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Reduction of Titanium Oxide in the Presence of Nickel by Supercooled Monatomic Hydrogen

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Today's contents

1. Introduction
   - ✓ Titanium
   - ✓ Thermodynamics for reduction of titanium oxide by hydrogen
2. Experimental and discussion
   - ✓ Reduction of titanium oxide by supercooled monatomic hydrogen
   - ✓ Reaction mechanism of molecular hydrogen and monatomic hydrogen
3. Summary

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Titanium

<u>Attractive features</u>

- Excellent specific strength and corrosion resistance.
- Unique properties.

  ex.) Ti-Ni alloy: Shape memory, Superelasticity.

<u>Production process</u>

- Kroll process

$TiO_2 + C + Cl_2$ — Chlorination

↓ → CO_2

$TiCl_4 + Mg$ — Magnesiothermic reduction

↓ → $MgCl_2$ — Vacuum distillation

Ti

Low productivity
High energy consumption

➡ It is desired to develop a new production process.

Reduction of titanium oxide by hydrogen gas

Merit of reduction of titanium oxide by hydrogen gas

- Simplify the production process.

Equilibrium partial pressure of O_2

$$2Ti + O_2 \rightleftarrows 2TiO$$

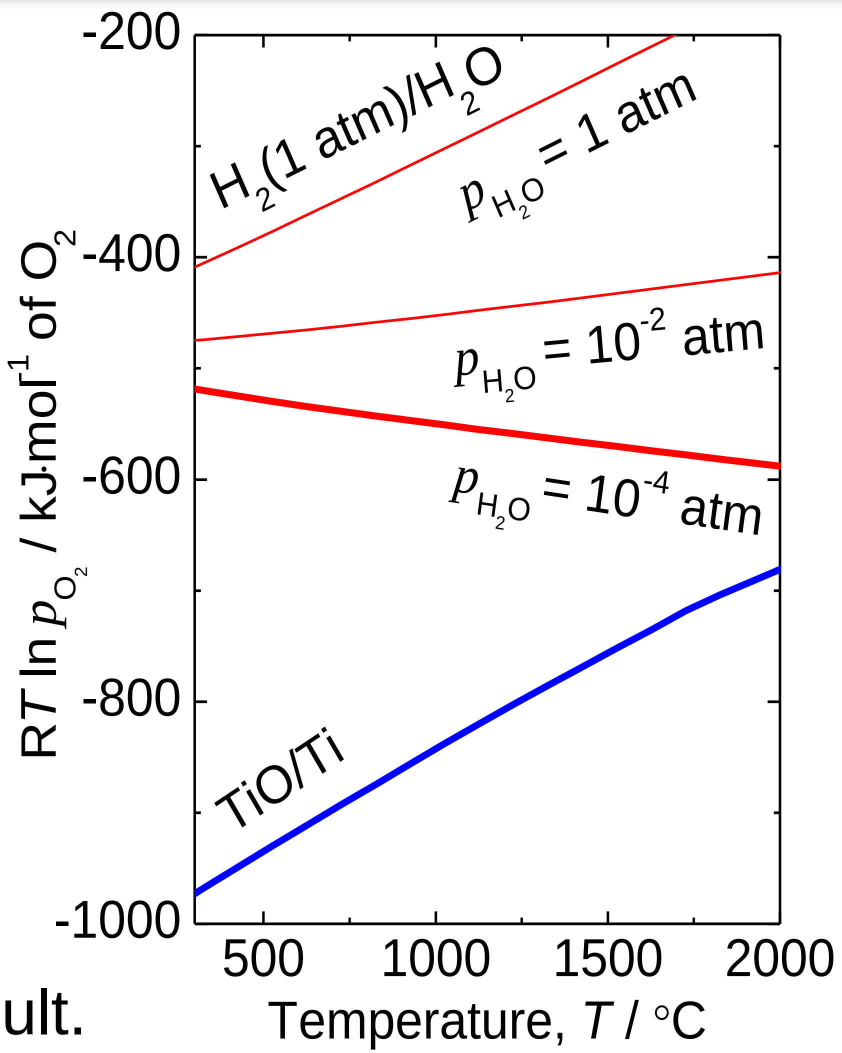
$$RT \ln p_{O_2} = \Delta G^\circ + 2RT \ln \frac{a_{TiO}}{a_{Ti}}$$

$$2H_2 + O_2 \rightleftarrows 2H_2O$$

$$RT \ln p_{O_2} = \Delta G^\circ + 2RT \ln \frac{p_{H_2O}}{p_{H_2}}$$

Because of $p_{H_2O} > 10^{-4}$ atm in gas boundary layer

➡ Reduction by hydrogen is difficult.



It might be possible to reduce TiO_2 to metallic state with controlling chemical potentials.

Control chemical potential

<u>The Gibbs energy change for reduction of TiO_2 by hydrogen</u>

$TiO_2 + 2H_2 = Ti + 2H_2O$ $\Delta G° = +359.1\ kJ{\cdot}mol^{-1}$ (1000 °C)

$$\Delta G = \Delta G° + RT \ln \frac{a_{Ti}\, p^2_{H_2O}}{a_{TiO_2}\, p^2_{H_2}}$$

$$= \Delta G° + 2.303\ RT\,(\boxed{\log a_{Ti}} + 2\log p_{H_2O} - \log a_{TiO_2} - 2\boxed{\log p_{H_2}})$$

<u>Previous works</u>

- Hydrogen reduction of TiO_2 in the presence of Pt at 1000 °C.

  TiO_2 + Pt (Ti : Pt = 1 : 3) ➡ Pt_3Ti

  We can obtain metallic titanium with decreased activity in alloy.

  However, the proceed of reaction depended on how much the affinity between titanium and alloying element is.

