Development of New Production Process of High Purity V Metal and V-Ti Alloys

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Vanadium?

The periodic table of elements

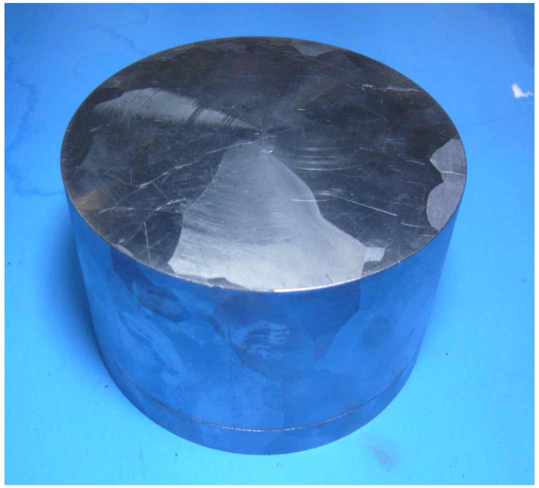
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Hydrogen 1 H																	Helium 2 He
Lithium 3 Li	Beryllium 4 Be											Boron 5 B	Carbon 6 C	Nitrogen 7 N	Oxygen 8 O	Fluorine 9 F	Neon 10 Ne
Sodium 11 Na	Magnesium 12 Mg											Aluminum 13 Al	Silicon 14 Si	Phosphorus 15 P	Sulfur 16 S	Chlorine 17 Cl	Argon 18 Ar
Potassium 19 K	Calcium 20 Ca	Scandium 21 Sc	Titanium 22 Ti	Vanadium 23 V	Chromium 24 Cr	Manganese 25 Mn	Iron 26 Fe	Cobalt 27 Co	Nickel 28 Ni	Copper 29 Cu	Zinc 30 Zn	Gallium 31 Ga	Germanium 32 Ge	Arsenic 33 As	Selenium 34 Se	Bromine 35 Br	Krypton 36 Kr
Rubidium 37 Rb	Strontium 38 Sr	Yttrium 39 Y	Zirconium 40 Zr	Niobium 41 Nb	Molybdenum 42 Mo	Technetium 43 Tc	Ruthenium 44 Ru	Rhodium 45 Rh	Palladium 46 Pd	Silver 47 Ag	Cadmium 48 Cd	Indium 49 In	Tin 50 Sn	Antimony 51 Sb	Tellurium 52 Te	Iodine 53 I	Xenon 54 Xe
Caesium 55 Cs	Barium 56 Ba	Lanthanum 57 La	Hafnium 72 Hf	Tantalum 73 Ta	Tungsten 74 W	Rhenium 75 Re	Osmium 76 Os	Iridium 77 Ir	Platinum 78 Pt	Gold 79 Au	Mercury 80 Hg	Thallium 81 Tl	Lead 82 Pb	Bismuth 83 Bi	Polonium 84 Po	Astatine 85 At	Radon 86 Rn
Francium 87 Fr	Radium 88 Ra	Actinium 89 Ac	Rutherfordium 104 Rf	Dubnium 105 Db	Seaborgium 106 Sg	Bohrium 107 Bh	Hassium 108 Hs	Meitnerium 109 Mt									

Features

① Low density (6.11 g/cm^3) and high-melting point (2188 K)

② High hydrogen storage ability at ambient temperature and pressure

③ The 20th largest crustal abundance among all elements



V metal

Application

Special steels

High thermal stability and tensile strength

↓

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

(http://popup5.tok2.com/home/trees2002/tabi/awaji2-2.htm.)

Ti–V alloys

High performance alloy

(Ref. Bridgestone Corp.)
(www.ikcc.jp/)

(Ref. PARIS MIKI Inc.)
(http://goddess.ocnk.net/)

Ti–V hydrogen storage alloy

V-25 mol%Ti alloy and V-50 mol%Ti alloy draw attention as an anode material of nickel hydride battery
→The use for electric vehicle

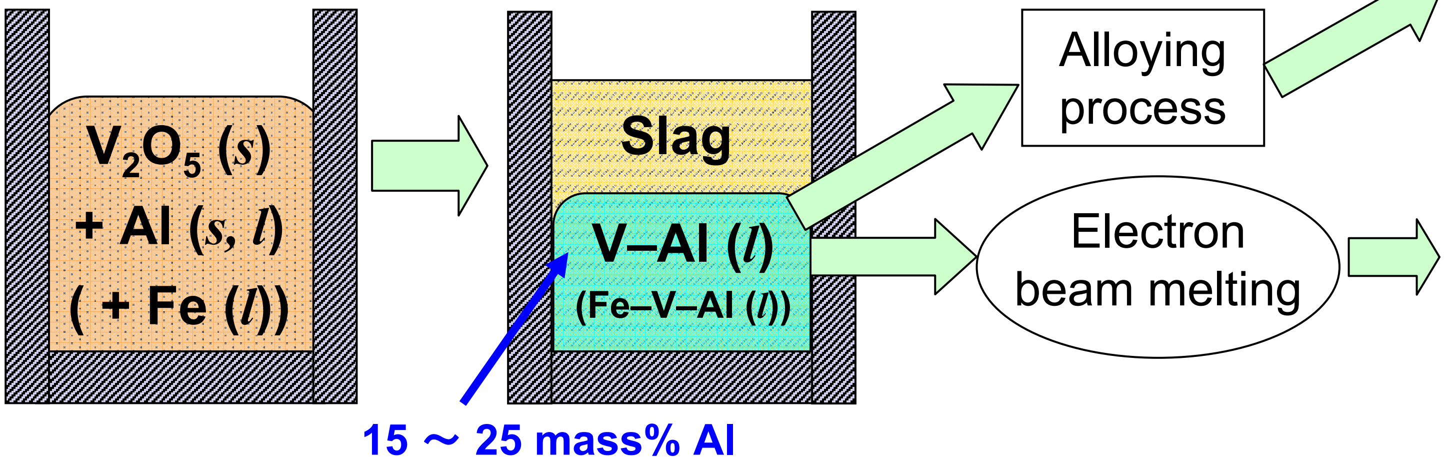
(Ref. Panasonic Co., Ltd.)
(http://panasonic.co.jp/corp/news/official.data/)

