Direct Production of Titanium Powder from Titanium Ore by Preform Reduction Process

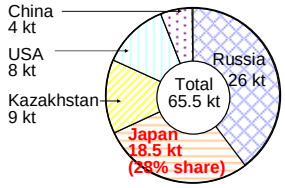
Haiyan Zheng [1*] and Toru H. Okabe [1]

1 Institute of Industrial Science, University of Tokyo, * Graduate Student

Introduction

Current status of industrial production of Ti

World production of Ti sponge (2003)



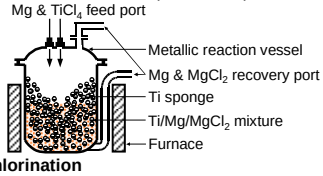
Comparison with common metals

Metal	Iron	Aluminum	Titanium
Symbol	Fe	Al	Ti
Melting point (K)	1809	933	1939
Density (g/cm³ at 298 K)	7.9	2.7	4.5
Specific strength ((kgf/mm²)/(g/cm³))	4~7	3~6	8~10
Clarke no.	4	3	9
Price (¥/kg)	50	600	3000
Production volume (t/world in 2003)	9.6×10^8	2.2×10^7	6.6×10^4

1/300, 1/15000

The Kroll process

Current commercial Ti production process



Chlorination

$Ti\ ore + C + 2\ Cl_2 \rightarrow TiCl_4\ (+ MCl_x) + CO_2$

Reduction

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

Electrolysis

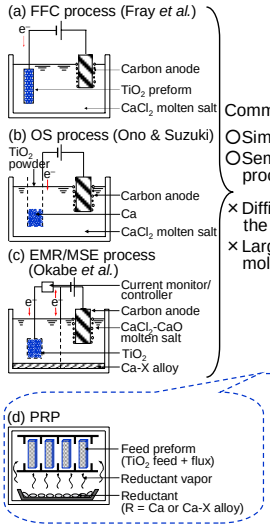
$MgCl_2 \rightarrow Mg + Cl_2$

Features of the Kroll process:

◎High-purity Ti can be obtained.
◎Metal/salt separation is simple.
○Chlorine circulation is established.
○Efficient Mg electrolysis can be utilized.
○Reduction and electrolysis can be carried out independently.
× Process is complicated.
× Reduction process is batch type.
× Production speed is low.
× Chloride wastes are produced.

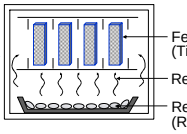
⇨ Production cost of Ti is high and its application is limited.

Direct reduction of TiO_2



Common features:
○Simple process
○Semi-continuous process
× Difficult to control the purity
× Large amount of molten salt

Preform reduction process (PRP)



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

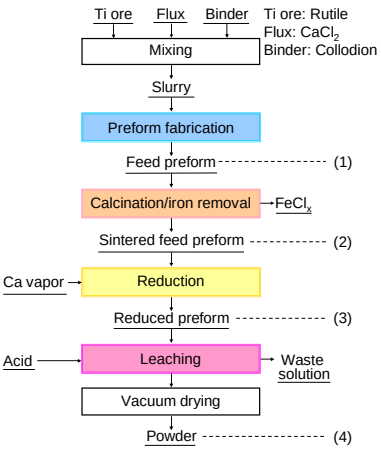
Features: ➞ **Simple and low-cost process**
◎Suitable for uniform reduction
◎Flexible scalability
○Possible to control the morphology of the powder by varying the flux content in the preform
○Possible to prevent the contamination from the reaction container and control purity
○Amount of waste solution is minimized
○Molten salt as a flux can be reduced in comparison with the other direct reduction process
△Leaching is required
× Difficult to produce calcium and control its vapor

Purpose of this study:

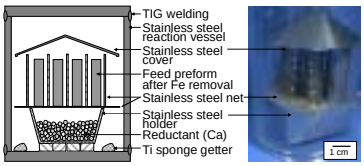
Development of a new smelting process for producing Ti with high purity and productivity and low cost

Research work

Flowchart of the PRP



Typical experimental apparatus for the reduction process



Experimental conditions

Table Experimental conditions in this study.

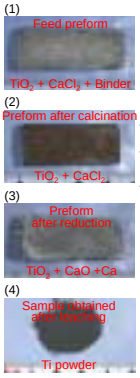
Exp. No. [a]	Cationic molar ratio $R_{Cat./Ti}$ [b]	Calcination Temp. $T_{cal.}$/K	Calcination Time $t'_{cal.}$/h	Reduction Temp. $T_{red.}$/K	Reduction Time $t'_{red.}$/h
A	0.2	1273	1	1273	6
B	0.3	1273	1	1273	6
C [c]	0.2	1273	2	1273	9
D [c]	0.3	1273	2	1273	9

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 the mole amounts of the cations in the flux and Ti, respectively.
c: C powder was added to the preform during the fabrication step in experiments C and D.

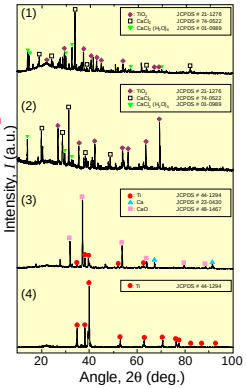
Experimental results 1

Exp. A, $R_{Cat./Ti} = 0.2$

Photographs



XRD patterns



Metallic Ti was successfully obtained after the experiment.

