Production of Titanium Powder Directly from Titanium Ore by Preform Reduction Process (PRP)

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Production of Titanium Powder Directly from Titanium Ore by Preform Reduction Process (PRP)

1. Introduction
  - Background
  - Previous research works
  - Purpose of this study

2. Experimental
3. Experimental results
4. Summary and future works

Titanium ?

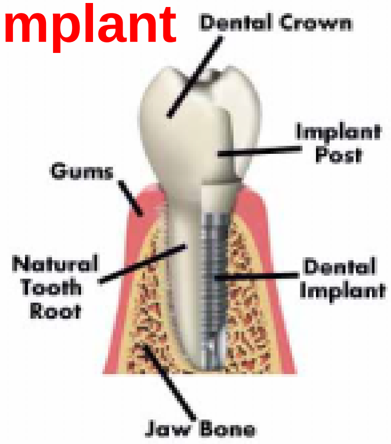
Features of Titanium

1. Light and high-strength
2. Corrosion resistance
3. Biocompatibility
4. 9th most abundant element in the earth’s crust

Japan Aerospace Exploration Agency

The JAPAN TITANIUM SOCIETY

Implant

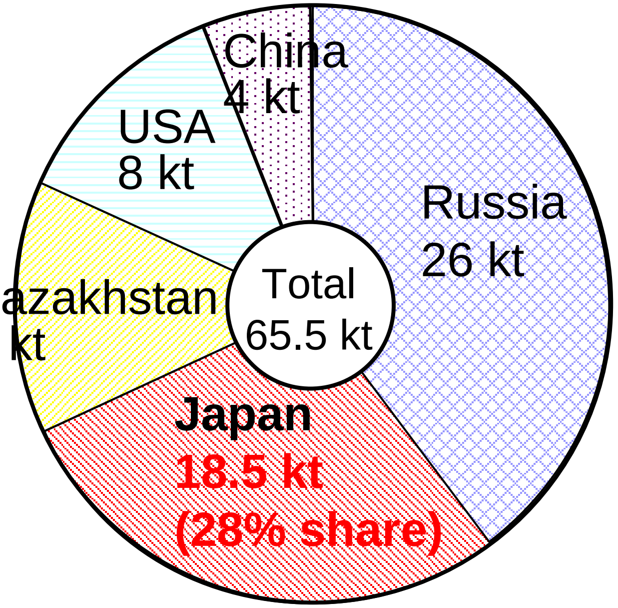


http://www.atlantadentalimplants.com/

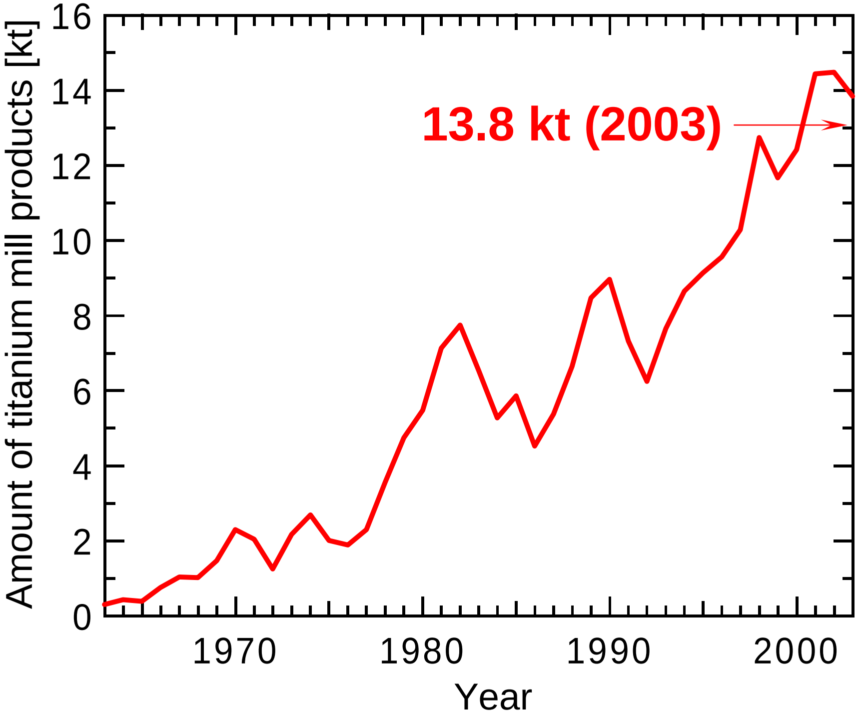
TMinato-Machi River Place (Osaka Japan)
http://www.city.osaka.jp/

Current status of titanium production

(a) Production of titanium sponge in the world (2003)



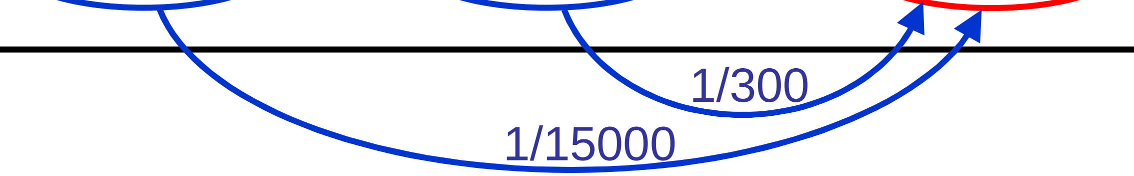
(b) Transition of production volume of titanium mill products in Japan



Japan has about 30% world market share,
and its titanium industry is growing steadily.

Comparison with common metals

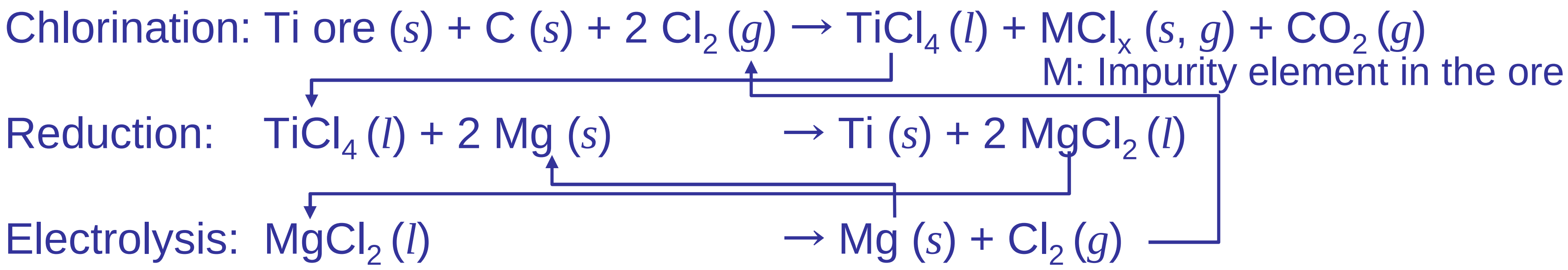
Metal	Iron	Aluminum	Titanium
Symbol	Fe	Al	Ti
Melting point (K)	1809	933	1939
Density (g/cm^3@298 K)	7.9	2.7	4.5
Specific strength ((kgf/mm^2)/(g/cm^3))	4~7	3~6	8~10
Clarke No.	4	3	9
Price (¥/kg)	50	200~600	1300~3000
Production volume (t/world@2003)	9.6 x 10^8	2.2 x 10^7	6.6 x 10^4


1/300

1/15000

Production volume of metallic Ti is substantially small compared to common metals.

Kroll process

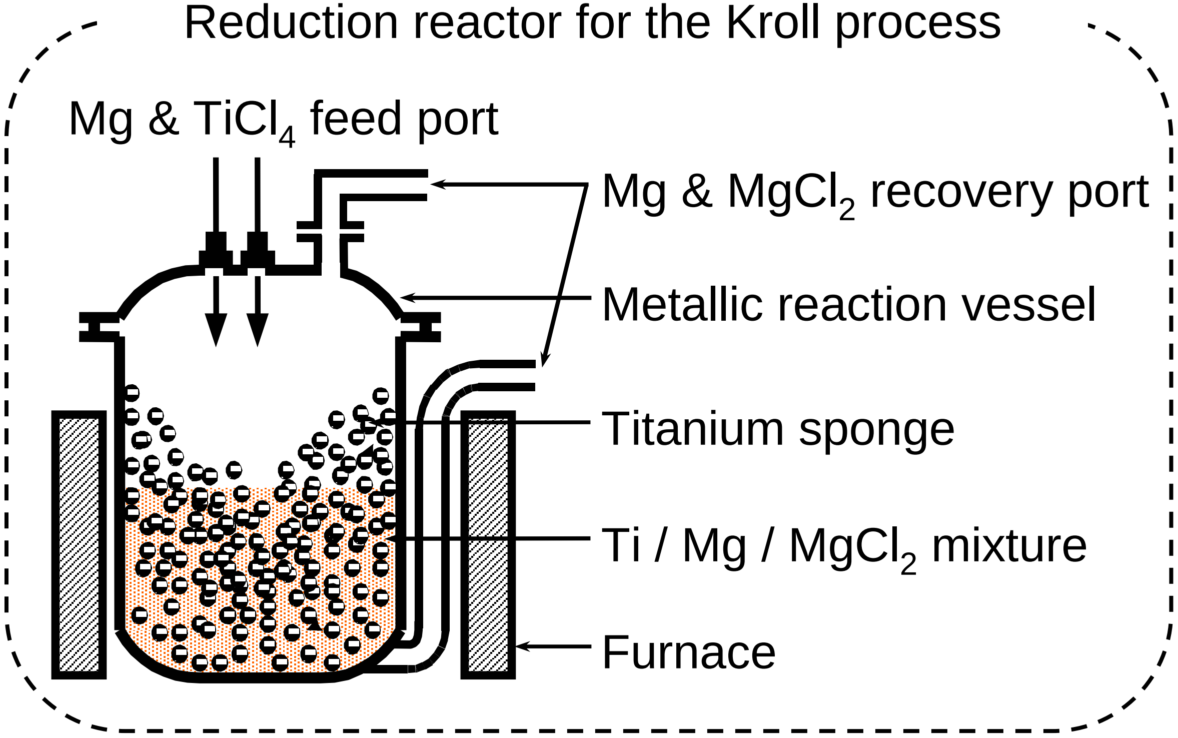


Chlorination: Ti ore (s) + C (s) + 2 Cl_2 (g) → $TiCl_4$ (l) + MCl_x (s, g) + CO_2 (g)

M: Impurity element in the ore

Reduction: $TiCl_4$ (l) + 2 Mg (s) → Ti (s) + 2 $MgCl_2$ (l)

Electrolysis: $MgCl_2$ (l) → Mg (s) + Cl_2 (g)



Reduction reactor for the Kroll process

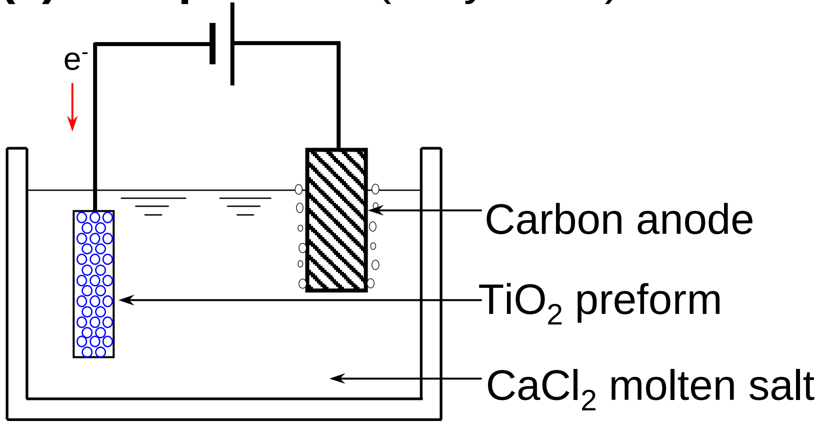
The essential advantage:
High-purity Ti obtainable

The critical disadvantage:

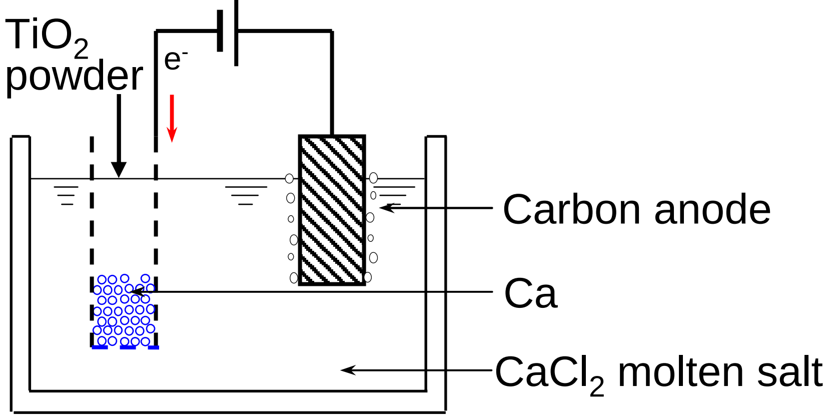
- Batch type process
- Labor and energy consuming
- Slow production speed
  → Low productivity

Various reduction processes for titanium oxides

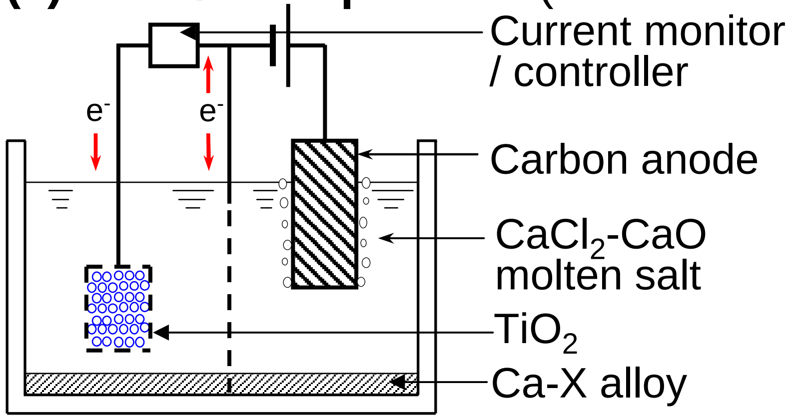
(a) FFC process (Fray *et al.*)



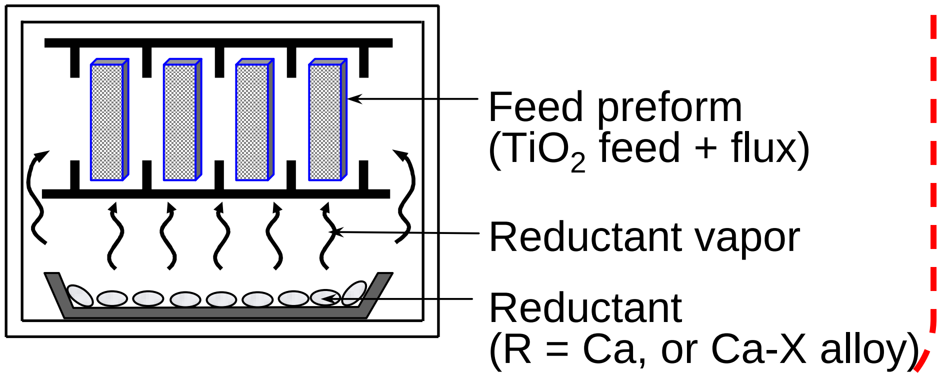
(b) OS process (Ono & Suzuki)



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



(d) Preform reduction process (PRP)

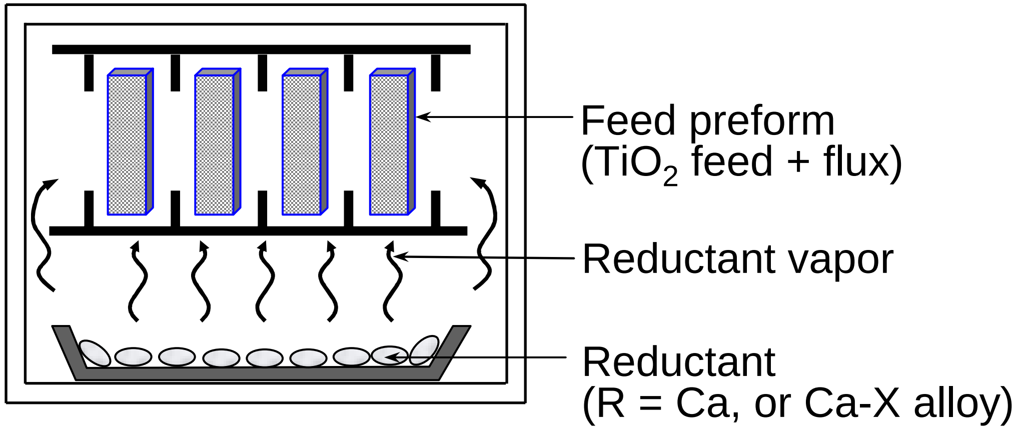


The purpose of this study

Development of a new smelting process for producing high purity titanium.

