20160328 1st seminar : My research topic

[CSSM]

The effects of nitrogen & oxygen on pure vanadium

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- Hydrogen Energy
- Metallic Hydrogen Membrane
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Introduction : Hydrogen Energy

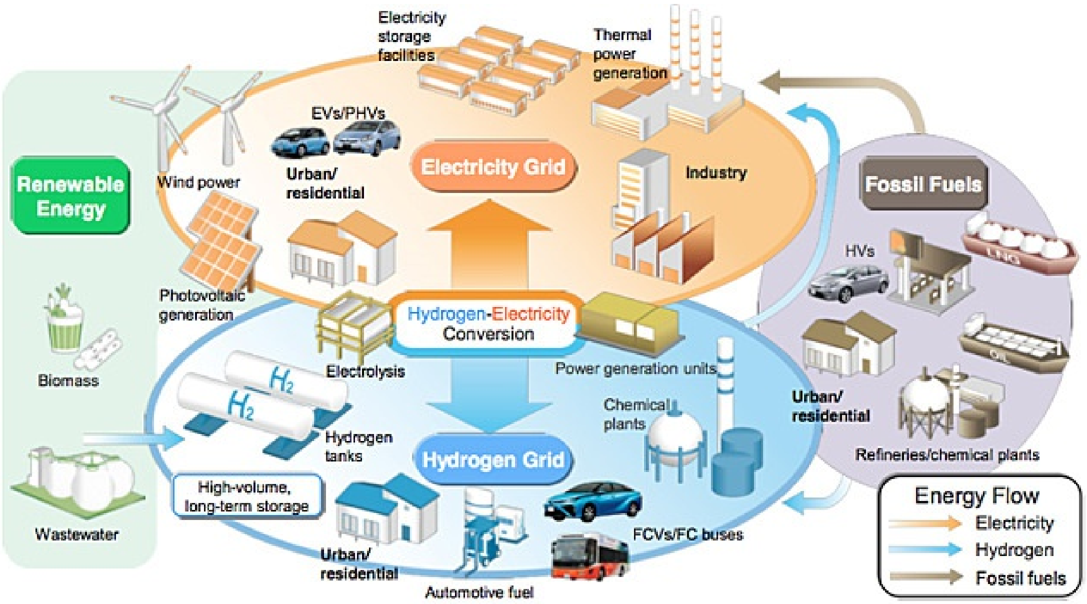


Table 1. Hydrogen Production Processes[1]

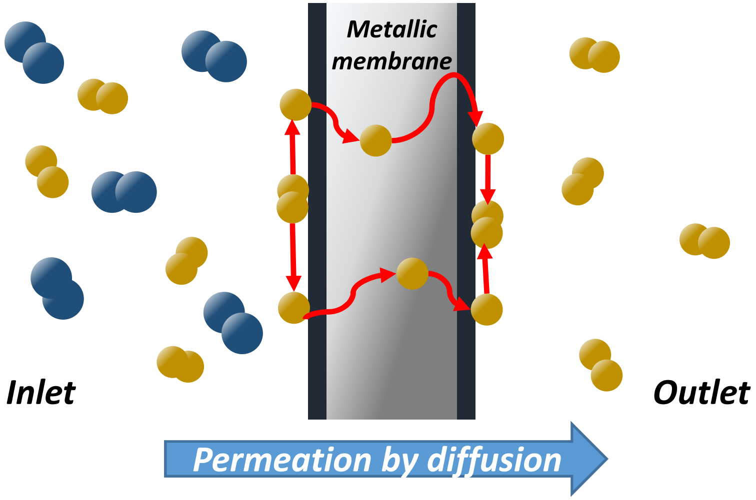
Feed source	H_2 in feed [%]
Steam reforming	64 ~ 96
Ethylene off-gas	35 ~ 98
Catalytic reformer off-gas	75 ~ 90
Chlorine off-gas	98
Dissociated ammonia	75
H_2CO cold box	94 ~ 99.5
EB-styrene off-gas	80 ~ 85
Methanol loop purge	68 ~ 84
Butadiene off-gas	79
Ammonia loop purge	60
Toluene HDA H_2 purge	57
Cyclohexane H_2 purge	42
LPG dehydrogenation	58
Coal gasification	35

Table 2. Comparison Hydrogen Purification Processes[1]

	Cryogenic Distillation	Getter	Pd-based Membrane
Method	Adsorption at ultra-low temperature	Adsorption impurities using Getter	Hydrogen permeation
Material	Liquid nitrogen, Activated carbon	Zirconium-based catalyst	Pd-based membrane
Operation temperature [℃]	-196	200	300 ~ 500
Recovery ratio [%]	95	99	95
Pressure drop [atm]	Very low	Very low	2 ~ 10 (Pressurization)
Capacity [Nm^3/h]	50 ~ 500	0.1 ~ 100	0.1 ~ 30
Strong points	Easy for maintenance, Large capacity oriented	Simplicity, High recovery ratio	Low capital and maintenance cost, High selectivity
Week points	Not suitable for small capacity	High demand of Getter cost	High pressure drop

Shin-Kun Ryi, The study of Pd-Cu-Ni ternary alloyed hydrogen membranes deposited on porous nickel supports, Thesis for the degree of doctor, Korea University (2007)

Introduction : Metallic Hydrogen Membrane



1) **Diffusion of hydrogen to the metal surface**
2) **Adsorption of hydrogen on the surface**
3) **Splitting of hydrogen molecules and incorporation into the metal**
4) **Diffusion of atoms in the lattice**
5) **Regeneration of hydrogen molecules on the permeated side surface**
6) **Desorption of the hydrogen molecules**
7) **Diffusion of the hydrogen molecules from the surface**

- **Crystalline or amorphous metallic membrane**
- **Non porous**
- **Lattice diffusion of atomic hydrogen**
- **Good selectivity, continuously operating**
- **Easley operating**

- Fick's first law

$$J = -D\frac{\Delta C}{t}$$

D : Diffusion coefficient

- Sievert's law

$$C = Ks \cdot P^{0.5}$$

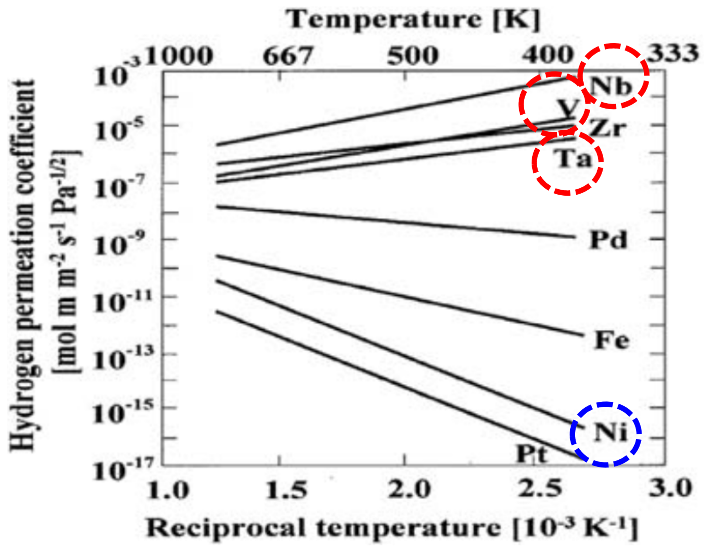
K_s : Solubility

- Permeability

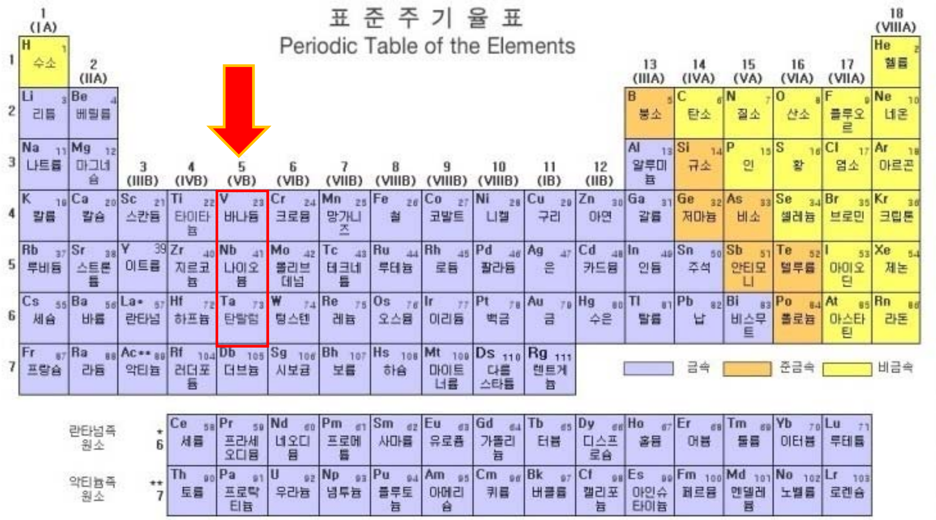
$$Q = Ks \cdot D$$

Introduction : Pd-based Hydrogen Membrane

- 1956, Hunter commercialized Pd membrane
- Pd-based alloy : Pd-Cu, Pd-Ag
- High permeability ~ 10^{-8} mol H_2 m^{-1} s^{-1} $Pa^{-0.5}$
- High cost ~ $ 19020/kg



