# Reduction of Titanium Oxide in Molten Salt Medium

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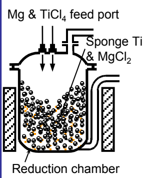
## Introduction

### Kroll Process




Chlorination:
$TiO_2 + C + 2\ Cl_2 \rightarrow TiCl_4 + CO_2$
Reduction:
$TiCl_4 + 2\ Mg \rightarrow Ti + MgCl_2$
Electrolysis:
$MgCl_2 \rightarrow Mg + Cl_2$
**Overall reaction**
$TiO_2 + C \rightarrow Ti + CO_2$

◎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

**At present, titanium is manufactured by the Kroll process.**

**Comparison between titanium and common metal.**

| | Ti | Al | Fe |
|---|---|---|---|
| Melting point | 1660 ℃ | 660 ℃ | 1540 ℃ |
| Price (¥ / kg) | 3,000 | 600 | 50 |
| Production vol. (t / year・world) | <100,000 | 20,000,000 | 800,000,000 |

<1/200　<1/8,000

A new process technology is essential for titanium production.

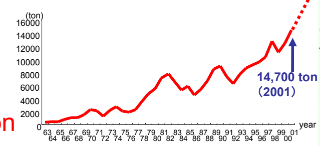
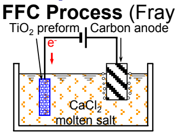



Fig. Transition of shipment of titanium mill product in Japan.

Kroll process is huge exothermic reaction
→It requires **several days** to produce titanium in large (ton) scale.

## Comparison with other studies

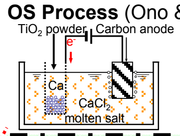
**FFC Process** (Fray et al., 2000)




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

◎Simple process
○Semi-continuous process
×Difficult metal / salt separation
×Reduction and electrolysis have to be carried out simultaneously
△Sensitive to carbon and iron contamination
△Low current efficiency

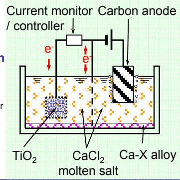
**OS Process** (Ono & Suzuki, 2002)




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

◎Simple process
○Semi-continuous process
×Difficult metal / salt separation
△Sensitive to carbon and iron contamination
△Low current efficiency

**EMR/MSE process**

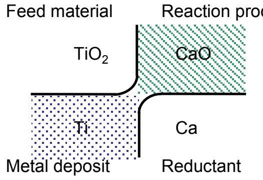



Reduction: **titanium reduction**
Cathode: $TiO_2 + 4\ e^- \rightarrow Ti + 2\ O^{2-}$
Anode: $Ca \rightarrow Ca^{2+} + 2\ e^-$
Electrolysis: **producing reductant**
Cathode: $Ca^{2+} + 2\ e^- \rightarrow Ca$
Anode: $C + x\ O^{2-} \rightarrow CO_x + 2x\ e^-$
**Over all reaction**
$TiO_2 + C \rightarrow Ti + CO_2$

◎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

## Electronically Mediated Reaction (EMR)

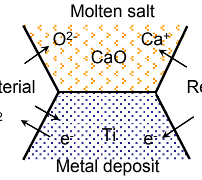
・**Conventional interpretation of metallothermic reaction**




Metallothermic reaction
$TiO_2 + 2\ Ca \rightarrow Ti + 2\ CaO$

Physical contact

・**Concept of EMR**




Electrochemical redox reactions
Cathode: $TiO_2 + 4\ e^- \rightarrow Ti + 2\ O^{2-}$
$CaCl_2$
Anode: $2\ Ca \rightarrow 2\ Ca^{2+} + 4\ e^-$

A feed material need not to make physical contact with a reductant.

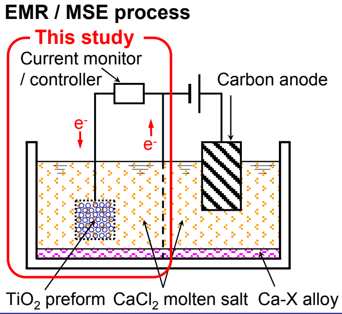
'Metallothermic Reduction as an Electronically Mediated Reaction (EMR)',
T. H. Okabe and D. R. Sadoway:
J. Materials Research, vol.13, no.12 (1998) pp.3372-3377.

## Experimental

**In this study**

Electrochemical reactions in the metallothermic reduction was utilized.

**EMR / MSE process**



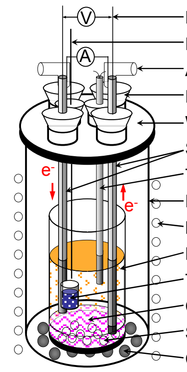




Fig. Schematic illustration of experimental apparatus for $TiO_2$ reduction using the EMR.

## Results

$TiO_2$　Binder　Flux (*e.g.* $CaCl_2$)

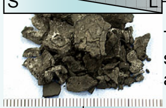
Preform fabrication

The intensity and Shape of the preform can be controlled by flux addition.

