高純度金属バナジウムの新製造法の開発

Development of New Production Process of High Purity Vanadium Metal

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Introduction

Vanadium?

The periodic table of the elements

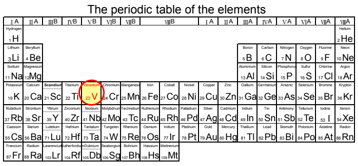


Table Abundance of elements in the earth's crust.

Crustal abundance (ppm)	Element
$> 10^5$	O, Si
$10^5 \sim 10^4$	Al, Fe, Ca, Na, K, Mg
$10^4 \sim 10^3$	Ti, H, P
$10^3 \sim 10^2$	V, Mn, S, C, Cl, ･･･
$10^2 \sim 10^1$	Cu, Ni, Zn, Nb, Co, Pb, ･･･
⋮	⋮
$10^{-1} \sim 10^{-2}$	Hg, Ag, Pd, Se
$10^{-2} \sim 10^{-3}$	Pt, Au, Rh, ･･･

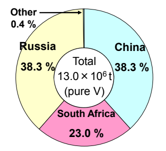
V metal

Feature of vanadium

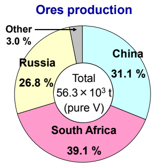
- Low density(6.11 g/cm^3) and high melting point (2188 K).
- The 20th largest crustal abundances among the all elements .
- Average abundance of vanadium in the earth's crust; 120ppm. (cf. Common (or base) metals such as Ni: 84ppm, Cu: 60ppm, Zn: 70ppm, Pb: 14ppm).

Resources and production

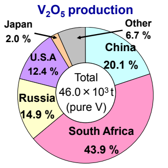
Confirmed reserve



Ores production



V_2O_5 production



Fe-V production

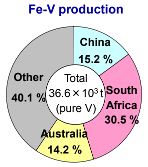
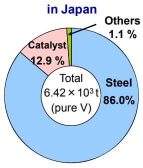


Table Amount of production and price of some metal elements in 2007.

Element	Amount of production (10^3 ton / year)	Price ($ · kg^{-1})
V	58	39
Fe	1,100,000	0.06
Al	29,000	3
Cu	15,000	7
Ni	1,600	40
Zn	11,000	3

Vanadium production in Japan



Application

Special steel

In the primary use, vanadium is consumed as an alloy element of steel.

High thermal stability and tensile strength

(Ref. Iron and Steel Institute of Japan)

Ti-V hydrogen storing alloy

Vanadium has high hydrogen storage ability. Ti-V alloy draws attention as a negative electrode material of nickel hydride battery, and has a potential to be used for lower-cost and higher-capacity battery.

It is important to develop a new production process of pure vanadium metal and vanadium alloy.

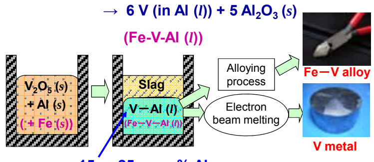
(Ref. Matsushita Electric Industrial Co., Ltd)

Commercial production process

Aluminothermic process

$$3\ V_2O_5\ (s) + 10\ Al\ (s)\ (+\ Fe\ (s)) \rightarrow 6\ V\ (\text{in Al}\ (l)) + 5\ Al_2O_3\ (s)$$

(Fe-V-Al (l))



15 ～ 25 mass% Al

Features

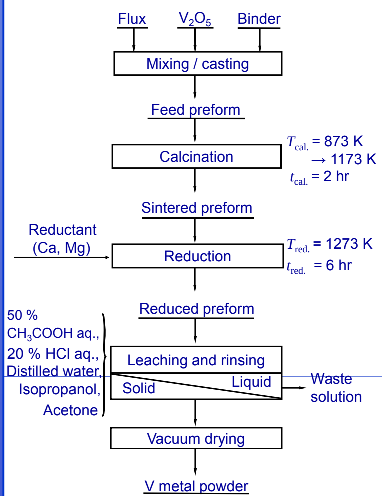
◎ Simple and economic process
○ First batch type process with rich scalability
× Difficult to control the purity
× Repeated removal of Al by the electron beam melting for some applications

Aim of this study

Development of simple and low-cost process for high purity vanadium metal or alloys

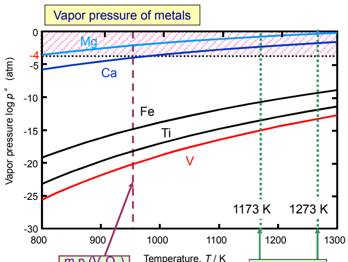
Experimental

Flowchart of our process

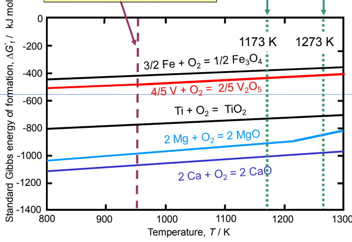


Thermodynamic analysis

Vapor pressure of metals



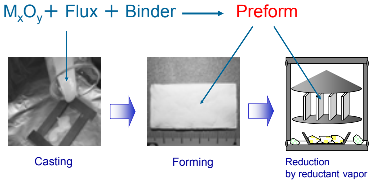
Ellingham diagram of oxides

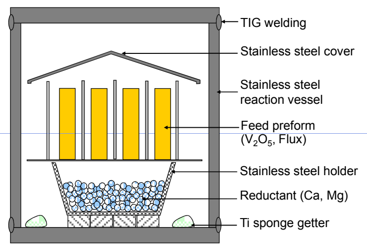


Preform reduction process (PRP)

