

ELECTROLYSIS OF MOLTEN $\text{CaCl}_2\text{-CaO}$ SALT FOR DIRECT REDUCTION PROCESS OF TITANIUM OXIDE

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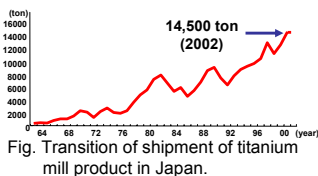
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Introduction

About titanium (Ti)

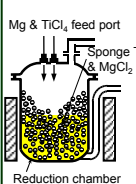
Comparison between titanium and common metals.

	Ti	Al	Fe
Melting point (°C)	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



At present, titanium is manufactured by the Kroll process.

Kroll Process



Chlorination:



Reduction:



Electrolysis:



Overall reaction



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

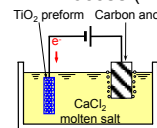
Huge exothermic reaction

It requires several days to produce titanium in large (ton) scale.

A new process technology is essential for titanium production.

Comparison among direct reduction processes of TiO_2

FFC Process (Fray et al., 2000)



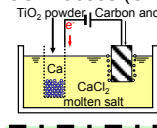
Electrolysis



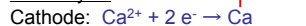
Simple process

- 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)



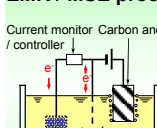
Electrolysis



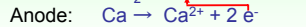
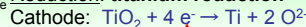
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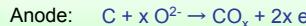
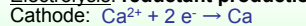
EMR / MSE process



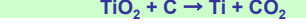
Reduction: titanium reduction



Electrolysis: reductant production



Over all reaction



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

Experimental

Electronically Mediated Reaction (EMR)

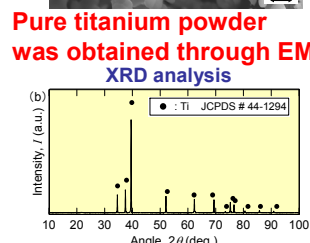
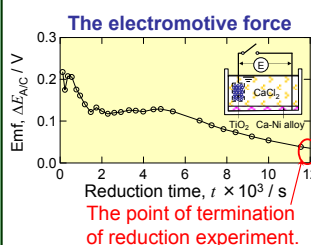
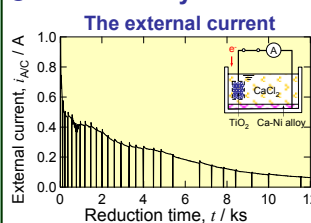
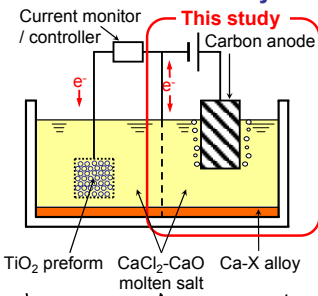


Fig. Variation of the external current and electromotive force at 1073 K.
Fig. Titanium powder obtained after reduction.
(a) SEM image.
(b) X-ray diffraction pattern (Cu K_α).

Molten Salt Electrolysis (MSE)



Once an efficient process for the production of the Ca alloy reductant is established, this method has the potential to be the next generation titanium production process.

To evaluate the optimum conditions for production of Ca-X alloy reductant, electrochemical properties of $\text{CaCl}_2\text{-CaO}$ molten salt were analyzed by cyclic voltammetry (CV).

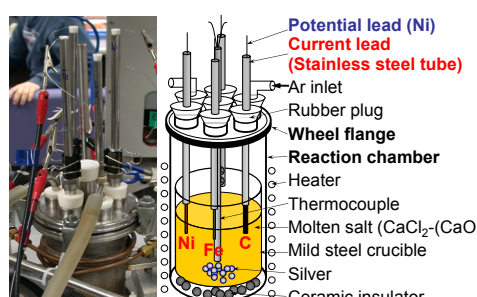


Fig. Schematic illustration of experimental apparatus.

	Cathodic reaction	Anodic reaction
Temperature	1100 K	1100 K
Working electrode	Fe	C
Counter electrode	C	Fe
Reference electrode	Ni/Ni ²⁺ or Ca/Ca ²⁺	Ni/Ni ²⁺ or Ca/Ca ²⁺

Results Electrochemical properties of $\text{CaCl}_2\text{-CaO}$ molten salt

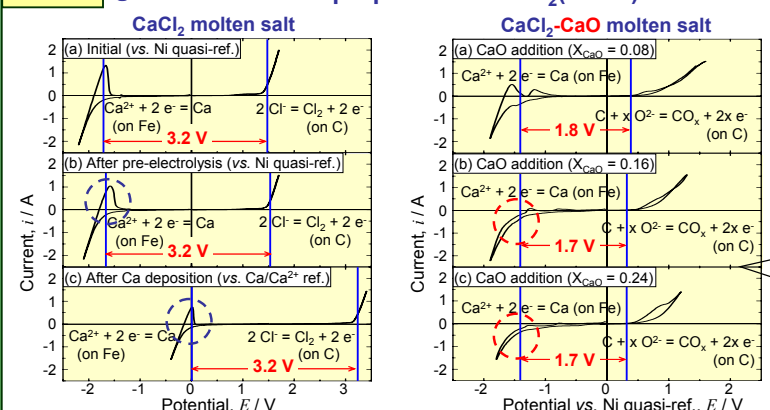


Fig. Cyclic voltammograms of CaCl_2 molten salt at 1100 K. (Cathode: Fe, $A_c = 26 \text{ mm}^2$, Anode: C, $A_a = 66 \text{ mm}^2$, Scan rate: $v_c = 100 \text{ mV/s}$, $v_a = 100 \text{ mV/s}$.)
 $\text{CaO ratio: } X_{\text{CaO}} = n_{\text{CaO}} / (n_{\text{CaCl}_2} + n_{\text{CaO}})$

Fig. Cyclic voltammograms of $\text{CaCl}_2\text{-CaO}$ molten salt at 1100 K. (Cathode: Fe, $A_c = 26 \text{ mm}^2$, Anode: C, $A_a = 66 \text{ mm}^2$, Scan rate: $v_c = 100 \text{ mV/s}$, $v_a = 100 \text{ mV/s}$.)

Conclusion

From cyclic voltammograms, it was demonstrated that...
 • Ca deposition from CaCl_2 molten salt can be monitored by cyclic voltammetry by using Ca/Ca^{2+} reference electrode.
 • When adding CaO to CaCl_2 molten salt, Ca is oxidized again to Ca^{2+} or eliminated from electrode just after Ca deposition.
 ⇒ Production of Ca by electrolysis of $\text{CaCl}_2\text{-CaO}$ molten salt is found to be difficult when CaO ratio is high.
 When Ca electrolysis is done for trial...
 (a) Voltage is about 3.2 V, and current efficiency is about 30%
 (b) Voltage is about 1.7 V, but current efficiency is almost 0%
 This reason is under investigation.

Future work

- To develop an efficient method for producing Ca alloy reductant by electrolysis of $\text{CaCl}_2\text{-CaO}$ molten salt.
- To evaluate current and energy efficiencies of MSE.

Establishment of EMR / MSE process