S. Uemiya, Topics in Catal., 29, 79 (2004).

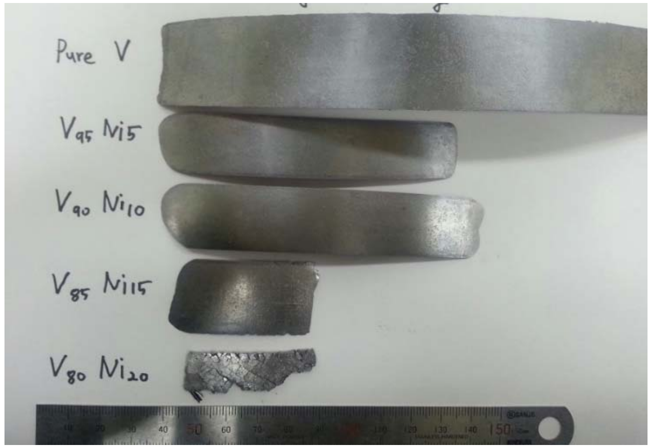


$$Q = Ks \cdot D$$

Introduction : V-based Hydrogen Membrane

- Optimization V-Ni alloy
- $ 14.41/kg (more than 1000times)
- Ni contents↑ → permeability↓, embrittlement resistance↑

Composition (at.%)	Permeability (mol m^{-1} s^{-1} Pa$^{-0.5}$)
V	3×10^{-7} 3.2×10^{-7}
$V_{91}Ni_9$	8.5×10^{-8}
$V_{85}Ni_{15}$	5×10^{-8} 3×10^{-8} 3×10^{-8}



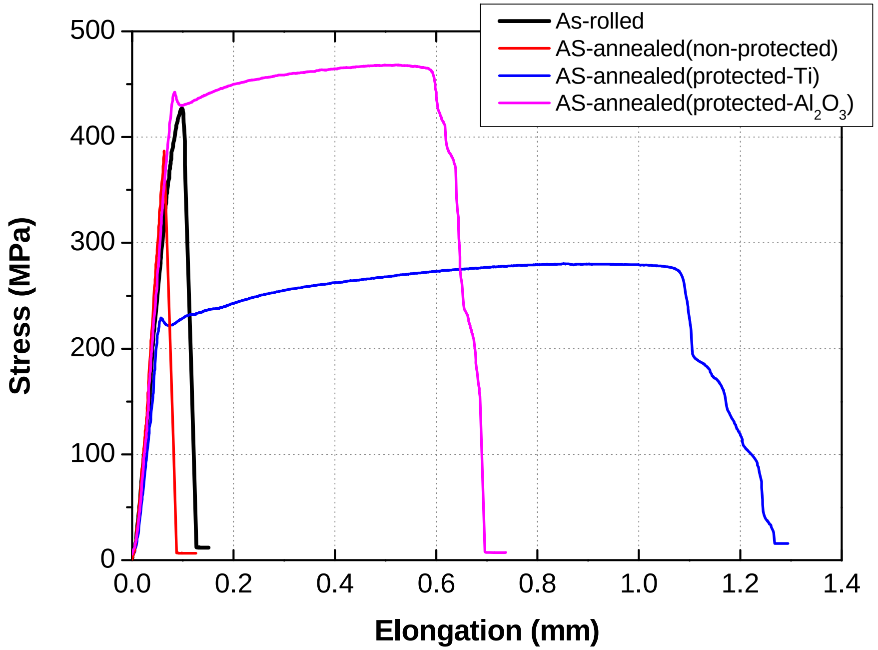
- Good resistance & Permeability ≒ palladium alloys
- But, hard to make a thin sheet

- Ni coating on the vanadium surface
  - Ni diffusion by heat treatment
  - Ni gradient in matrix
  - Use good workability of pure V

→

- V-Ni cladding
- Ni electroplating
- Ni electroless plating

Introduction : Motivation



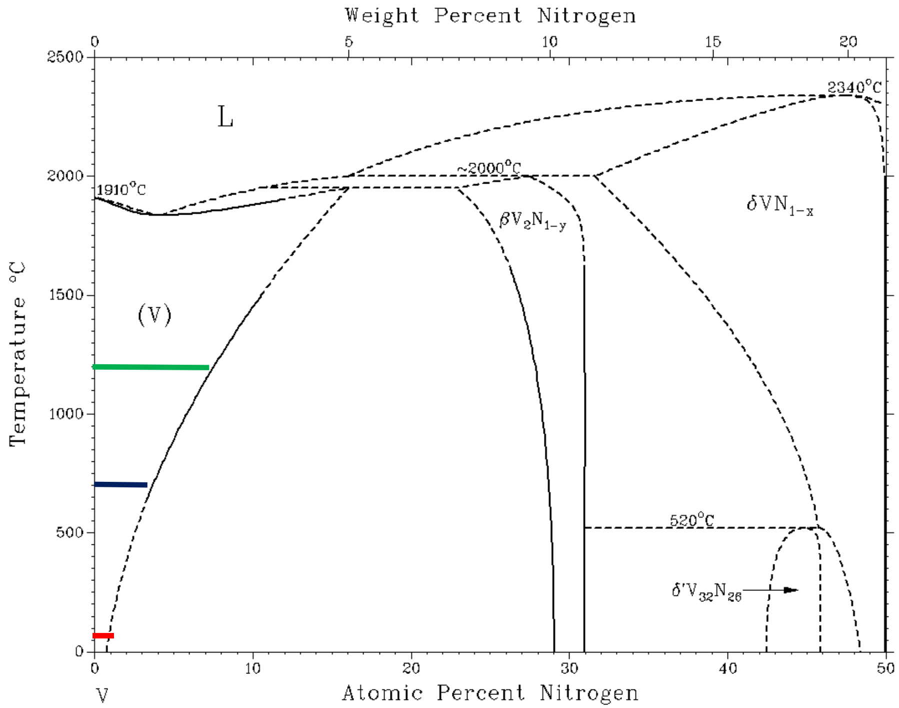
(wppm)

	O	N
As-rolled	512	3
As-annealed(Non-P)	2438	4156
As-annealed(P-Ti)	523	1
As-annealed(P-Al_2O_3)	2387	1

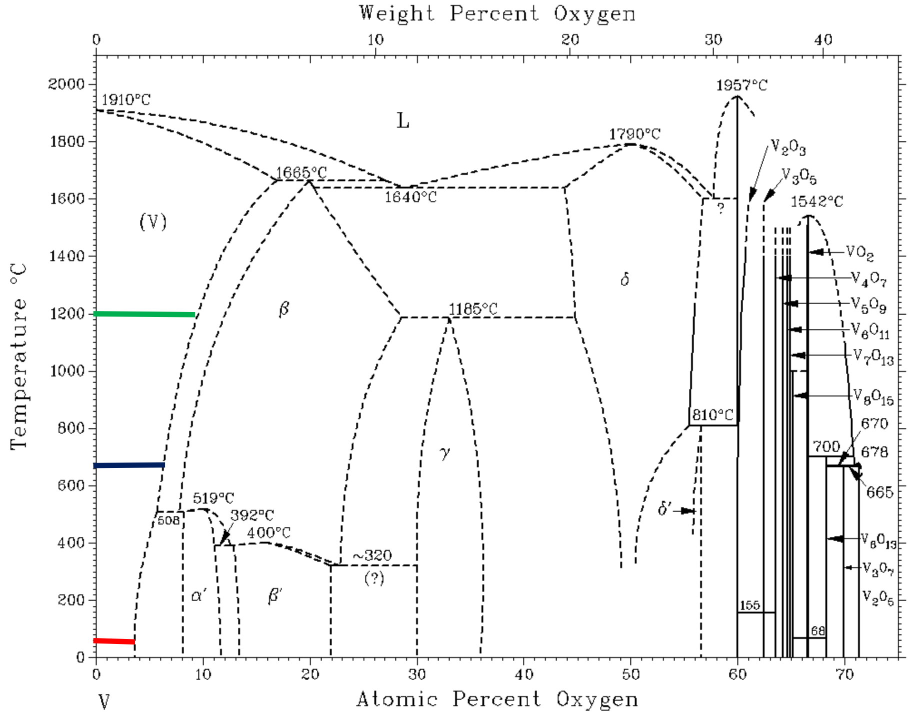
The effects of oxygen and nitrogen on mechanical property of vanadium

The effects of initial oxygen and nitrogen level on vanadium with hydrogen

❖ V-N phase diagram



❖ V-O phase diagram



Solubility (approx)		
T(℃)	Nitrogen (wt%, at%)	Oxygen (wt%, at%)
RT	0.28, 1	1.13, 3.5
650 or 700	0.93, 3.3 (700)	1.97, 6 (650)
1200	2.03, 7	3.01, 9

2. Experimental methods

- Processing
- Characterization

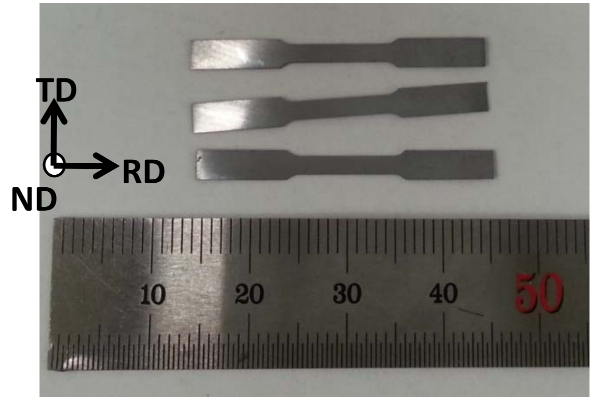
Experimental methods : Processing

As-received (pieces) → Arc melting suction casting → As-Ingot → Cold rolling → As-rolled → Wire cutting → Tensile specimens (as-rolled)

