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Korea Institute of Science and Technology

Enhanced initial hydrogenation of TiFe-based hydrogen storage alloys

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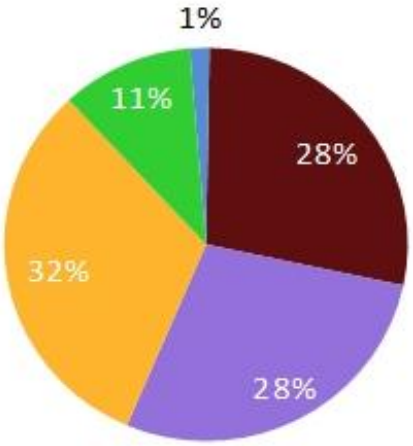
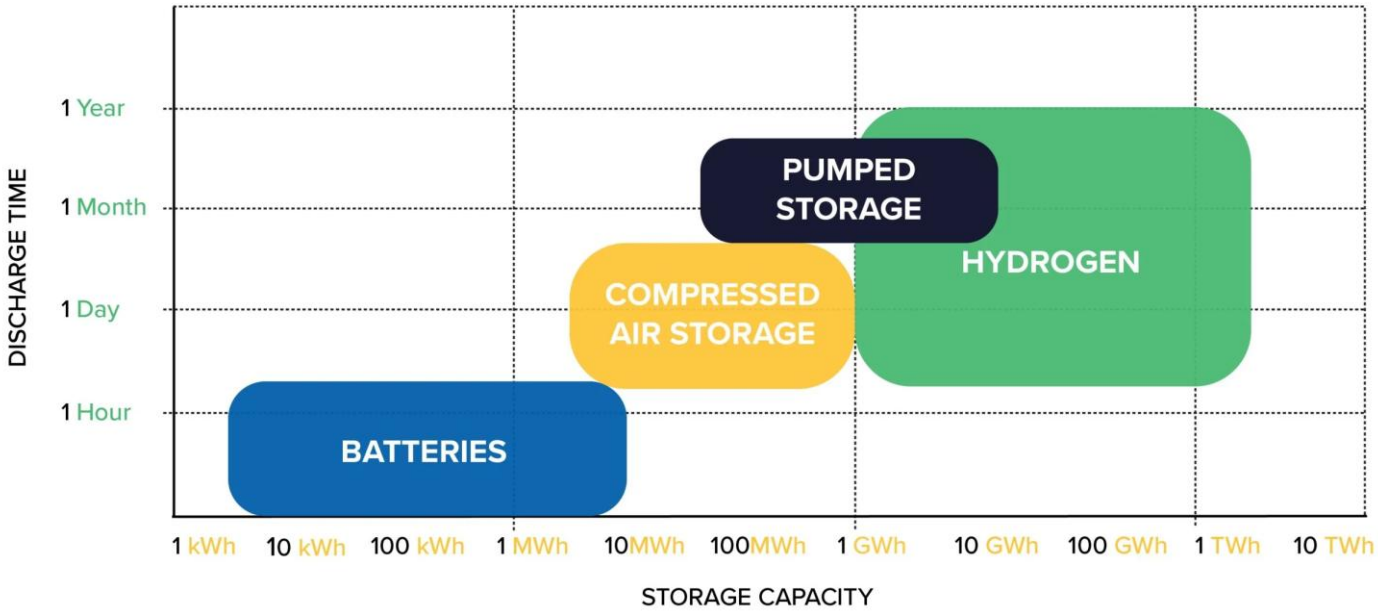
Storage solutions for renewable energy



Korea 600 TWh (2024)

