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真空溶融塩電解法
～純度の高い金属精錬が効率よく行える～

京都大学　工学研究科材料工学専攻
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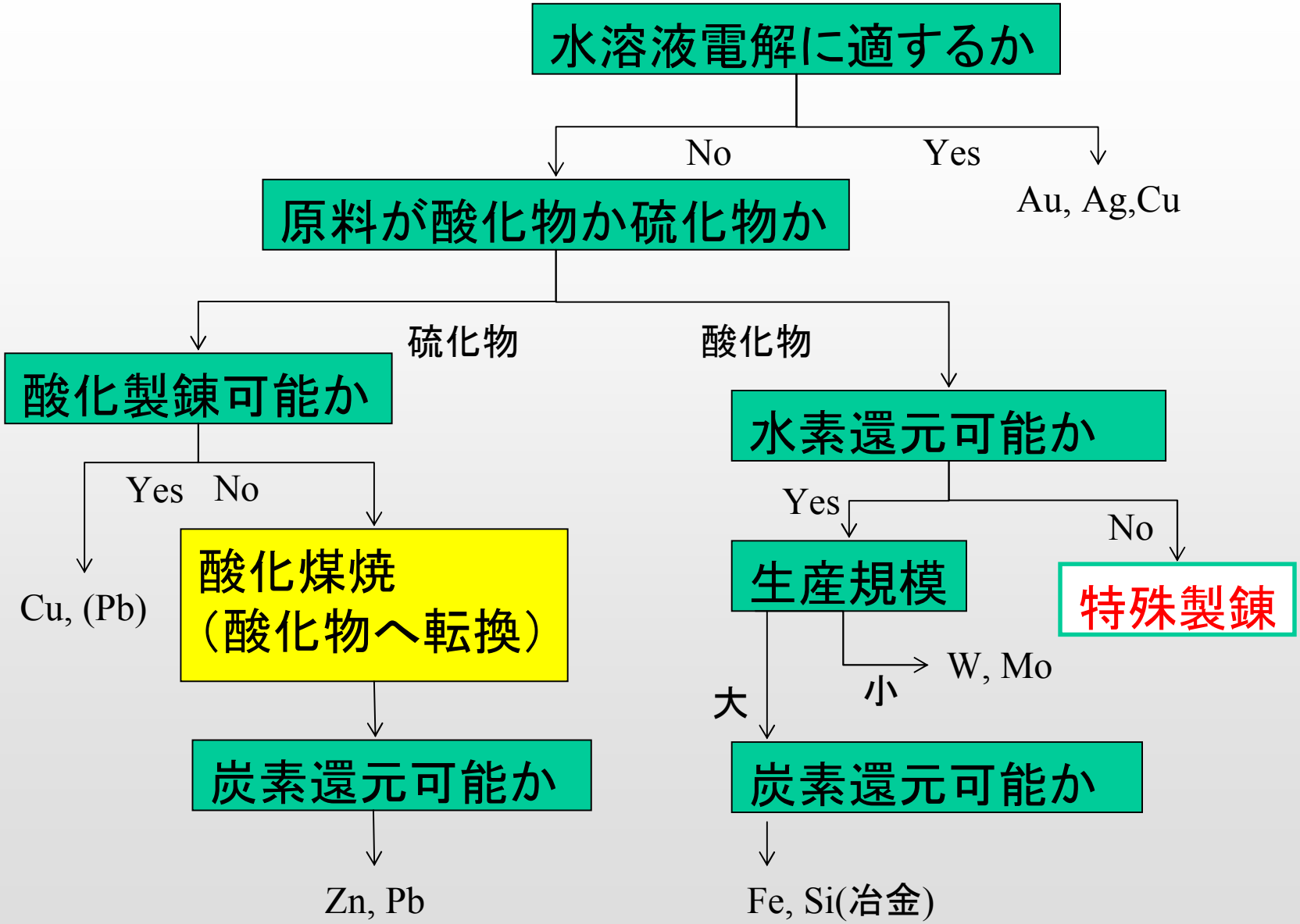
製錬(精錬)プロセス


水溶液電解に適するか
No
Yes
Au, Ag,Cu
原料が酸化物か硫化物か
硫化物
酸化物
酸化製錬可能か
Yes
No
Cu, (Pb)
酸化煤焼
(酸化物へ転換)
炭素還元可能か
Zn, Pb
水素還元可能か
Yes
No
特殊製錬
生産規模
大
小
W, Mo
炭素還元可能か
Fe, Si(冶金)

