IEEC 2026, Sep 7-9, Ostravice, Czech Republic
Research session: Storage Materials (Sep 8th)

Optimizing reversible hydrogen storage capacity and activation characteristics in TiFe-based alloys by oxygen addition

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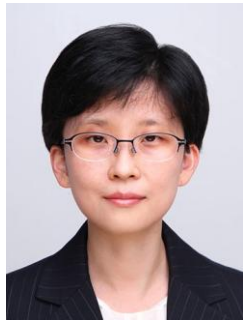

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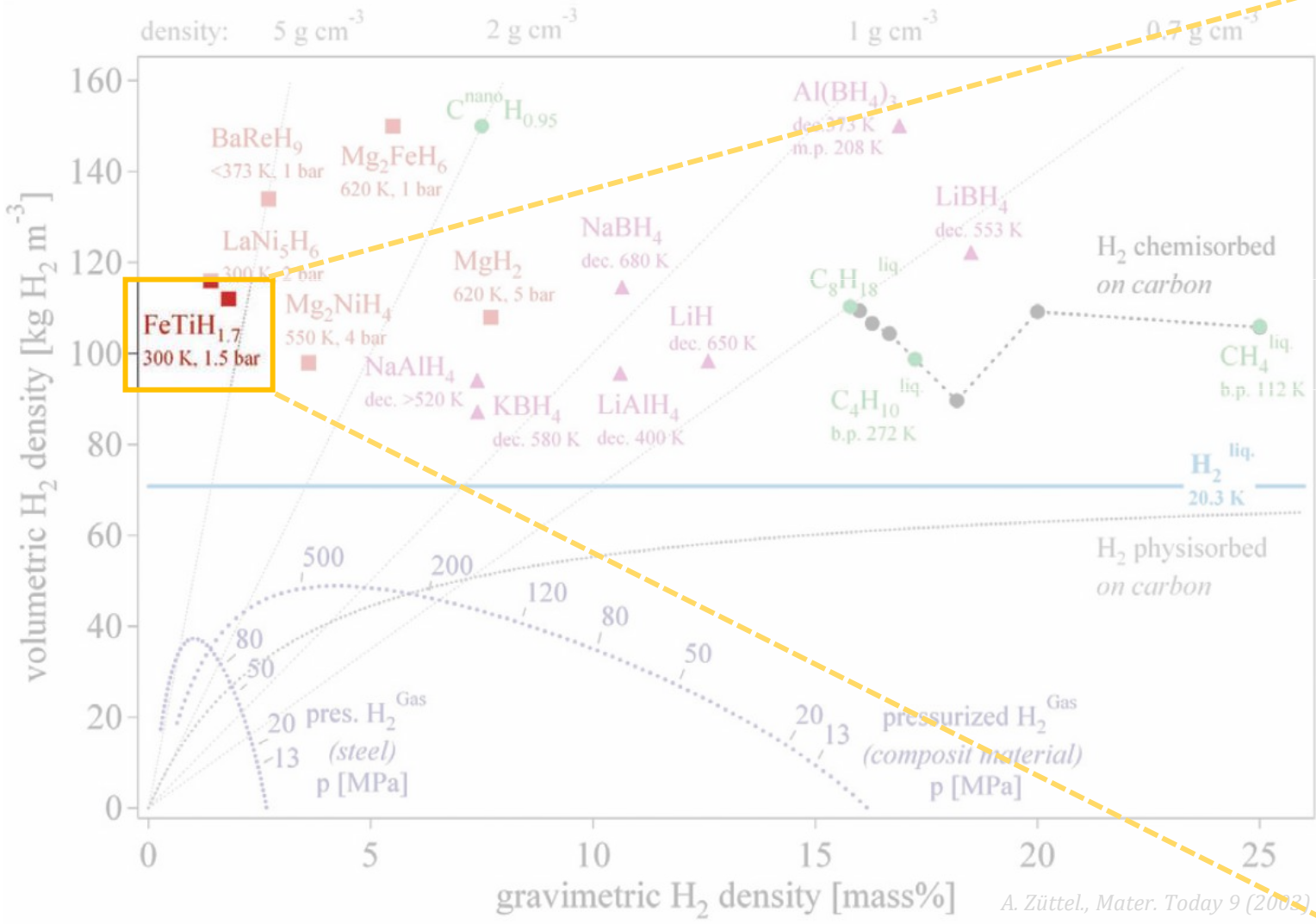
KIST 한국과학기술연구원 Korea Institute of Science and Technology

nst 국가과학기술연구회 National Research Council of Science & Technology

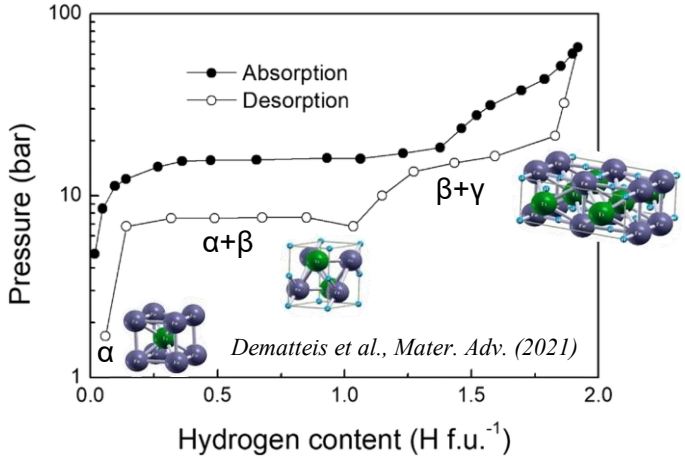
NRF 한국연구재단

TiFe hydrogen storage alloy : initial hydrogenation issue



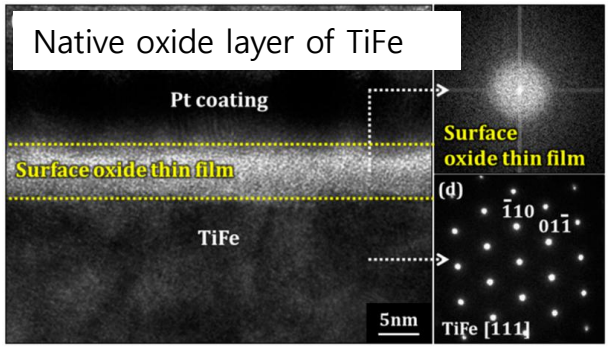
A. Züttel., Mater. Today 9 (2003)

TiFe B2 phase



Dematteis et al., Mater. Adv. (2021)

- RT reversible H-storage alloy
- Difficulties in initial hydrogenation

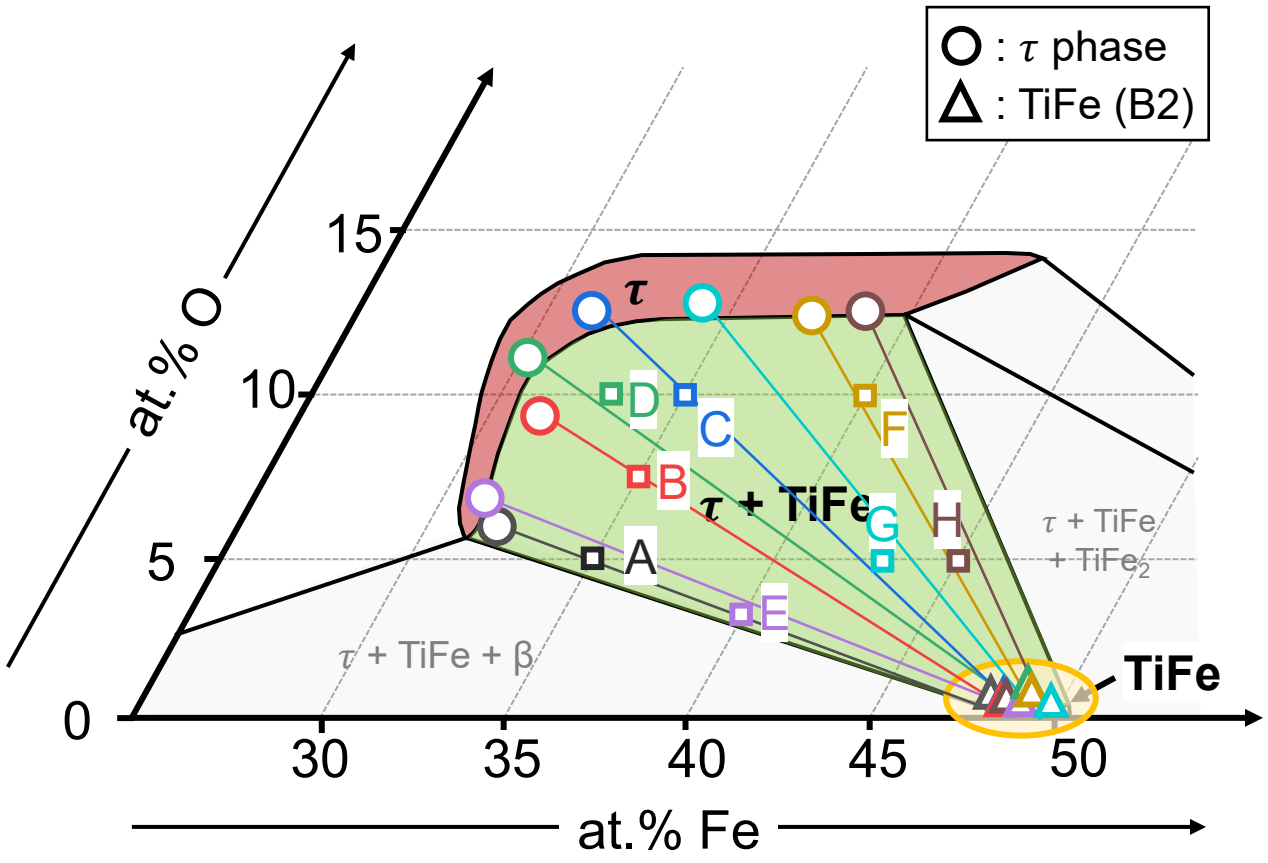


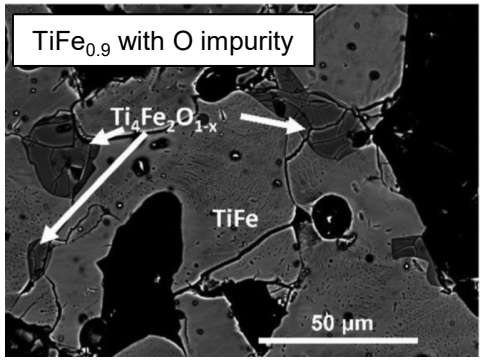
K. B. Park et. al., Metals, 12 (2022)

$Ti_4Fe_2O_x$ ternary phase (τ phase) in TiFe-based alloys

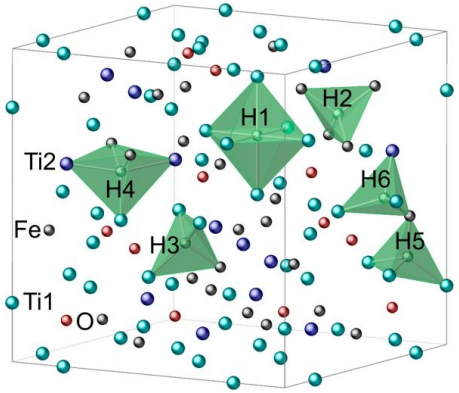
Ti-Fe-O isothermal phase diagram at 1000°C

(Reproduced from *Rupp (1984)*, verified with samples heat-treated at 1000oC, 72h)

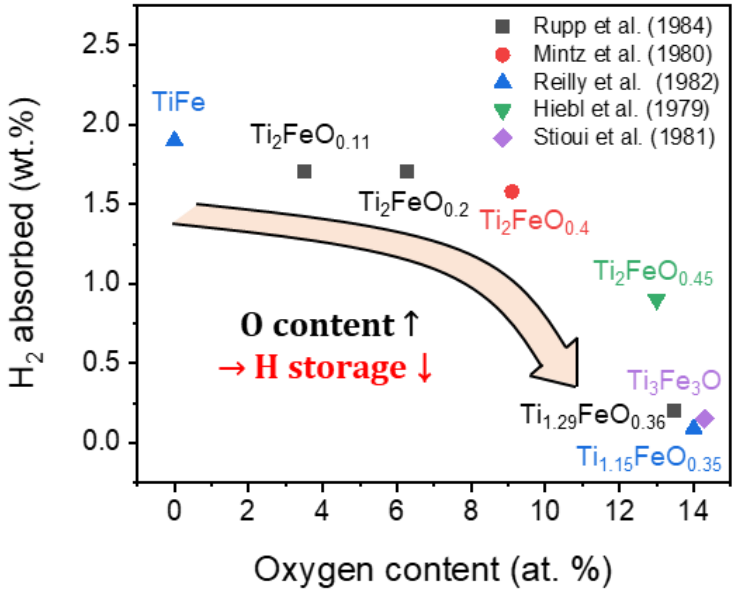




Liu et al, Int. J. Hydrogen Energy (2023).



$Ti_4Fe_2O_x$ (τ phase): O-stabilized Intermetallic compound



Previous reports on hydrogenation of τ phase

Journal of the Less-Common Metals, 104 (1984) 51 - 63

ON THE CHANGE IN PHYSICAL PROPERTIES OF $Ti_{4-x}Fe_{2+x}O_y$ DURING HYDROGENATION
I: ACTIVATION BEHAVIOUR OF TERNARY OXIDES $Ti_{4-x}Fe_{2+x}O_y$ AND β-Ti*

BERNHARD RUPP
Institut für Physikalische Chemie a
Vienna (Austria)

(Received March 15, 1984)

Fig. 2. Partial isothermal section of the Ti–Fe–O phase diagram at 1273 K.

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 48 (2023) 32011–32024

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The mechanistic role of $Ti_4Fe_2O_{1-x}$ phases in the activation of TiFe alloys for hydrogen storage

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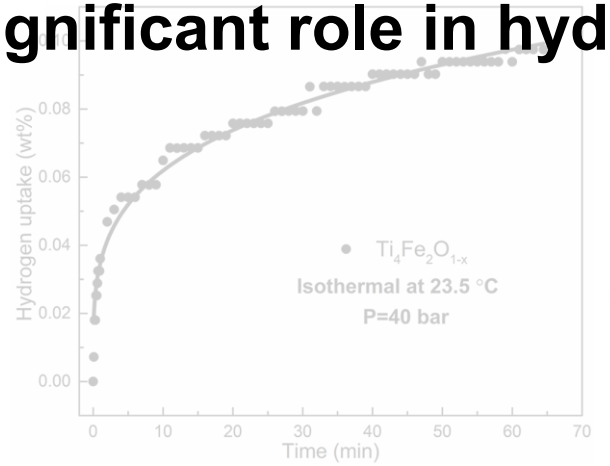
How oxygen content in TiFe alloys affects their hydrogenation behavior?

Does τ-phase actually plays a significant role in hydrogenation?

Hydrogenation behaviour of bulk multiphase alloys

Hydrogenation conditions	*"Ti_2Fe"*[a]	*"$Ti_2FeO_{0.11}$"*[b]	*$Ti_2FeO_{0.2}$*[c]
0.09 MPa, 373 K	—	—	Hydride (1.3 wt.% H)
0.09 MPa, 473 K	—	Weak reaction, TiH_x, $Ti_{4-x}Fe_{2+x}O_y$ hydride	Violent reaction
0.09 MPa, 673 K	Very weak reaction	Good reaction, TiH_x, $Ti_{4-x}Fe_{2+x}O_y$ hydride	Violent reaction
4 MPa, 293 K	—	Violent reaction, TiH_x, $Ti_{4-x}Fe_{2+x}O_y$ hydride	Violent reaction, hydride (1.64 wt.% H)

Low oxygen content in τ phase would be beneficial for hydrogenation



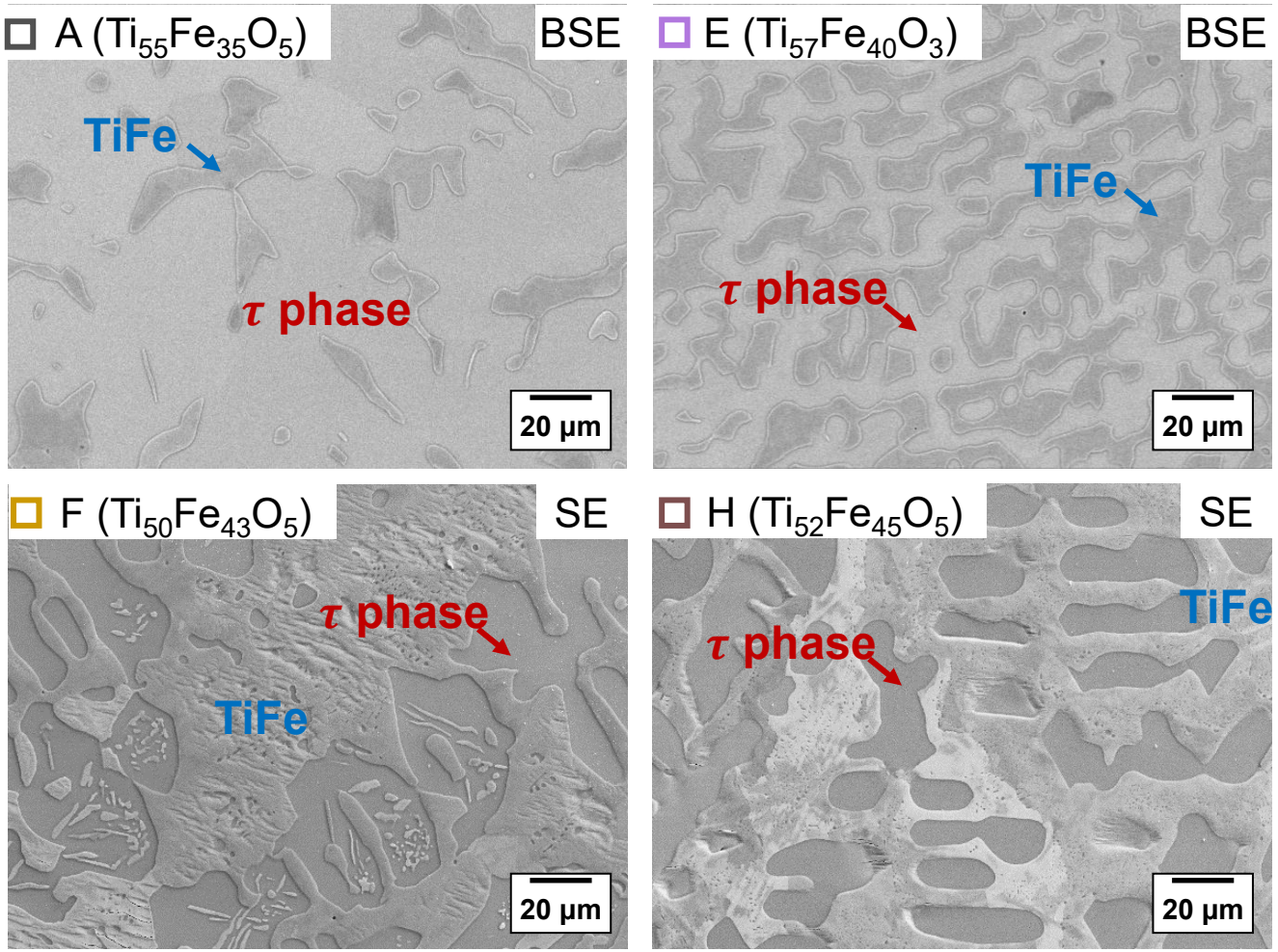
But in some conditions, the τ phase hydrogenated quite slow and even does not absorbs H much (~0.1 wt.% level).

