Reduction of Titanium Oxide to Titanium Alloy by Hydrogen

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Outline

- Titanium alloy
- Reduction of titanium oxide to Ti-Pt alloy
- Reduction of titanium oxide to Ti-Ni alloy
- Summary

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Introduction

Titanium alloys have many unique features and they are used in various situations.

Ti-Ni alloy; Shape Memory, Superelasticity

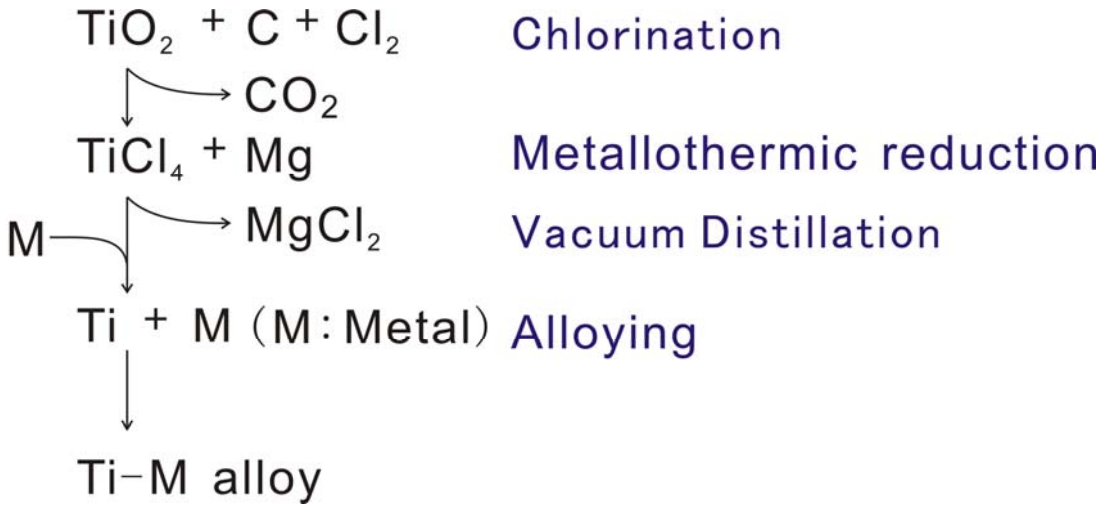
Photographs; Daido Steel Co., ltd., Wacoal Co.

However, titanium alloy is very expensive for its production cost.

It is necessary to develop a new process of titanium alloy.

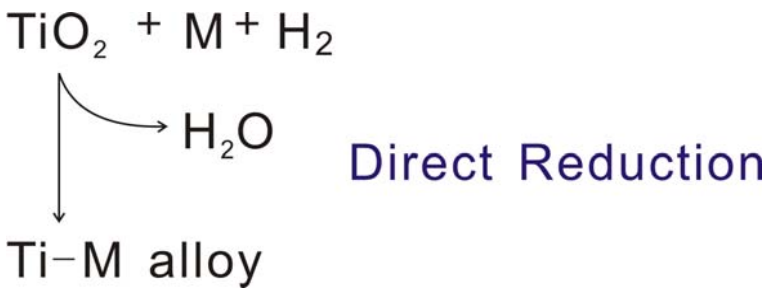
Production process of titanium base alloy

Current production process



This process is very complicated and consumes much energy.

New production process



This process is very simple and clean!

Thermodynamics of the new process at 1000°C

In the case of reducing TiO_2 to pure titanium

① $TiO_2+2H_2 = Ti +2H_2O$ —— $\Delta G^\circ_1 = 359.563 \quad (kJ\cdot mol^{-1}) > 0$

The Gibbs energy is positively large.

It is very difficult to reduce TiO_2 to pure titanium by hydrogen.

When some other metal coexists with TiO_2 (In our process)

