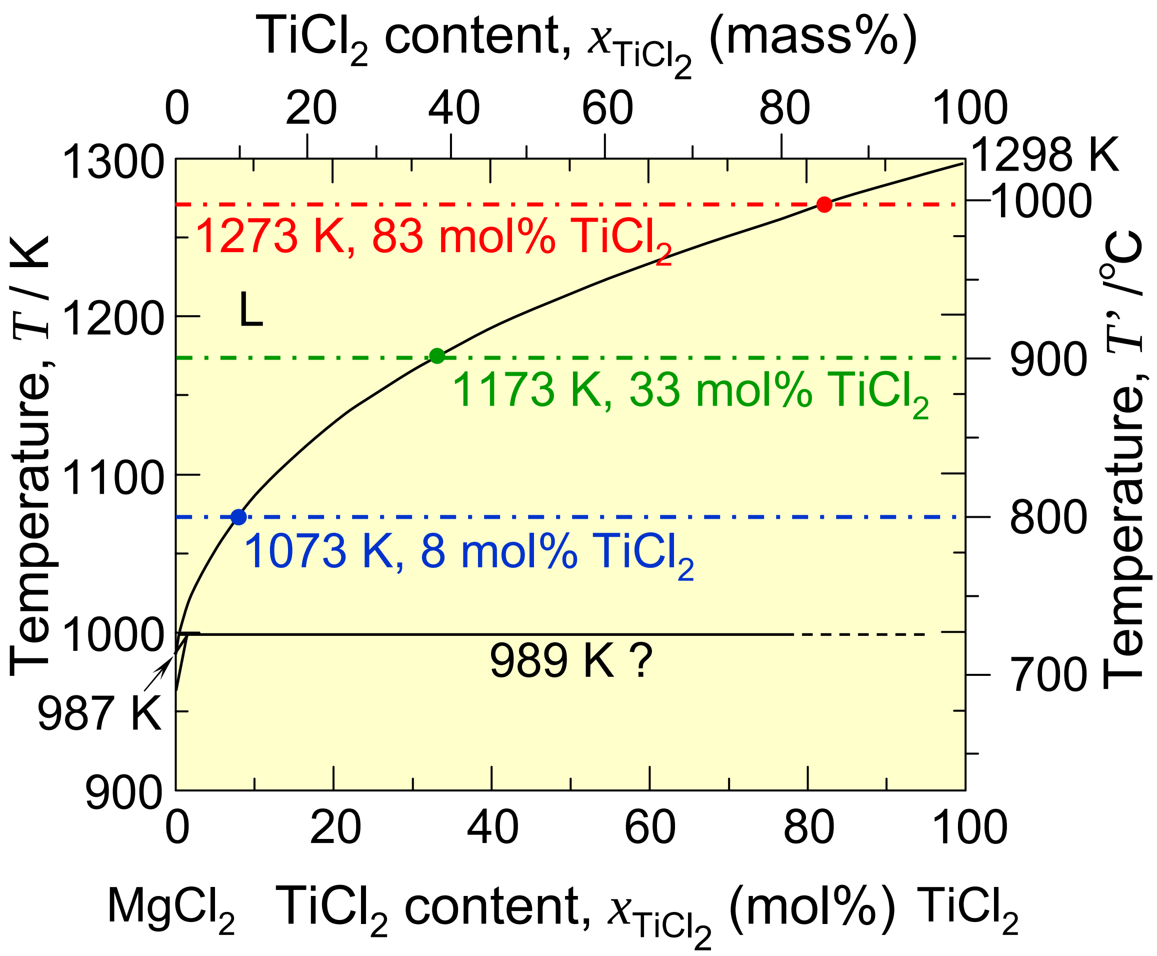
For improving efficiency of $TiCl_x$ formation

1. $TiCl_2$ formed on surface of metallic Ti has to be removed.
2. Reaction of $TiCl_2$ with $TiCl_4$ has to be prevented.

Titanium Subchloride Synthesis by Reaction of $TiCl_4$ with Ti in Molten Salts

Experimental Procedure

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

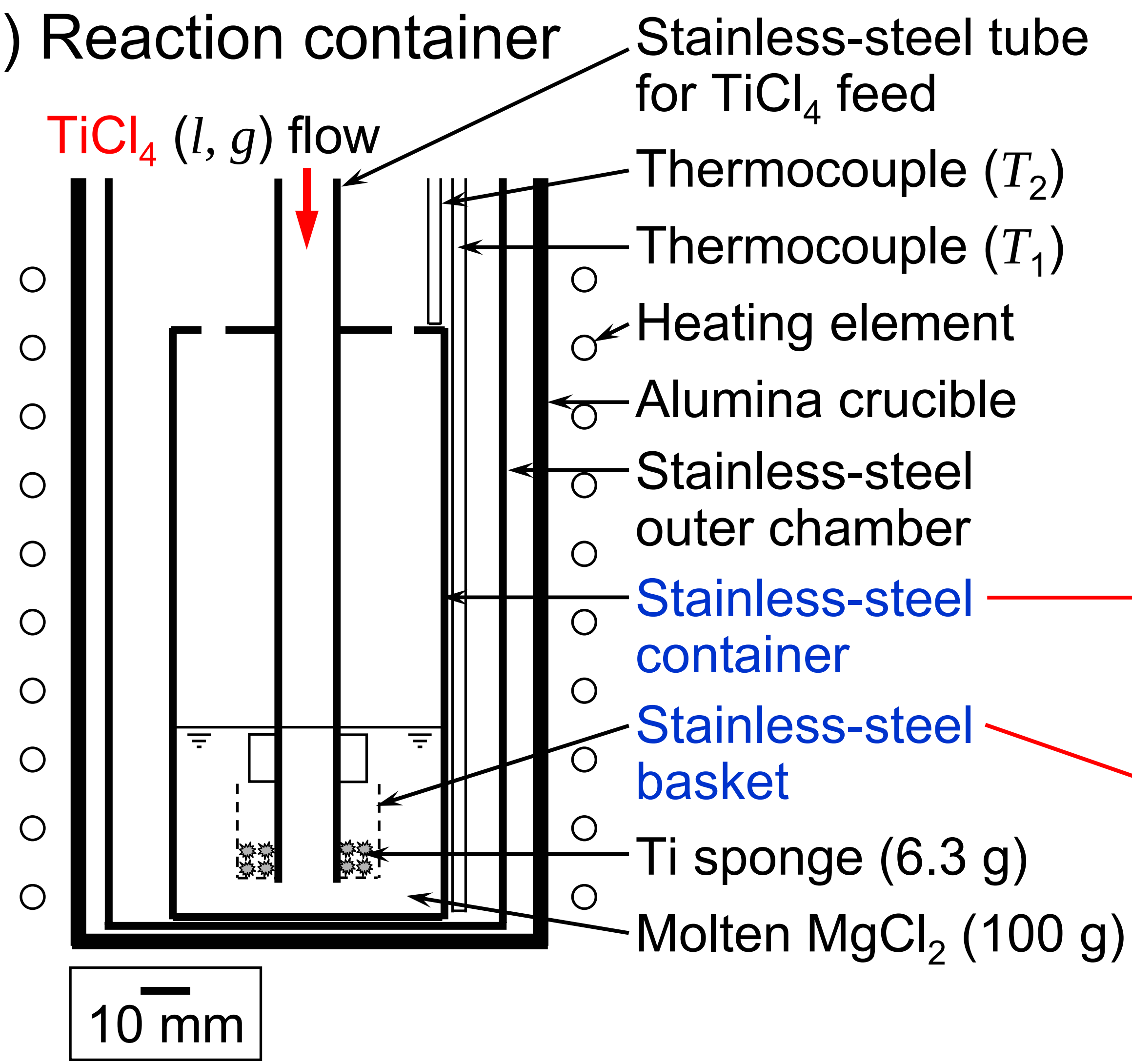


- $MgCl_2$ is expected to work as a medium that removes $TiCl_2$ film formed on the surface of metallic titanium by dissolving and accumulates $TiCl_2$ in its interior.

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

Experimental Procedure

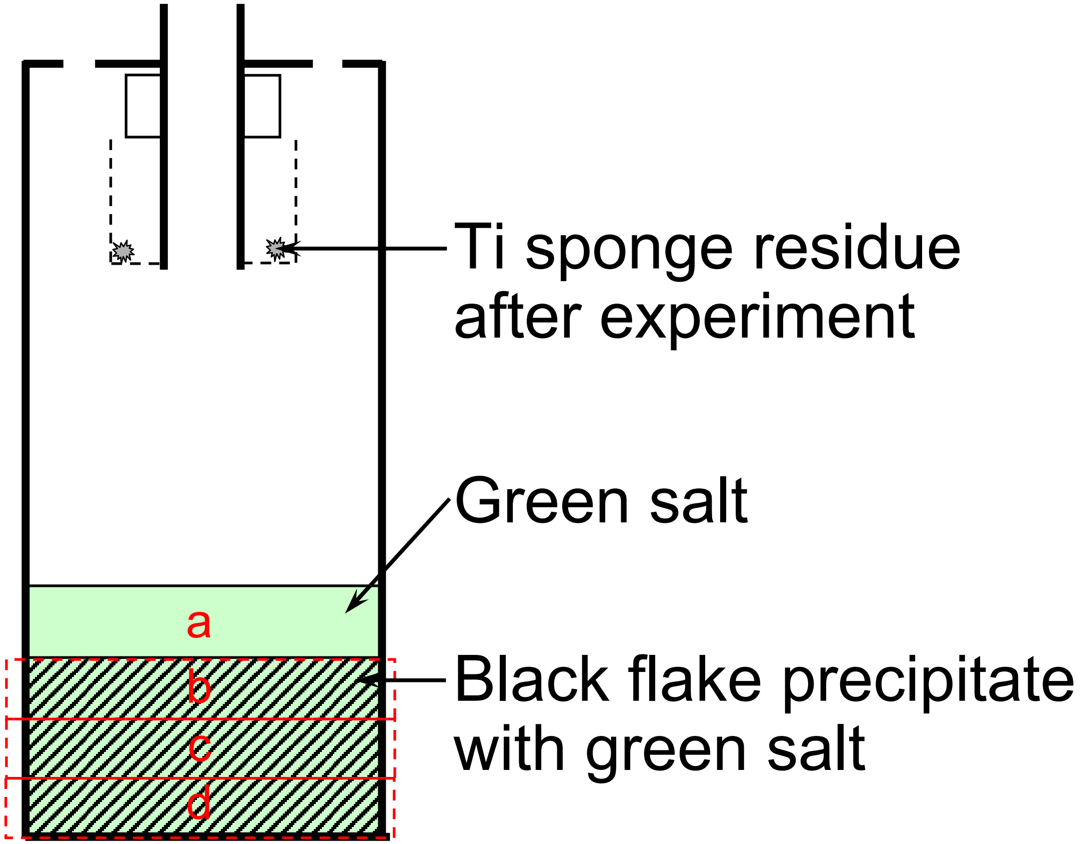
(a) Reaction container



(b) Photo

Experimental Results

Status of solidification of the salt



Experimental Results

Table Analytical results of the obtained samples (Exp. 3A).

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	2.33	74.63	23.01	0.03	<0.02	<0.01	4.35
b	7.07	72.25	20.62	0.01	<0.02	0.04	2.31
c	8.87	71.85	19.24	0.01	<0.02	0.03	2.39
d	9.58	71.34	18.95	0.08	<0.02	0.04	2.26

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

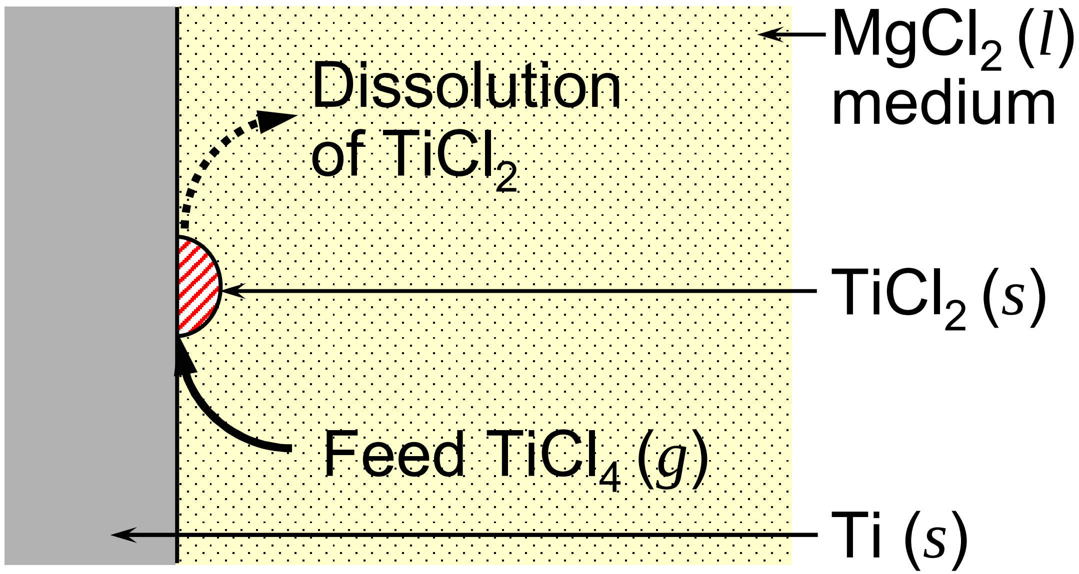
- Concentration of Ti in the salt recovered from the upper part of the reaction container was low, and that in the salt recovered from the lower part of the reaction container was relatively high.

- Value of x in $MgCl_2$–$TiCl_x$ was calculated to be 2.24~2.47 (lower part).

Experimental Results

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}' (%)
3A	0.56	64	80
3B	0.16	46	93
3C	0.13	49	84



- It was demonstrated that efficiency of $TiCl_x$ formation was improved by using molten $MgCl_2$ as a reaction medium.

Conclusions

In order to establish a new semi-continuous and high-speed Ti production process based on the magnesiothermic reduction of titanium subchlorides, a novel synthetic process of titanium subchlorides ($TiCl_x$, x = 2, 3) by reaction of $TiCl_4$ with metallic Ti was investigated.

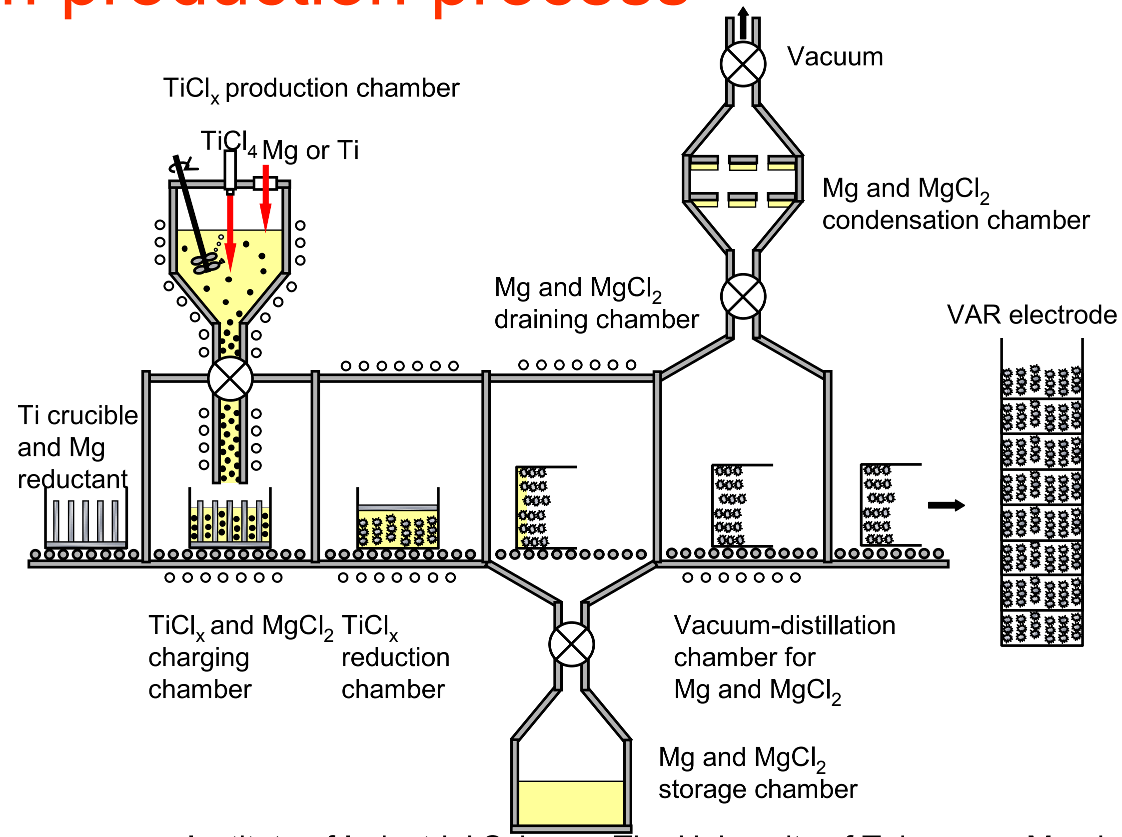
- Efficiency of $TiCl_x$ formation produced by direct reaction of $TiCl_4$ with Ti was low.

- It was demonstrated that efficiency of $TiCl_x$ synthesis can be improved when using molten $MgCl_2$ as a reaction medium.

Future Works

- More efficient production process of $TiCl_x$ from $TiCl_4$
- Enrichment process of $TiCl_x$

  → Establishment of a continuous and high-speed titanium production process



これ以後補足資料

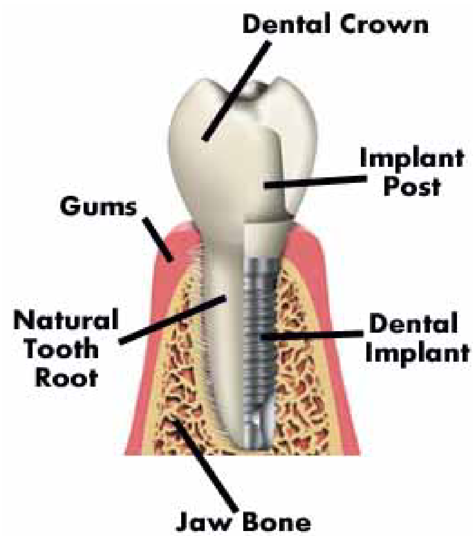
Feature of Titanium

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

Aerospace industry

Japan Aerospace Exploration Agency

Dental material

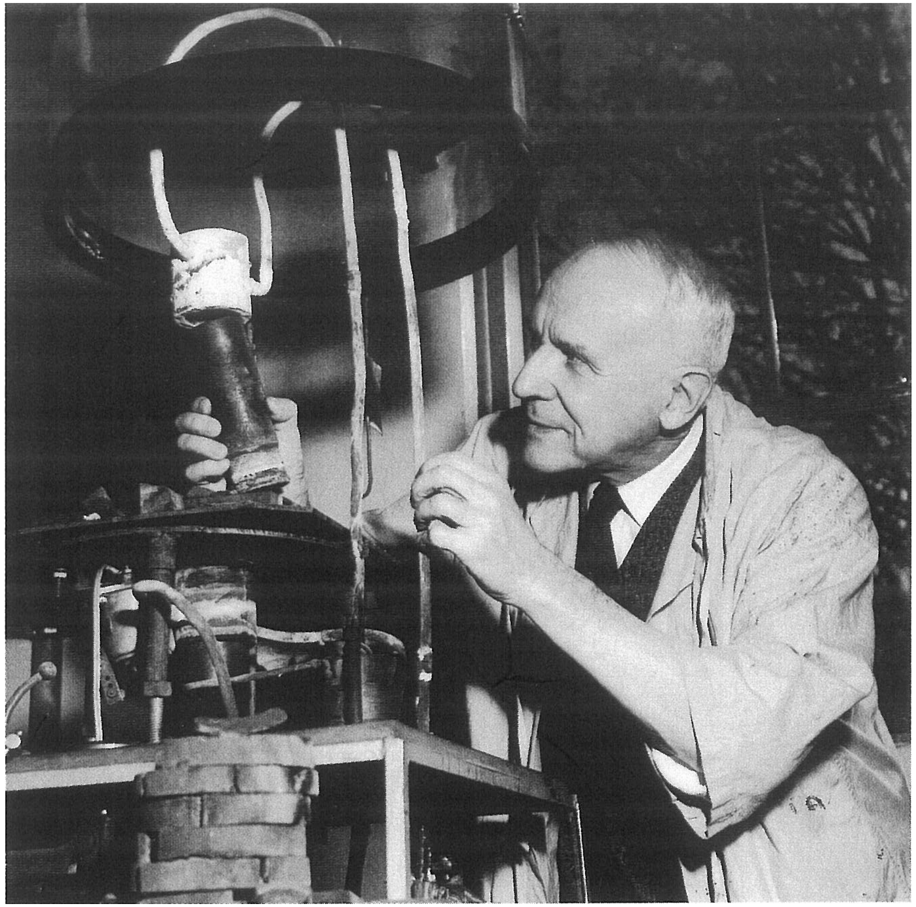


http://village.infoweb.ne.jp/~etou/indexhome.htm

Power generation plant

Japan Titanium Society

Chapter Ⅰ Father of Titanium Industrial Production



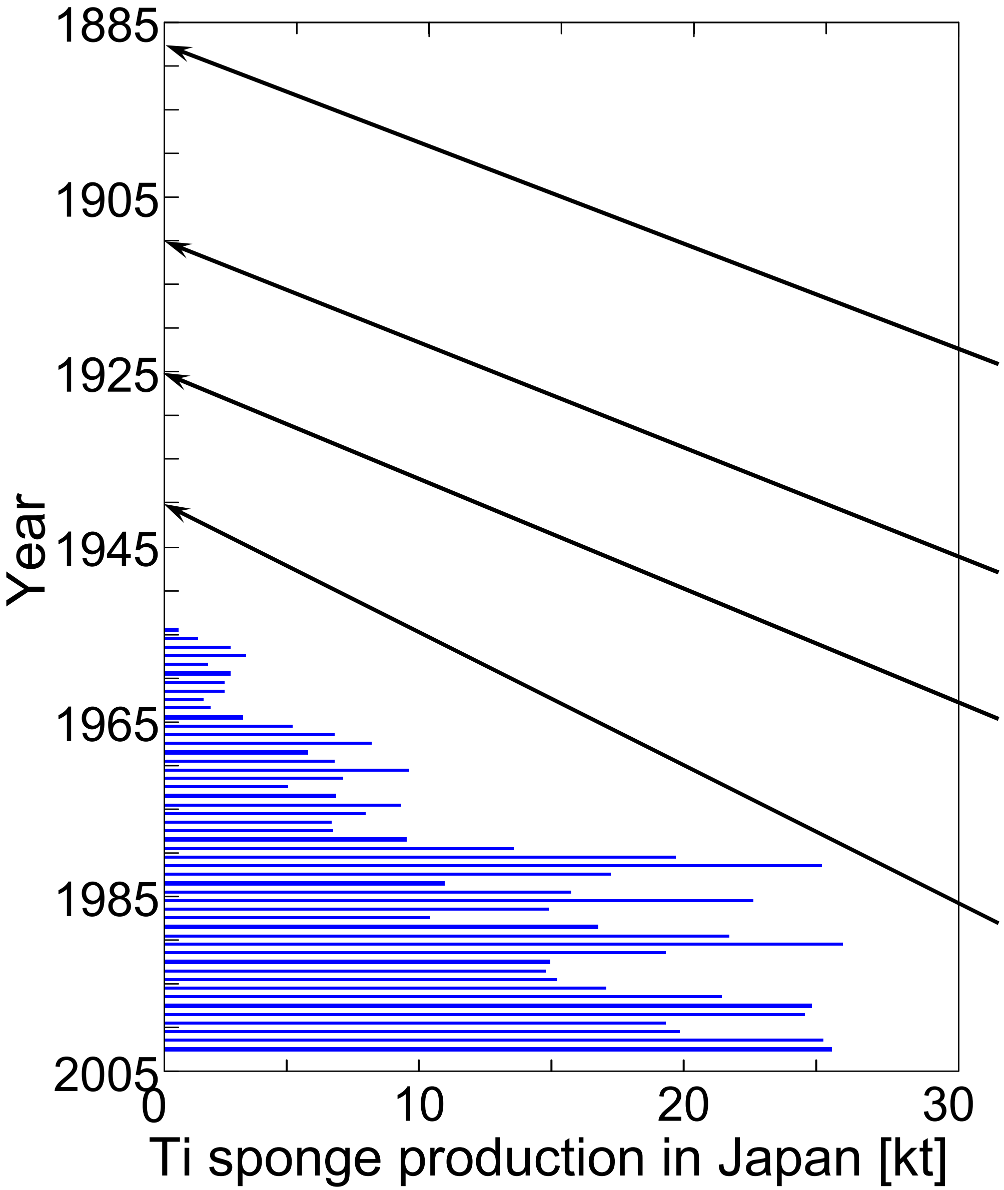
William J. Kroll
(1889.11.24-1973.3.30)

[William J. Kroll – A Luxembourg Scientist, Edited by Fondation Nicolas Lanners, Luxembourg 1998, Cover page.]

Chapter I　Father of Ti Industrial Production

William J. Kroll
(1889.11.24-1973.3.30)

[William J. Kroll – A Luxembourg Scientist, Edited by Fondation Nicolas Lanners, Luxembourg 1998, p.63.]



1791 **Gregor**: Discovery of titanium element

1795 **Klaproth**: Denominated as "Titanium"

1887 **Nilson, Petterson**:
Reduction of $TiCl_4$ by Na

1910 **Hunter**: Reduction of $TiCl_4$ by Na

1925 **van Arkel**, **DeBore**:
Thermal dissociation of $TiCl_4$

1940 **Kroll**: Reduction of $TiCl_4$ by Mg

Current titanium production process based on the Kroll process.