- High productivity, low cost process has to be developed for replacing the Kroll process

Preform reduction process (PRP)

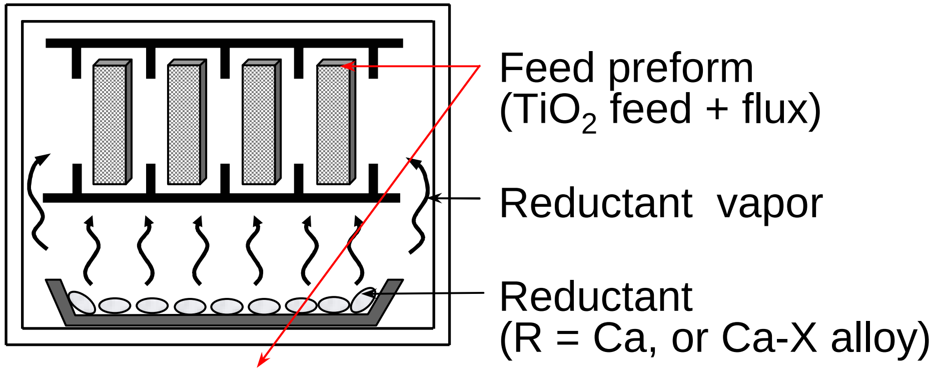


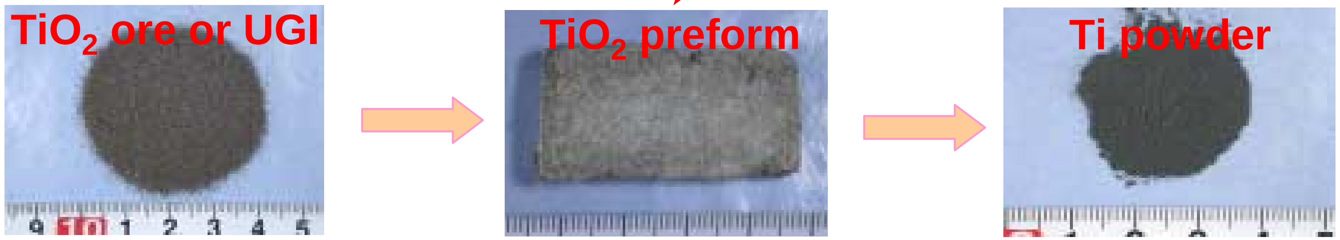
TiO_2 (*s*, feed preform) + Ca (*g*) → Ti (*s*, powder) + CaO (*s*, flux)

Production of Titanium Powder Directly from Titanium Ore by Preform Reduction Process (PRP)

1. Introduction
2. **Experimental**
    - Concept of PRP
    - Flowchart of this study
    - PRP experiment with no carbon powder
    - PRP experiment with carbon powder
3. Experimental results
4. Summary and future works

Preform Reduction Process (PRP) ?





Starting material   Preform   Powder

$$TiO_2\ (s,\ \text{feed preform}) + Ca\ (g)\ \rightarrow\ Ti\ (s,\ \text{powder}) + CaO\ (s,\ \text{flux})$$

Advantages of Preform Reduction Process: → **“simple and low-cost process”**

● Suitable for uniform reduction
● Flexible scalability
● Possible to control the morphology of powder by varying the flux content in the preform
● Possible to prevent the contamination from reaction container
● Amount of waste solution is minimized
● Molten salt as a flux can be reduced compared to other direct reduction process

Disadvantages of Preform Reduction Process:

▲ Leaching process is required
✕ Calcium production and control of calcium vapor is difficult

Ellingham diagram of some selected oxides

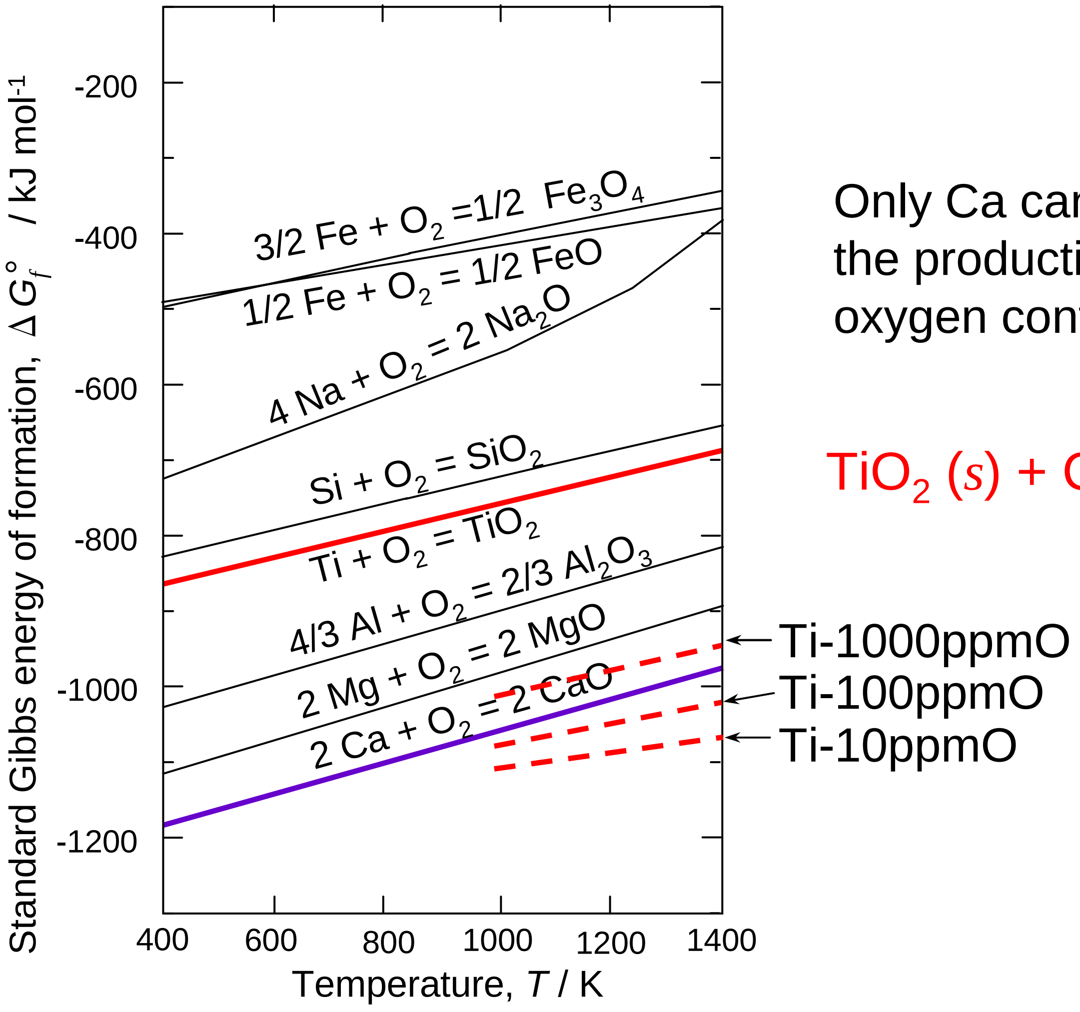


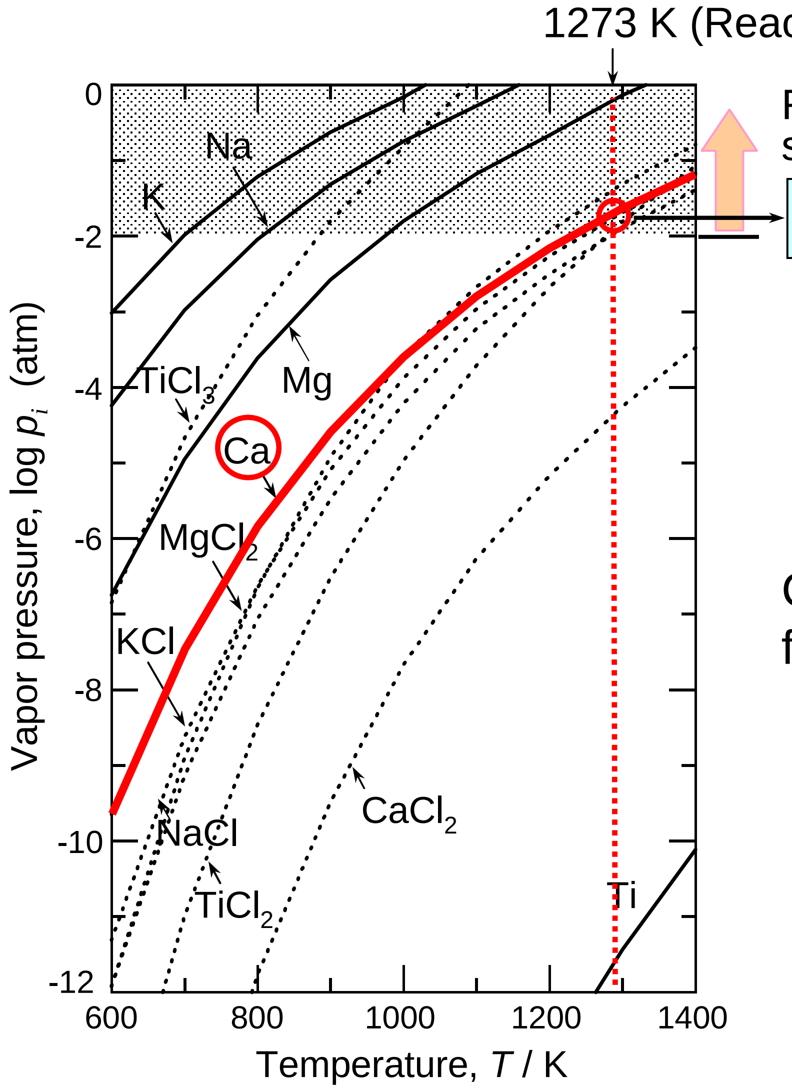
Fig. Ellingham diagram of some selected oxides.

Only Ca can be utilized as reductant for the production of metallic Ti with low oxygen content directly from Ti ore.

$$TiO_2\ (s) + Ca\ (g) \rightarrow Ti\ (s) + CaO\ (s)$$

~500ppmO

Vapor pressure of some selected metals and chlorides



Range of vapor pressure feasible for supplying reductants in vapor form

The vapor pressure of Ca: 0.024 atm @ 1273 K

Ca reductant can be supplied as vapor form for reducing Ti ore or TiO_2 in the PRP.

Fig. Vapor pressure of selected metals and chlorides.

Starting materials

Previous study: Artificial feed materials

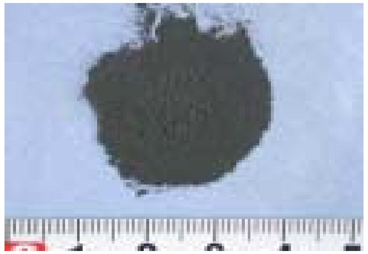
TiO_2 powder

Or

Upgraded ilmenite (India)


De-ionized ilmenite ore

Titanium Powder



99 % up matellic titanium powder was obtained by using titanium oxide (TiO_2) or upgraded ilmenite (UGI) as the staring materials.

This study: Natural titanium ore (Rutile, South Africa) used as feed material

Rutile ore (South Africa)

XRF analysis (mass %)				
Ti	**Fe**	Al	Ca	Cl
96.82	**2.11**	1.01	0.07	(0.00)

So far, it was difficult to produce high-purity Ti directly from natural Ti ore!

Experimental procedure

Ti ore: Rutile
Flux: $CaCl_2$
Binder: Collodion

Ti ore → Mixing
Flux → Mixing
Binder → Mixing

Mixing → Slurry → Preform fabrication

Preform fabrication: Rutile+$CaCl_2$+Binder
T: Room temp.; t': 6 hr
e.g. 40mm × 20mm × 8mm

Preform fabrication → Feed preform → Calcination/iron removal

Calcination/iron removal: T: 1273 K; t': 1 hr~ 2hr

Calcination/iron removal → $FeCl_x\uparrow$

Calcination/iron removal → Sintered feed preform → Reduction

Reduction: T: 1273 K, t': 6 hr~9 hr

Calcium vapor → Reduction

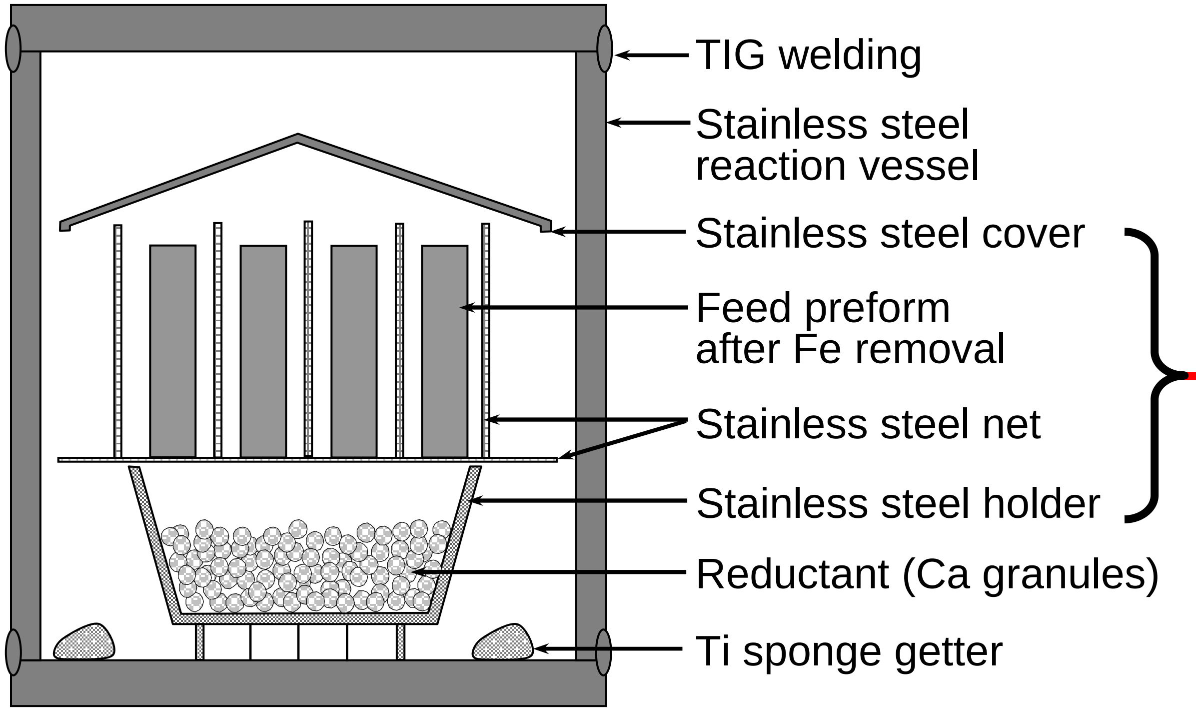
Reduction → Reduced preform → Leaching

Leaching:
T: RT
50% CH_3COOH aq.,
t': 6 hr
20% HCl aq.,
t': 1 hr

Leaching → Waste solution

Leaching → Vacuum drying → Powder

Experimental apparatus for the reduction process in PRP



TIG welding

Stainless steel reaction vessel

Stainless steel cover

Feed preform after Fe removal

Stainless steel net

Stainless steel holder

Reductant (Ca granules)

Ti sponge getter

Fig. Schematic illustration of the experimental apparatus for the reduction experiment.

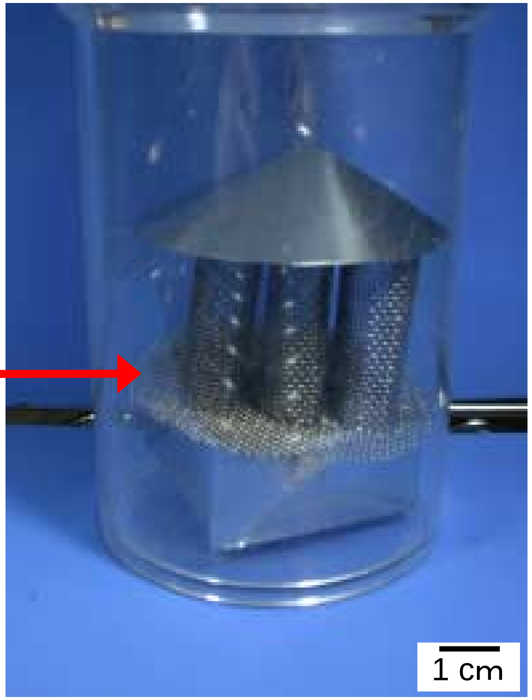


Fig. Arrangement of stainless steel net and holder tentatively installed in transparent container.

Experimental conditions

Table Experimental conditions in this study.

Exp.	Mass of sample, w_i / g				Cationic Molar ratio.,	Calcination		Reduction	
	Feed	Flux	Binder	Additive		Temp.,	Time,	Temp.,	Time,
	Ti ore[a]	$CaCl_2$	Collodion	Carbon powder	$R_{Cat. / Ti}$[b]	$T_{cal.}$ / K	$t'_{cal.}$ / hr	$T_{red.}$ / K	$t'_{red.}$ / hr
$A_{(C-2)}$	7.74	2.52	5.58	-	0.2	1273	1	1273	6
$B_{(C-7)}$	6.65	3.86	6.01	-	0.3	1273	1	1273	6
$C_{(PCD-2)}$	6.26	1.74	4.26	0.2	0.2	1273	2	1273	9
$D_{(PCD-4)}$	5.65	2.35	5.79	0.2	0.3	1273	2	1273	9

[a] Natural rutile ore produced in South Africa after pulverization.