Commercial production process

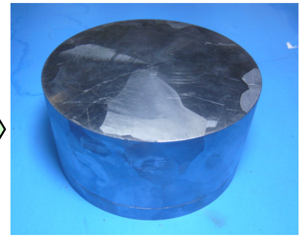
Aluminothermic reduction process (ATR)

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

(Fe–V(–Al) (l))



Fe–V alloy



High purity V metal

Features

- ◎ Simple and economical process
- ○ Flexible method for alloying
- × Difficult to control the purity
- × Repeated removal of Al by the electron beam melting for high purity V metal

Aim of this study

High purity vanadium metal and Ti–V alloy

① New demand for hydrogen storing alloys

② Abundance of V feed in the earth

However conventional process is not suitable for producing high purity vanadium metal and Ti–V alloys!!

Development of a simple and low-cost production process for high purity vanadium metal and Ti–V alloys

Experimental

Preform Reduction Process (PRP)

$$MO_x + Flux + R \rightarrow M + RO_x$$

Flux, MO_x, Binder

↓

Mixing / Casting

↓

Preform fabrication

↓

Reduction

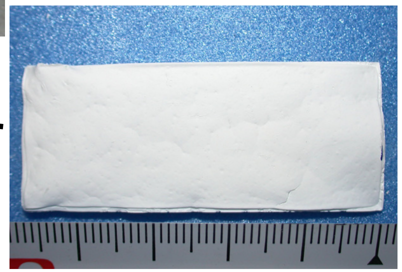
↓

Leaching

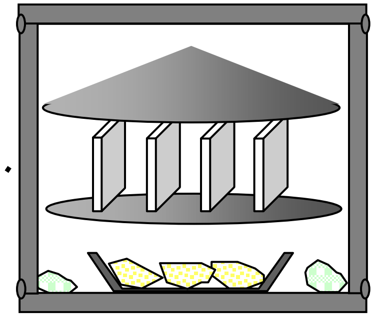
↓

Metal powder

Casting



Preform fabrication



Reduction by reductant vapor

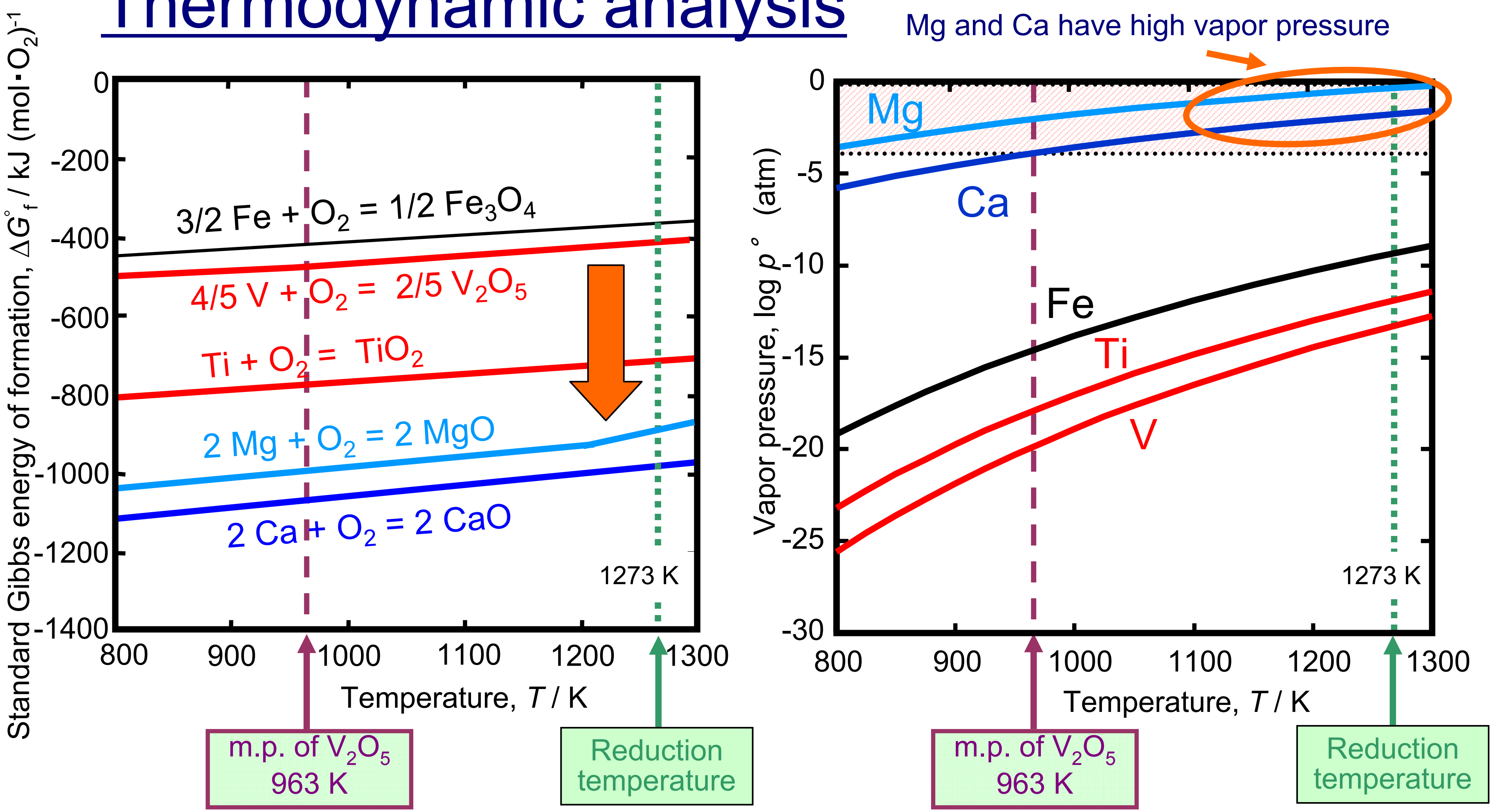