- Coal
- Natural gas
- Nuclear
- Renewable
- Others

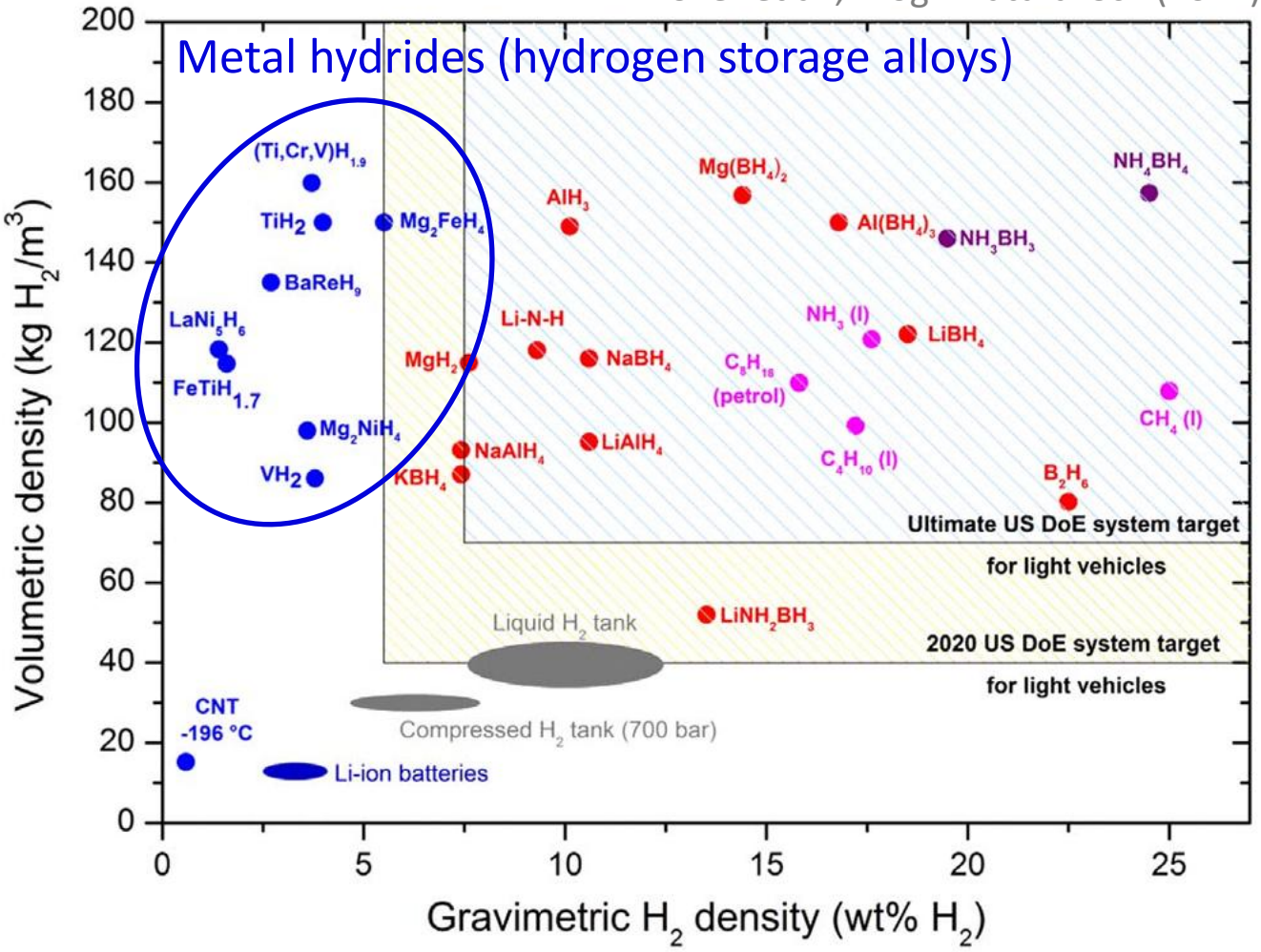


Energy Storage News (2020)

- Renewable energy portion expected to be 20 % in 2030s in Korea
- Effective storage solution necessary due to fluctuation of renewable energy
- Hydrogen is the most effective solution in long-term massive energy storage (day-year, GWh-TWh scales)