99.7% pure V | T=3 mm | T=0.35 mm

Mechanical polishing & Annealing → As-annealed (T=0.3 mm)

- Heat treatment With Nitrogen → Nitrogen absorption
- Heat treatment With Oxygen → Oxygen absorption



➢ Wire cutting

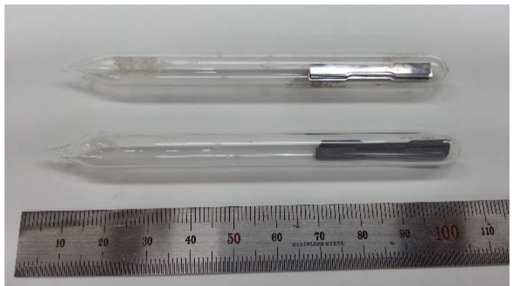
: Small size rectangular dog-bone shape decreased at the same ratio from ASTM subsize rectangular tension test specimens

➢ Mechanical polishing & Annealing

: Sand paper 2000 grade & 1200℃, 1hr, flowing gettered Ar, with Ti granules to prevent oxidation

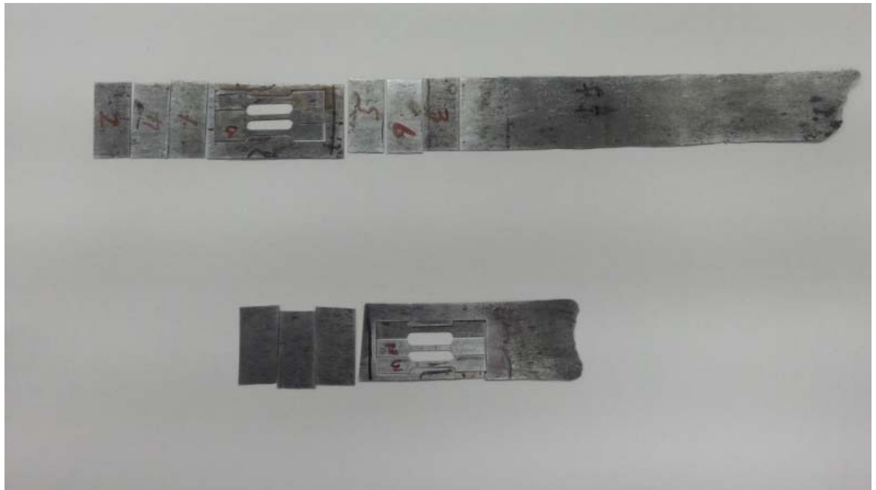
➢ Absorption heat treatment

: Quartz sealing with gas, Temperature & time calculated by various diffusion coefficients



- **Arc Suction melting caster**

- **After rolling**

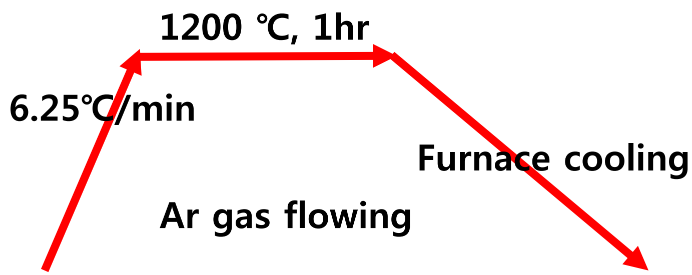


● Heat treatment system

- Gettering furnace

- Stack and protect

As-rolled 4 EA tensile test specimens
Ti granules(99.99%)_Alfa Aesar
Alumina crucible, plate



- **Ar 100% (1000cc/min)**

- After heat treatment

Non-protect

Experimental methods : Characterization

1. Tensile Test

Gatan Microtest 300
1.0mm/min (2.115 X $10^{-3}s^{-1}$)

2. ON analysis

ELTRA ON-900
Burn at 3000℃, Oxygen&Nitrogen contents measurement

3. Vickers hardness Test

Mitutoyo HM-122
Diamond indenter, 0.1 kgf load

4. EBSD

SEM Hitachi S-4300SE, EBSD Bruker e-Flash
Electro-polishing 10%Perchliric acid+90%methanol, -30℃, 22V, 15 flow rate, 30s

5. XRD

Bruker D8 advance
2-Theta : 40~100degree, 40kv, 40mV,
step size 0.02, time 2s, rotation 30rpm, fluo configuration

6. CS analysis

LECO CS600
Carbon&Sulfur contents measurement

7. Nano-SIMS

CAMECA Nano-SIMS 50
Cs+ gun, Impact Energy 19keV, Current 0.4pA

8. FIB & TEM

FIB : FEI Nova 600 NanoLab
5~30kV, 1.1nm image resolution(15kV)
TEM : FEI Talos F200X (super X-EDS)
200kV, 0.16nm > image resolution, with unparalleled advances in EDS signal detection and 3D chemical characterization with compositional mapping

3. Results

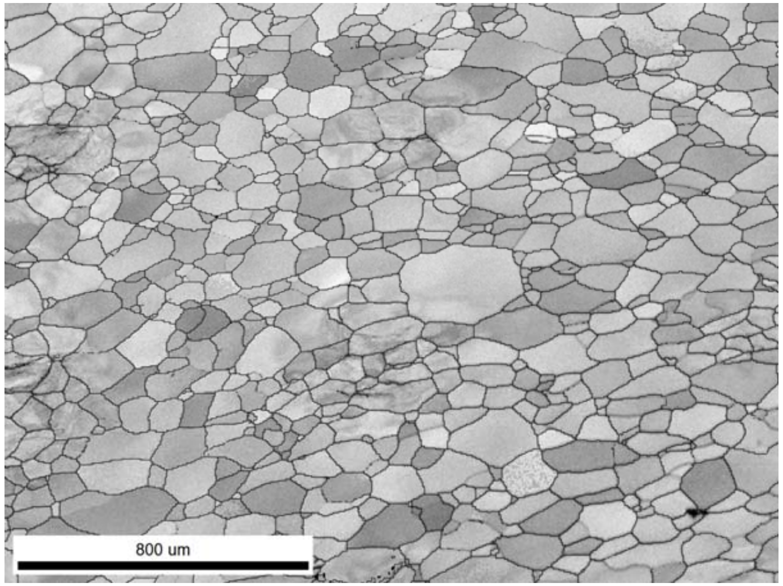
- Composition
- Tensile test
- Microstructure
- Micro-Vickers hardness
- XRD
- Nano-SIMS
- TEM

Results : Composition

(wppm)

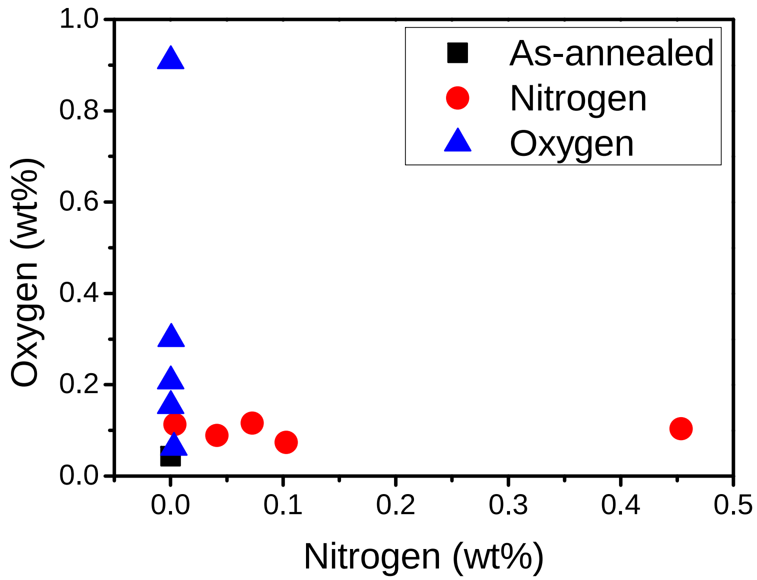
	N	O	C	S	V
As-Received	28	262	182	35	Bal.
As-rolled	1	463	270	37	Bal.