Features

◎ Effective control of purity and morphology

◎ Flexible scalability

◎ Suitable for uniform reduction

Thermodynamic analysis



The calcined preforms are reduced by Mg or Ca vapor above 1173 K.

In the preform reduction process (PRP), mechanical strength of preform is required at elevated temperature.

Flowchart of this study

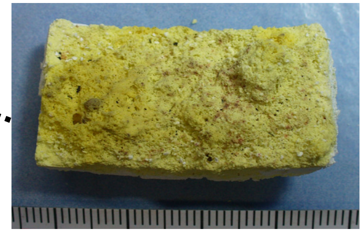
Flux : CaO, MgO, $CaCl_2$

Binder : Collodion

Flux → Mixing / casting
V_2O_5, TiO_2 → Mixing / casting
Binder → Mixing / casting

Mixing / casting
↓
Preform fabrication
↓
Feed preform

↓
Calcination (**873 K → 1173 K, 2 h**)



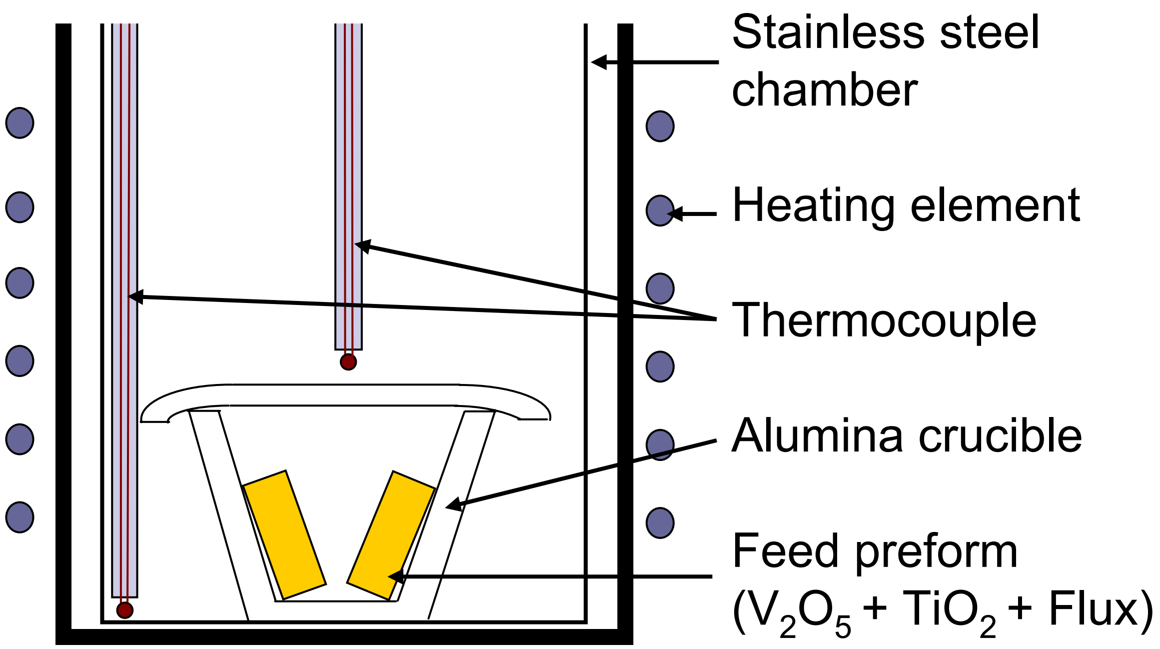
↓
Reduction ← Reductant (Ca or Mg), **1273 K, 6 h**
↓
Reduced preform

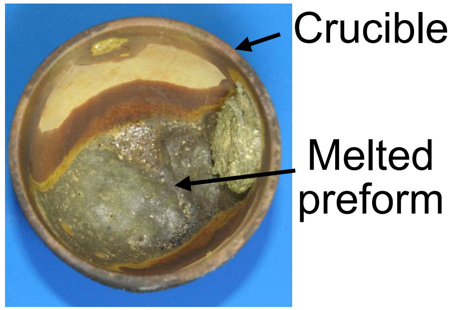
↓
Leaching ← 50% CH_3COOH aq., 20% HCl aq., Distilled water, Isopropanol, Acetone
S | L → Waste solution
↓
Vacuum drying
↓
V powder (Ti–V alloy)

Experimental procedure 【Calcination】

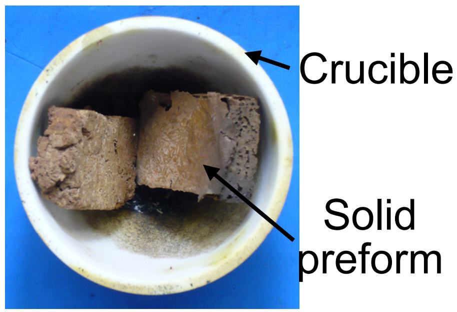
■ V_2O_5 (+ TiO_2) + CaO / MgO / $CaCl_2$ → $Ca_xV_yO_z$ / $Mg_xV_yO_z$
⇒ Vanadium complex oxide has high melting point.

