Selective Chlorination of Titanium Ore by Electrochemical Method

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Introduction

Features of titanium

Lightweight and high strength
Corrosion resistant
Biocompatibility
Some titanium alloys:
shape-memory effect
superelasticity

Applications

Aircraft
Spacecraft
Chemical plant
Implant
Artificial bone
etc.

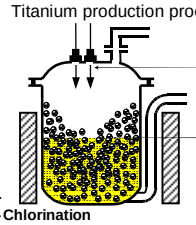
Comparison between titanium and common metals

	Ti	Al	Fe
Melting point (℃)	1660	660	1,540
Price (¥ / kg)	3,000	600	50
Production vol. (t / year･world)	< 50,000	20,000,000	800,000,000
	< 1/400		< 1/16,000

Ilmenite (Ti ore) $ 0.1 ～ 0.2 / kg Ti
×50 ～ 100
Sponge titanium $ 10 / kg Ti
×2 ～ 5
Bulk metal Bars & rods $ 18 ～ 20 / kg Ti
$ 30 ～ 50 / kg Ti

The Kroll process

Titanium production process

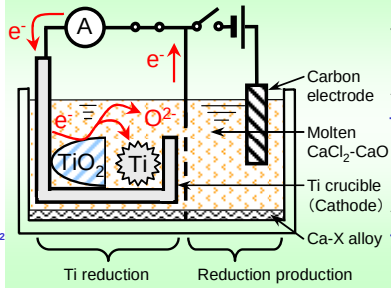


Chlorination
Ti ore + C + 2 Cl_2 → $TiCl_4$ (+ $FeCl_x$) + CO_2
Reduction
$TiCl_4$ + 2 Mg → Ti + 2 $MgCl_2$
Electrolysis
$MgCl_2$ → Mg + Cl_2

Features of the Kroll process:

◎ 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.
× Batch-type reduction process is used.
× Production speed is low.
× Chloride wastes cannot be utilized.

New Ti reduction process (EMR / MSE process)

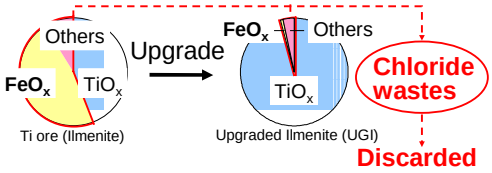


Reduction:
Titanium reduction
Cathode:
TiO_2 + 4 e^- → Ti + 2 O^{2-}
Anode:
Ca → Ca^{2+} + 2 e^-
Electrolysis:
Reductant production
Cathode:
Ca^{2+} + 2 e^- → Ca
Anode:
C + x O^{2-} → CO_x + 2x e^-
Overall reaction
TiO_2 + C → Ti + CO_2

Features of the EMR process:

◎Resistant to iron and carbon contamination
○Semi-continuous process
○Reduction and electrolysis operations can be carried out independently.
× Difficult metal / salt separation with oxide system
×Complicated cell structure
△Complicated process

Wastes from the Kroll process



Issues related to chloride wastes:

1. Disposal cost and environmental burden
2. Additional chlorine gas has to be purchased.
3. Effective utilization has not been established.

Upgrading Ti ore for minimizing chloride wastes

New process

Ti smelting process using low-grade Ti ore

This study

Low-grade Ti ore ($FeTiO_x$) + MCl_x ($CaCl_2$) → Selective chlorination → Upgraded Ti ore (TiO_2) + $FeCl_x$ ($+AlCl_3$)
$FeCl_x$ + Ti scrap → Chlorine recovery → Fe + $TiCl_4$
Upgraded Ti ore → Ti smelting → Ti metal

Advantages:

1. Material cost can be reduced by using low-grade ore.
2. Chlorine circulation in the Kroll process can be improved.
3. This process can also be applied to the new Ti production processes by the direct reduction of TiO_2.

Earlier studies (pyrometallurgical methods)

Experiment

FeO_x (*s*) + $MgCl_2$ (*l*) = $FeCl_x$ (*l*) + MgO (*s*)

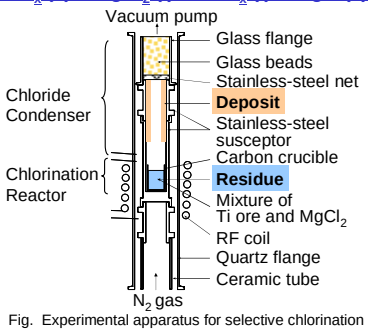


Fig. Experimental apparatus for selective chlorination of titanium ore using $MgCl_2$ as a chlorine source.