[b] Cationic molar ratio, $R_{Cat. / Ti} = N_{Cat.} / N_{Ti}$, where $N_{Cat.}$ and N_{Ti} are mole amount of cation in flux and that of titanium, respectively.

Calcination: Fe removal

Reduction: Ti powder production

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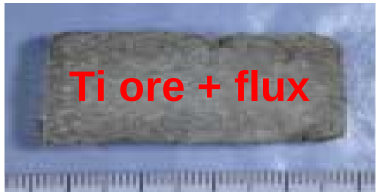
1. Introduction
2. Experimental
3. **Experimental results**
   - Analytical data by XRD, XRF, and SEM
4. Summary and future works

Experimental results: Images and XRD

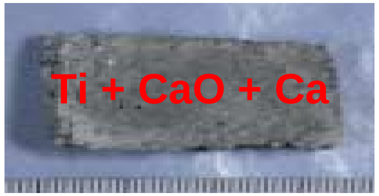
Exp. A, Cationic molar ratio, R = 0.2

(a) Fabricated feed preform

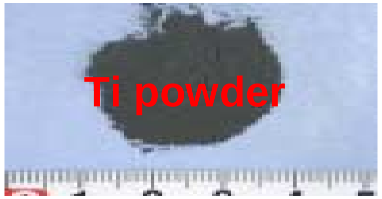


(b) After calcination

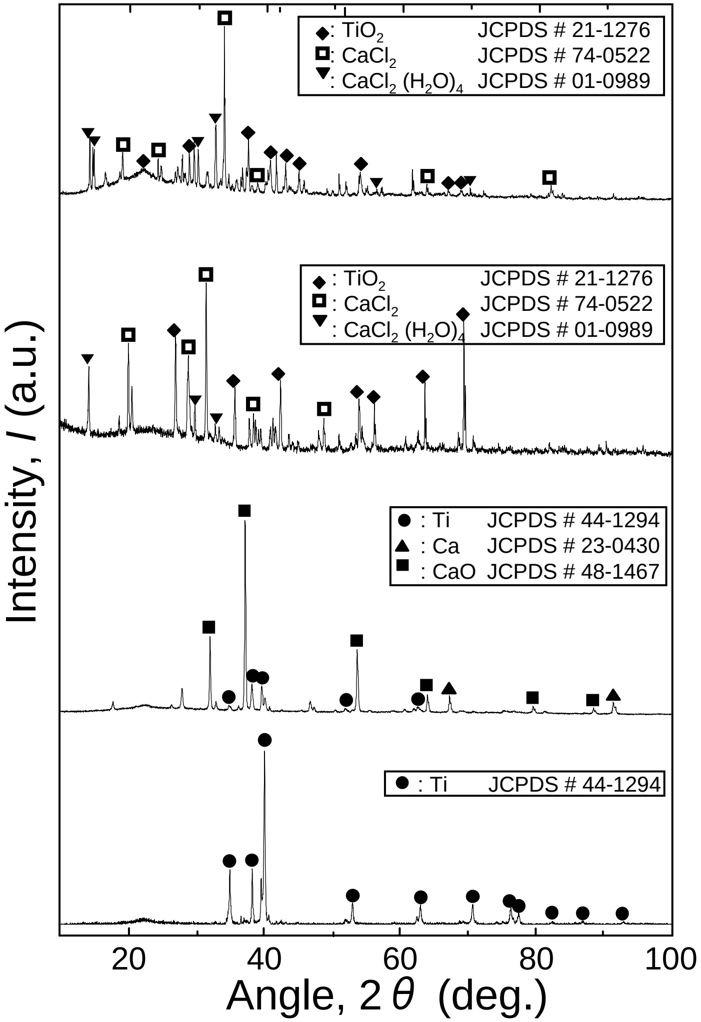
(c) After reduction



(d) After leaching



XRD patterns



$TiO_2 + CaCl_2 + CaCl_2(H_2O)_4$

$TiO_2 + CaCl_2 + CaCl_2(H_2O)_4$

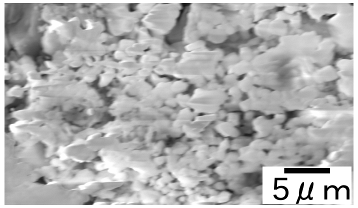
Ti + CaO + Ca

Ti

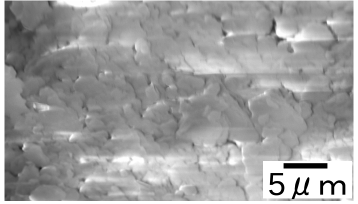
Experimental results: SEM images and XRF

SEM images

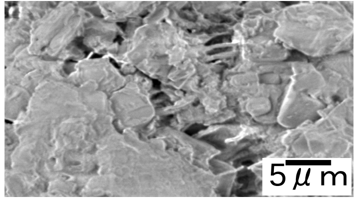
(a) Fabricated feed preform



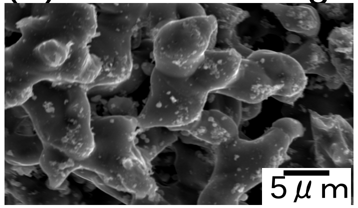
(b) After calcination



(c) After reduction



(d) After leaching



Exp. B, Cationic molar ratio, *R* = 0.3

Step	XRF analysis (mass %)				
	Ti	**Fe**	Al	Ca	Cl
(a)	68.00	**1.07**	0.44	11.66	18.83
(b)	60.68	**0.42**	0.33	14.88	23.70
(c)	17.74	0.07	(0.00)	67.42	14.76
(d)	99.10	0.03	0.30	0.58	(0.00)

Iron removal ratio is 56 %

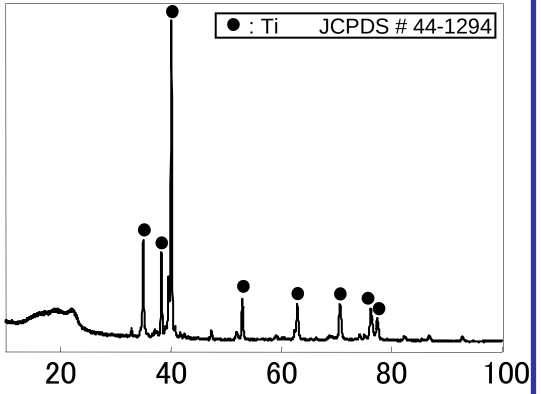
Iron removal ratio:
$(C_{Fe,\ Bef.}/C_{Ti,\ Bef.} - C_{Fe,\ Aft.}/C_{Ti,\ Aft.}) / (C_{Fe,\ Bef.}/C_{Ti,Bef.})$

Experimental results: XRD, SEM images, and XRF

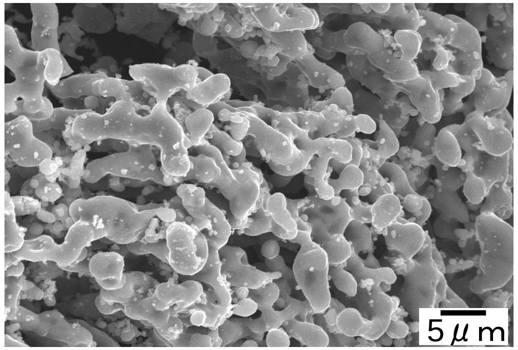
Exp. C, Cationic molar ratio, $R = 0.2$, Carbon powder: 0.2 g

After leaching

XRD pattern



SEM images



Step	XRF analysis (mass %)				
	Ti	**Fe**	Al	Ca	Cl
(a) After fabrication	67.64	**1.36**	0.50	10.20	20.29
(b) After calcination	65.99	**0.13**	0.08	11.65	22.15
(c) After reduction	18.79	**0.10**	(0.00)	67.98	13.09
(d) After leaching	98.23	**0.23**	0.56	0.98	(0.00)

Iron removal ratio is 90 %.

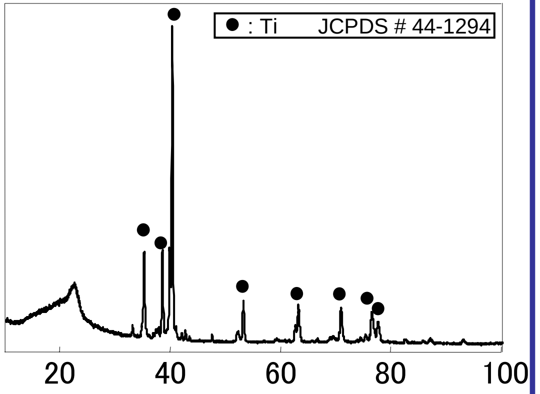
Iron removal ratio:
$(C_{Fe,\ Bef.}/C_{Ti,\ Bef.} - C_{Fe,\ Aft.}/C_{Ti,\ Aft.}) / (C_{Fe,\ Bef.}/C_{Ti,Bef.})$

Experimental results: XRD, SEM images, and XRF

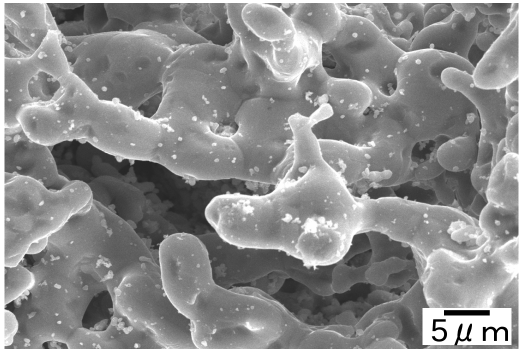
Exp. D, Cationic molar ratio, $R = 0.3$, Carbon powder: 0.2 g

After leaching

XRD pattern



SEM images



Step	XRF analysis (mass %)				
	Ti	**Fe**	Al	Ca	Cl
(a) After fabrication	46.11	**0.79**	0.17	19.88	33.06
(b) After calcination	49.63	**0.30**	0.16	18.05	31.85
(c) After reduction	19.98	**0.09**	(0.00)	66.25	13.61
(d) After leaching	98.44	**0.14**	0.68	0.73	(0.00)

Iron removal ratio is 65 %.

Iron removal ratio:
$(C_{Fe,\ Bef.}/C_{Ti,\ Bef.} - C_{Fe,\ Aft.}/C_{Ti,\ Aft.}) / (C_{Fe,\ Bef.}/C_{Ti,Bef.})$

Composition and yields of the obtained Ti product

Exp. C and D

Table Analytical results of the titanium samples obtained after leaching.

Exp.	Cationic molar ratio, $R_{\text{Cat./Ti}}$	Concentration of element i in obtained Ti powder, C_i (mass %)					Yield (%)
		Ti	Fe	Al	Ca	Cl	
C	0.2	98.23	0.23	0.56	0.98	(0.00)	79.02
D	0.3	98.44	0.14	0.73	0.68	(0.00)	87.74

[a] Natural rutile ore produced in South Africa after pulverization.

[b] Cationic molar ratio, $R_{\text{Cat. / Ti}} = N_{\text{Cat.}} / N_{\text{Ti}}$, where $N_{\text{Cat.}}$ and N_{Ti} are mole amount of cation in flux and that of titanium, respectively.

Still high for practical application, but will be improved.

Loss occurred mainly at leaching process.

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4. **Summary and future works**

Summary

1. Iron was successfully removed by selective chlorination in the calcination step, and 90 % of iron was removed.

2. When carbon powder is added to the preform, the effect of iron removal became more efficient. Titanium powder with 98 mass % purity was obtained with the yield of 88 %.

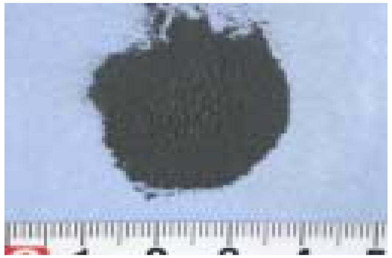
3. High-purity metallic titanium powder (99 mass % up) was obtained directly from natural titanium ore (rutile ore) by Preform Reduction Process (PRP).

Future Works

1. Development of more effective method for removing iron directly from titanium ore.
2. Development of efficient recycling system of $CaCl_2$ flux, and residual Ca reductant.

The ultimate object:
→ establishing an innovative process for producing high-purity titanium powder with low-cost.

Natural Ti Ore or UGI



Low iron, low oxygen Ti powder

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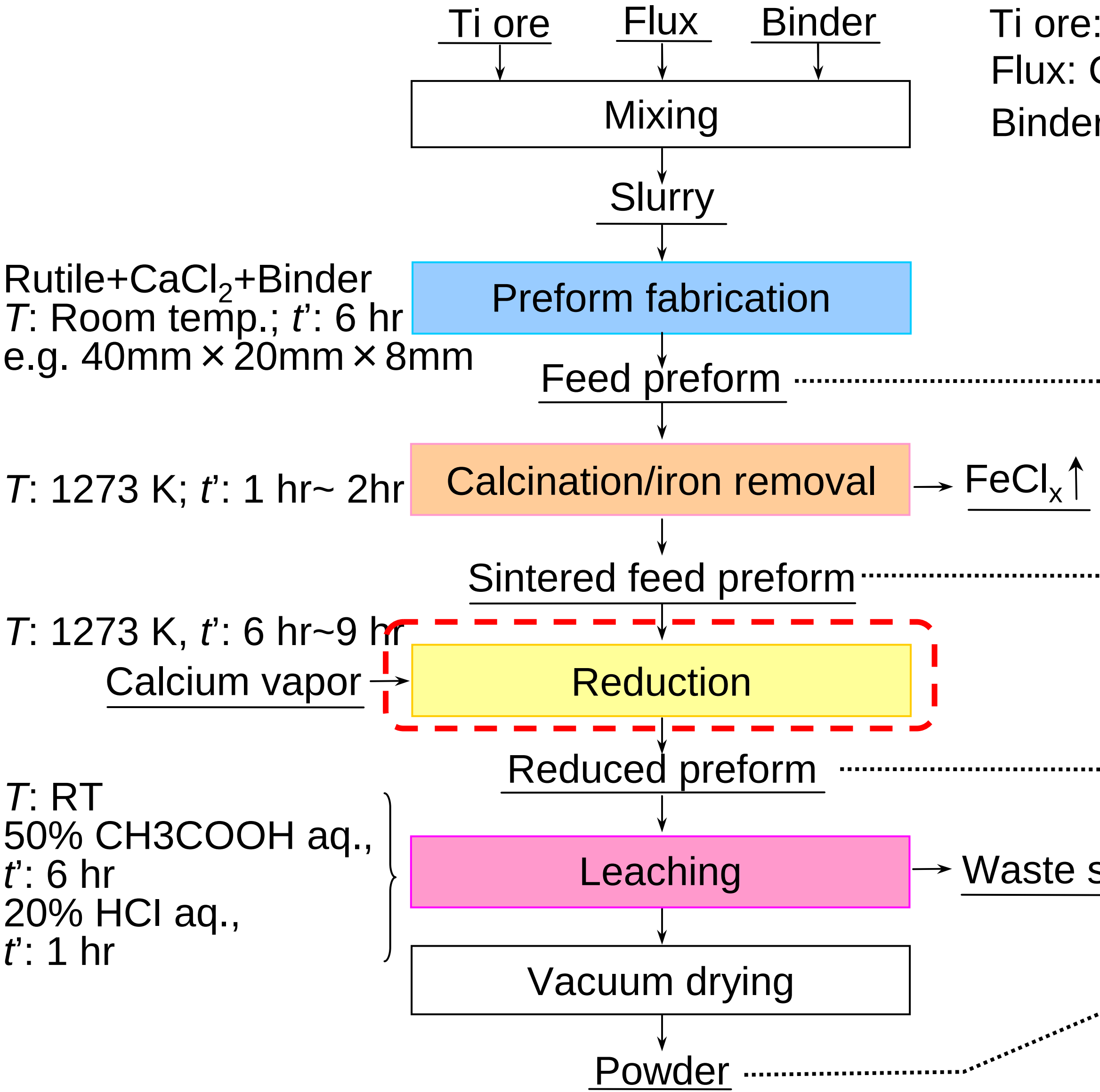


Ti ore, Flux, Binder → Mixing → Slurry → Preform fabrication → Feed preform → Calcination/iron removal → Sintered feed preform → Reduction → Reduced preform → Leaching → Vacuum drying → Powder

Ti ore: Rutile
Flux: $CaCl_2$
Binder: Collodion

Preform fabrication:
Rutile+$CaCl_2$+Binder
T: Room temp.; *t*': 6 hr
e.g. 40mm × 20mm × 8mm

Calcination/iron removal:
T: 1273 K; *t*': 1 hr~ 2hr
→ $FeCl_x$↑

Reduction:
T: 1273 K, *t*': 6 hr~9 hr
Calcium vapor →

Leaching:
T: RT
50% CH3COOH aq.,
t': 6 hr
20% HCl aq.,
t': 1 hr
→ Waste solution

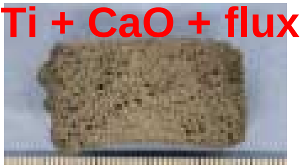
Ti ore + flux

→0.8~1.4 mass % Fe

90 % Fe removal

TiO_2 feed in flux

→~0.13 mass % Fe



Ti + CaO + flux

Ti powder

98 mass % up purity
0.14 mass % Fe
88 % yield

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Reference

History of Titanium

1791

First discovered by William Gregor, a clergyman and amateur geologist in Cornwall, England

1795

Klaproth, a German chemist, gave the name titanium to an element re-discovered in Rutile ore.