特殊製錬

溶融塩電解

- チタン、タンタル、ニオブ、シリコン、ナトリウム、カリウム、マグネシウム、カルシウム、ウラン…
- 希土類

スカンジウム、イットリウム、ランタノイド

今日は、チタンの溶融塩電解について説明

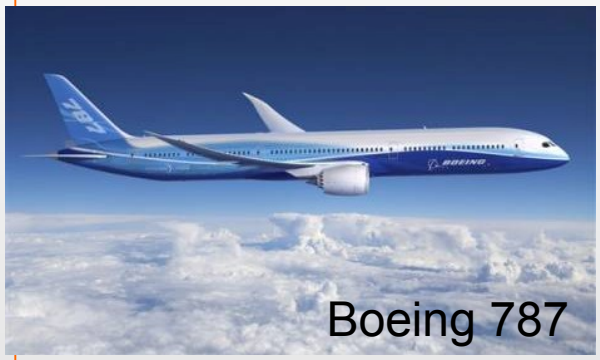
チタンの特徴

軽い・強い
高い比強度

耐食性
海水には完全耐食

Ti

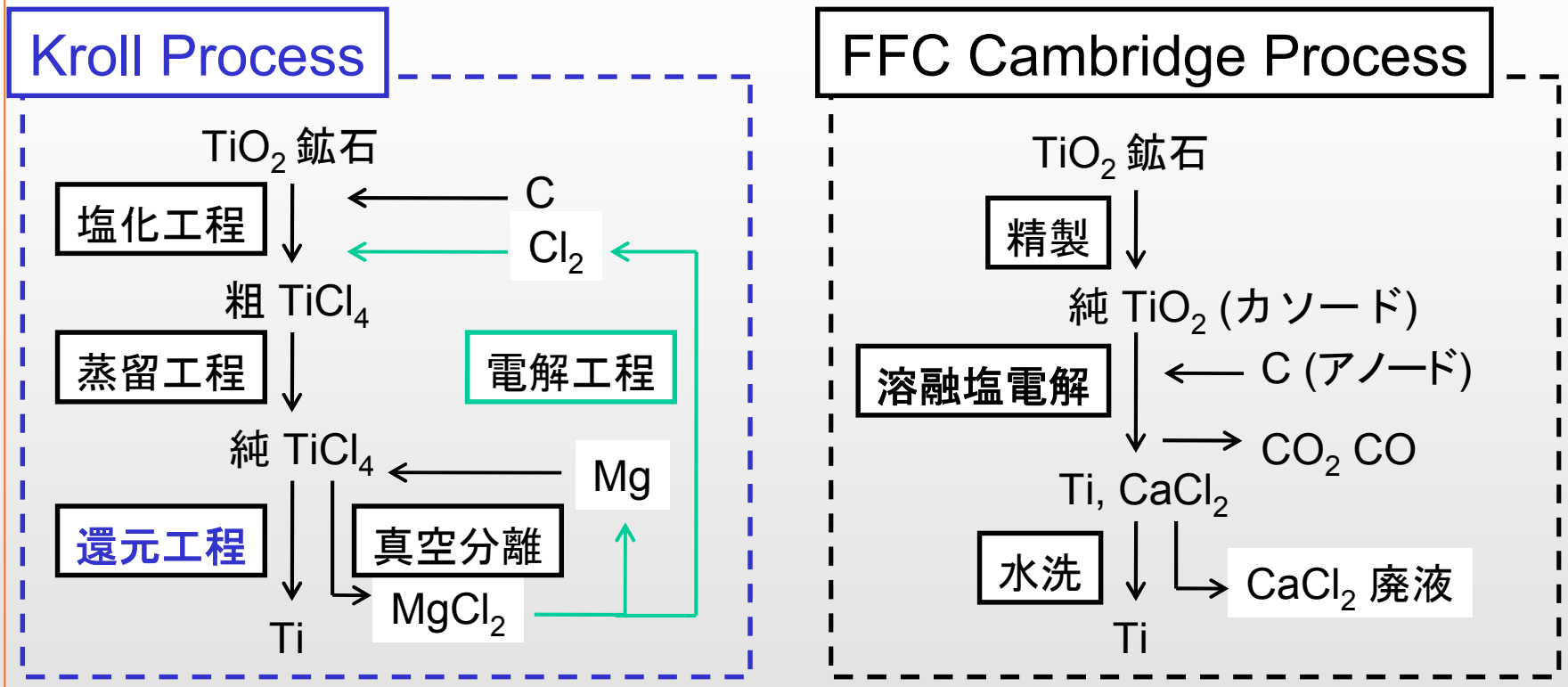
豊富な資源
クラーク数10 位



	チタン	鉄	ステンレス鋼	アルミニウム
生産量 / 万 t	15	95000	1635	3800
価格 / ¥ kg^{-1}	1800	70	600	320

製錬プロセスの困難さ

チタンの製錬法について



Kroll Process

長所
- 高純度のチタンを得られる (5N程度)
- $MgCl_2$ の再利用が可能

短所
- 還元反応の発熱が大きい
- 還元されたチタンが反応容器に固着
→速度が制限される

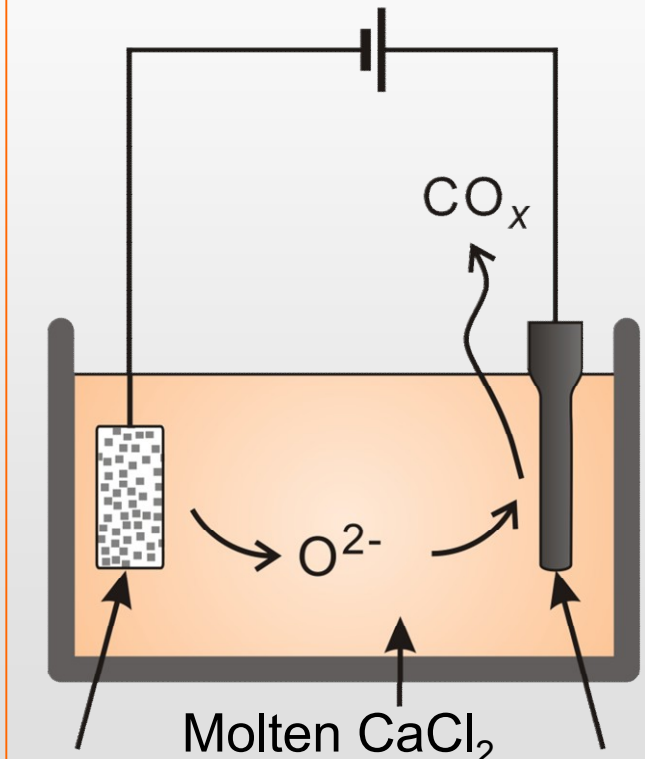
FFC Cambridge Process

長所
- 半連続化が可能

短所
- TiO_2 の高純度化
- 生成されるチタンへの炭素汚染

Background – TiO_2 electrolysis

FFC Cambridge Process[2]