- $T_{m.p.}(V_2O_5)$ = 963 K
- Calcined temperature : $T_{cal.}$ = 873 K → 1173 K
  Calcined time : $t'_{cal.}$ = 2 h





Preforms without flux
→Melted at Low temp. !



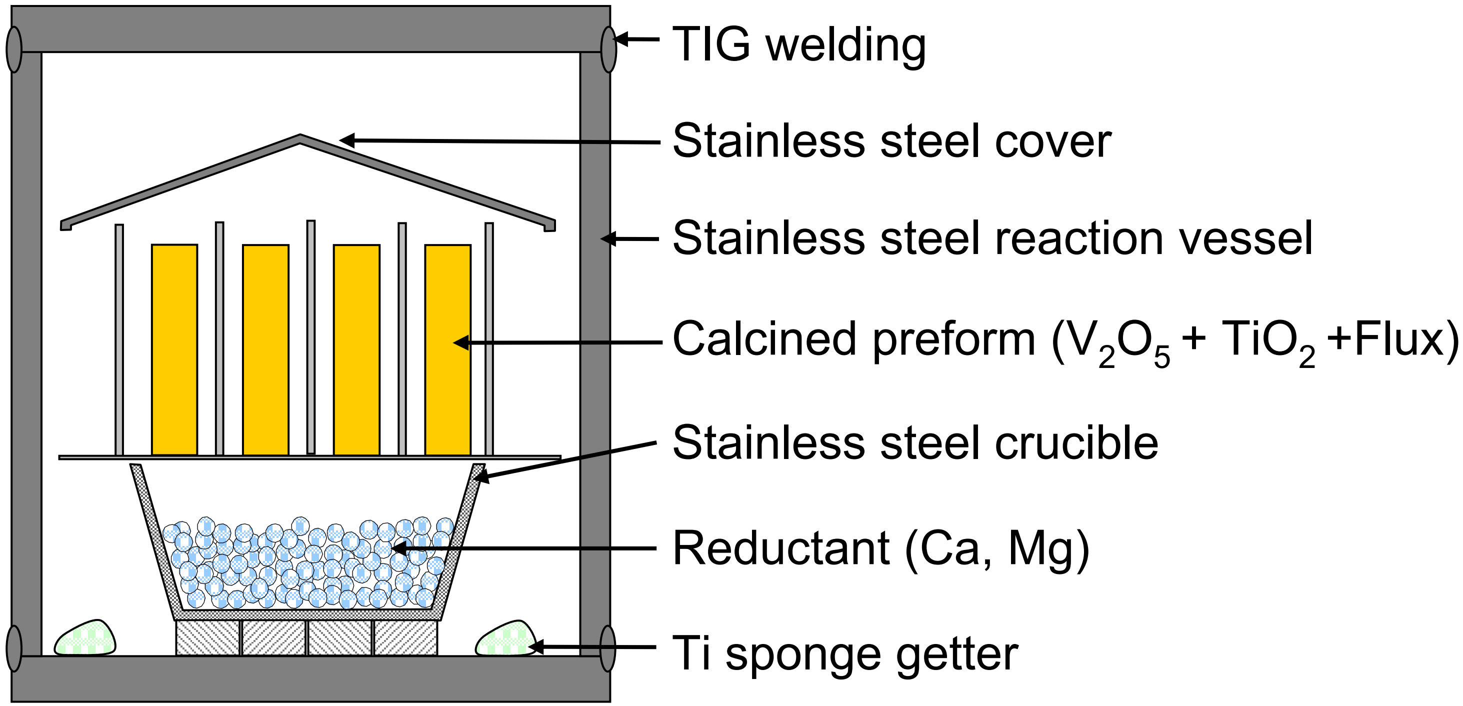
Preforms with flux

Experimental procedure 【Reduction】

■ V_2O_5 (+ TiO_2) + Flux + R → 2 V(–Ti) + RO_x
⇒Reduction of preform by Ca or Mg vapor