② $Ti+3M = M_3Ti$ —— ΔG°_2

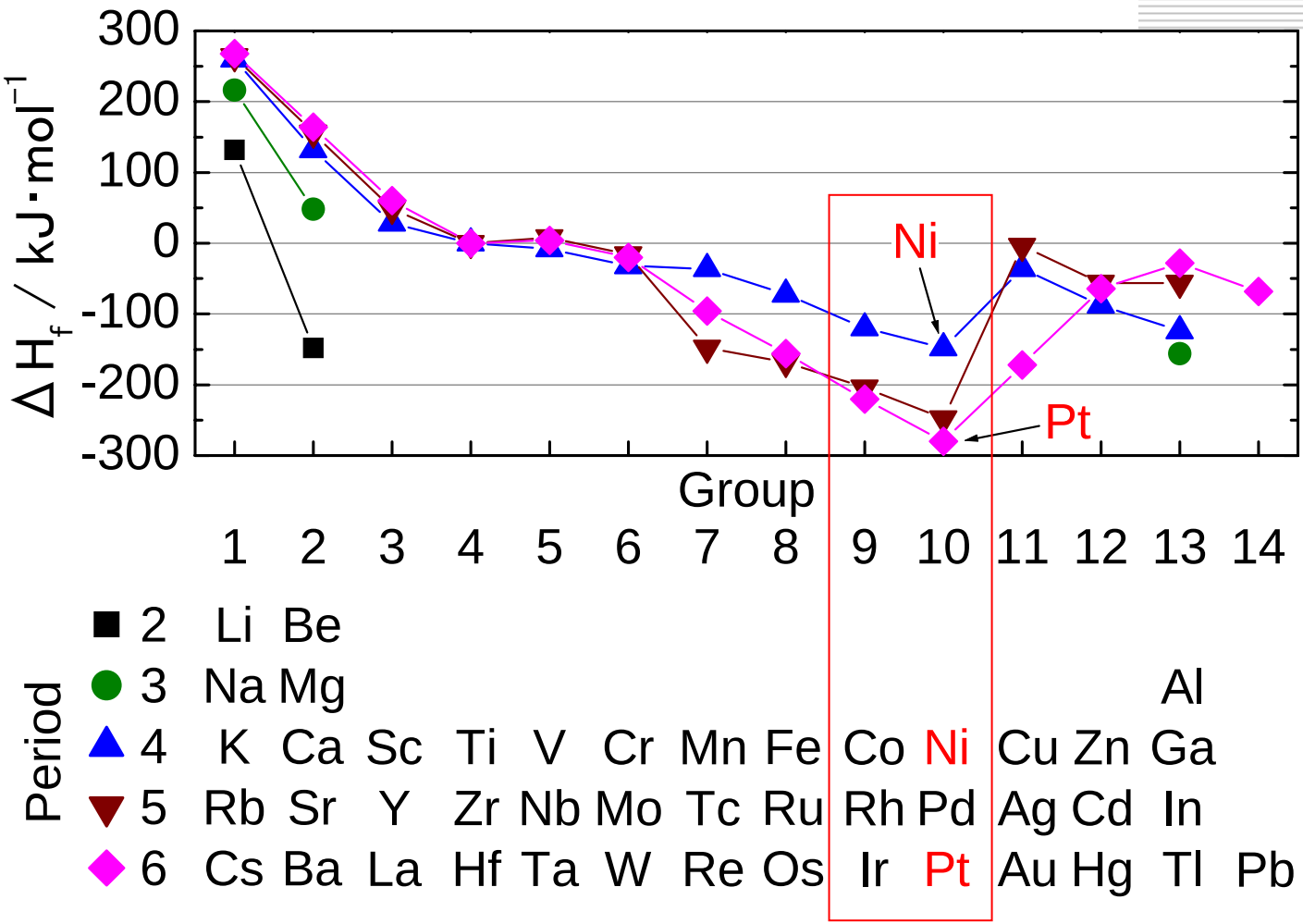
③ $TiO_2+2H_2+3M = M_3Ti +2H_2O$ —— ΔG°_3

$$\Delta G^\circ_3 = \Delta G^\circ_1 + \Delta G^\circ_2$$

If ΔG°_2 is negatively large, it is possible to reduce TiO_2 to M_3Ti.

ΔG°_2 was estimated by the formation enthalpy and the formation entropy. $(\Delta G^\circ_2 = \Delta H_f - T\Delta S_f)$

Estimate the formation enthalpy of M_3Ti (ΔH_f)



The order of the formation enthalpy is as follows.

Pt<Pd<Ir<Rh<Au<Ru<Al, Os<Be, Ni, Tc

Estimate the formation entropy of M_3Ti (ΔS_f) at 1000°C

The formation entropy of typical M_3Ti is as follows

	Al_3Ti	Ni_3Ti	Pt_3Ti
ΔH_f / kJ mol^{-1}	-182.310	-152.205	-341.833
$-T\Delta S_f$ / kJ mol^{-1}	27.755	39.615	42.663

Comparing the value of ΔH_f, the value of $T\Delta S_f$ is not so large that it does not affect the order of ΔG°_2.

ΔG°_2 can be estimated by the formation enthalpy of M_3Ti.

The metals chosen in this study

- Platinum（Pt）; it has the negatively largest value of ΔH_f.

- Nickel（Ni）; it has relatively large negative value of ΔH_f and the alloy is practical.