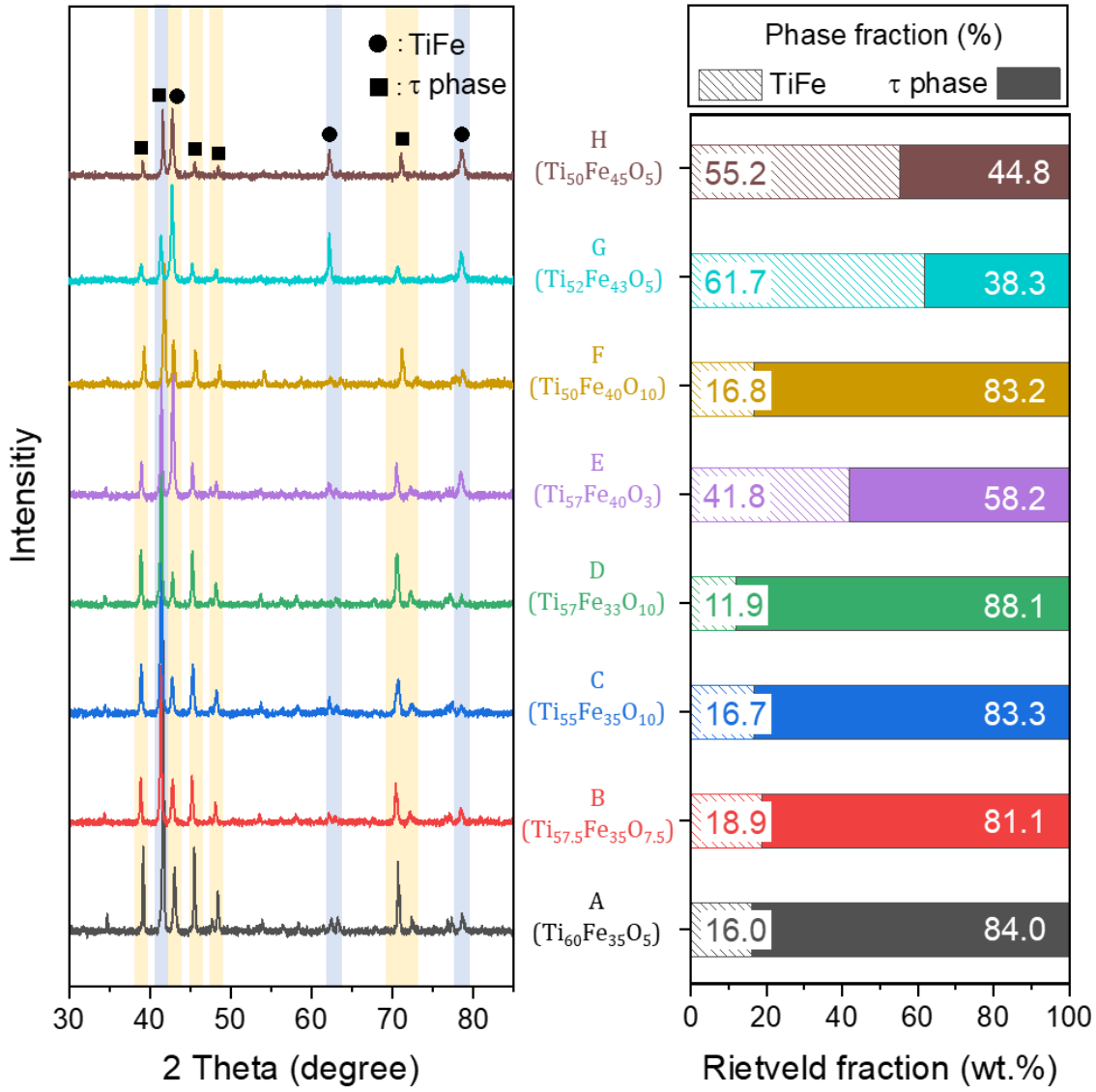
(1) $TiFe_{0.9}$ and $TiFe_{0.95}$ can be activated at room temperature, and their hydrogen sorption kinetics can be improved within a few hydrogenation cycles.
(2) The activation of $TiFe_x$ alloys with higher Ti/Fe ratios at room temperature is attributed to the presence of $Ti_4Fe_2O_{1-x}$, which can absorb hydrogen, crack, and create a path for the hydrogenation of TiFe.
(3) The activation of $TiFe_x$ alloys can be adjusted by controlling the Ti/Fe ratios. Higher Ti/Fe ratios lead to an increase in the amount of the $Ti_4Fe_2O_{1-x}$ phase.

*The alloys in both reports (and also in most of other reports) have a significant amount of bcc-β phase too.

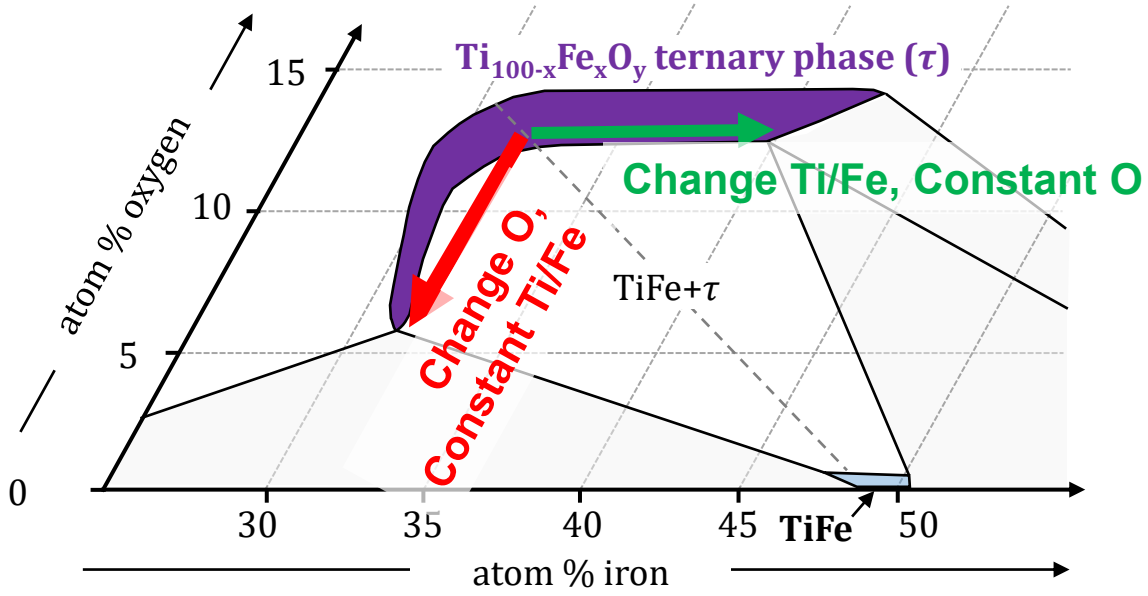
B2 + τ dual-phase microstructure (without bcc-β phase)

Arc-melted from high-purity Ti+Fe+TiO_2, annealed at 1273 K for 72 h



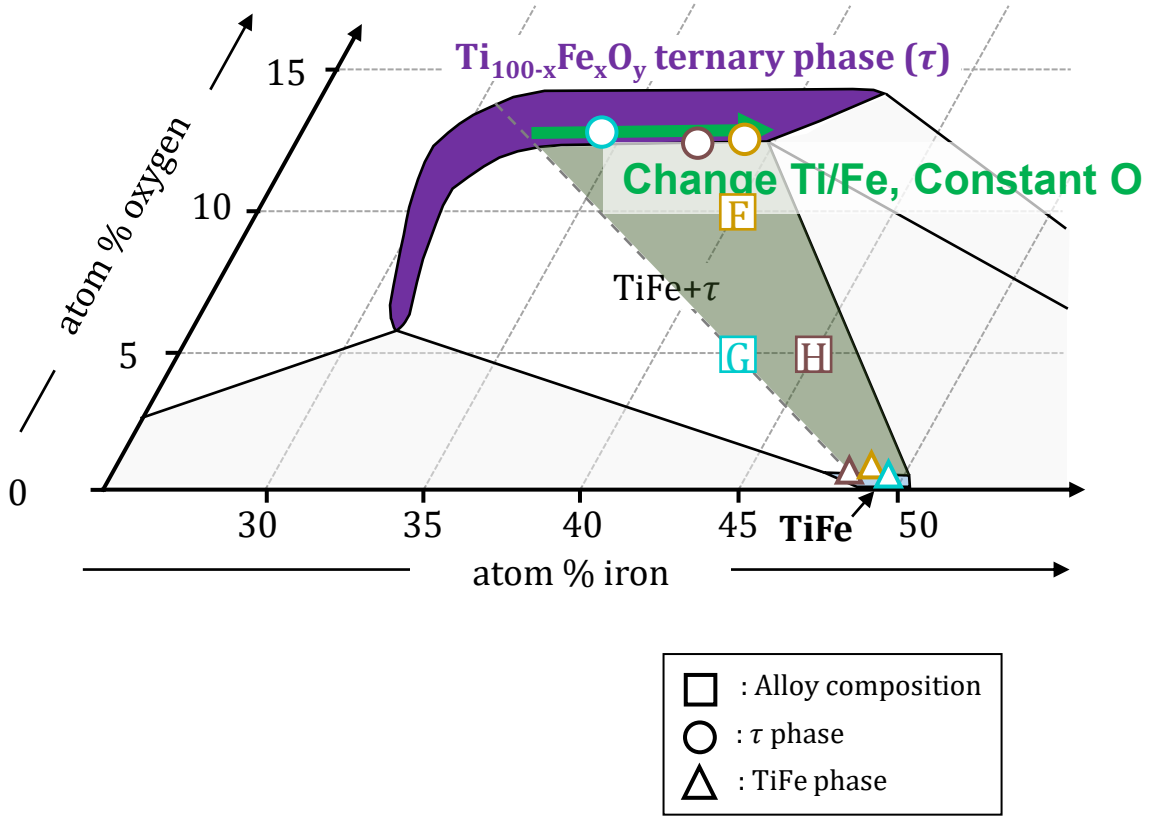


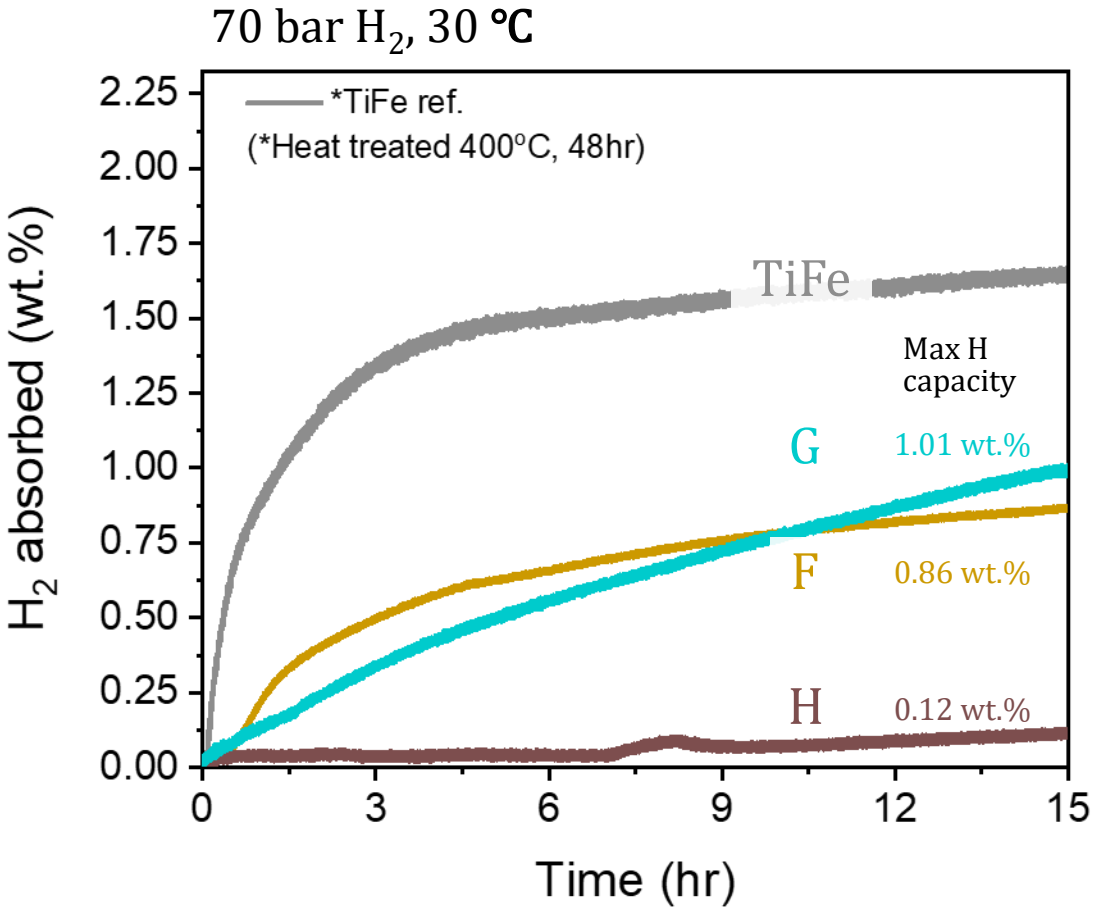
1st H-absorption behavior vs. τ phase chemistry



□ : Alloy composition
○ : τ phase
△ : TiFe phase

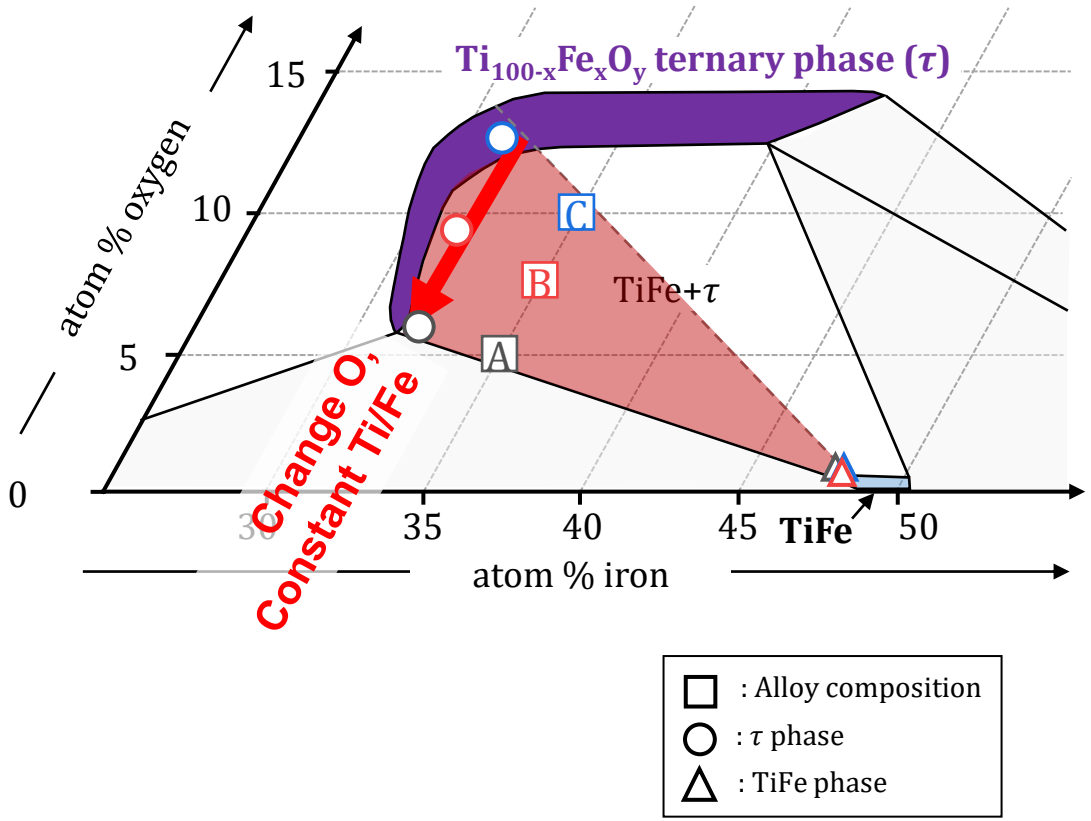
1st H-absorption behavior vs. τ phase chemistry