◆ Reduction temperature : $T_{red.}$ = 1273 K

◆ Reduction time : $t'_{red.}$ = 6 h



Production of Vanadium Metal

Result【Calcination】

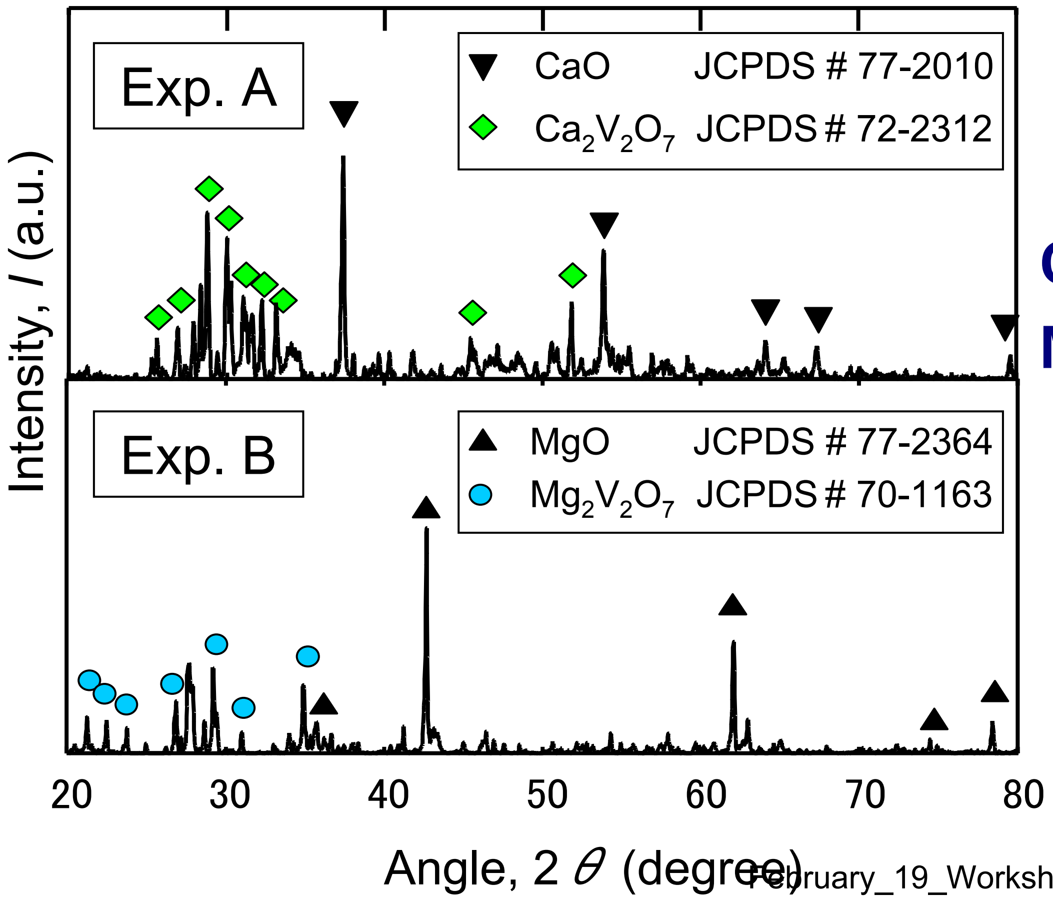
Calcined V_2O_5 and flux

$T_{cal.}$: 873 K → 1173 K

$t'_{cal.}$: 2 h

$$V_2O_5 + 2\ CaO \rightarrow Ca_2V_2O_7$$

$$V_2O_5 + 2\ MgO \rightarrow Mg_2V_2O_7$$

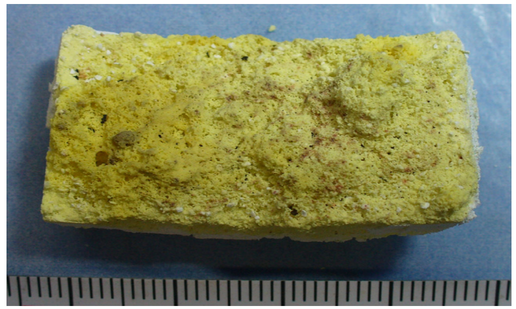


V_2O_5 m.p. 963 K

→ Melt at reduction temp.