Electrolysis of TiO_2 in molten $CaCl_2$
- potential alternative to the current process

Reactions

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

Advantages

- Possible to be operated semi-continuously.
- Simple process

Problems

- Low-cost TiO_2 purification process is not established.
- Low current efficiency[3]
- Carbon contamination[3]

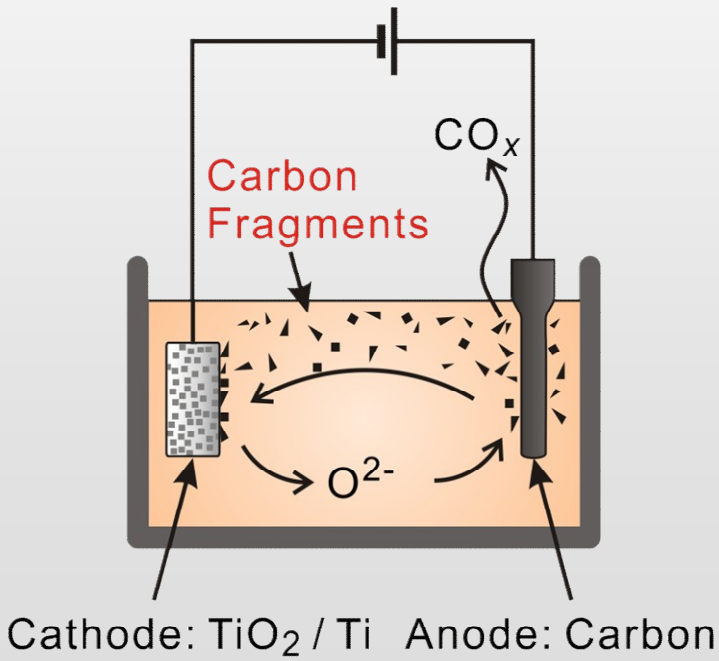
[2] G. Z. Chen, D. J. Fray, and T. W. Farthing, *Nature*, **407**, 361 (2000).
[3] S. Jiao and D. J. Fray, *Metall. Mater. Trans. B*, **41B**, 74 (2010).

Background – Carbon contamination

How does the carbon come to cathode from anode?