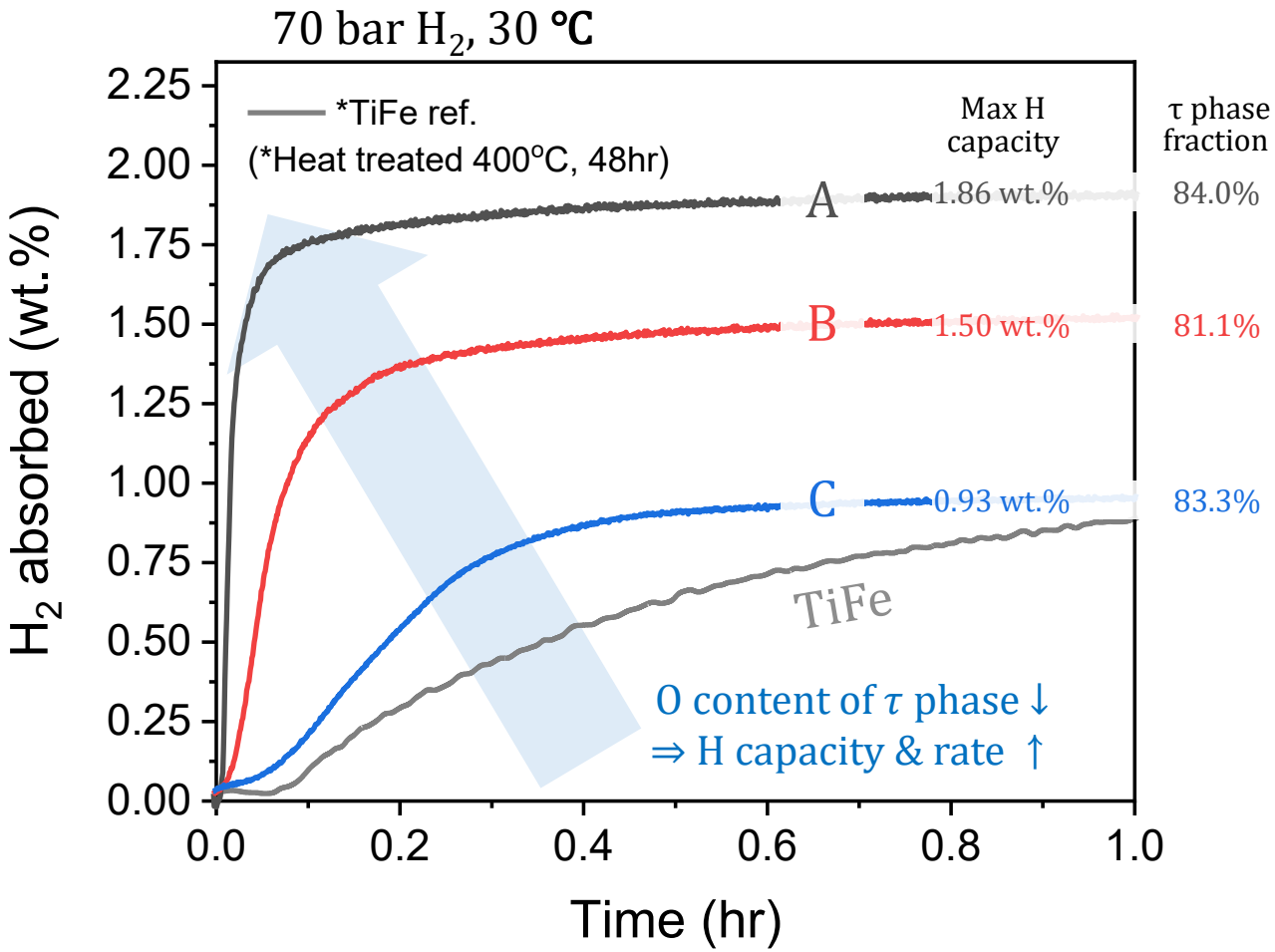




Increasing Fe is not preferable for rapid & high-capacity H storage

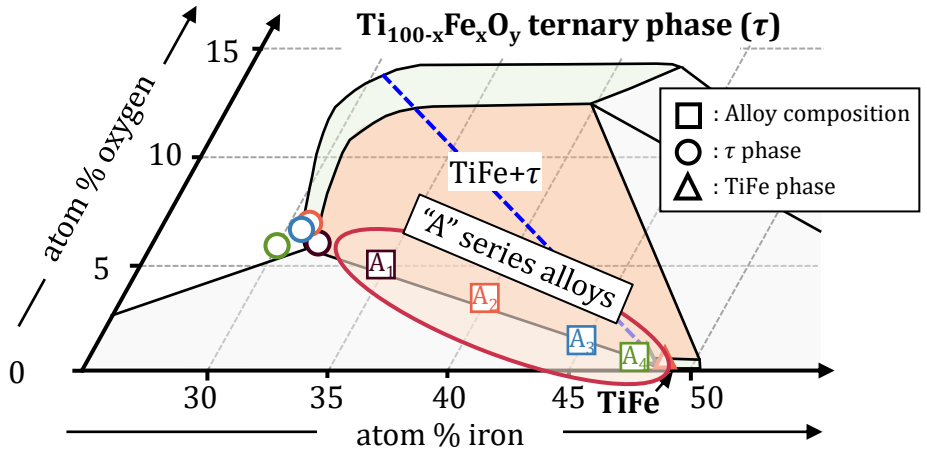
1st H-absorption behavior vs. τ phase chemistry

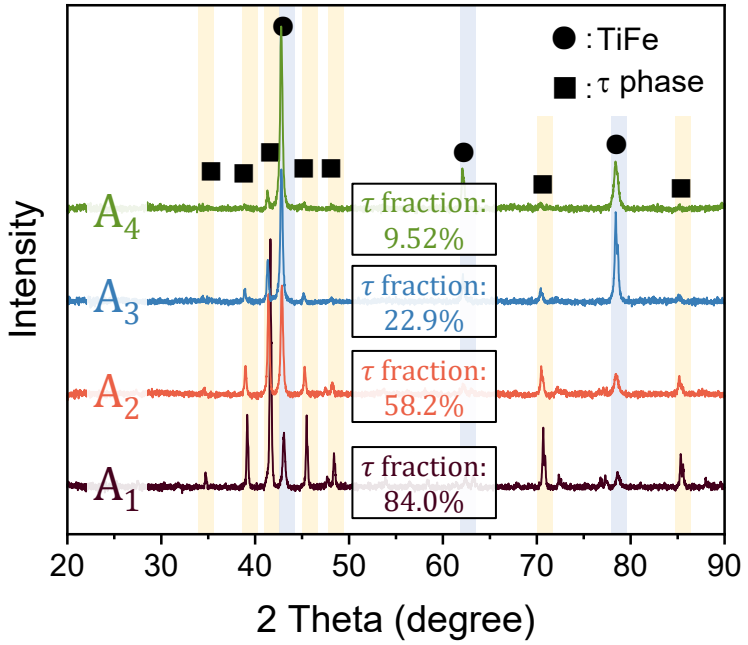


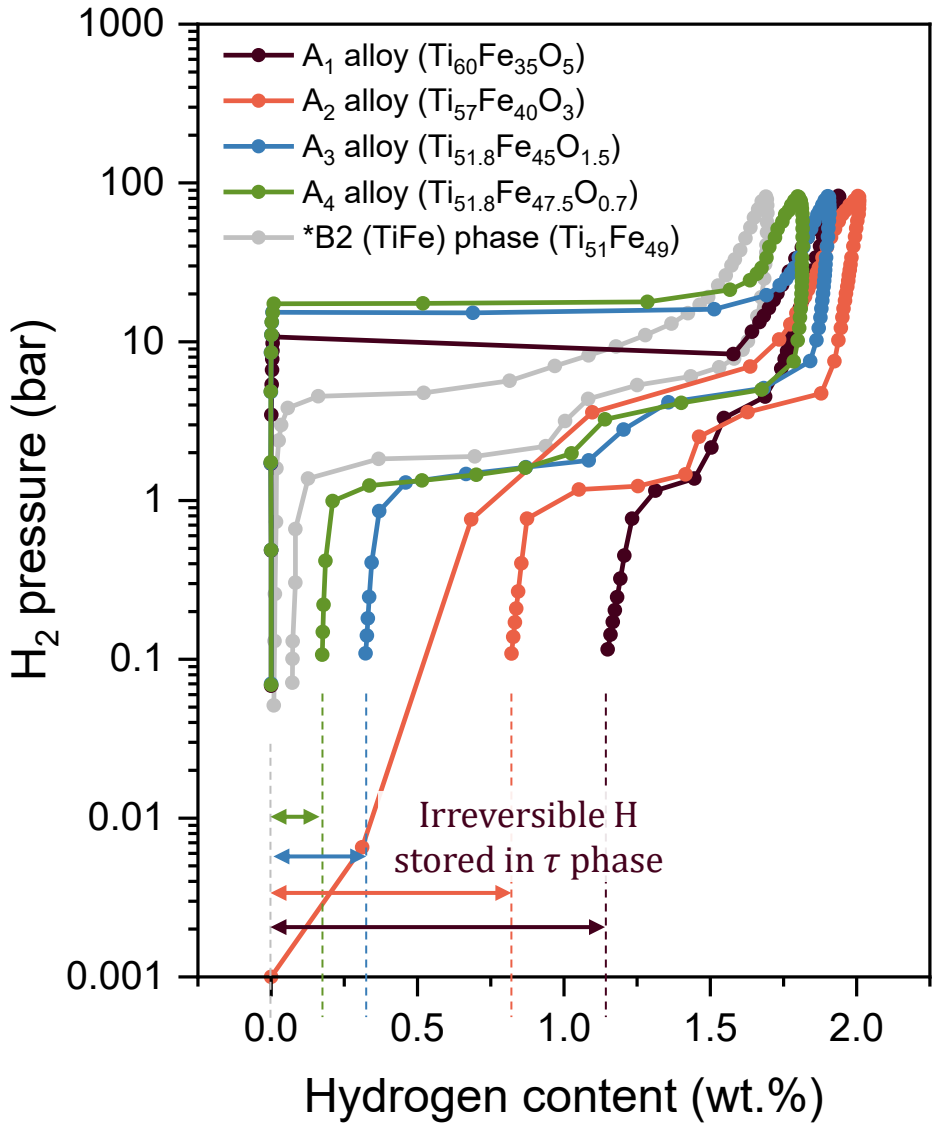


Reducing O, or increasing O vacancies is preferable for rapid & high-capacity H storage

Optimizing reversible H-capacity in B2 + τ alloys

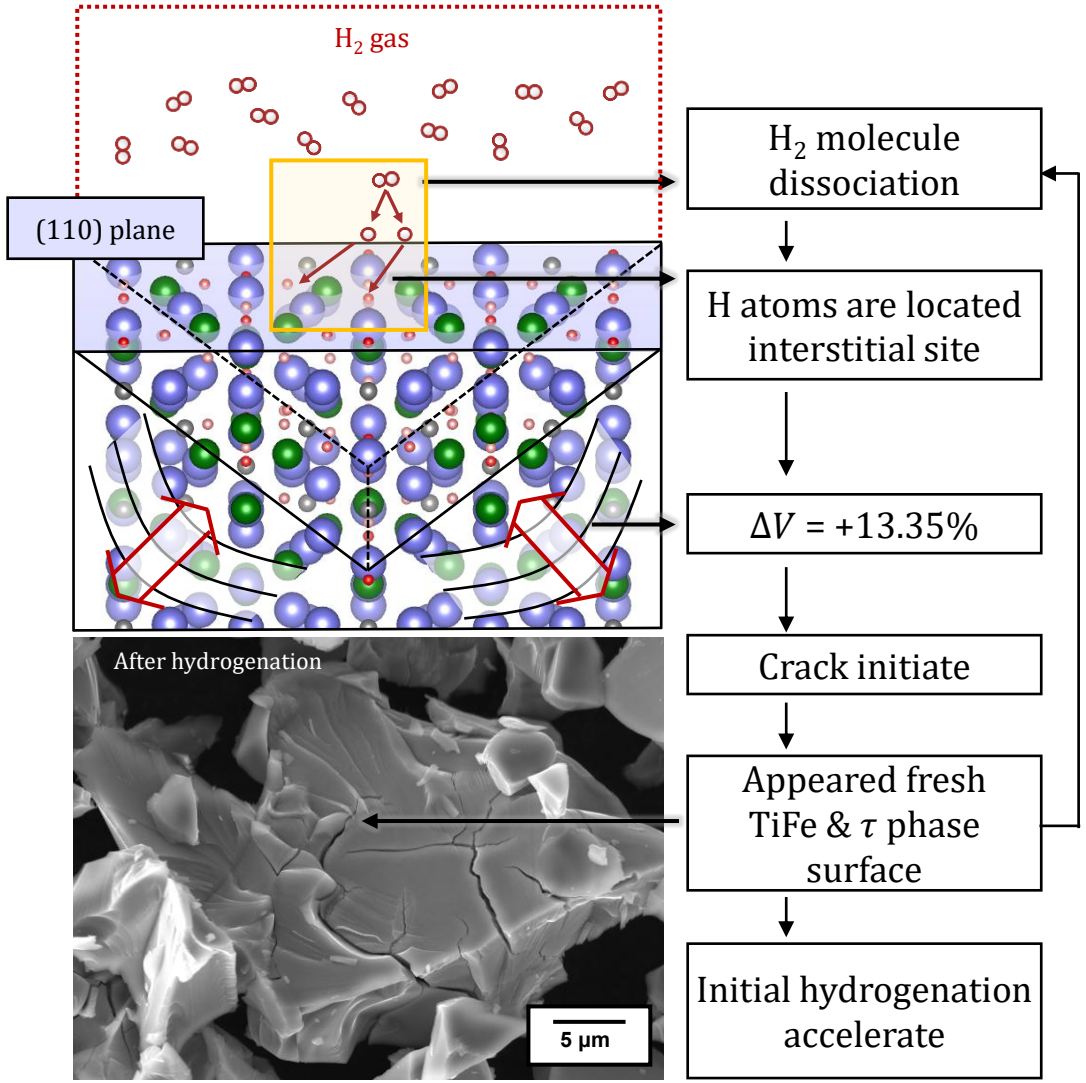






A_1-A_4 alloys were tested without additional activation process,
*while $Ti_{51}Fe_{49}$ was pre-activated at 400°C, 48h before the measurement .

τ phase-induced easy hydrogenation of TiFe alloys



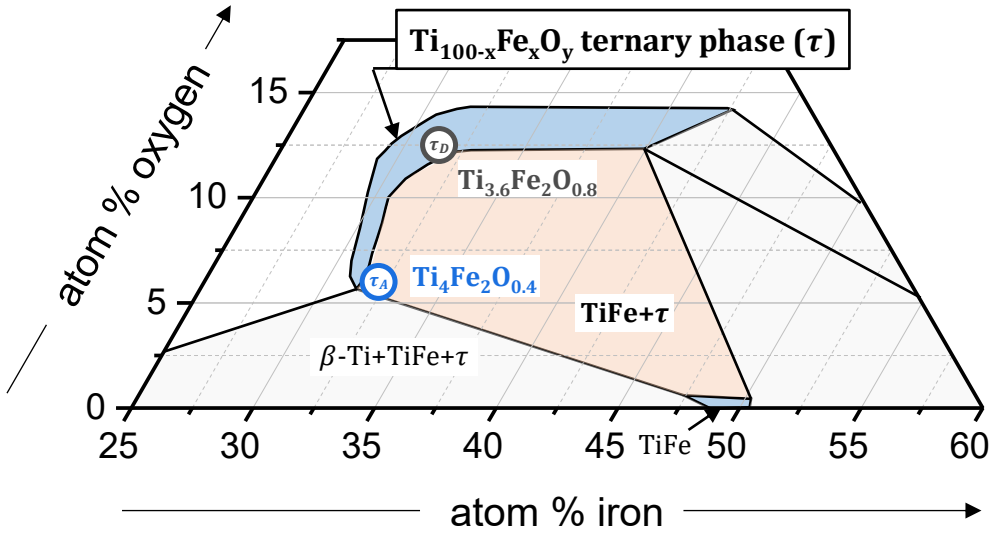
(1) Preferential hydrogenation & V-expansion of τ phase

(2) Cracking of TiFe to accommodation the V-expansion

(3) Hydrogen ingress to TiFe via fresh surfaces in cracks

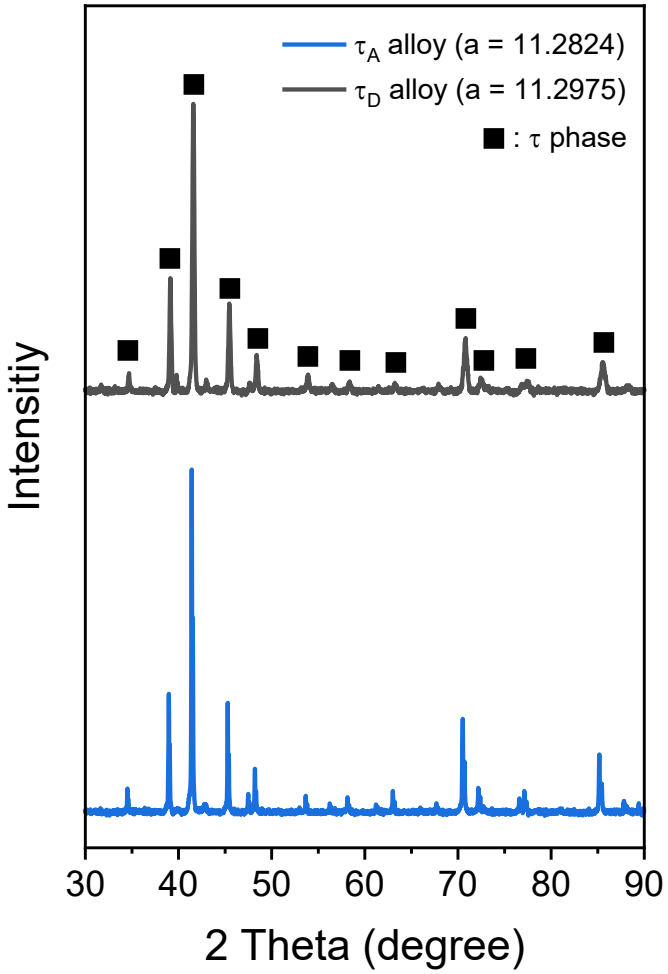
How τ phase can readily hydrogenated in terms of its structure?