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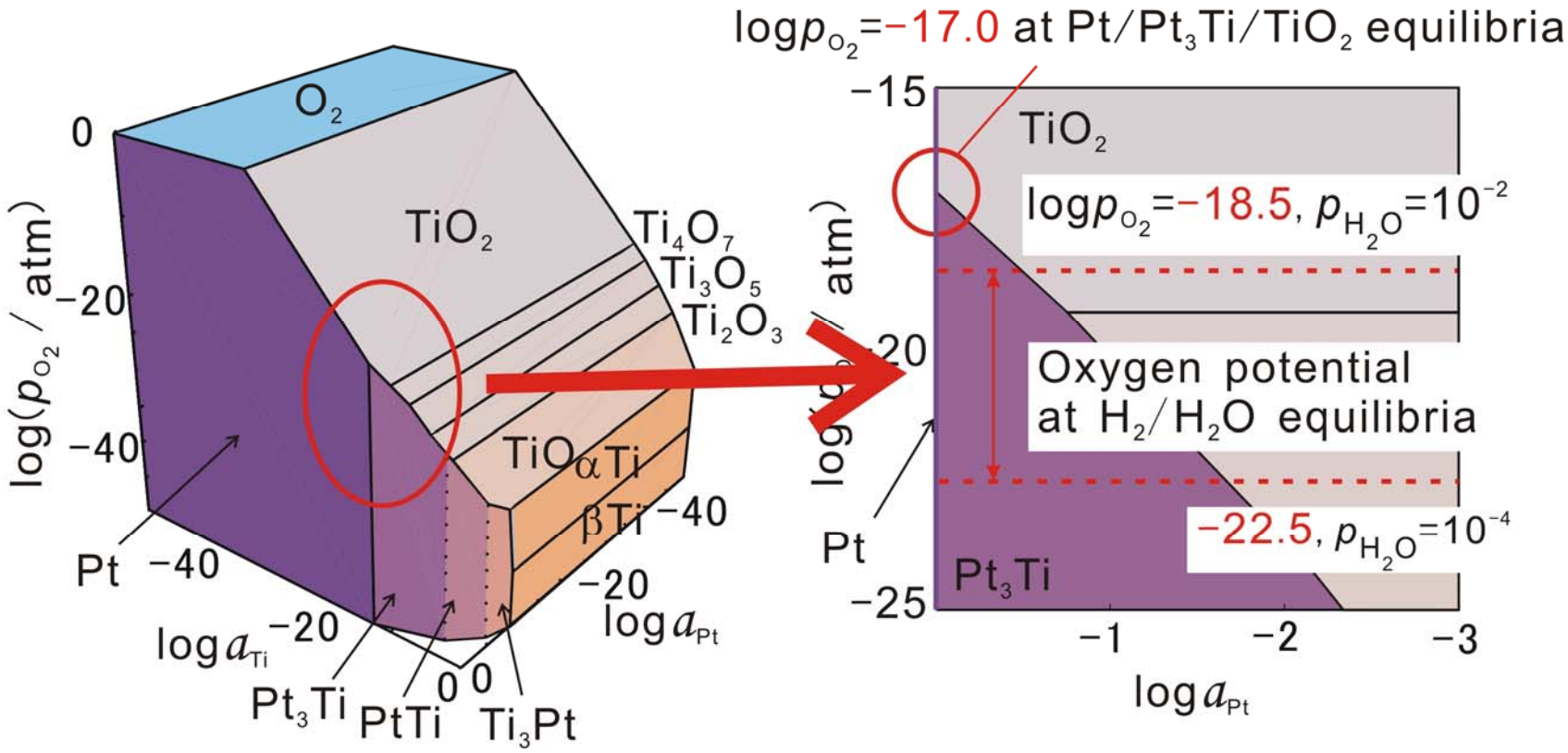
Thermodynamic estimation of the possibility of the process

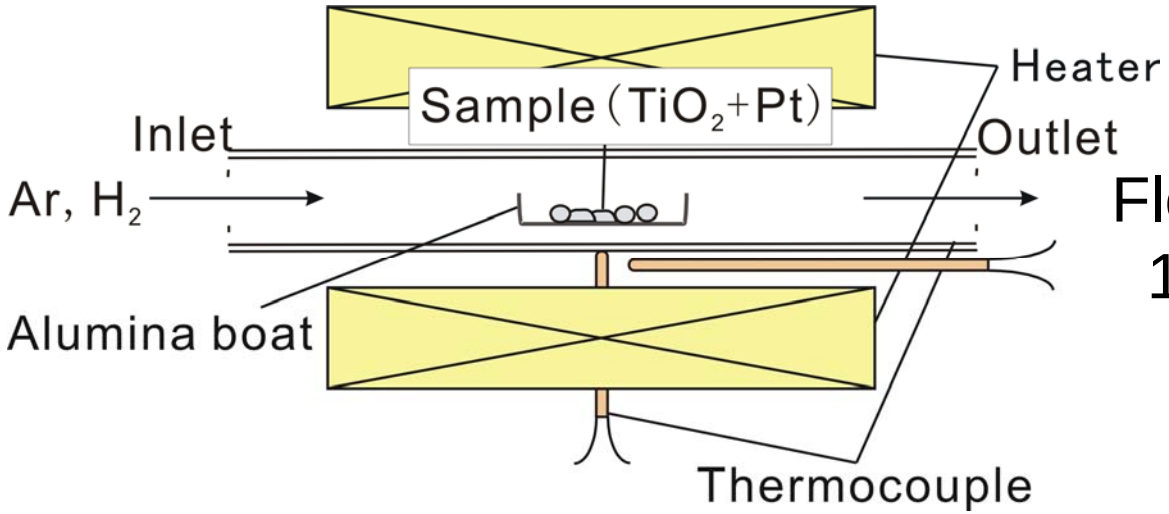


$\log p_{O_2}$ at $Pt/Pt_3Ti/TiO_2$ equilibria > $\log p_{O_2}$ at H_2/H_2O equilibria

It is possible to reduce TiO_2 to Pt_3Ti by hydrogen.

Experimental 1; Reduction by hydrogen

Set-up



Flow rate
100 ml min^{-1}

Sample

Prepared by mixing TiO_2 (rutile type) powder and Pt powder to the atomic ratio of 1 : 3 by ball milling