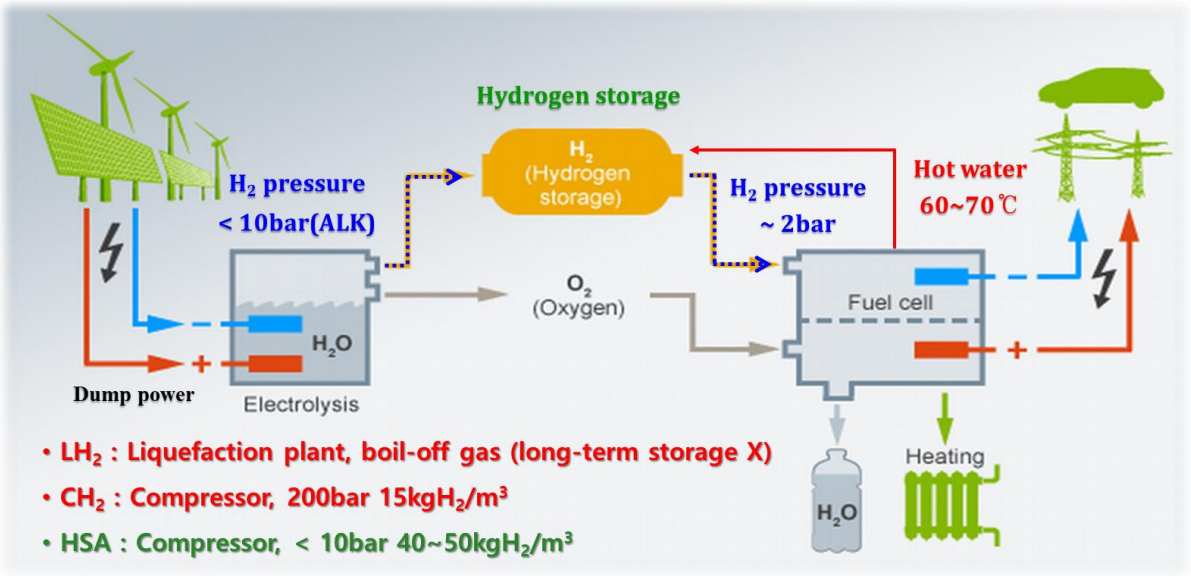
Hydrogen storage density

Moller et al., Progr. Natural Sci. (2017)



Hydrogen storage using metal hydrides operating at room temperature (i.e., hydrogen storage alloys) can be the effective solution for renewable energy storage

Hydrogen energy storage system in Korea



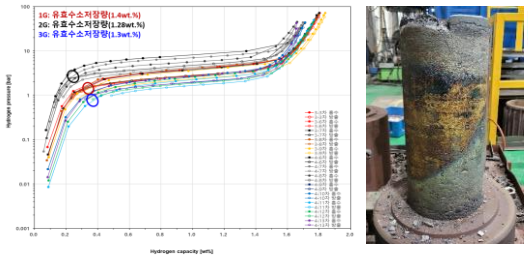
Global top project (‘24-’29), 50 kg H_2 below 10 bar

EWP KOREA EAST-WEST POWER CO.,LTD.

+

SUNG WON ENTERPRISE CO.,LTD

Solid-state hydrogen storage system

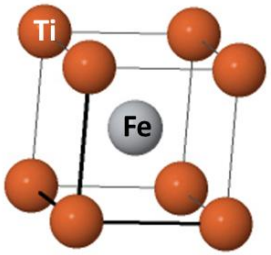


KPCM KIST KITECH 한국생산기술연구원

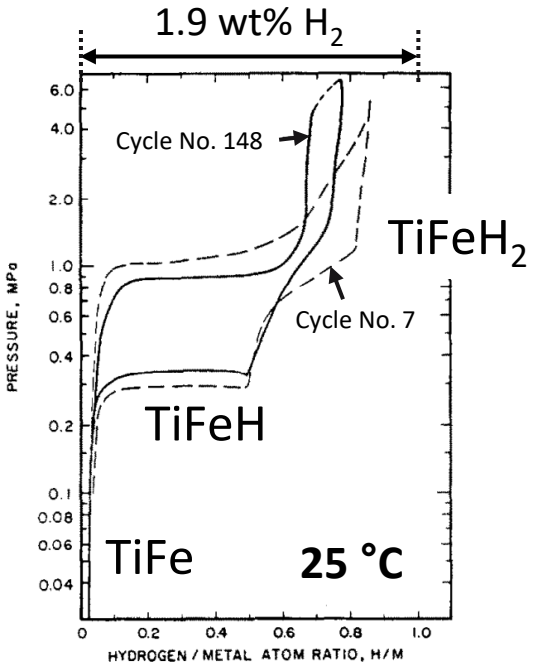
AB_2–type alloy (> 30k USD/ton)