$Ca_2V_2O_7$
$Mg_2V_2O_7$

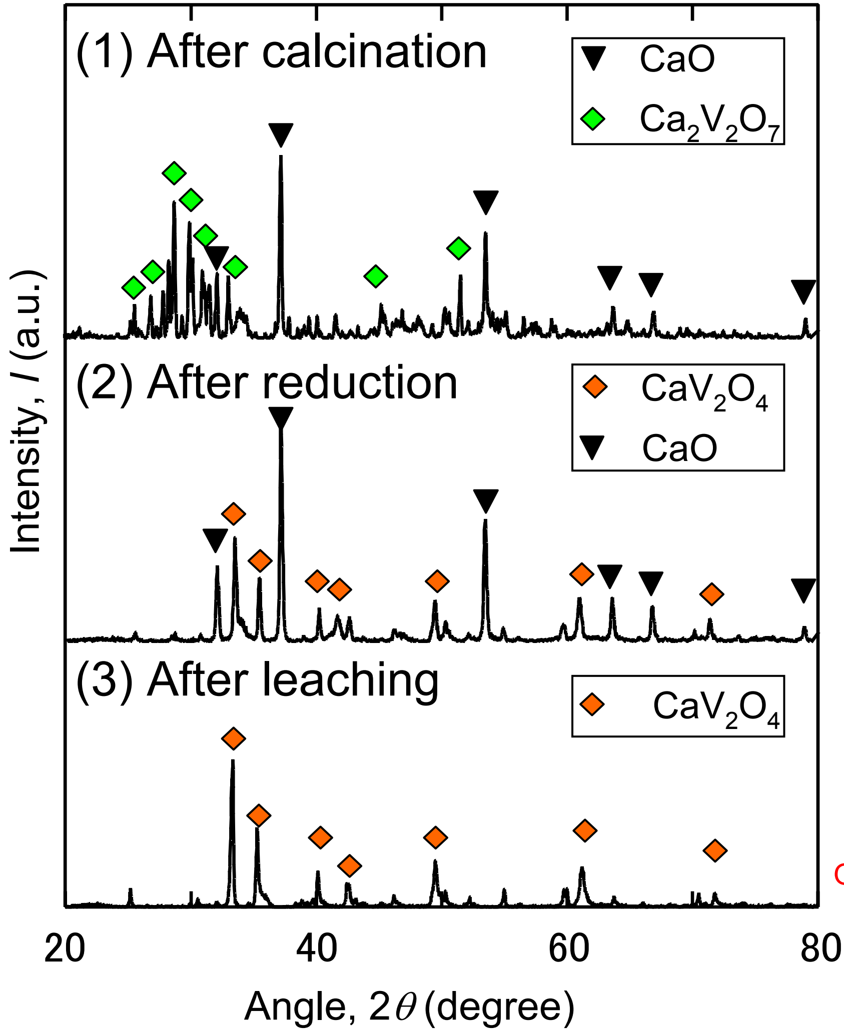
Physically strong solid even at 1273 K



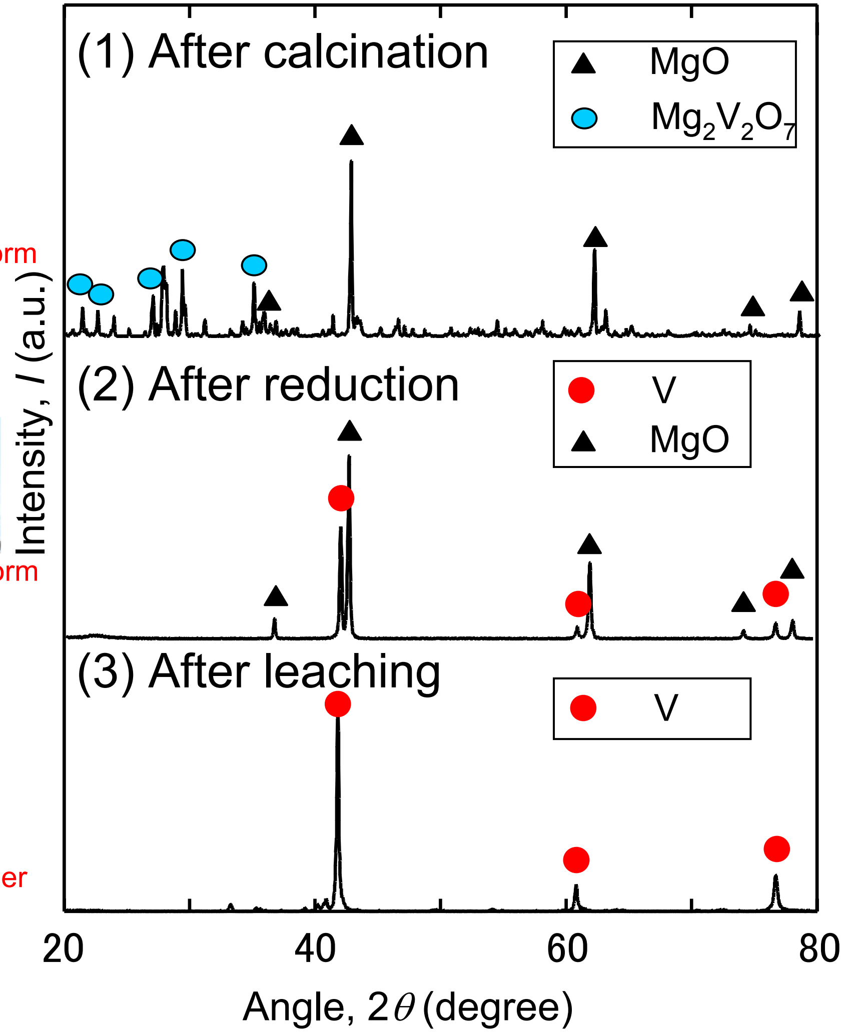
V_2O_5 preform mixed with flux

Result 【Reduction】

exp. A (Flux : CaO, Reductant : Ca)



exp. B (Flux : MgO, Reductant : Mg)



Result 【Purity】

Table　Component analysis by XRF.

Exp. #	Reductant	Flux	Composition of element i, C_i (mass%)				
			C_V	C_{Ca}	C_{Mg}	C_{Fe}	C_{Cr}
exp.A	Ca	CaO	79.0	20.4	―	0.1	0.4
exp.B	Mg	MgO	99.7	―	0.2	0.01	0.03

◆Reduction temperature : $T_{red.}$ = 1273 K

◆Reduction time : $t'_{red.}$ = 6 h

Obtained V metal powder

In the exp. B, high purity vanadium was successfully obtained.