Origin1 : Anode fragments

Emitted with anode consumption

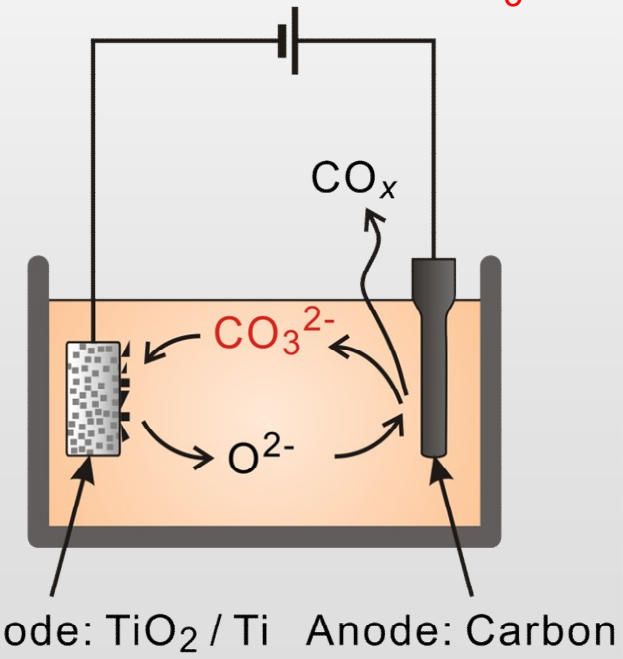


Preventable physically by diaphragm

Origin2 : Carbonate ions

Cathode : $CO_3^{2-} + 4e^- \rightarrow C + 3O^{2-}$

Anode : $C + 3O^{2-} \rightarrow CO_3^{2-} + 4e^-$



Unpreventable by diaphragm

Proposal : Electrolysis under vacuum

Vacuuming

↓

Acceleration of CO_3^{2-} decomposition and CO_x removal

↓

Prevention from carbon contamination

But no one has ever tried
molten salt electrolysis under vacuum.

Cathode

$TiO_2 + 4e^- \rightarrow Ti + 2O^{2-}$

~~$CO_3^{2-} + 4e^- \rightarrow C + 3O^{2-}$~~ prevented

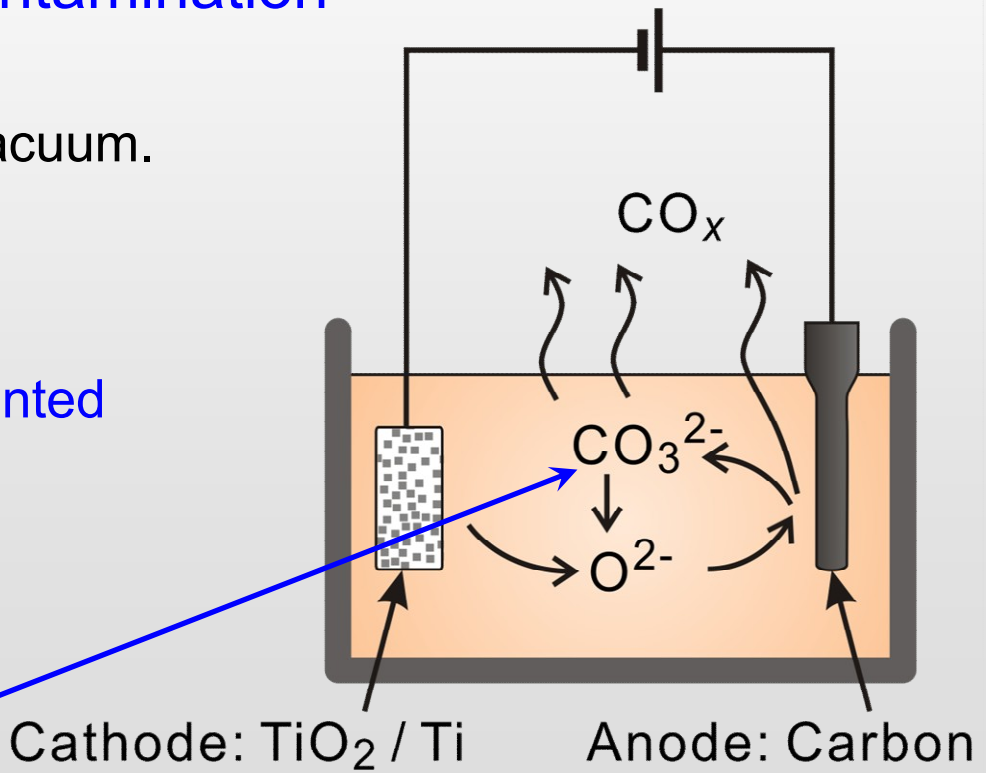
Anode

$C + xO^{2-} \rightarrow CO_x + 2xe^-$

$C + 3O^{2-} \rightarrow CO_3^{2-} + 4e^-$

Electrolyte

$CO_3^{2-} \rightarrow O^{2-} + CO_2$ accelerated



Objective

Revealing the effect of vacuuming during TiO_2 electrolysis

- Examine the acceleration of the decomposition of CO_3^{2-}
  → Weight loss measurement of $CaCl_2$ - $CaCO_3$
- Investigate whether vacuuming is effective on the electrolysis
  → Electrolysis of TiO_2 in $CaCl_2$