Experimental condition:
T = 1100 K; t ' = 1 h; Atmosphere: N_2;
Ti ore (UGI): 4 g, $MgCl_2$: 2 g

Results

XRF analysis

Residue after selective chlorination → Fe was selectively chlorinated.

Table Analytical results of titanium ore, the sample obtained after selective chlorination, and the sample after reduction.

	Concentration of element *i*, C_i (mass %)[a]				
	Ti	Fe	Si	Al	V
Ti ore (UGI from Ind.)	95.10	**2.29**	0.41	0.12	0.75
After exp.	96.45	**0.43**	0.44	0.37	1.50
After reduction[b]	98.30	**0.05**	0.38	0.12	0.52

a: Value determined by XRF analysis
b: Dechlorinated Ti ore was reduced by calciothermic reduction.

Iron was removed from Ti ore by chemical methods.

This study (electrochemical method)

Thermodynamic analysis

Ti ore: mixture of FeO_x and TiO_x

Fe-Cl-O and Ti-Cl-O systems, T = 1100 K

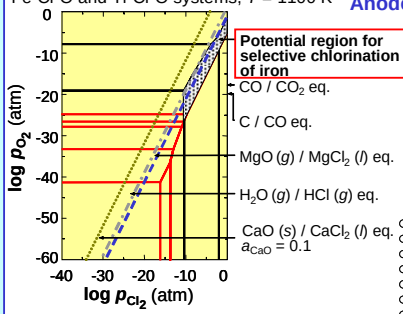


Fig. Chemical potential diagram for Fe-Cl-O and Ti-Cl-O systems at 1100 K.

Iron removal from Ti ore by selective chlorination using $MgCl_2$ is thermodynamically feasible.

Experiment

Selective chlorination･Iron removal process
Cathode: Fe^{n+} + n e^- → Fe ; Ca^{2+} + 2 e^- → Ca
Anode: 2 Cl^- → Cl_2 + 2 e^-
FeO_x + C + Cl_2 → $FeCl_x$ (*l*, *g*) + CO_x

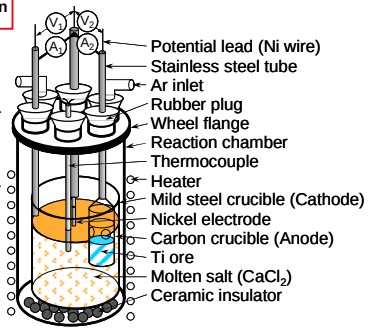


Fig. Schematic illustration of experimental apparatus in this experiment.

Experimental condition:
T = 1100 K; t' = 9 h; Atmosphere: Ar;
Voltage, E = 1.5 V

Results

Potentiostatic electrolysis

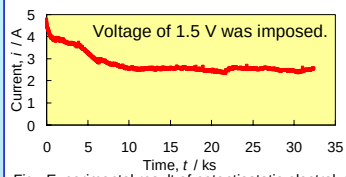


Fig. Experimental result of potentiostatic electrolysis (Voltage, E = 1.5 V; Time, t' = 9 h ≒ 32 ks)

Average current at approximately 3 A passed for 9 h.

XRF analysis

After the electrochemical treatment, Fe was selectively chlorinated and removed.

Table Analytical results of titanium ore (starting sample) and the sample obtained after electrochemical selective chlorination.

	Concentration of element *i*, C_i (mass %)[a]					
	Ti	Fe	Si	Al	V	Fe / Ti (%)
Ti ore	42.62	**48.72**	2.19	2.23	0.64	**114**
After exp.	78.38	**16.22**	0.97	0.88	1.76	**20.7**

82% of Fe was successfully removed.

Iron was removed from Ti ore by the electrochemical method.

Conclusions

Selective chlorination of Ti ore by the electrochemical method was investigated, and 80 mass% Fe was successfully removed from low-grade Ti ore.

Future works

- **A more efficient process for producing Fe-free Ti ore by the electrochemical method will be investigated.**
- **Behavior of chlorine in selective chlorination will be investigated.**

Ultimate goals:

Low-cost Ti production directly from low-grade Ti ore will be established.

Ti ore (TiO_2 + FeO_x) ← **Low-value ore**
Selective chlorination → $FeCl_x$
Fe-free TiO_2
Ti smelting ····· **Direct reduction of oxides**
Ti metal ← **Metal**