Chapter Ⅰ Abundance of Titanium in the Earth's Crust

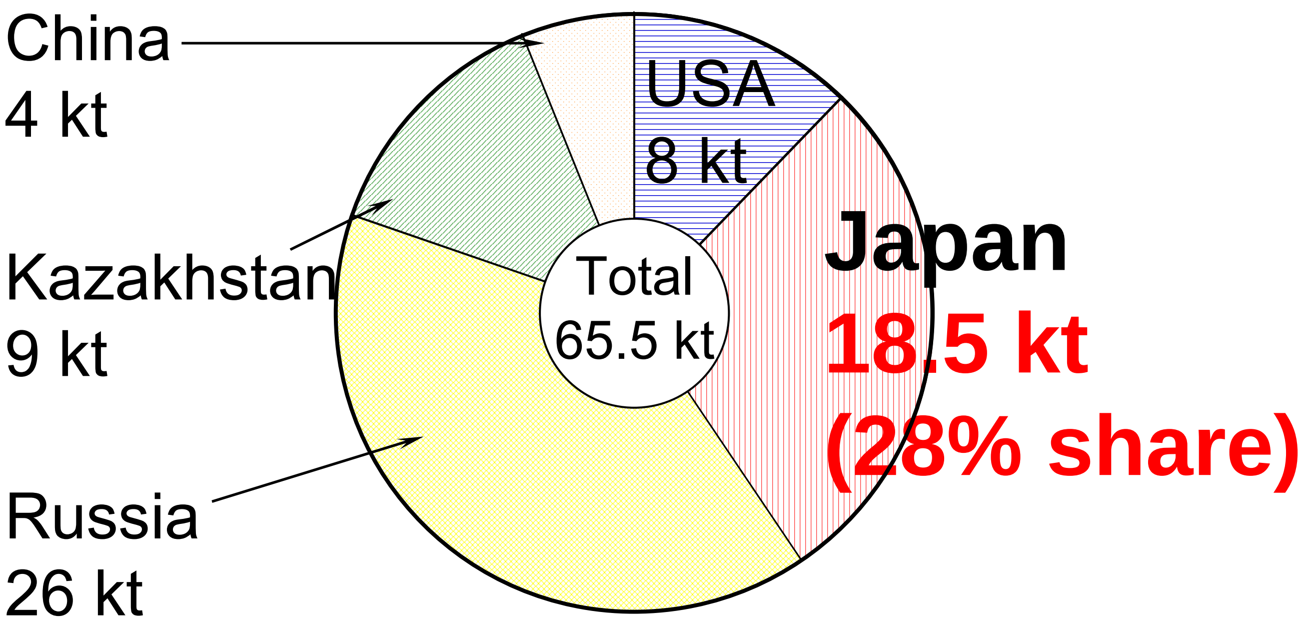
Rank	Element	Clarke No.
1	^{8}O	49.50
2	^{14}Si	25.80
3	^{13}Al	7.56
4	^{26}Fe	4.70
5	^{20}Ca	3.39
6	^{11}Na	2.63
7	^{19}K	2.40
8	^{12}Mg	1.93
9	^{1}H	0.87
10	**^{22}Ti**	**0.46**
11	^{17}Cl	0.19
12	^{25}Mn	0.09
13	^{15}P	0.08
14	^{6}C	0.08
15	^{16}S	0.03

Rank	Element	Clarke No.
16	^{7}N	0.03
17	^{9}F	0.03
18	^{39}Rb	0.03
19	^{56}Ba	0.02
20	^{40}Zr	0.02
21	^{24}Cr	0.02
22	^{38}Sr	0.02
23	^{23}V	0.02
24	^{28}Ni	0.01
25	^{29}Cu	0.01
26	^{74}W	6×10^{-3}
27	^{3}Li	6×10^{-3}
28	^{58}Ce	4.5×10^{-3}
29	^{27}Co	4×10^{-3}
30	^{50}Sn	4×10^{-3}

Titanium is the 10th most abundant element in the earth's crust.

Chapter Ⅰ Current Status of Titanium Production

Production of Ti sponge in the world (2003)



[S. Nakamura: Industrial Rare Metals, (Tokyo, Japan: Arumu publish co., 2004), pp. 52–55.]

Chapter I Comparison with common metals

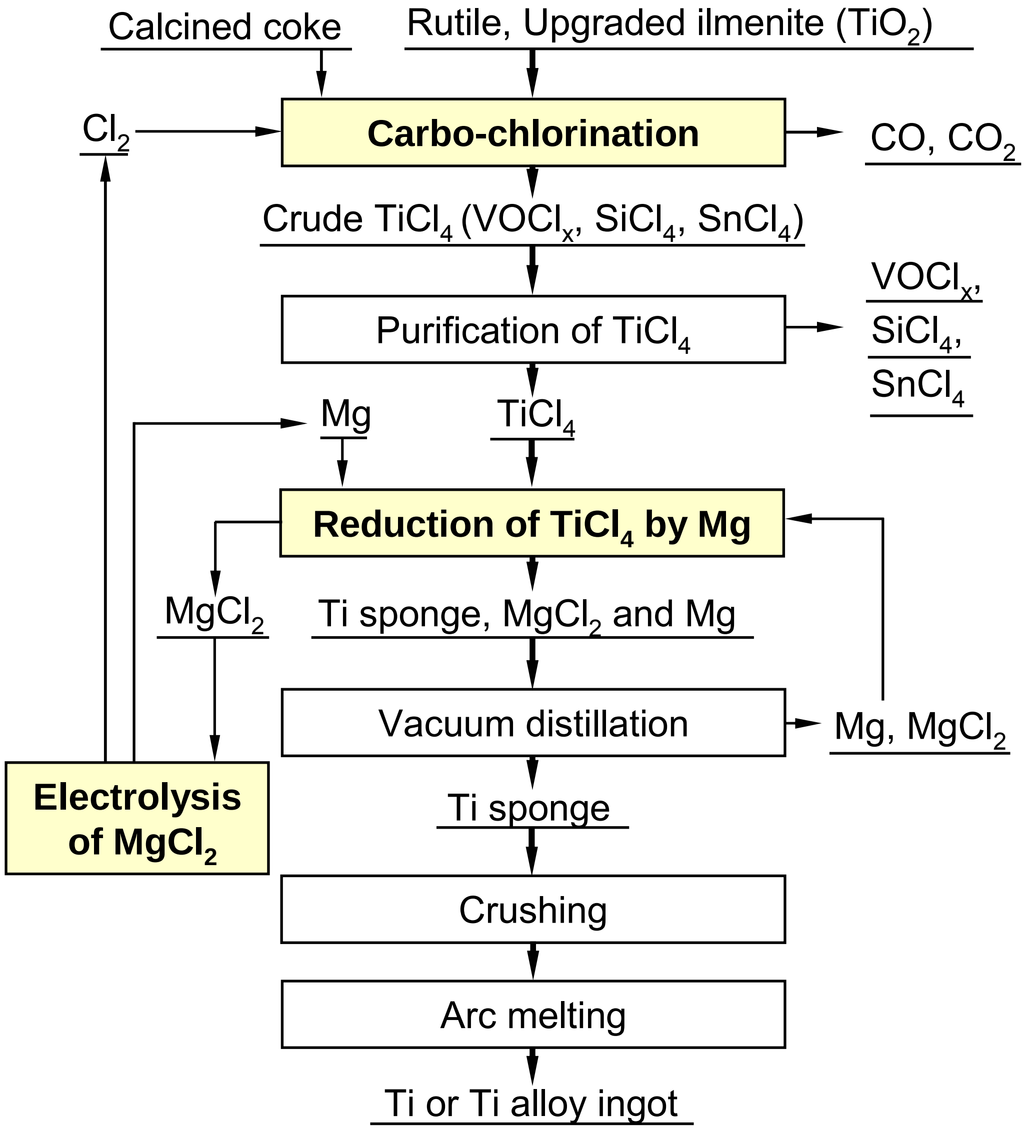
Metal	Iron	Aluminum	Titanium
Symbol	Fe	Al	Ti
Melting point (°C)	1536	660	1680
Density (g/cm^3@25 °C)	7.9	2.7	4.5
Specific strength [$(kgf/mm^2)/(g/cm^3)$]	4.1(Pure) 6.7(SUS304)	2.2(Pure) 8.9(0.5Mg0.5Si)	5.1(Pure) 24.6(6Al4V)
Clarke No.	4	3	10
Price (¥/kg)	50	600	3000
Production volume (t/world@2003)	9.6×10^8	2.2×10^7	6.6×10^4

1/300

1/15000

Although titanium is the 10th most abundant element in the earth's crust, its production volume is very small.

Chapter I Production Process of Titanium Subchlorides

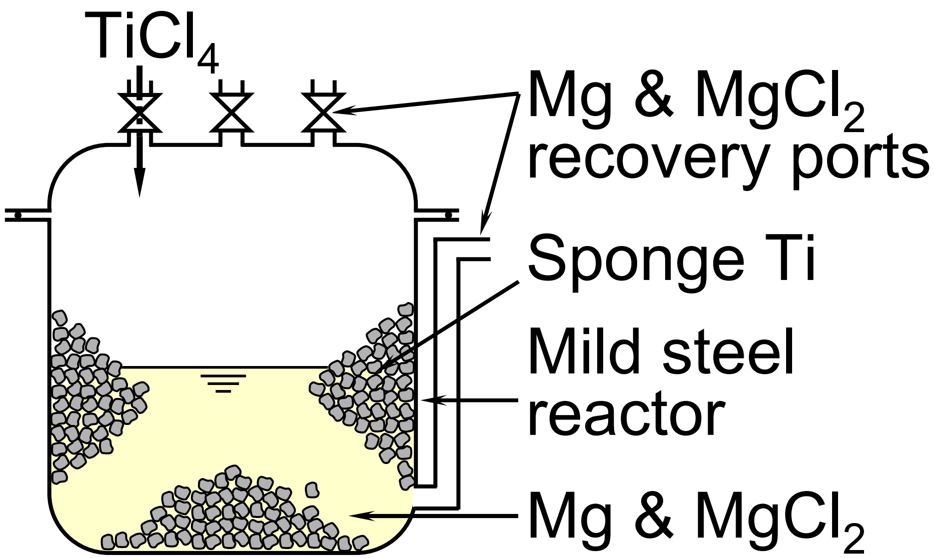


The Kroll Process

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

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

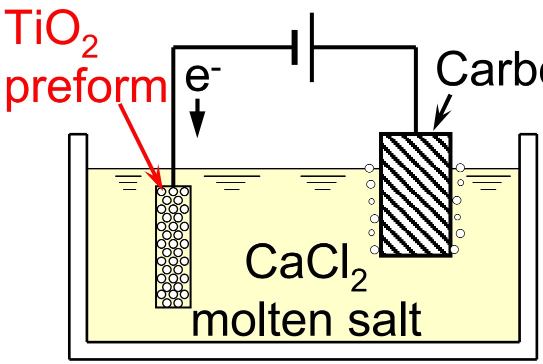
Electrolysis: $MgCl_2 \rightarrow Mg + Cl_2$



◎High-purity Ti can be obtained.
◎Metal/salt separation is easy.
○Chlorine circulation is Established.
○Efficient Mg electrolysis can be utilized.
○Reduction and electrolysis can be carried out independently.
×Process is complicated.
×Reduction process is a batch type.
×Production speed is low.

Reduction speed of Ti is less than 1 t/day·batch, which is one of the contributors to its high cost.

(a) FFC Process (Fray *et al.*)

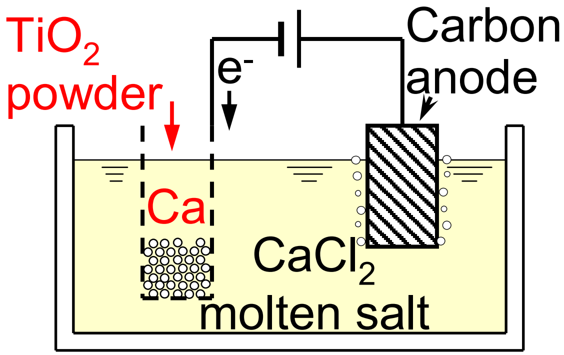


Electrolysis

Cathode: $TiO_2 + 4e^- \rightarrow Ti + 2O^{2-}$ (a1)

Anode: $C + x\,O^{2-} \rightarrow CO_x + 2x\,e^-$ (a2)

(b) OS Process (Ono & Suzuki)



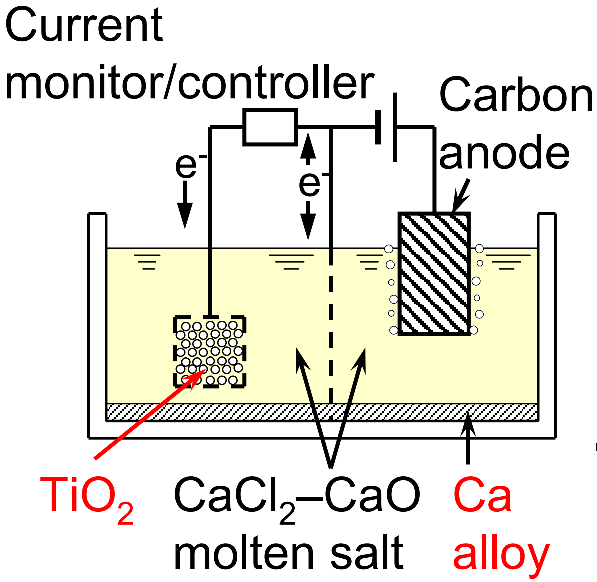
$TiO_2 + 2Ca \rightarrow Ti + 2O^{2-} + Ca^{2+}$ (b1)

Electrolysis

Cathode: $Ca^{2+} + 2e^- \rightarrow Ca$ (b2)

Anode: $C + x\,O^{2-} \rightarrow CO_x + 2x\,e^-$ (b3)

(c) EMR/MSE Process (Okabe *et al.*)



Cathode: $TiO_2 + 4e^- \rightarrow Ti + 2O^{2-}$ (c1)

Anode: $2Ca \rightarrow 2Ca^{2+} + 4e^-$ (c2)

<u>Electrolysis</u>

Cathode: $Ca^{2+} + 2e^- \rightarrow Ca$ (c3)

Anode: $C + x\,O^{2-} \rightarrow CO_x + 2x\,e^-$ (c4)

Overall reaction

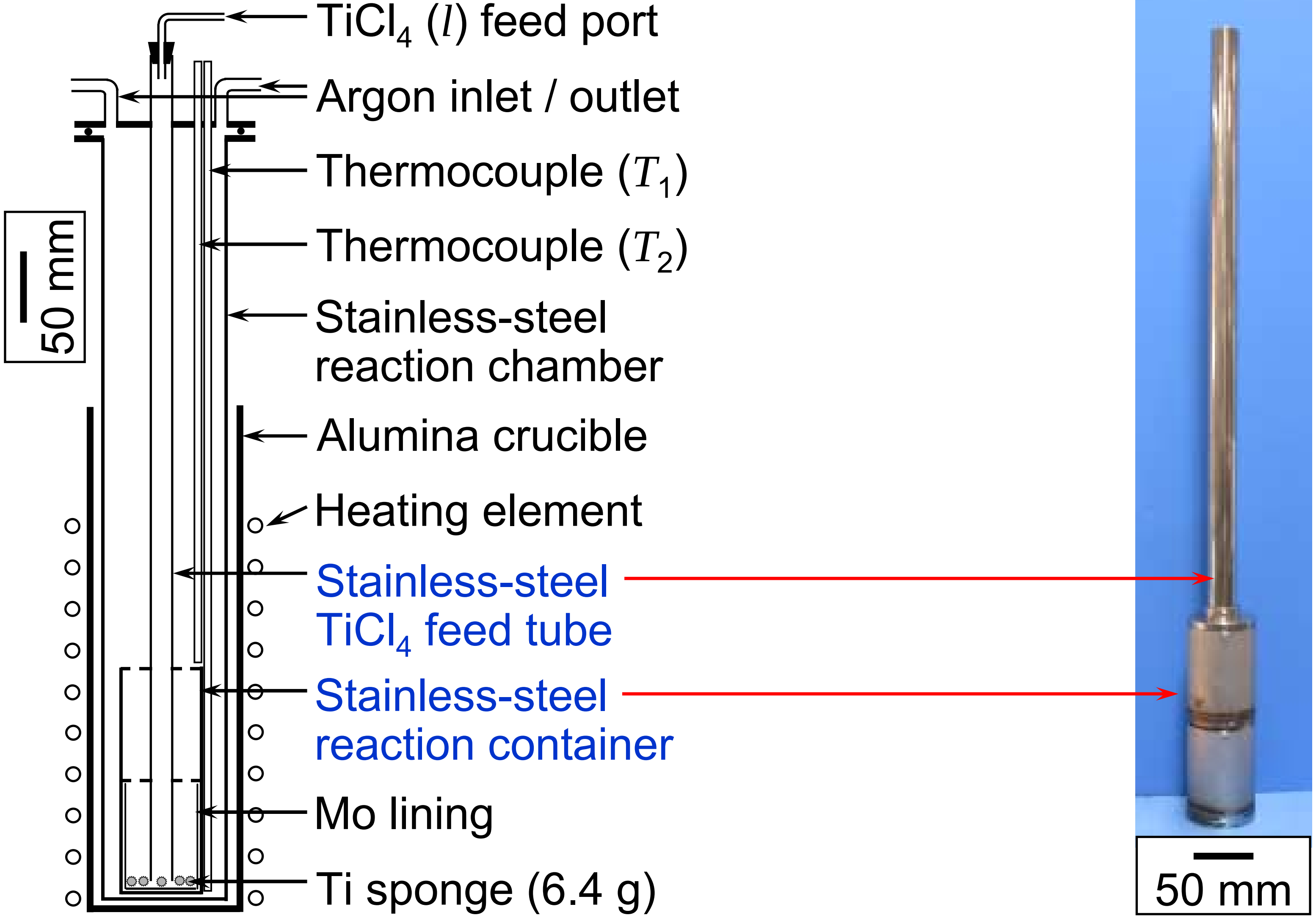
$TiO_2 + C \rightarrow Ti + CO_2$ (d)

Difficulties in using TiO_2:

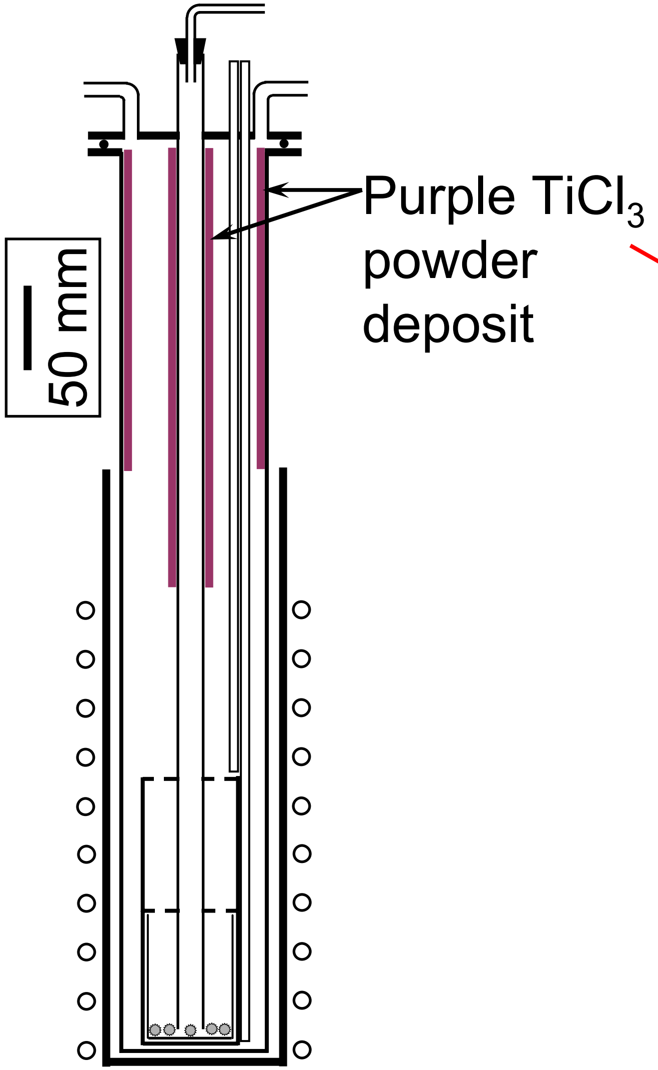
- Production of high-purity TiO_2 feed is expensive.
- Energy efficiency is low.
- Metal/salt separation is difficult.
- Purity control of obtained Ti is difficult.

Experimental Apparatus

(a) Gas flow type reaction container (Type I) (b) Photo

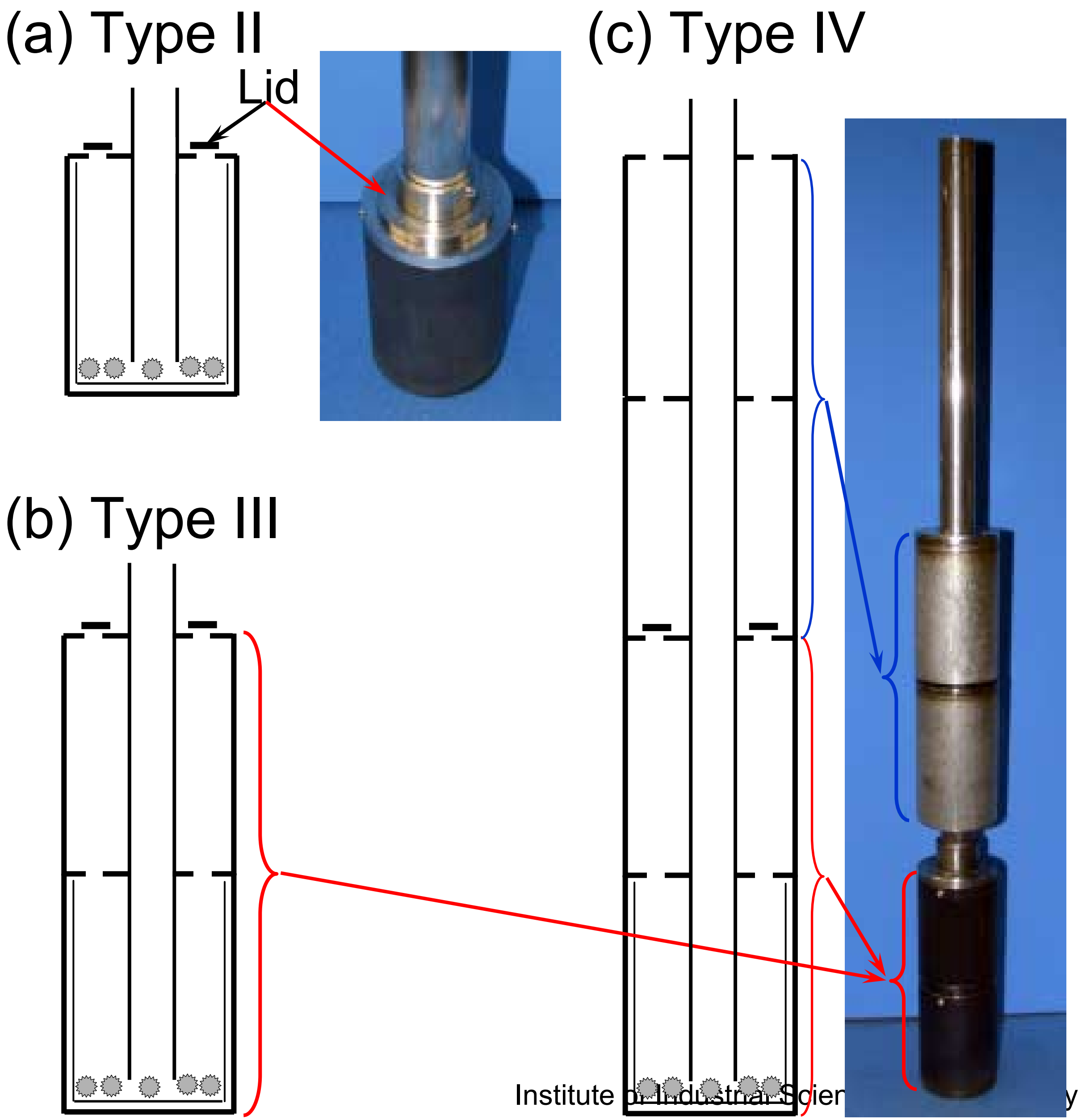


Experimental Apparatus



スポンジTiの表面に極わずか$TiCl_2$が生成していたが，分離・回収はできなかった.