1887

Nilson and Pettersson produced metallic titanium containing large amounts of impurities

1910

M. A. Hunter produced titanium with 99.9% purity by the sodiothermic reduction of $TiCl_4$ in a steel vessel.

(119 years after the discovery of the element)

1946

W. Kroll developed a commercial process for the production of titanium: Magnesiothermic reduction of $TiCl_4$..

Titanium was not purified until 1910, and was not produced commercially until the early 1950s.

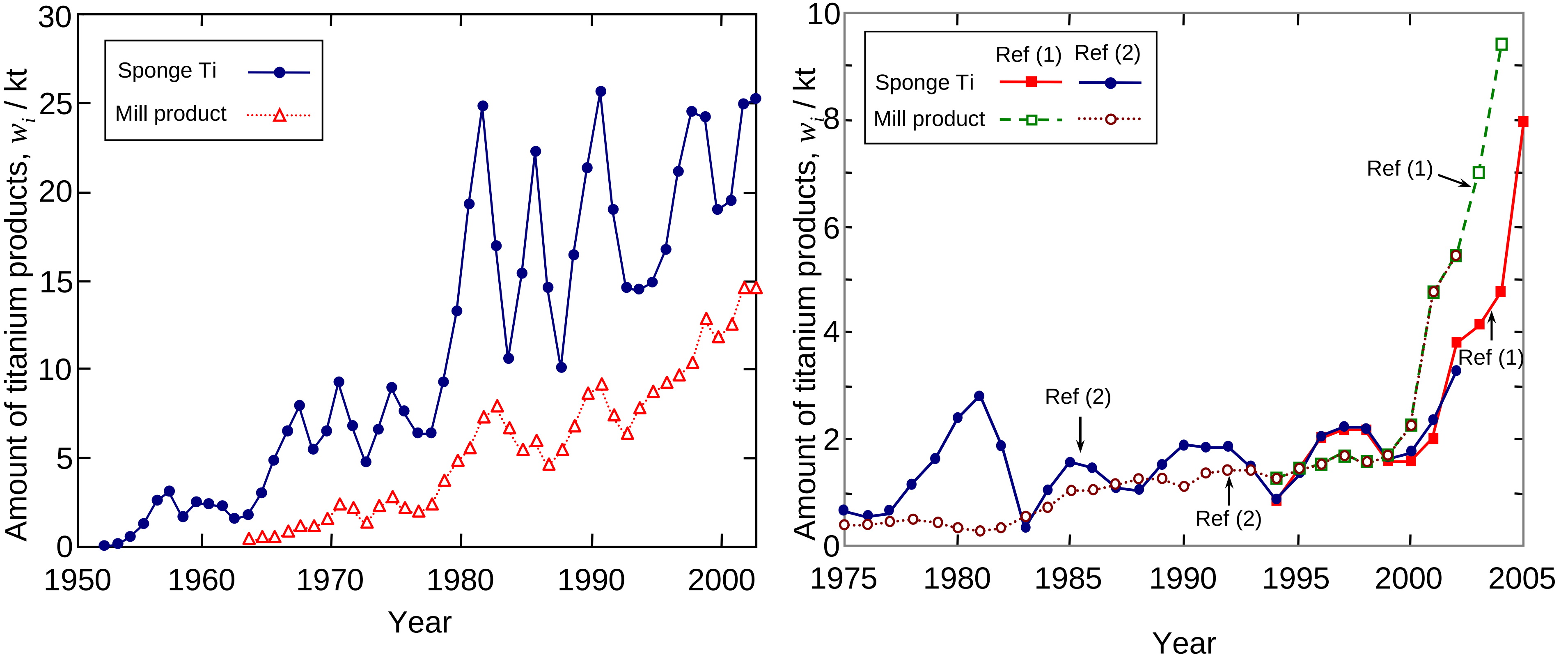
Titanium is the 10th most abundant element in the earth's crust

Rank	Element	Clark #.
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

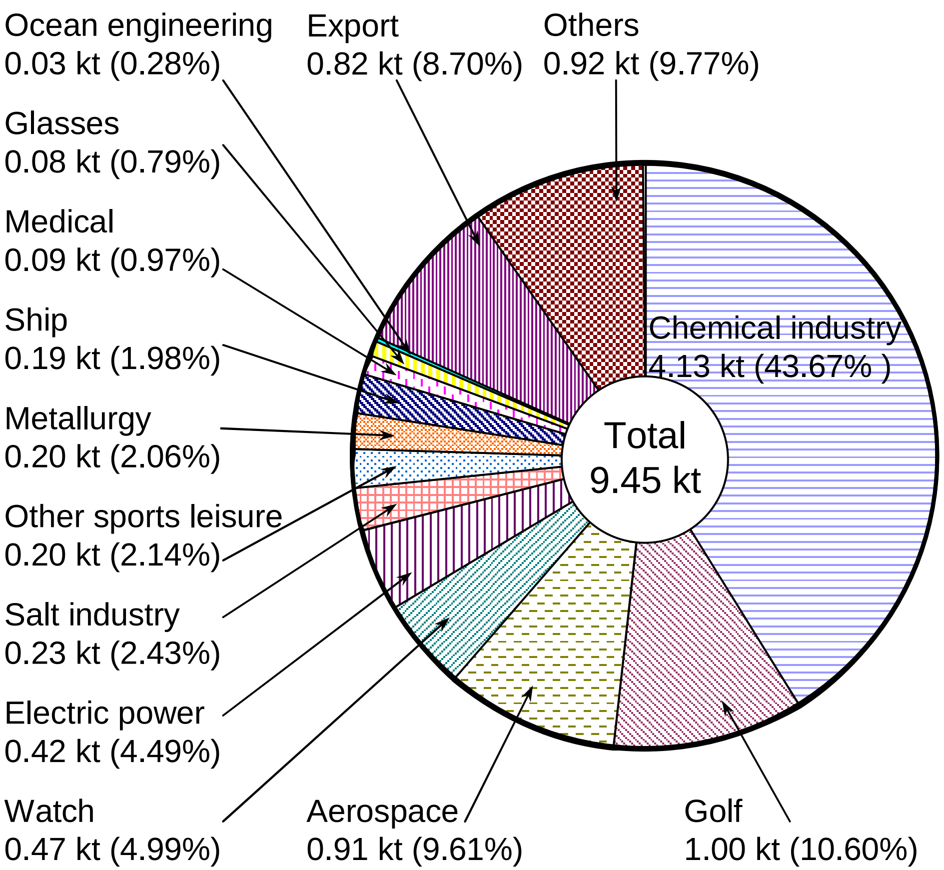
The tenth most abundant element

Rank	Element	Clark #.
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}

Exhausting element…

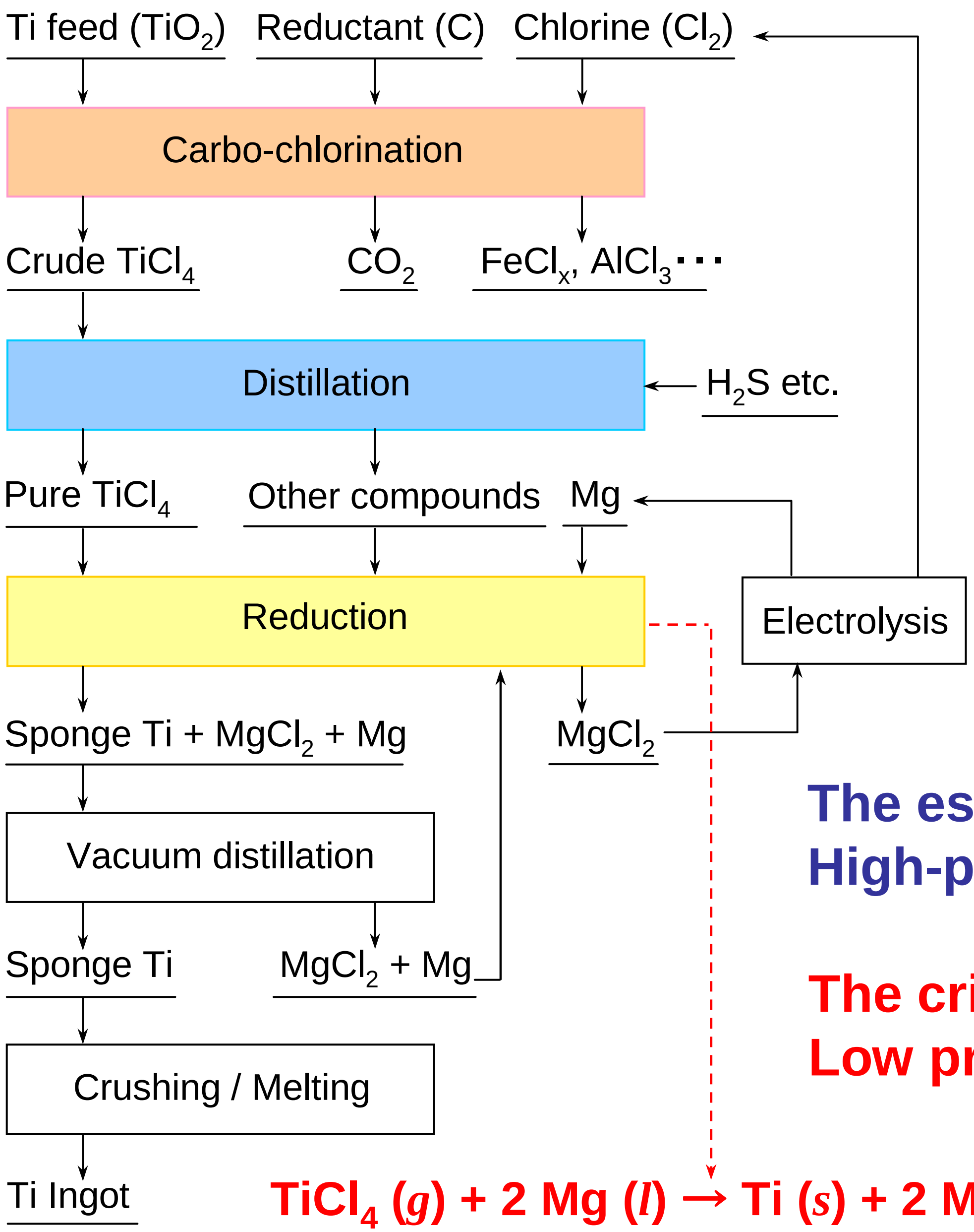


Transition of production volume of titanium sponge and mill products in China.
Ref(1): China Titanium Association (Courtesy of Mr. Akiyama, JTS)
Ref(2): China Titanium Association (H. Z., Private communication)



Shipments of titanium mill product in various field’s application in China (2004).

The Kroll process

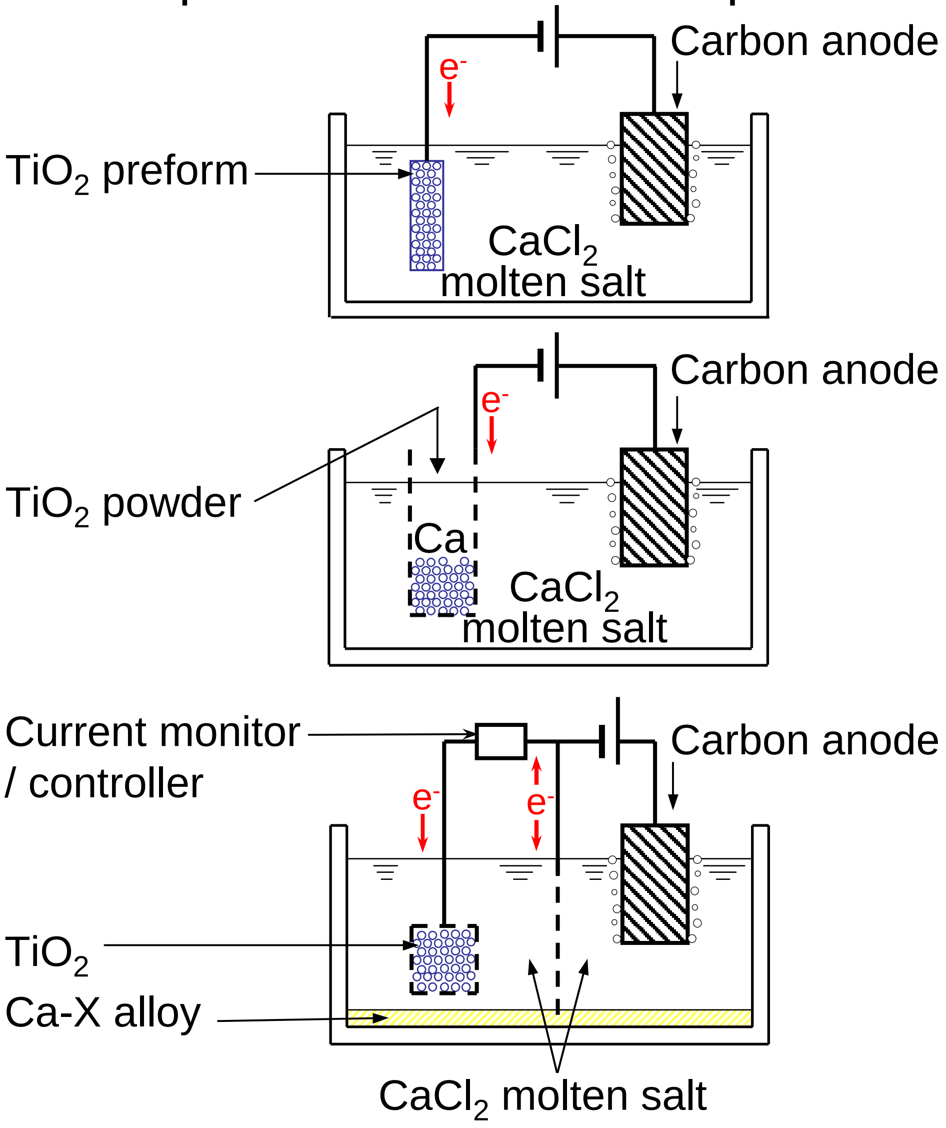


The essential advantage:
High-purity titanium available.

The critical disadvantage:
Low productivity.