- Hydrogen reduction of TiO_2 in the presence of Ni at 1000 °C.

  TiO_2 + Ni (Ti : Ni = 1 : 3) ➡ Ti_4O_7 + Ni

Control chemical potential

The Gibbs energy change for reduction of TiO_2 by hydrogen

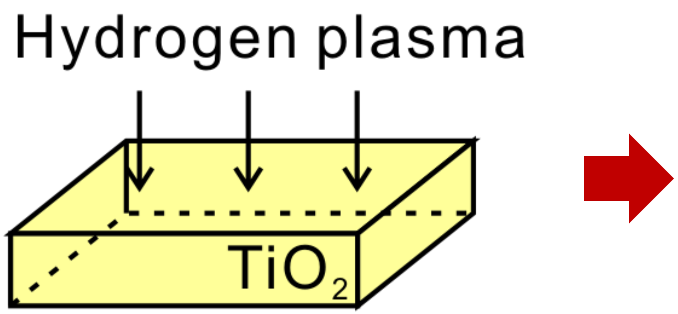
$TiO_2 + 2H_2 = Ti + 2H_2O$ $\Delta G° = +359.1\ kJ \cdot mol^{-1}$ (1000 °C)

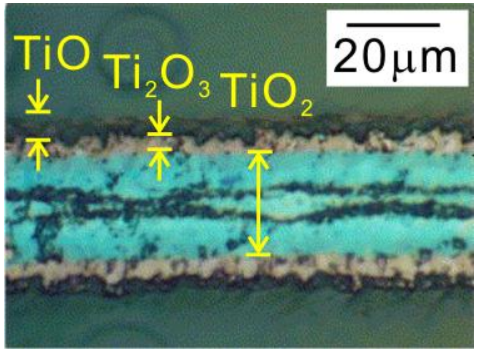
$$\Delta G = \Delta G° + RT \ln \frac{a_{Ti}\, p^2_{H_2O}}{a_{TiO_2}\, p^2_{H_2}}$$

$$= \Delta G° + 2.303\ RT\ (\log a_{Ti} + 2 \log p_{H_2O} - \log a_{TiO_2} - 2 \log p_{H_2})$$

Previous works

- Reduction of TiO_2 at 800 °C by low temperature hydrogen plasma





Optical micrograph of the cross section

(Huet *et al*)

This result clearly indicates that the partial pressure of hydrogen was hypothetically increased.

Objective in this study

Combining two previous studies

① Alloying with nickel (Decrease log a_{Ti})

② Utilizing nonequilibrium hydrogen (Increase log p_{H_2})

⬇

Produce titanium nickel alloy by hydrogen reduction.

Reduction of titanium oxide in the presence of nickel by supercooled monatomic hydrogen was examined.

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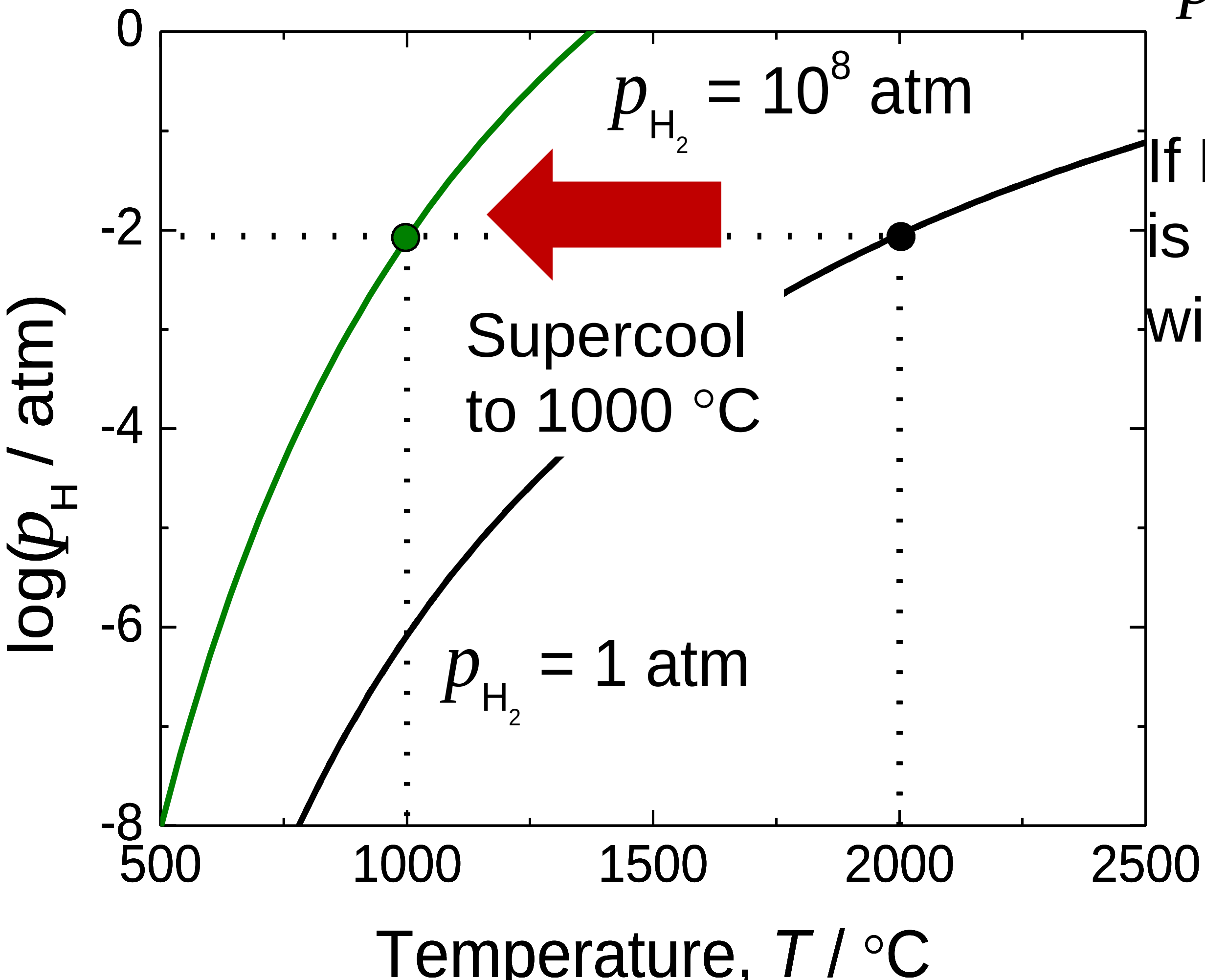
Supercooled monatomic hydrogen