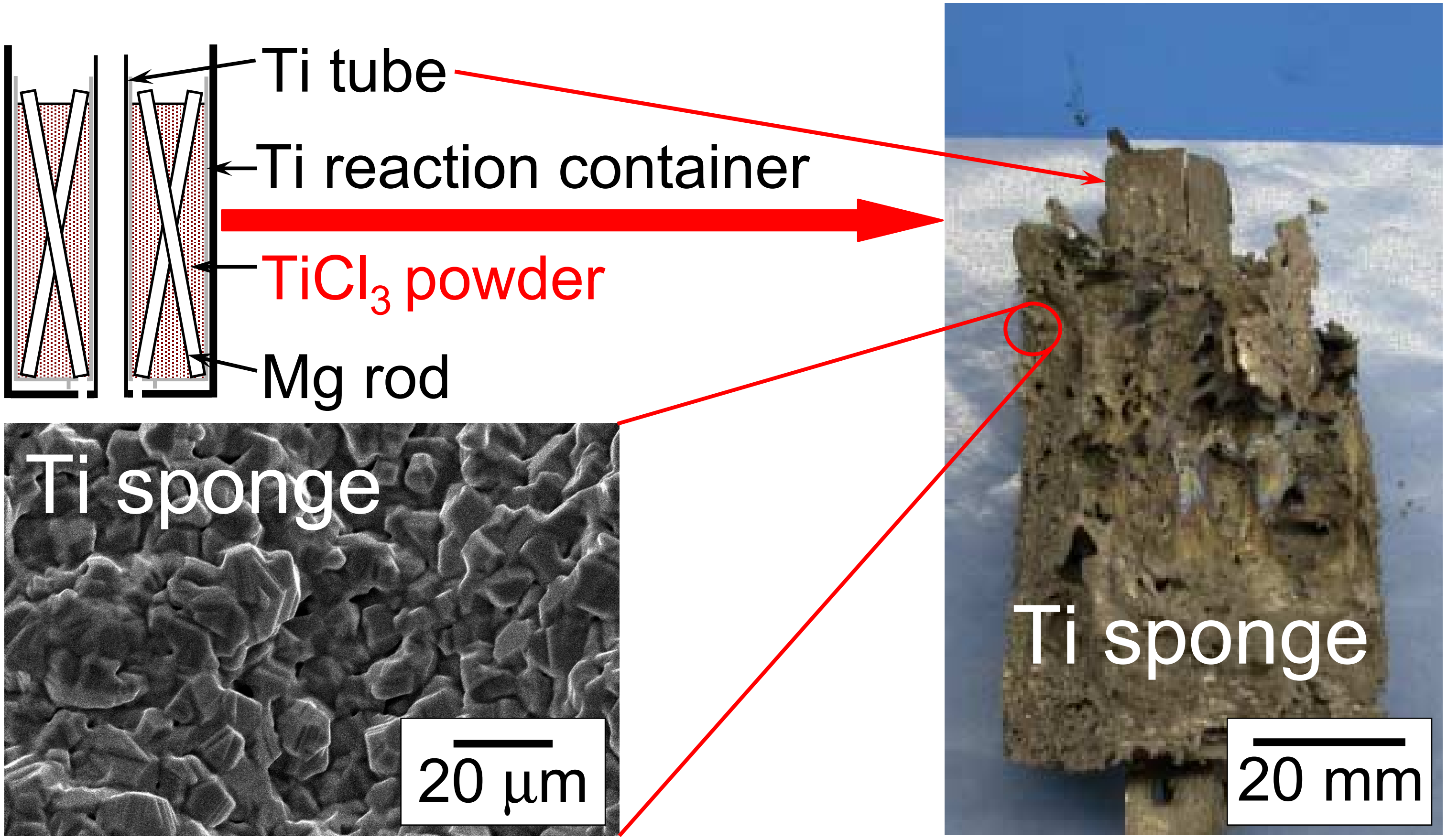
Experimental Apparatus



反応容器内の気流を閉じ込めようとしたが，効果はでなかった.

Achievement in the Previous Study

Before Exp. **After Exp.**

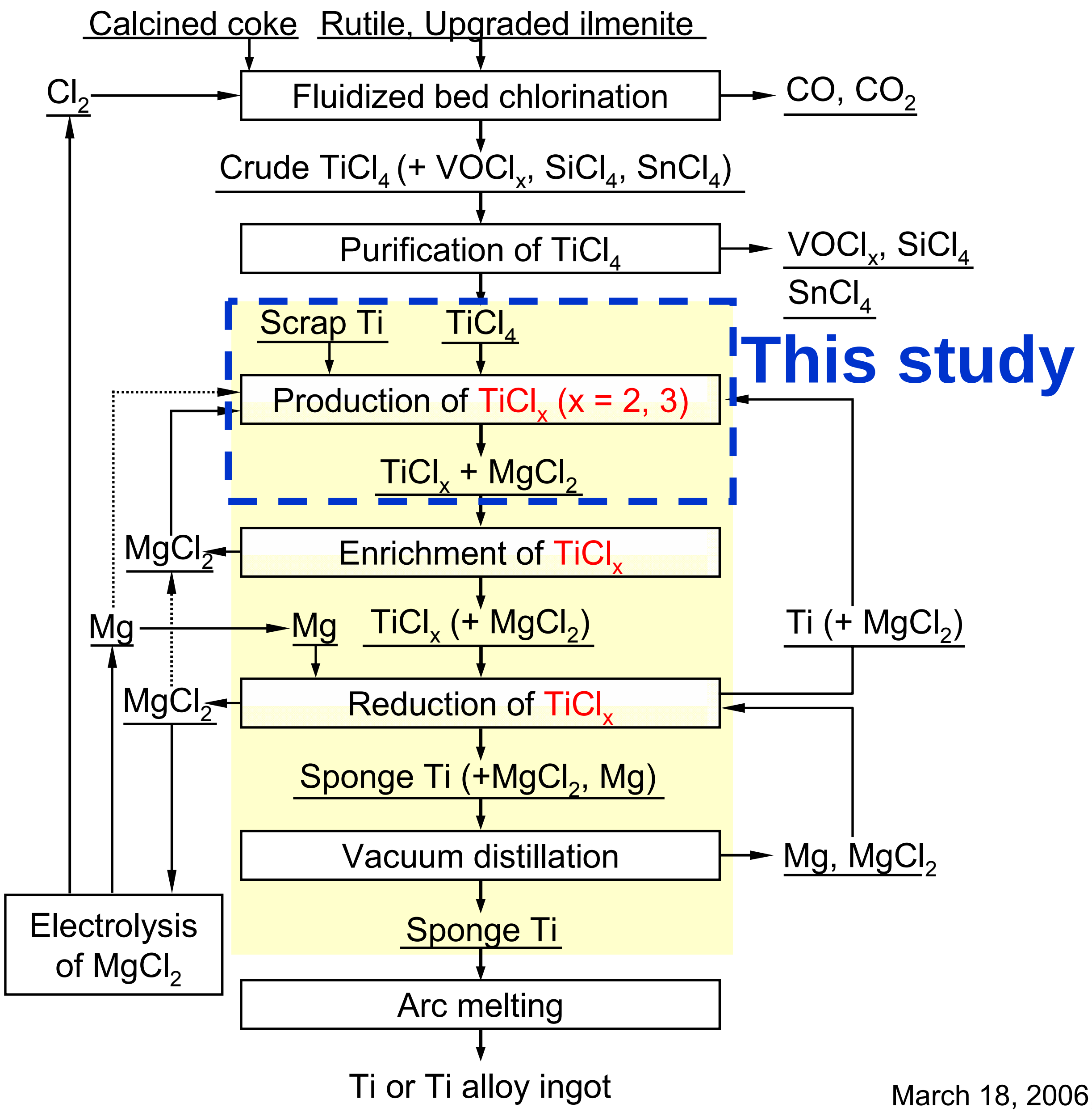


Pure metallic Ti was successfully obtained by the subhalide reduction process.

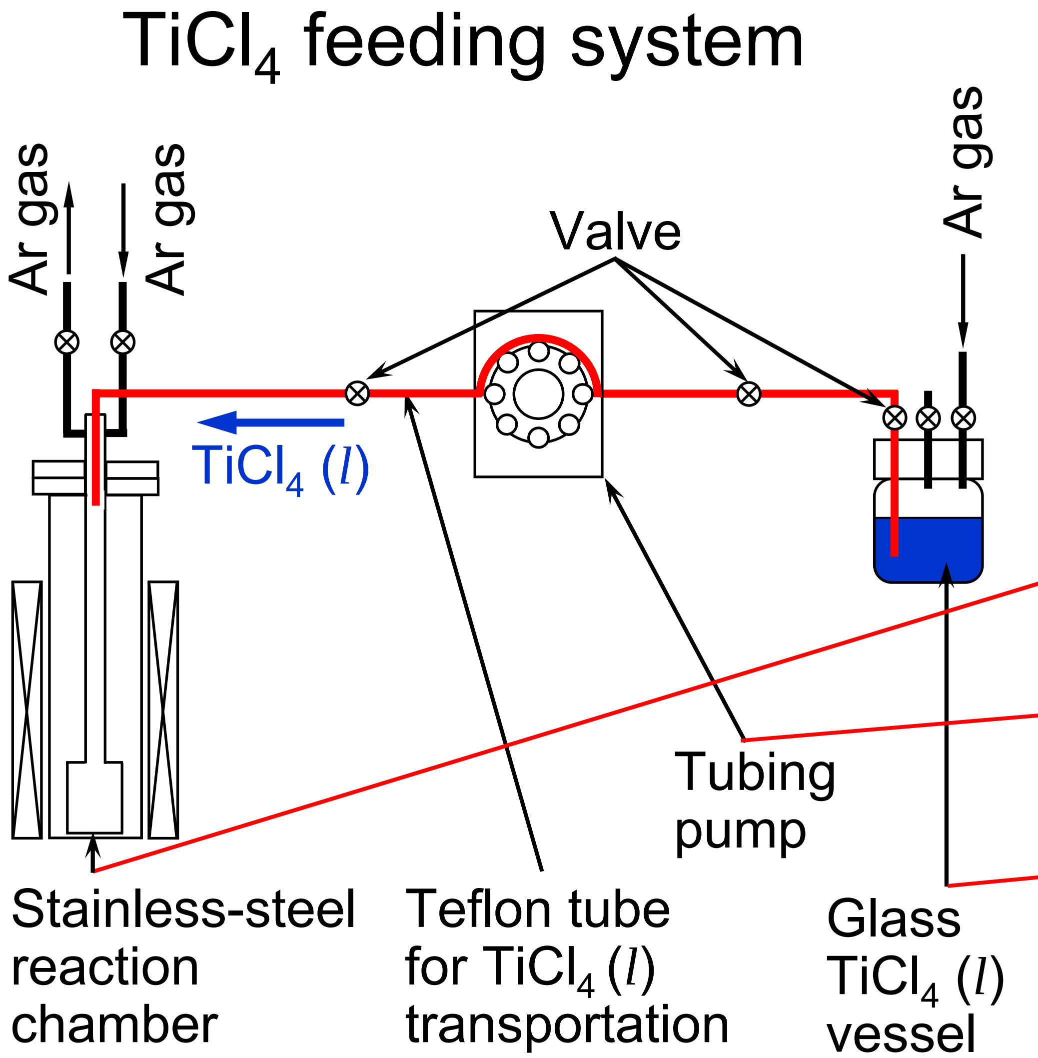
Part I

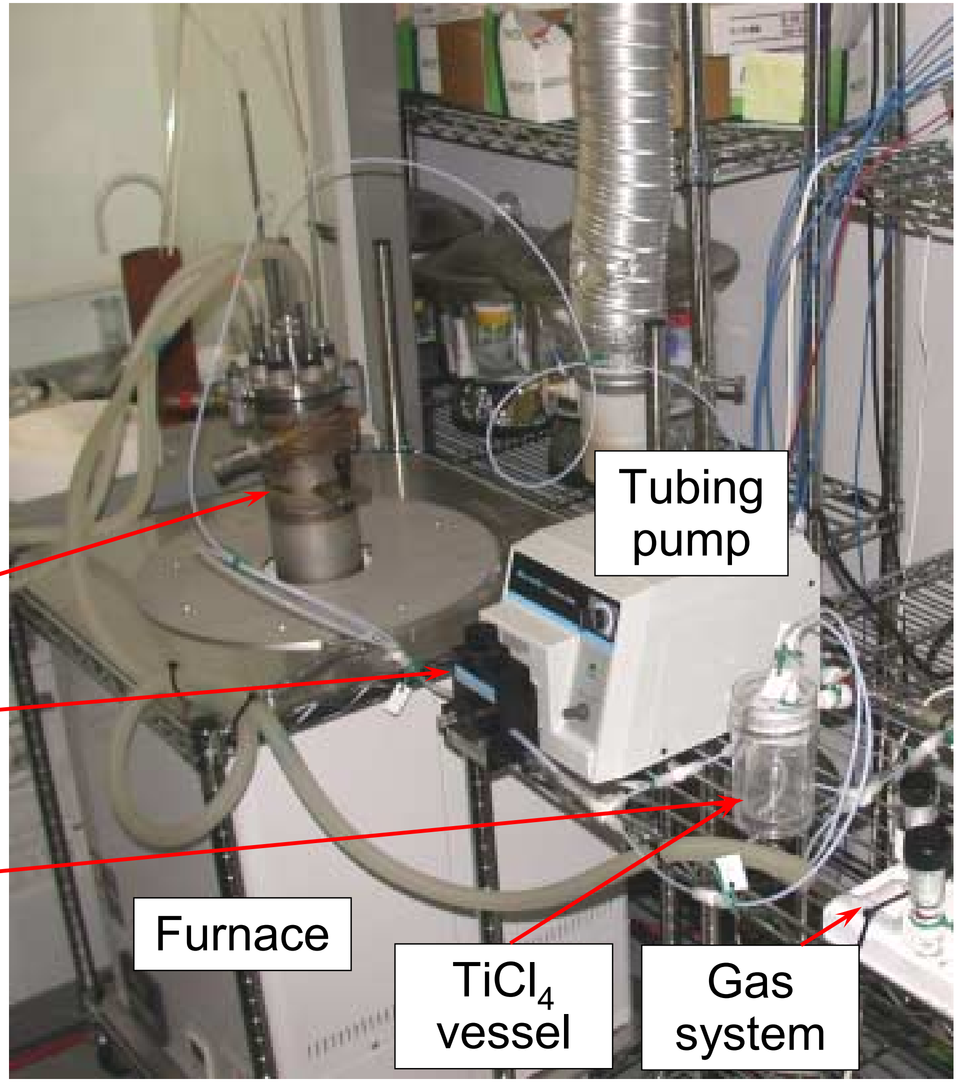
Titanium Subchloride Synthesis by Reaction of $TiCl_4$ with Ti

Production Process of Titanium Subchlorides



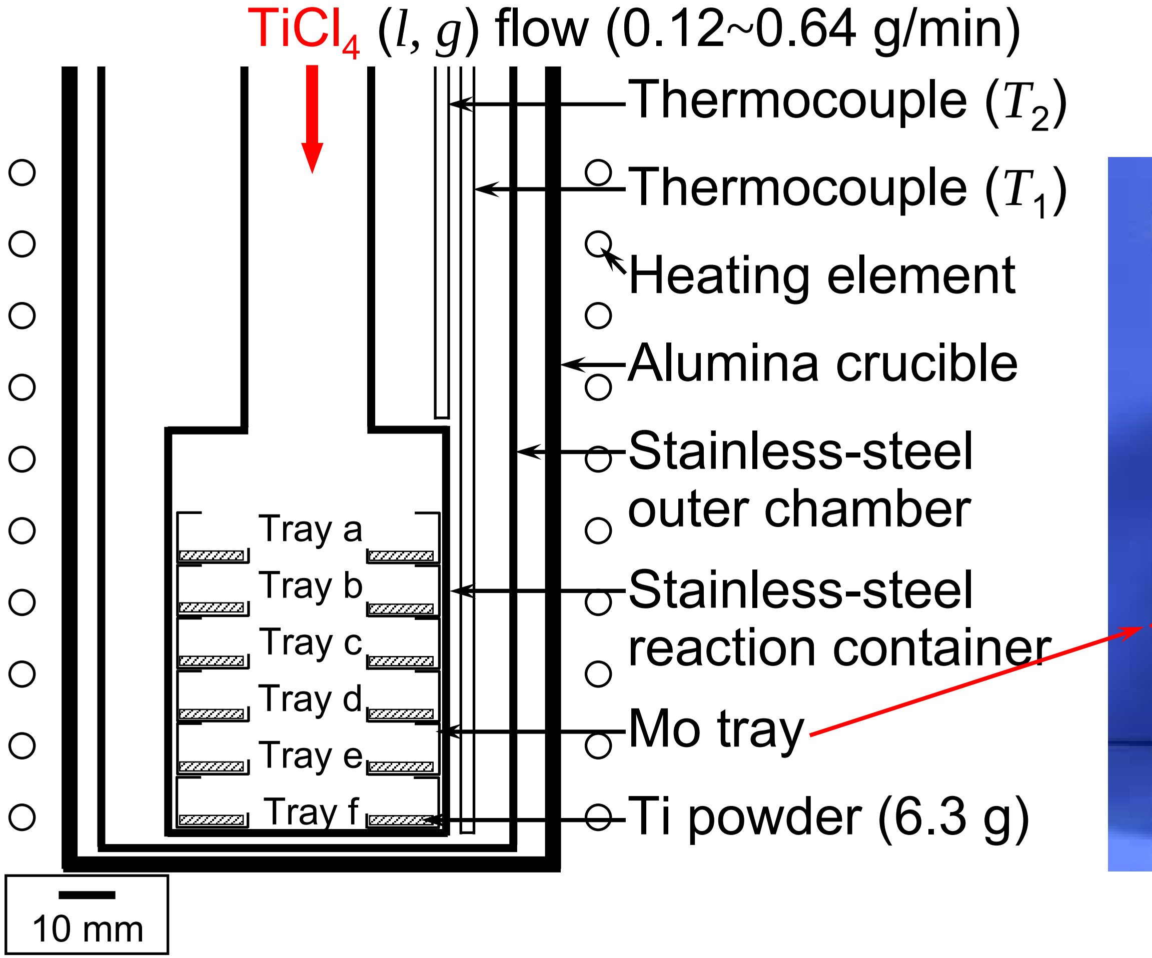
Part I: Experimental Apparatus



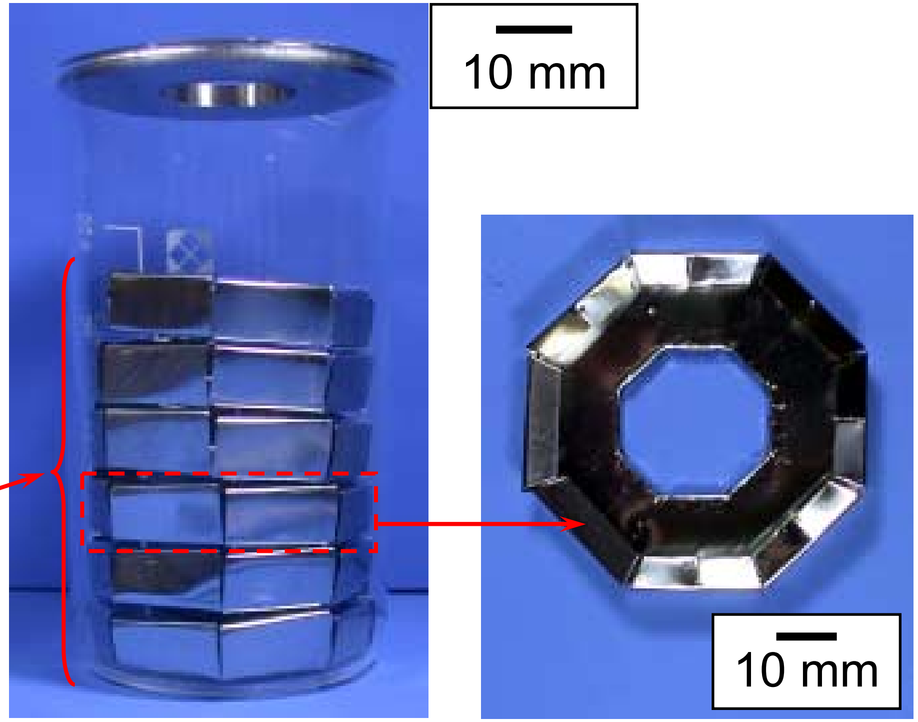


Part I: Experimental Apparatus

(a) Closed-type reaction container



(b) Mo trays used for $TiCl_x$ synthesis tentatively installed in transparent beaker.

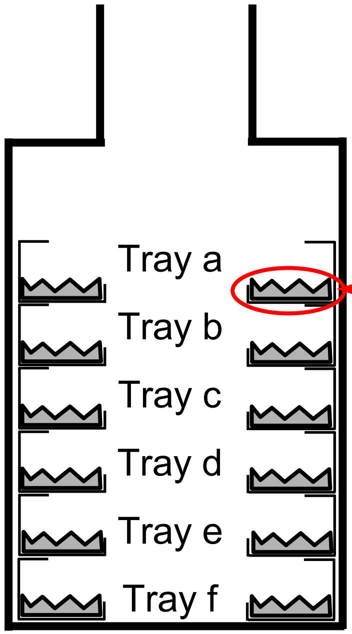


$$Ti\ (s) + TiCl_4\ (g) \rightarrow 2\ TiCl_2\ (s);\ \Delta G_f^\circ = -18.9\ \text{kJ/mol @ 1273 K}$$

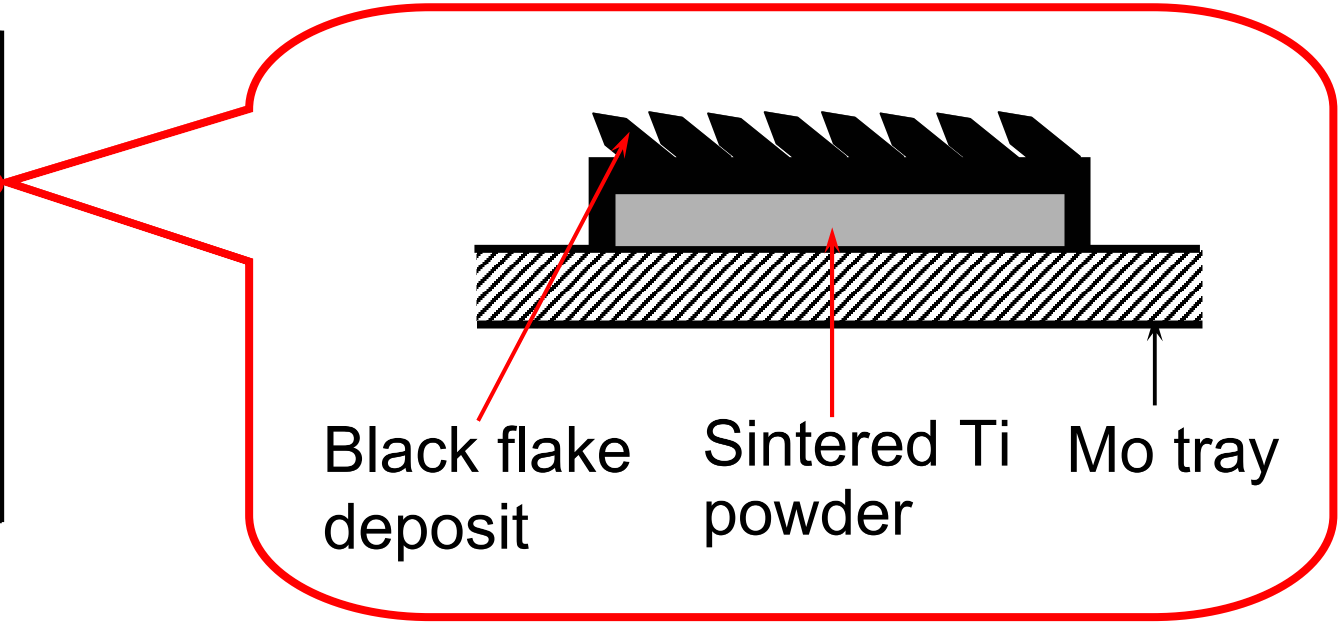
Part I: Experimental Results

Appearance of the products after the synthesis experiment

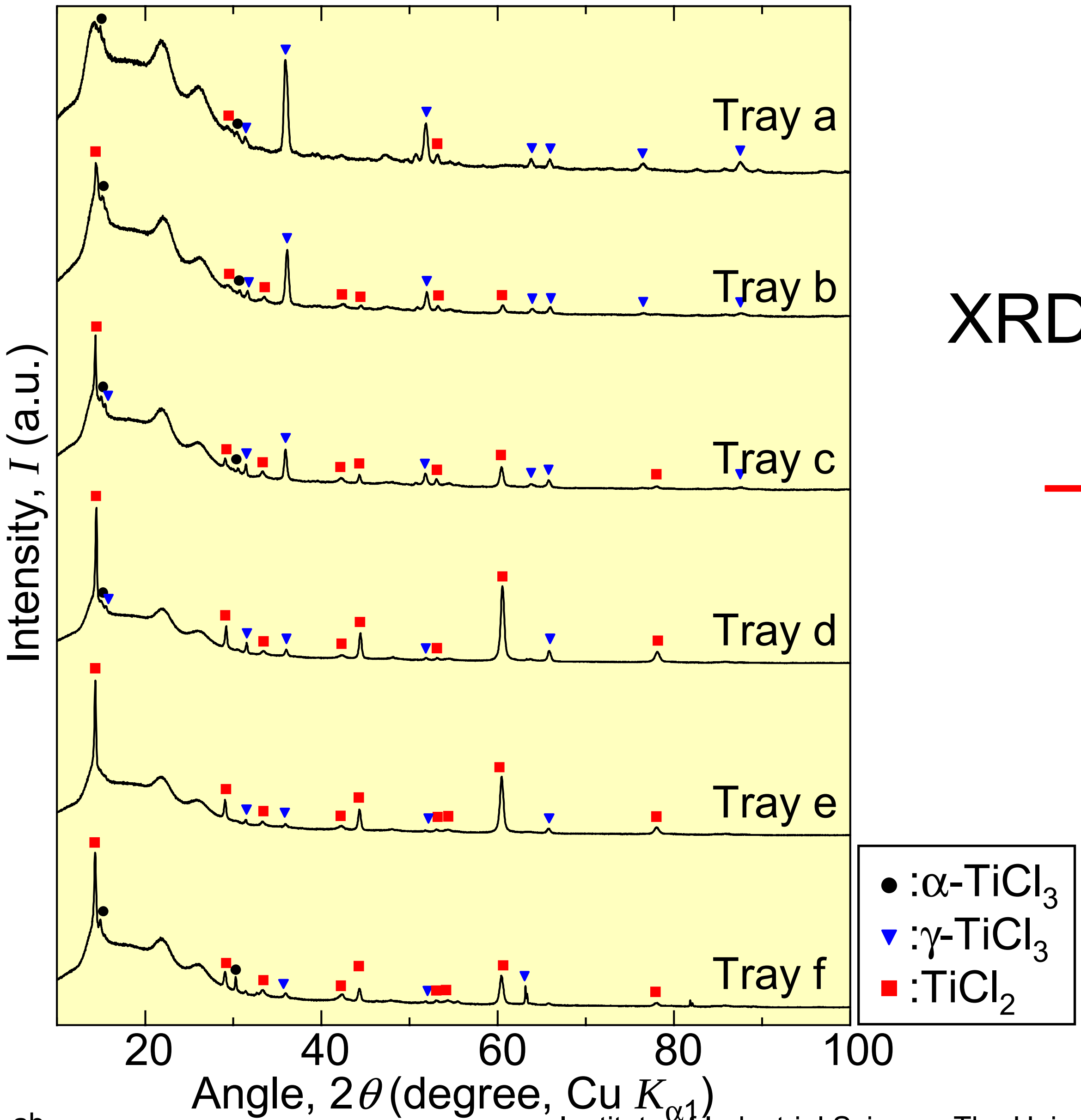
(a) Closed-type reaction container



(b) Form of black flake deposit



Part I: Experimental Results



XRD pattern of the products

→ $TiCl_2$ (+ γ-$TiCl_3$)

Part I: Experimental Results

Table Analytical results of the obtained samples (Exp. 2D[c]).

