Dream & Objective of Okabe Lab.

Innovational Technology to Transform Rare Metals into Common Metals

Development of innovative materials processing

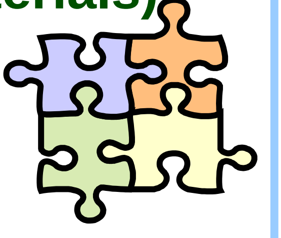
Development of a new rare metal production process

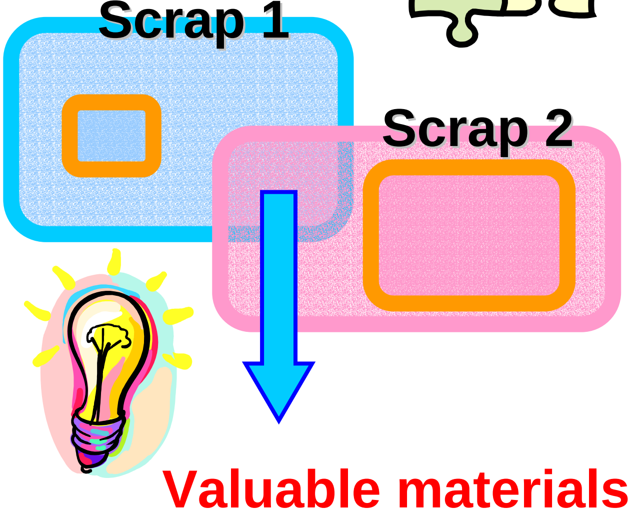
Innovative process

New process for producing highly pure metallic titanium directly from titanium ore

Environmentally sound rare metal processing

Development of a new recycling process involving scrap (or waste materials) combination





Valuable materials

Idea to transform scrap into valuable materials

Contribution to society by the development of an innovative and environmentally sound material processing

Resource Recovery and Materials Process Engineering Laboratory

2005/11/15
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New Titanium Production Process

High-speed Titanium Production Process Using Titanium Subhalides
Environmentally Sound Process Utilizing Titanium Scraps

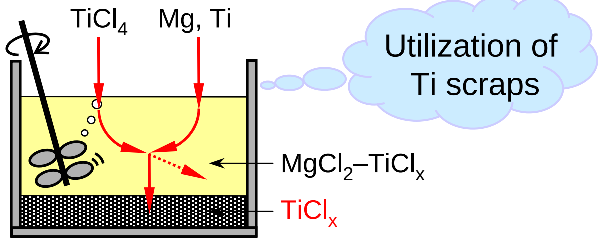
High-speed Ti production process

Ti production process using Ti subhalides ($TiCl_x$, x = 2, 3)

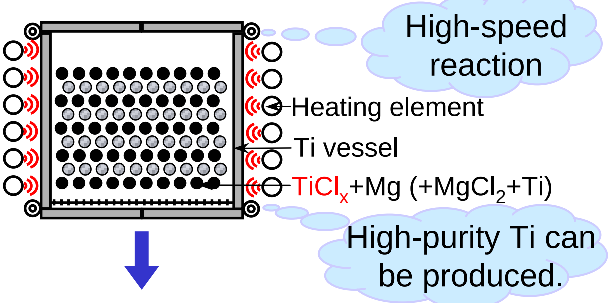
① $TiCl_4(l, g) + Mg(l, g) \rightarrow TiCl_x(s, l) + MgCl_2(l)$
$TiCl_4(l, g) + Ti(s, \text{scrap}) \rightarrow TiCl_x(s, l)$

② $TiCl_x(s, l) + Mg(l, g) \rightarrow Ti(s) + MgCl_2(l, g)$

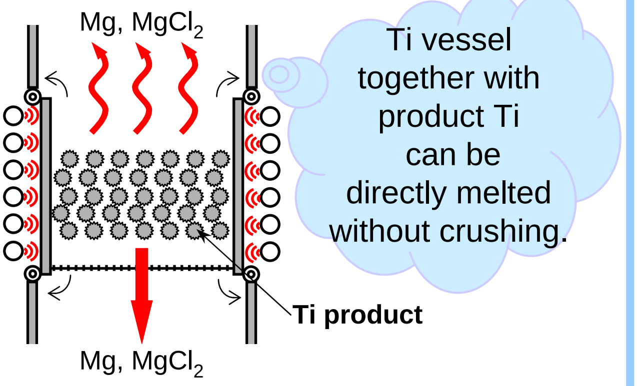
Step1: Production and enrichment of $TiCl_x$



Step2: High-speed reduction of $TiCl_x$



Step3: Removal of reaction product $MgCl_2$

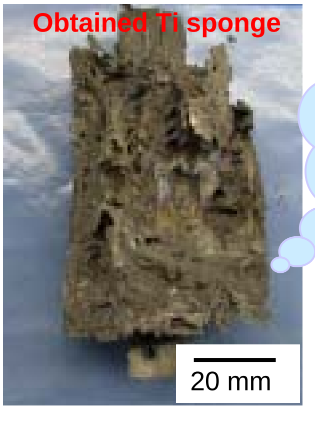


Features and experimental result

Comparison of Kroll process and new process

	Kroll process	New process
Process type	Batch-type, limited speed	**(Semi-)Continuous, high-speed**
Feed material	$TiCl_4$ (l, g)	**$TiCl_2$, $TiCl_3$ (s, l)**
Heat of reduction	High (ΔH = –434 kJ molTi)	**Low (ΔH = –94 ~ –191 kJ molTi)**
Reactor material	Mild steel (Iron contamination unavoidable)	**Titanium (No iron contamination)**
Reactor size	Large (Crush and melt)	**Small (No crush and direct melt)**
Flux, sealant	Not used	Ti, $MgCl_2$
Common features	Magnesiothermic reduction of chlorides Removal of $MgCl_2$ and Mg from Ti sponge by vacuum distillation Production of high-purity Ti with low oxygen content	

Experiment for the magnesiothermic reduction of $TiCl_3$



Ti with 99.2% purity was efficiently obtained using Ti vessel.

New technologies for this process are under development.

Feasibility of new Ti production process based on the magnesiothermic reduction of Ti subhalides using Ti vessel was demonstrated.

