Selective Chlorination of Titanium Ore and Production of Titanium Powder by Preform Reduction Process

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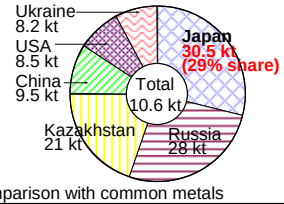
Introduction

Current status of industrial production of Ti

World production of Ti sponge (2005)



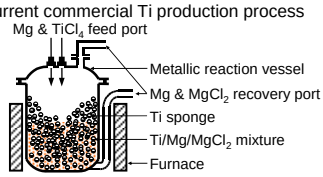
Comparison with common metals

Metal	Iron	Aluminum	Titanium
Symbol	Fe(-C)	Al	Ti
Melting point (K)	1809	933	1939
Density (g/cm^3 at 298 K)	7.9	2.7	4.5
Specific strength ((kgf/mm^2)/(g/cm^3))	4.1(Pure)	3~6	8~10
Clarke no.	4	3	9
Price (¥/kg)	50	600	3000
Production volume (t/world in 2005)	1.1 x 10^9	3.2 x 10^7	1.3 x 10^5

1/300
1/10000

The Kroll process

Current commercial Ti production process



Chlorination

TiO_2 (Ti ore) + C + Cl_2 → $TiCl_4$ (+ MCl_x) + CO_x

Reduction

$TiCl_4$ + Mg → Ti + $MgCl_2$

Electrolysis

$MgCl_2$ → Mg + Cl_2

Overall reaction: TiO_2 + C → Ti + CO_x

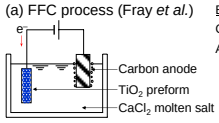
Features of the Kroll process:

◎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.

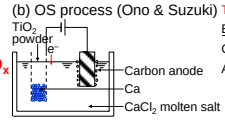
Direct reduction of TiO_2

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



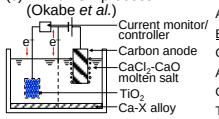
Electrolysis
Cathode: $TiO_2 + 4e^- \rightarrow Ti + 2O^{2-}$
Anode : $C + x\,O^{2-} \rightarrow CO_x + 2x\,e^-$

(b) OS process (Ono & Suzuki) $TiO_2 + 2Ca \rightarrow Ti + 2O^{2-} + 2Ca^{2+}$



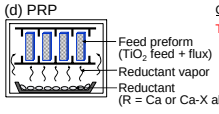
Electrolysis
Cathode: $Ca^{2+} + 2e^- \rightarrow Ca$
Anode : $C + x\,O^{2-} \rightarrow CO_x + 2x\,e^-$

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



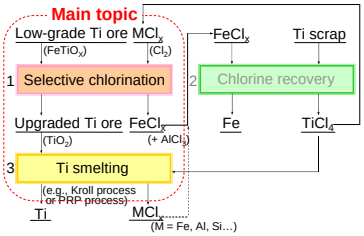
Cathode: $TiO_2 + 4e^- \rightarrow Ti + 2O^{2-}$
Anode : $2Ca \rightarrow 2Ca^{2+} + 4e^-$
Electrolysis
Cathode: $Ca^{2+} + 2e^- \rightarrow Ca$
Anode : $C + x\,O^{2-} \rightarrow CO_x + 2x\,e^-$
Overall reaction
$TiO_2 + C \rightarrow Ti + CO_2$

(d) PRP



Calciothermic reduction
$TiO_2 + 2Ca \rightarrow Ti + 2CaO$

Concept of this study



Producing Ti environmentally with low-cost

1. The feasibility of utilizing low-grade Ti ore directly in the Ti smelting process
   → Using selective chlorination for removing Fe from low-grade Ti ore with metal chlorides.
2. The chlorine recovery using Ti metal scraps.
3. The development of direct production of Ti metallic powder by Prefrom Reduction Process (PRP).

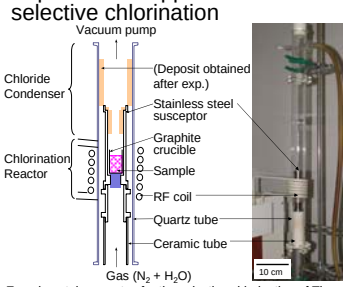
Purpose of this study

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

Research work

Part 1 Selective Chlorination Experiment

Experimental apparatus for selective chlorination



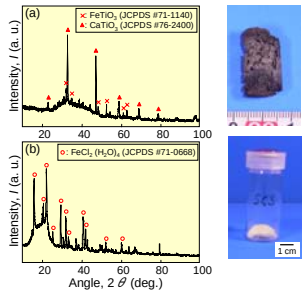
Experimental apparatus for the selective chlorination of Ti ore using Radio Frequency furnace

Experimental conditions

Exp. No.	Mass of Feed Materials, *w* / *g*		Temp.	Time
	Ti ore[a]	$CaCl_2$	$T_{red.}$/K	$t'_{red.}$/h
SA	3.03	1.98	1073	6
SS	3.00	3.00	1293	6

a: Ilmenite produced in Vietnam.