Tray No.	Concentration of element i, C_i (mass%)						x value in $TiCl_x$
	Ti [a]	Cl [b]	Fe [a]	Ni [a]	Cr [a]	Mo [a]	
a	36.38	62.53	0.27	0.64	0.12	0.06	2.32
b	36.13	62.90	0.17	0.69	0.06	0.05	2.35
c	37.21	61.79	0.20	0.67	0.07	0.05	2.24
d	37.20	62.54	0.10	0.07	0.06	0.02	2.27
e	39.27	60.45	0.10	0.05	0.09	0.03	2.08
f	38.82	60.72	0.22	<0.01	0.18	0.05	2.11

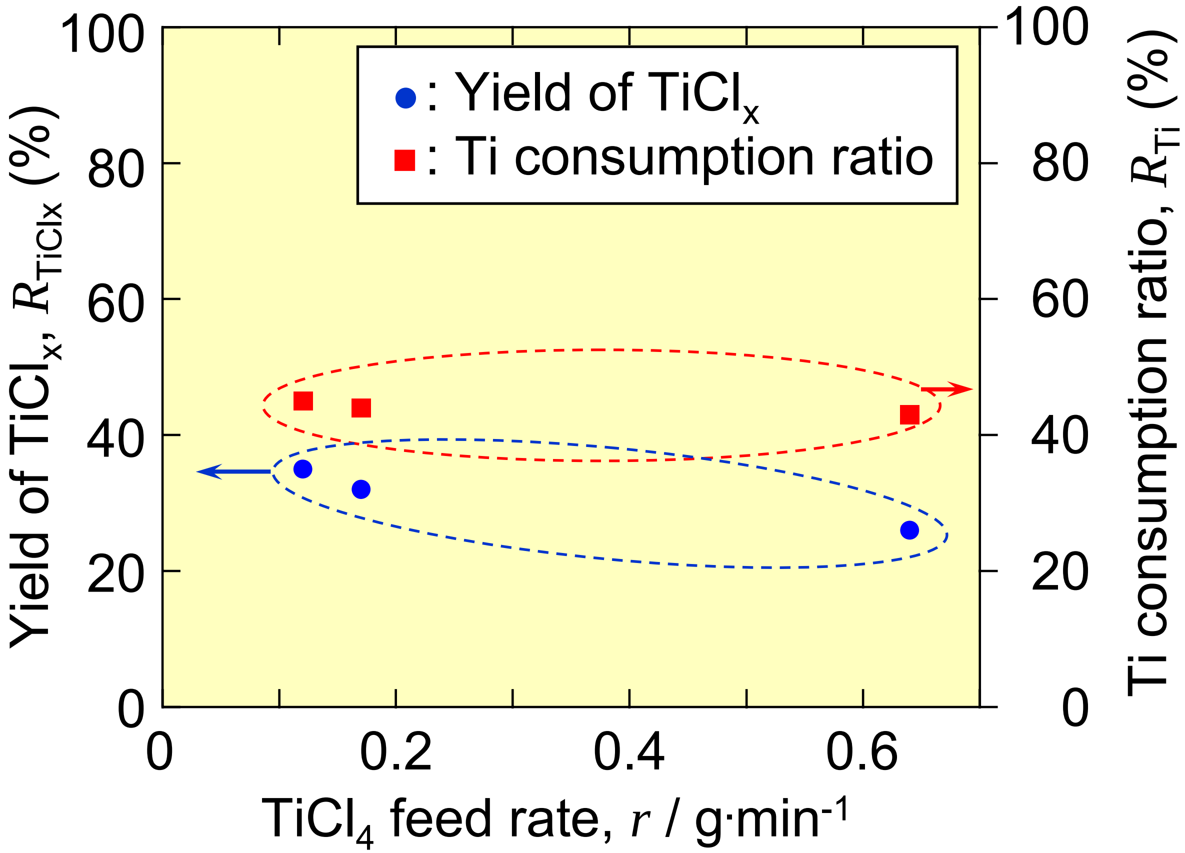
a: Determined by ICP-AES.
b: Determined by potentiometric titration method.
c: $TiCl_4$ feed rate, r = 0.12 g/min

Exp. No.	Concentration of element i, C_i (mass%) [a]						x value in $TiCl_x$
	Ti [b]	Cl [c]	Fe [b]	Ni [b]	Cr [b]	Mo [b]	
2A	39.13	60.05	0.19	0.49	0.20	0.03	2.07
2B	36.01	63.34	0.16	0.31	0.16	0.04	2.38
2C[d]	38.46	60.45	0.68	0.24	0.17	<0.01	2.13
2D	37.50	61.82	0.18	0.42	0.10	0.04	2.23

a: Average of 6 samples obtained from each tray.
b: Determined by ICP-AES.
c: Determined by potentiometric titration method.
d: Stainless-steel tray was used.

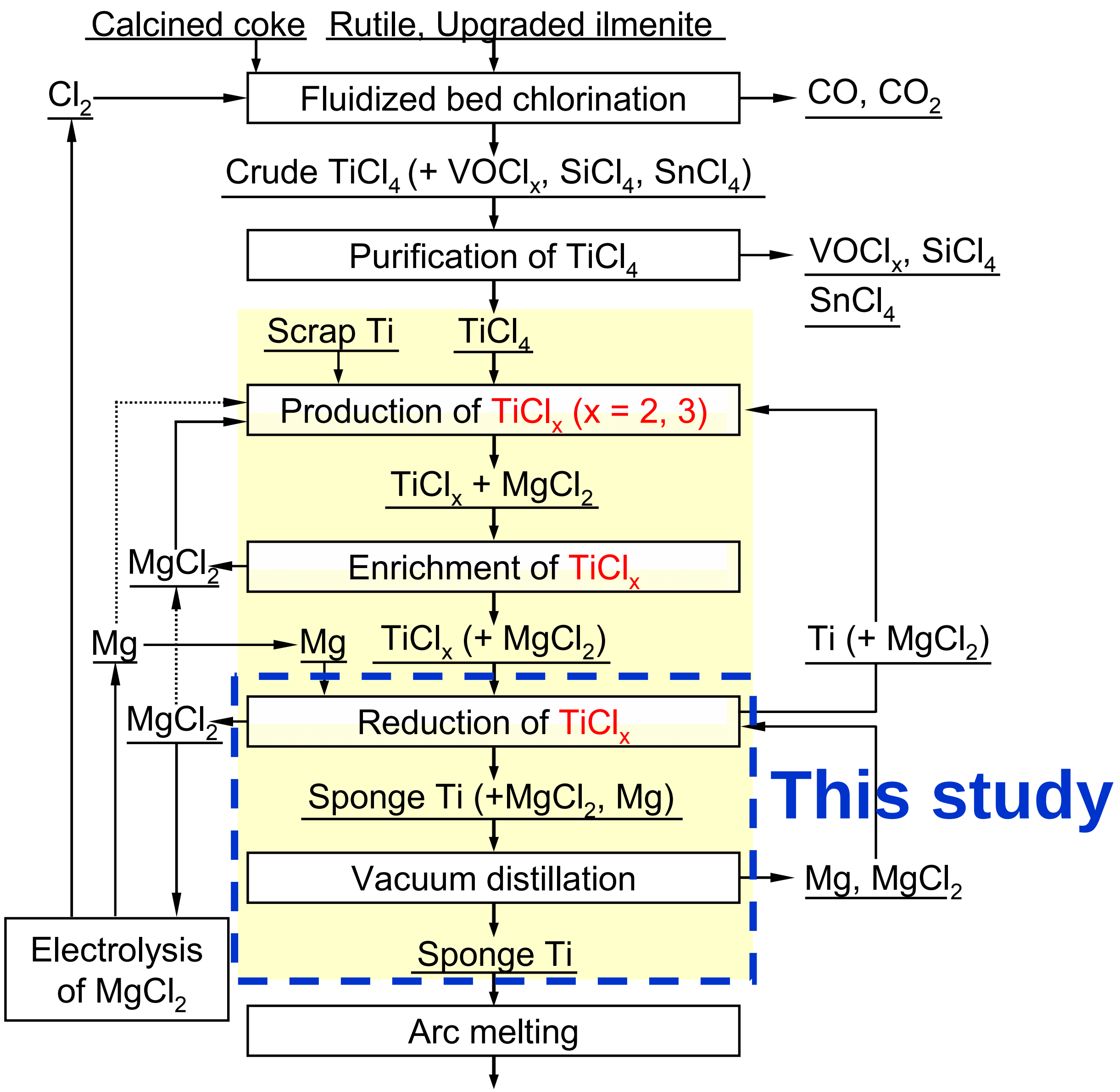
aa, z, y, ab

Efficiency of $TiCl_x$ formation

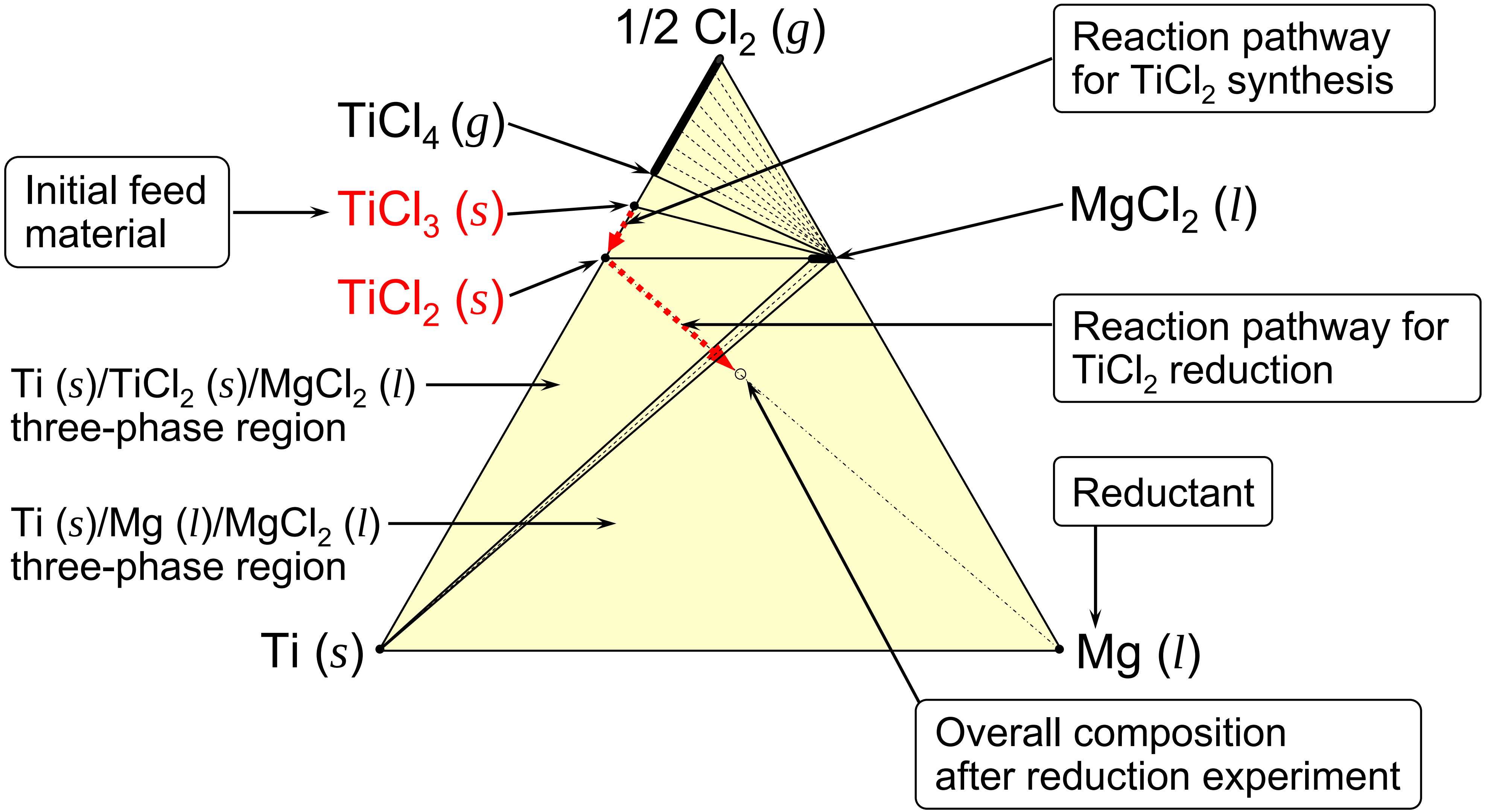


- Yield of the recovered $TiCl_x$ sample was 23~35%, and it decreased with increasing $TiCl_4$ feed rate.
- Consumption ratio of the feed Ti was 42~45%, and the ratio was independent of $TiCl_4$ feed rate.

Chapter V　Production Process of Titanium Subchlorides

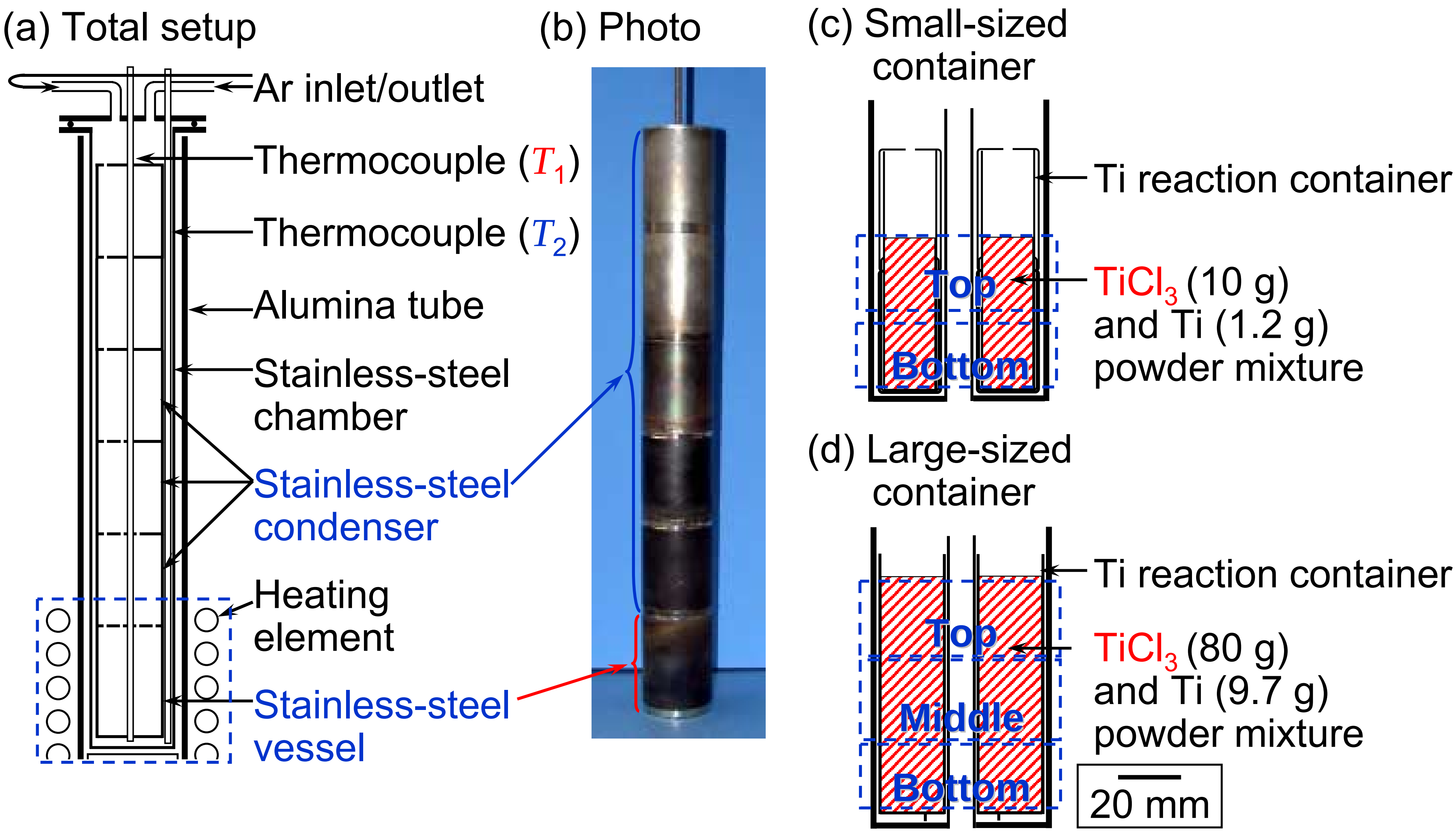


Chapter V Phase Diagram for the Ti–Mg–Cl system at 1073 K

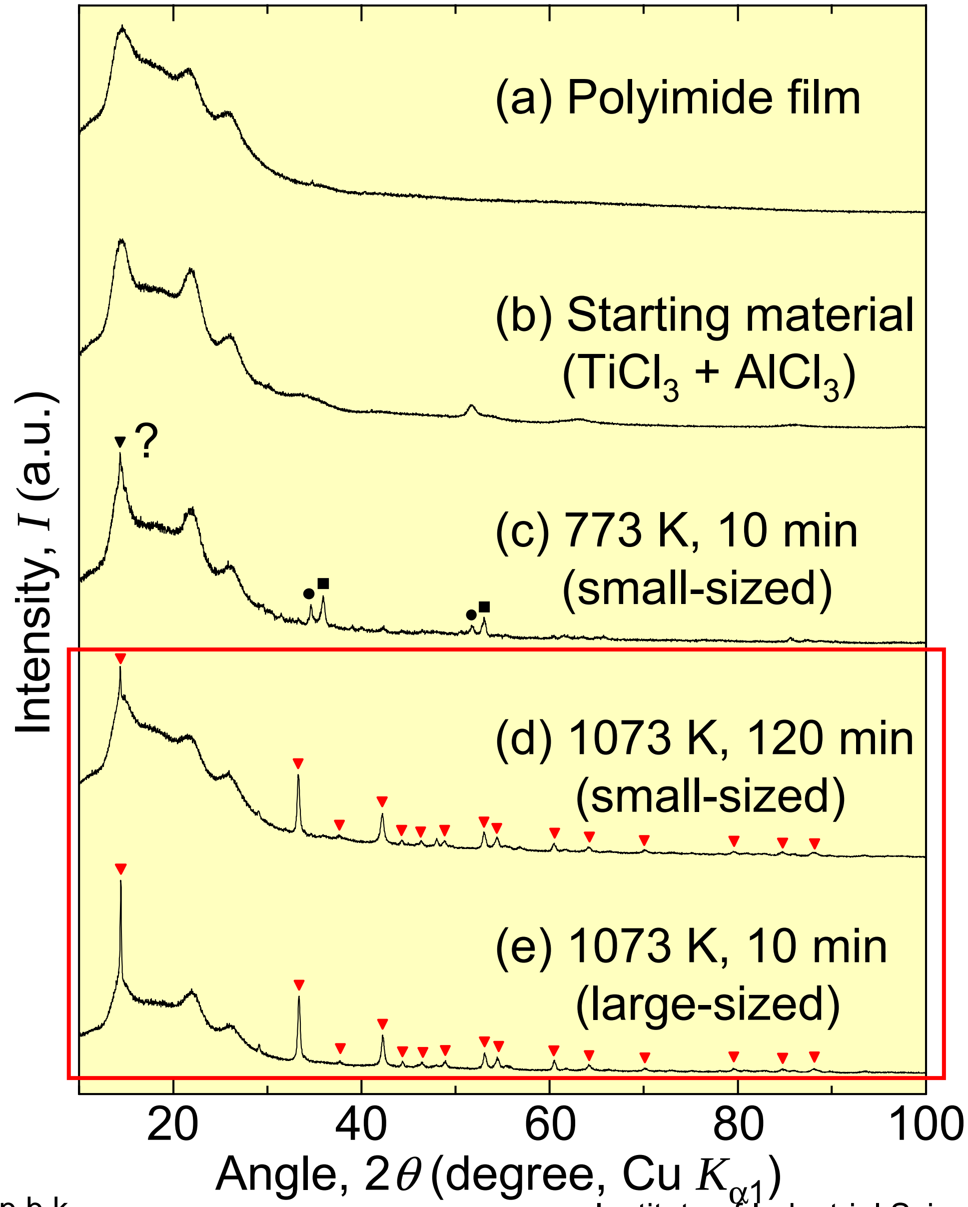


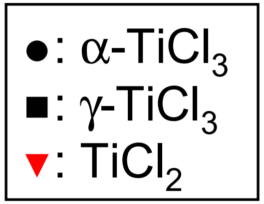
[Ref. Okabe *et al*.: J. Japan Inst. Metals 61 (1997) pp. 610-618.]

Chapter V Experimental Apparatus



Experimental Results





XRD pattern of the products

$TiCl_2$ was obtained.

PDF #29-1357, γ-$TiCl_3$: PDF #29-1359, $TiCl_2$: PDF #10-0315 and 73-0751.

Table Analytical results of the obtained $TiCl_2$ samples.

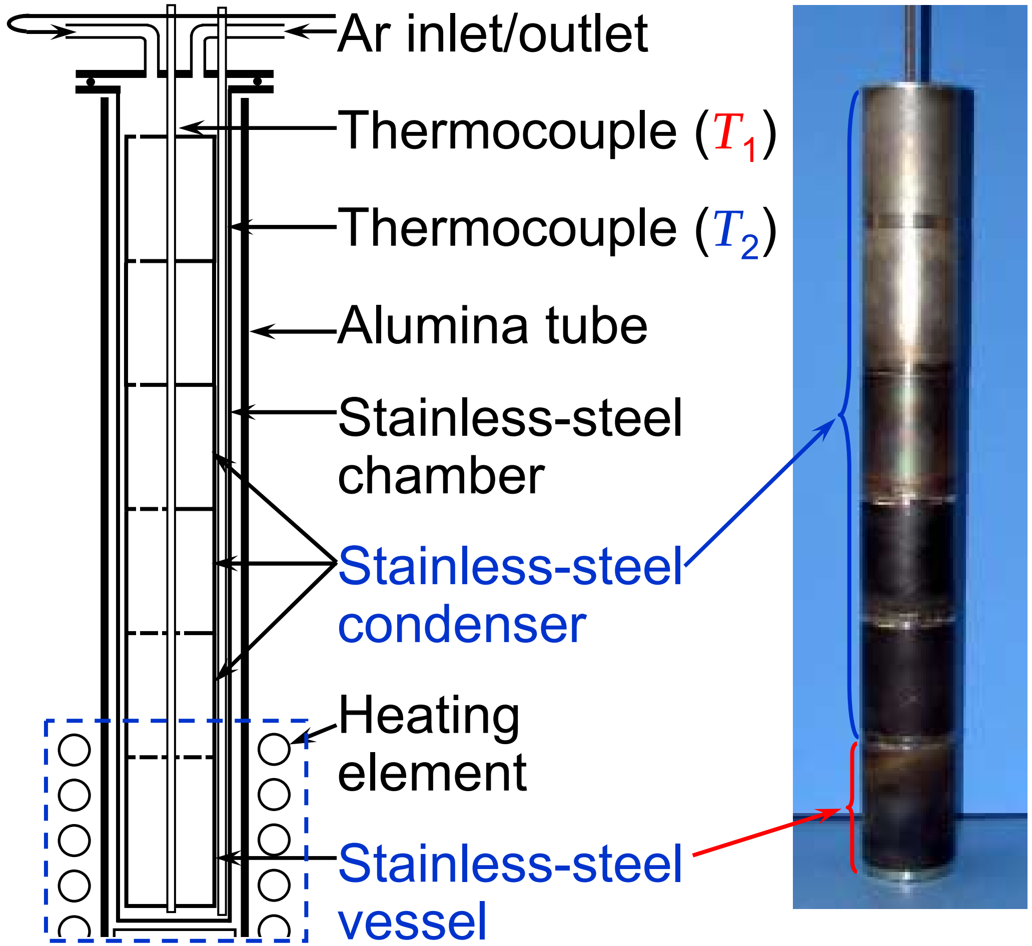
Sample	Concentration of element *i*, C_i (mass%)				Yield (%)	Calculated value of x in $TiCl_x$
	Ti [c]	Fe [c]	Al [c]	Cl [d]		
Feed [a]	24.31 [b]	0.03	4.50 [b]	71.12 [b]	–	2.95
$4A_{top}$	42.81	0.13	0.05	57.01	51	1.80
$4A_{bot}$	43.18	0.05	0.63	56.14		1.76
$4B_{top}$	37.10	0.06	0.19	62.61	94	2.28
$4B_{mid}$	39.54	0.05	0.10	60.29		2.06
$4B_{bot}$	40.25	0.07	0.10	59.56		2.00

a: Supplied by Toho Titanium Co., Ltd.
b: Nominal value.
c: Determined by ICP-AES.
d: Determined by potentiometric titration method.