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0511_011_Ti_subhalide.ppt

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011_Ti_e
2005_Ti_subhalide

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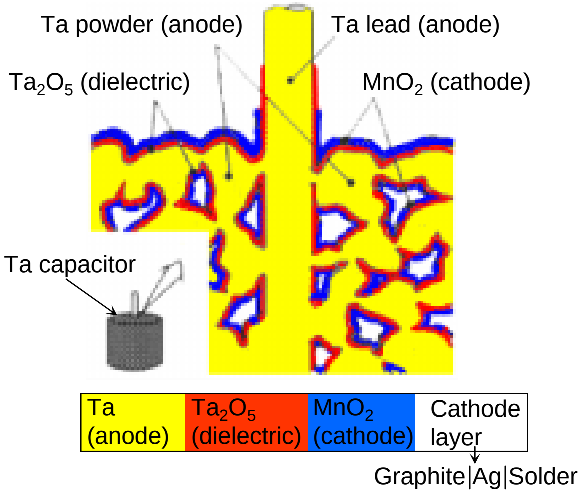
New Niobium/Tantalum Production Process

Electrochemical Pulverization of Bulk Metal for Producing Fine and Highly Pure Ta and Nb Powders

Background & new process

Background

Tantalum (Ta) capacitors have the largest capacity per unit volume, and they are thermally stable. The anode of a Ta capacitor is fabricated using Ta powder, which is very expensive primarily due to limited Ta resources.

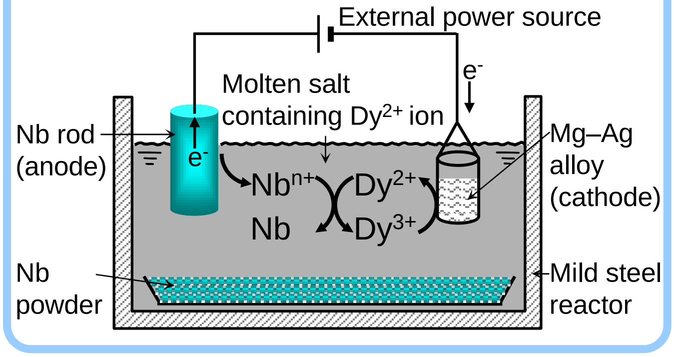


Recent trend in the miniaturization of electrical appliances has increased the demand for high performance Ta capacitors. If the abundant and cheap Nb can substitute Ta for capacitors, Nb capacitor has the potential to become the next generation capacitor.

New process: Electrochemical Pulverization (EP)

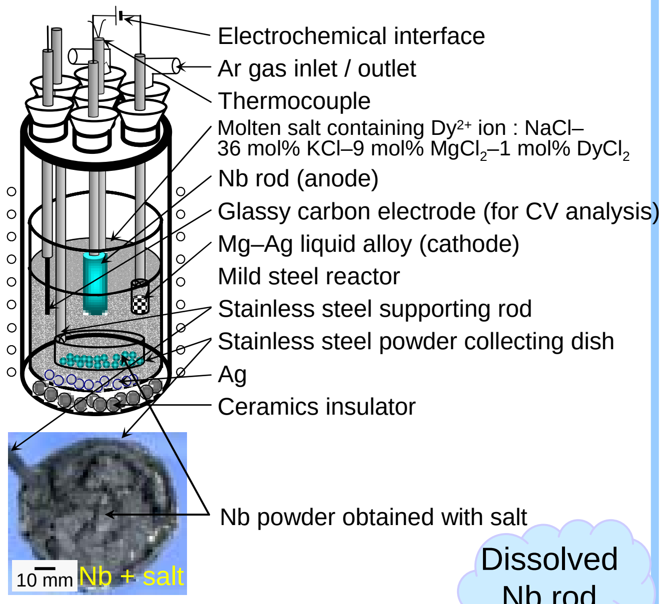
Anode: Nb (bulk) → Nb^{n+} + n e^-
(Anodic dissolution of Nb rod)
Cathode: n Dy^{3+} + n e^- → n Dy^{2+}
(Regeneration of Dy^{2+} ion, reductant)
In molten salt: Nb^{n+} + n Dy^{2+} → Nb (powder) + n Dy^{3+}
(Reduction of Nb^{n+} ions)

Overall reaction: Nb (bulk) → Nb (powder)

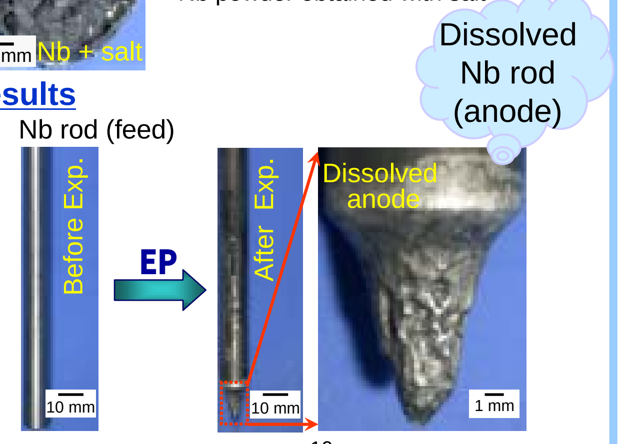


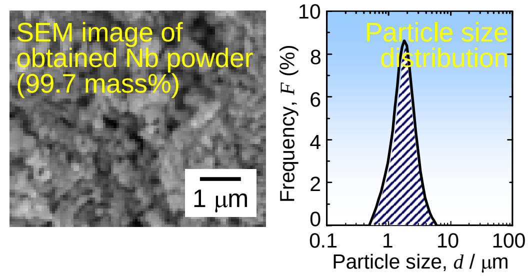
Experimental & results

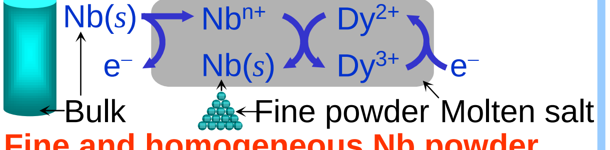
Experimental apparatus



Results







Fine and homogeneous Nb powder is successfully obtained

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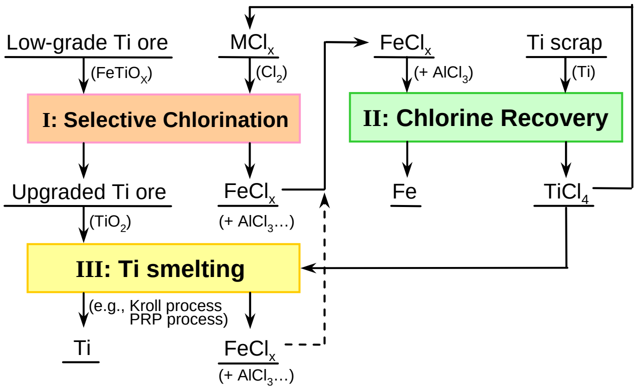
New Titanium Production Process