Single τ-phase alloys with different O contents: τ_A and τ_D

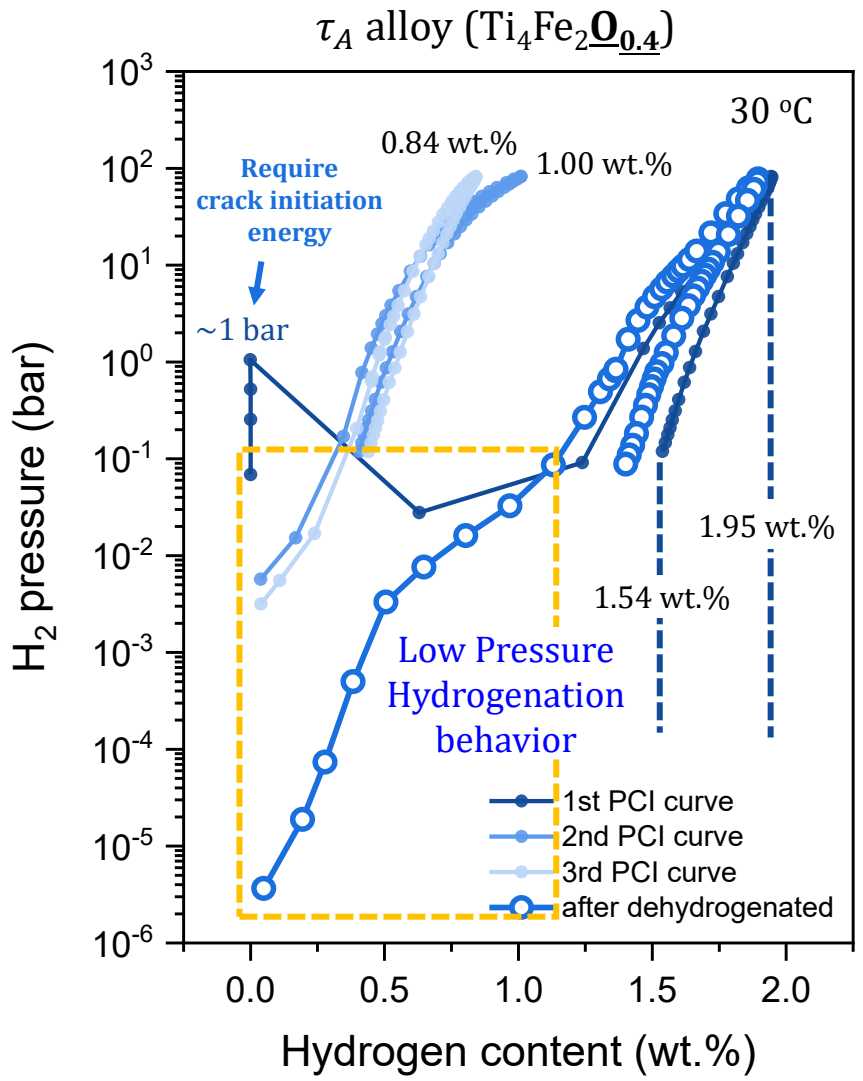


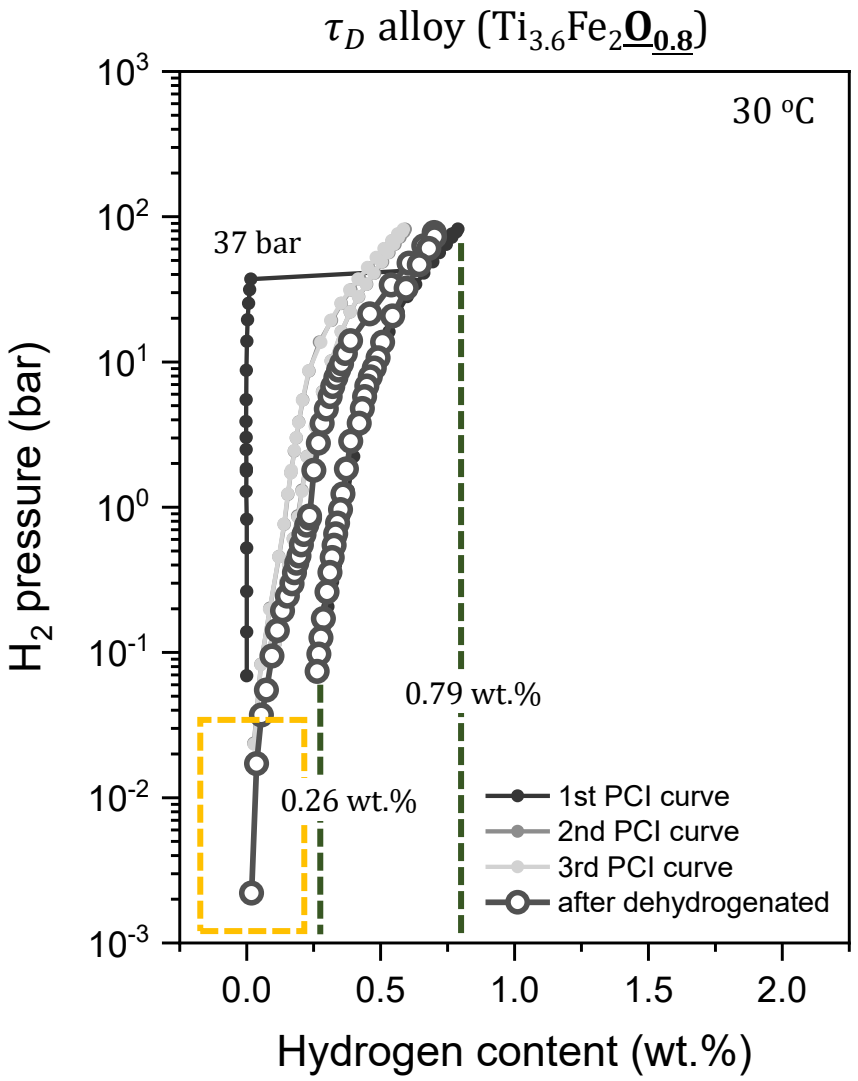
Alloys	Target chemical composition (at.%)			
	Ti : Fe : O ratio	Ti	Fe	O
τ_A	4 : 2 : **0.4**	61.6	31.1	6.3
τ_D	3.6 : 2 : **0.8**	55.9	31.3	12.8

*1,000°C, 72hr heat treatment after arc-melting



Hydrogenation behavior of τ single phase alloys

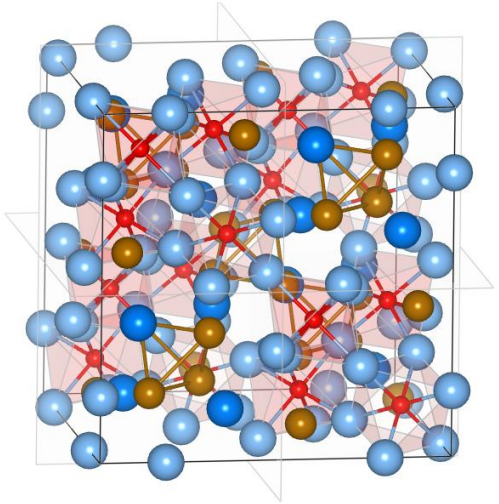




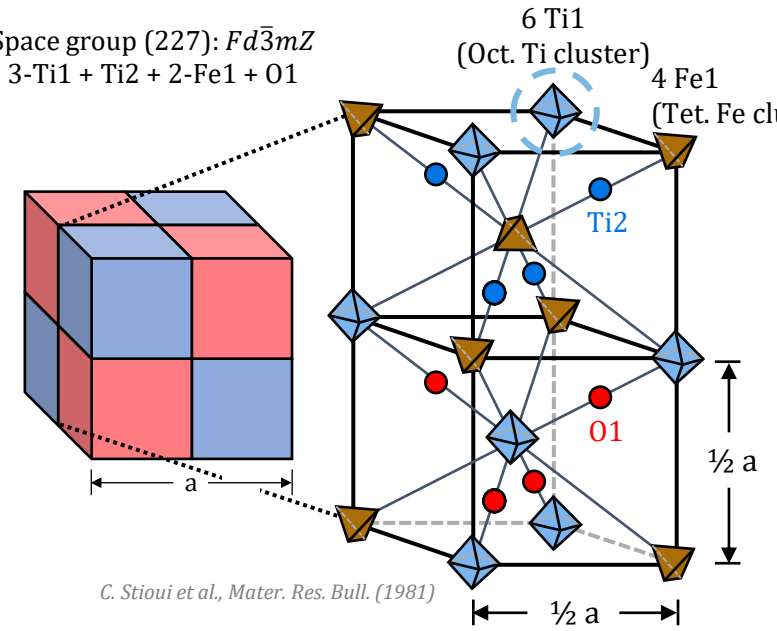
Hydrogenation of τ_A phase with a low oxygen content starts at extremely low H_2 pressure level.

H-Interstitials in τ phase with O vacancy

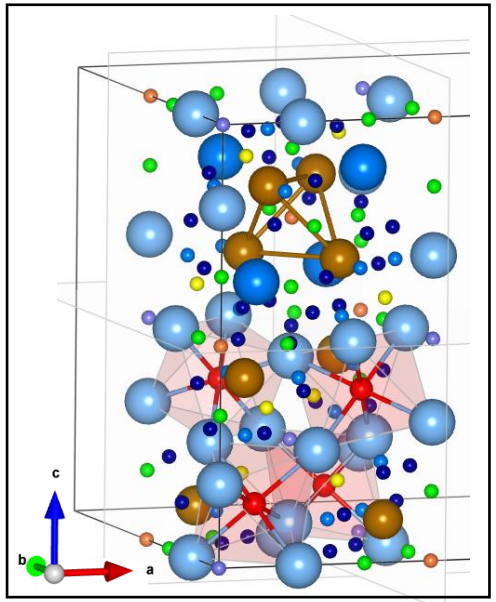
- **The τ phase structure**



Space group (227): $Fd\bar{3}mZ$
3-Ti1 + Ti2 + 2-Fe1 + O1

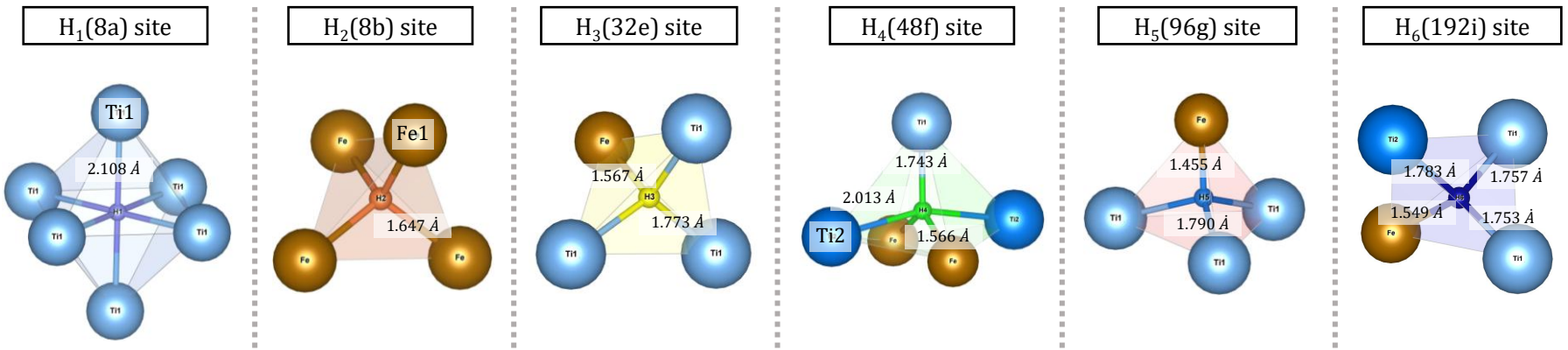


C. Stioui et al., Mater. Res. Bull. (1981)



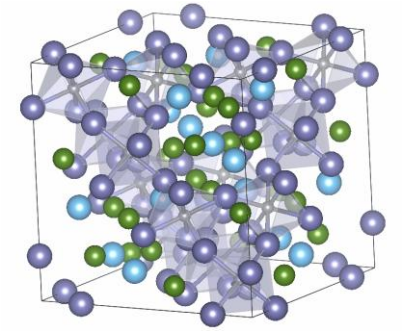
T. J. Ha et. al., J. Alloys Compd., 891 (2022)

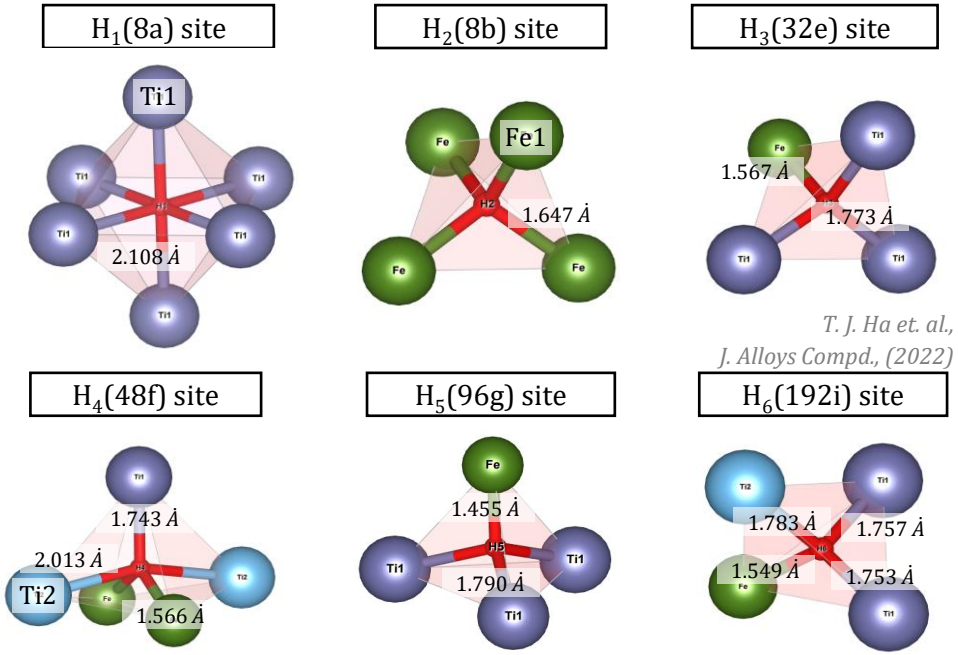
- **Types of H interstitial sites in τ phase**



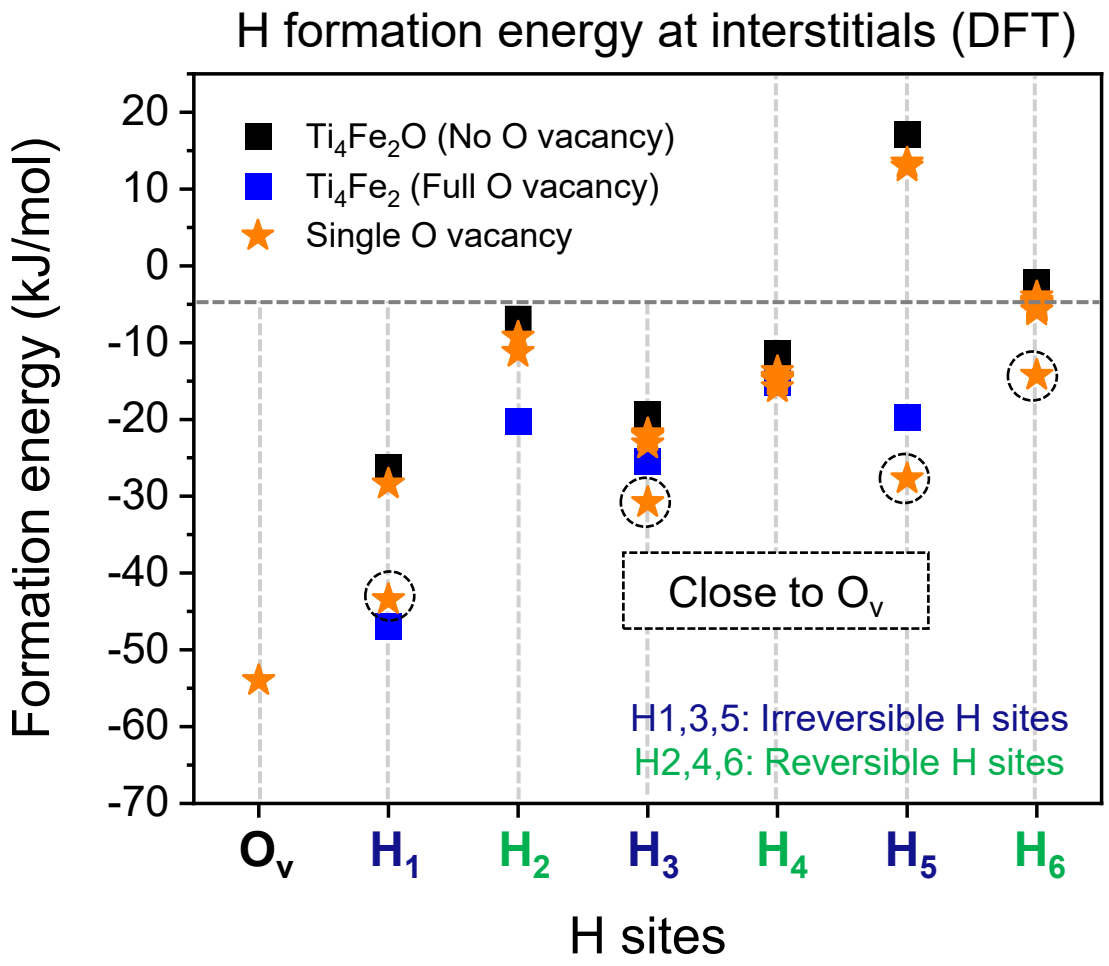
O vacancy effects on H-formation energy at interstitial sites