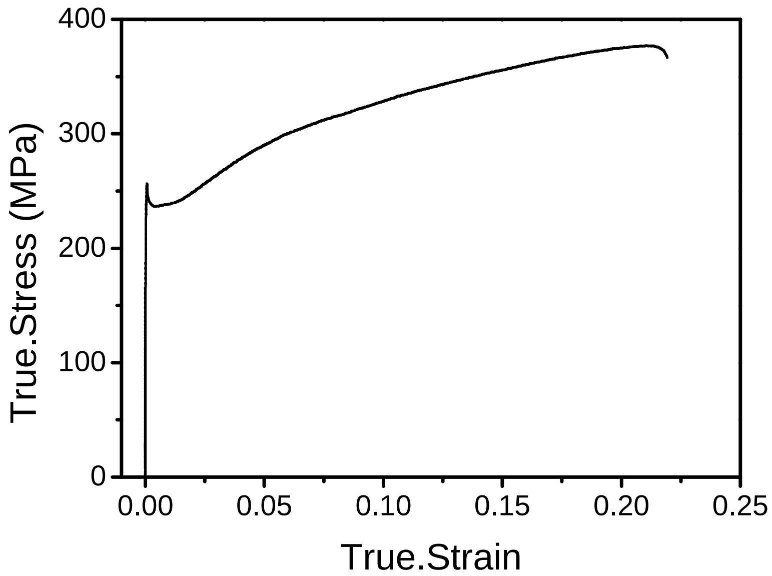
➢ After Annealing treat



Upper Yield Strength (YS) : 256.2 MPa
Lower YS : 235.4 MPa
Ultimate tensile strength (UTS) : 308.1 MPa
%EL : 27.5%
Values were get from Eng S-S curve

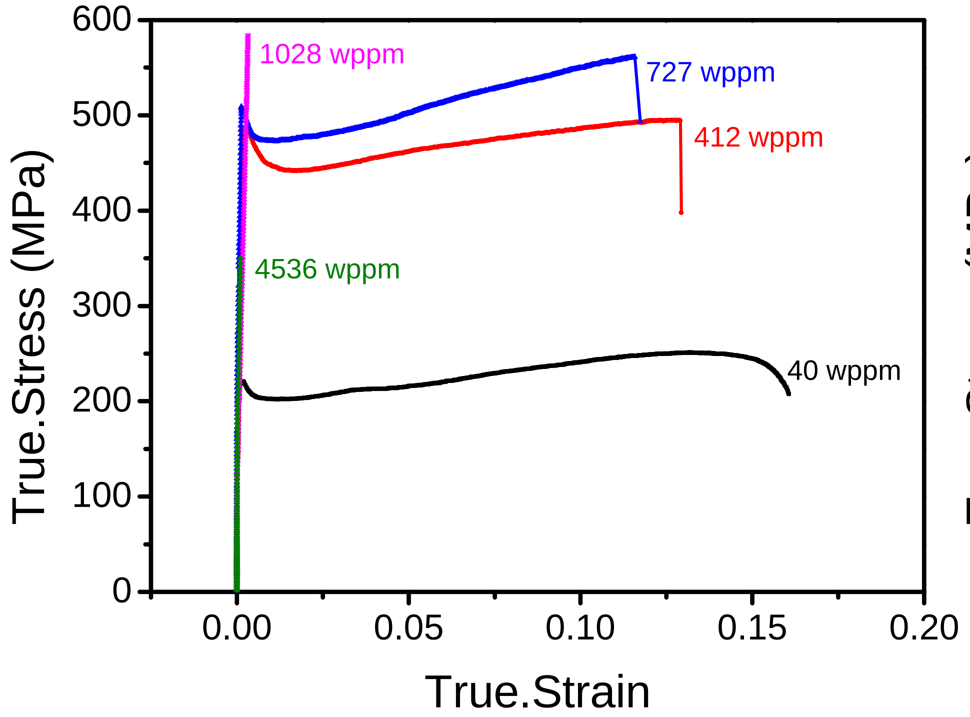
Grain size : 150μm
HV0.1 : 118.21±1.8266



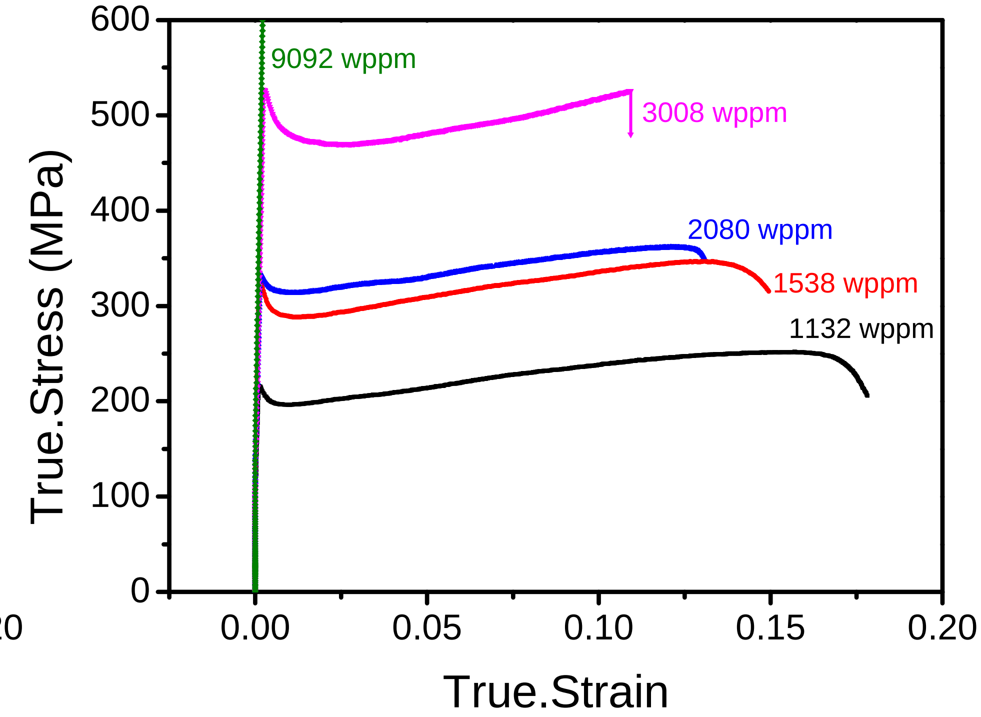


Results : Tensile test

- **For nitrogen**

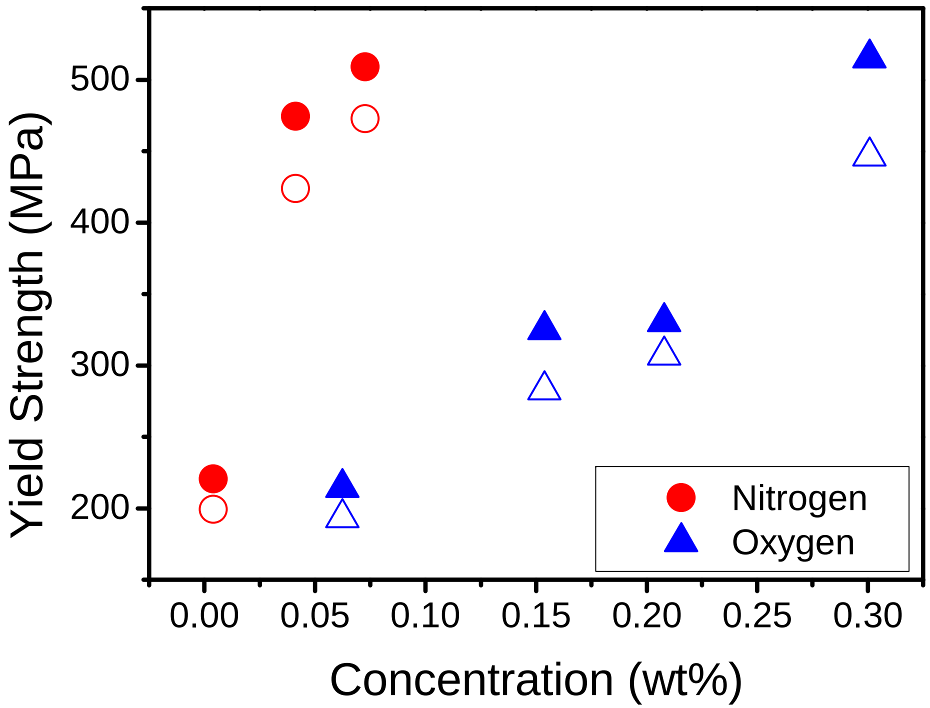


- **For oxygen**

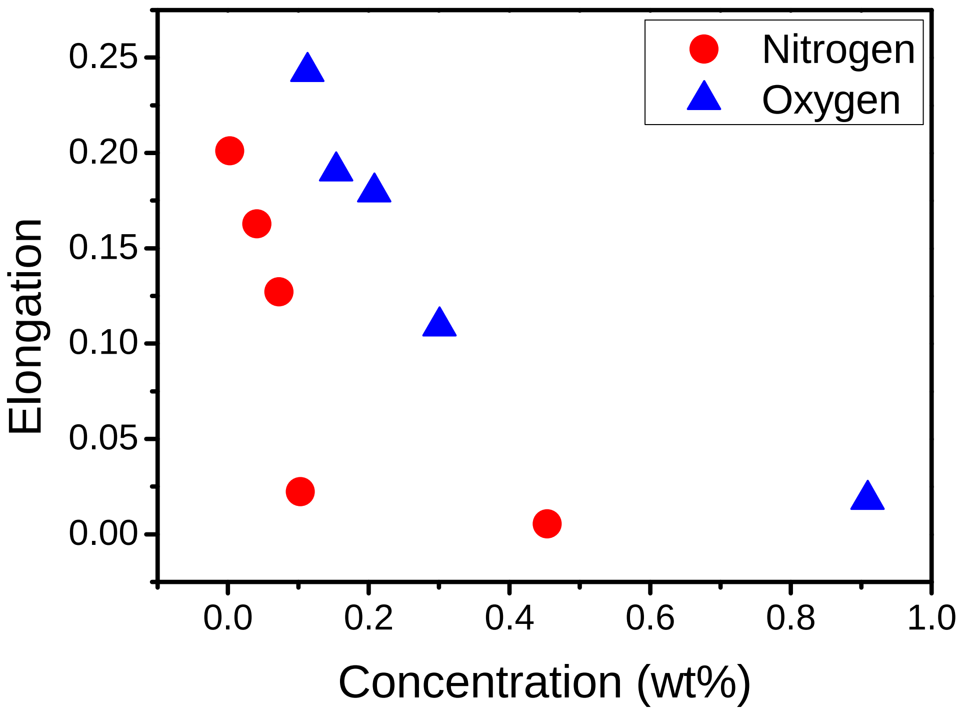


- Nitrogen treatment : 700℃, 11day(264hr) +WQ → 450㎛
- Oxygen treatment : 650℃, 6day(144hr) +WQ → 350㎛