Iron Removal from Titanium Ore by Selective Chlorination and Effective Utilization of Chloride Wastes and Titanium Scrap
Development of New Environmentally Sound Process

New process using low-cost low-grade Ti ore



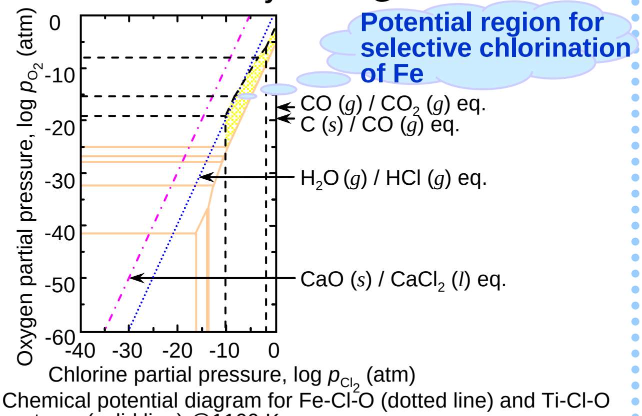
The research objective is to develop a new environmentally sound process using low-cost low-grade Ti ore.

Ti feed with low Fe concentration obtained by selective chlorination can be reduced to metallic Ti in Kroll process or other new Ti smelting processes.

Thermodynamic analysis and experimental

I: Selective Chlorination

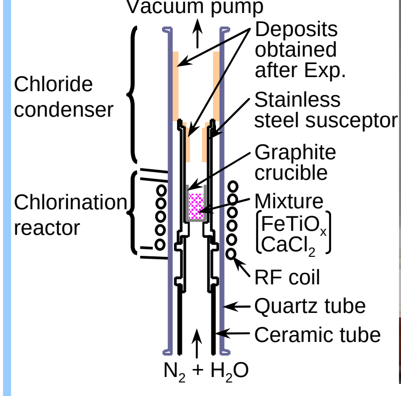
Fe-Cl-O & Ti-Cl-O Systems @ 1100 K



Chemical potential diagram for Fe-Cl-O (dotted line) and Ti-Cl-O systems (solid line) @1100 K.

$$H_2O\ (g) + CaCl_2\ (s, l) \rightarrow HCl\ (g) + CaO(s)$$

$$FeO_x\ (FeTiO_x, s) + HCl\ (g) \rightarrow FeCl_x\ (g)\uparrow + H_2O\ (g)$$



Fe was removed from Ti ore.

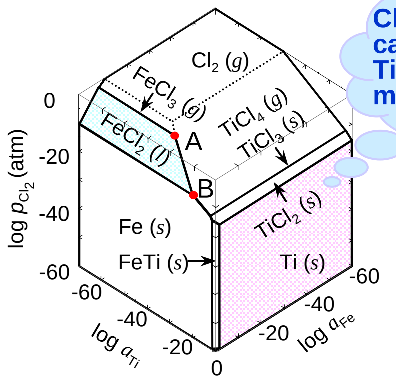
Utilization of low-grade Ti ore

Decrease in production cost of Ti

Fe was selectively removed from Ti ore.

II: Chlorine Recovery

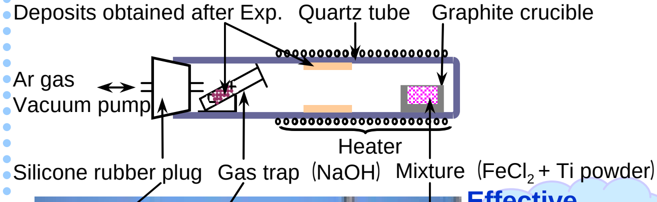
Fe-Ti-Cl System @ 1100 K

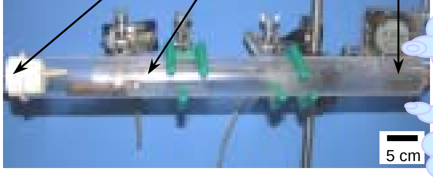


Chlorine in FeCl$_x$ can be recovered as TiCl$_4$ (g) by using metallic Ti.

Chemical potential diagram for Fe-Ti-Cl system @1100 K.

$$FeCl_2\ (l, g) + Ti\ (s) \rightarrow Fe\ (s) + TiCl_4\ (g)\uparrow$$





Effective utilization of chloride wastes and Ti scrap is possible.

Environmental burden is decreased.

Ti feed material was produced, at the same time, chlorine in FeCl$_x$ was recovered.

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0511_009_Ti_scrap.ppt

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009_Ti_e
2005_Ti_scrap

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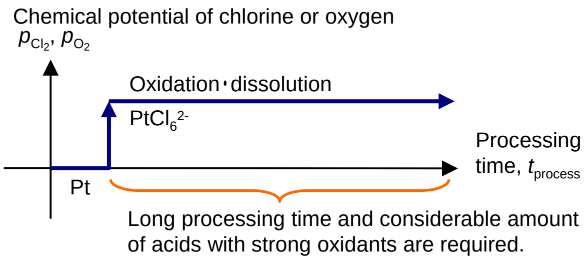
Efficient Recovery Process of Precious Metals

New Environmentally Sound Recovery Process of Precious Metals Using Reactive Metal and Chloride Vapor Treatment

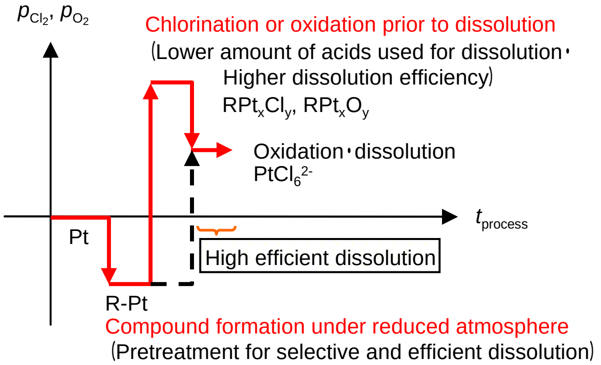
New hydrometallurgical recovery process of precious metals