Weight loss measurement

in glove box

$CaCl_2$ $CaCO_3$

weight measurement

heating up — Ar 1atm

decomposition

vacuum or Ar 1atm

800 °C

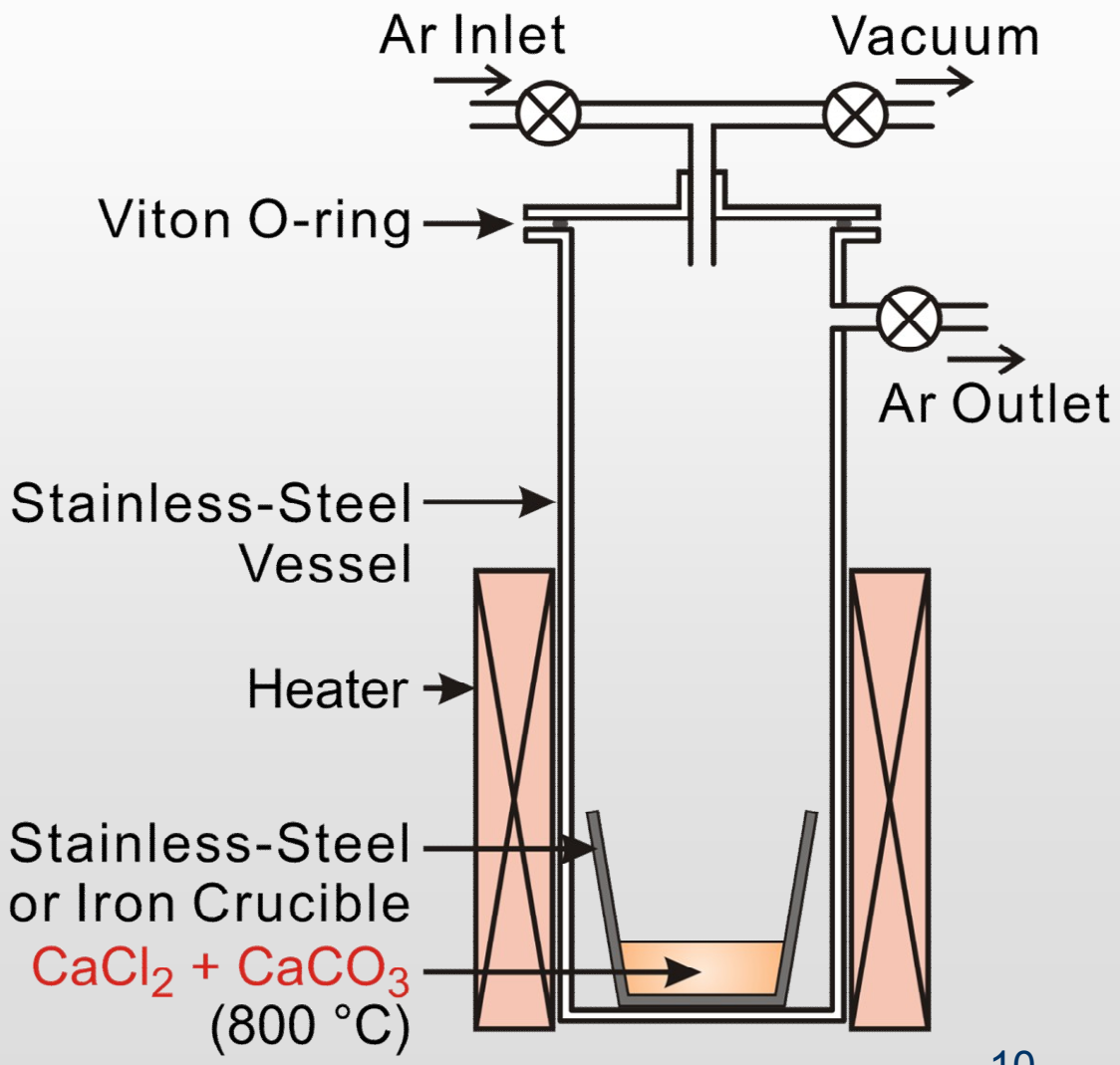
$CaCO_3 \rightarrow CaO + CO_2$

weight loss

cooling down — Ar 1atm

in glove box

weight measurement



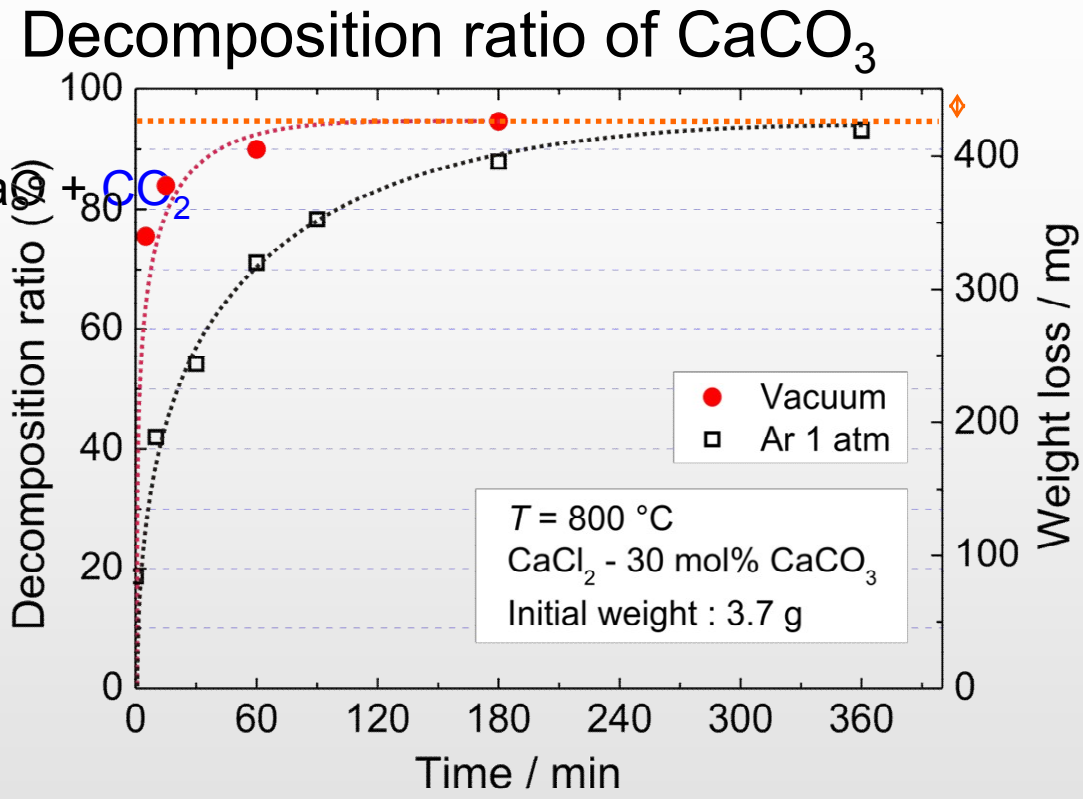
Weight loss measurement

Supposed reaction:

$$CaCO_3 \rightarrow CaO + CO_2$$

Theoretical weight loss is 44% of $CaCO_3$ weight.

$$\text{Decomposition ratio} = \frac{\text{(Weight loss)}}{0.44 \times (\text{Initial weight of } CaCO_3)}$$



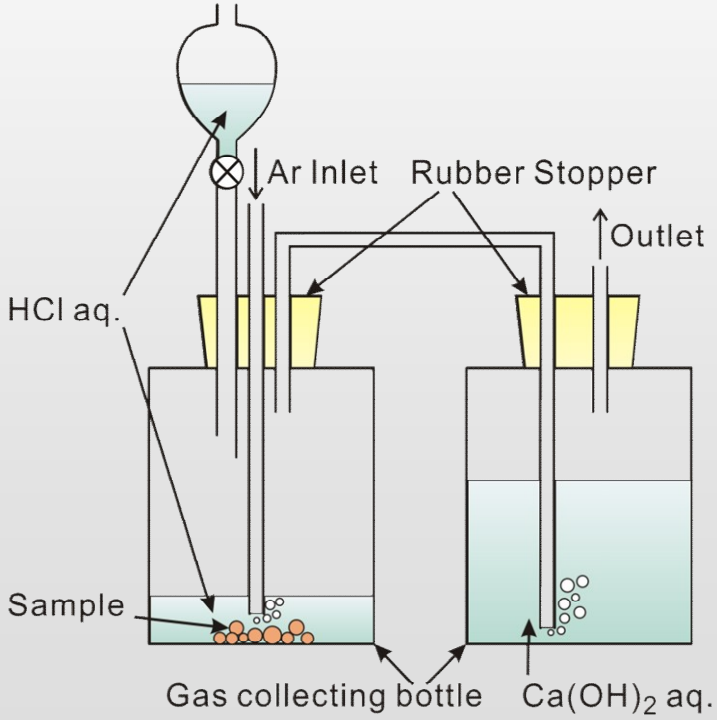
- Vacuuming accelerated decomposition of $CaCO_3$.
- Decomposition ratio did not reach 100%.
  → Small amount of $CaCO_3$ remained?