Reduction Temperature

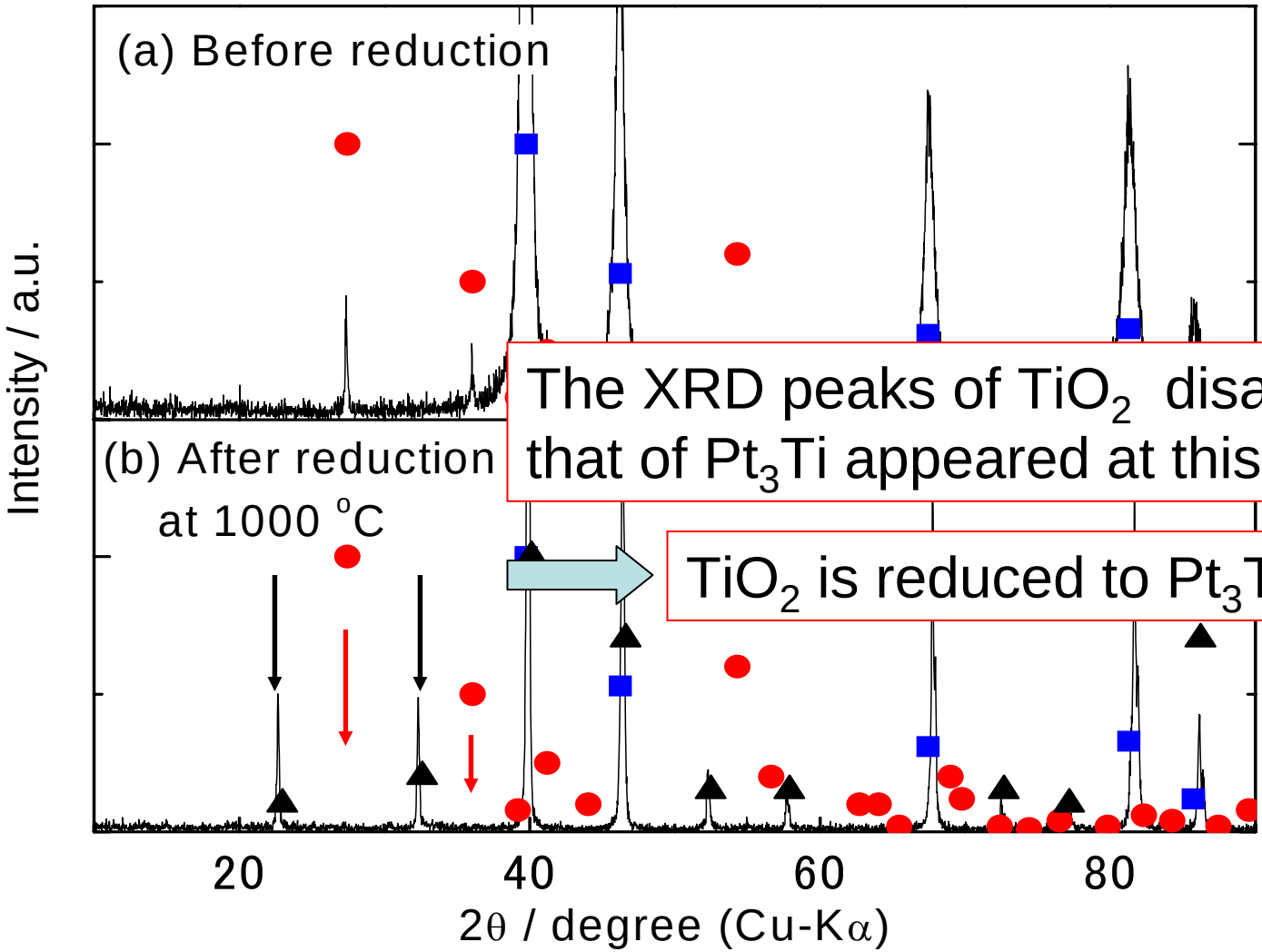
1000℃

Analysis

X-ray Diffraction (XRD); identify products

The results of reduction by hydrogen at 1000 ˚C

X-ray diffraction pattern



The XRD peaks of TiO_2 disappeared and that of Pt_3Ti appeared at this temperature.

TiO_2 is reduced to Pt_3Ti by hydrogen!