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

Comparison of various new processes for titanium production



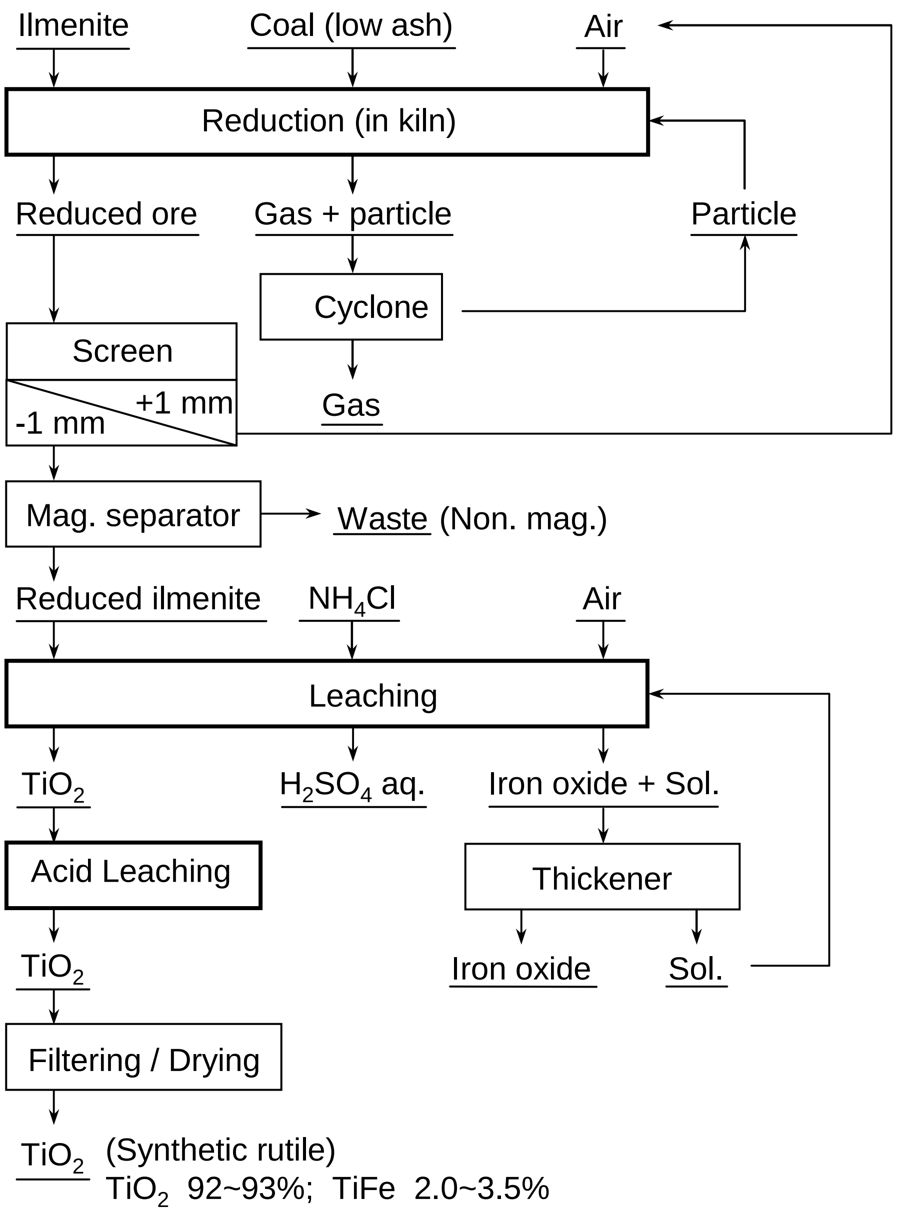
(a) FFC process

(b) OS process

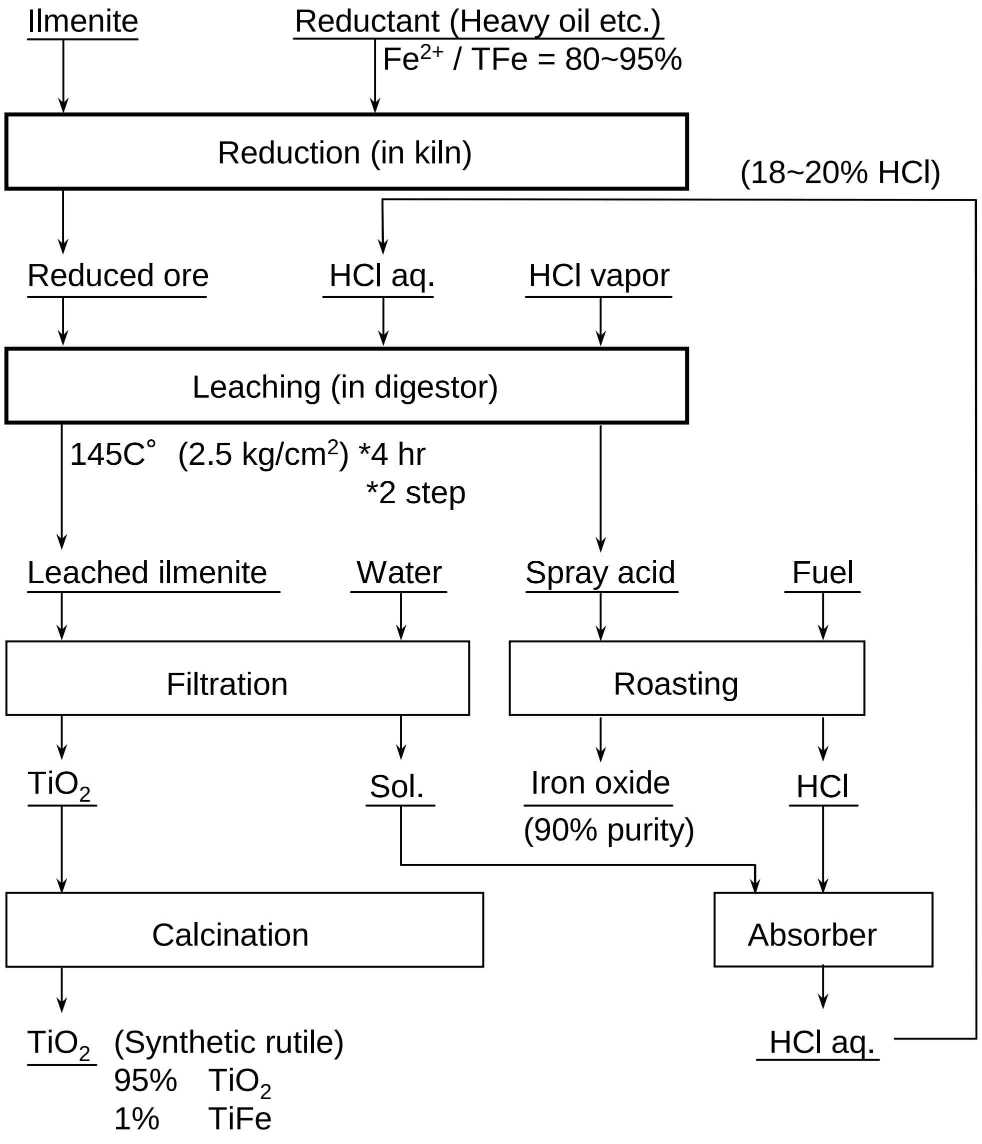
(c) EMR / MSE process (Oxide system

Fig. Comparison of various reduction processes of titanium oxide in molten calcium chloride medium.

Arial: 16



Flowchart of the Beacher process.



Ilmenite

Reductant (Heavy oil etc.)

Fe^{2+} / TFe = 80~95%

Reduction (in kiln)

(18~20% HCl)

Reduced ore

HCl aq.

HCl vapor

Leaching (in digestor)

145C° (2.5 kg/cm^2) *4 hr
*2 step

Leached ilmenite

Water

Spray acid

Fuel

Filtration

Roasting

TiO_2

Sol.

Iron oxide
(90% purity)

HCl

Calcination

Absorber

TiO_2 (Synthetic rutile)
95% TiO_2
1% TiFe

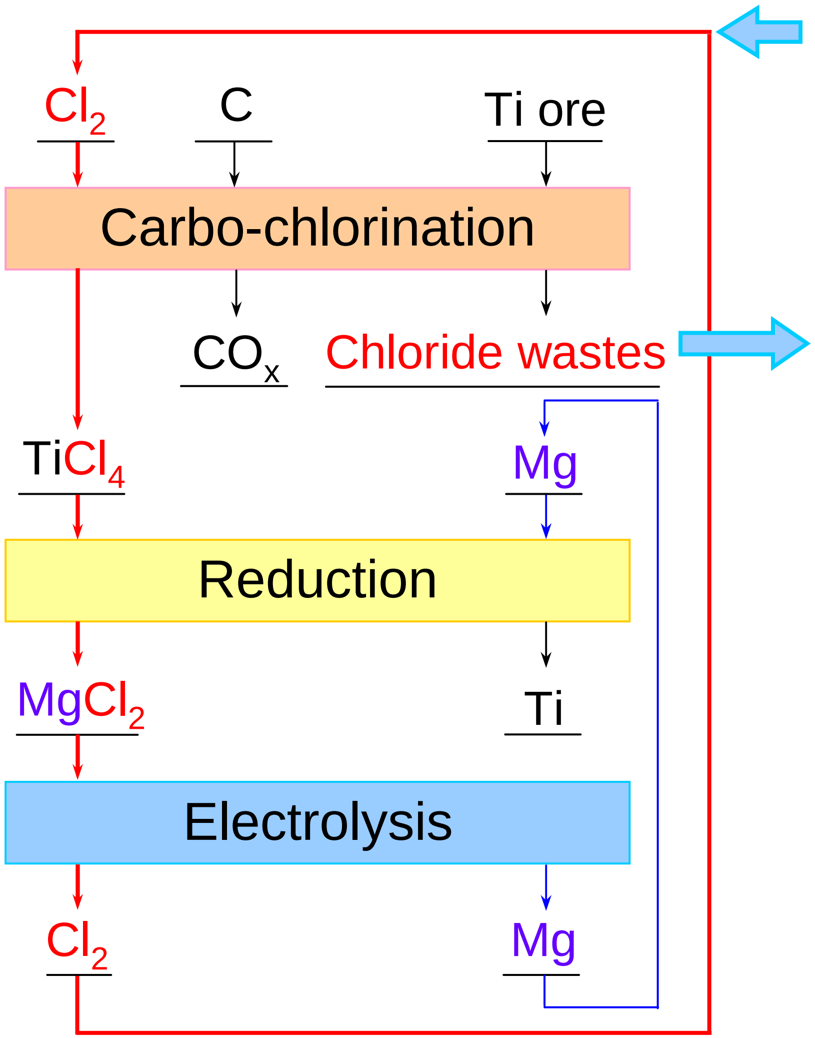
HCl aq.

Flowchart of the Benilite process.

Features of reductant and feed materials in metallothermic reduction process.

	$TiCl_4$	TiO_2
Mg	◎ Possible to remove Mg and $MgCl_2$ by distillation. Possible to efficiently eletrosis $MgCl_2$ Easy to control purity (strong contamination of carbon)	× Impossible to remove oxygen
Na	○ Difficult to remove Na Difficult to control the temperature Easy to purity control (strong resistance to Ni contamination)	× Impossible to remove oxygen
Ca	△ High enegy loss Difficult to remove Ca or $CaCl_2$ ？Cost of the reductant production	○ Difficult to purity control Difficult to remove Ca or $CaCl_2$ ？Cost of the reductant production
	↑ Process with strong resistace to Oxygen	

Chlorine cycle in the Kroll process



Cl_2 C Ti ore

Carbo-chlorination

CO_x Chloride wastes

$TiCl_4$ Mg

Reduction

$MgCl_2$ Ti

Electrolysis

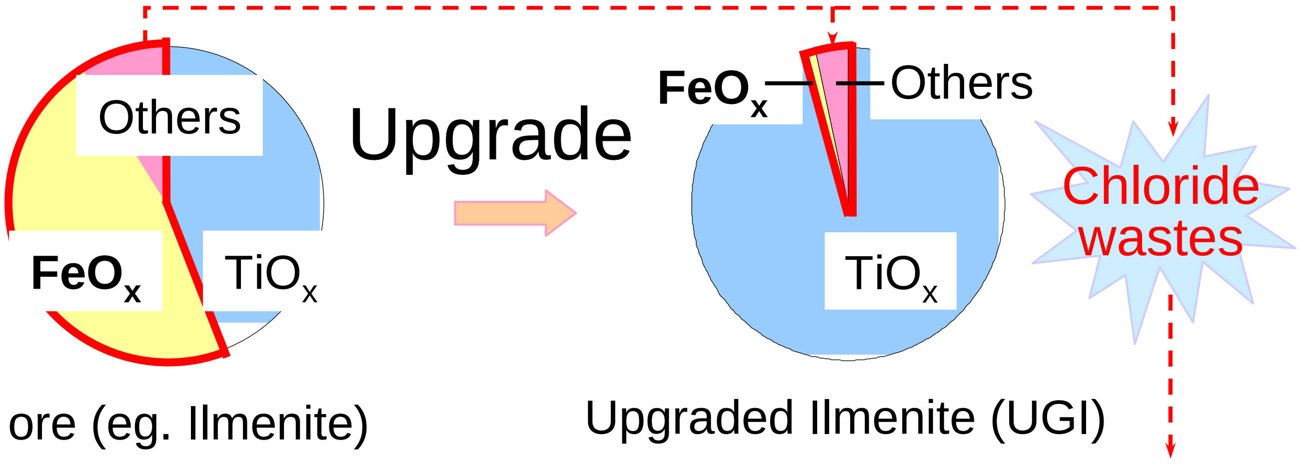
Cl_2 Mg

Additional Cl_2 supply to compensate for chlorine loss

Chlorine loss

Chlorine in the Kroll process is recycled, but the generation of chloride waste causes chlorine loss in the process.

Upgrading Ti ore for minimizing chloride wastes



Discarded

Problems:

When low-grade ore is used, a large amount of chloride wastes (e.g., $FeCl_x$) are generated in the Kroll process.
→ Disposal cost of chloride wastes
→ Environmental issues
→ Causes chlorine loss in the process

Current:

Currently expensive upgraded ore is used for reducing chloride waste and environmental burden.

Gibbs energy change

Table Gibbs energy change of formation and reaction in the Fe-Ti-O system.

Reactions	Gibbs energy change, ΔG^{o}_{f} or ΔG^{o}_{r} (kJ/mol)				Ref.
	1100 K	1200 K	1300 K	1273 K^{a}	
Fe (*s*) + 0.5 O_2 (*g*) = FeO (s)	-200.709	-194.362	-187.999	-189.717	1
	-192.476	-185.817	-179.133	-180.937	2
	-200.670	-271.184	-270.265	-189.667	4
	-190.021	-183.792	-177.563	-179.244	8
Ti (*s*) + O_2 (*g*) = TiO_2 (*s*)	-744.912	-727.229	-709.392	-714.208	1
	-745.367	-727.312	-709.436	-714.262	2
	-744.807	-727.113	-709.265	-714.084	4
	-742.567	-724.883	-707.200	-711.975	7
	-717.417	-700.250	-683.083	-687.718	8
Fe (*s*) + Ti (*s*) + 1.5 O_2 (*g*) = $FeTiO_3$ (*s*)	-956.608	-931.690	-906.600	-913.374	1
2 Fe (*s*) + Ti (*s*) + 2 O_2 (*g*) = Fe_2TiO_4 (*s*)	-1164.697	-1133.483	-1102.214	-1110.66	1
	-1164.870	-1133.57	-1102.23	-1110.69	2
TiO_2 (*s*) + Fe (*s*) + 0.5 O_2 (*g*) = $FeTiO_3$ (*s*)	-211.696	-204.461	-197.208	-199.166	1
				-202.3	5
	-209.946	-204.558	-199.171	-200.625	8
TiO_2 (*s*) + 2 Fe (*s*) + O_2 (*g*) = Fe_2TiO_4 (*s*)	-417.785	-406.254	-392.822	-396.452	1
	-419.503	-406.258	-392.794	-396.428	2
				-393.2	5
TiO_2 (*s*) + FeO (*s*) = $FeTiO_3$ (*s*)	-10.987	-10.099	-9.209	-9.449	1
	-26.462	-25.05	-24.638	-24.749	3
	-17.829	-18.955	-20.081	-19.777	6
	-20.042	-18.833	-17.625	-17.951	7
				-12.6	1, 5
				-21.4	2, 5
				-12.6	4, 5
				-23.1	5, 8
				-21.381	8
TiO_2 (*s*) + 2 FeO (*s*) = Fe_2TiO_4 (*s*)	-18.367	-17.53	-17.022	-17.018	1
	-34.551	-34.707	-34.528	-34.554	2
				-13.8	1, 5
				-31.3	2, 5
				-13.9	4, 5
				-34.7	5, 8

a: interpolated

References

[1] I. Barin, Thermochemical Data of Pure Substances, 3rd ed., (Weinheim, Federal Republic of Germany, VCH Verlagsgesellschaft mbH, 1997).

[2] Outokumpu HSC Chemistry® for Windows, Version 5.0, (Finland, Outokumpu Research Oy Information Service, 2002).

[3] O. Knacke, O. Kubaschewski, and K. Hesselmann, Thermochemical Properties of Inorganic Substances, 2nd ed., (Berlin, Federal Republic of Germany, Springer-Verlag, 1991).

[4] NIST-JANAF Thermochemical Tables 4th ed., U.S. Bureau of Standards (1998).

[5] S. Ito, Phase Equilibria of the Titanium-Iron-Oxygen system as 1,273 K on Titanium Extraction Processing, (Journal of the Mining and Materials Processing Institute of Japan (Vol. 112, p.867-972, 1996).

[6] J. S. J. Van Devender, Kinetics of Selective Chlorination of ilmenite, (Thermochimica Acta, vol. 124, p. 205-215, 1988).

[7] Special Lecture for the Process Design of the Recycling Material, Distributed Documents, (Summer term, 2003)

[8] O. Kubaschewski, High Temp. High pressures 4.1 (1972).

a: Interpolated

TiO_x + FeO = $Ti_xFe_yO_z$

ΔG_r = -30 ~ -9 kJ / mol

Table Starting materials used in this study.

Materials	Form	Purity or conc. (%)	Note / Supplier
Rutile[a]	Powder	93.1[c]	Produced in South Africa.
$CaCl_2$	Powder	95.0 up	Kanto Chemicals., Inc.
Collodion[b]	Aqueous	5.0[d]	Wako Pure Chemical Industries, Ltd.
Ca	Chip	98.0 up	Mintech Japan K. K.
Ti	Sponge	98.0 up	Toho Titanium Co., Ltd.
CH_3COOH	Aqueous	99.7 up	Kanto Chemicals., Inc.
HCl	Aqueous	35.0[d]	Kanto Chemicals., Inc.
2-Propanol	Liquid	99.5 up	Wako Pure Chemical Industries, Ltd.
Acetone	Liquid	99.0 up	Wako Pure Chemical Industries, Ltd.

[a] Natural rutile ore produced in South Africa.
[b] 5 mass% nitro cellulose, 23.75 mass% ethanol, 71.25 mass% diethylether.
[c] Purity of TiO_2 in the ore.
[d] Concentration of the solution.

Ito-san

Table Titanium ore used in this study.