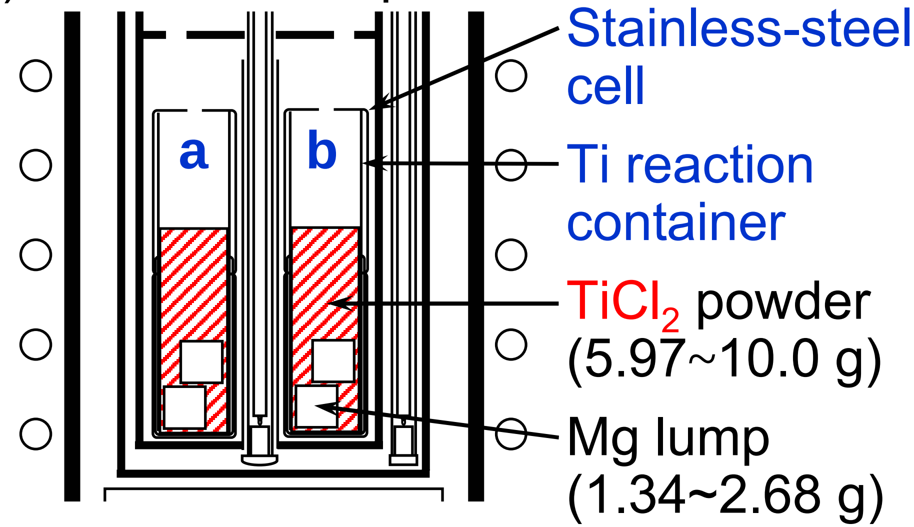
b,k

Experimental Apparatus

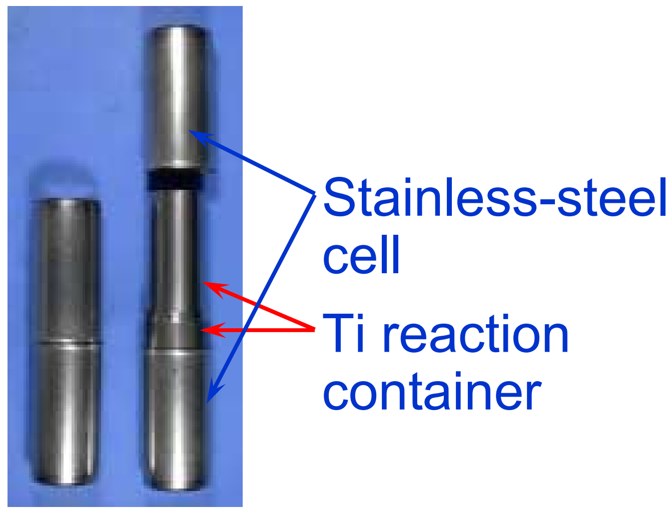
(a) Total setup (b) Photo



(c) Container setup

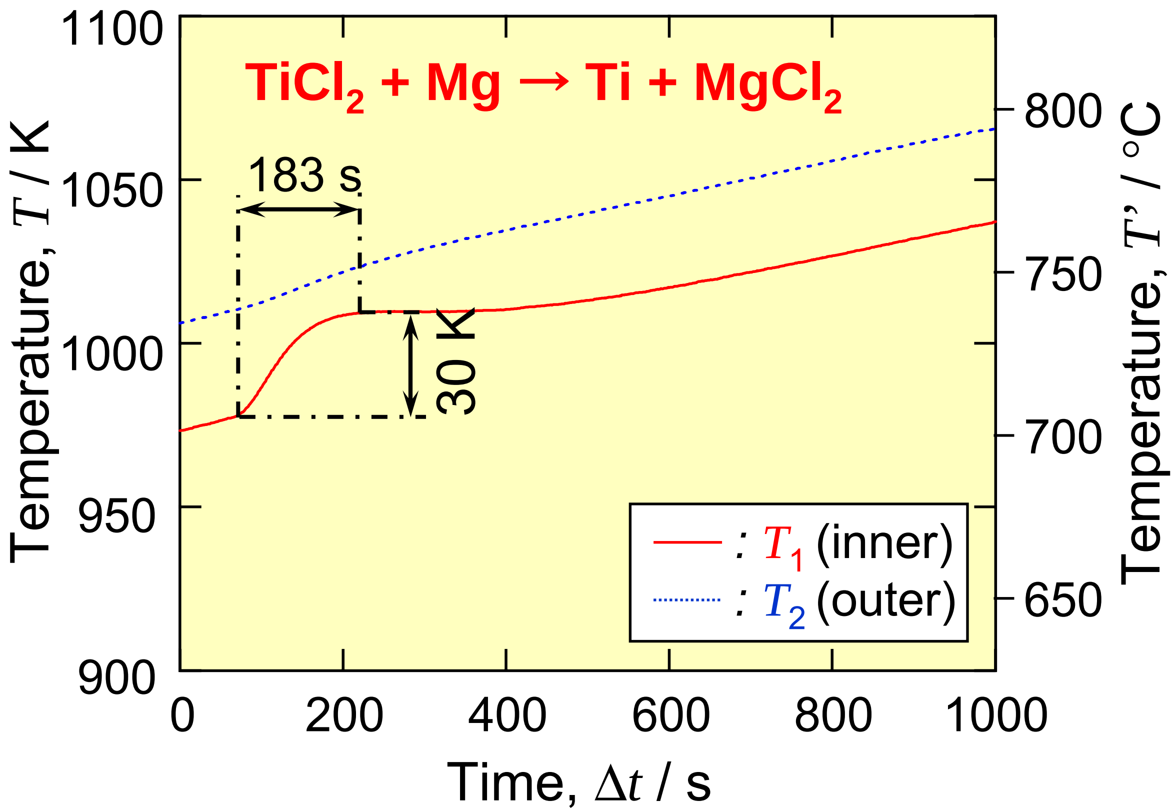


(d) Photo



➡ Leaching or vacuum distillation

$TiCl_2$の還元反応の温度履歴



クロール法によるチタンの生成速度

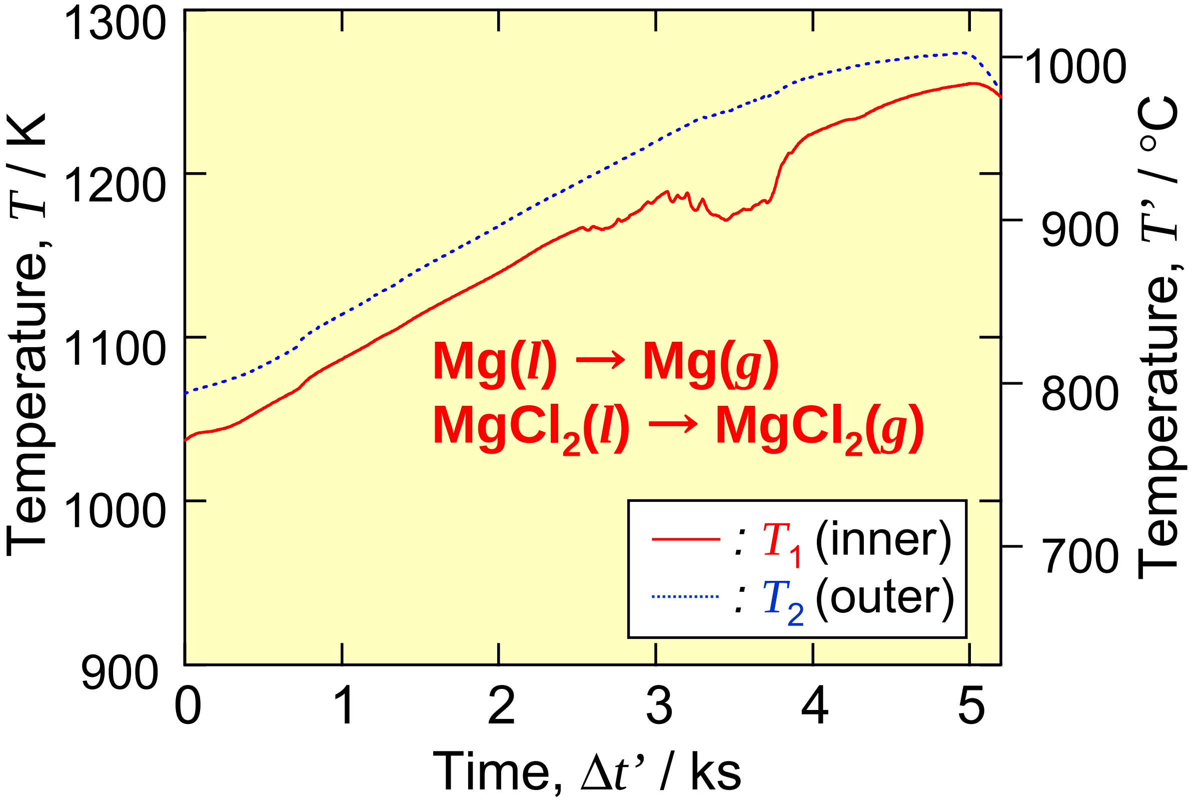
下崎ら: 0.006 kg/m^2·s @ 1000 K
[0.06 kg/m^3·s @ 1000 K (推定)]

野田ら: 0.009 kg/m^2·s @ 1100 K?
[0.009 kg/m^3·s @ 1100 K? (推定)]

本実験条件におけるチタンの生成速度

0.76 kg/m^3·s @ 1000 K
[0.061 kg/m^2·s @ 1000 K]

副生成物の真空蒸留の温度履歴



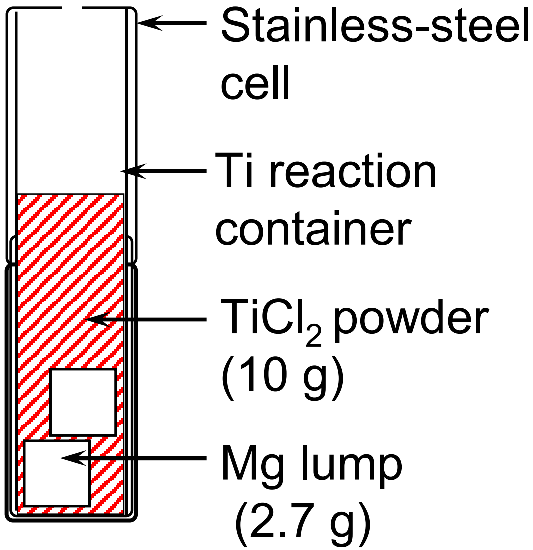
途中の温度ドロップは副生成物の$MgCl_2$および余剰の金属マグネシウムの蒸発により熱が奪われたものと考えられる.

($p^\circ_{MgCl_2}$ = 520 Pa (5.1×10^{-3} atm), $\Delta H^\circ_{evap,\ MgCl_2}$ = 188 kJ/mol @ 1150 K)

生成物の外観

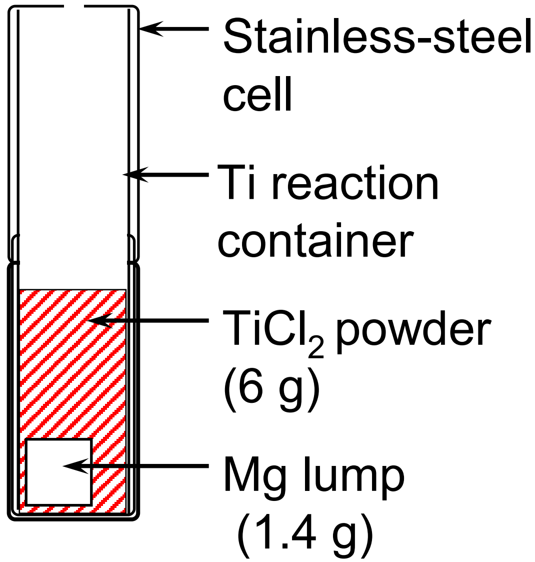
(a) Leaching

(b) Initial setup for (a)



(c) Vacuum distillation

(d) Initial setup for (c)



Ti reaction container was not damaged.

生成物の析出相と組成

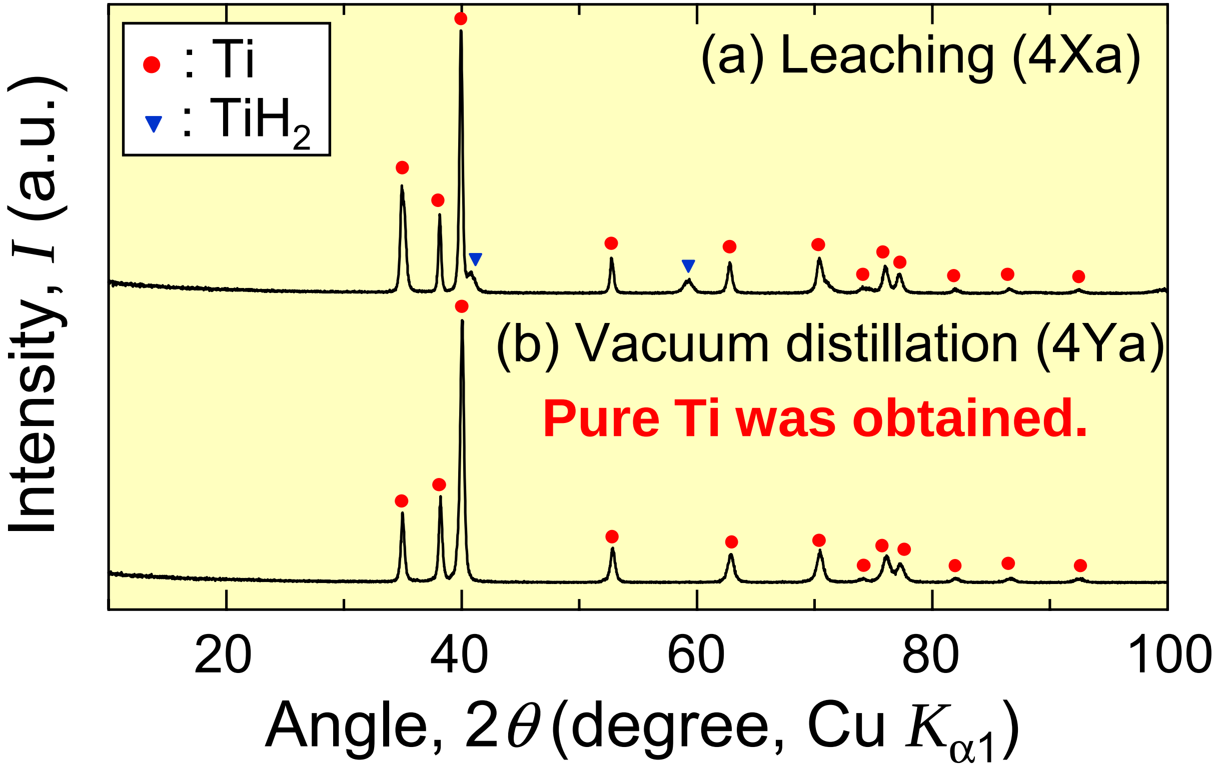

: Ti
: TiH_2
(a) Leaching (4Xa)
(b) Vacuum distillation (4Ya)
Pure Ti was obtained.
Intensity, I (a.u.)
20
40
60
80
100
Angle, 2θ (degree, Cu $K_{\alpha 1}$)

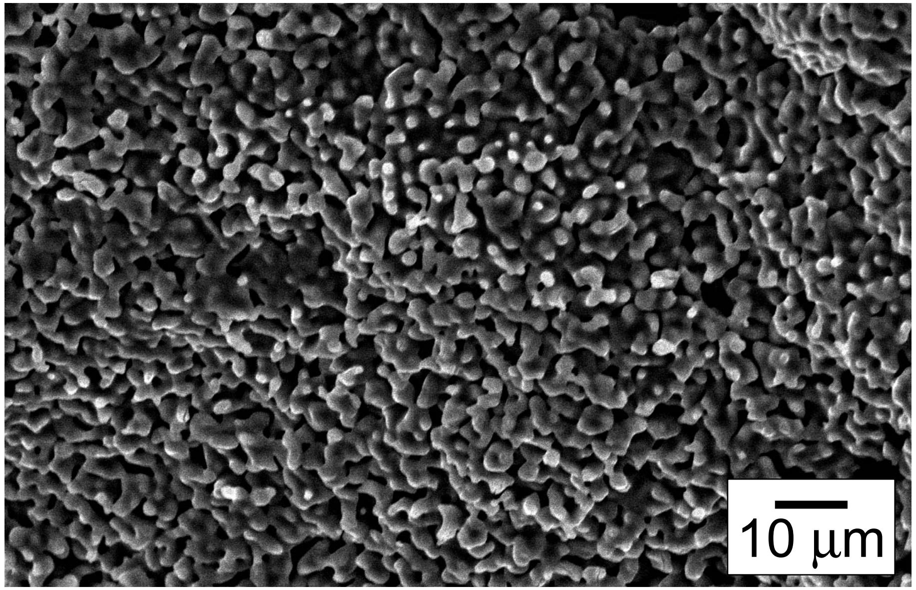
Table Analytical results of the Ti sample recovered by leaching (4X) and vacuum distillation (4Y).

Code	Concentration of element i, C_i (mass%) [a]						Yield
	Ti	Fe	Ni	Cr	Mg	Al	(%)
4Xa	99.71	0.16	0.04	<0.01	0.06	0.03	99
4Xb	99.19	0.10	<0.01	0.05	0.50	0.16	>89[b]
4Ya	99.75	0.22	<0.01	0.03	<0.01	<0.01	98
4Yb	99.72	0.16	<0.01	<0.01	<0.11	0.10	99

a: Determined by XRF; the value excludes carbon and gaseous elements.
b: This value includes the uncertainty due to mechanical separation.

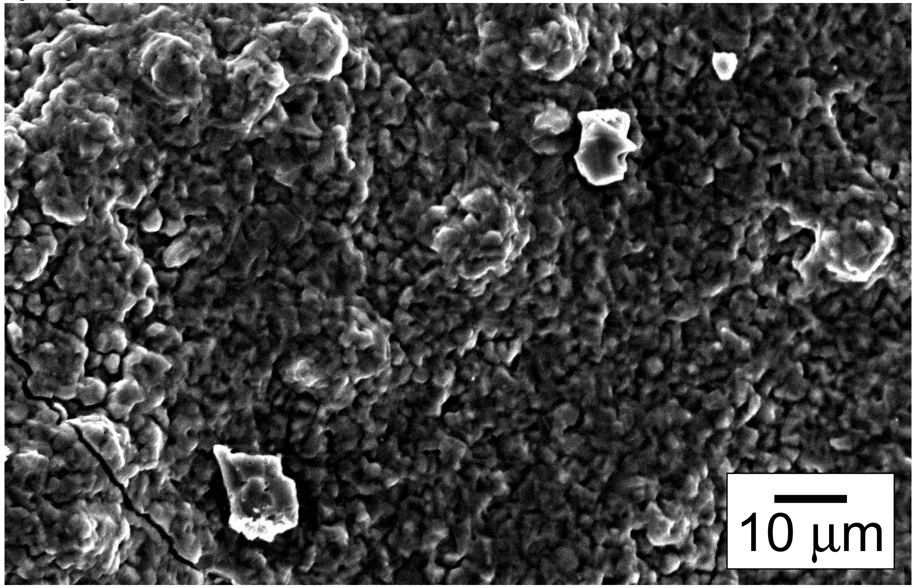
生成物の微細構造

(a) Leaching



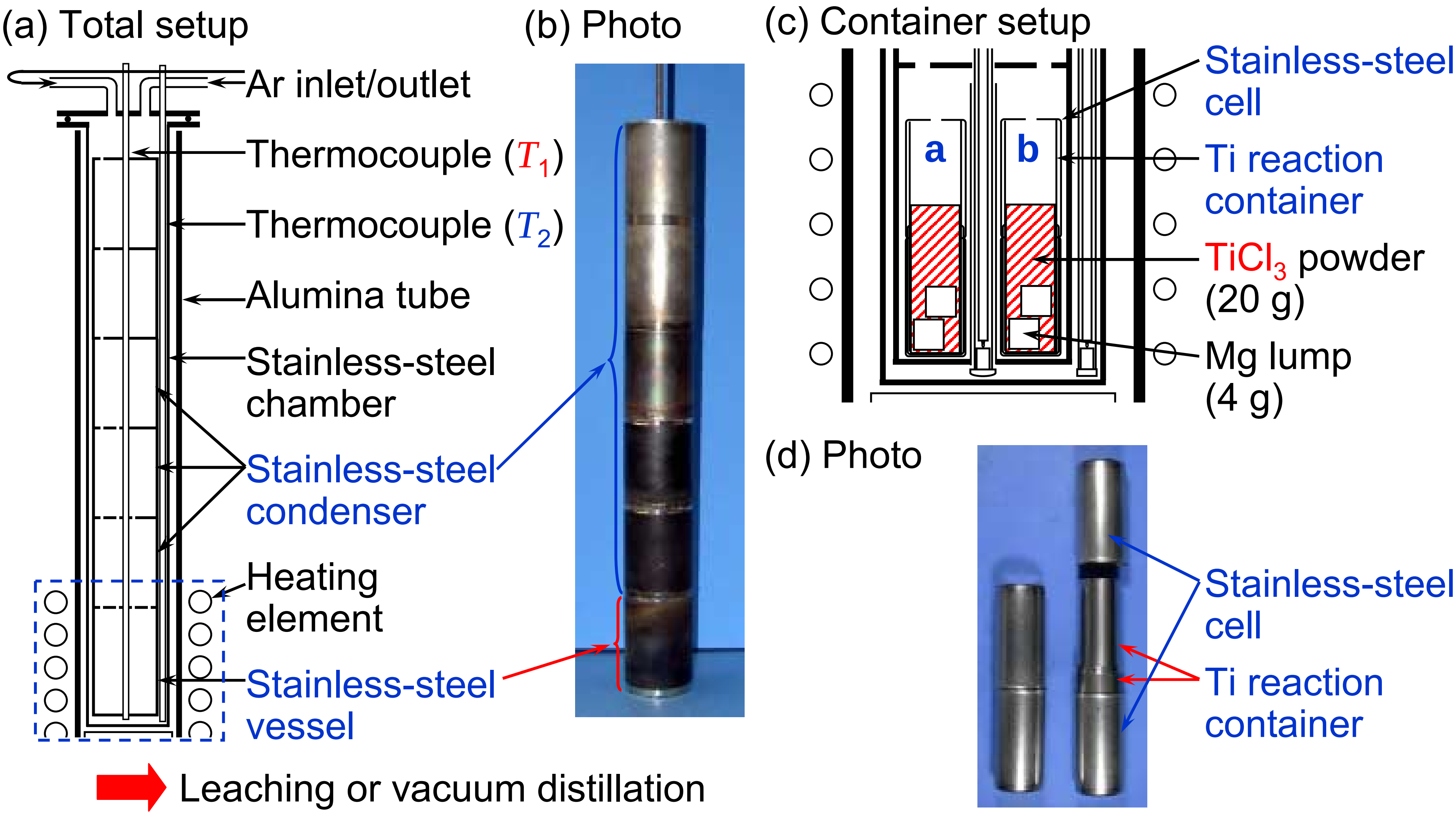
Coral like structure

(b) Vacuum distillation



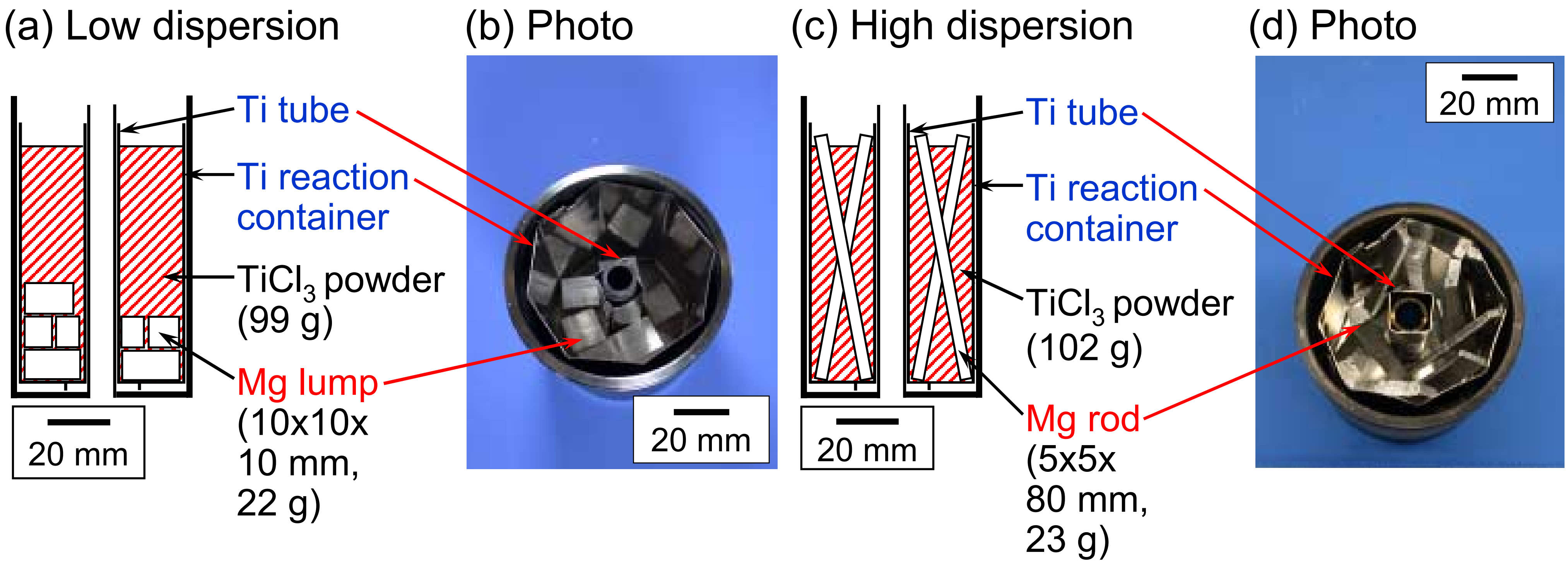
Primary particles were sintered.