Equilibrium partial pressure of monatomic hydrogen

$H_2 \rightleftarrows 2H$ $$\log p_H = \frac{1}{2}\left(\log p_{H_2} - \frac{\Delta G^\circ}{2.303\,RT}\right)$$

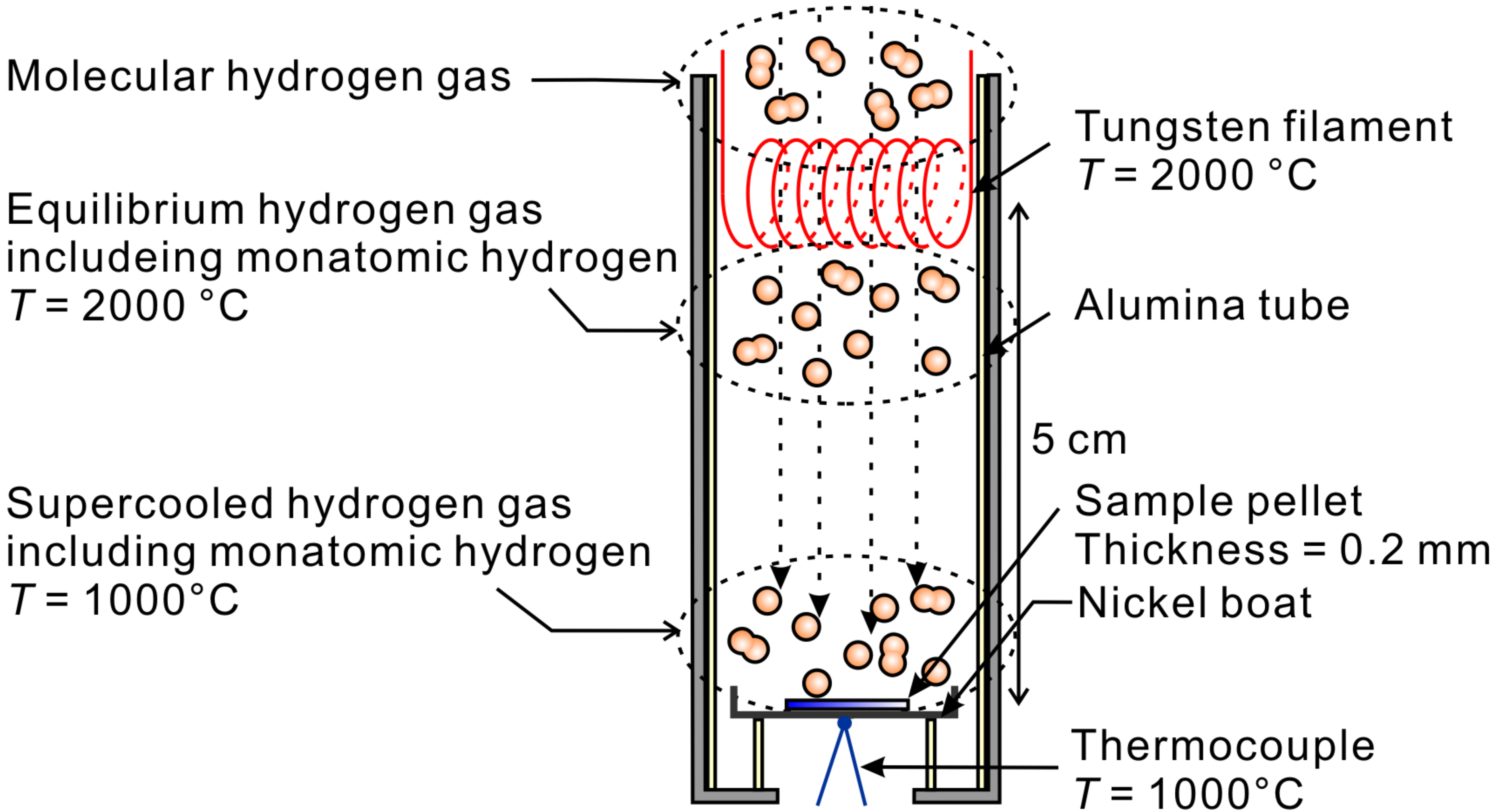


In equilibrium with H_2, $p_H = 10^{-2}$ atm at 2000 °C

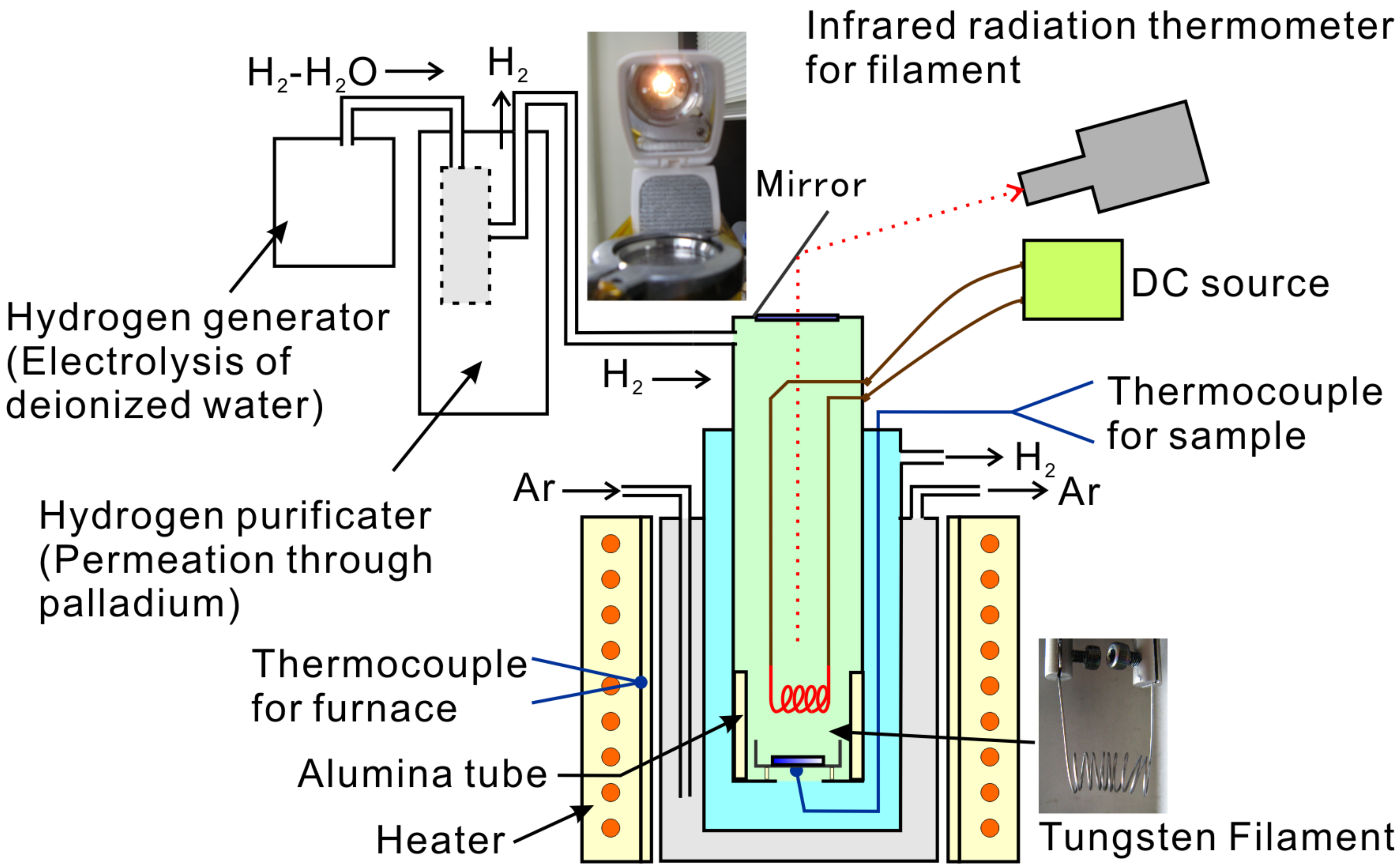
If H generated at 2000 °C is supercooled to 1000 °C with keeping p_H,

Based on the assumption of local equilibrium, partial pressure of supercooled hydrogen gas corresponds to 10^8 atm.

Hot-wire method



Experimental Apparatus



Experimental procedure

TiO_2 powder + Ni powder

↓ Mix by ball-milling (8 hours)
Ti : Ni = 1 : 3

Mixed powder

↓ Uniaxis press
(412 MPa, 10 min.)

Sample pellet

↓ Reduction
(H_2 flow rate = 100 ml·min^{-1}
Treatment time = 12 hours)