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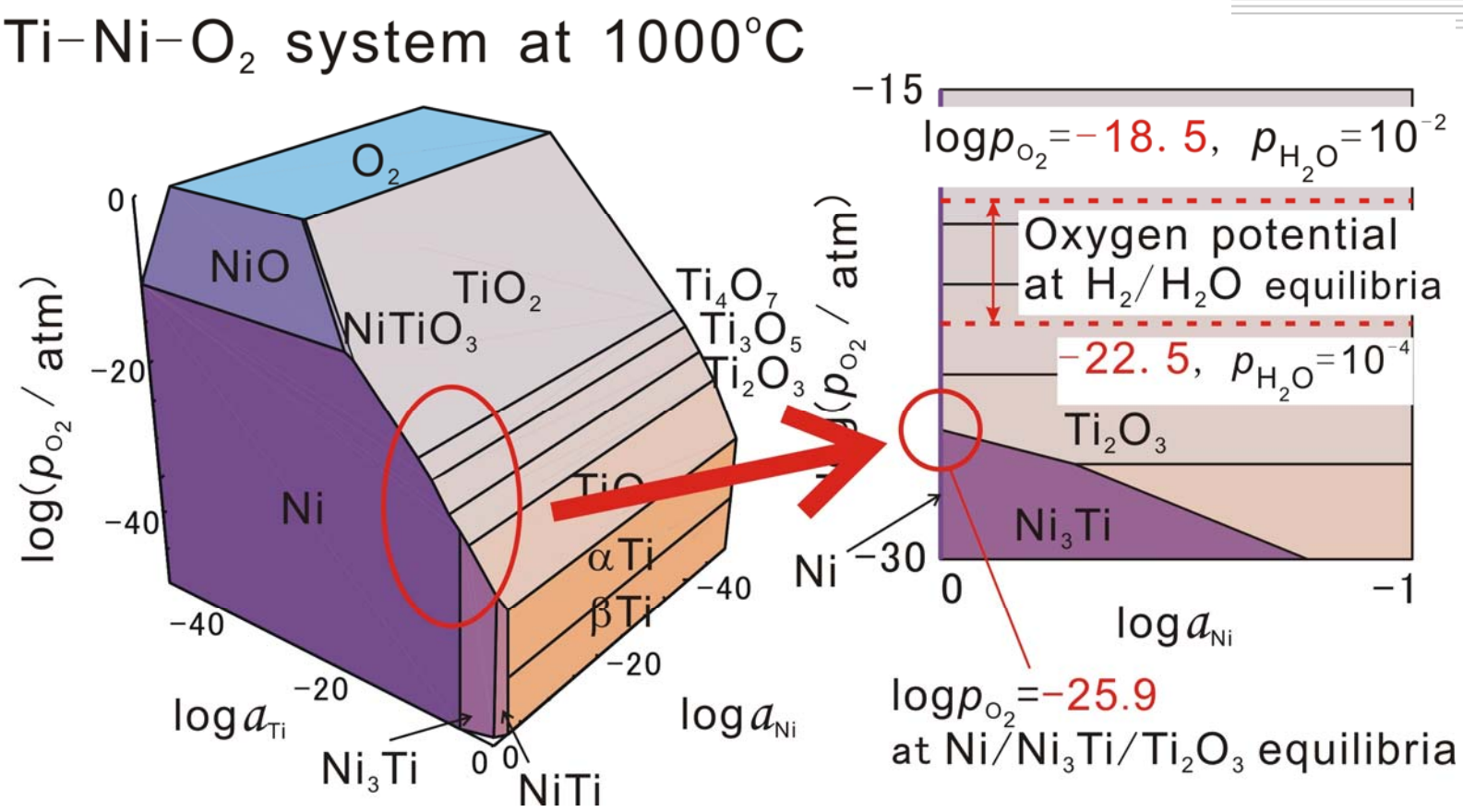
Thermodynamic estimation of the possibility of the process



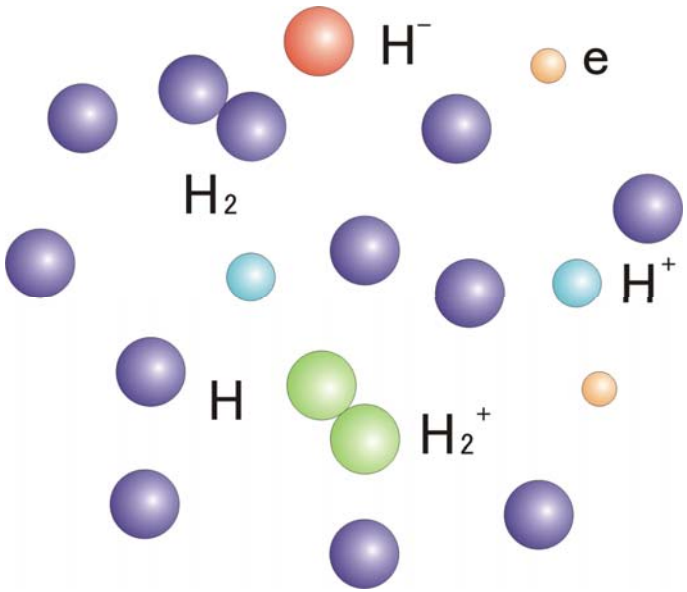
$\log p_{O_2}$ at $Ni/Ni_3Ti/Ti_2O_3$ equilibria $<$ $\log p_{O_2}$ at H_2/H_2O equilibria

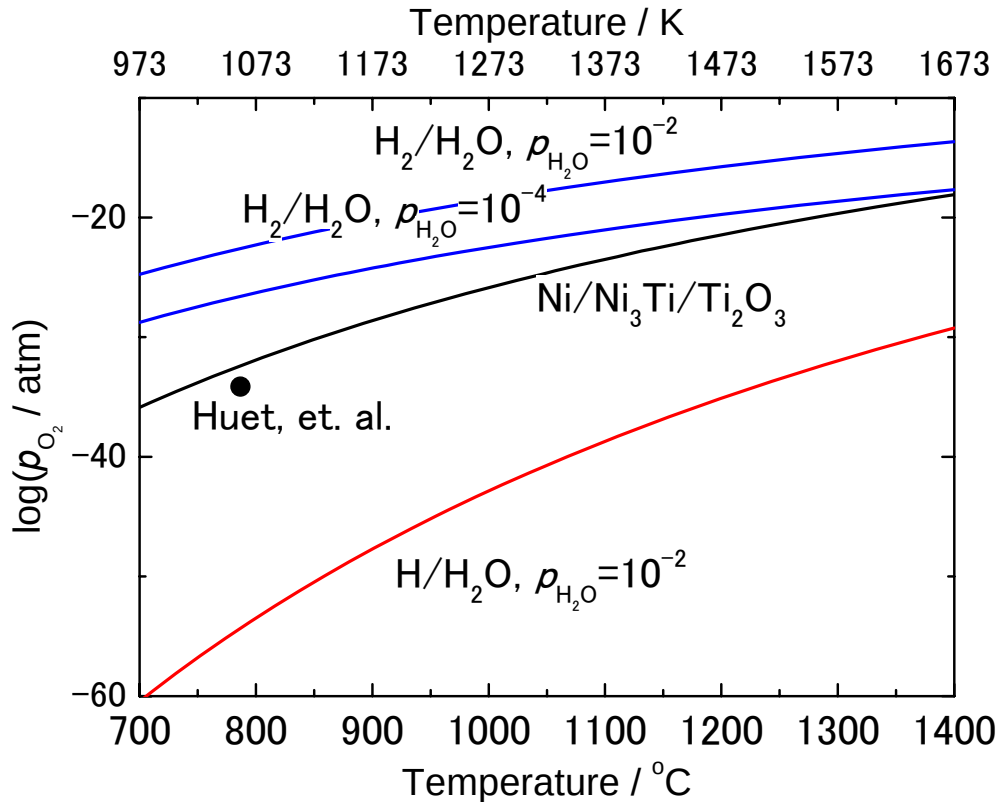
It is difficult to reduce TiO_2 to Ni_3Ti by hydrogen.