Comparison between conventional process and new process

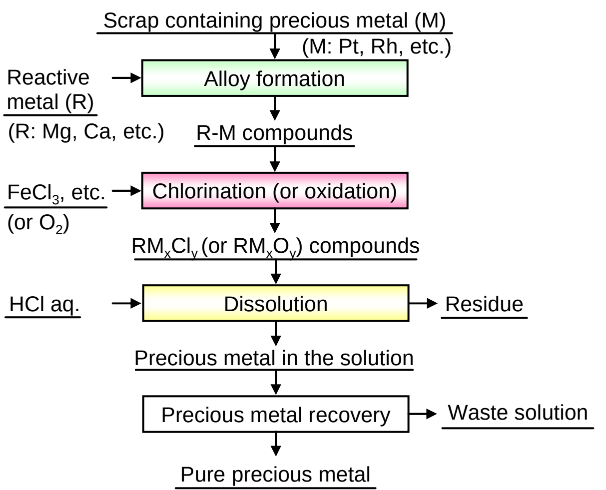
(a) Conventional leaching process



(b) Reactive metal treatment followed by chlorination or oxidation



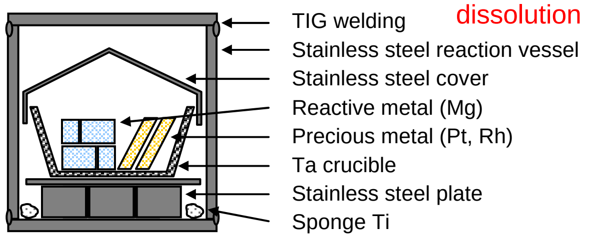
New recovery process for precious metals using reactive metal and chloride vapor treatment



Experimental procedure and results

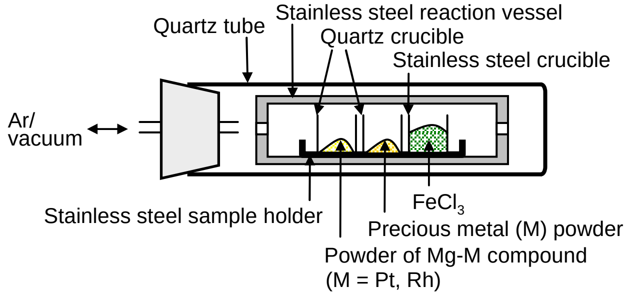
Synthesis of R-M compounds

Selective and high-speed dissolution

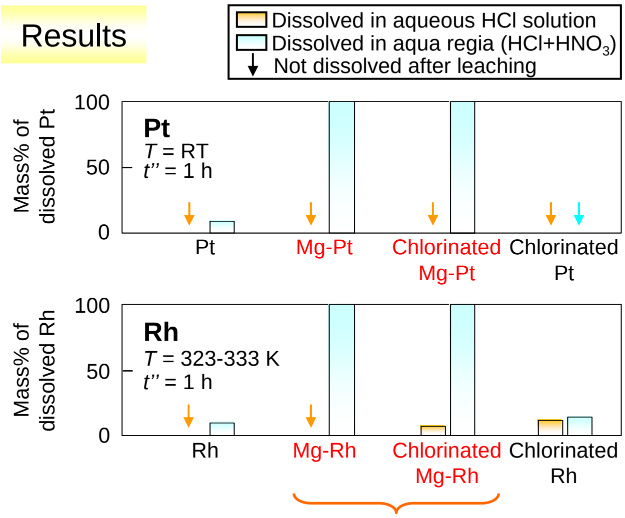


Chlorination of R-M compounds

Minimizing amount of toxic waste solution
Utilizing chloride wastes



Results



Dissolution efficiencies in aqua regia after alloy formation and chlorination were significantly enhanced.

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2005_PGM_scrap

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New Ti Production Process Directly from Ti Ore

Development of New Ti Production Process Using Low-grade Ti Ore
Selective Chlorination and Fe Removal by Electrochemical Method

New Ti smelting process

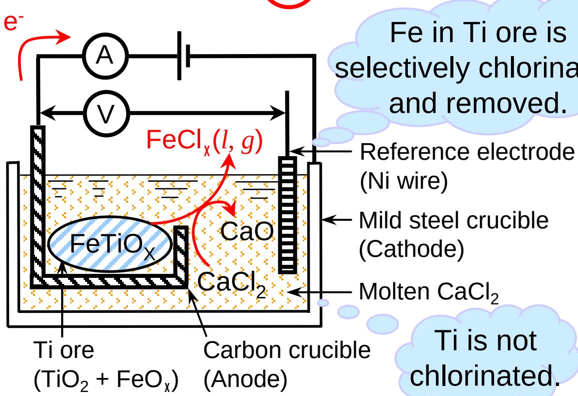
Fe in Ti ore is selectively chlorinated and removed by a new smelting process in which Cl potential in molten salt is controlled by electrochemical method.

1. Selective chlorination, Fe removal

Cathode: $Fe^{n+} + n\,e^- \rightarrow Fe$; $Ca^{2+} + 2\,e^- \rightarrow Ca$

Anode: $2\,Cl^- \rightarrow Cl_2 + 2\,e^-$

$FeO_x\ (FeTiO_x) + Cl_2 \rightarrow FeCl_x(l, g) + O^{2-}$



Fe in Ti ore is selectively chlorinated and removed.

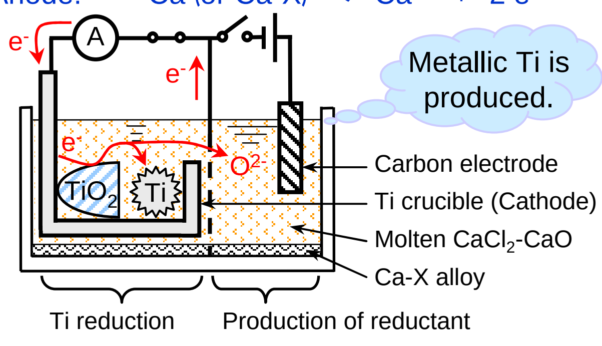
Ti is not chlorinated.

2. TiO_2 reduction process

(Metallic Ti is produced by new reduction process, e.g. EMR/MSE process)

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

Anode: $Ca\ (or\ Ca\text{-}X) \rightarrow Ca^{2+} + 2\,e^-$

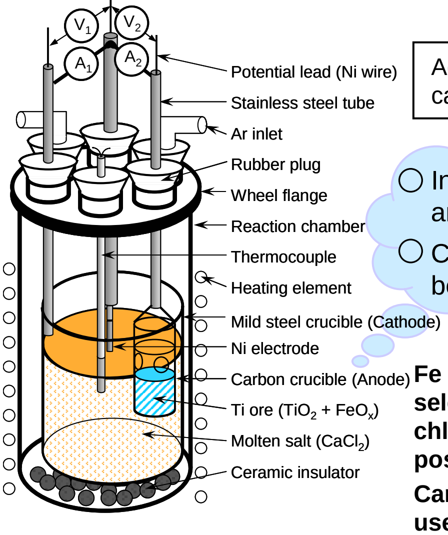


Metallic Ti is produced.