Reduced sample

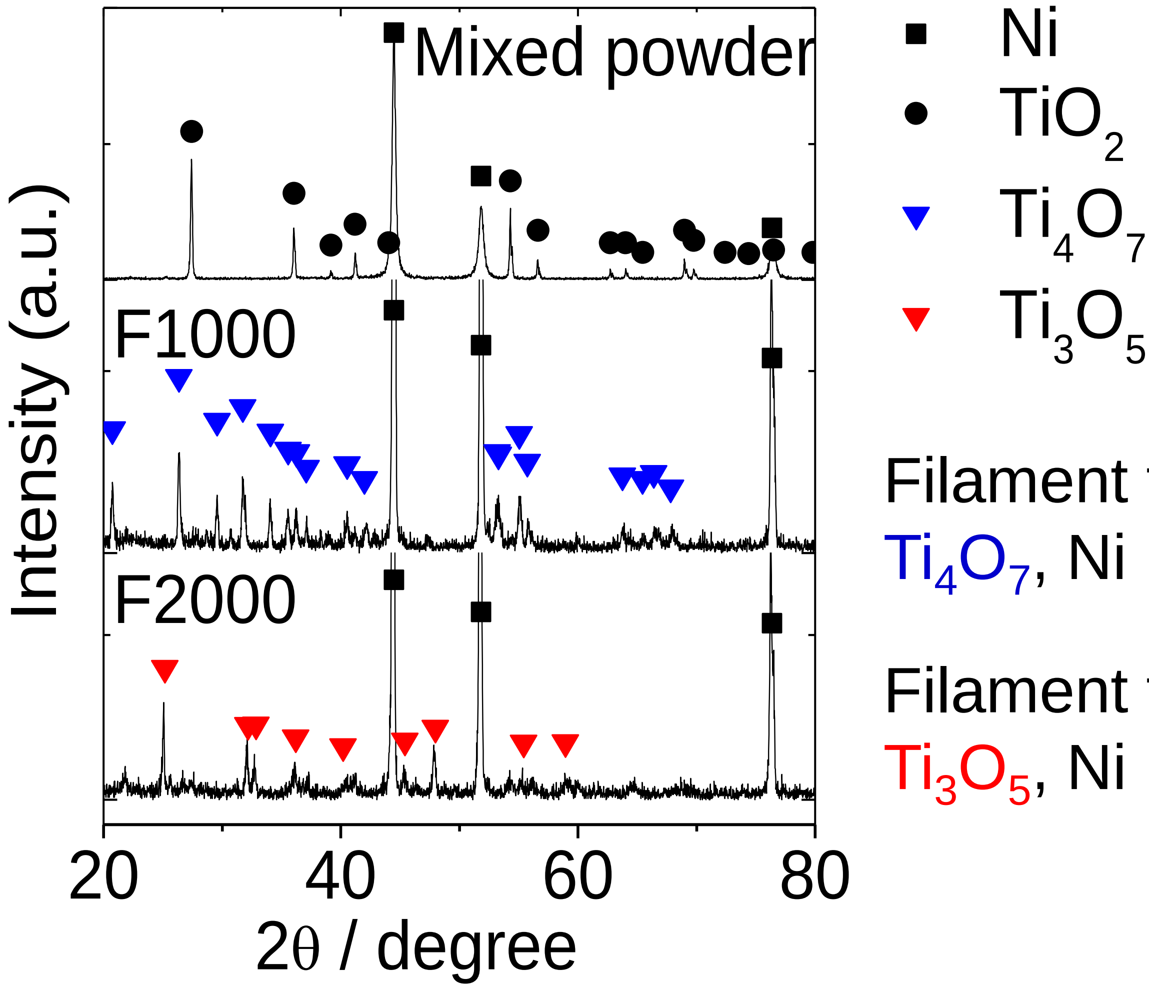
Temperature conditions

Sample	Temperature [°C]	
	Sample	Filament
F1000	1000	(1000)
F2000	1000	2000

Analysis

- X-ray diffraction analysis (XRD)
- Field emission scanning electron microscopy (FE-SEM)
- Energy-dispersive X-ray microscopy (EDX)

XRD analysis of reaction products



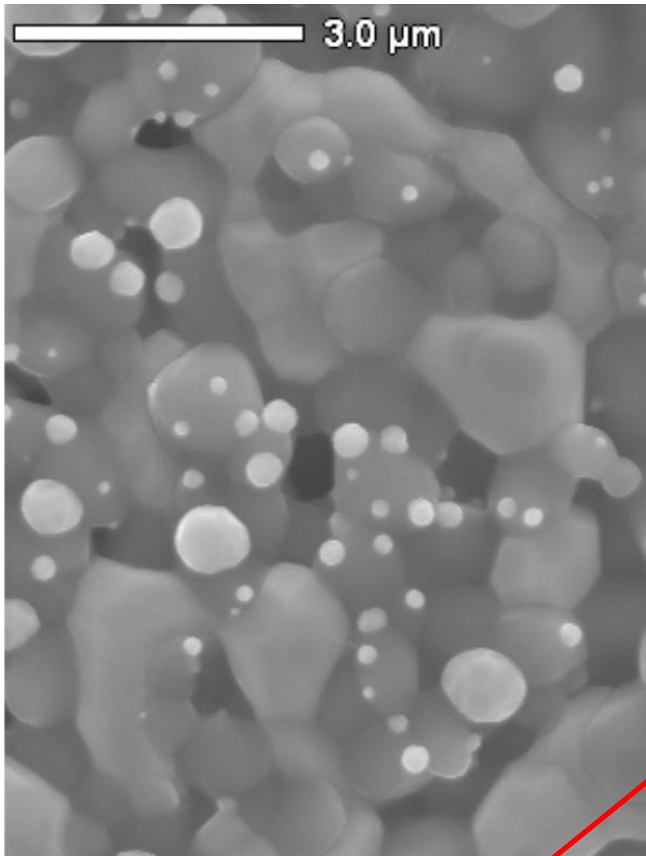
Filament temperature: 1000 °C
Ti_4O_7, Ni