Enhance reduction ability of hydrogen

Possibility of hydrogen plasma reduction

Hydrogen plasma consists of mainly monatomic hydrogen, and partially proton, electron, and so on.





The hydrogen plasma has higher reduction ability than the hydrogen molecule.

Experimental 2; Reduction by hydrogen plasma

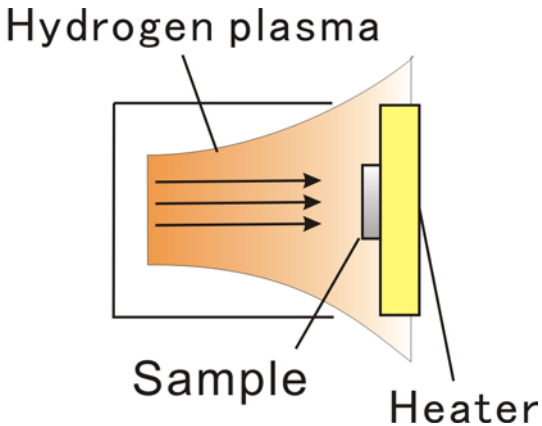
Sample

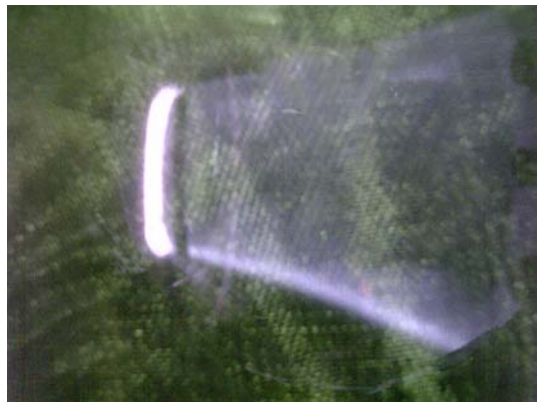
Prepared by mixing TiO_2 (rutile type) powder and Ni powder to the atomic ratio of 1 : 3, and then, forming to pellet.

Hydrogen plasma

Generated by RF plasma equipment

Pressure [Pa]	H_2 flow rate [ml min^{-1}]	Microwave power [W]	Treatment time [min]
100	100	1500	360