$Ti_{64}Fe_{32}O_{16}$, Space group: Fd-3m





T. J. Ha et. al., J. Alloys Compd., (2022)

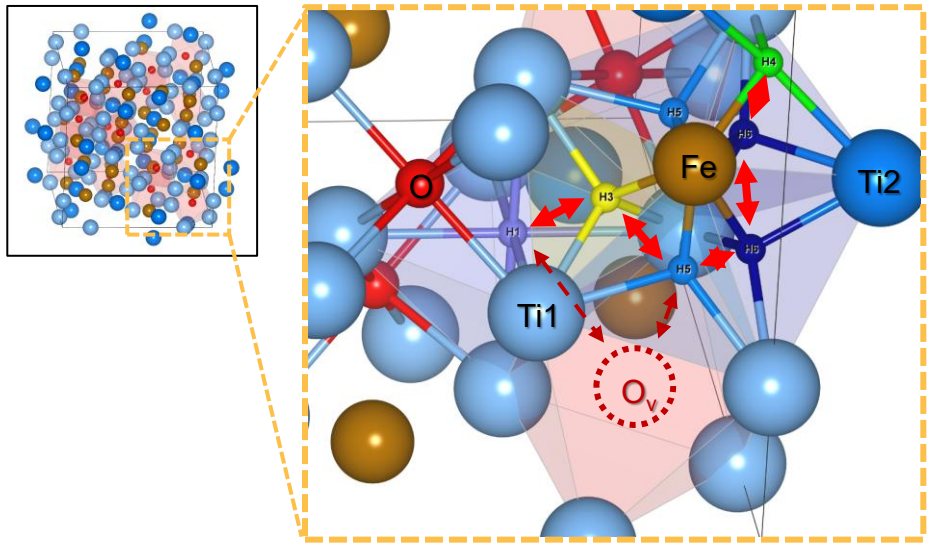


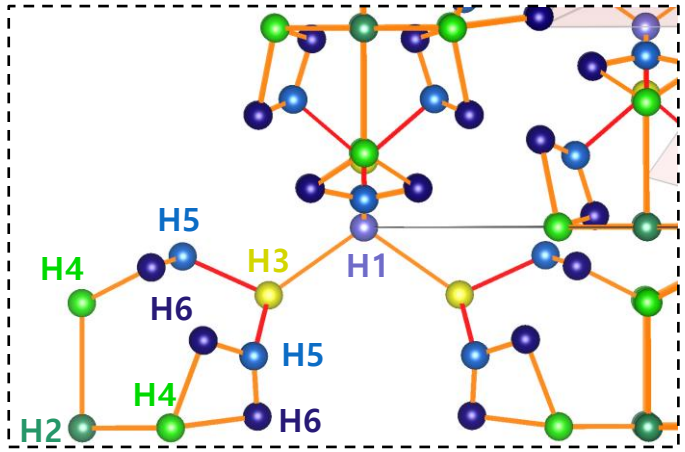
Formation of O_v stabilizes H-interstitial sites
→ Increase of H capacity

H diffusion path in τ phase with O vacancy

- **H diffusion path between interstitials (DFT, NEB)**

τ **phase structure**

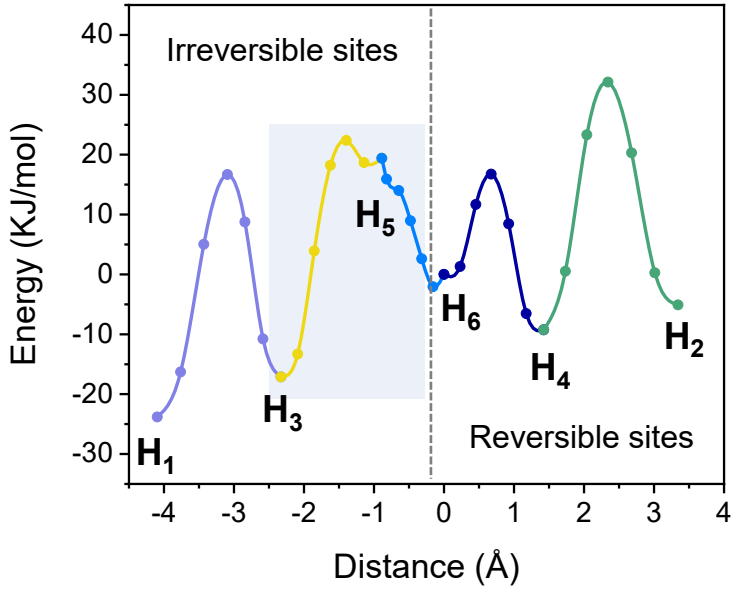




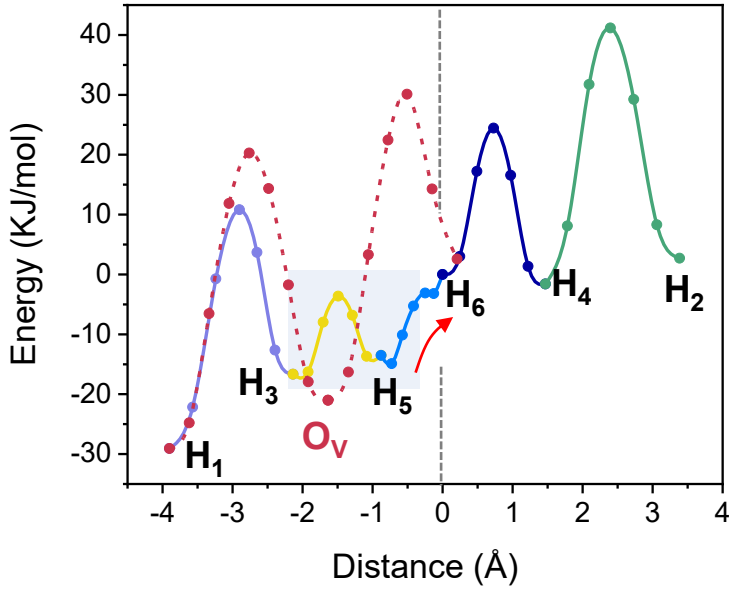
H2→H4→H6
→H5→H3→H1

- **Diffusion barrier energy between the interstitial sites**

without Oxygen vacancy

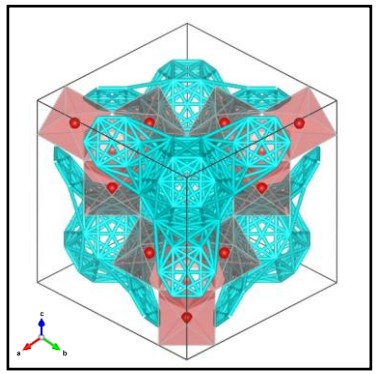


with Oxygen vacancy



O_V opens up H-diffusion network between reversible and irreversible H sites

H6 (192i) network



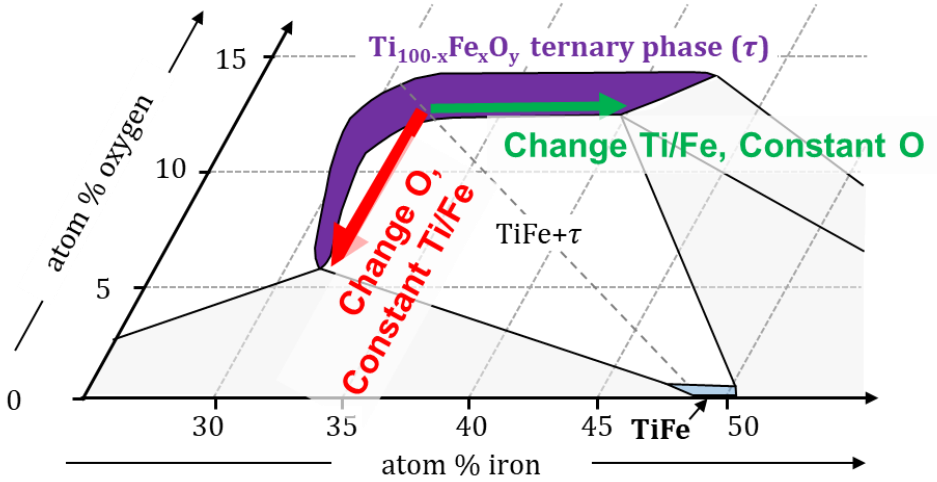
Conclusions: Hydrogenation of $Ti_4Fe_{2+x}O_y$ (τ) phase

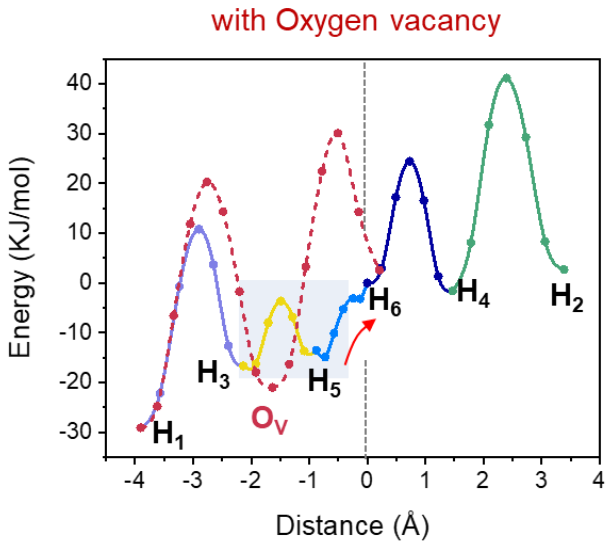
(1) Excess amount of O addition in atomic percent scale leads to formation of $Ti_4Fe_{2+x}O_y$ (τ) phase, of which hydrogenation behavior highly depends on its chemistry.

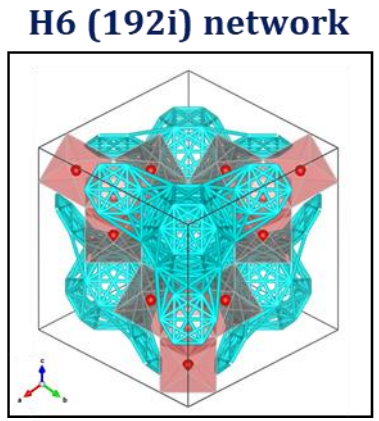
(2) Reducing O content, or formation of oxygen vacancy, in τ phase increases both hydrogenation rate and H-capacity, while the majority of H-capacity in the phase is irreversible at RT.

(3) O vacancies not only stabilizes the H-interstitial sites but also opens up the diffusion path network between reversible and irreversible sites in τ phase , which leads to easy hydrogenation.

(4) Forming dual-phase microstructure of TiFe B2 and τ phases enables hydrogenation of the alloys without additional activation processes, and also decreases plateau pressure of B2 phase.







Thank you for your attention

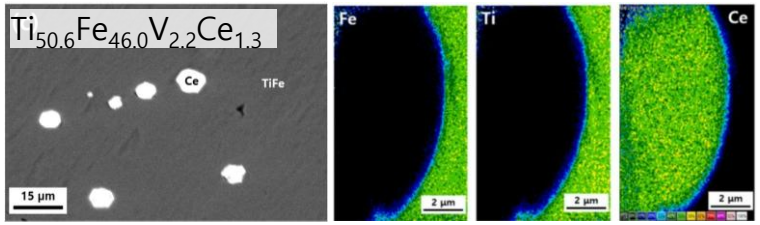
한국과학기술연구원
Korea Institute of Science and Technology

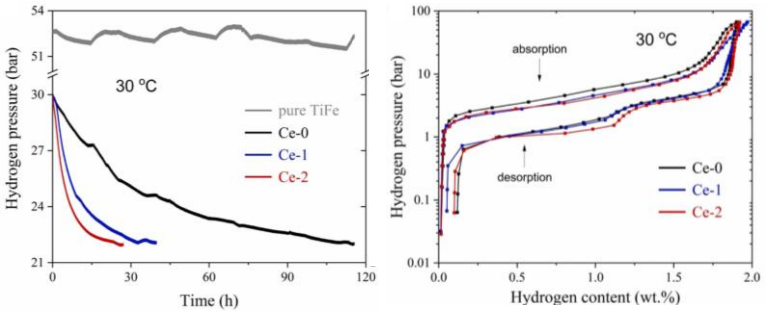
Alloy design for easy activation of TiFe

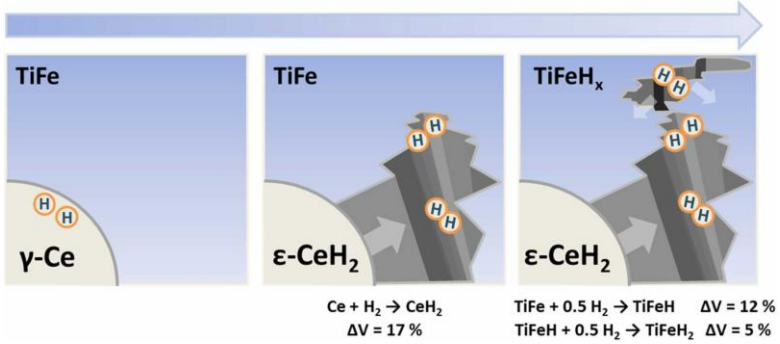
AB-M type (M = metal)

Ti-Fe-V-Ce

Ha et al., Nano Energy (2023).



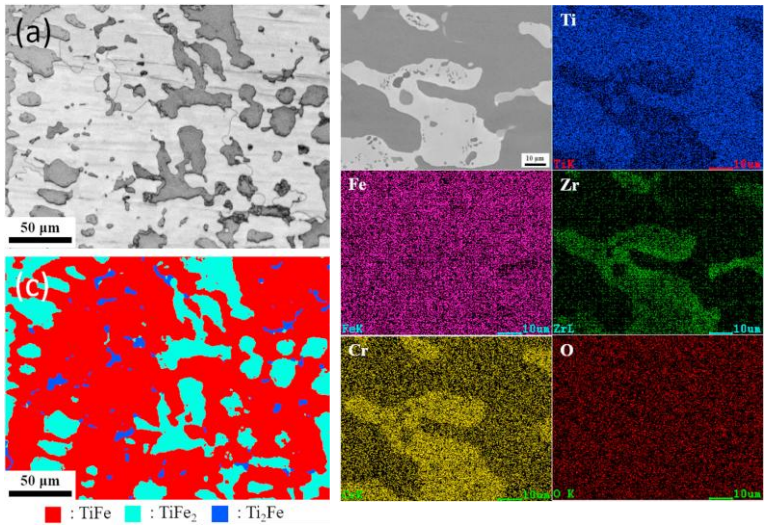


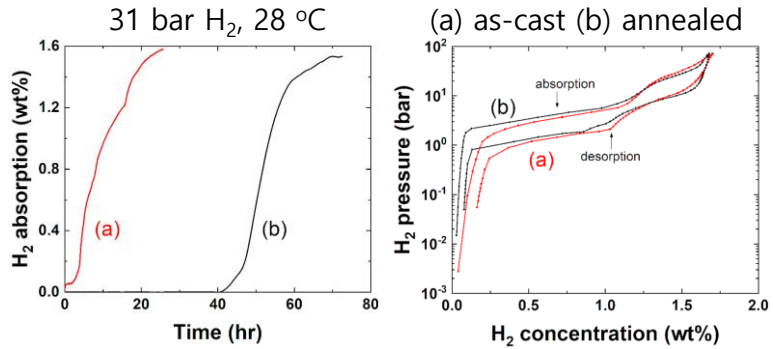


AB+AB_2 type

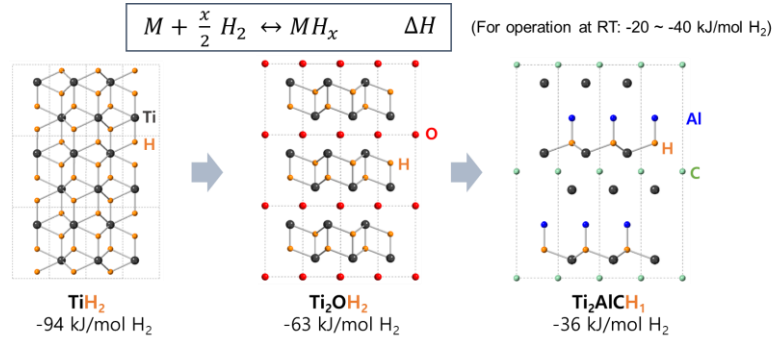
$TiFe+ZrCr_2$

Ha et al., J. Alloys Compd. (2021).



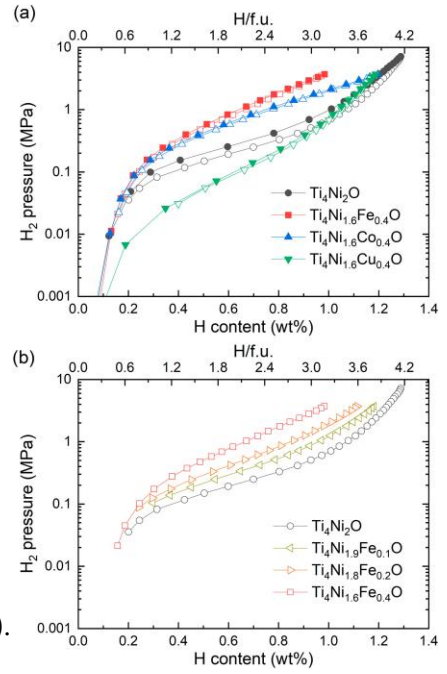


Ti-M-X type (X= C,O,N,..)



H-storage ?

Ti_4Fe_2O
Ti_3AlC_2
Ti_2AlN
Ti_5Si_3
…

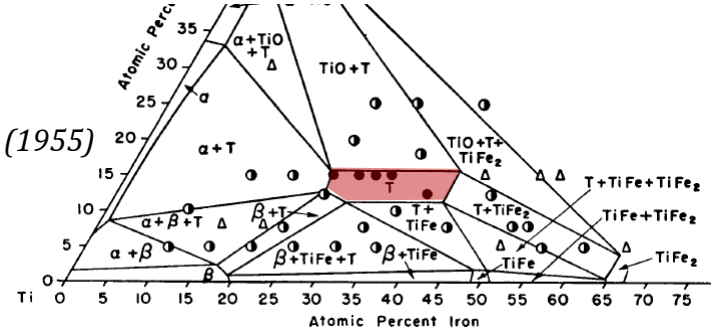


Ha et al., J. Alloys Compd. (2022).