Sample	Concentration of element *i*, C_i (mass%)[a]											Note
	Ti	Si	Nb	Al	Fe	V	Cr	Mn	Ca	Mg	Ni	
UGI[b]	95.47	0.45	0.54	0.13	1.87	1.46	ND[d]	0.03	ND[d]	0.07	ND[d]	040524
	95.85	0.37	0.62	0.04	2.04	1.04	ND[d]	0.05	ND[d]	ND[d]	ND[d]	040721
Rutile[c]	93.10	1.58	0.62	0.66	2.27	1.42	ND[d]	0.16	0.01	0.16	0.03	040524
	93.55	1.05	0.64	0.35	1.32	1.72	1.29	ND[d]	0.09	ND[d]	ND[d]	040721

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

b : Up-graded ilmenite produced in India by the Beacher process.

c : Natural rutile ore produced in South Africa.

d : Not detected. Below detection limit of XRF (<0.01%).

Table 3-1 Analytical results of obtained titanium powder by preform reduction process using UGI[a].

Exp. #	Flux	Cationic molar ratio, $R_{\mathrm{Cat.\,/\,Ti}}$[b]	Reduction temp., $T_{\mathrm{red.}}$ / K	Concentration of element i, C_i (mass%)[c]					Note
				Oxgen, C_{O}	Aluminum, C_{Al}	Calcium, C_{Ca}	Titanium, C_{Ti}	Iron, C_{Fe}	
A-1	$CaCl_2$	0.2	1273	(0.00)	0.40	0.11	98.94	0.57	040510_$CaCl_2$_Ca_1273_6h_11-1
A-2	$CaCl_2$	0.3	1273	(0.00)	0.25	0.12	99.41	0.22	040510_$CaCl_2$_Ca_1273_6h_5-2
A-3	$CaCl_2$	0.3	1273	(0.00)	0.17	0.10	99.24	0.50	040510_$CaCl_2$_Ca_1273_6h_6-1
A-4	$CaCl_2$	0.2	1273	0.13	0.13	0.92	98.58	0.32	Refer Mashimo's data[d].
A-5	$CaCl_2$	0.2	1273	(0.00)	0.19	0.11	99.70	0.01	Refer Mashimo's data[d].
A-6	$CaCl_2$	0.3	1273	(0.00)	0.24	0.03	99.60	0.13	Refer Mashimo's data[d].
A-7	$CaCl_2$	0.3	1273	(0.00)	0.19	0.04	99.71	0.08	Refer Mashimo's data[d].

a : Up-graded ilmenite produced in India by the Beacher process (See Table 2-2).

b : Cationic molar ratio, $R_{\mathrm{Cat.\,/\,Ti}} = N_{\mathrm{Cat.}} / N_{\mathrm{Ti}}$, where $N_{\mathrm{Cat.}}$ and N_{Ti} are mole amount of flux and of titanium, respectively.

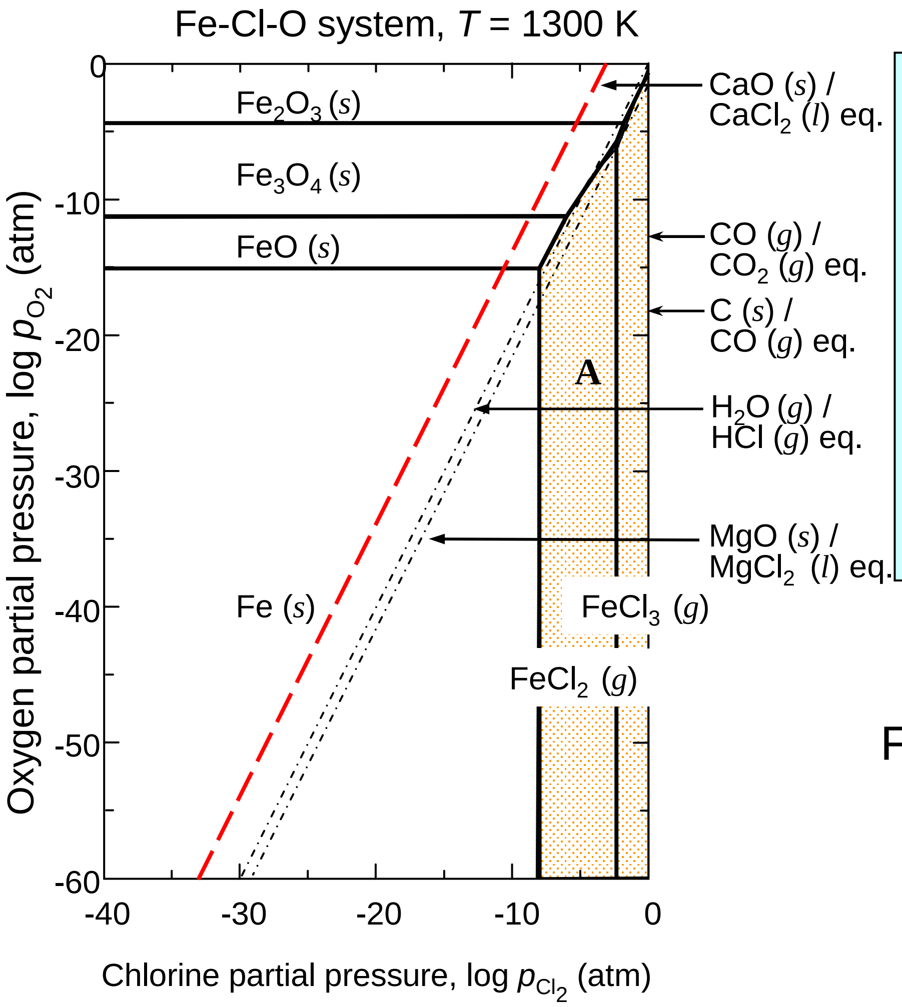
c : Analyzed by EDS. Values in parenthesis are listed for reference.

d : Yuichi. Mashimo, Bachelor thesis, Chiba Institute of Technology (2004).

Properties of $TiCl_x$

	$TiCl_4$	$TiCl_3$	$TiCl_2$
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	425	1035
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}

Mechanism of iron removal (FeO_x chlorination)



Ⅰ:

$$H_2O\ (g) + CaCl_2\ (l) \rightarrow 2\ HCl\ (g) + CaO\ (s)$$

$$FeO_x\ (FeTiO_x,\ s) + HCl\ (g) \rightarrow FeCl_2\ (l,\ g) + H_2O\ (g)$$

Ⅱ:

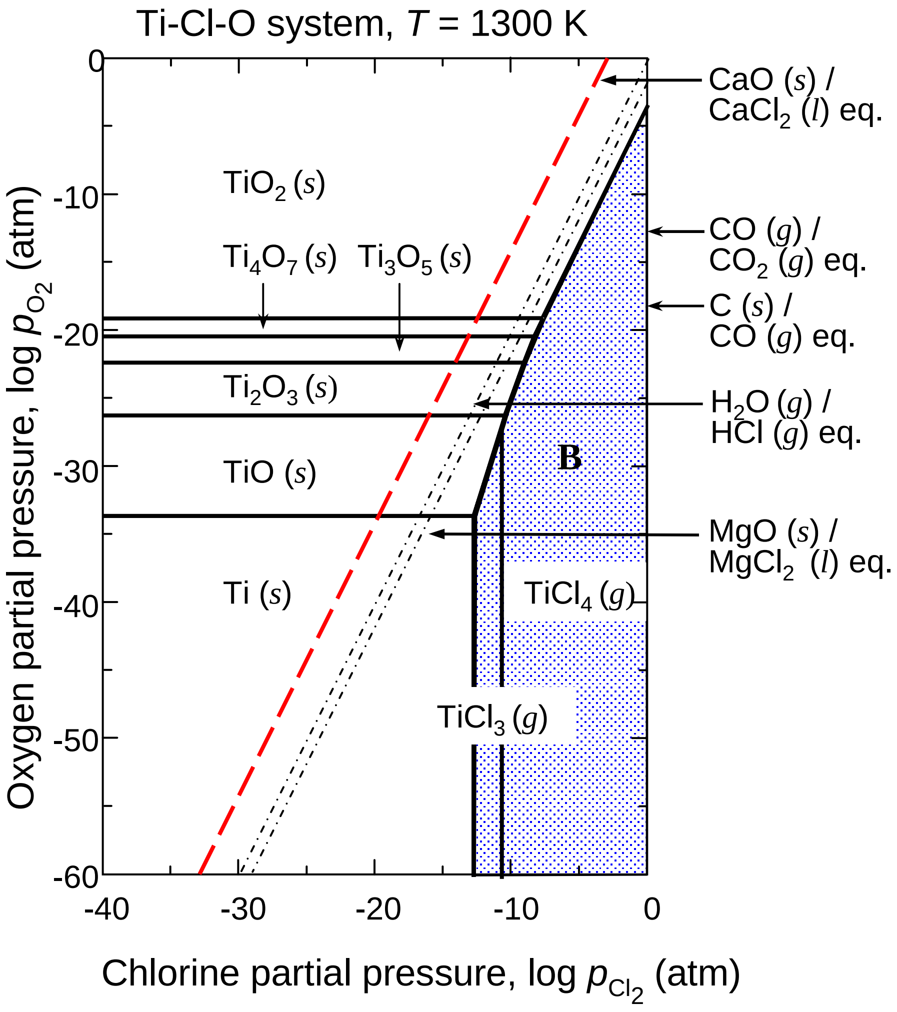
$$FeO_x\ (FeTiO_x,\ s) + CaCl_2\ (l) \rightarrow FeCl_x\ (g) + \underline{CaO\ (CaTiO_x,\ s)}$$

$$a_{CaO} << 1$$

FeO_x can be chlorinated using $CaCl_2$ + H_2O.

Fig. Chemical potential diagram of the Fe-Cl-O system at 1300 K.

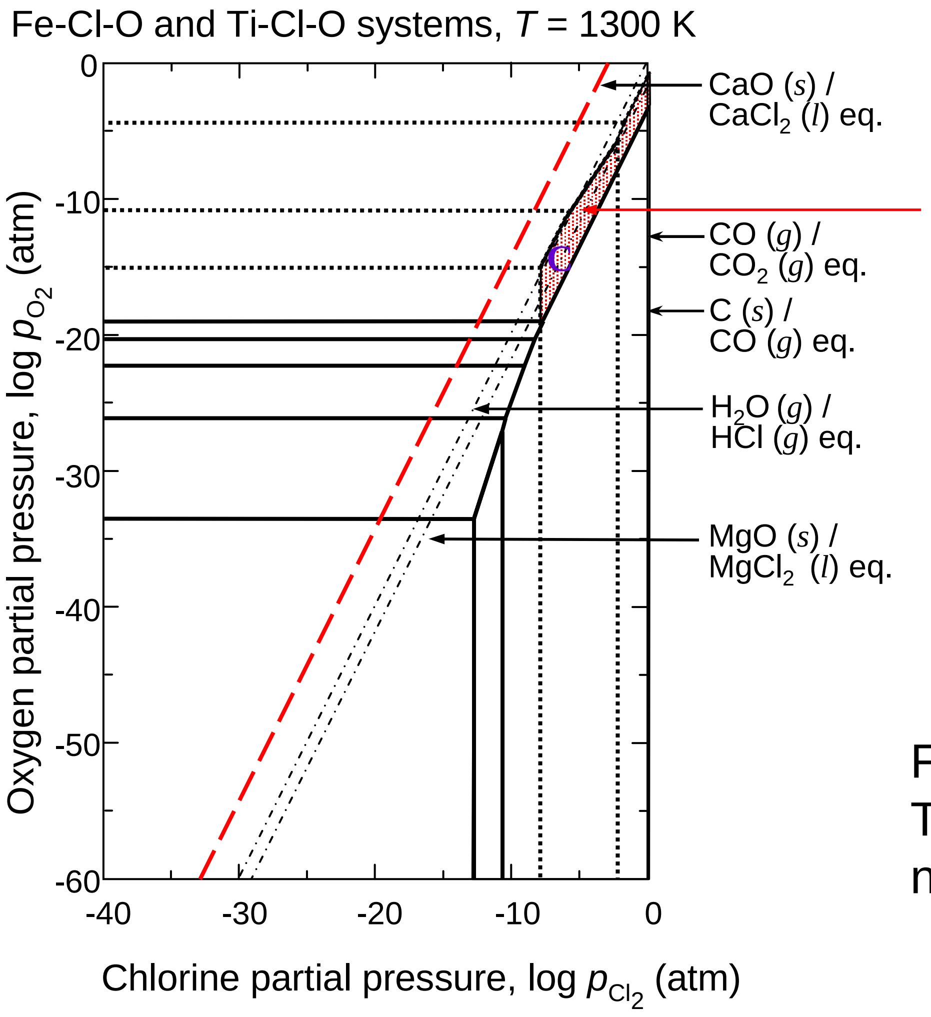
Mechanism of iron removal (TiO_x chlorination)



TiO_x can not be chlorinated using $CaCl_2$, nor $CaCl_2$+H_2O.

Fig. Chemical potential diagram of the Ti-Cl-O system at 1300 K.

Mechanism of iron removal Ti ore chlorination



$$\mathrm{FeO}_x\ (\mathrm{FeTiO}_x,\ s) + \mathrm{HCl}\ (g) \rightarrow \mathrm{FeCl}_x\ (g)\uparrow + \mathrm{H_2O}\ (g)$$

$$\mathrm{FeO}_x\ (\mathrm{FeTiO}_x,\ s) + \mathrm{CaCl_2}\ (l) \rightarrow \mathrm{FeCl}_x\ (g)\uparrow + \underset{a_{\mathrm{CaO}} \ll 1}{\underline{\mathrm{CaO}\ (\mathrm{CaTiO}_x,\ s)}}$$

⇩

FeO_x can be chlorinated using $CaCl_2$+H_2O.
TiO_x can not be chlorinated using $CaCl_2$, nor $CaCl_2$+H_2O.

Fig. Combined chemical potential diagram of the Fe-Cl-O (dotted line) and Ti-Cl-O (solid line) systems at 1300 K.

Mechanism of iron removal Ti ore chlorination

Fe-Cl-O and Ti-Cl-O systems, *T* = 1300 K

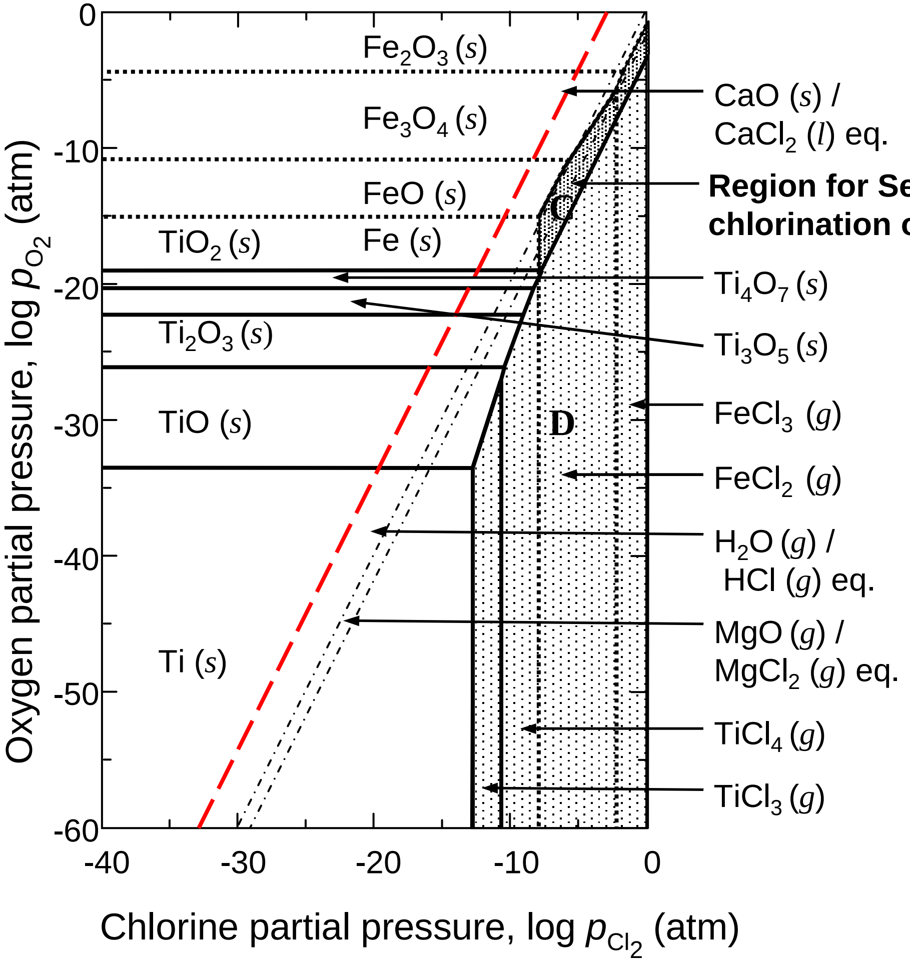
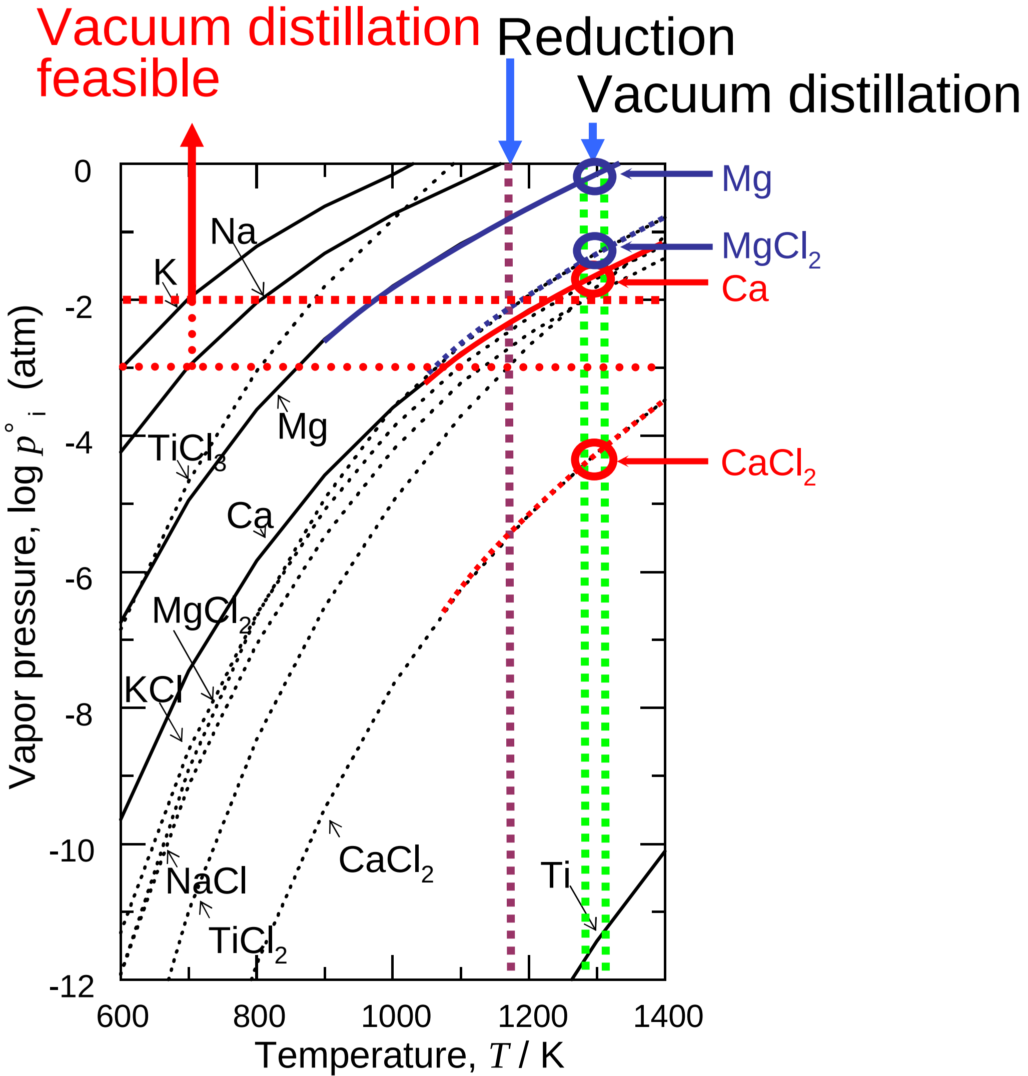