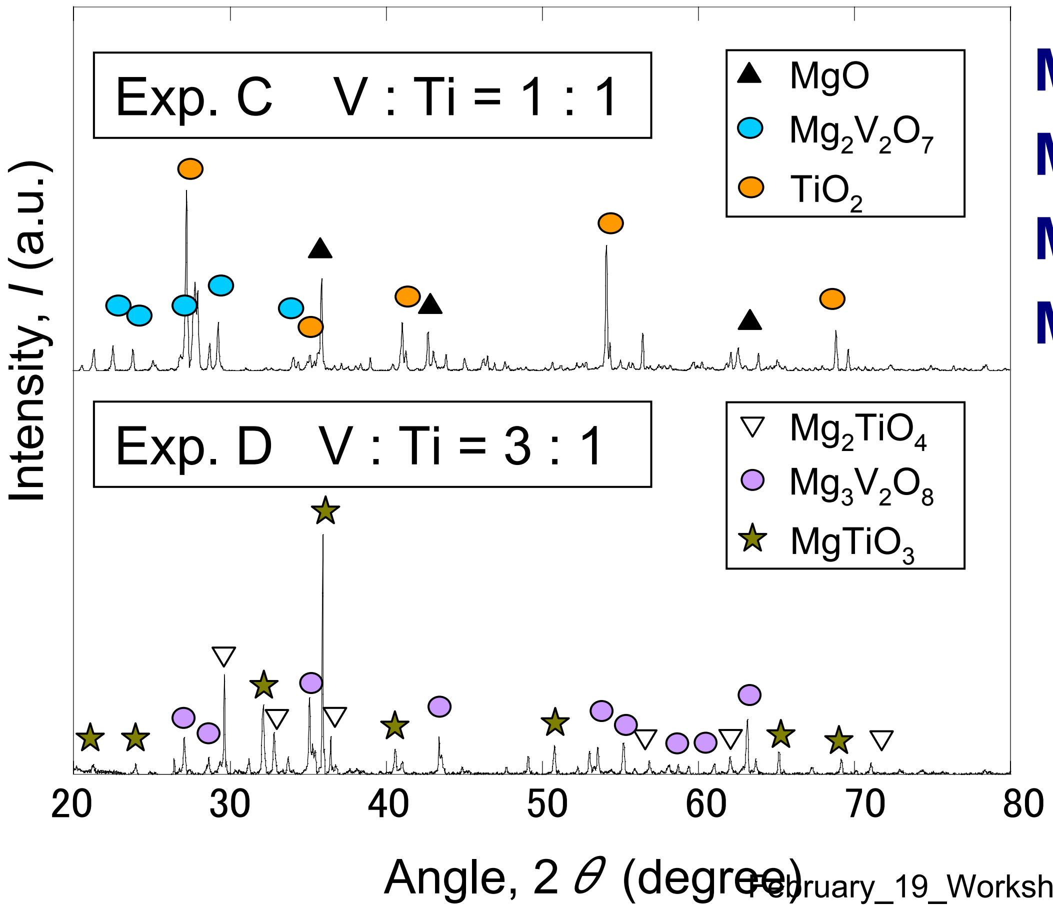
Production of Ti–V Alloy

Result【Calcination】

Calcined V_2O_5, TiO_2, and flux

$T_{cal.}$: 873 K → 1173 K
$t'_{cal.}$: 2 h
Flux : MgO + $CaCl_2$

$$V_2O_5 + 2\,TiO_2 + 3\,MgO + CaCl_2 \rightarrow \text{Complex Oxides}$$



$MgTiO_3$
$Mg_2Ti_2O_8$
$Mg_2V_2O_7$
$Mg_3V_2O_8$

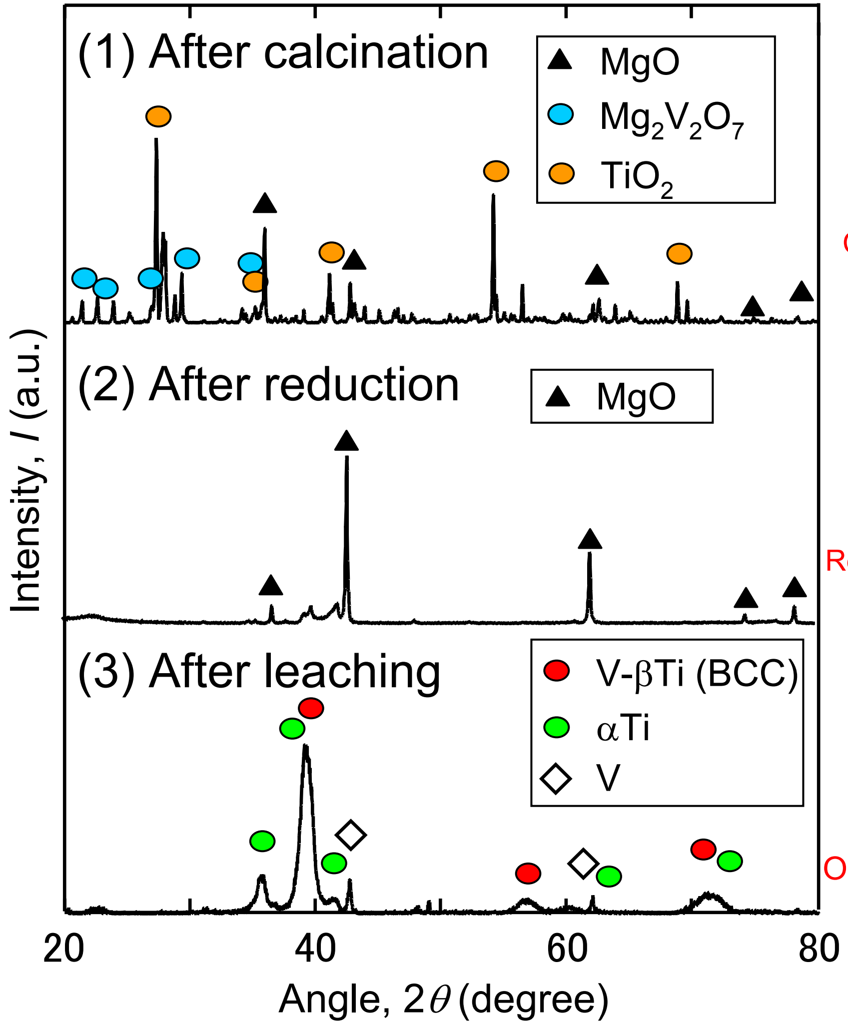
Solid even at 1273 K

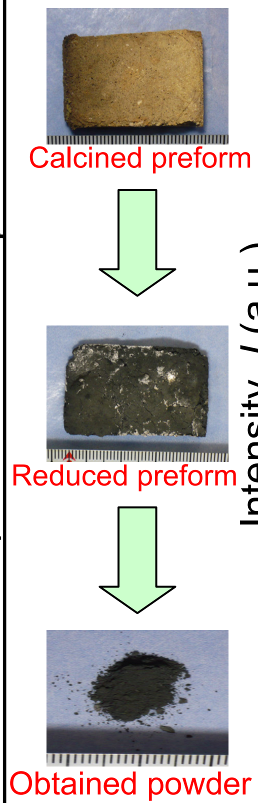
Preform (Complex Oxides)