New smelting process for producing metallic Ti directly from Ti ore is under investigation.

Experimental apparatus and result

Experimental apparatus for Fe removal



Advantage of carbon crucible

○ Inert at high anodic potential
○ Cl potential can be increased.

Fe removal by selective chlorination is possible.

Carbon can not be used for Ti reduction electrode (cathode).

Experimental result

Table Analytical results of Ti ore and residue after selective chlorination.

	Concentration of element i, C_i (mass %)[a]			Fe / Ti (%)
	Ti	Fe	Ca	Mass ratio
Before exp.[b]	42.62	48.72	0.33	114.8
After exp.	47.22	3.40	47.92	7.2

a: Determined by XRF analysis.
b: Ilmenite ($FeTiO_x$) from China.

Fe in Ti ore was successfully removed. Fe removal ratio should be improved.

Technique for removing Fe down to ppm level is currently under investigation.

Selective chlorination and Fe removal in Ti ore by electrochemical method was demonstrated.

Future work

Development of new smelting process for producing metallic Ti directly from Ti ore after Fe removal.

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New Scandium Production Process

New Production Process of Very Scarce Scandium
Production of Al-Sc Alloy by Alloying with Al after Reduction of Sc_2O_3

What is Scandium?

Scandium (Sc) is classified as a rare earth metal (RE) as well as yttrium (Y) and lanthanid.

Atomic number	21 ←light metal
Atomic weight	44.96
Density (g/cm^3)	2.99
Melting point (℃)	1541
Clarke number (ppm)	5.5 (50th)
Price (¥/g)	4,000～30,000

Price of Sc is higher than those of Pt and Au.

There is no commercial Sc ore deposits specialized in Sc production, because of scarcity of Sc in the earth's crust.

Sc is currently recovered from the by-product of U or W smelting process.

⬇

Recently Sc is focused as a by-product of new Ni production process.

Main application of Sc


Bicycle for road race

Al-Sc alloy is used as structural material.


MIG29 Metal halide lamp

ScI_3 is encapsulated.

Sc is expected as future material supporting high-tech industry.

⬇

Demand for Sc is expected to increase.

Experimental procedure

Conventional production process：

$$2\ ScF_3 + 3\ Ca \rightarrow 2\ Sc + 3\ CaF_2$$

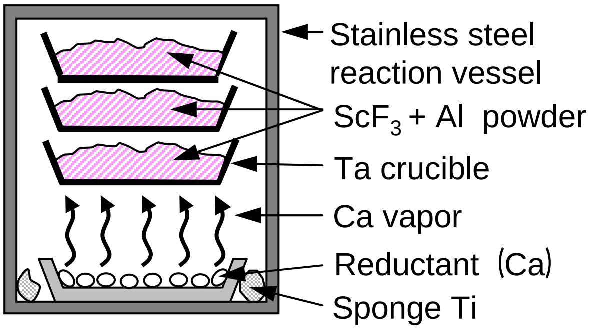
Because metallic Sc is chemically reactive, recovery of Sc by leaching process is difficult.

⬇

Sc can be extracted and separated by alloying with collector metal such as Al.

Research Plan (I)：Calciothermic reduction

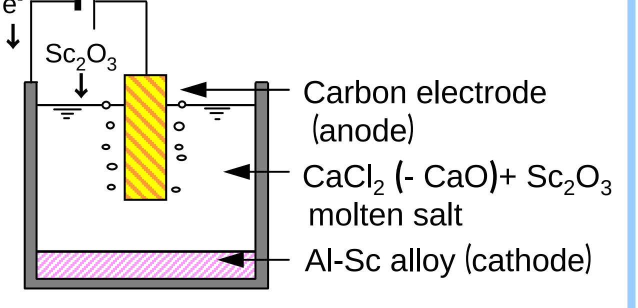
$$2\ ScF_3 + 6\ Al + 3\ Ca \rightarrow 2\ Al_3Sc\ (\text{or Al-Sc(l) alloy}) + 3\ CaF_2$$



Research Plan (II)：Molten Salt Electrolysis

Cathode：$Sc_2O_3 + Al + 6e^- \rightarrow$ Al-Sc(l) alloy $+ 3\ O^{2-}$

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



Study goal

Development of new process for producing Sc or Al-Sc alloy directly from Sc_2O_3

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006_Sc_e
2005_Sc

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New Production Process of Nb and Ta for Capacitors

Production of Nb for Capacitors by Preform Reduction Process

Production process of powder for capacitors

Comparison between Nb and Ta

	Niobium	Tantalum
Symbol of element	Nb	Ta
Atomic number	41	73
Atomic weight	92.9	180.9
Density	8.56 g/cm^3	16.65 g/cm^3
Melting point	2468 ℃	2980 ℃
Boiling point	4758 ℃	5534 ℃
Resistivity (20℃)	12.5 μΩ・cm	12.4 μΩ・cm
Clarke number	2×10^{-3} (34 th)	1×10^{-3} (40 th)
World production	23000 ton	2300 ton
Demand in Japan	3900 ton	550 ton
Price(in round numbers)	55 $/kg	700 $/kg

Production volume of Nb is **10 times** that of Ta, price of Nb is **less than one-tenth** that of Ta.

Nb powder is emerging as a substitute material of Ta for use in capacitor.

Uniform Nb powder with purity higher than 99.9% and particle size of 0.2〜1.0 μm is required for capacitor application.