Sample temperature

800 ˚C

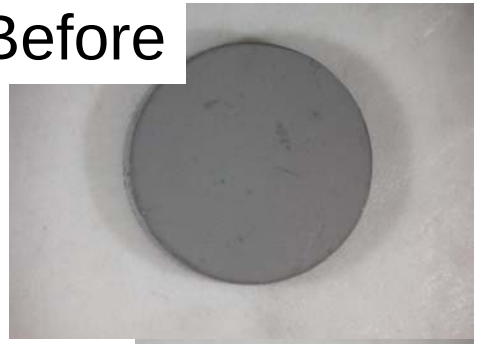
Analysis

Grazing Incidence X-ray Analysis;
identify products on the surface of samples

The results of reduction by hydrogen plasma at 800 ˚C

Photograph

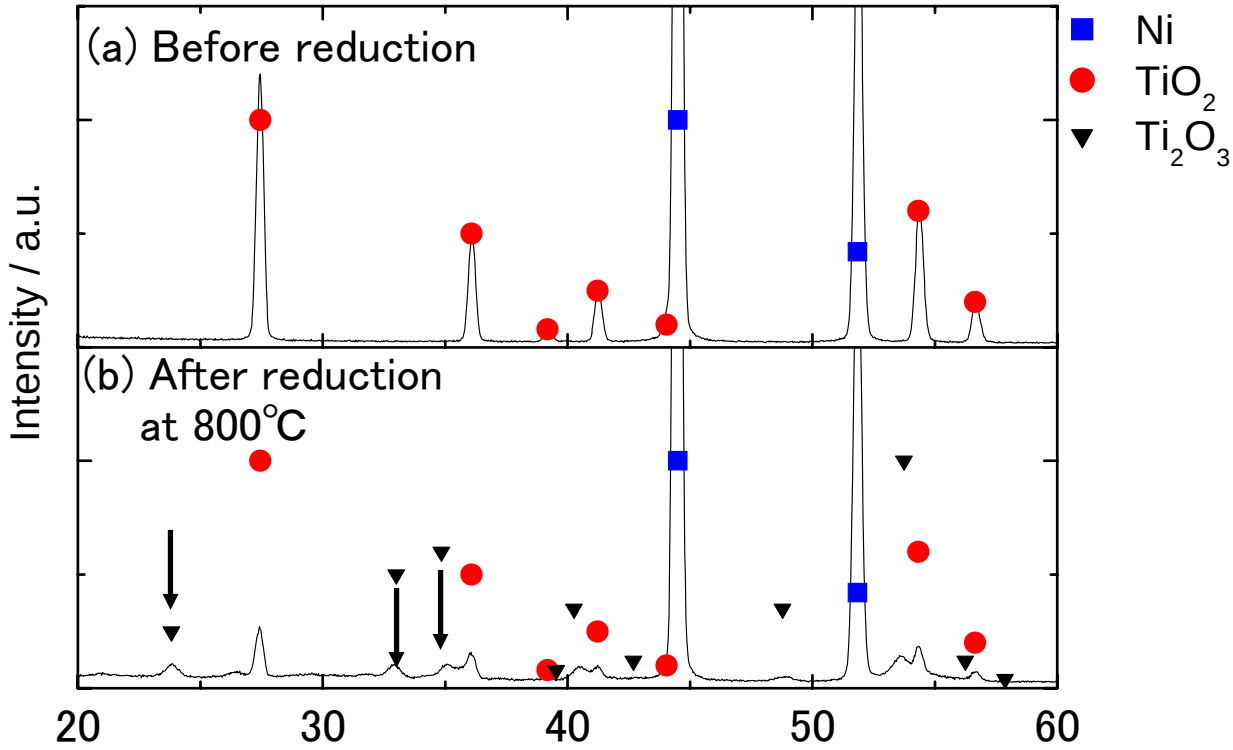
(a) Before



(b) After

1 cm

Grazing incidence X-ray analysis

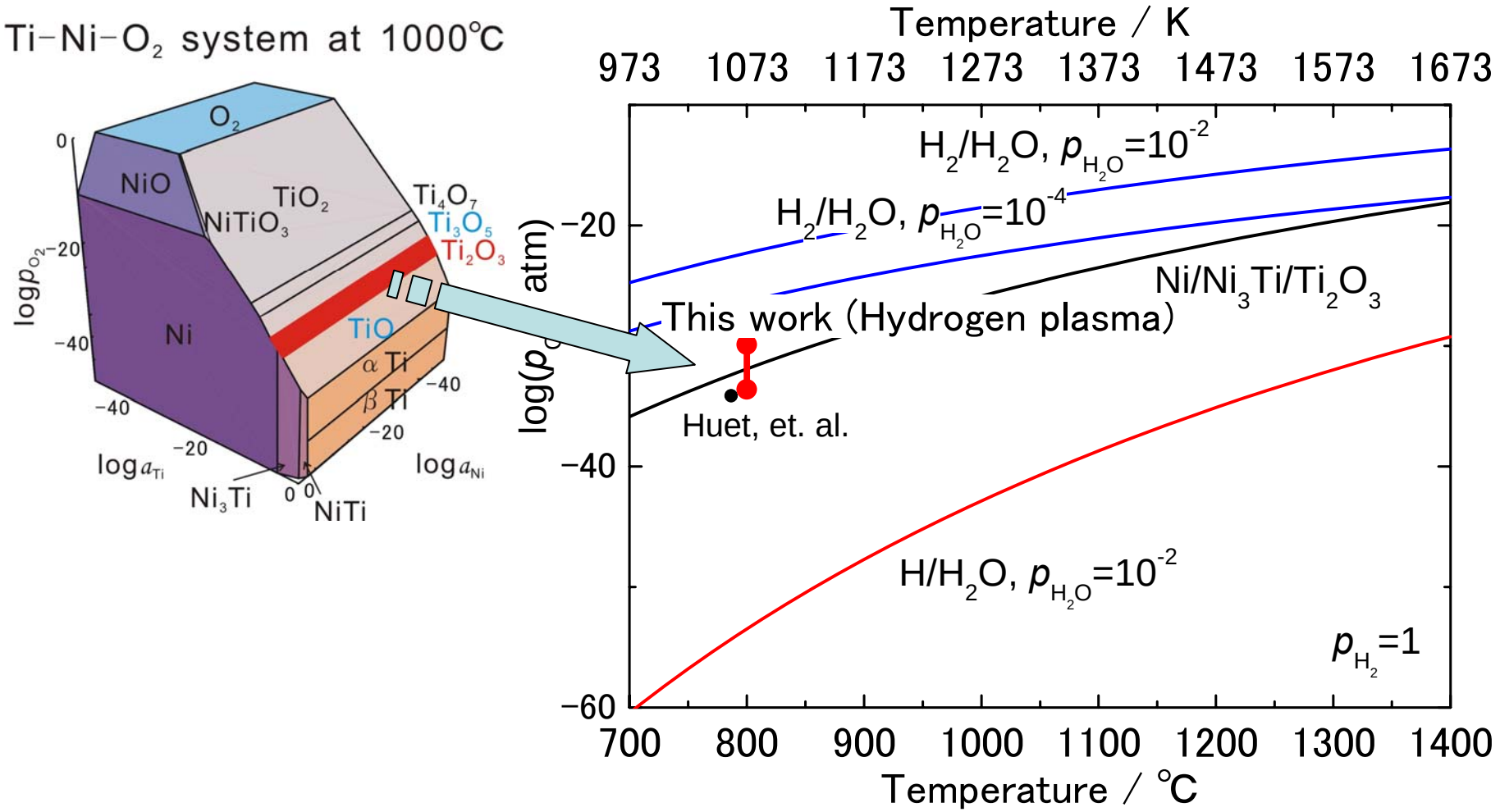


The color of the surface changed to black.