Results : Tensile test

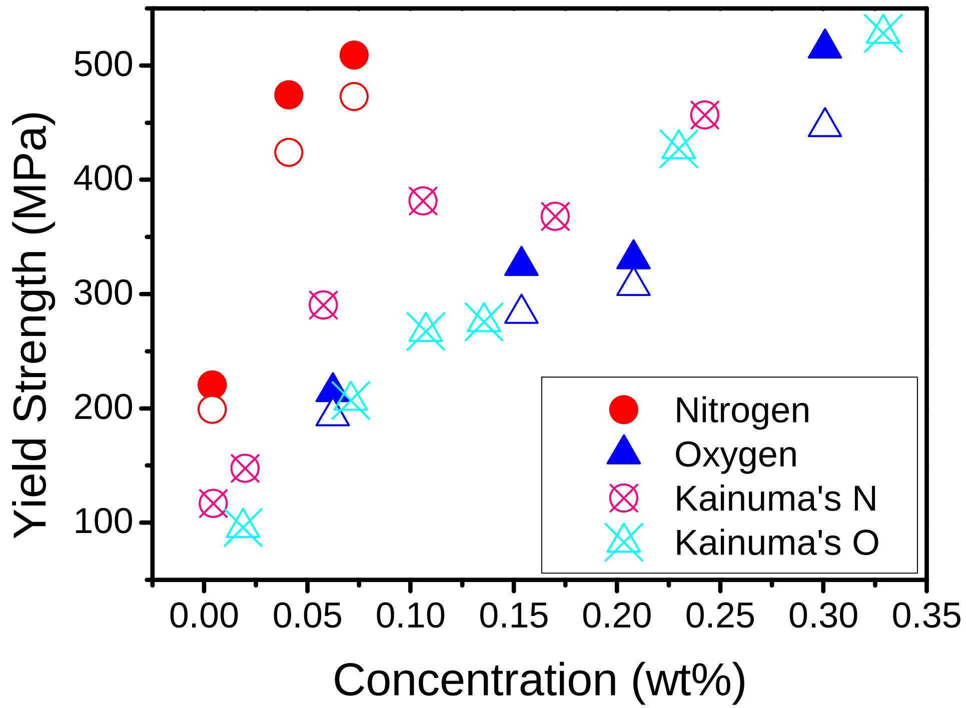


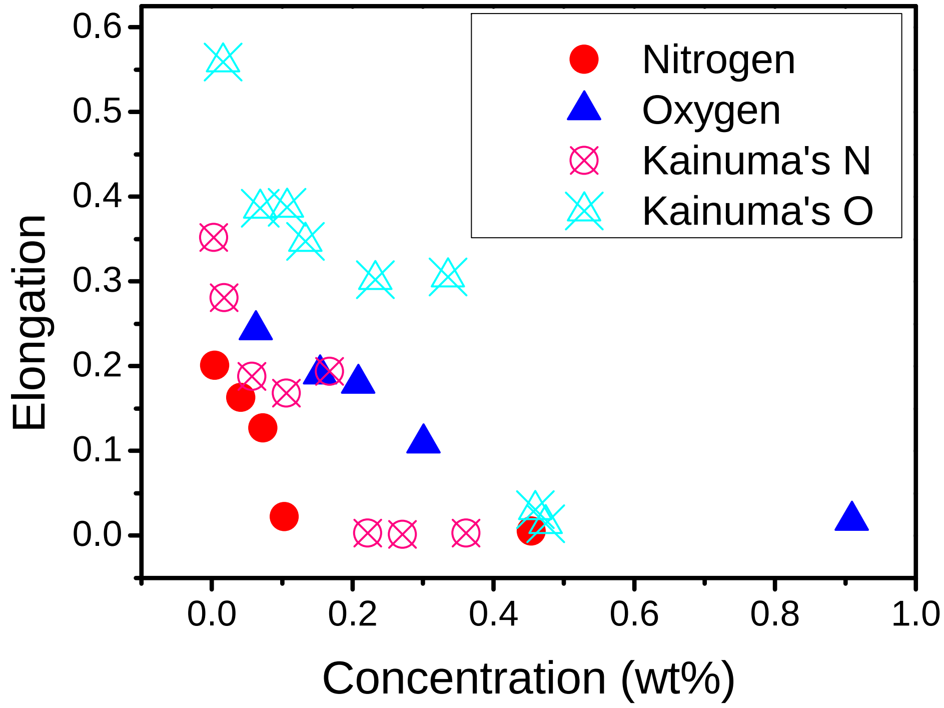
Close : upper YS, open : lower YS



- **Nitrogen** : above 0.10 wt% N brittle fracture
- **Oxygen** : above 0.27 wt% O brittle fracture

Results : Tensile test





- **Kainuma's test condition**

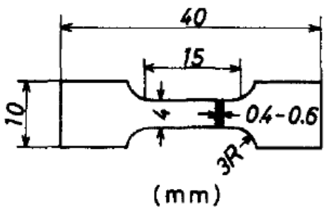


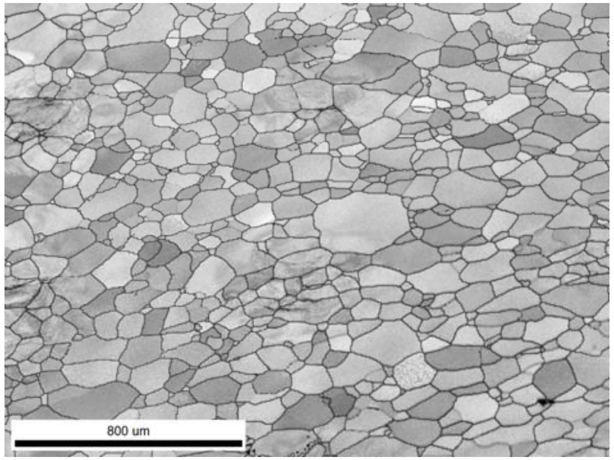
Fig. 1. Tensile specimen of vanadium and V–Mo alloys.

- Crosshead speed : 0.017mm/s (1.1 X $10^{-3}s^{-1}$)
- 15mm gauge-length
- They used 0.2% proof stress = YS
- 200 wppm O, 65 wppm N, 80 wppm C

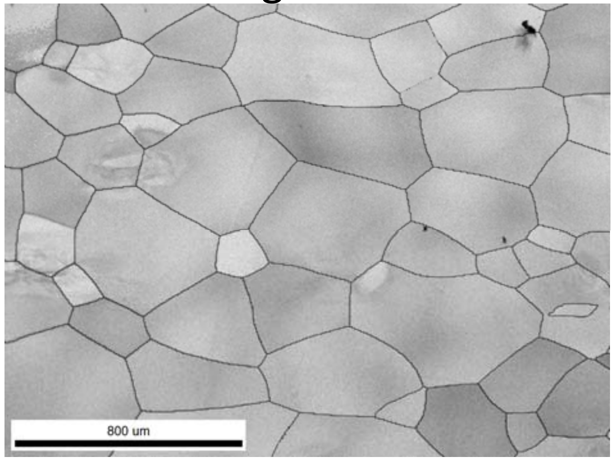
- Crosshead speed : 0.017mm/s (2.1 X $10^{-3}s^{-1}$)
- 7.88mm gauge-length
- 270 wppm C