$$V_2O_5 + 5\ R \rightarrow 2\ V + 5\ RO_x$$

M_xO_y + Flux + Binder → Preform





Features

◎ Suitable for uniform reduction
◎ Flexible scalability
○ Possible to control the morphology of the powder by varying the flux content in the preform
○ Possible to prevent the contamination from the reaction container and to control the purity
○ Amount of waste solution is minimized.
○ Molten salt as a flux can be reduced in comparison with the other direct reduction process.
× Difficult to produce reductant and to control its vapor

PRP is simple and low-cost process for high purity products.

Problem

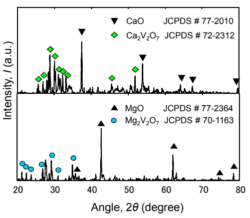
The melting point of vanadium pentoxide (V_2O_5) is low (963 K), and it is difficult to fabricate mechanically strong solid preform. Reduction has to be carried out at temperature higher than 1173 K to maintain enough vapor pressure of Ca or Mg.

CaO or MgO was added to feed preform in order to synthesize complex oxides ($Ca_xV_yO_z$, $Mg_xV_yO_z$) during calcination. The obtained feed preform has a mechanical strength at elevated temperature and suitable for handling during processing.

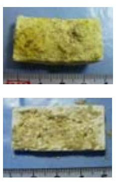
Results

Calcination process

X-ray diffraction pattern



Appearance



Condition for calcination

The calcination temperature was raised from 873 K to 1173 K during 2 hr of calcination period.

- Complex oxides ($Ca_2V_2O_7$ or $Mg_2V_2O_7$) was synthesized after calcination.
- Calcined sample maintained its shape form.

→ This can be used as a feed preform for reduction experiment.

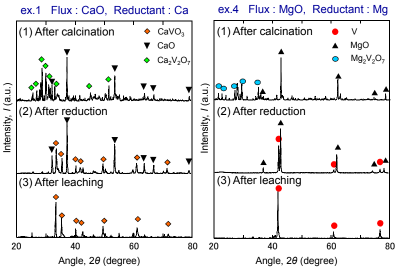
Reduction process

Weight change of the samples

Table Experimental condition and mass of samples after each step.

Exp. #	Reductant	Flux	Mass of preform, w_{pre} / g (V_2O_5 + 3CaO / V_2O_5 + 3MgO)	Mass of reductant, w_R / g (Ca / Mg)	Mass of sample after reduction, w_1 / g	Mass of sample after leaching, w_2 / g
ex.1	Ca	CaO	3.474	3.976	3.642	1.805
ex.2	Ca	MgO	3.670	4.906	3.955	0.981
ex.3	Mg	CaO	3.604	2.573	4.435	1.071
ex.4	Mg	MgO	3.937	3.345	5.086	0.729

X-ray diffraction pattern



X-ray fluorescence spectrometry

Table Analytical results of vanadium powder obtained by PRP.

Exp. #	Reductant	Flux	[a]Composition of sample (mass%) V	Ca	Mg	Fe	Cr
ex.1	Ca	CaO	79.0	20.4	—	0.1	0.4
ex.2	Ca	MgO	85.4	13.0	—	0.3	0.5
ex.3	Mg	CaO	86.0	2.4	10.6	0.2	0.5
ex.4	Mg	MgO	99.7	—	0.2	0.01	0.03

[a]Determined by XRF ; value excludes carbon and gaseous elements.

Condition for reduction

- Temperature :1273 K, Time : 6 hr

- In using Mg vapor as a reductant, pure vanadium metal was obtained. The purity of the obtained vanadium powder was 99.7 mass%.
- In using Ca vapor as a reductant, $Ca_2V_2O_7$ in the preform was reduced to CaV_2O_4 after reduction. At this stage, vanadium metal was not produced.

The reason for incomplete reduction by Ca vapor is not well understood. The difference of the results between Mg and Ca reductant is partially due to the difference of their vapor pressure. The vapor pressure of Mg (0.458 atm) is 26 times larger than Ca (0.018 atm) at 1273 K.

Current status

The feasibility of the preform reduction process (PRP), based on the thermal reduction of V_2O_5, was demonstrated.

- Complex oxide containing V_2O_5 was synthesized by the calcination process in order to increase the mechanical strength of feed preform.
- Vanadium powder with 99.7 mass% purity was obtained by magnesiothermic reduction.

Future work

- Investigation of residual oxygen concentration, and evaluation of total vanadium yield.
- Development of production process of Ti-V alloys.
- Analysis of reduction mechanism by utilizing the chemical potential diagram for the system involving oxygen, calcium, magnesium, and vanadium.