Experimental results of selective chlorination



XRD patterns of the residue in crucible (a) and the deposit (b) inside the SUS susceptor

After experiment:

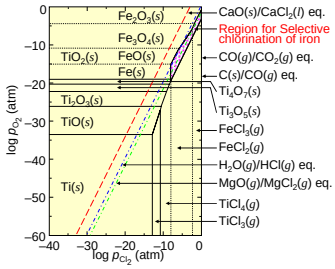
C_{Fe}: 53.7% → 16%

Generation of $CaTiO_3$ and $FeCl_2$

Iron removal directly from Ti ore was carried out successfully.

Discussion

Mechanism of iron removal (Ti ore chlorination)



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

The reactions considered in this study:

FeO_x ($FeTiO_x$,*s*) + HCl(*g*) → $FeCl_x$(*g*) ↑ + H_2O(*g*)

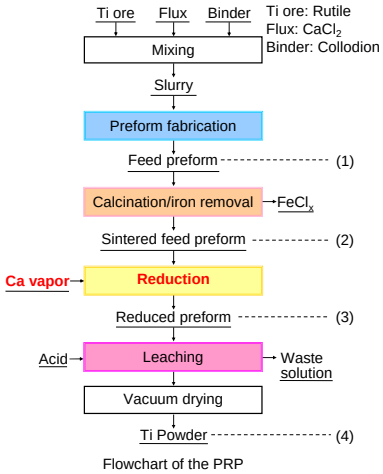
FeO_x ($FeTiO_x$,*s*) + $CaCl_2$(*l*) → $FeCl_x$(*g*) ↑ + CaO ($CaTiO_x$,*s*)

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.**

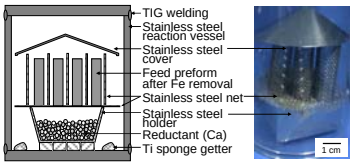
Part 2 Preform Reduction Process (PRP)

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



Flowchart of the PRP

Experimental apparatus for PRP



Schematic illustration of the experimental apparatus for reduction of de-ironized Ti ore by preform reduction process (PRP)

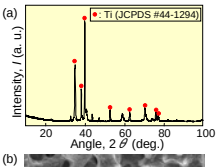
Experimental conditions

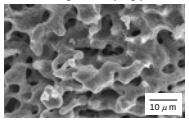
Exp. No.[a]	Cationic molar ratio	Calcination		Reduction	
		Temp.	Time	Temp.	Time
	$R_{Cat./Ti}$[b]	$T_{cal.}$/K	$t'_{cal.}$/h	$T_{red.}$/K	$t'_{red.}$/h
PE	0.2	1273	1	1273	6
PCD[c]	0.3	1273	1	1273	9

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 the experiment PCD.

Experimental results 1 of PRP

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





(c) Concentration of element *i*, C_i (mass %)

Ti	Fe	Ca	Al	O
99.2	0.02	0.42	0.36	(0.00)

X-ray diffraction (XRD) pattern (a), scanning electron microscopic (SEM) image (b), and energy dispersive spectrometric results (c) of Ti powder obtained by PRP.

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

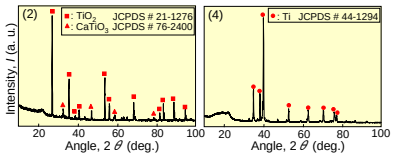
Experimental results 2 of PRP

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

Analytical results of the obtained samples after each step

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.



XRD patterns of the obtained samples after calcination (2) and leaching (4)

Iron removal in calcination step was carried out successfully.

Conclusion

Selective chlorination experiment for removing iron contained in low-grade Ti ore (ilmenite), and preform reduction process (PRP) for producing high-purity metallic Ti powder directly from natural Ti ore (rutile) were carried out in this study.

- **Iron was directly removed from ilmenite by selective chlorination using $CaCl_2$.**
- **Metallic Ti powder with a purity exceeding 99% was obtained directly from rutile by suing PRP.**

In the future, the detailed mechanism of the selective chlorination reactions and mass balance will be investigated.
In addition, a more effective method for removing iron from Ti ore by the selective chlorination method will be investigated for developing a low-cost innovative process for producing high purity Ti powder.