Filament temperature: 2000 °C
Ti_3O_5, Ni

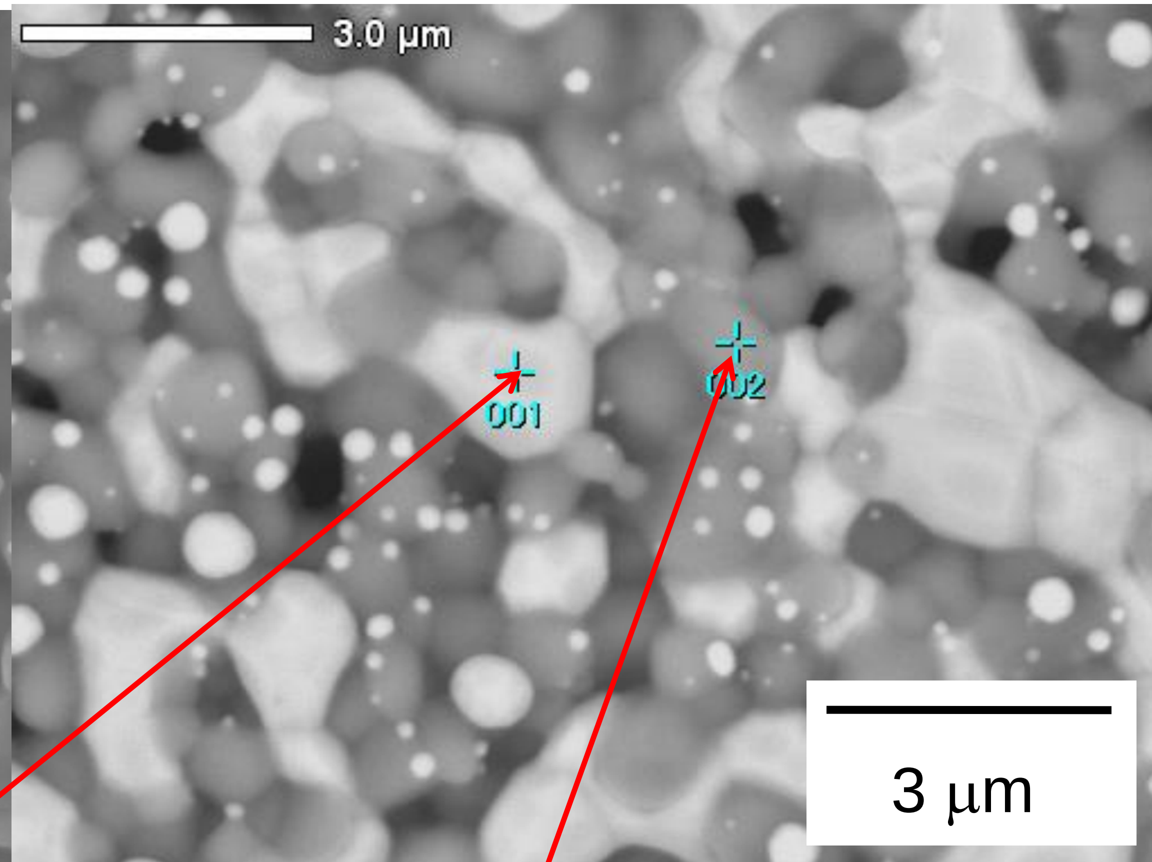
TiO_2 was reduced to lower oxide by supercooled hydrogen gas including monatomic hydrogen than by usual hydrogen gas.

EDX analysis of reaction products

Secondary electron im



Backscattered electron image of F1000

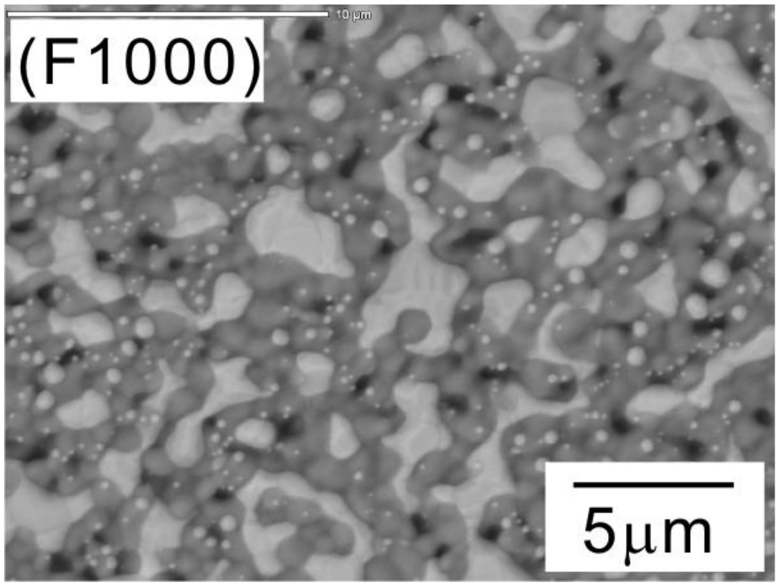


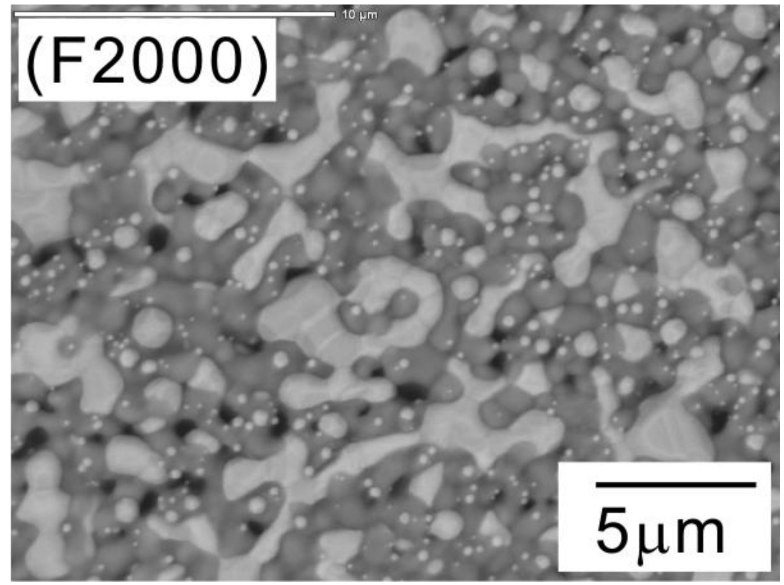
Ti : 1.8 %
Ni : 98.2 %
} Nickel phase

Ti : 63.6 %
Ni : 4.7 %
O : 31.8 %
} Titanium oxide phase

EDX analysis of reaction pruducts

Backscattered electron image (composition image)