Chapter VI Experimental Apparatus



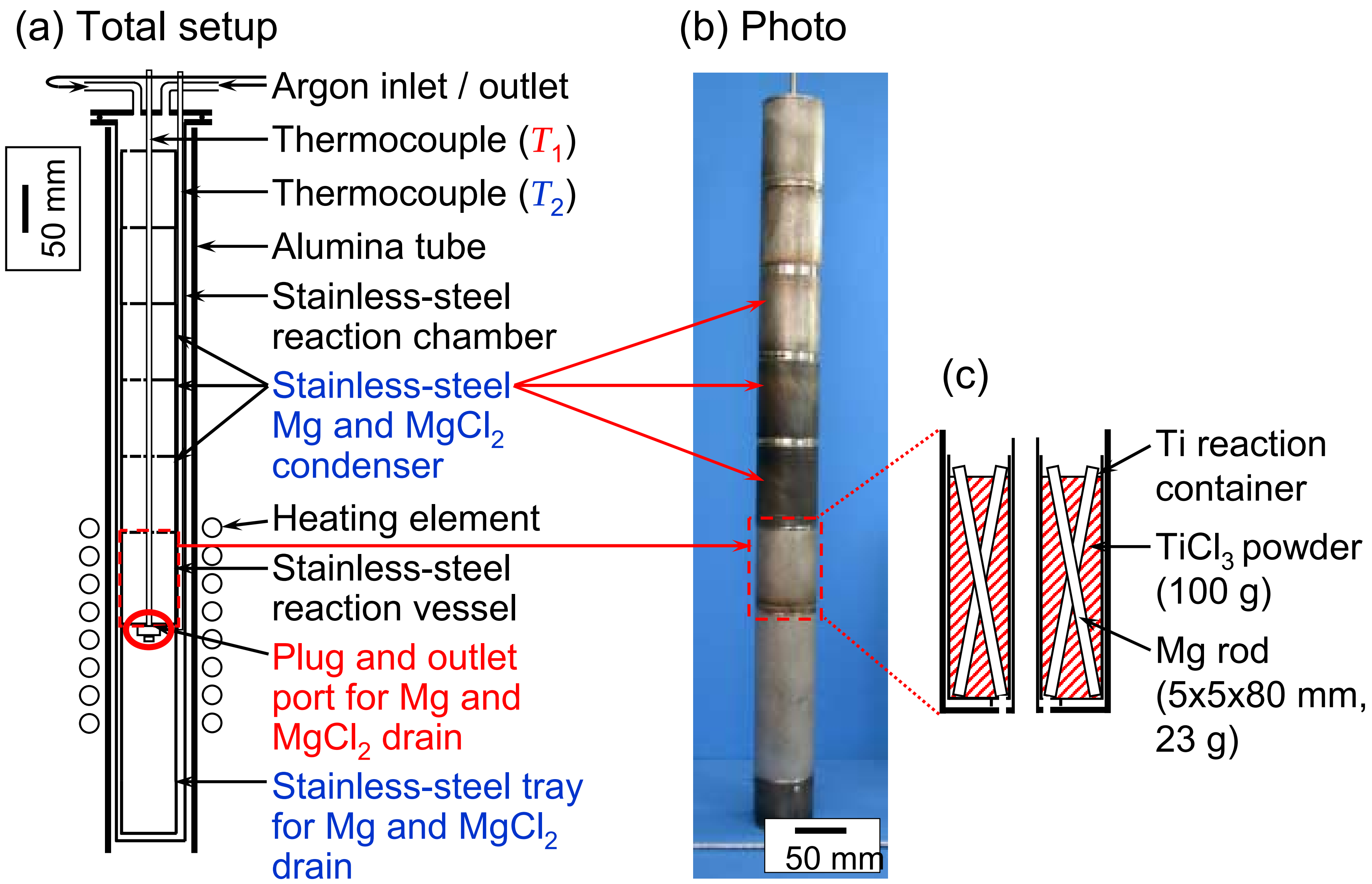
➡ Leaching or vacuum distillation

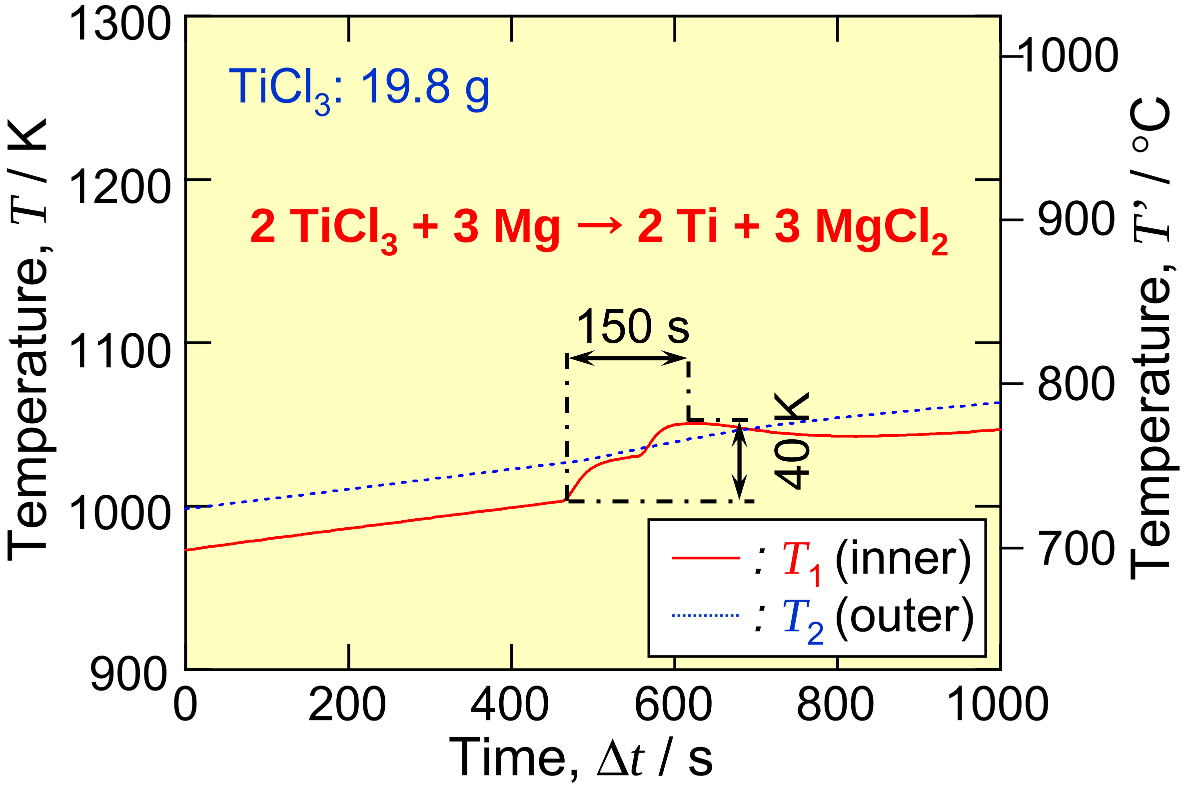
Mgの分散状態を変化させた実験



m, i

Experimental Apparatus



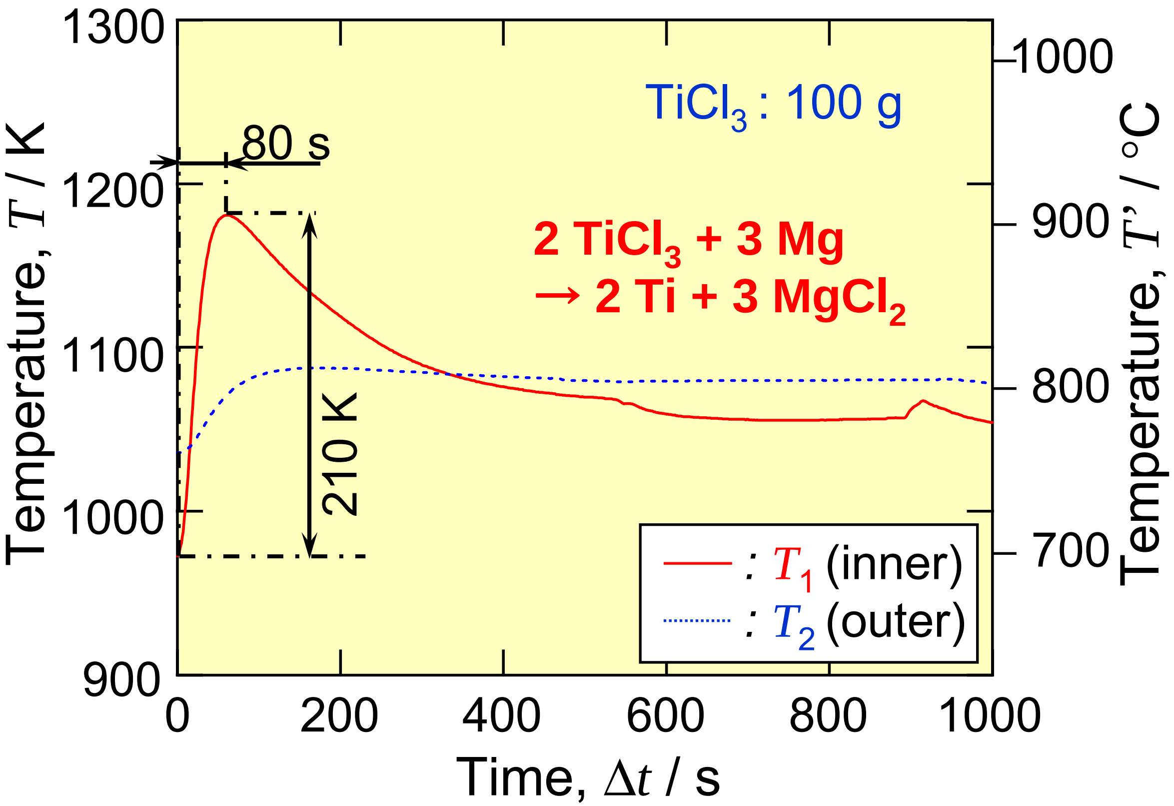


二段階の温度上昇が観測された.

$TiCl_3$ (*s*) + 1/2 Mg (*l*) → $TiCl_2$ (*s*) + 1/2 $MgCl_2$ (*l*);
　ΔH° = –96 kJ/mol @ 1000 K

$TiCl_2$ (*s*) + Mg (*l*) → Ti (*s*) + $MgCl_2$ (*l*);
　ΔH° = –91 kJ/mol @ 1000 K

Experimental Results



$TiCl_3$の投入量が多い実験では，一段階の急激な温度上昇が観測された.

本実験条件におけるチタンの生成速度

0.54 kg/m^3·s @ 1000 K

[0.043 kg/m^2·s @ 1000 K

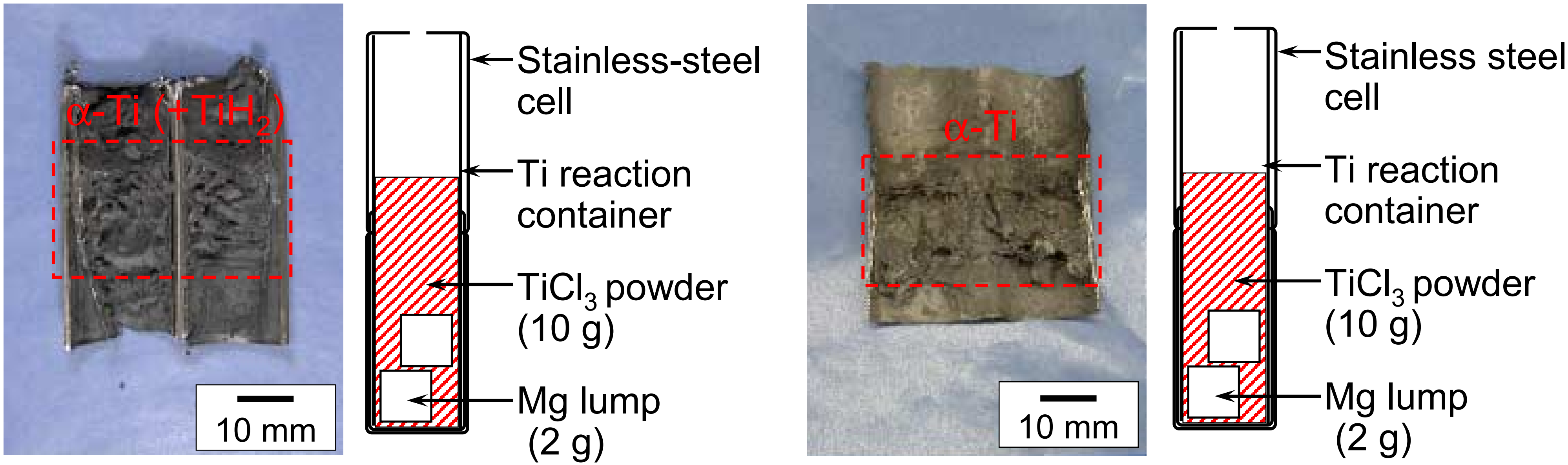
生成物の外観

(a) Leaching

(b) Initial setup of (a)

(c) Vacuum distillation

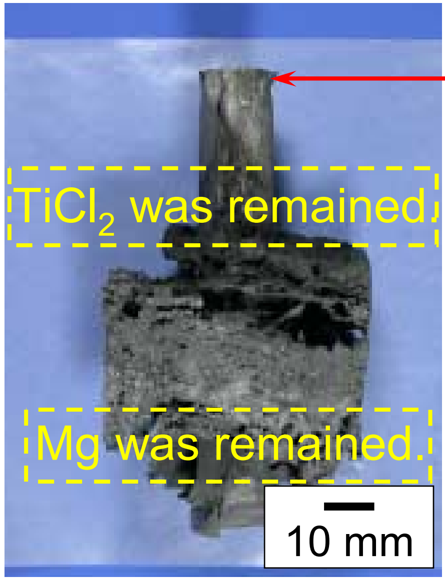
(d) Initial setup of (c)



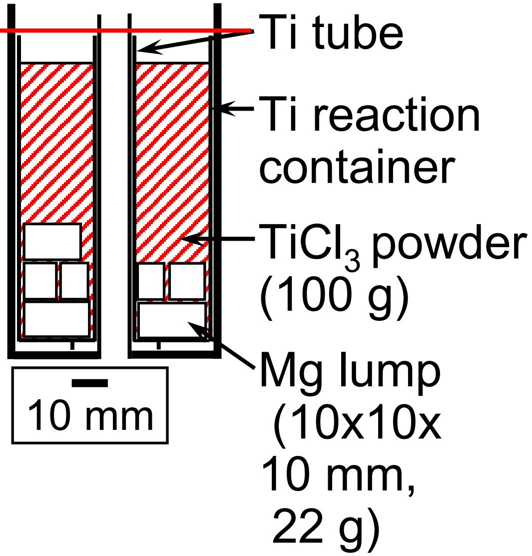
Ti reaction container was not damaged.

生成物の外観

(a) Low dispersion

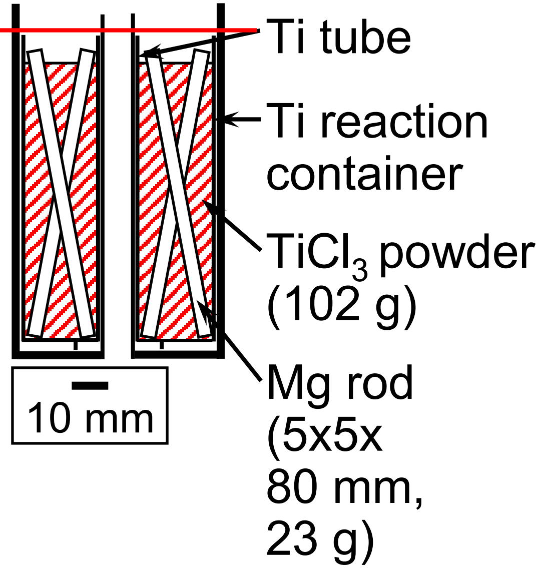


(b) Initial setup of (a)

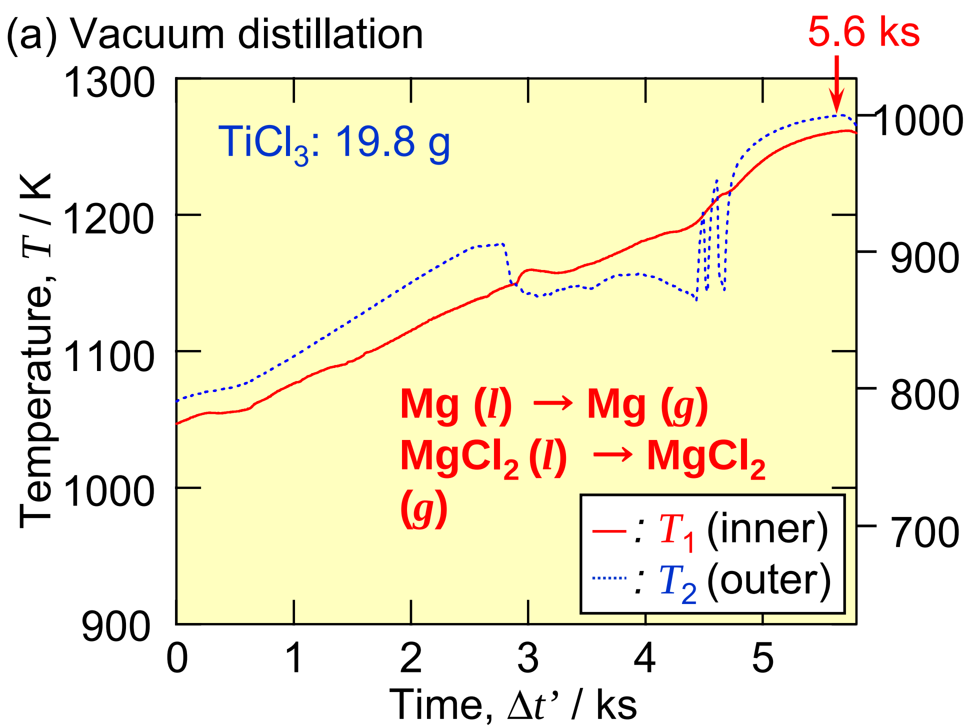


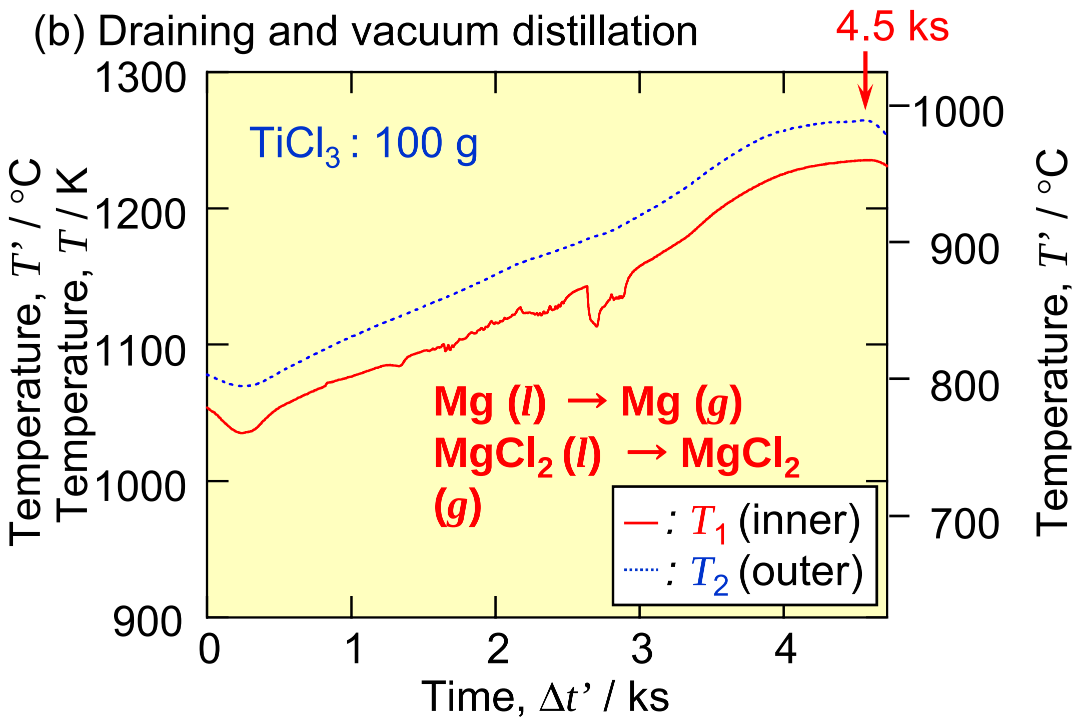
(c) High dispersion

(d) Initial setup of (c)

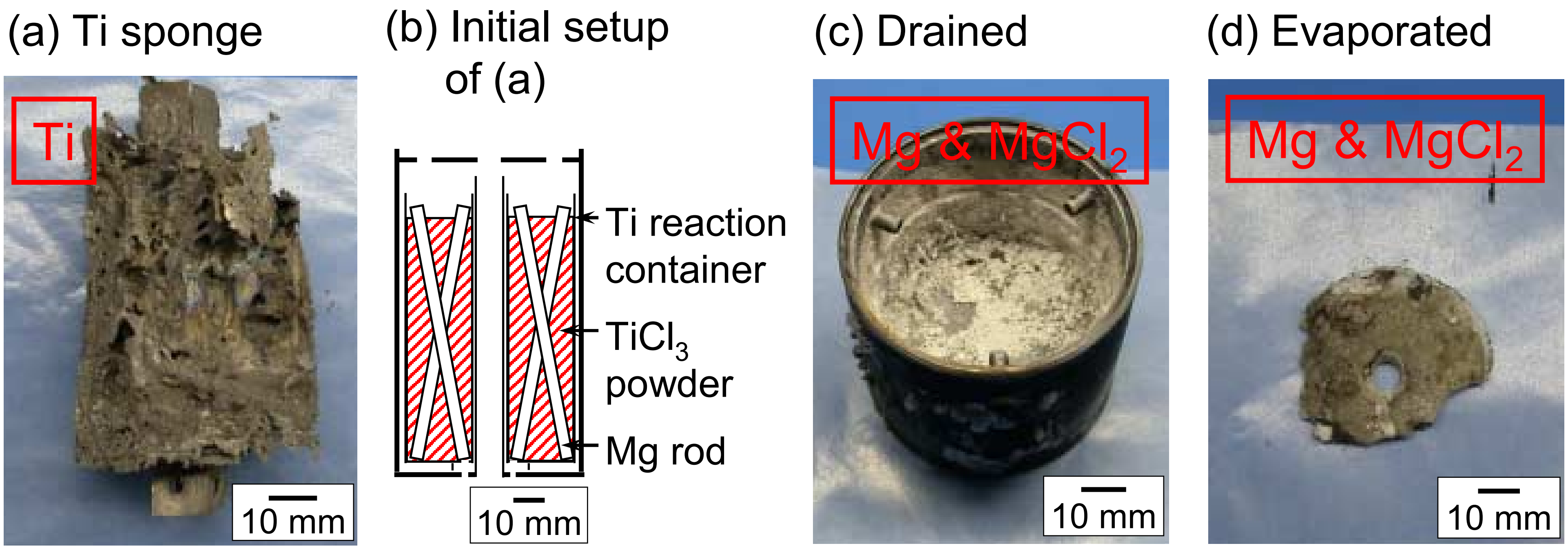


Experimental Results





生成物の外観


(a) Ti sponge
Ti
10 mm
(b) Initial setup of (a)
Ti reaction container
$TiCl_3$ powder
Mg rod
10 mm
(c) Drained
Mg & $MgCl_2$
10 mm
(d) Evaporated
Mg & $MgCl_2$
10 mm

Experimental Results

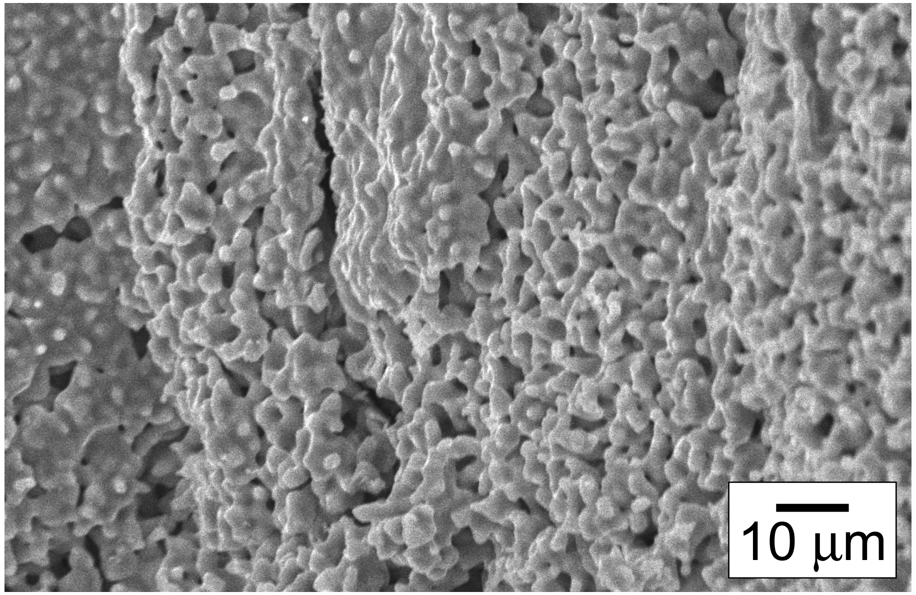
Table Analytical results of the Ti sample.

Exp.	Concentration of element i, C_i (mass%) [a]						Yield (%)
	Ti	Fe	Ni	Cr	Mg	Al	
5A [c]	96.35	0.13	<0.01	0.03	0.02	3.47	81
5B [d]	99.37	0.16	<0.01	0.02	<0.01	0.44	99
5C [b,d]	95.79	1.74	0.33	0.36	<0.01	1.77	80
5D [c]	99.26	0.29	<0.01	<0.01	0.10	0.36	66
5E [c]	99.52	0.12	<0.01	<0.01	0.11	0.24	91
5X [e]	99.04	0.18	0.02	0.02	0.09	0.65	82
5Y [e]	99.18	0.50	<0.01	<0.01	0.09	0.21	87

a: Determined by XRF, and the value excludes carbon and gaseous elements.
b: Stainless-steel reaction container was used.
c: Recovered by leaching.
d: Recovered by vacuum distillation.
e: Recovered by draining and vacuum distillation.