Preform Reduction Process (PRP)

Nb_2O_5 ＋ Flux ＋ Binder → Preform

Chemical reaction：

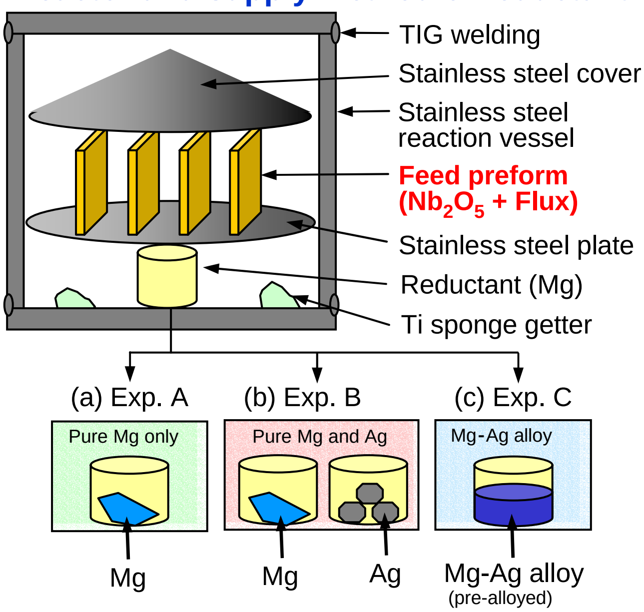
$Nb_2O_5 + 5\,Mg \rightarrow 2\,Nb + 5\,MgO$

＜Features＞

- **No emission of waste solution containing fluorine**
- **Flexible scalability, and homogeneous powder available**
- **Small amount of molten salts required**
- **(Semi–)Continuous and high-speed process**

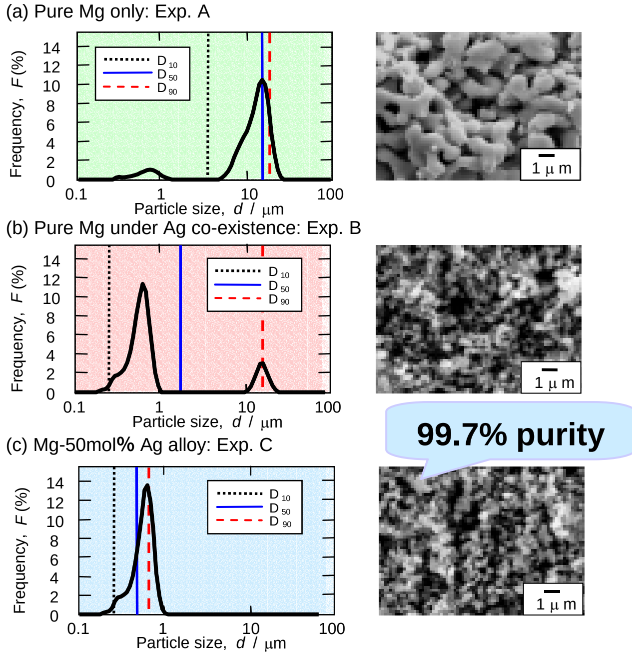
Experimental procedure and results

Reactor and supply method of reductant



Particle size distribution and SEM image

$T_{red.}$ = 1273 K, $t'_{red.}$ = 24 h, Flux = $CaCl_2$, $X_{cat./Nb}$ = 0.2



Highly pure and fine Nb powder was produced by controlling Mg vapor pressure using Mg-Ag alloy.

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2004_Nb_Ta_PRP

Institute of Industrial Science, The University of Tokyo

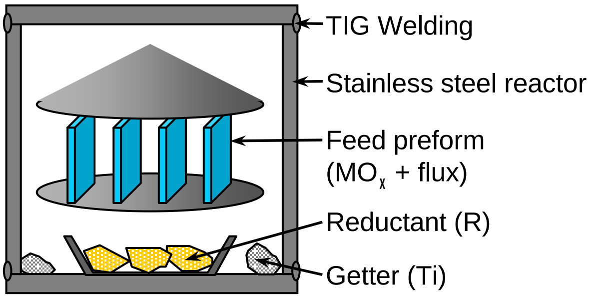
New Titanium Production Process (PRP)

Conversion of Ti into Common Metal by Process Innovation

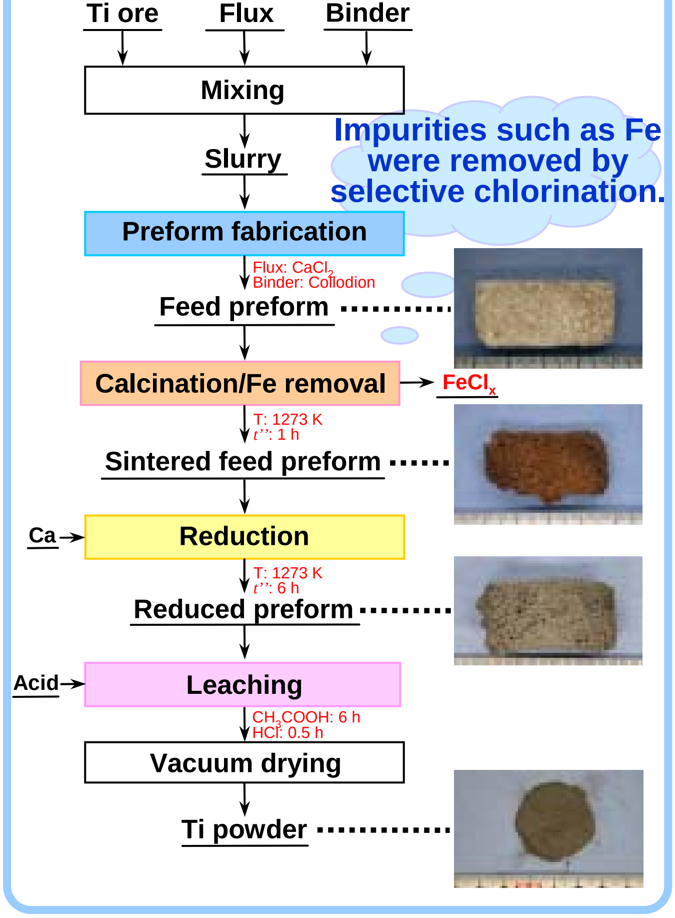
New process for producing Ti powder directly from Ti ore

Experimental apparatus for preform reduction process (PRP)

$MO_x + R \rightarrow M + RO_x$ M = Ti, Nb, Ta R = Ca, Mg…



Experimental procedure of PRP

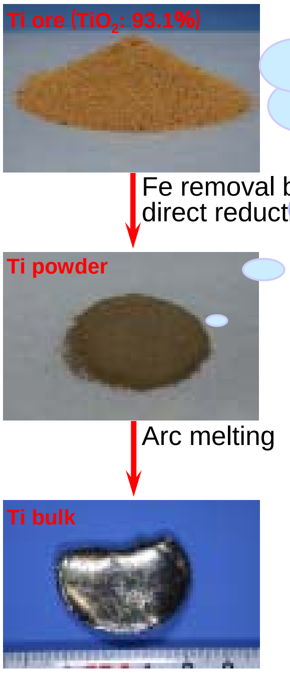


Features and experimental results

Comparison of Kroll process and this process

	Kroll process	This process
Process type	Batch-type, limited speed (Complex)	**(Semi-)Continuous, high-speed (Simple)**
Feed material	$TiCl_4$ (*l*,*g*)	**TiO_2(*s*)**
Reductant	Mg	**Ca**
Reactor size	Large (Crush)	**Small (No crush, flexible scalability)**
Flux, sealant	Not used	**$CaCl_2$**

Experimental results



Metallic Ti powder with purity of 99 mass% was obtained.