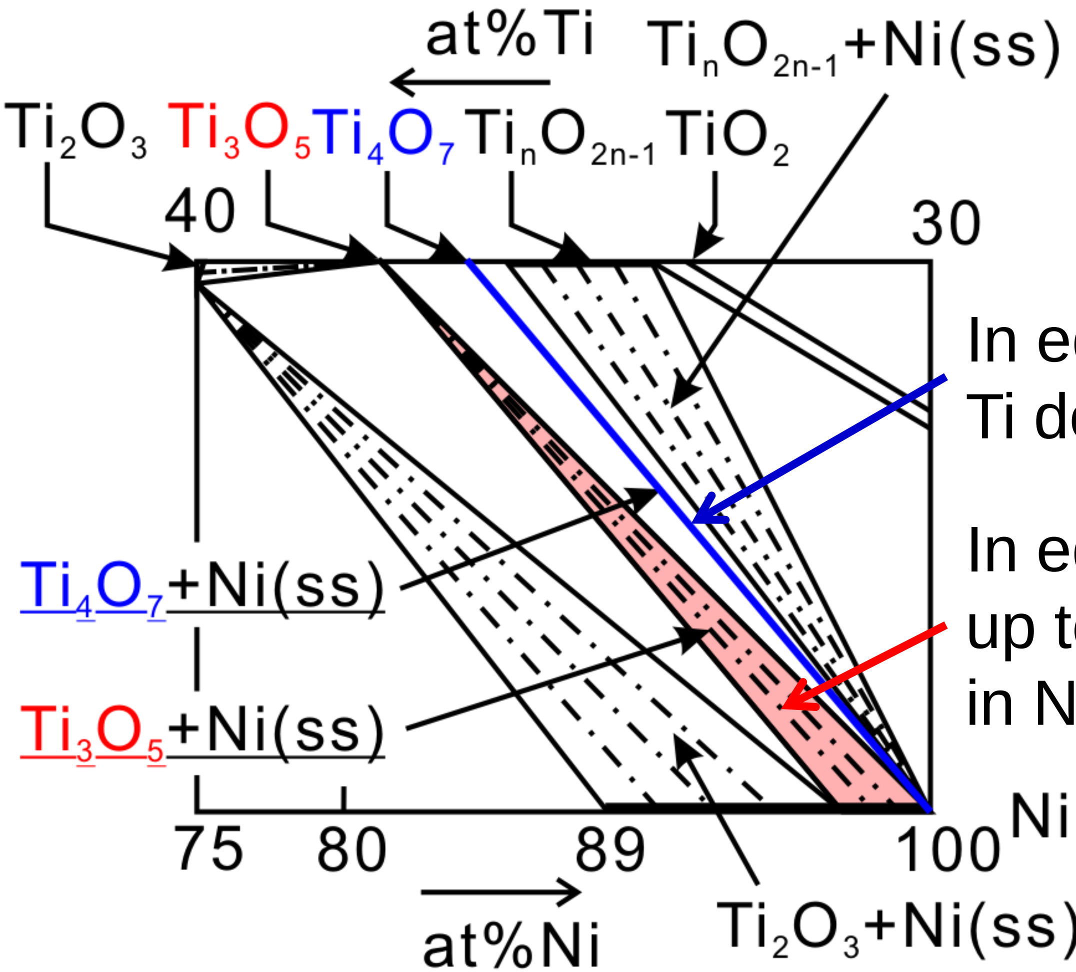


Sample	Ti concentration in Ni(ss) [at%]
F1000	1.8 ± 0.5
F2000	1.6 ± 0.4

Ti concentration in Ni(ss) was independent of filament temperature.

Log a_{Ti} is not different with each other.

Phase diagram of Ti-Ni-O system



Ti-Ni-O system at 927 °C [1]

In equilibrium with Ti_4O_7, Ti does not dissolve in Ni(ss).

In equilibrium with Ti_3O_5, up to 3 at% of Ti dissolves in Ni(ss).

[1] Chattopadhyay and Kleykamp, Z. Metallkde, 74(1983)

In the result of reduction by usual hydrogen gas (F1000),

- Ti_4O_7 was observed by XRD
- Ti concentration in Ni(ss) by EDX was 1.8 at%.

Contradiction

Detectable depth in EDX and XRD analysis

Penetration depth of electron beam and X-ray

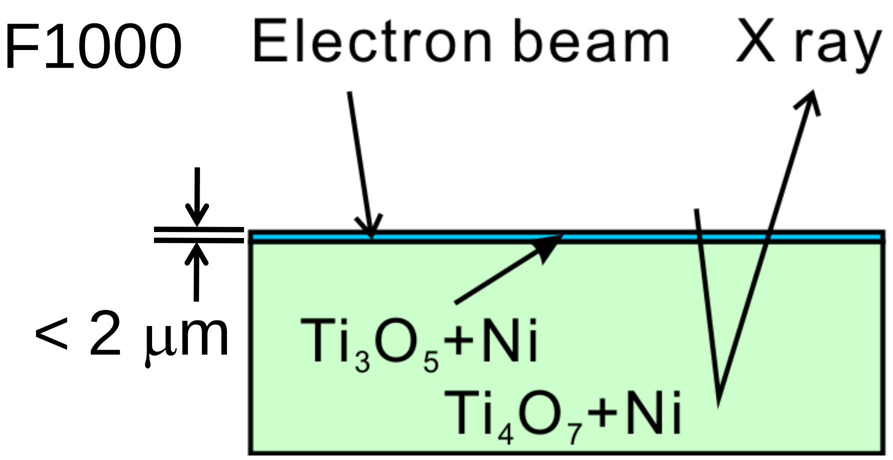
- Electron beam into nickel: 0.4 ~ 4 μm.