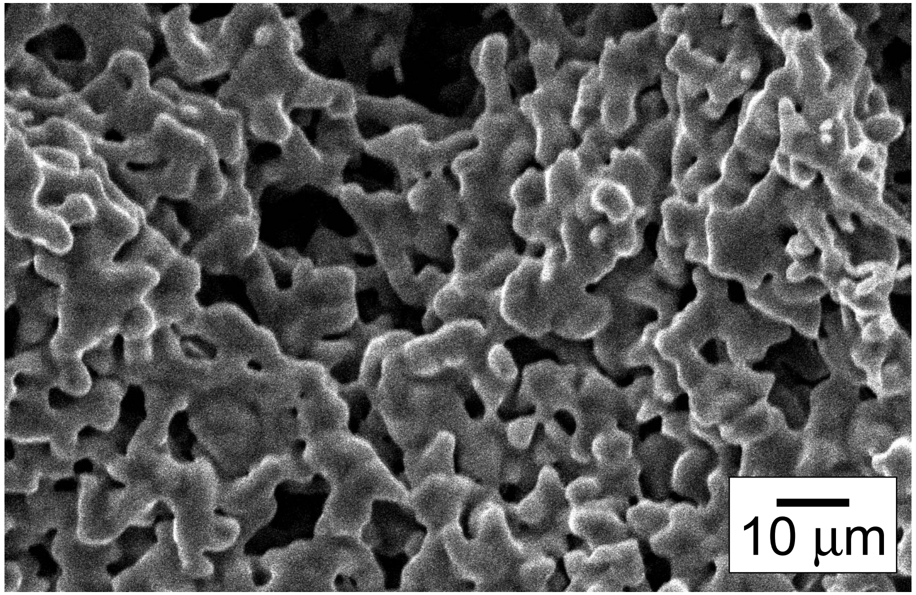
Experimental Results

(a) $TiCl_3$: 19.7 g, leaching



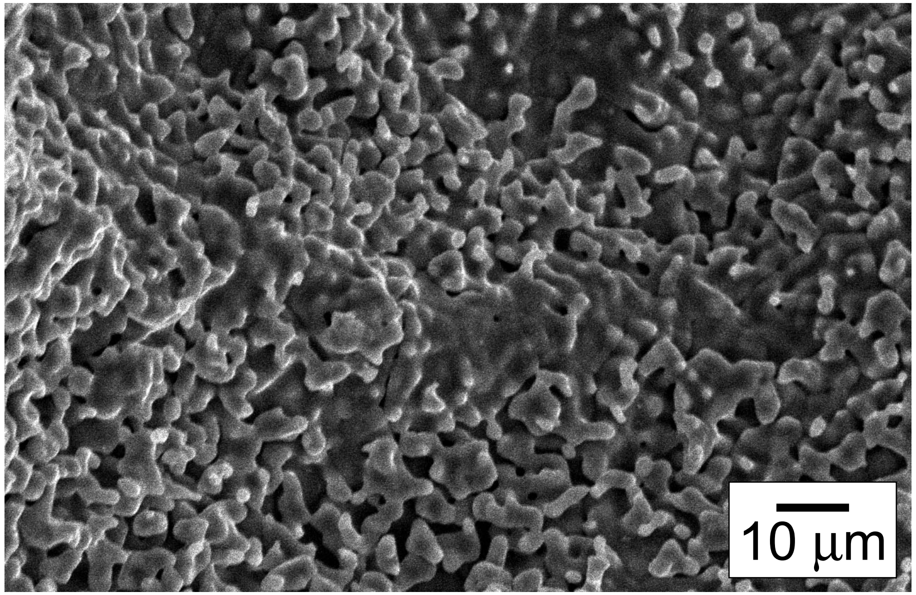
Coral like structure

(b) $TiCl_3$: 19.8 g, vacuum distillation



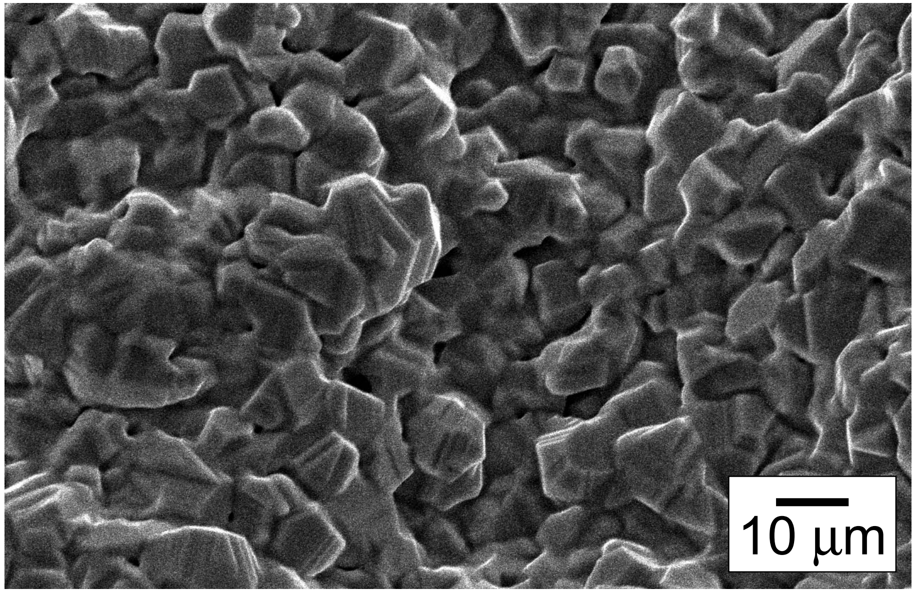
Primary particles were sintered.

(a) $TiCl_3$: 102 g, leaching



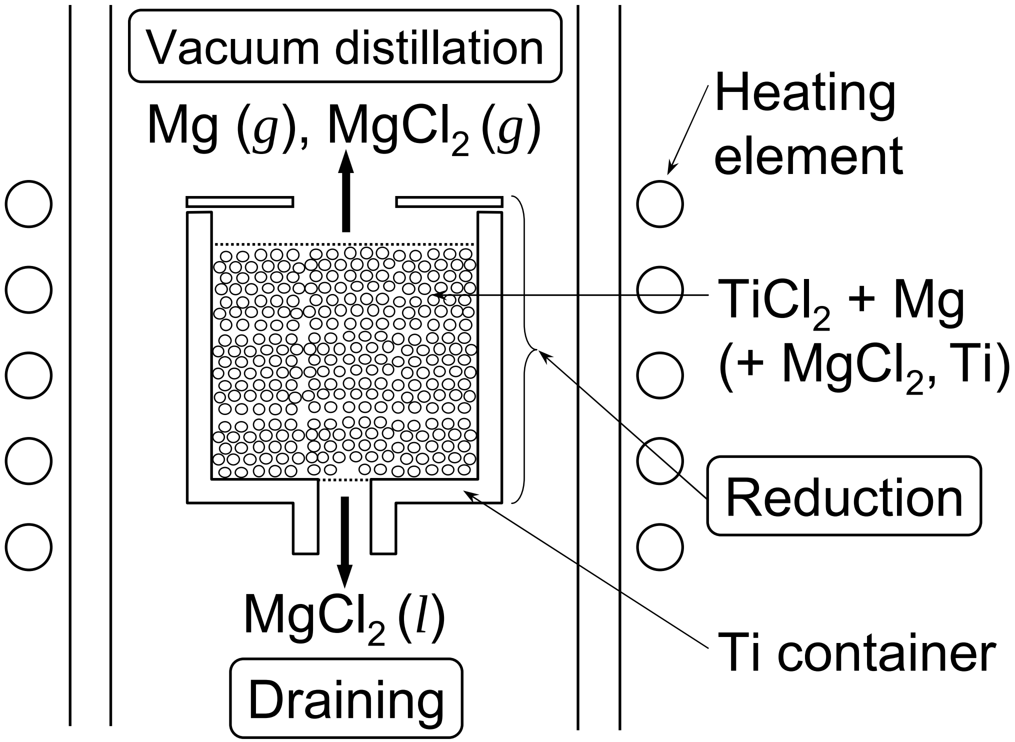
Coral like structure

(b) $TiCl_3$: 100 g, draining and vacuum distillation



Primary particles were sintered.

Conclusions



サブハライド還元法

$TiCl_x$ (x = 2, 3) + Mg (l)
→ Ti (s) + $MgCl_2$(l)

チタンの高速（半）連続還元プロセスの開発

↓

チタンの飛躍的な普及を目指す

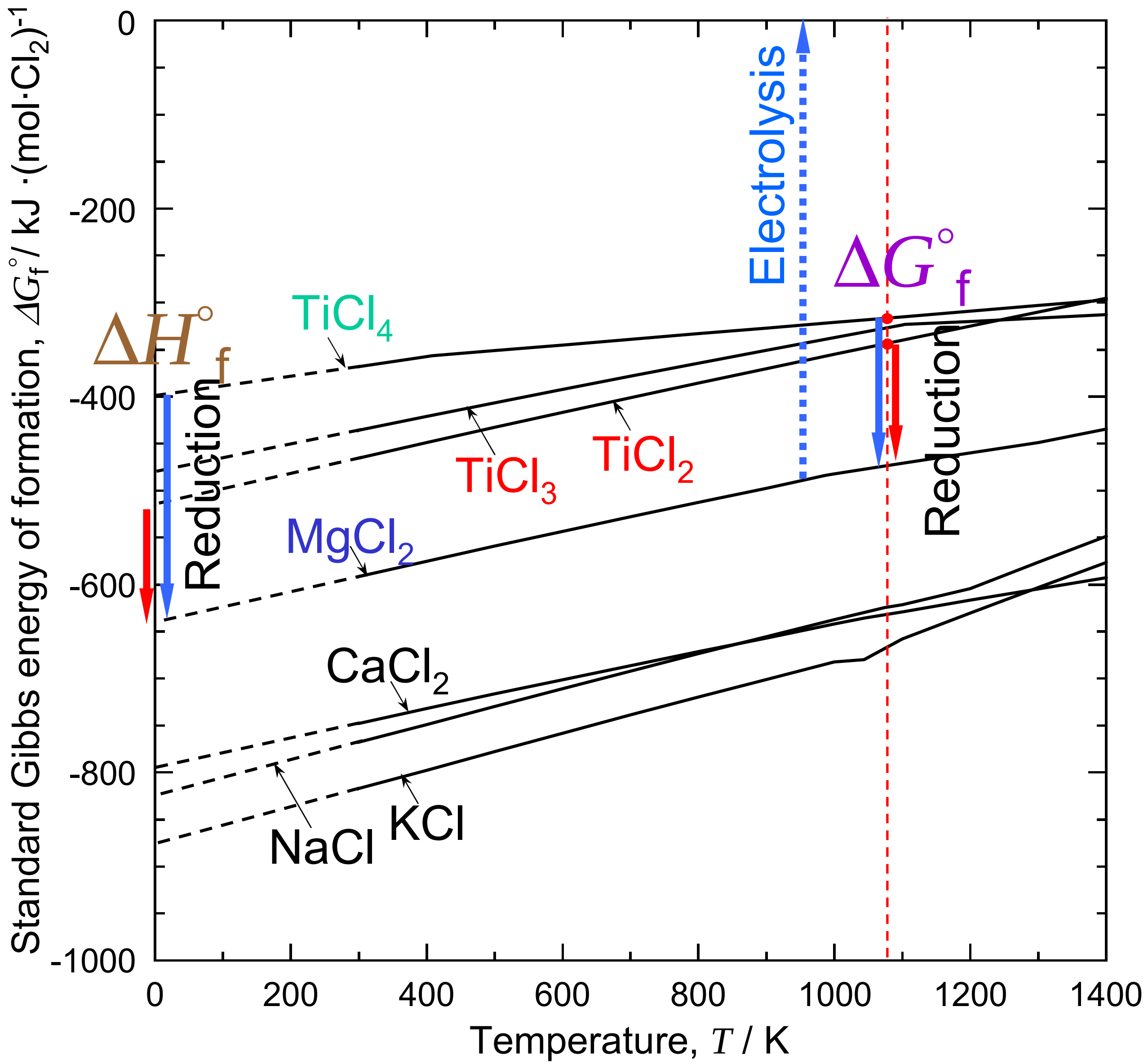
Chapter VII Epilogue

Fig. The table centerpiece made of aluminum, which was crafted for Emperor Napoleon III in 1858. (Carnegie Museum of Art, Pittsburgh, Pennsylvania, cover page of JOM, Nov. 2000)

Aluminum was changed from a rare metal to a common metal by the process innovation, and it contributed to develop our society.

Can titanium be a common metal?

Chapter Ⅰ Gibbs Energy of Formation of Chloride



$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$$

Heat of reduction is halved by utilizing titanium subhalides

Fig. Standard Gibbs energy of formation of several Chlorides.[Ref. I. Barin, Thermochemical Data of Pure Substances, VCH Verlagsgesellschaft, Weinheim, (1989).]

Chapter I Mass Balance of Titanium Production

$TiCl_4$	+	2 Mg	→	Ti	+	2 $MgCl_2$
3.96 ton		1.02 ton		1 ton		3.98 ton
2.33 m^3		0.59 m^3		0.22 m^3		1.71 m^3

ΔH° = –8980 MJ (2.50 MW·h)

1/2

$TiCl_2$	+	Mg	→	Ti	+	$MgCl_2$
2.48 ton		0.51 ton		1 ton		1.99 ton
0.79 m^3		0.29 m^3		0.22 m^3		0.85 m^3

ΔH° = –1900 MJ (0.53 MW·h)

Vapor Pressure

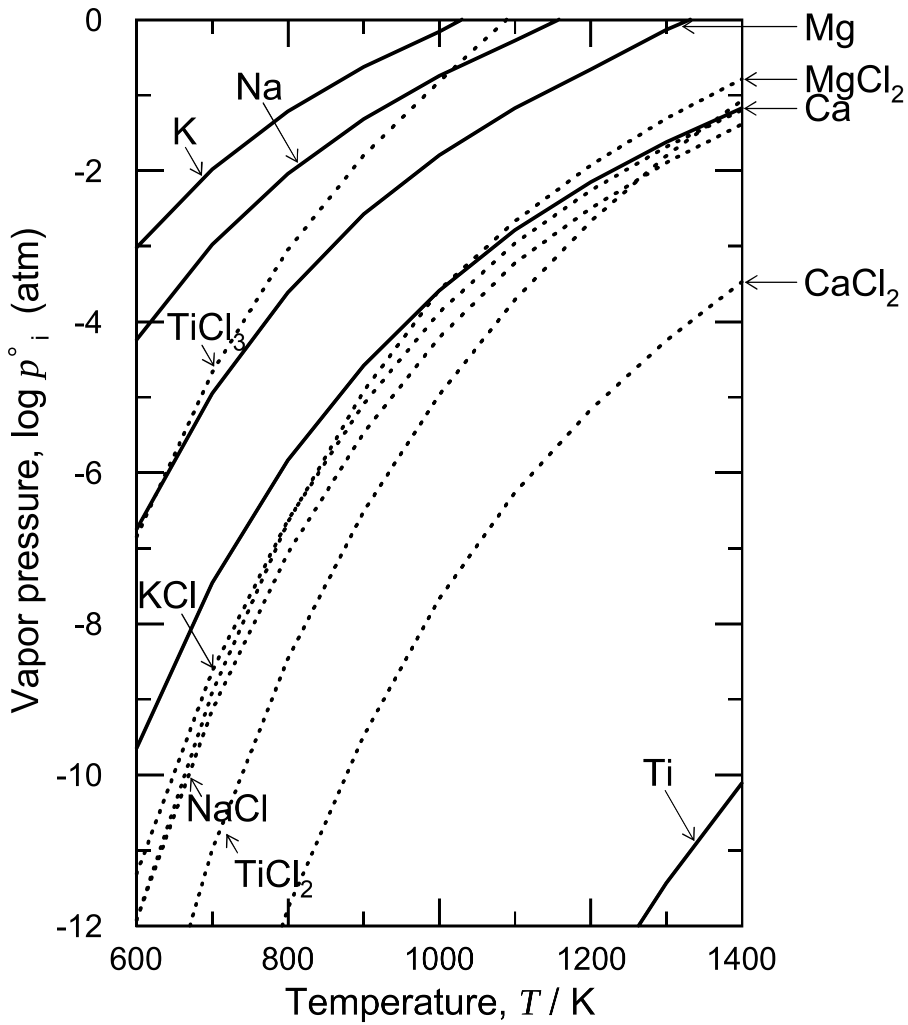


Fig. Vapor pressure of several chemical species.
[Ref. I. Barin, Thermochemical Data of Pure Substances, VCH Verlagsgesellschaft, Weinheim, (1989).]

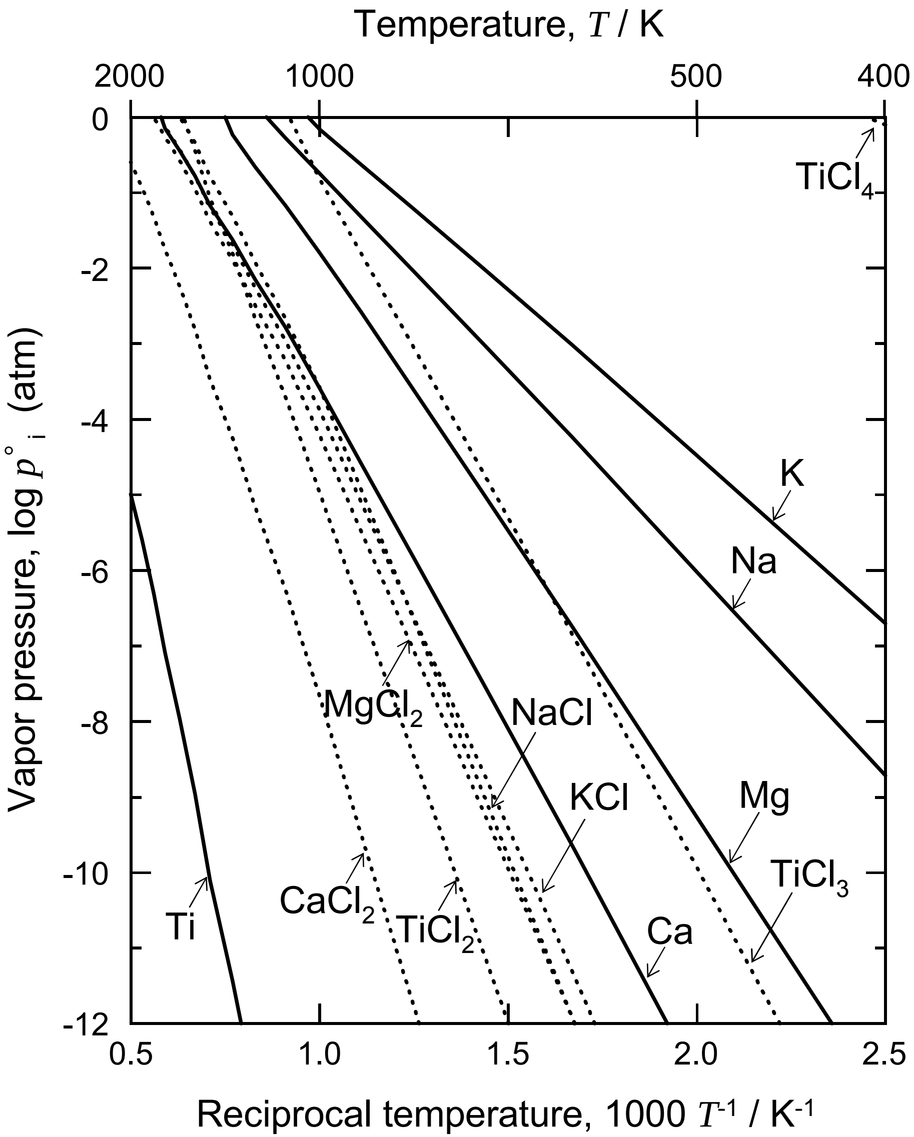
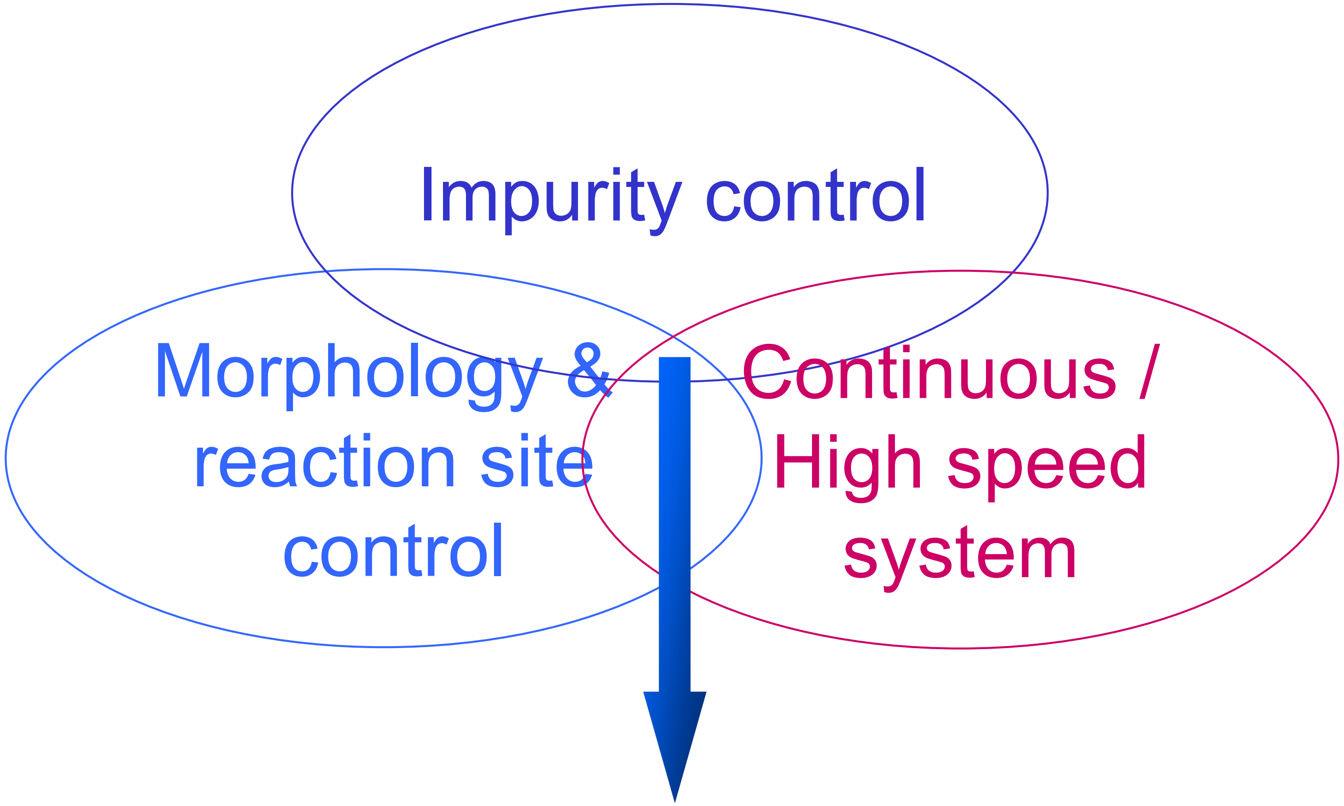


Fig. Vapor pressure of several chemical species.
[Ref. I. Barin, Thermochemical Data of Pure Substances, VCH Verlagsgesellschaft, Weinheim, (1989).]

Chapter Ⅰ Key Factors of the Development of a New Titanium Reduction Process

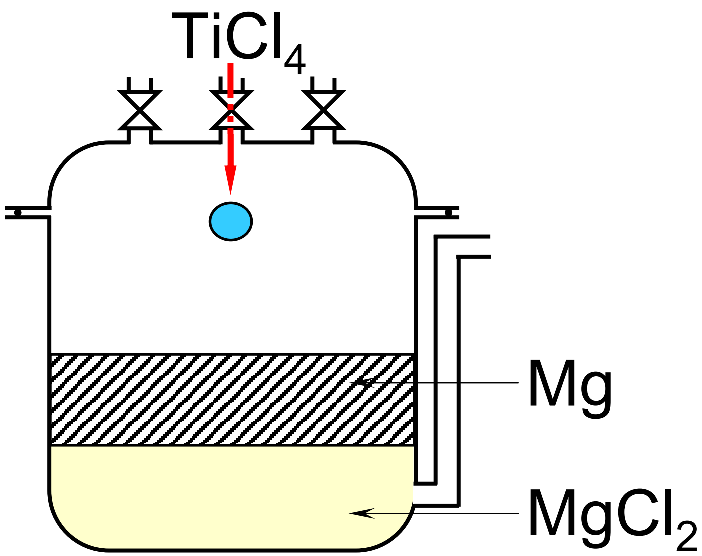


Low cost reduction process

Vapor Pressure

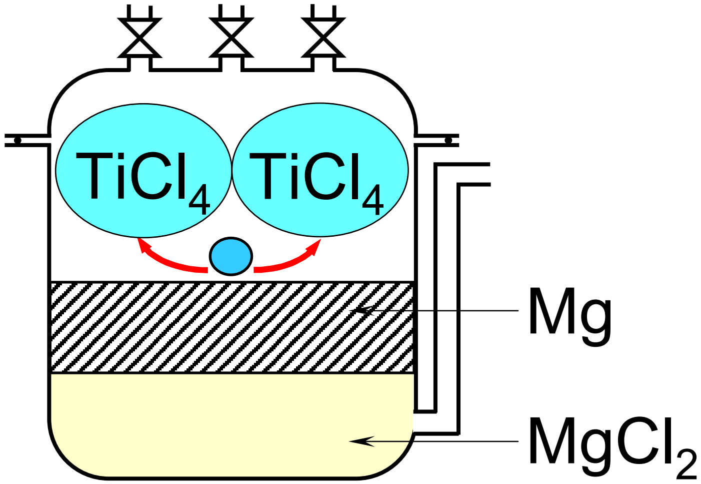
	Advantages	Disadvantages
Kroll	◎High purity titanium available ◎Easy metal / salt separation ○Established chlorine circulation ○Utilizes efficient Mg electrolysis ○Reduction and electrolysis operation can be carried out independently	×Complicated process ×Slow production speed ×Batch type process
FFC	◎Simple process ○Semi-continuous process	×Difficult metal / salt separation ×Reduction and electrolysis have to be carried outsimultaneously △Sensitive to carbon and iron contamination △Low current efficiency
OS	◎Simple process ○Semi-continuous process	×Difficult metal / salt separation △Sensitive to carbon and iron contamination △Low current efficiency
EMR / MSE	◎Resistant to iron and carbon contamination ○Semi-continuous process ○Reduction and electrolysis operation can be carried out independently	×Difficult metal / salt separation when oxide system ×Complicated cell structure △Complicated process
PRP	◎Effective control of purity and morphology ◎Flexible scalability ◎Resistant to contamination ○Small amount of fluxes necessary	×Difficult recovery of reductant ×Environmental burden by leaching
This study	◎High speed reduction process ○Semi-continuous process ○Titanium scrap enable ○Facilities for Kroll process can be utilized	×Difficulty of $TiCl_2$ handling △Multiple reduction process

1. $TiCl_4$ is dropped into a reactor.