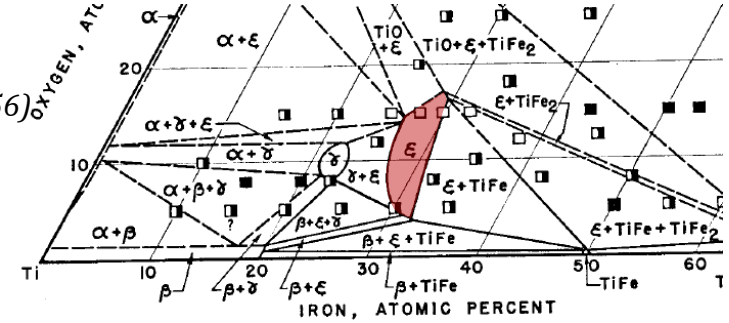
Ti-Fe-O ternary phase diagram?

Reported Ti-Fe-O
ternary phase diagrams for 1000 °C

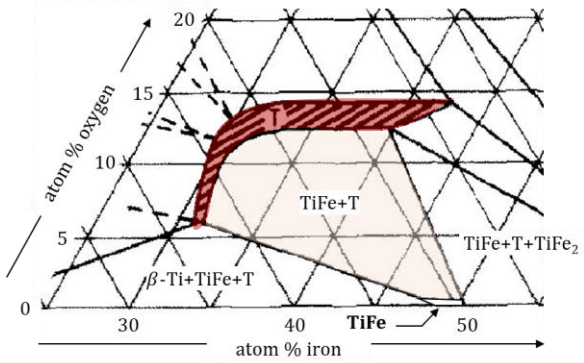
W. Rostoker (1955)



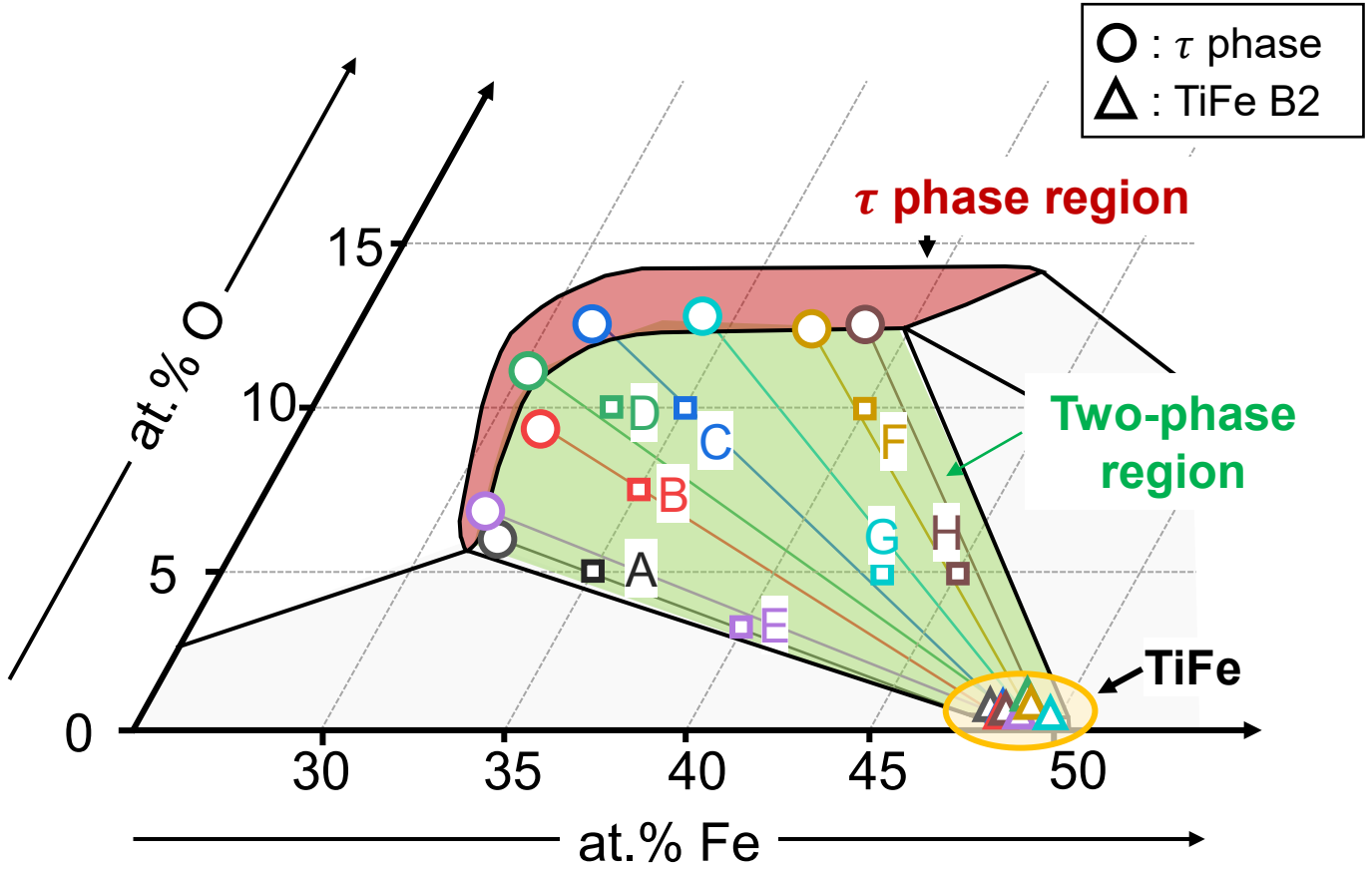
E. Ence (1956)



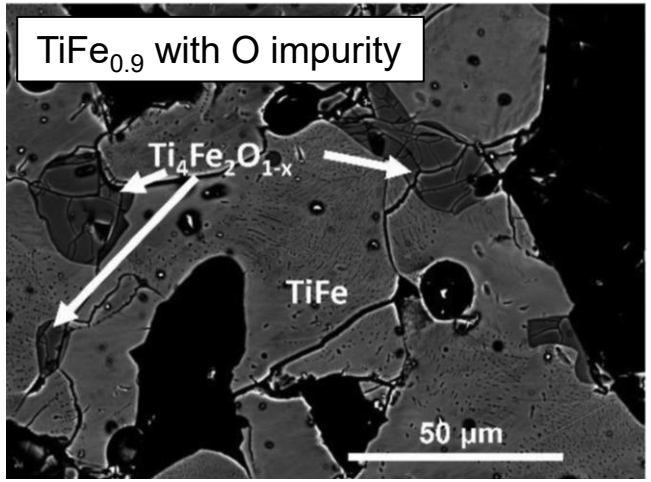
B. Rupp (1984)



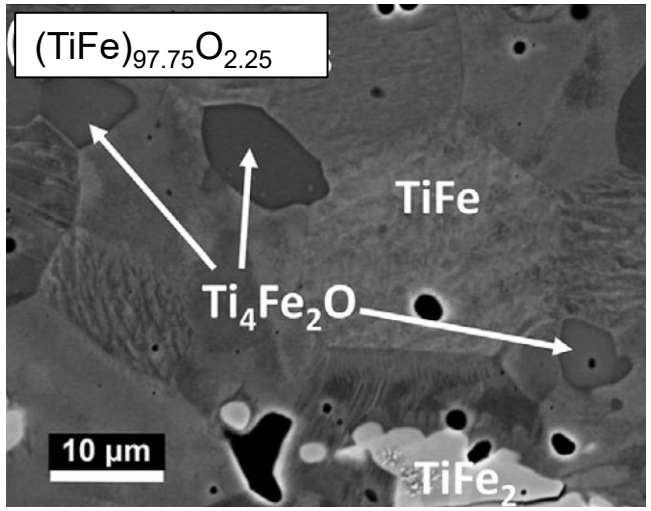
Verified τ & two-phase region (B2 + τ)
using XRD(phase fraction), EDS & AES(composition)



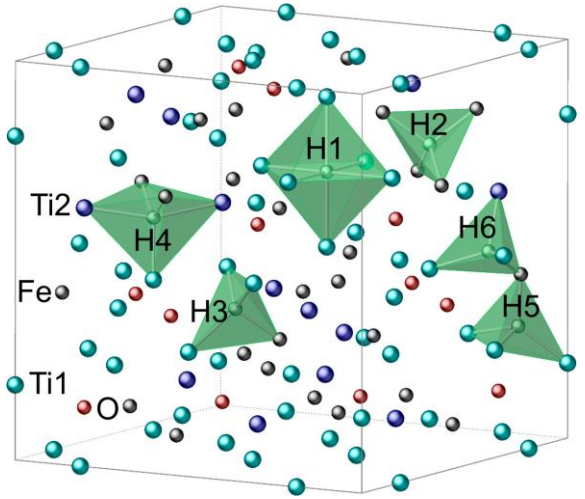
$Ti_4Fe_2O_x$ ternary phase (τ phase) in TiFe-based alloys



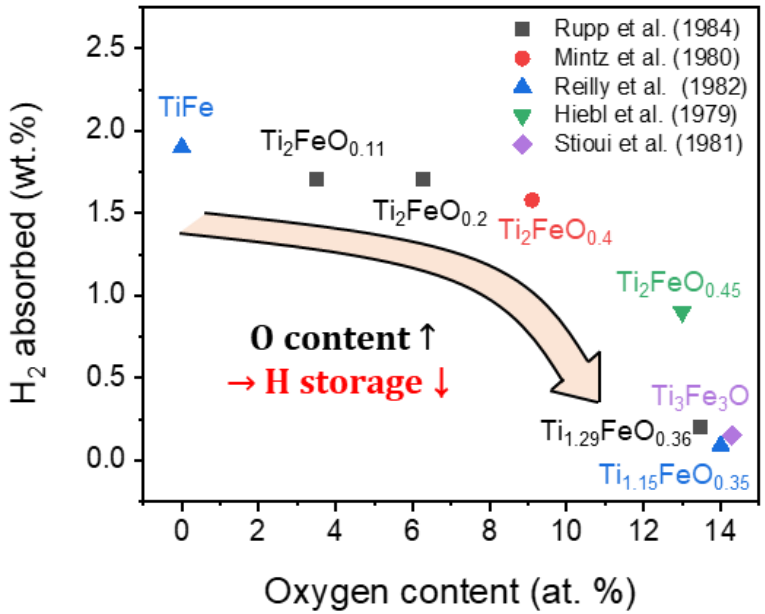
Liu et al, Int. J. Hydrogen Energy (2023).



Liu et al, Int. J. Hydrogen Energy (2023).



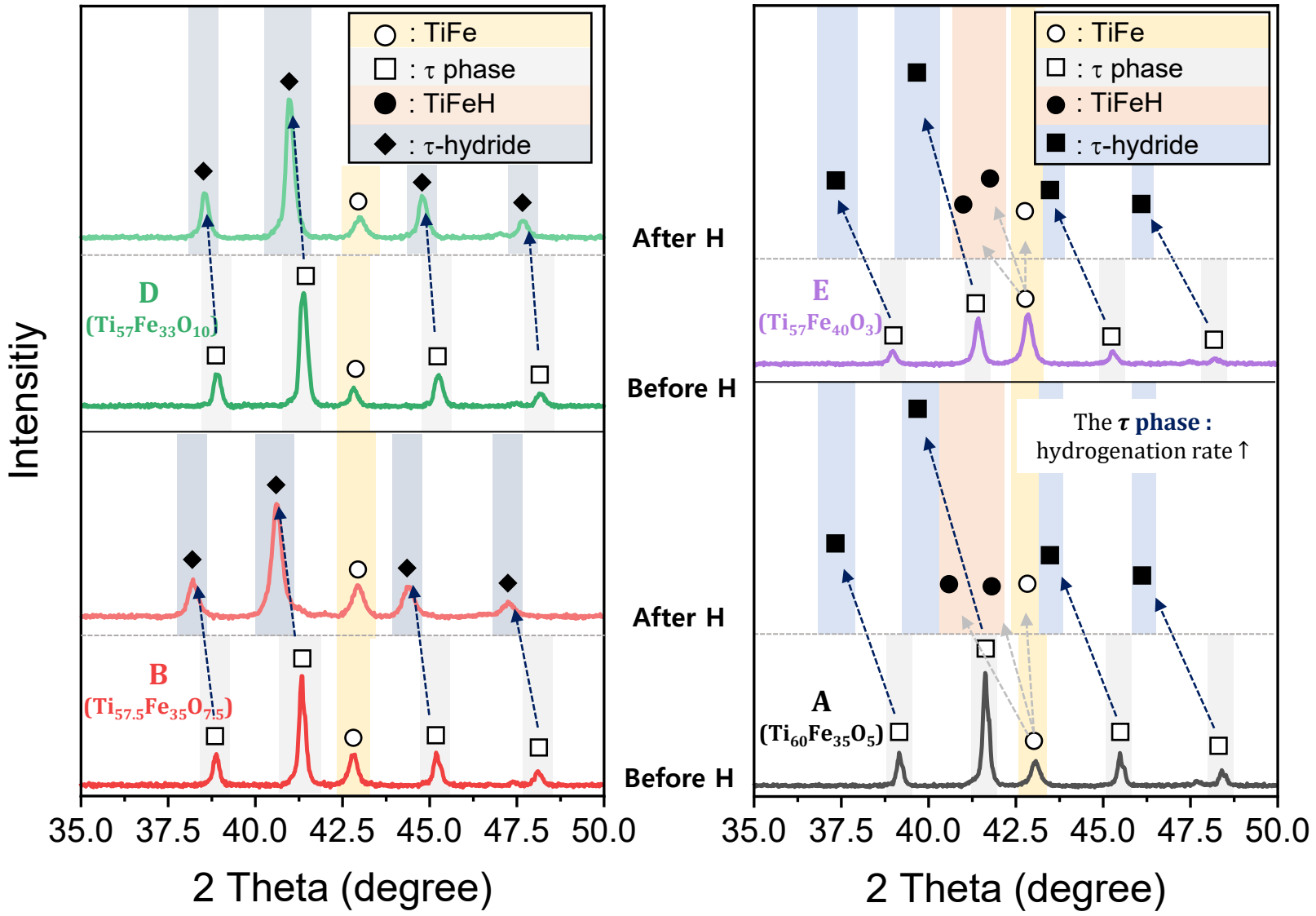
$Ti_4Fe_2O_x$ (τ phase):
Oxygen-stabilized
Intermetallic compound



How oxygen content in TiFe alloys affects their hydrogenation behavior?

Does τ-phase plays a significant role in hydrogenation?

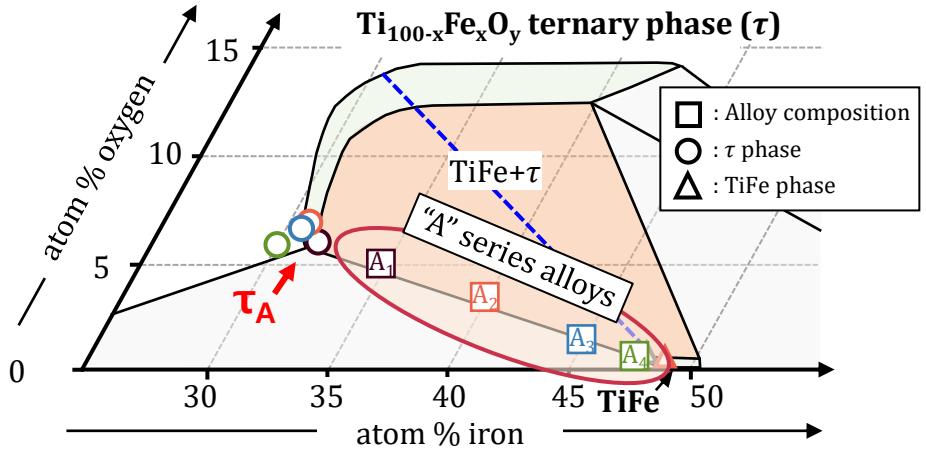
XRD patterns before & after H-absorption