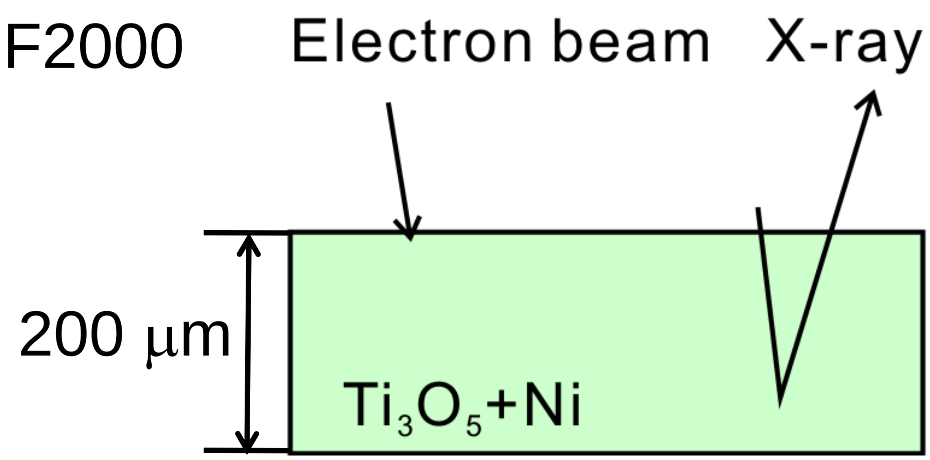
  ➡ EDX gives surface information.

- X-ray into the mixture of titanium oxide and nickel: 20 ~ 200 μm.

  ➡ XRD gives bulk information.

Ti_3O_5 layer of F1000 might be too thin to be detected in XRD analysis.

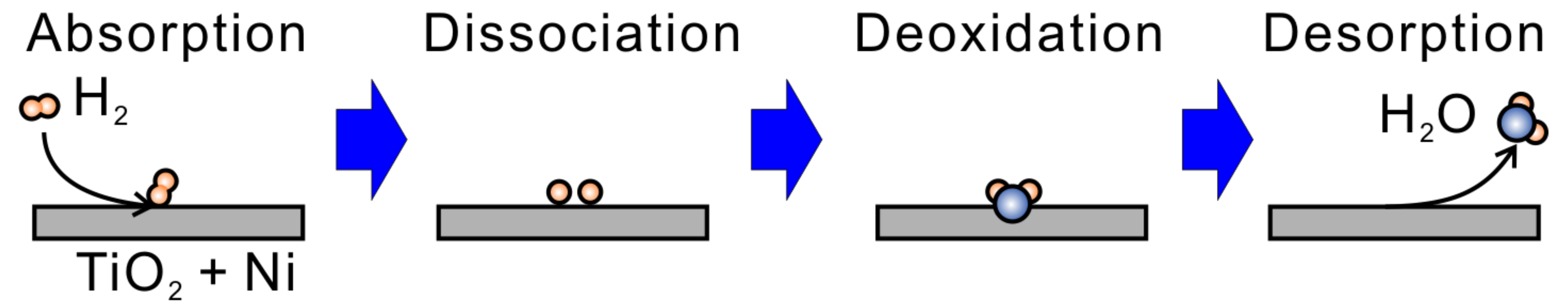




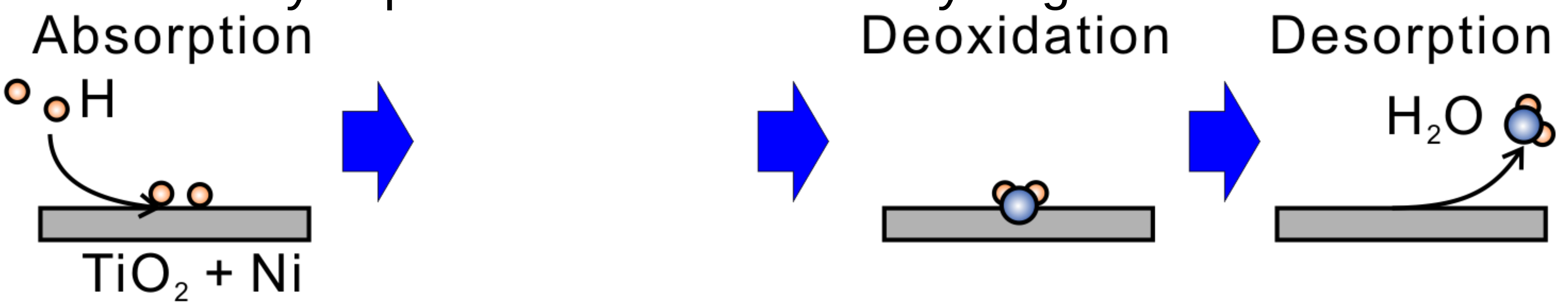
Thickness of Ti_3O_5 layer: F1000 << F2000

Reaction mechanism

Reduction by molecular hydrogen



Reduction by supercooled monatomic hydrogen



Reduction rate: Monatomic Hydrogen >> Molecular hydrogen

By utilizing supercooled monatomic hydrogen, the reduction ability was kinetically enhanced and Ti_3O_5 layer grew wider.

Summary

• We could not obtain metallic titanium by reduction of titanium oxide in the presence of nickel by supercooled monatomic hydrogen. But we obtained the following findings.

Sample	Temperature [°C]		Detected phase by XRD	Ti concentration in Ni(ss) [at%]
	Sample	Filament		
F1000	1000	1000	Ti_4O_7, Ni	1.8 ± 0.5
F2000	1000	2000	Ti_3O_5, Ni	1.6 ± 0.4

• In bulk, titanium oxide obtained after reduction by supercooled hydrogen gas including monatomic hydrogen is different from the oxide obtained after reduction by usual hydrogen gas.

• The Ti concentration suggests that the chemical potential of oxygen on pellet surface is independent of filament temperature.

• Reduction rate by supercooled hydrogen gas including monatomic hydrogen is faster than that by usual hydrogen gas. As the result, the detected phase was different in bulk.