TiFe-based hydrogen storage alloy

Alloy	Hydrogen capacity (wt% H_2)	Operation Temp.	Material Cost
TiFe (AB)	~1.9	R.T.	Low
$TiZrMn_{1.6}V_{0.4}$ (AB_2)	~1.6	R.T.	Medium
$LaNi_5$ (AB_5)	~1.5	R.T.	High



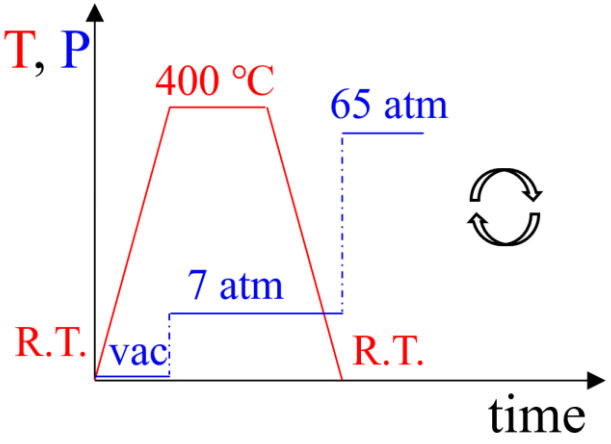
BCC B2



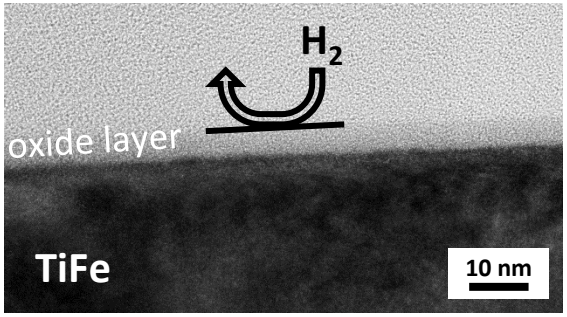
PCT curve of TiFe alloy

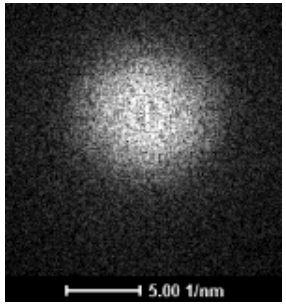
(1) TiFe ↔ TiFeH + 1/2 H_2 (0.95 wt% H_2)

(2) TiFeH ↔ $TiFeH_2$ + 1/2 H_2 (0.95 wt% H_2)



Cyclic harsh process for initial (first) hydrogenation to modify oxide layers





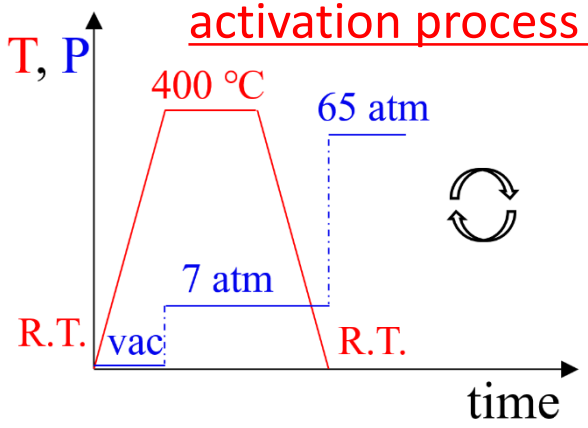
TEM analysis of surface oxide layers in a TiFe alloy
(Courtesy of Dr. H. Kim, 2018, unpublished work)

Reilly, J. J., and R. H. Wiswall. "Formation and properties of iron titanium hydride." Inorganic Chemistry 13.1 (1974): 218-222.
Goodell, P. D., G. D. Sandrock, and E. L. Huston. "Kinetic and dynamic aspects of rechargeable metal hydrides." *Journal of the Less Common Metals* 73.1 (1980): 135-142.