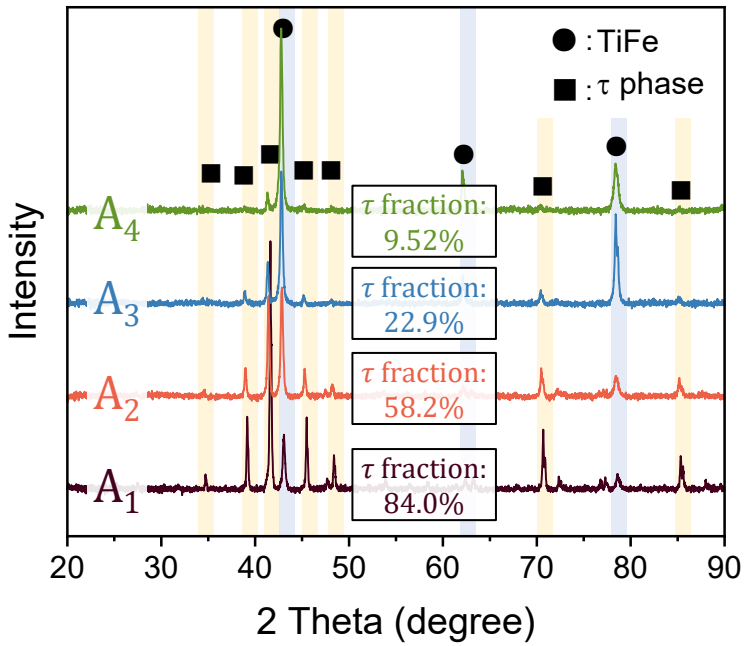


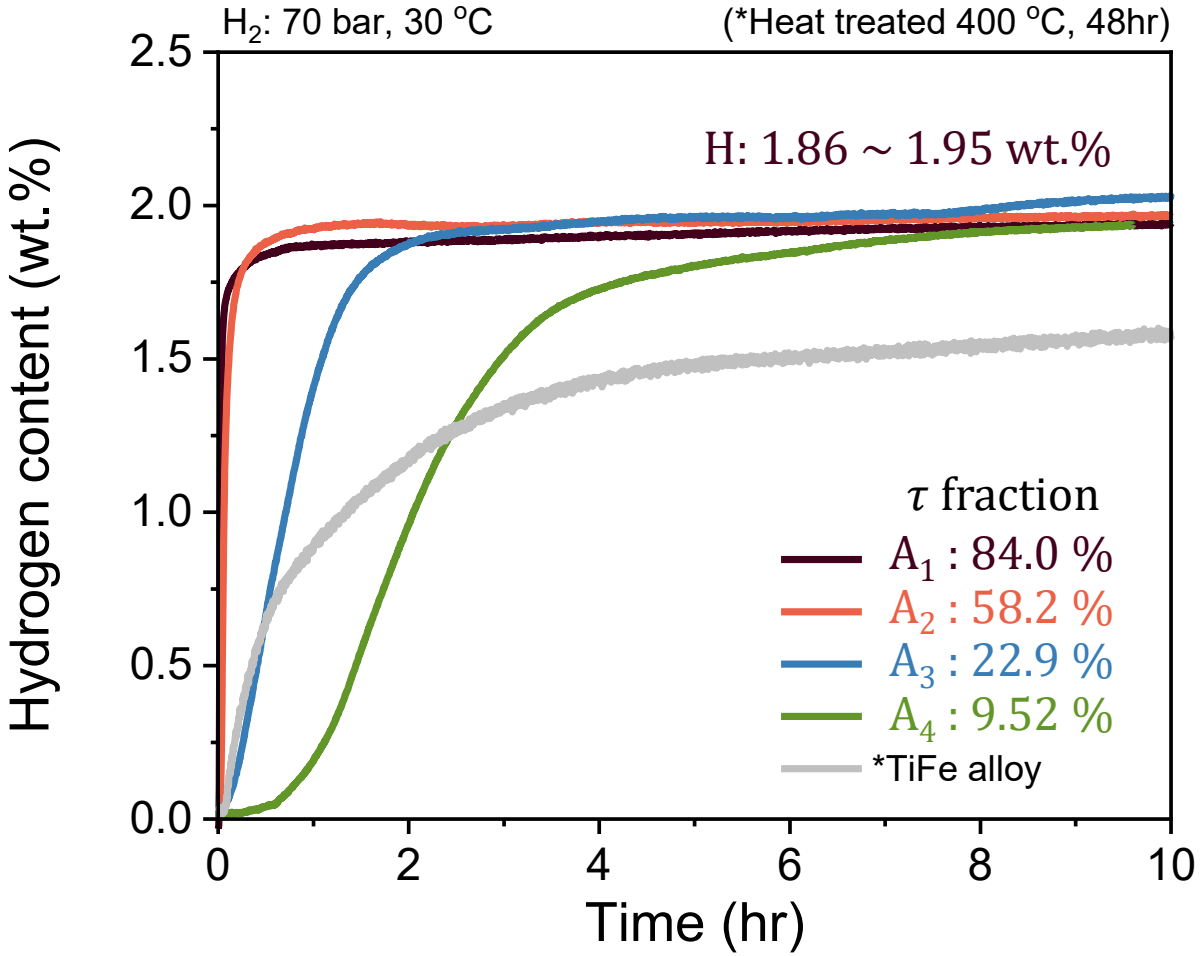
Peak shifts of τ-phase,
no new peaks evolved

→ Hydrogenation of τ-phase does not change its crystal structure.
Hydrogen goes to interstitial sites and accompanies just volume change of unit cell.

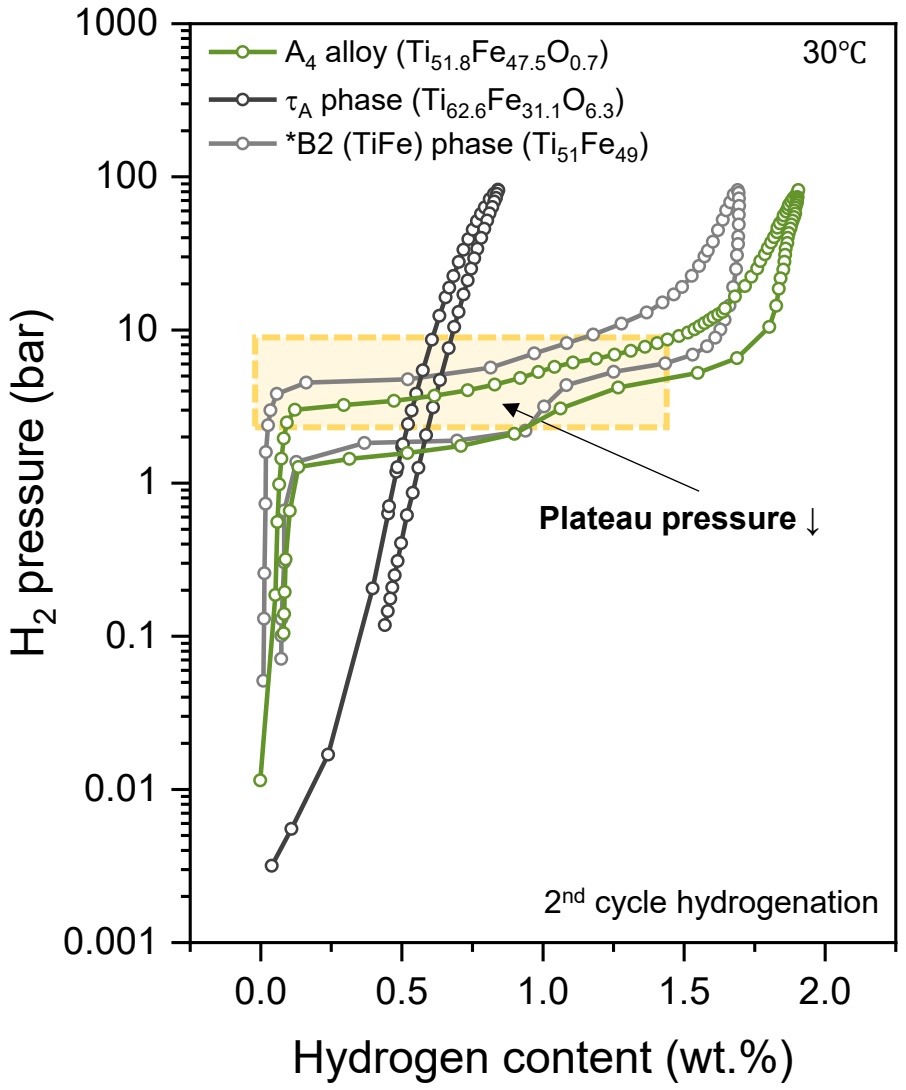
Hydrogenation of dual-phase alloys with τ_A phase

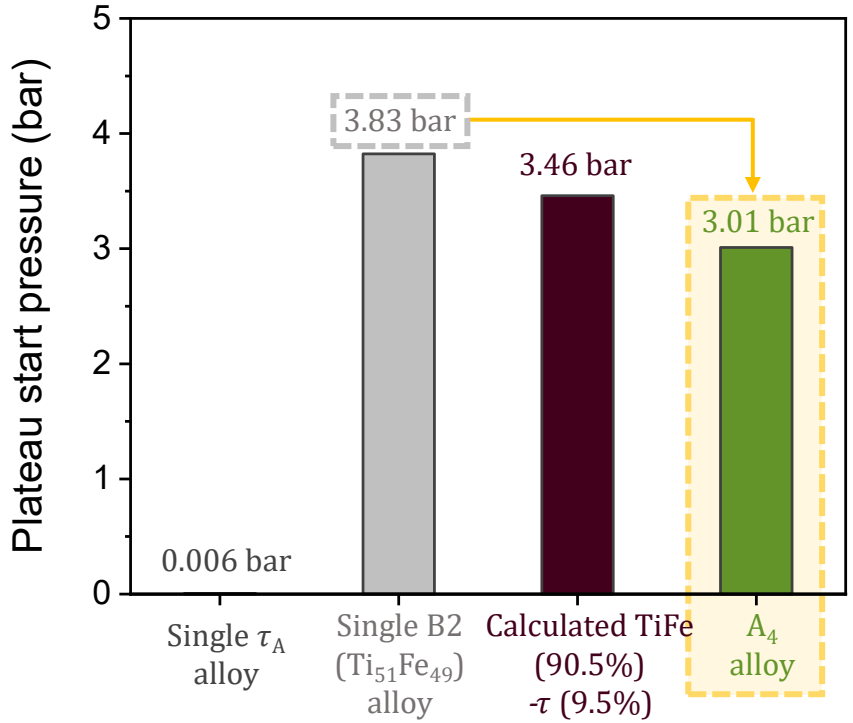






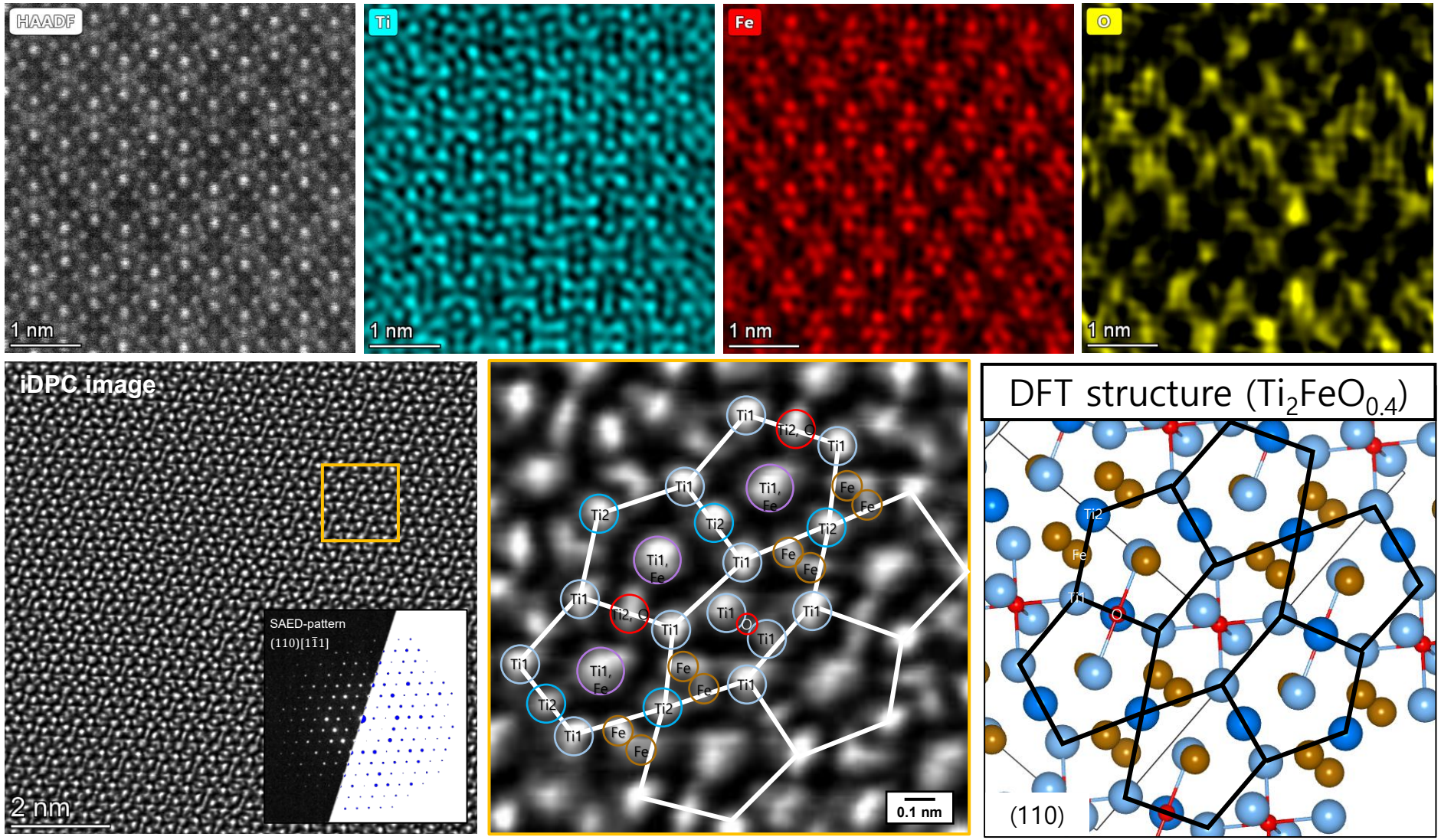
Interface effect between TiFe B2 and τ phases





- B2 + τ dual-phase microstructure lowers plateau pressure of B2 phase compared to the single B2 alloy.
  *Plateau pressure = equilibrium pressure of hydride formation

Atomic arrangement in τ phase confirmed by HRTEM



Hydrogen storage methods

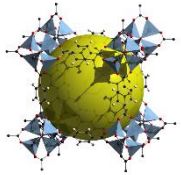
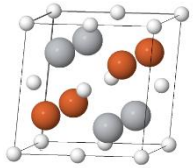
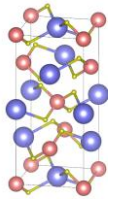
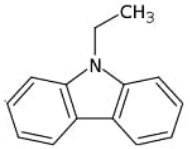
- **Hydrogen**, the greenest energy source

  $(2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + 286\ kJ/mol)$

  Technical challenges :

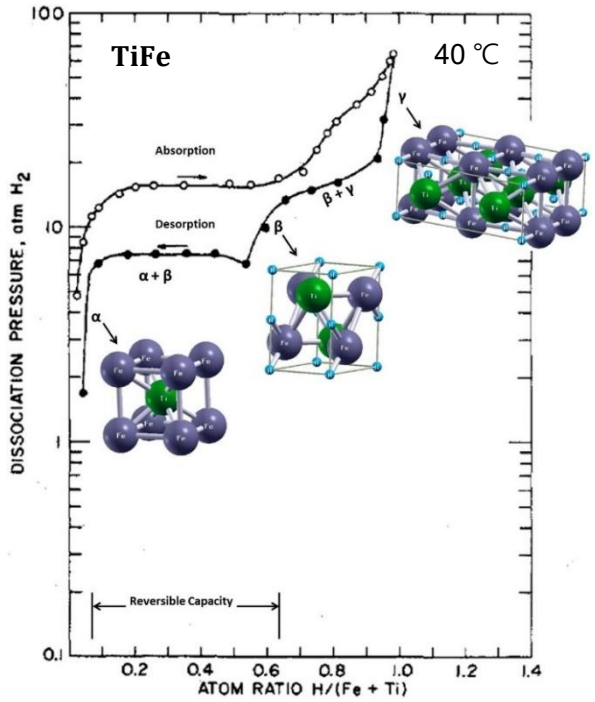
  (i) Packing hydrogen as dense as possible
  (to reach the highest gravimetric/volumetric density)

  (ii) The reversibility of H uptake-release for storage

Liquid hydrogen	**Cryo-adsorption**	**Metal hydride**	**Compressed hydrogen**	**Complex hydride**	**Chemical hydride**
					
Liq. H_2	**Activated carbon**	**TiFe, $LaNi_5$ etc.**	**Gas H_2**	**$NaAlH_4$**	**LOHC**
70 kg H_2/m^3	40 kg H_2/m^3	110 kg H_2/m^3	40 kg H_2/m^3	90 kg H_2/m^3	57 kg H_2/m^3
Operating pressure					
1 – 5 bar	10 – 100 bar	10 – 30 bar	350 – 700 bar	10 – 50 bar	1 – 60 bar
Operating temperature					
-253 °C	-200 ↑ °C	0 - 50 °C	25 °C	70 - 170 °C	250-320 °C

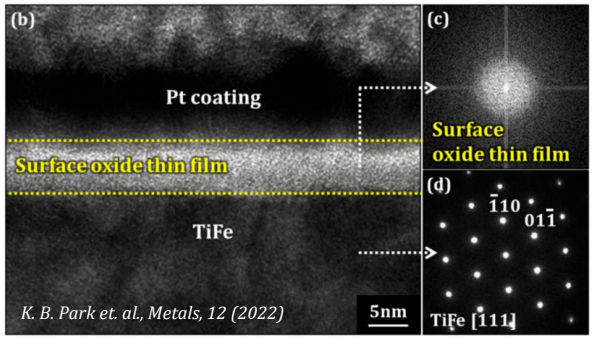
Characteristics of TiFe alloy & Ti-Fe-O phase in TiFe alloys

- **TiFe Pressure-Composition curve**



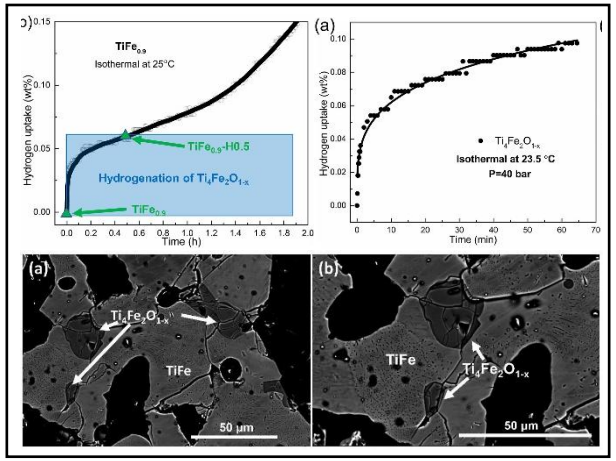
J. Reilly, Inorg. Chem., 13 (1974)

- **Surface oxidation layer of TiFe**



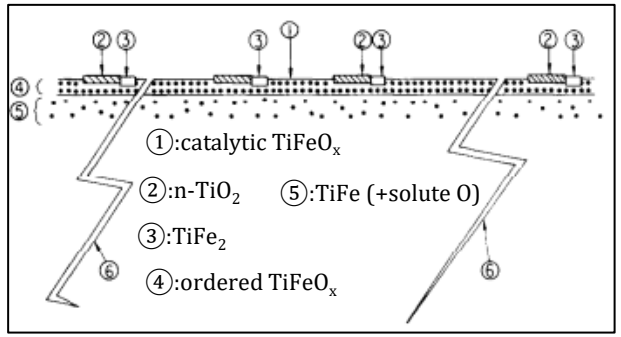
K. B. Park et. al., Metals, 12 (2022)