New process for producing highly pure Ti powder directly from low-grade Ti ore is under development.

New process for producing highly pure metallic Ti powder directly from feed oxides was developed.

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004_Ti_e
2004_Ti_PRP

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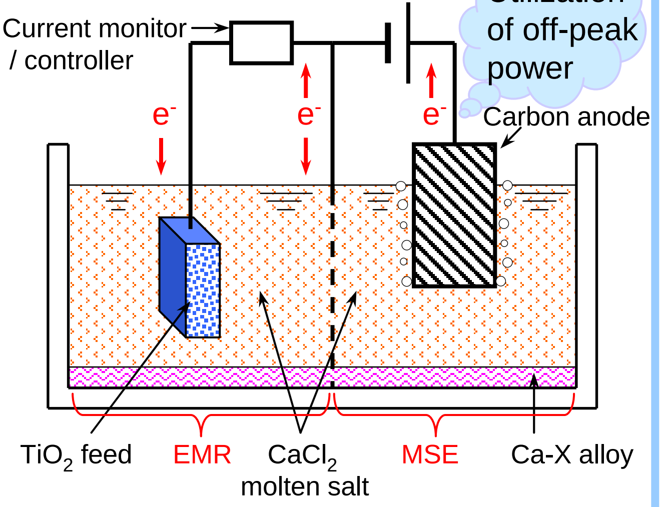
New Titanium Production Process (EMR)

Research on Innovative Technology and New Production Process of Titanium
Conversion of Resource Abundant Rare Metal into Common Metal

New Ti reduction process

EMR / MSE process



<u>EMR: Electronically Mediated Reaction</u>

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

Anode: $Ca \rightarrow Ca^{2+} + 2e^-$

<u>MSE: Molten Salt Electrolysis</u>

Cathode: $Ca^{2+} + 2e^- \rightarrow Ca$

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

Overall reaction

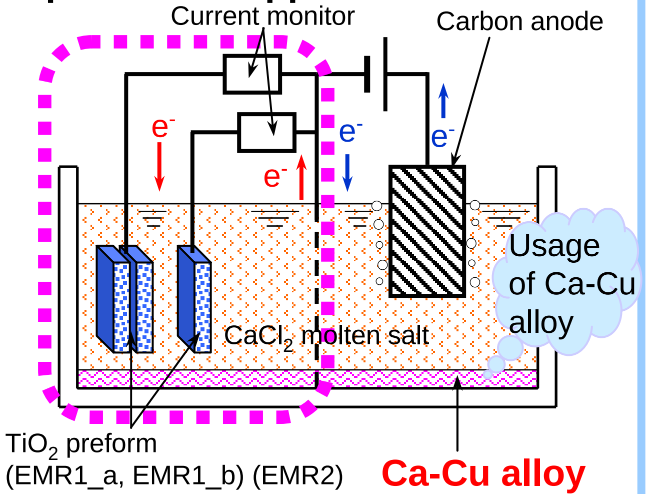
$$TiO_2 + C \rightarrow Ti + CO_2$$

Comparison of the Kroll process and this process

Kroll process	EMR / MSE process
◎ High-purity Ti obtainable ○ Established chlorine and Mg circulation ○ Utilization of efficient Mg electrolysis ○ Reduction and electrolysis operations can be carried out independently	◎ Direct reduction from oxide ◎ Resistant to iron and carbon contamination ◎ (Semi-)continuous process ○ Reduction and electrolysis operations can be carried out independently
×Batch type process ×Complicated process ×Slow production speed ×Huge exothermmic reaction	× Utilization of Ca reductant × Difficult meal / salt separation when oxide system is used × Complicated cell structure △ Complicated process

Demonstration experiment for EMR process

Experimental apparatus



Experimental result

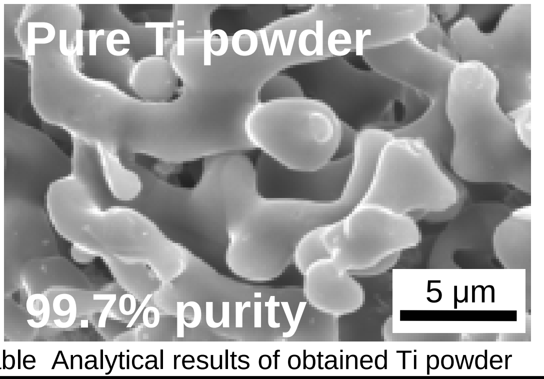


Table Analytical results of obtained Ti powder

	Concentration of element i, C_i (mass%)			
	Ti[a]	Ca[a]	Cl[a]	O[b]
EMR1_a	99.7	0.19	(0.09)	0.25
EMR1_b	99.6	0.18	(0.15)	0.37
EMR2	99.7	0.21	(0.08)	-

[a]: Determined by XRF (Detection limit: 300 ppm)
[b]: Determined by inert gas fusion-infrared absorption spectroscopy (LECO)

<u>2500 ppmO</u>

Homogeneous Ti powder free of Cu was obtained even though Ca-20 mol%Cu alloy reductant was used.

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2005/11/15
Takashi Abiko (Isao Obana)
0511_003_Ti_EMR.ppt

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003_Ti_e
2004_Ti_EMR

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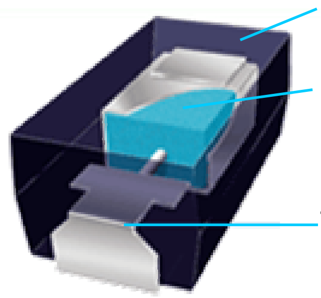
Recycling Process for Tantalum

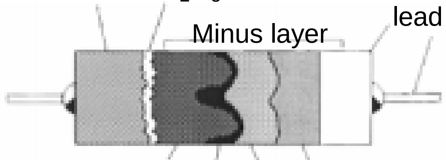
New Environmentally Sound Process for Recovery of Tantalum from High Performance Capacitor

Features of Ta capacitor

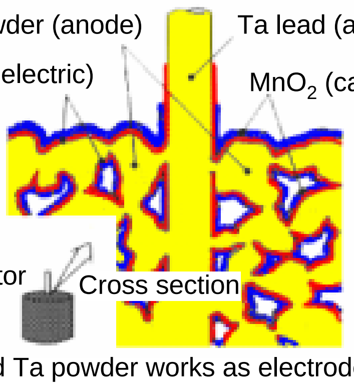
Structure of Ta capacitor



Schematic illustration of its interior



Cross section of Ta electrode



Sintered Ta powder works as electrode.