Effect of rare-earth element addition

Problem

Cyclic harsh activation process of TiFe



Previous studies

1) $TiFe_{0.9}Mn_{0.1}$ + Ce [1)]

2) TiFe + mischmetal [2)]

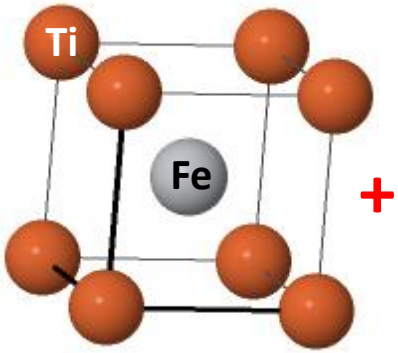
The addition of rare-earth elements enables initial hydrogenation of TiFe alloys at reduced temperature and pressure conditions

This study

1) V addition[3)]

2) Ce addition

a=2.979Å
b=2.979Å
c=2.979Å
α=90.000°
β=90.000°
γ=90.000°



BCC B2
cubic structure

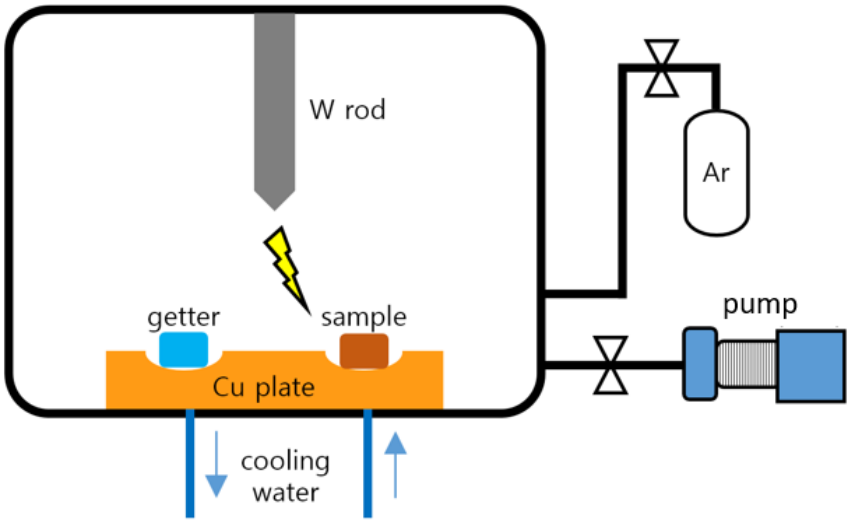
+ rare-earth

To understand how rare-earth element addition plays a positive role

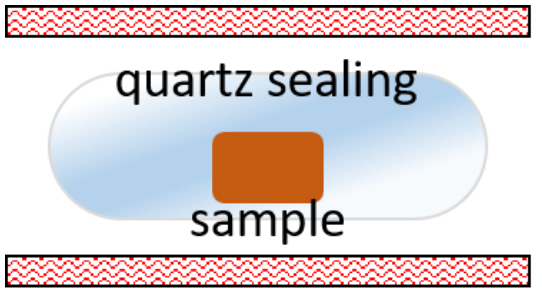
1) Leng, Haiyan et al., *International Journal of Hydrogen Energy* 42.37 (2017): 23731-23736.
2) Sandrock, G. D., Hydrides for energy storage. Pergamon, 1978. 353-393.
3) Faisal, Mohammad et al., *Materials* 14.17 (2021): 4829.