- **Oxygen addition effect of TiFe alloy**

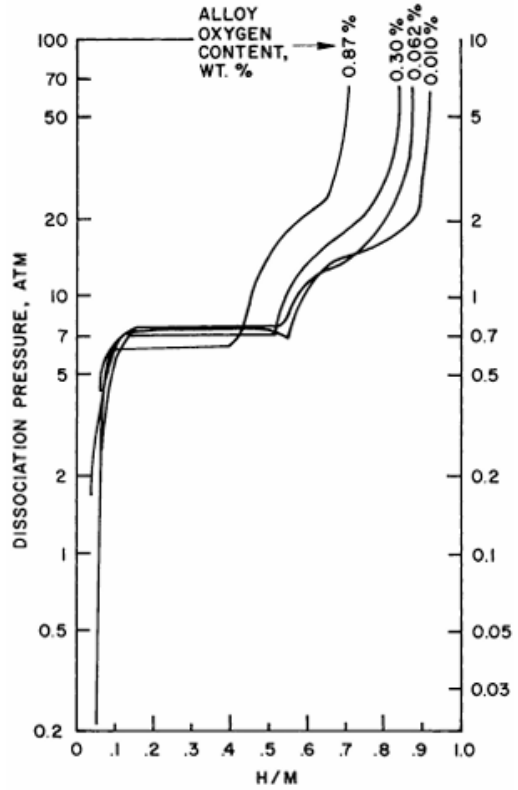


H. Liu et al., Int. J. Hydro. Eng., 48 (2023)

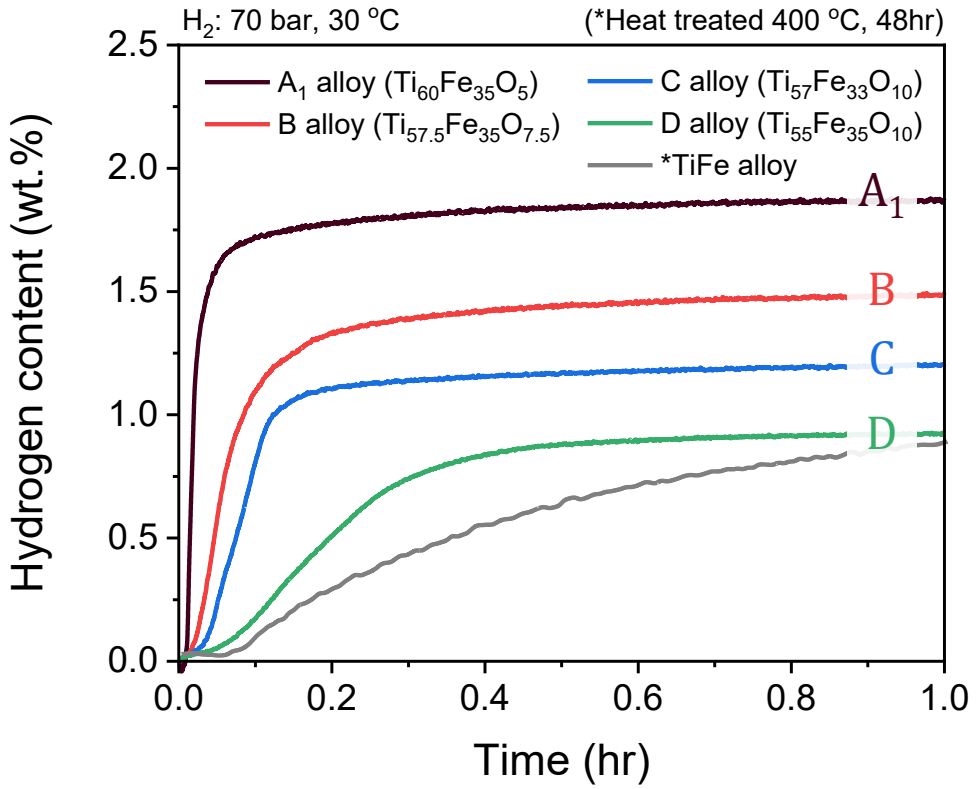
FeTi ↓ + O_2 metastable $FeTiO_x$	(CsCl structure) (metal atoms still have the CsCl structure with a threefold increase in the cell size)
↓ + O_2 metastable ternary oxide (f.c.c.)	$a_0 < 1.1$ nm [5]
↓ + O_2 stable f.c.c. $Fe_7Ti_{10}O_3$	$a_0 \approx 1.121$ nm

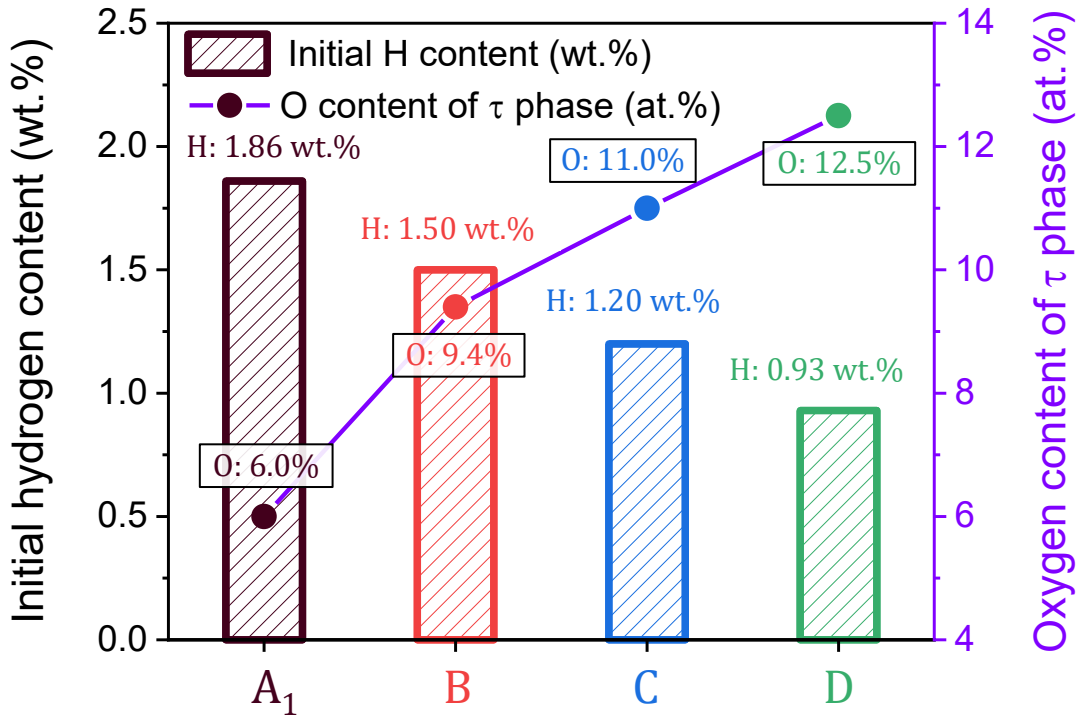


T. Schober., J. Less. Comm. Metals, 89 (1983)

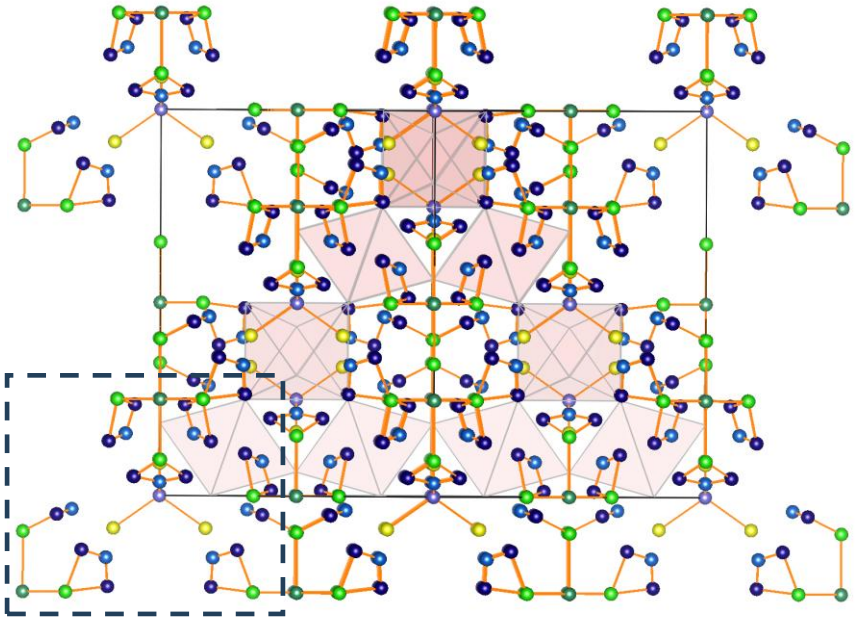


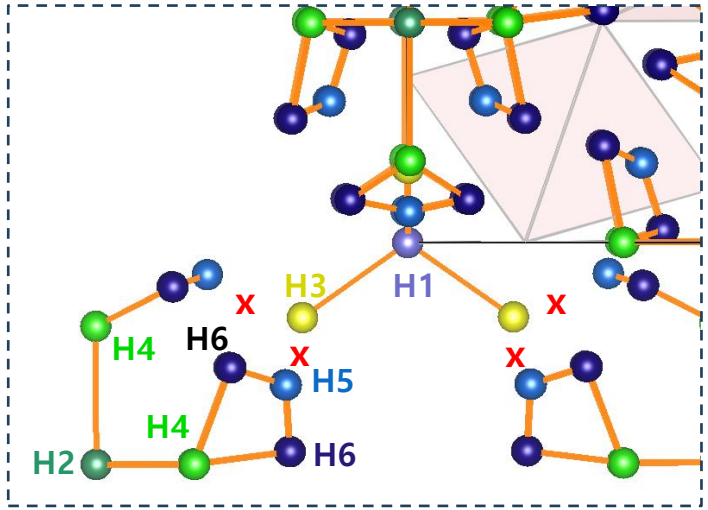
G. D. Sandrock, Hydrides for Energy Storage, 1978, Pages 353-393


H2: 70 bar, 30 °C
(*Heat treated 400 °C, 48hr)
A1 alloy (Ti60Fe35O5)
B alloy (Ti57.5Fe35O7.5)
C alloy (Ti57Fe33O10)
D alloy (Ti55Fe35O10)
*TiFe alloy
A1
B
C
D
Hydrogen content (wt.%)
Time (hr)
0.0
0.5
1.0
1.5
2.0
2.5
0.0
0.2
0.4
0.6
0.8
1.0

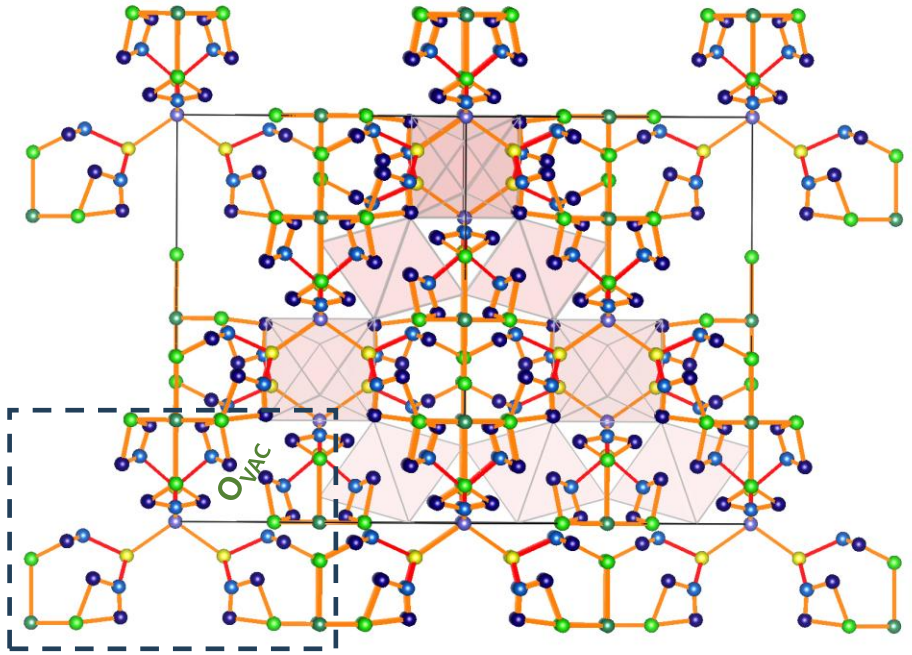

Initial H content (wt.%)
O content of τ phase (at.%)
H: 1.86 wt.%
H: 1.50 wt.%
H: 1.20 wt.%
H: 0.93 wt.%
O: 6.0%
O: 9.4%
O: 11.0%
O: 12.5%
A1
B
C
D
Initial hydrogen content (wt.%)
Oxygen content of τ phase (at.%)
0.0
0.5
1.0
1.5
2.0
2.5
4
6
8
10
12
14

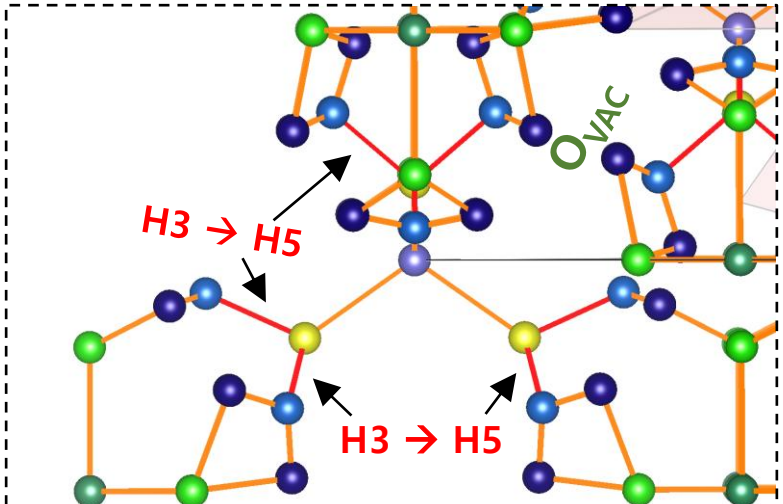
No O Vacancy





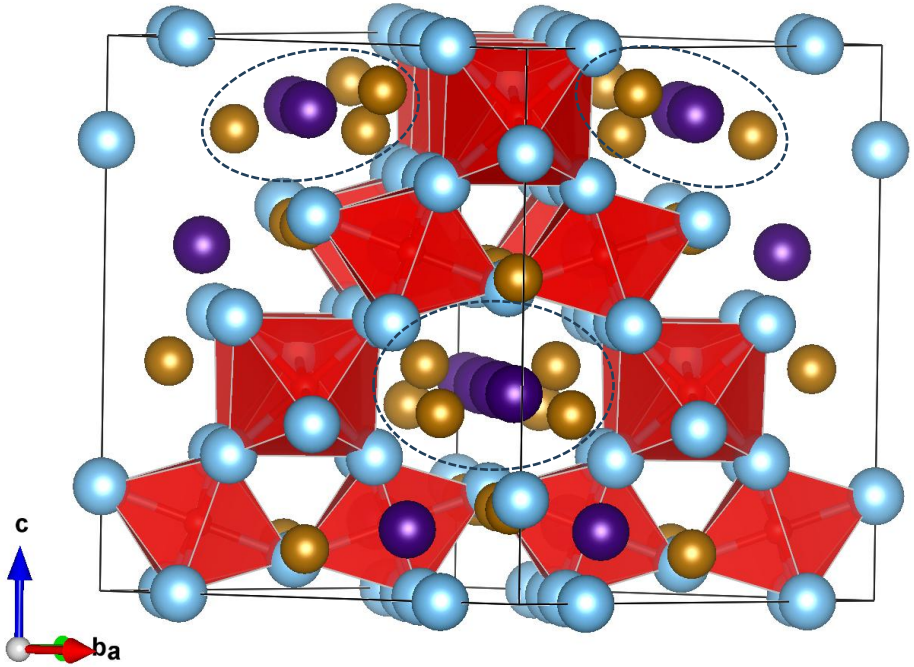
With O Vacancy

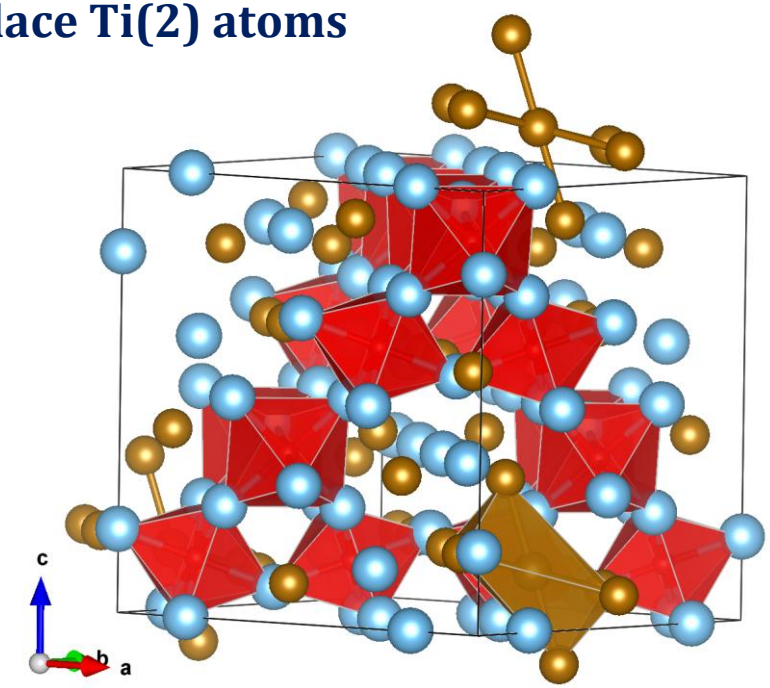




Excess Fe effect in the τ phase

- **Excess Fe will replace Ti(2) atoms**





H_6(192i) site