Weight loss measurement

Why did not decomposition ratio reach 100 %?

- Small amount of $CaCO_3$ remained?

  → It was investigated whether $CaCO_3$ remained in the sample.



If $CaCO_3$ remains,
white precipitation appears in the right bottle.

Left bottle : $2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O$

Right bottle : $CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H$

precipitation

→ $CaCO_3$ did not remain in the sample which decomposition ratio was 95%.

Weight loss measurement

Why did not decomposition ratio reach 100 %?

- Small amount of $CaCO_3$ remained?

  → $CaCO_3$ content in the sample was analyzed by the chemical method.

  → $CaCO_3$ did not remain in sample which decomposition ratio was 95%.

- Another reaction occurred ?

$$\frac{\text{Weight loss}}{\text{Initial weight of } CaCO_3} \text{ is...}$$

Supposed reaction	: $CaCO_3 \rightarrow CaO + CO_2$ (1)	44%
Another reaction	: $CaCO_3 \rightarrow CaO_2 + CO$ (2)	28%
Another reaction	: $CaCO_3 + \underline{Fe}_{\text{crucible}} \rightarrow CaO + FeO + CO$ (3)	28%

→ Apparent decomposition ratio did not reach 100%.

➡ Anyway the acceleration was confirmed,
we carried out electrolysis of TiO_2.

Electrolysis

TiO_2 powder

↓

Pressing 392 MPa 10 min

↓

Sintering air 900 °C 24 hours

↓

Envelopment by Ni mesh

↓

Electrolysis

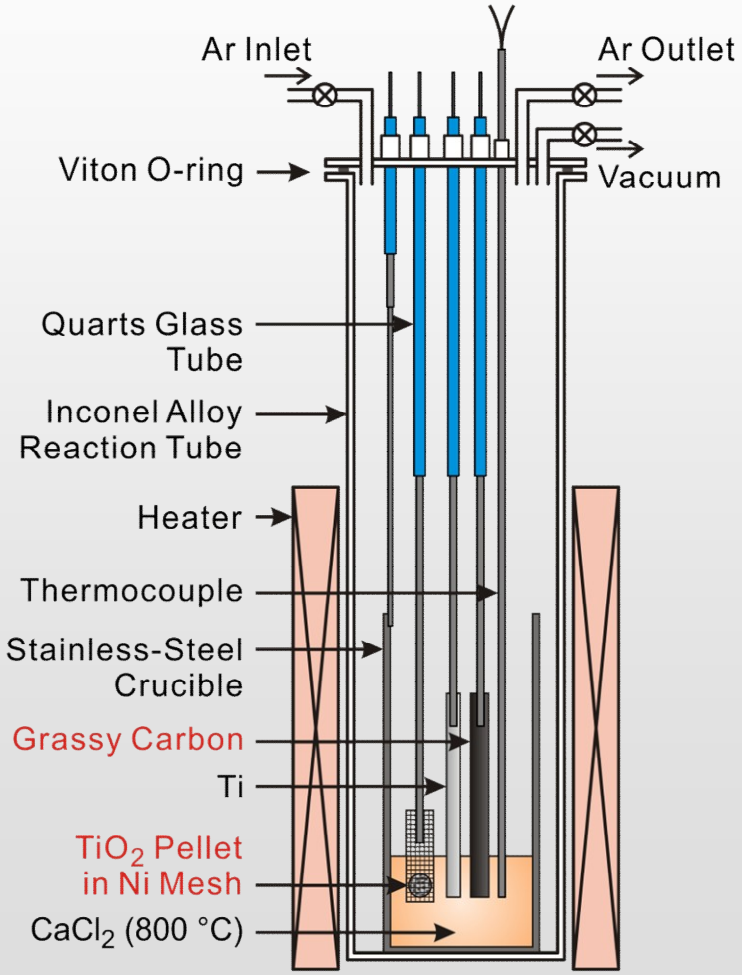
cell voltage at 3.0 V
5 hours
800 °C
vacuum / Ar 1 atm