Results : Microstructure

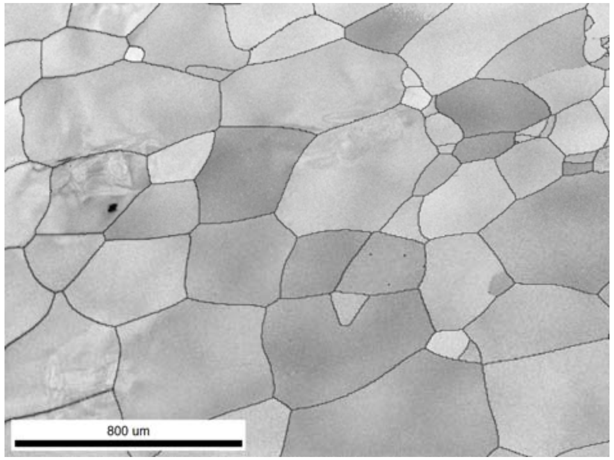
- As-annealed



- As-nitrogen treated



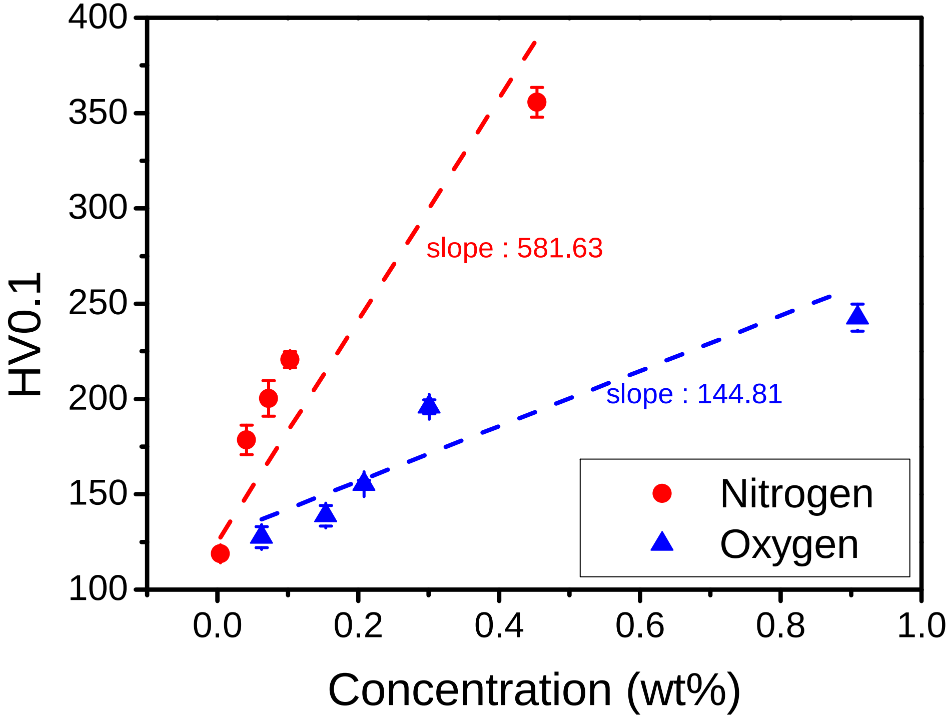
- As-oxygen treated

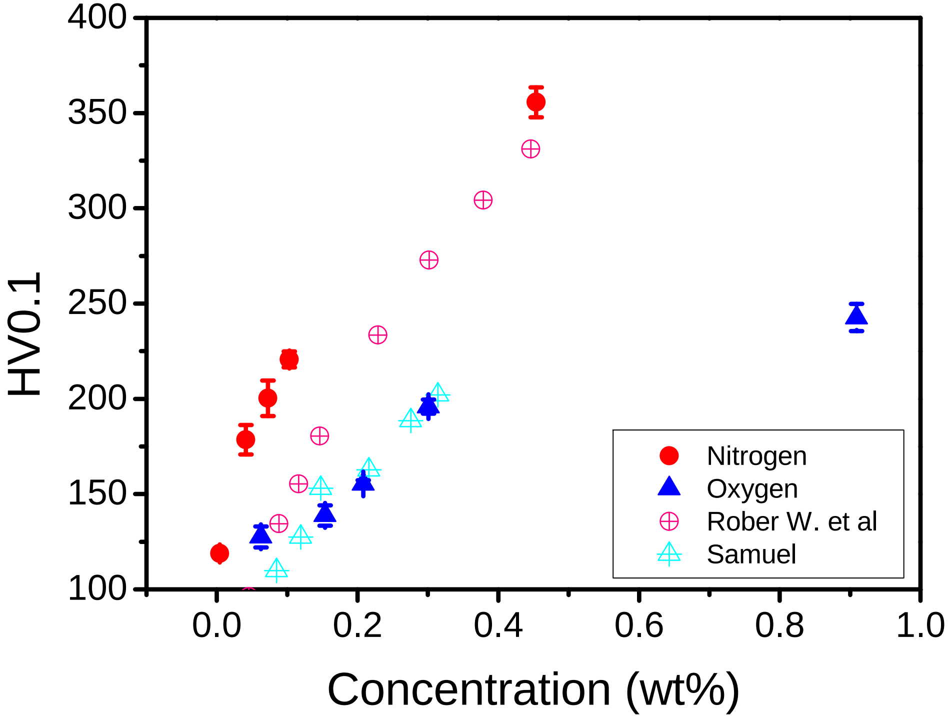


- Nitrogen treatment : 700℃, 11day(264hr) +WQ → 400㎛
- Oxygen treatment : 650℃, 6day(144hr) +WQ → 400㎛

During nitrogen and oxygen treatment, grain grew (150㎛ → 400㎛)
Even grain grow, strength increase (effective solid-solution > Hall-petch)

Results : micro-Vickers hardness

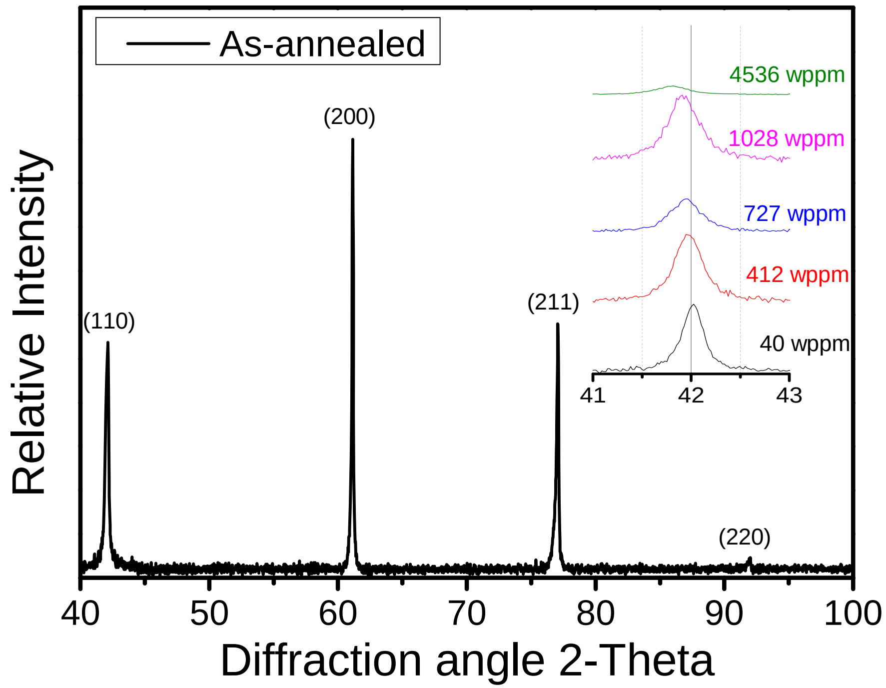




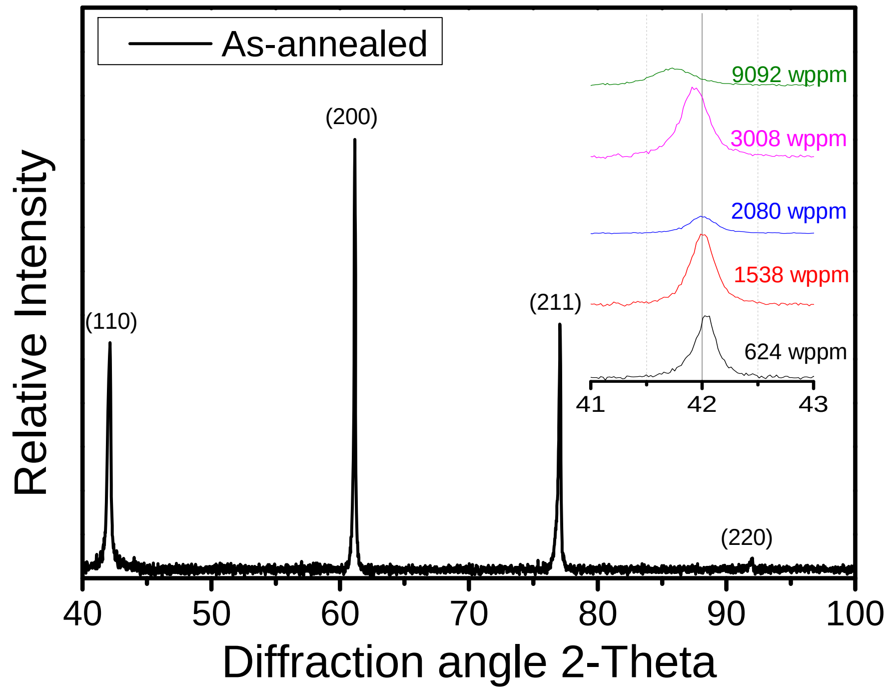
- Tensile and hardness results show nitrogen is more effective for solid-solution hardening than oxygen.