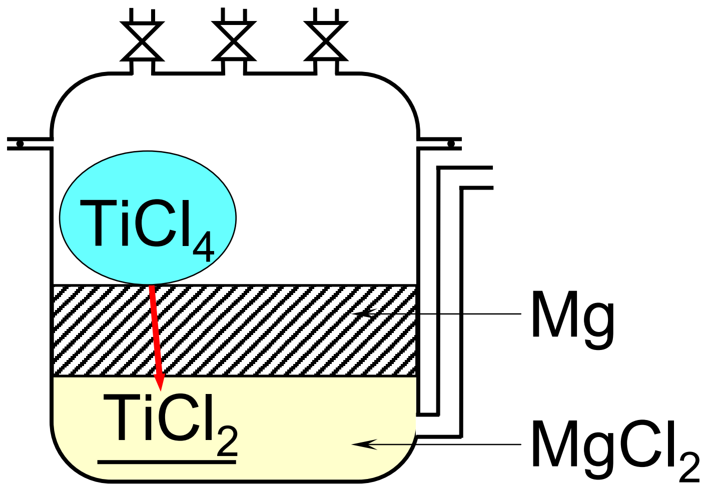
2. $TiCl_4$ vaporizes.

$$TiCl_4\ (l) \rightarrow TiCl_4\ (g)$$



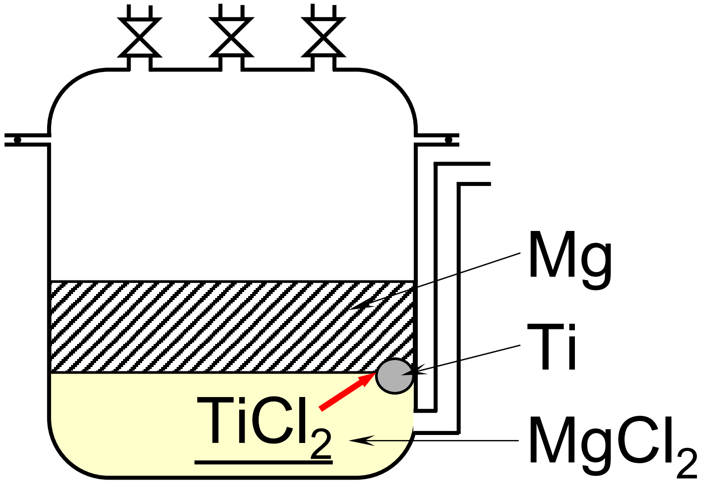
3. A part of gaseous $TiCl_4$ is reduced to $TiCl_2$ by Mg, and $TiCl_2$ dissolves into molten $MgCl_2$.

$$TiCl_4\ (g) + \underline{Mg}\ (l) \rightarrow TiCl_2\ (l) + MgCl_2\ (l)$$



4. $TiCl_2$ is reduced to Ti by Mg.

$$TiCl_2\ (l) + \underline{Mg\ (l)} \rightarrow Ti\ (s) + MgCl_2\ (l)$$



5. A part of gaseous $TiCl_4$ is directly reduced to Ti by Mg.

$$TiCl_4\ (g) + 2\ Mg\ (l) \rightarrow Ti\ (s) + 2\ MgCl_2\ (l)$$

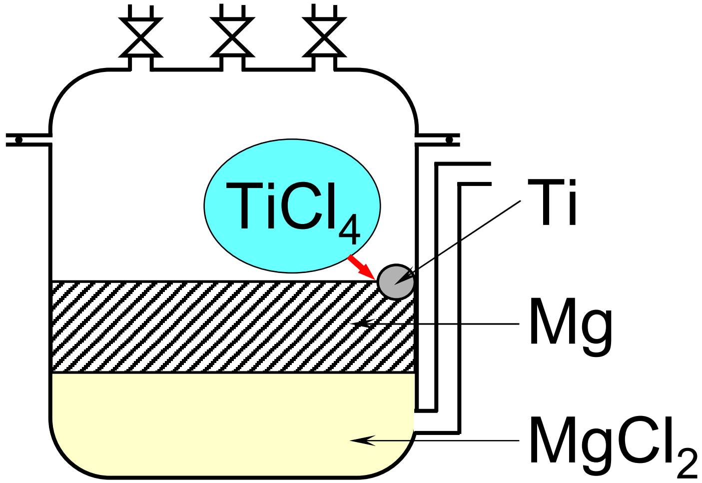


Table Physical properties of chemical species used in this study.

Symbol of chemical species	Name of chemical species	Molecular weight	Density at 20 °C, d_{20} / g·cm^{-3}	Melting point, T_m' / °C	Melting point, T_m / K	Boiling point, T_b' / °C	Boiling point, T_b / K	Sublimation point T_s' / °C	Sublimation point T_s / K
Ti	Titanium	47.88 [a]	4.5 [a]	1680 [a]	1953 [a]	3262 [a]	3535 [a]	— [a]	— [a]
				1660 [d]	1933 [d]	3300 [d]	3573 [d]	— [d]	— [d]
$TiCl_2$	Titanium (II) chloride	118.77 [b]	3.13 [c]	1035 [c]	1308 [c]	1500 [c]	1773 [c]	— [c]	— [c]
				— [e]	— [e]	— [e]	— [e]	1307 [e]	1580 [e]
$TiCl_3$	Titanium (III) chloride	154.22 [b]	no data	— [e]	— [e]	— [e]	— [e]	830 [e]	1103 [e]
$TiCl_4$	Titanium (VI) chloride	189.67 [b]	1.702 [c]	-24.1 [c]	249.1 [c]	136.5 [c]	409.7 [c]	— [c]	— [c]
				-24.1 [e]	249.1 [e]	134.9 [e]	408 [e]	— [e]	— [e]
Mg	Magnesium	24.31 [a]	1.74 [a]	659 [a]	932 [a]	1103 [a]	1376 [a]	— [a]	— [a]
				649 [d]	922 [d]	1090 [d]	1363 [d]	— [d]	— [d]
$MgCl_2$	Magnesium (II) chloride	95.21 [b]	2.325 [c]	714 [c]	987 [c]	1412 [c]	1685 [c]	— [c]	— [c]
				714 [d]	987 [d]	1410 [d]	1683 [d]	— [d]	— [d]
Cl_2	Chlorine	70.90 [b]	3.21 x 10^{-3} [d]	-101 [c]	172 [c]	-34.6 [c]	238.6 [c]	— [c]	— [c]
				-101 [d]	172 [d]	-34.1 [d]	239.1 [d]	— [d]	— [d]

a: *Kinzoku Data Book*, 3rd ed. , (ed. by Japan Inst. Metals, Maruzen, Tokyo, 1993) pp. 1-11.
b: Calculated from reference a.
c: M. Nakahara: *Dictionary of Inorganic Compounds & Complexes*, (Koudansya, Tokyo, 1997) p 87.
d: R. Kubo *et al.* : *Rikagaku Jiten*, 4th ed. , (Iwanami Shyoten, Tokyo, 1992) pp 159-784.
e: I. Barin: *Thermochemical Data of Pure Substances*, (VCH Verlagsgesellschaft, Weinheim, 1989)

Table Temperature at specific vapor pressure

	Temperature at vapor pressure 0.01 atm		Temperature at vapor pressure 0.1 atm	
	$T'_{p0.01}$ / °C	$T_{p0.01}$ / K	$T'_{p0.1}$ / °C	$T'_{p0.1}$ / K
$TiCl_2$	1010	1283	1133	1407
$TiCl_3$	613	887	707	980
Mg	701	975	859	1133
$MgCl_2$	922	1195	1085	1358

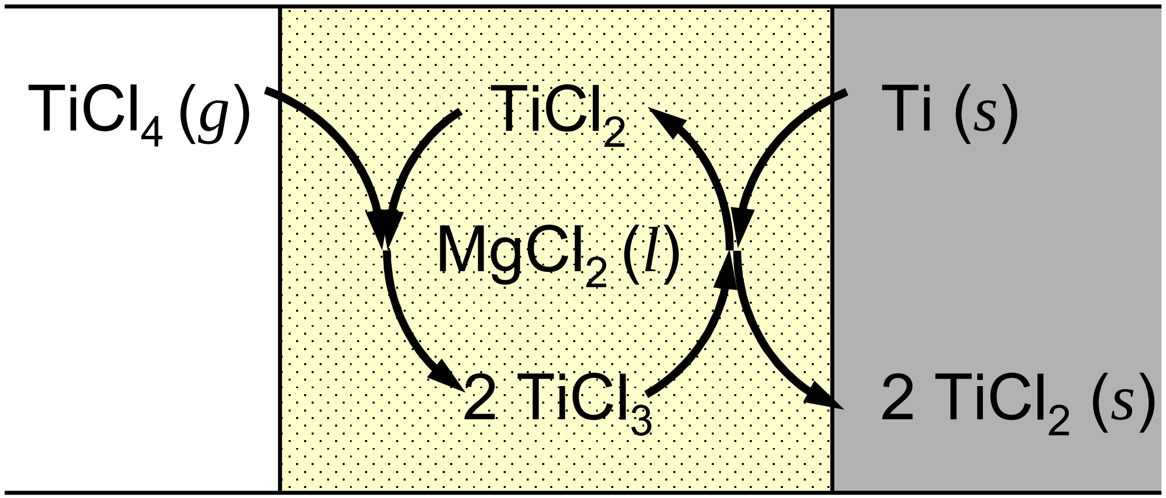
Table
Composition of titanium tri-chloride [a] used in this study

Element i	Composition of element i	
	x'_i (mass%)	x_i (mol%)
Ti	24.3	18.9
Cl	71.1	74.8
Al	4.5	6.3
$TiCl_{2.96}$	77.6 [b]	75.1 [b]
$AlCl_3$	22.4 [b]	24.9 [b]

a: Supplied by Toho titanium Co., Ltd.
b: Calculated value.

This chemical is produced as a catalyst for polymerization of polypropylene.

$TiCl_x$生成反応のメカニズム



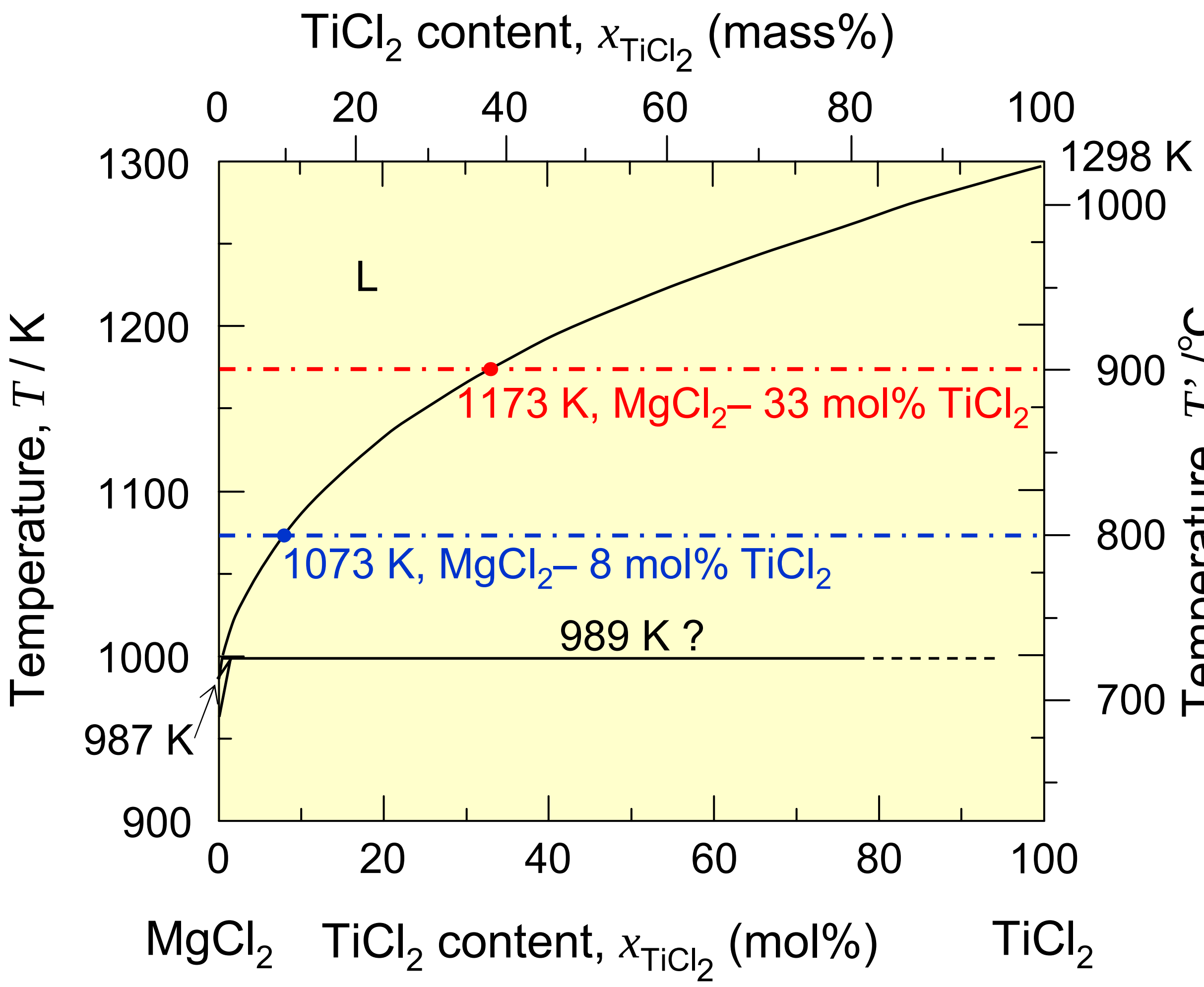
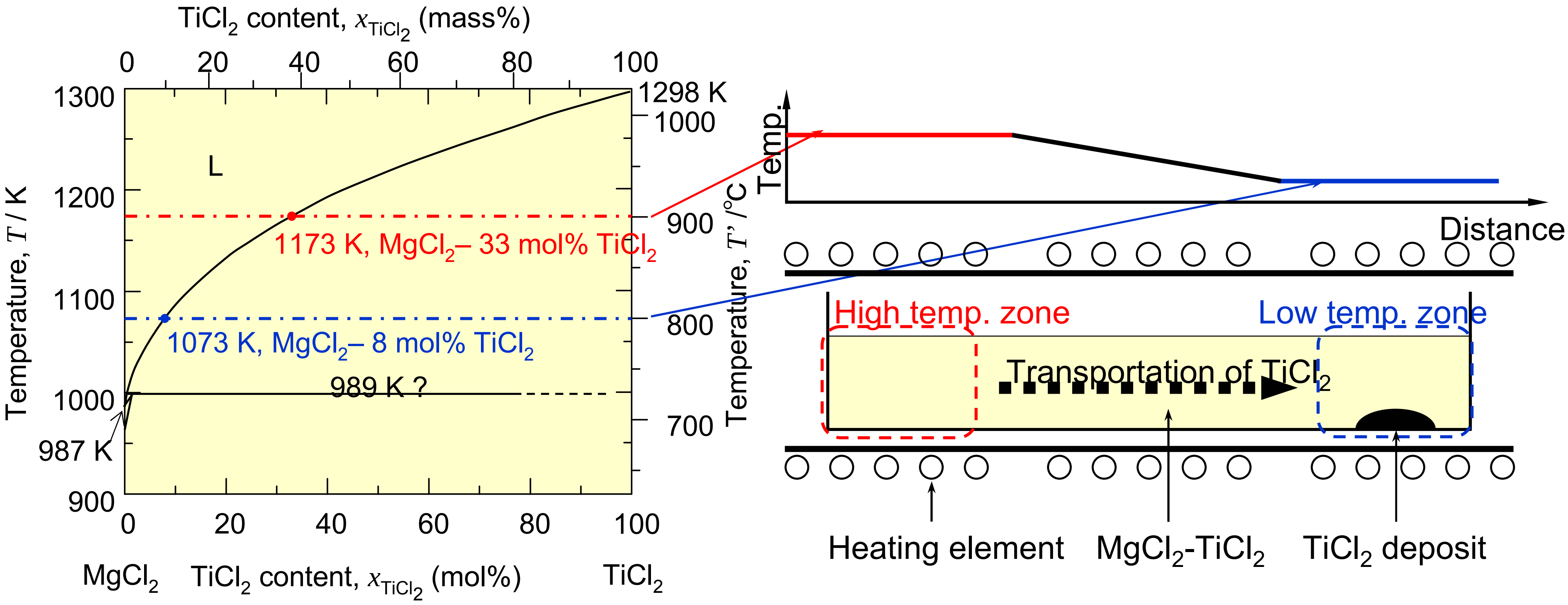


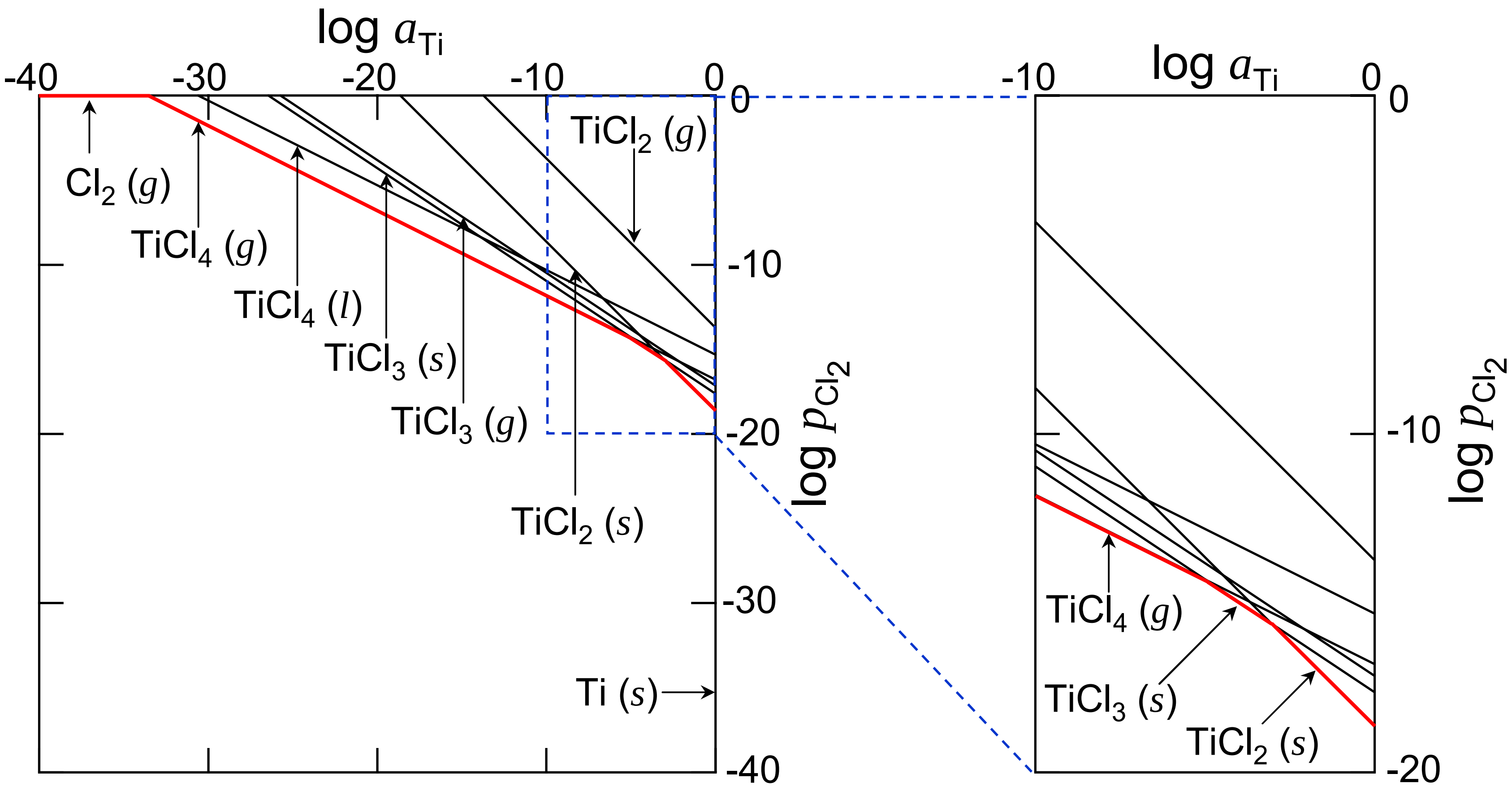
Fig. Phase diagram for the $MgCl_2$-$TiCl_2$ system.
[Ref. K. Komarek and P. Herasymenko:
J. Electrochem. Soc. 105 (1958) p 210.]

Enrichment of $TiCl_x$



Potential diagram for Ti-Cl binary system

T = 1000 K



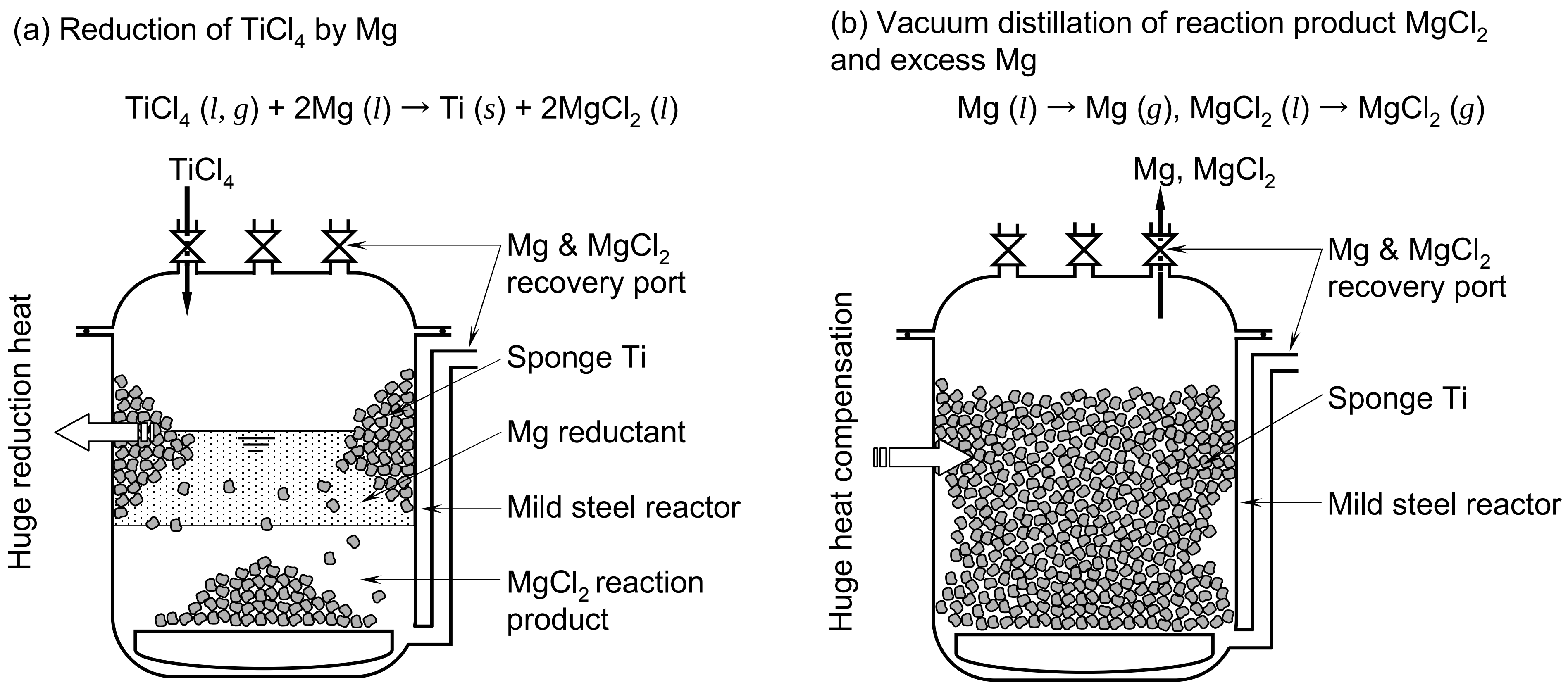


Fig. 1-3 Schematic illustration of (a) the reduction process, and (b) vacuum distillation process for titanium production based on the Kroll process.

Phase diagram for Ti-Fe binary system