Fig. Combined chemical potential diagram of the Fe-Cl-O (dotted line) and Ti-Cl-O (solid line) systems at 1300 K.

FeO_x ($FeTiO_x$, *s*) + HCl (*g*)
$\rightarrow FeCl_x(g)\uparrow + H_2O(g)$
FeO_x ($FeTiO_x$, *s*) + $CaCl_2$ (*l*)
$\rightarrow FeCl_x(g)\uparrow + \underline{CaO\ (CaTiO_x,\ s)}$
$a_{CaO} << 1$

FeO_x can be chlorinated using $CaCl_2$+H_2O.
TiO_x can not be chlorinated using $CaCl_2$, nor $CaCl_2$+H_2O.

Temperature Dependence of vapor pressure of some chlorides, e.g. Mg and Ca



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

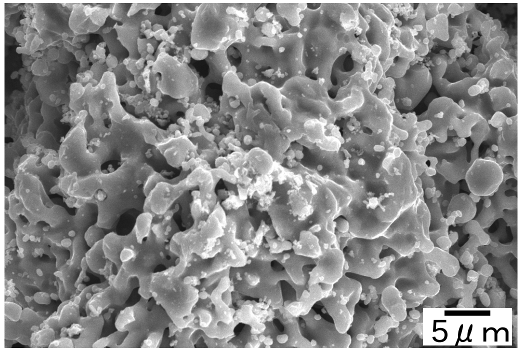
Experimental results: XRD, SEM images, and XRF

Exp. D, Cationic molar ratio, R = 0.3, Carbon powder: 0.2 g

After leaching

XRD analysis
未完成！

SEM images



Step	XRF analysis (mass %)				
	Ti	**Fe**	Al	Ca	Cl
(a) After fabrication	56.83	**0.77**	0.18	15.19	27.03
(b) After calcination	49.51	**0.30**	0.19	18.39	31.61
(c) After reduction	20.56	**0.09**	(0.00)	65.65	13.65
(d) After leaching	98.00	**0.18**	0.86	0.97	(0.00)

Iron removal ratio is 61 %

Composition and yields of the obtained Ti product

Exp. C and D

Table Analytical results of the titanium samples obtained after leaching.

Exp.	Cationic molar ratio $R_{\text{Ca/Ti}}$	Concentration of element i in obtained Ti powder, C_i (mass %)					Yield (%)
		Ti	Fe	Al	Ca	Cl	
C	0.2	98.23	0.23	0.56	0.98	(0.00)	79.02
D	0.3	98.00	0.18	0.86	0.97	(0.00)	92.07

[a] Natural rutile ore produced in South Africa after pulverization.

[b] Cationic molar ratio, $R_{\text{Cat. / Ti}} = N_{\text{Cat.}} / N_{\text{Ti}}$, where $N_{\text{Cat.}}$ and N_{Ti} are mole amount of cation in flux and that of titanium, respectively.

UGI

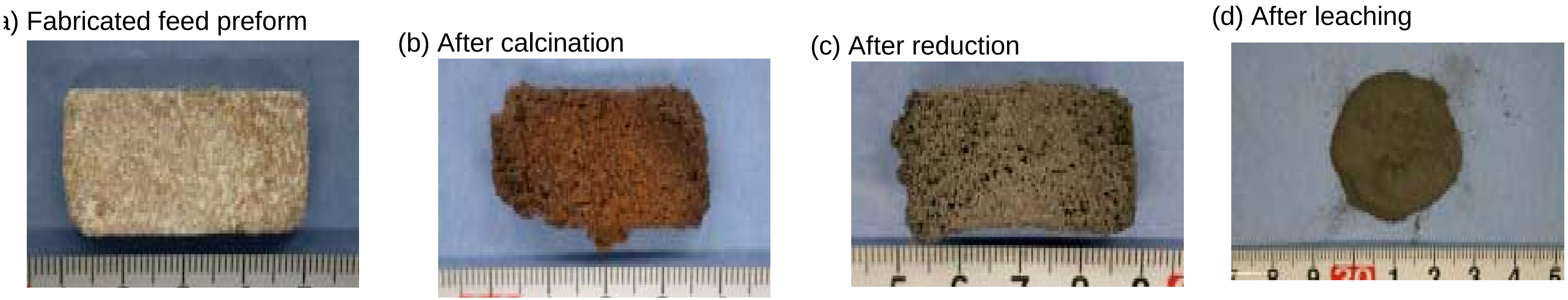
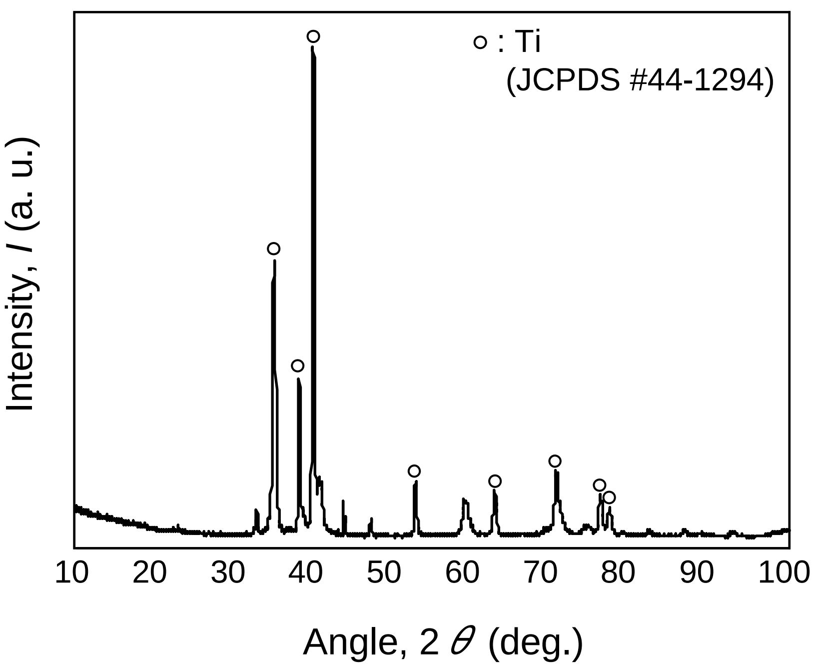
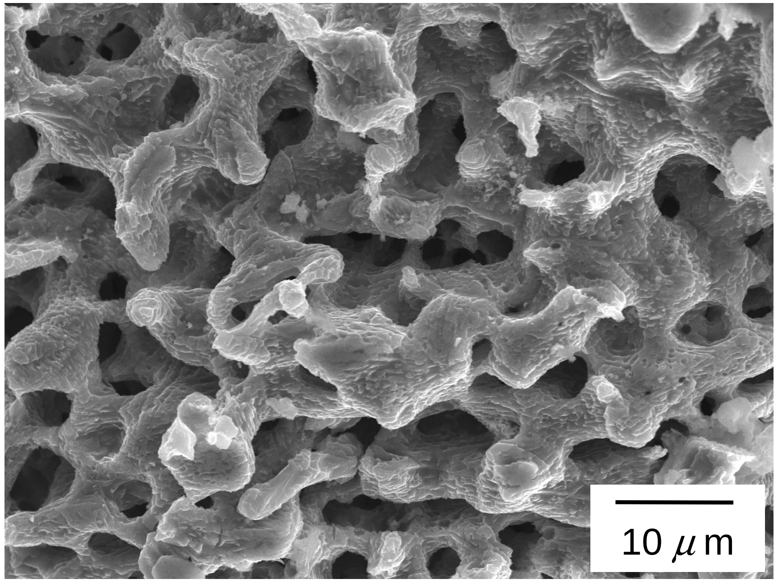

a) Fabricated feed preform
(b) After calcination
(c) After reduction
(d) After leaching

Figure 7: (a) Fabricated platy feed preform. (Flux: $CaCl_2$, Binder: Collodion)
(b) After calcination. (Temp.: $T_{cal.}$ = 1273 K, holding time: $t'_{cal.}$ = 1 h.)
(c) After reduction. (Temp.: $T_{red.}$ = 1273 K, holding time: $t'_{red.}$ = 6 h.)
(d) Titanium powder obtained after leaching. Ito-san

(a)



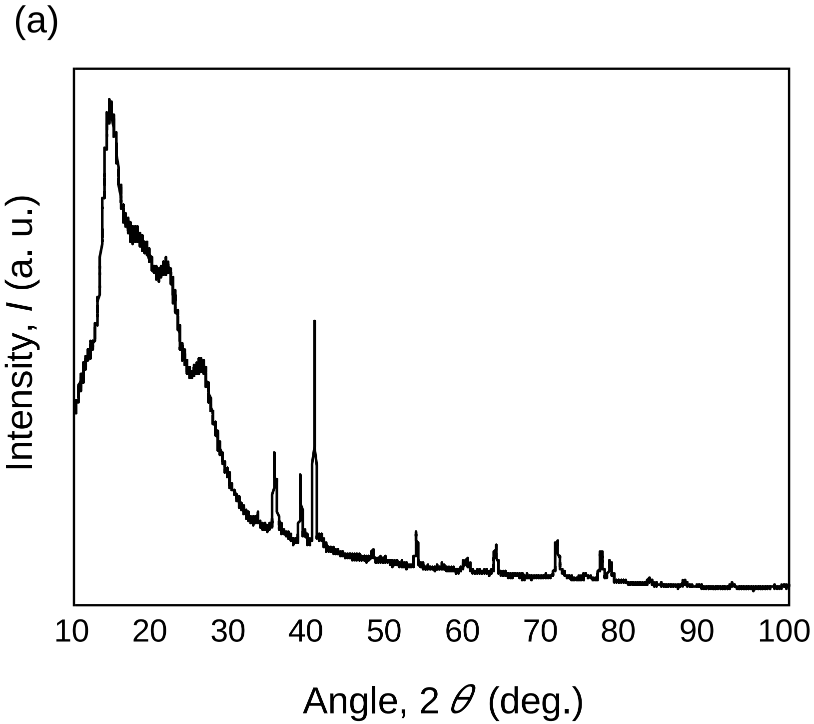
(b)

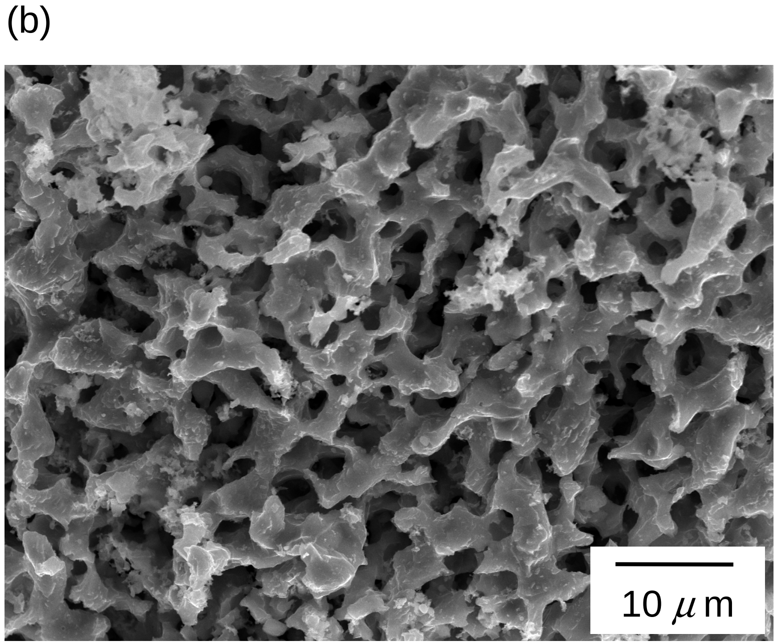


Ti	Fe	Ca	Al	O
99.20	0.02	0.42	0.36	n.d.

Ti powder

Figure (a) XRD pattern of titanium powder obtained by PRP
(b) Scanning electron microscopic image and EDS
(E_1_1_2)

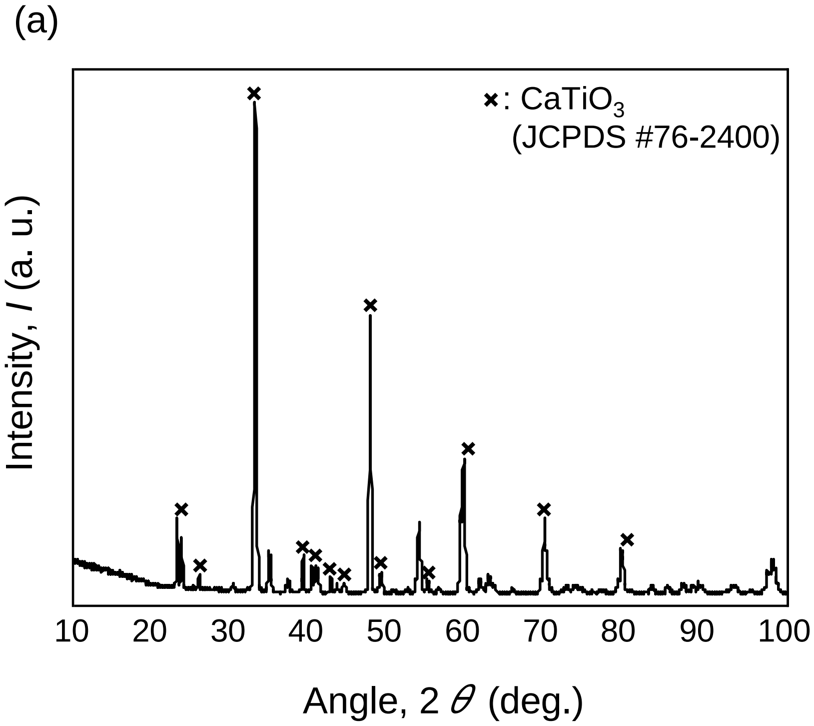


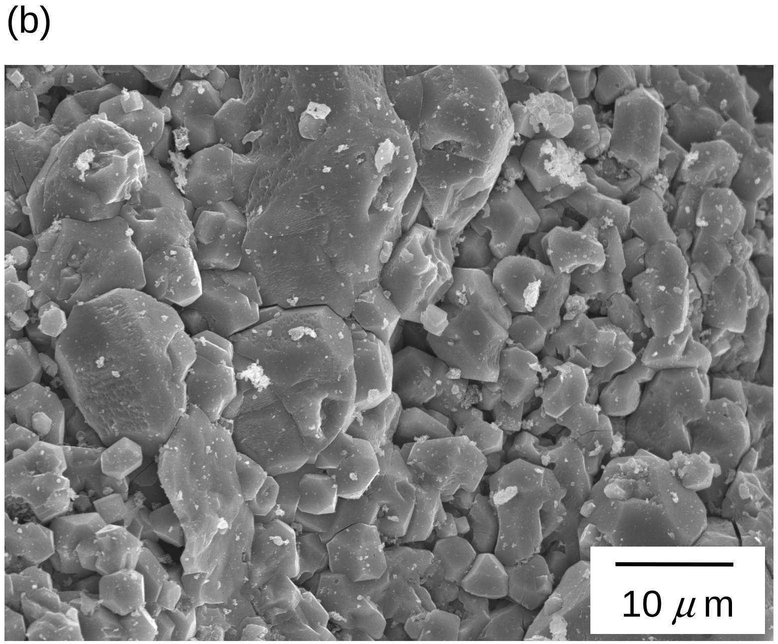


Ti	Fe	Ca	Al	O
99.59	n.d.	0.44	0.30	n.d.