Results : X-ray diffraction

- **For nitrogen**



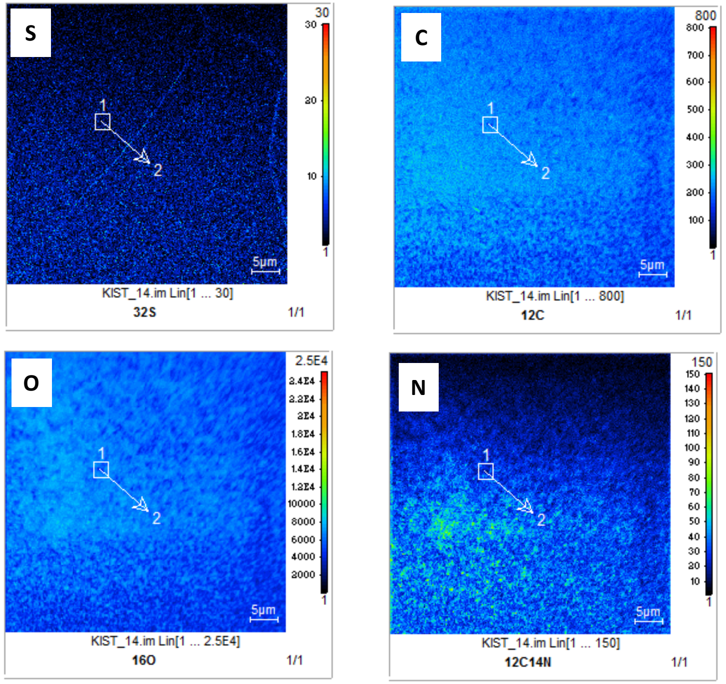
- **For oxygen**

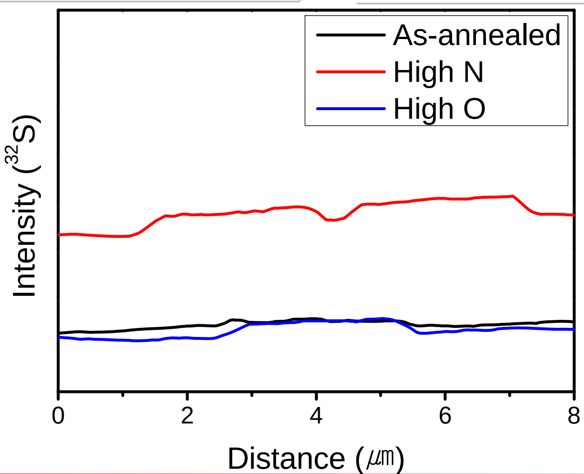


- Increasing contents, XRD peaks shift to the left

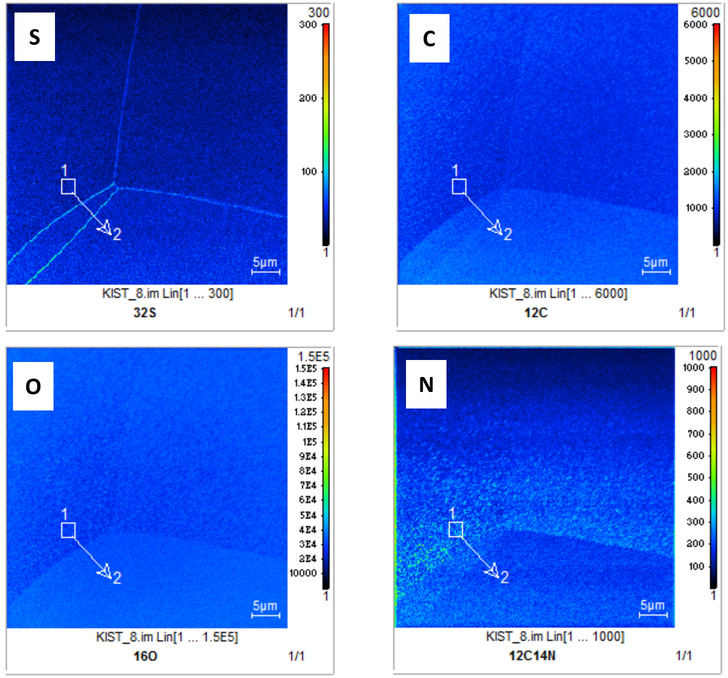
Results : Nano-SIMS

As-annealed

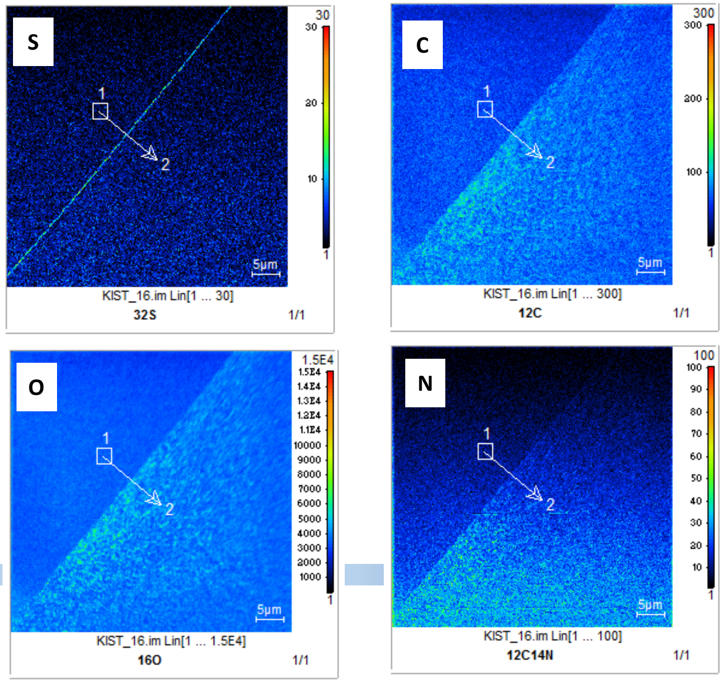




High N

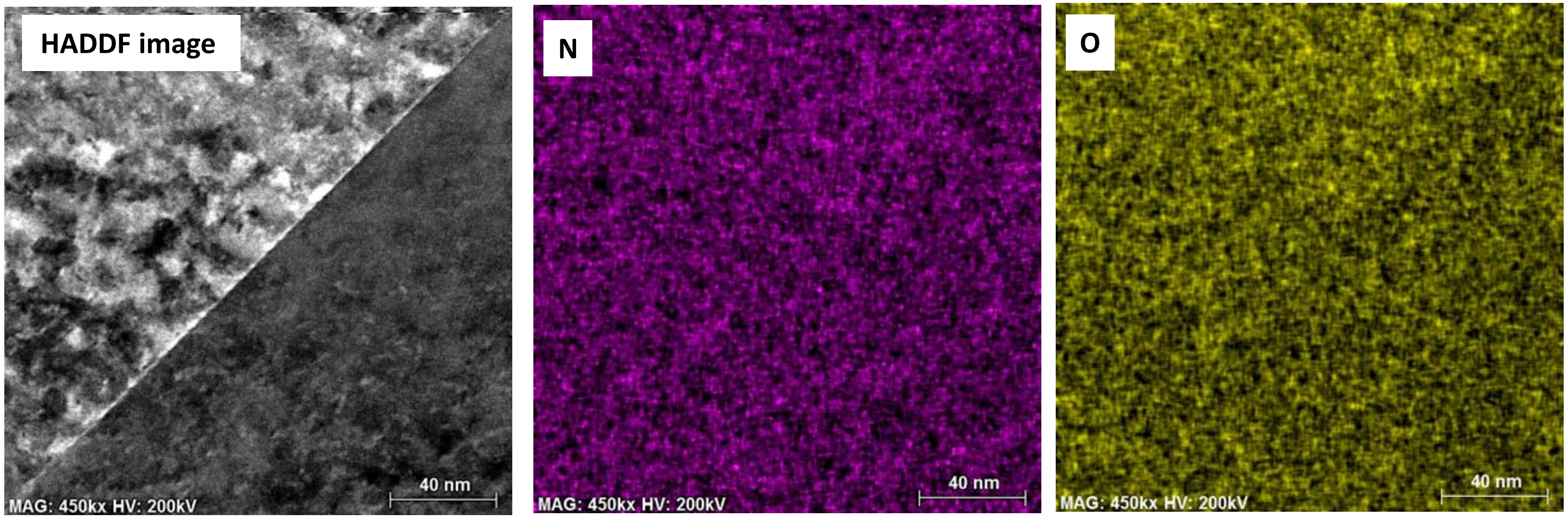


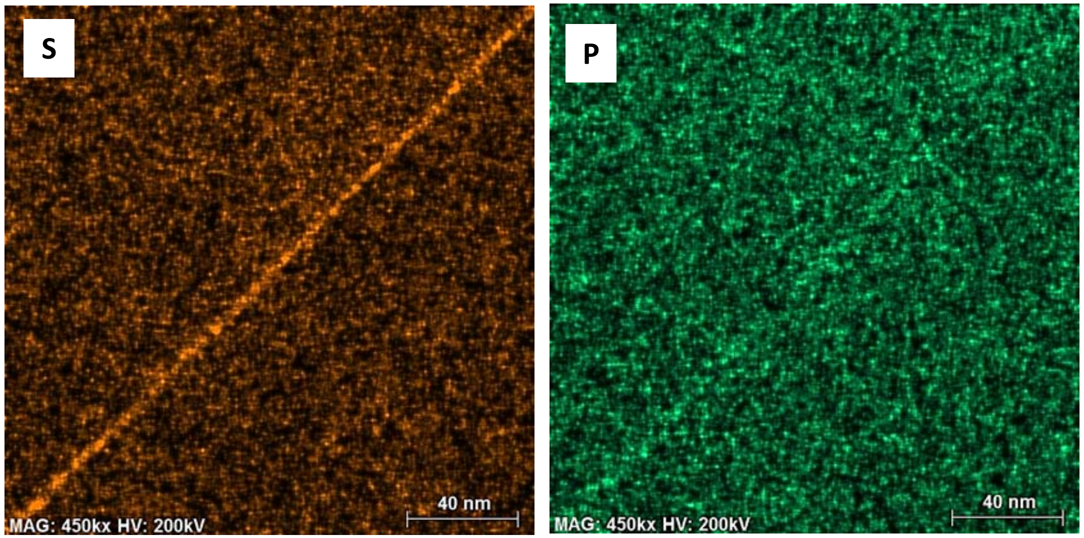
High O



Results : TEM

EDS mapping : High N





- S, P are segregated in grain boundary

4. Summary

- Vanadium, BCC metal, yield point phenomenon
- Both nitrogen and oxygen concentration increase → YS and flow stress , %EL
- Nitrogen is more effective for solid-solution hardening than oxygen
- Both nitrogen and oxygen do not be segregated in grain boundary
- S is segregated in grain boundary