- Capacitance per unit volume higher than those of other capacitors
- High thermal stability

High performance capacitor

Ta is scarce and expensive rare metal.

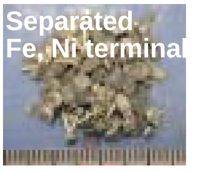
Development of recovery process of Ta from capacitor is important.

Recycling of Tantalum

Ta capacitor was oxidized at elevated temperature.

After oxidation, Ta electrode maintained its original shape, while fireproof epoxy resin was converted into powder consisting SiO_2.

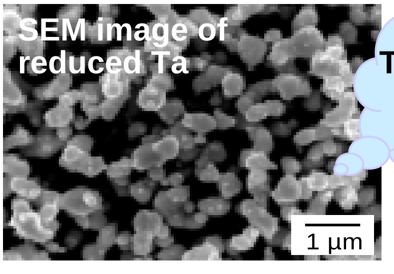
Fe and Ni terminals were separated by magnetic separation.



Powder containing SiO_2 was mechanically separated.

After crushing, Cu terminal was separated by sieving.

Impurities were removed by leaching with acid, and Ta was recovered as Ta_2O_5.



Ta with purity of 99% was obtained.

Recovery process of Ta from capacitor was established.

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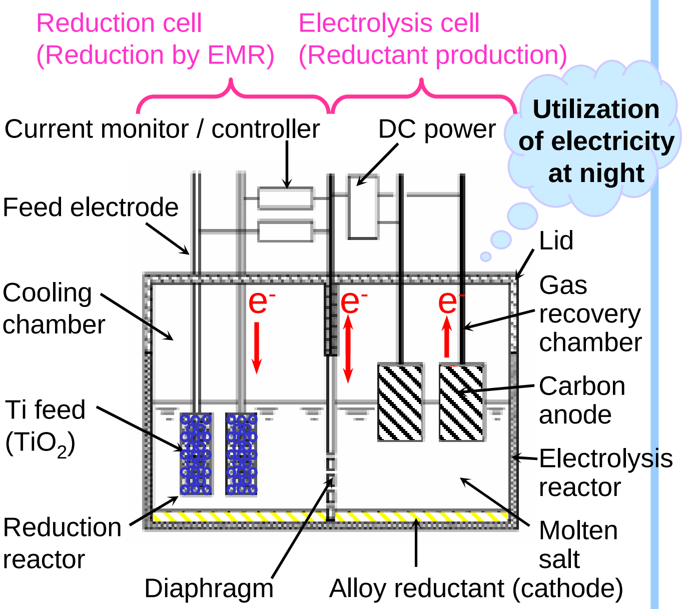
New Production Process of Rare Metal

Development of New Production Process for Conversion of “Rare Metal” into “Common Metal”

New Ti production process



Schematic illustration of EMR/MSE process

Reduction (EMR)

Cathode: $TiO_2 + 4e^- \rightarrow Ti + 2O^{2-}$ (1)

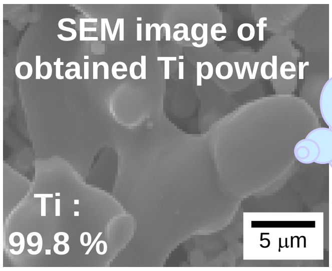
Anode: $Ca \rightarrow Ca^{2+} + 2e^-$ (2)

Production of reductant (MSE)

Cathode: $Ca^{2+} + 2e^- \rightarrow Ca$ (3)

Anode: $C + xO^{2-} \rightarrow CO_x + 2xe^-$ (4)

Overall $TiO_2 + C \rightarrow Ti + CO_2$ (5)

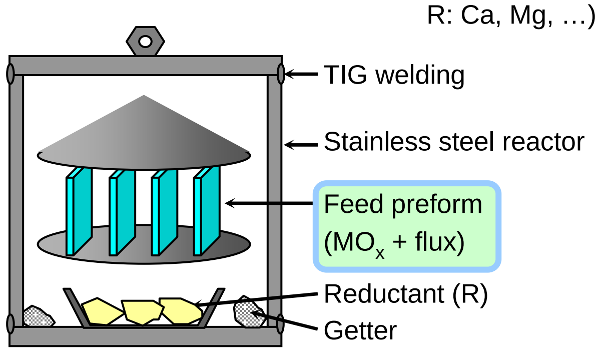


Scaling-up of this process is under investigation.

Next-generation low-cost production process of Ti is under development.

New industrial process for producing highly pure rare metal powder by Preform Reduction Process

$MO_x + xR \rightarrow M + xRO$ (M: Nb, Ta, Ti, … R: Ca, Mg, …)



Schematic illustration of reactor for PRP

Preform fabrication

Flux: CaO, $CaCl_2$

Binder: Collodion

After calcination

Temp.: 800~1000 °C

Holding time: 1 h

After reduction

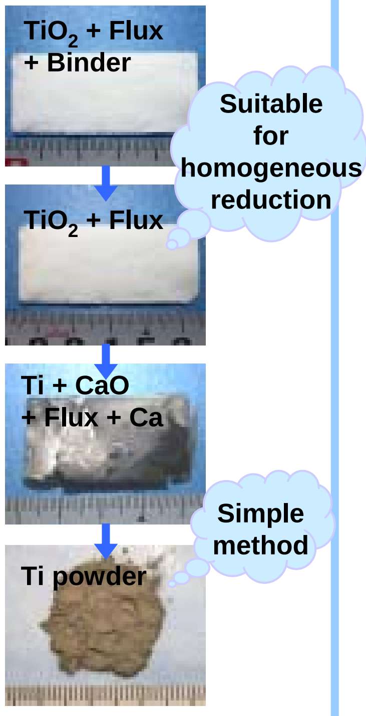
Temp.: 800~1000 °C

Holding time: 6 h

Ti powder obtained after leaching

Acetic acid: 6 h

Hydrochloric acid: 0.5 h



New industrial process for producing rare metal powder with high purity and controlled morphology was developed.

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