Experimental results 2

Exp. B, $R_{Cat./Ti} = 0.3$

SEM images

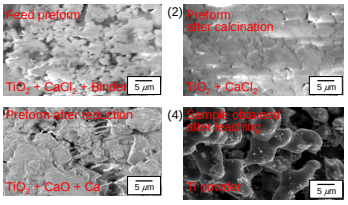


Table Analytical results of the obtained sample.

Step	Concentration of element i, C_i [a] (mass %) Ti	Fe	Al	Ca	Cl
(1)	68.00	1.07	0.44	11.66	18.83
(2)	60.68	0.42	0.33	14.88	23.70
(3)	17.74	0.07	(0.00)	67.42	14.76
(4)	99.10	0.03	0.30	0.58	(0.00)

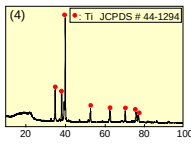
a: Determined by X-ray fluorescence analysis, and the value excludes carbon and gaseous elements.

- **Metallic Ti exhibiting a coral-like structure was obtained.**
- **Purity of Ti was greater than 99 mass %.**

Experimental results 3

Exp. C, $R_{Cat./Ti} = 0.2$, C powder: 0.2 g

XRD pattern



SEM image

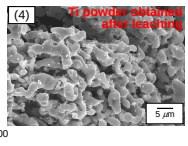


Table Analytical results of the obtained sample.

Step	Concentration of element i, C_i [a] (mass %) Ti	Fe	Al	Ca	Cl
(1)	67.64	1.36	0.50	10.20	20.29
(2)	65.99	0.13	0.08	11.65	22.15
(3)	18.79	0.10	(0.00)	67.98	13.09
(4)	98.23	0.23	0.56	0.98	(0.00)

a: Determined by X-ray fluorescence analysis, and the value excludes carbon and gaseous elements.

Iron removal efficiency was improved when C powder was added to the preform.

Experimental results 4

Table Composition of the samples obtained after leaching and yield of Ti powder

Exp. No.	Cationic molar ratio $R_{Cat./Ti}$ [a]	Concentration of Ti and Fe in the obtained Ti powder C [b] (mass %) Ti	Fe	others	Iron removal ratio [c] (%)	Yield (%)
A	0.2	98.16	0.88	1.76	59	-
B	0.3	99.10	0.03	0.87	56	-
C	0.2	98.23	0.23	1.54	90	79
D	0.3	98.44	0.14	1.42	65	88

a: Cationic molar ratio, $R_{Cat./Ti} = N_{Cat.}/N_{Ti}$, where $N_{Cat.}$ and N_{Ti} are the mole amounts of the cations in the flux and Ti, respectively.
b: Determined by X-ray fluorescence analysis, and the value excludes carbon and gaseous elements.
c: Iron removal ratio: $(C_{Fe}/C_{Ti\ (Before)} - C_{Fe}/C_{Ti\ (After)})/(C_{Fe}/C_{Ti\ (Before)})$

- **High-purity metallic Ti powder was obtained directly from natural Ti ore.**
- **Iron removal ratio was enhanced when C powder was added to the preform.**
- **Ti powder with a yield of 88% was obtained.**

Discussion

Mechanism of iron removal (Ti ore chlorination)

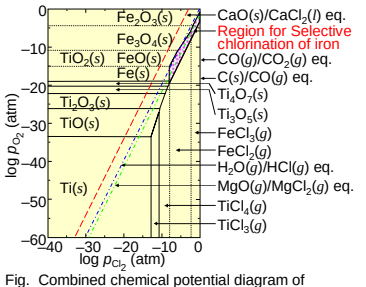


Fig. Combined chemical potential diagram of the Fe-Cl-O (dotted line) and Ti-Cl-O (solid line) systems at 1300 K.

$FeO_x\ (FeTiO_{x'}s) + HCl(g) \rightarrow FeCl_x(g) \uparrow + H_2O(g)$

$FeO_x\ (FeTiO_{x'}s) + CaCl_2(l) \rightarrow FeCl_x(g) \uparrow + \underline{CaO\ (CaTiO_{x'}s)}$, $a_{CaO} << 1$

- **FeO_x can be chlorinated using $CaCl_2 + H_2O$.**
- **TiO_x cannot be chlorinated using $CaCl_2$ or $CaCl_2 + H_2O$.**

Conclusion

The feasibility of the preform reduction process (PRP), based on the calciothermic reduction of natural Ti ore, was demonstrated.

- **90% of iron was successfully removed by selective chlorination during the calcination step.**
- **When C powder was added to the preform, iron was removed more efficiently, and Ti powder with a purity of 98% and yield of 88% was obtained.**
- **It was experimentally demonstrated that high-purity metallic Ti powder (greater than 99 mass %) was obtained directly from natural Ti ore (rutile ore) by the PRP.**

Currently, the development of a more effective method for the direct removal of iron from Ti ore, analysis of the detailed mechanism of selective chlorination, and development of an efficient recycling system of $CaCl_2$ flux and the residual Ca reductant are under investigation.