Preparation of Ti-Fe-V-Ce alloys

Arc button melting (~10 g)



Homogenization



furnace

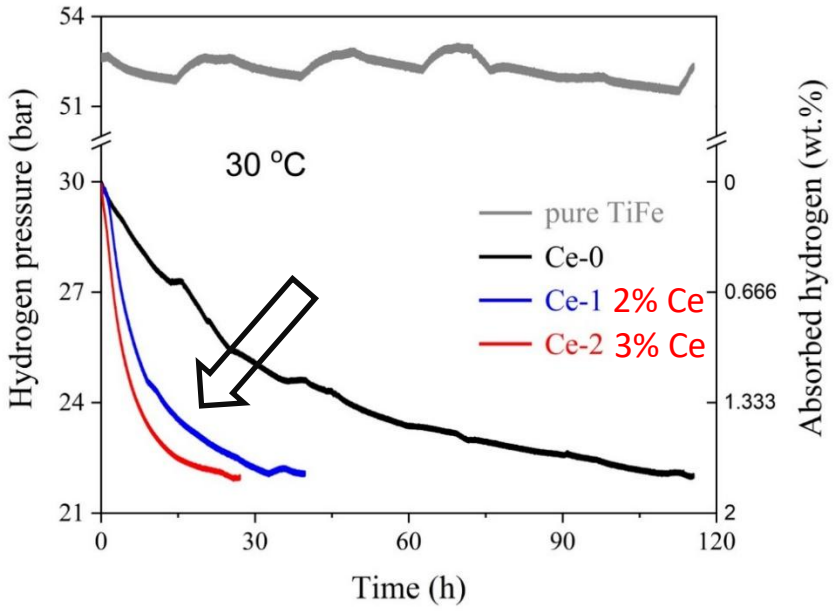
7 days at 1,000 °C

Composition of the prepared alloy samples in wt% (at%)

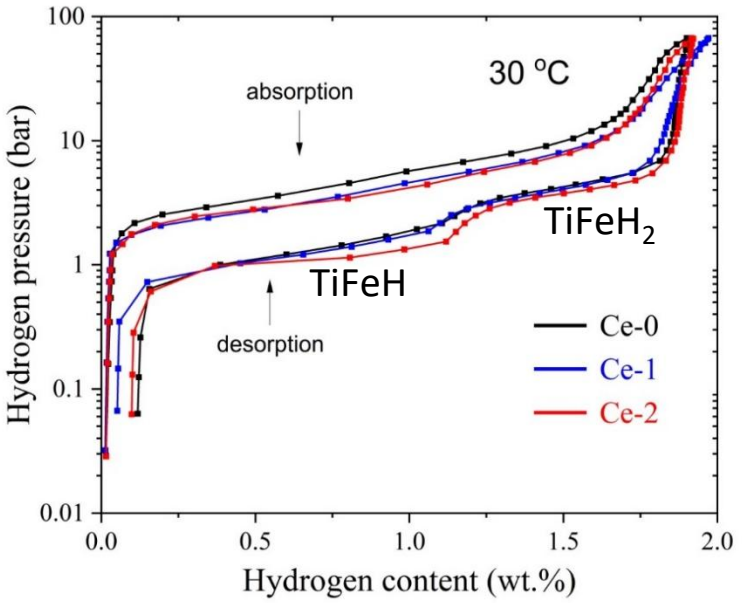
Alloy	Ti	Fe	V	Ce
Ce-0	50.7 (47.0)	46.5 (50.3)	2.8 (2.7)	-
Ce-1	50.47 (46.13)	46.4 (49.47)	2.33 (2.27)	0.80 (2.13)
Ce-2	50.57 (45.83)	46.00 (48.67)	2.17 (2.13)	1.27 (3.40)