Result 【Reduction】

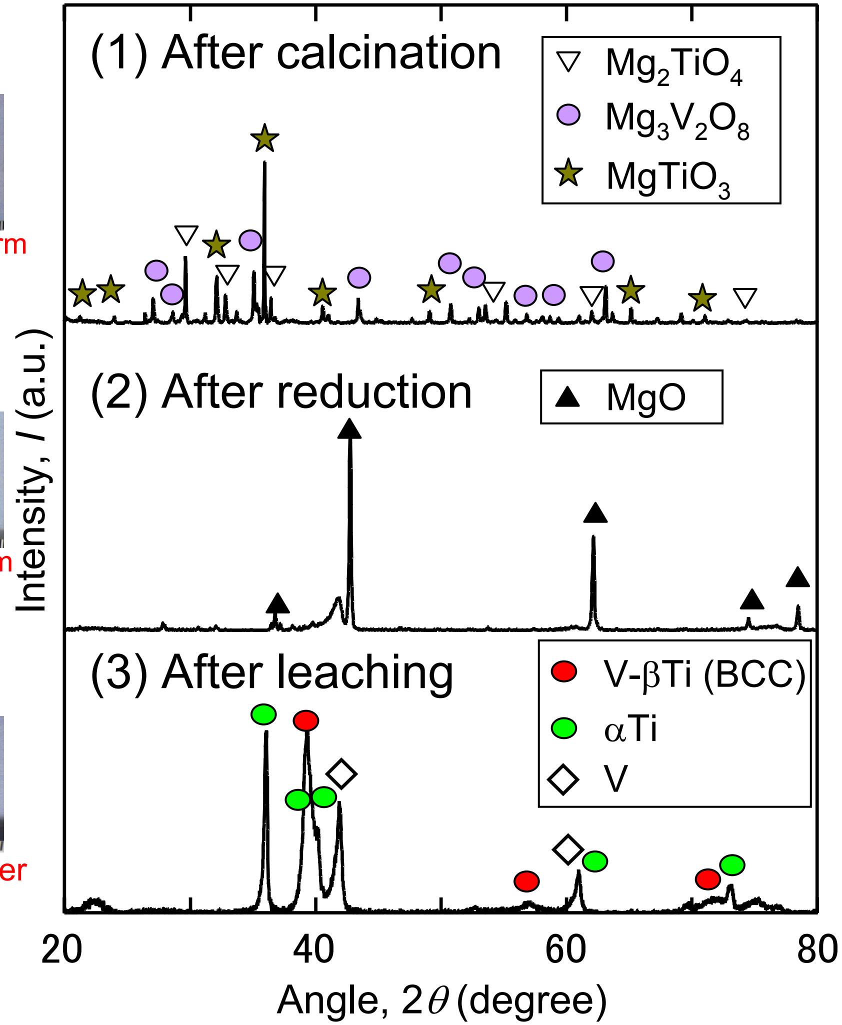
$T_{cal.}$ = 873 K → 1173 K, $t'_{cal.}$ = 2 h
$T_{red.}$ = 1273 K, $t'_{red.}$ = 6 h
R = Mg, Flux = $MgO + CaCl_2$

exp. C V : Ti = 1 : 1





exp. D V : Ti = 3 : 1



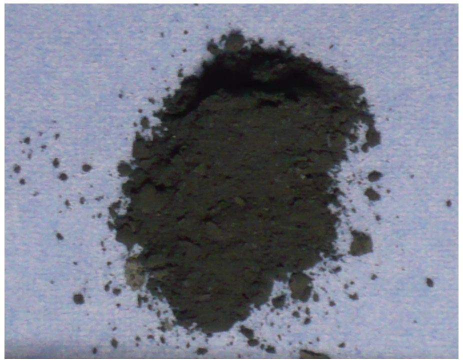
Result 【Purity】

Table Composition analysis by XRF and LECO.

Exp. #	Flux	Normal V / Ti mass ratio $C_V^{calc.}/C_{Ti}^{calc.}$	Composition of element i, C_i (mass%)				V / Ti mass ratio C_V / C_{Ti}
			C_V [a]	C_{Ti} [a]	C_{Mg} [a]	C_O [b]	
exp. C	$MgO + CaCl_2$	1.06	42.5	54.8	2.3	0.64	0.78
exp. D	$MgO + CaCl_2$	3.19	79.4	18.8	—	1.06	4.22

a: Analyzed by XRF
b: Analyzed by LECO

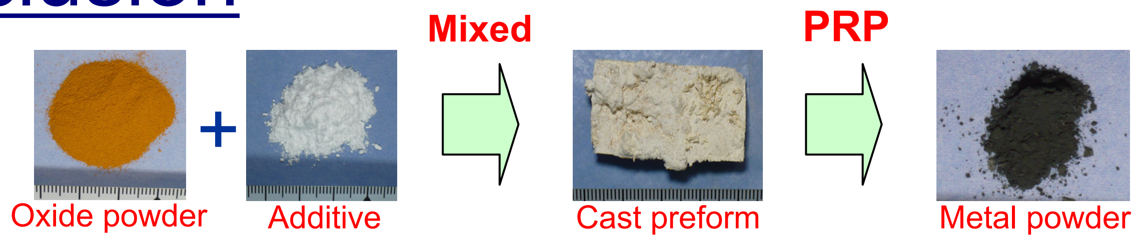
- ◆Reduction temperature : $T_{red.}$ = 1273 K
- ◆Reduction time : $t'_{red.}$ = 6 h
- ◆Reductant : R = Mg



Obtained Ti-V alloy powder

In the Exp. C, V–βTi alloy with low-oxygen concentration was obtained.

Conclusion



Production of high purity vanadium metal and Ti–V alloy by PRP was investigated.

- ◆ Vanadium powder with 99.7 mass% purity was obtained by magnesiothermic reduction of feed preform.
- ◆ V–βTi alloy with low oxygen concentration can be obtained by magnesiothermic reduction.

It was demonstrated that high purity vanadium metal and Ti–V alloy can be produced.

Acknowledgement

The authors are grateful to Prof. S. Yamaguchi of The University of Tokyo for his generous support and valuable discussion.

Thanks are also due to Okabe's Lab. members for providing technical assistance and various support.

The expense of the author (A. Miyauchi) was supported by the grant from the Foundation for the Promotion of Industrial Science.

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