Ti powder

Figure (a) XRD pattern of titanium powder obtained by PRP
(b) Scanning electron microscopic image and EDS
(E_2_1_2_rutile)

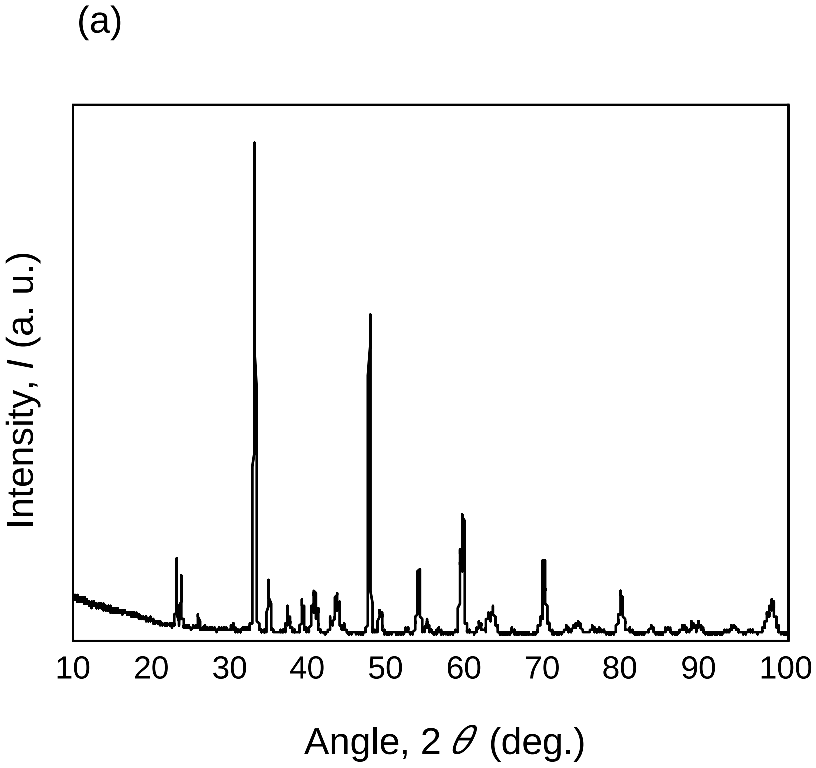


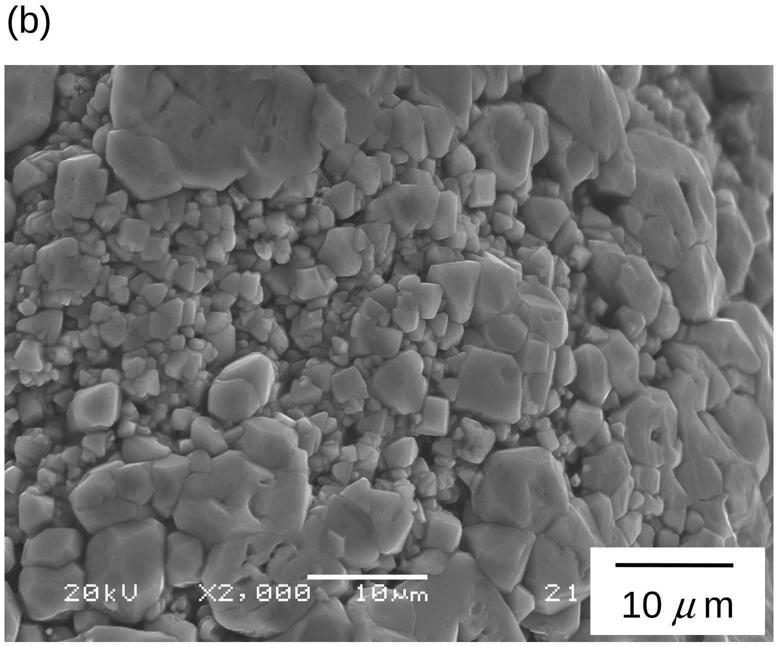


Ti	Fe	Ca	Al	O
29.03	0.27	28.83	0.84	41.04

$CaTiO_3$

Figure (a) XRD pattern of titanium powder obtained by PRP
(b) Scanning electron microscopic image and EDS
(E_5_1_2_ilmenite)

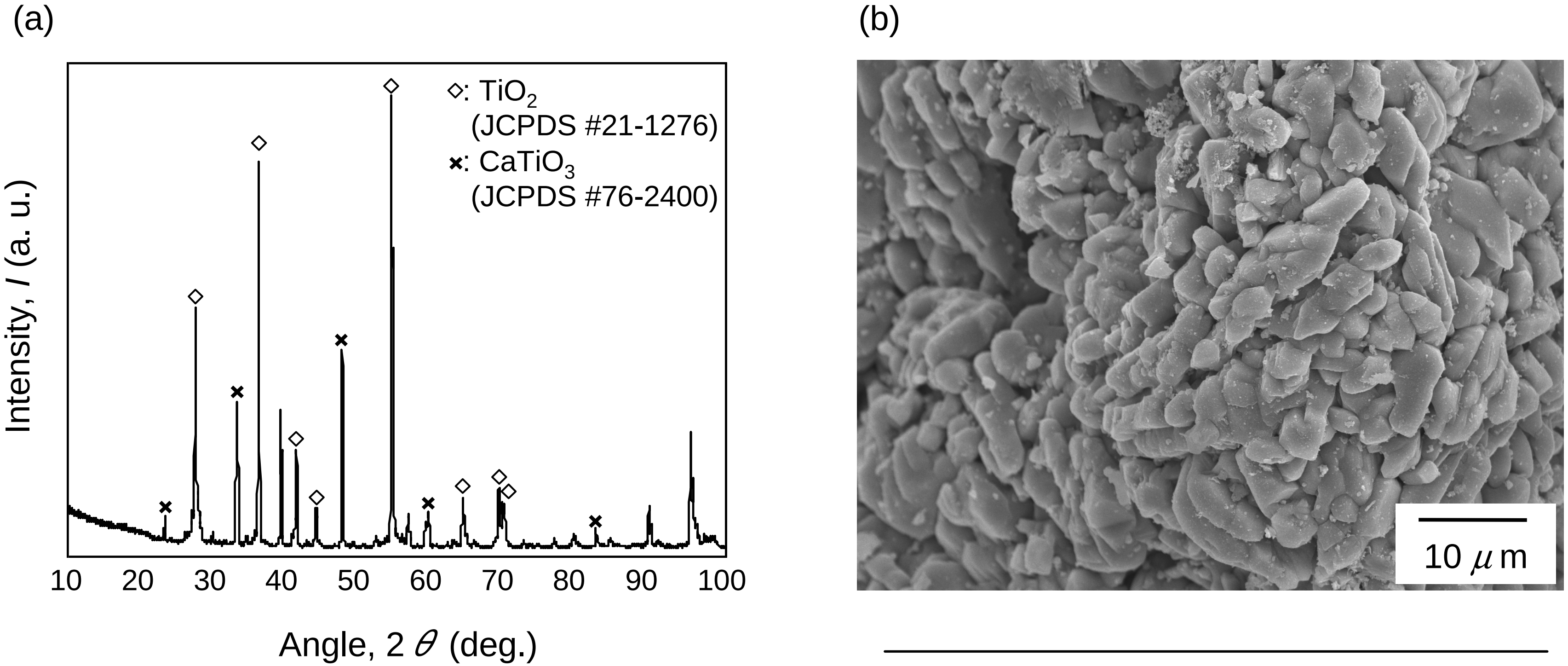




Ti	Fe	Ca	Al	O
28.26	0.23	26.94	0.51	44.06

$CaTiO_3$

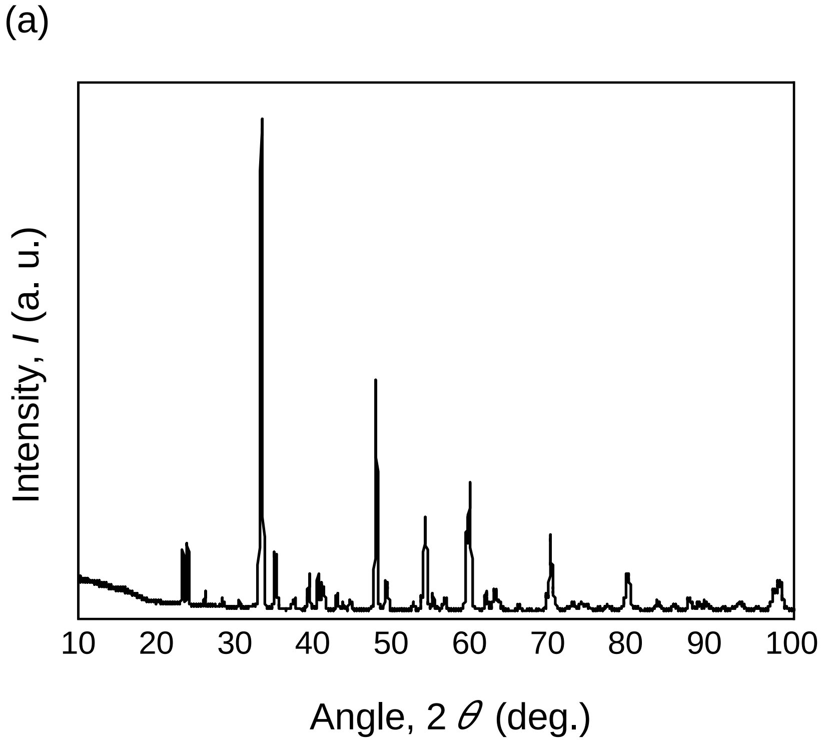
Figure (a) XRD pattern of titanium powder obtained by PRP
(b) Scanning electron microscopic image
(B_2_1_1_rutile)

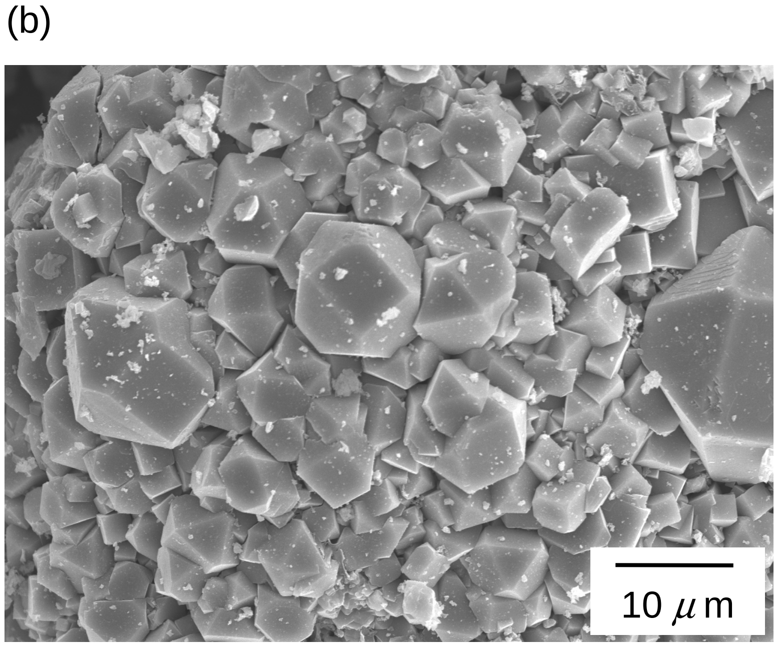


Ti	Fe	Ca	Al	O
55.21	n.d.	4.79	6.24	33.77

TiO_2

Figure (a) XRD pattern of titanium powder obtained by PRP
(b) Scanning electron microscopic image
(E_6_1_1_ilmenite)



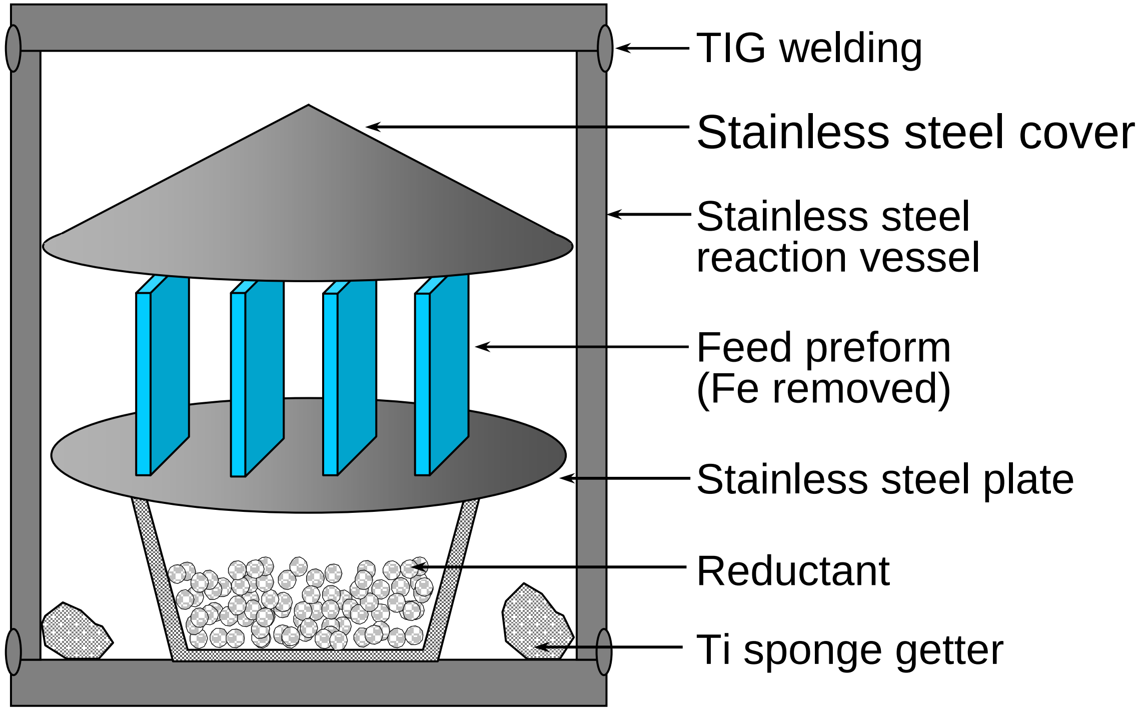


Ti	Fe	Ca	Al	O
33.24	n.d.	28.45	0.42	37.89

$CaTiO_3$

Figure (a) XRD pattern of titanium powder obtained by PRP
(b) Scanning electron microscopic image
(B_1_1_2_rutile?)

Reduction Experimental



Schematic illustration of the experimental apparatus for reduction.

Materials: Preform (Mixture of Ti ore, $CaCl_2$ and Binder)
T: 1273 K
t': 6 h
Reductant: Ca shot

Arial: 16

Starting Materials

Sample name	Concentration of element *i*, C_i (mass%)[a]										XRF file name
	Al	Si	Ca	Ti	V	Cr	Mn	Fe	Ni	Nb	
ilmenaite[b]	1.60	2.30	0.10	47.62	0.56	n.d.	1.78	45.49	0.03	n.d.	04070101
ilmenaite[c]	0.75	2.19	n.d.	44.46	0.36	n.d.	3.43	48.38	n.d.	0.21	04070103
Haiyan's analysis	0.07	0.44	n.d.	43.83	0.36	n.d.	3.77	51.34	0.04	0.15	
UGI[d]	0.05	0.42	0.03	94.68	1.02	n.d.	1.30	1.96	n.d.	0.52	04072111
UGI[e]	0.04	0.36	n.d.	95.84	1.04	n.d.	0.05	2.03	n.d.	0.62	04072110

a: Value determined by XRF analysis, n.d.notes not detected (below 0.01 mass%).

b: Natural ilmenite ore produced in Australia.

c: Natural ilmenite ore produced in Viet Nam.

d: Up-graded ilmenite by the Beacher process. The ore was produced in Australia.

e: Up-graded ilmenite by the Benilite process. The ore was produced in India.

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