Reference

[1] Shin-Kun Ryi, The study of Pd-Cu-Ni ternary alloyed hydrogen membranes deposited on porous nickel supports, Thesis for the degree of doctor, Korea University (2007)
[2] S. Uemiya, Topics in Catal., 29, 79 (2004).
[3] Kainuma, "EFFECTS OF OXYGEN, NITROGEN AND CARBON ADDITIONS ON THE MECHANICAL PROPERTIES OF VANADIUM AND V/MO ALLOYS", Journal of Nuclear Materials, 80 (1979) 339-347
[4] Robert W. Thompson and 0. N. Carlson, "THE EFFECT OF NITROGEN ON THE STRAIN AGING AND BRITTLEDUCTILE TRANSITION OF VANADIUM", Metals, Ceramics and Materials (UC -25), (1964)
[5] Samuel Arthur Bradford, "The effect of oxygen on physical and mechanical properties of vanadium", PhD thesis, Iowa State University (1961)

Appendix

❖ Experimental methods : Processing

- **Arc melting suction casting**

Bought from Alfa Aesar, 99.7% vanadium pieces
With Ti getter
After suction, 10x40x4mm(width X length X thickness)

- **Cold rolling**

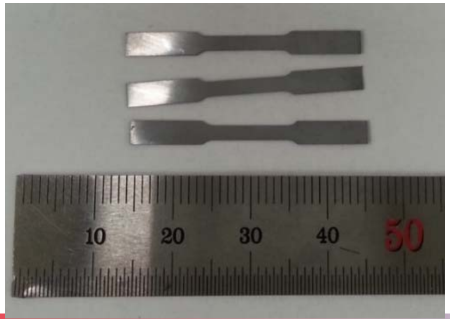
About 91.25% reduction (4mm → 0.35mm)

- **Specimen making**

Decrease same ratio from subsize ASTM dog-bone shape

- **Recrystallization treatment**

Pre-polishing surface (use only 2000grade)
1200℃, 1hr, in flowing gettered Ar(99.9999% Ar +gas purifying), with Ti granules to prevent +Furnace cooling
(4 specimens)

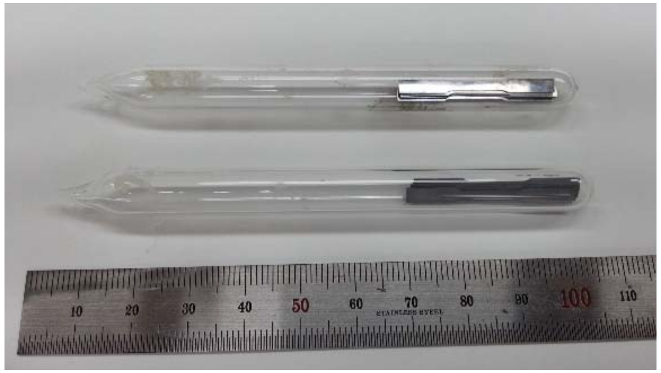


- **Nitrogenating**

Quartz sealing without or with various pressure of nitrogen. (before filling and sealing, over 3 times 99.9999% Ar purging were done), filling 99.9999% N_2
700℃, 11day(264hr) +WQ
(4 specimens)

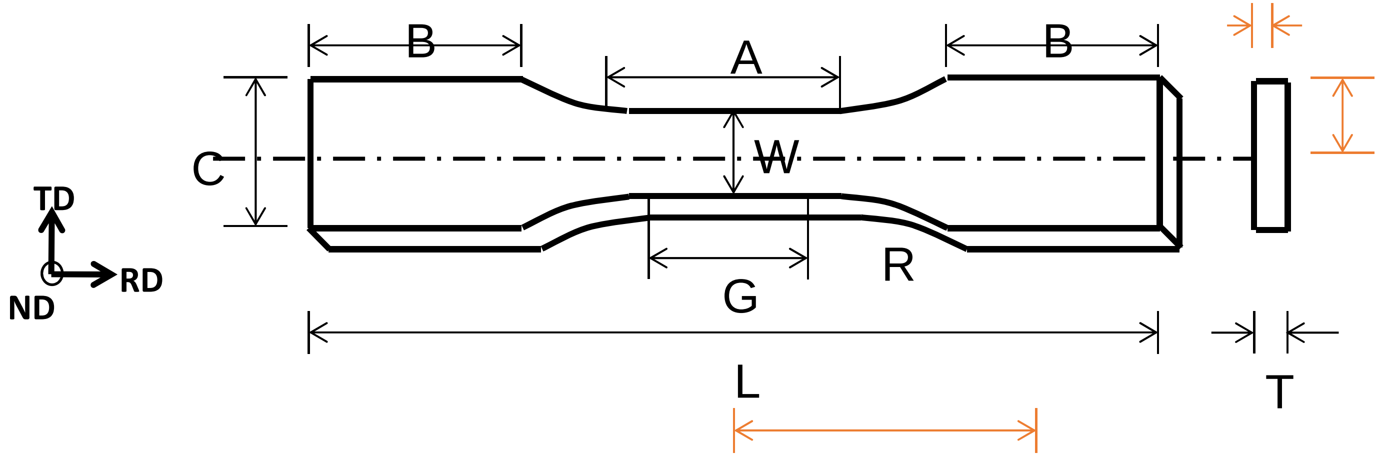
- **Oxygenating**

Quartz sealing withour or with various pressure of oxygen. (before filling and sealing, over 3 times 99.9999% Ar purging were done), filling 99.9999% O_2
650℃, 6day(144hr) +WQ
(4 specimens)



Appendix : Tensile specimen dimension

Rectangle specimen	G	W	R	A	B	C	L	T
Subsize specimen(mm)	7.88	1.97	1.89	10.08	9.45	3.15	31.5	0.315(0.31~0.32)



TEM (Talos F200X)

투과전자현미경

Talos™ F200X is a 200 kV FEG Scanning Transmission Electron Microscope (S/TEM), which is designed for fast, precise and quantitative characterization of nano-materials. It accelerates nano-analysis of materials based on higher data quality, faster acquisition, and simplified, easy and automated operation. Talos is a system which can be operated completely remotely and which has enhanced environmental immunity. It combines outstanding quality in high-resolution STEM and TEM imaging with unparalleled advances in EDS signal detection and 3D chemical characterization with compositional mapping.

Model

FEI (Talos F200 X)

Location L5117A Tel.02-958-4940

Specifications

- Accelerating voltage : 80 ~ 200 kV
- Image resolution : < 0.16 nm
- Magnification : 25 ~ 1,500,000 X
- Tomography holder : ± 75°

Applications

- BF/DF/STEM/SADP/HAADF/DPC
- High resolution structure analysis
- High brightness and high stability source X-FEG with Super-X EDS
- Electron 3D Tomography

Appendix : Diffusion coefficient

✓ Nitrogen

Thickness : 0.0315 cm

Diffusion coefficient (D, cm^2/sec)	The activation energy (Q)	R value	Temperature (K)	Time (hr)	Ref
$0.0417\exp(\frac{-35459}{RT})$	35.459 kcal/mole	1.9872041 cal/K mole	973	152.2534	[1]
$0.076\exp(\frac{-1.504}{RT})$	1.504 eV/atom	0.0000816154 eV/K atom	973	280.3113	[2]
$0.018\exp(\frac{-35100}{RT})$	35.1 kcal/mole	1.9872041 cal/K mole	973	**292.9513**	[3]
$0.05021\exp(\frac{-151040}{RT})$	151.04 kJ/mole	8.3144621 J/K mole	973	176.0997	[4]

[1] J. Less-common metals, 26 (1972) 325-326
[2] Appl. Phys. A 34, 49-56 (1984)
[3] Stanley, J. T. and Wert, C. A. Acta Met. 3: 107. 1955.
[4] F.A. Schmidt and J.C. Warner, J. Less Common Metals, v. 13, pp. 493-500, 1967.

264 hrs (11days) Using [3], 0.03 cm
→ 312 hrs (13days)

✓ Oxygen

Diffusion coefficient (D, cm^2/sec)	The activation energy (Q)	R value	Temperature (K)	Time (hr)	Ref
$0.0246\exp(\frac{-29495}{RT})$	29.495 kcal/mole	1.9872041 cal/K mole	923	26.9818	[1]
$0.003\exp(\frac{-28200}{RT})$	28.2 kcal/mole	1.9872041 cal/K mole	923	**109.209**	[2]
$0.019\exp(\frac{-29300}{RT})$	29.3 kcal/mole	1.9872041 cal/K mole	923	31.411	[3]
$0.02661\exp(\frac{-124710}{RT})$	124.71 kJ/mole	8.3144621 J/K mole	923	29.5594	[4]

[1] J. Less-common metals, 26 (1972) 325-326
[2] Stanley, J. T. and Wert, C. A. Acta Met. 3: 107. 1955.
[3] Powers, R. W. Acta Met. 2: 604. 1954.
[4] R.W. Powers, Acta Met., v. 2, pp. 605-607, 1953.

144 hrs (6days) Using [2], 0.035cm
→ 120 hrs (5days)