Reduction

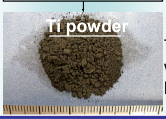
Separation

S　L → $CaCl_2$ - CaO



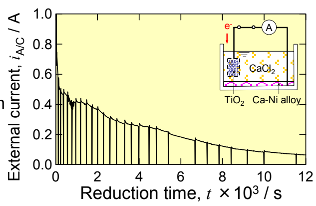
The preform became slightly deformed after reduction.

Acid → Leaching / Drying → Waste solution

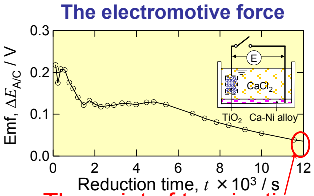



The metal powder was obtained after leaching.

**The external current**




**The electromotive force**




The point of termination of reduction experiment.

Fig. Variation of the external current and electromotive force at 1073 K.

**SEM image**


Pure titanium powder was obtained using the EMR.

**XRD analysis**

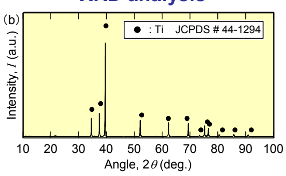



Fig. Titanium powder obtained after reduction.
(a) SEM image.
(b) X-ray diffraction pattern (Cu $K_\alpha$).

**Impurity content**

**Table** Analytical results of the titanium powder obtained using an EMR at 1173 K

| Exp. # | Impurity content $C_i$ [a] (mass %) Ti | Ca | Fe | Ni | Cl | O | EMR ratio $X_{EMR}$ [b] (%) |
|---|---|---|---|---|---|---|---|
| B1 | 99.8 | 0.13 | 0.07 | 0.04 | 0.00 | (0.00) | 1.2 |
| | | 0.23[c] | 0.27[c] | 0.16[c] | | | |
| B2 | 99.6 | 0.14 | 0.04 | 0.13 | 0.11 | (0.00) | 4.1 |
| | | 0.26[c] | 0.11[c] | 0.23[c] | | | |
| C1 | 99.9 | 0.02 | 0.06 | 0.02 | 0.05 | (0.00) | 6.2 |
| | | 0.17[c] | 0.55[c] | 0.11[c] | | 0.65[d] | |
| C2 | 99.9 | 0.10 | 0.00 | 0.00 | 0.04 | (0.00) | 3.6 |
| | | 0.16[c] | 0.27[c] | 0.05[c] | | 0.57[d] | |
| C3 | 99.9 | 0.01 | 0.00 | 0.00 | 0.00 | (0.00) | 5.1 |
| | | 0.15[c] | 0.20[c] | 0.04[c] | | 0.35[d] | |

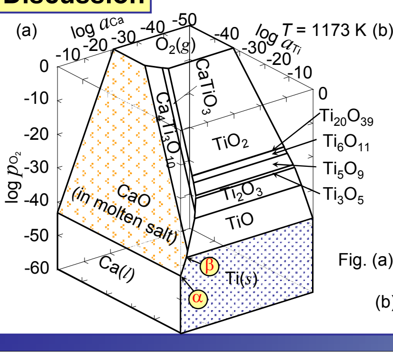
[a]: Determined by EDS analysis. Values in parenthesis are listed for reference.
[b]: $X_{EMR} = 100 ´ Q_{exp.} / Q_{thoe.}$, where $Q_{exp.}$ is amount of electric charge passed through external circuit, and Qthoe. is the theoretical electric charge necessary for reducing $TiO_2$.
[c]: Determined by ICP-AES analysis.
[d]: Determined by inert gas fusion-infrared absorption spectroscopy (LECO) analysis.

Low Ni even though Ca-18~21.5 mass % Ni alloy was used as a reductant.　3500 ppmO

Impurities such as iron or carbon can be trapped on the anode (Ca-Ni alloy).

**High purity powder titanium can be manufactured from $TiO_2$ using the EMR.**

## Discussion




(b) 3-D chemical potential diagram
Indicates that a reductant calcium need not to make physical contact with titanium oxides.

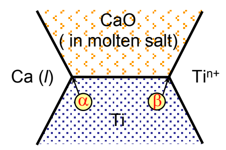



Fig. (a) Three-dimensional chemical potential diagram for the system Ti-Ca-O at 1173 K.
(b) Depiction of the reaction pathway consistent with the chemical potential diagram.

## Conclusion

**EMR / MSE process** (Oxide system)

・$TiO_2$ was reduced by metallotheimic reaction through an electronically mediated reaction (EMR), and titanium powder was produced.

・Using EMR, titanium powder with 99.9% (metallic purity) containing 3500 ppm oxygen was obtained.

・EMR/MSE process is suitable for developing a (semi-)continuous and energy saving process.