↓

Washing by water

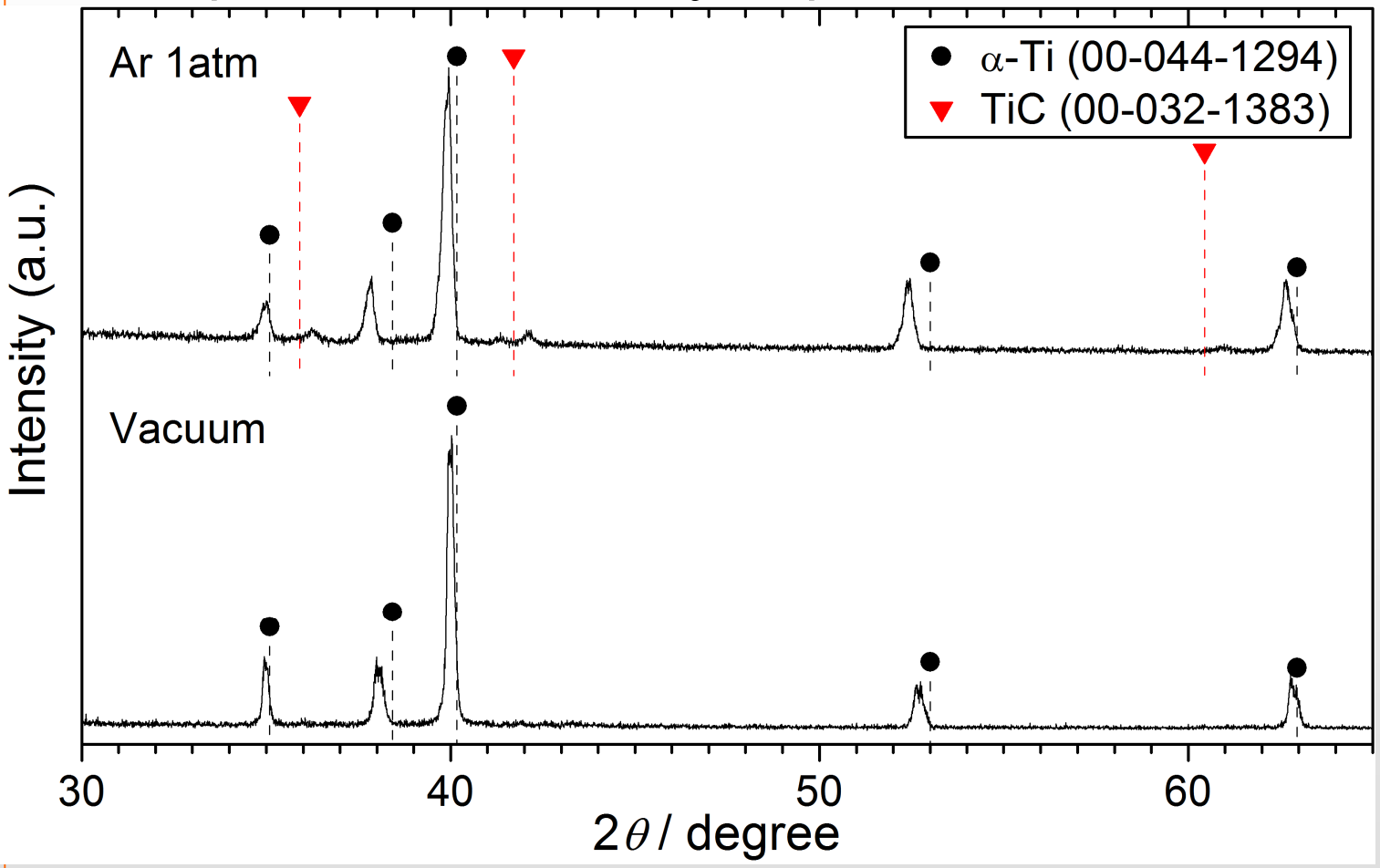
↓

XRD analysis



Electrolysis

XRD patterns of electrolysis products



Ti and TiC

Ti only!

TiC formation was prevented in electrolysis under vacuum!

→ Vacuuming is effective for prevention from carbon contamination.

Summary

- Weight change measurements of $CaCl_2$-$CaCO_3$
  → Vacuuming accelerated the decomposition of CO_3^{2-}.
- Electrolysis of TiO_2 in $CaCl_2$
  → Vacuuming prevented the formation of TiC.

Vacuuming is effective for prevention
from carbon contamination in TiO_2 electrolysis.

新技術の特徴

- 純度の高い金属の製造
- 金属製錬の効率化（電力損失の軽減）
- 装置が簡便である

想定される用途

- チタン製造
- 溶融塩電解法を用いている金属製錬
- 希土類の製錬

- チタン、タンタル、ニオブ、シリコン、ナトリウム、カリウム、マグネシウム、カルシウム、ウラン…
- 希土類：スカンジウム、イットリウム、ランタノイド

本技術に関する知的財産権

発明の名称	「電気分解による金属の製造方法」
出願番号	特願2010-291739
出願人	国立大学法人　京都大学
発明者	宇田哲也、林彰平

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