The peaks of Ti_2O_3 appeared, but the peaks of Ni_3Ti did not appear.

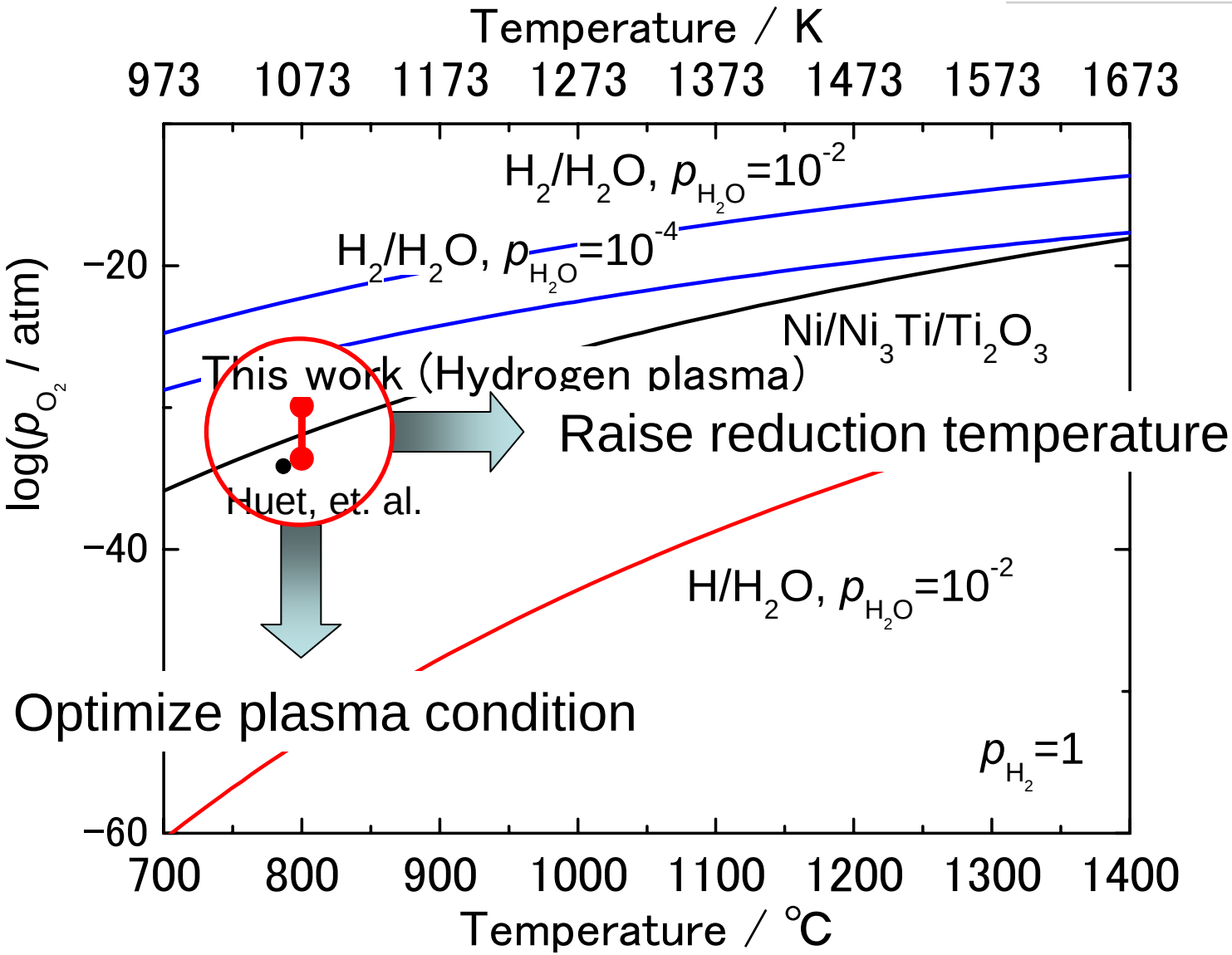
TiO_2 on the surface was reduced to Ti_2O_3 but Ni_3Ti was not obtained by hydrogen plasma at 800 ˚C.

Estimate the oxygen potential of hydrogen plasma



The oxygen potential of hydrogen plasma takes almost the same potential value required for Ni_3Ti.

As next work…


Temperature / K
973 1073 1173 1273 1373 1473 1573 1673
H_2/H_2O, $p_{H_2O}=10^{-2}$
H_2/H_2O, $p_{H_2O}=10^{-4}$
Ni/Ni_3Ti/Ti_2O_3
This work (Hydrogen plasma)
Raise reduction temperature
Huet, et. al.
H/H_2O, $p_{H_2O}=10^{-2}$
Optimize plasma condition
$p_{H_2}=1$
log(p_{O_2} / atm)
−20
−40
−60
700 800 900 1000 1100 1200 1300 1400
Temperature / ℃

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1. TiO_2 coexisting with Pt was reduced to Pt_3Ti by hydrogen at 1000 ˚C.
2. Ti-Ni alloy was not formed by hydrogen plasma reduction.
3. TiO_2 was reduced to Ti_2O_3 by hydrogen plasma at 800 ˚C.

End

Thank you for your attention !