Initial (first) hydrogenation of Ti-Fe-V-Ce alloys

Profiles for initial hydrogenation 30 °C



PCT curves after initial hydrogenation

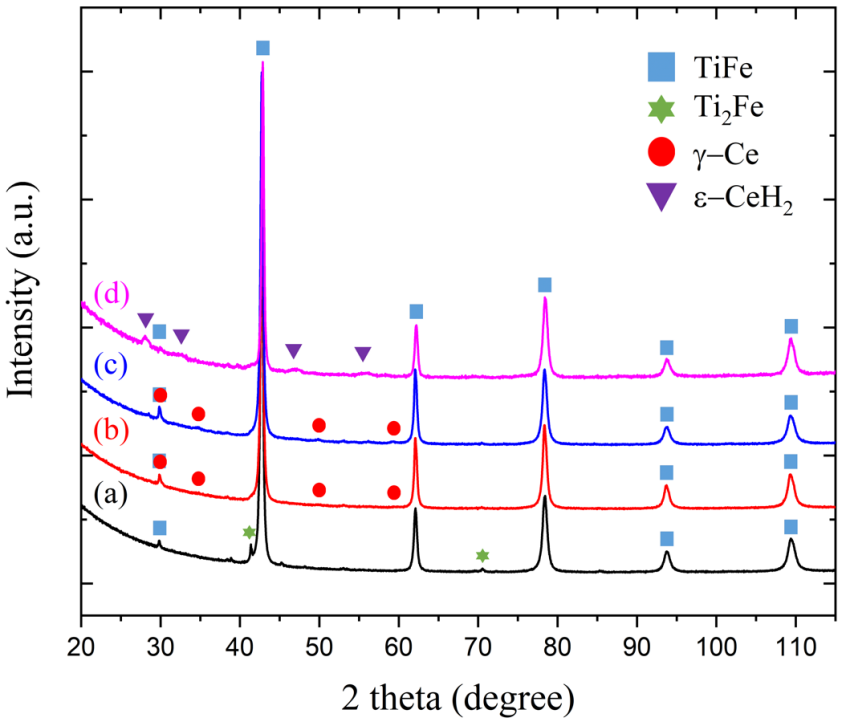


- No room temperature hydrogenation without alloying elements (pure TiFe)
- The V addition enables slow initial hydrogenation at room temperature
- The Ce addition dramatically enhances initial hydrogenation kinetics
- PCT curves do not change with the Ce addition
- Two-stage dehydrogenation (two hydrides) observed from PCT curves

T. Ha et al., "Crucial role of Ce particles during initial hydrogen absorption of AB-type hydrogen storage alloys", Nano Energy **112**, 108483 (2023)

Phase analysis of Ti-Fe-V-Ce alloys

XRD patterns



- TiFe with B2 structure as a major phase (> 97 %)
- No V-related phases
- γ-Ce with FCC structure observed
- A trace of Ti_2Fe observed in Ce-0
- γ-Ce transforms into ε-CeH_2 after hydrogenation at 30 bar for 40 h

Ce-2 after initial hydrogenation for 40 h

Ce-2 (as-prepared)

Ce-1 (as-prepared)

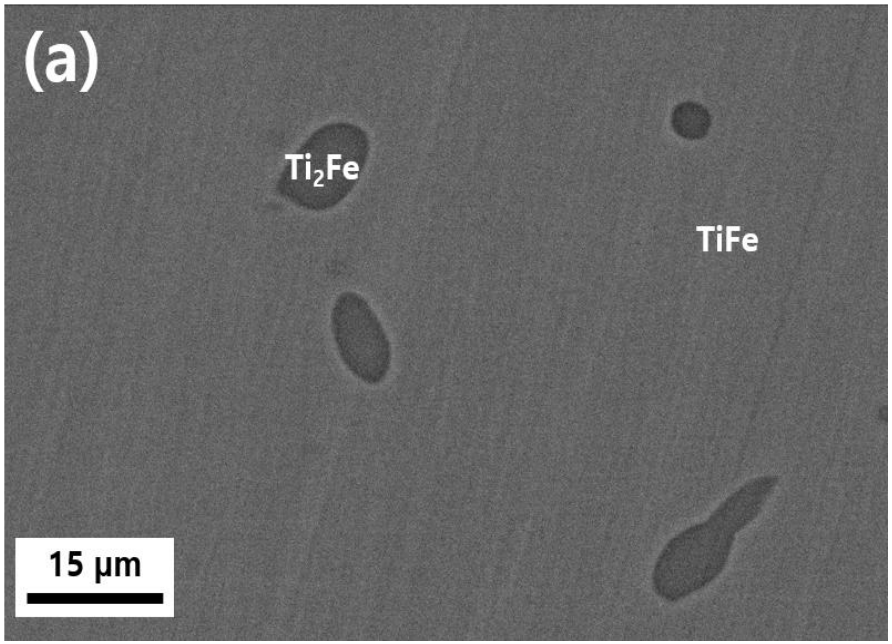
Ce-0 (as-prepared)

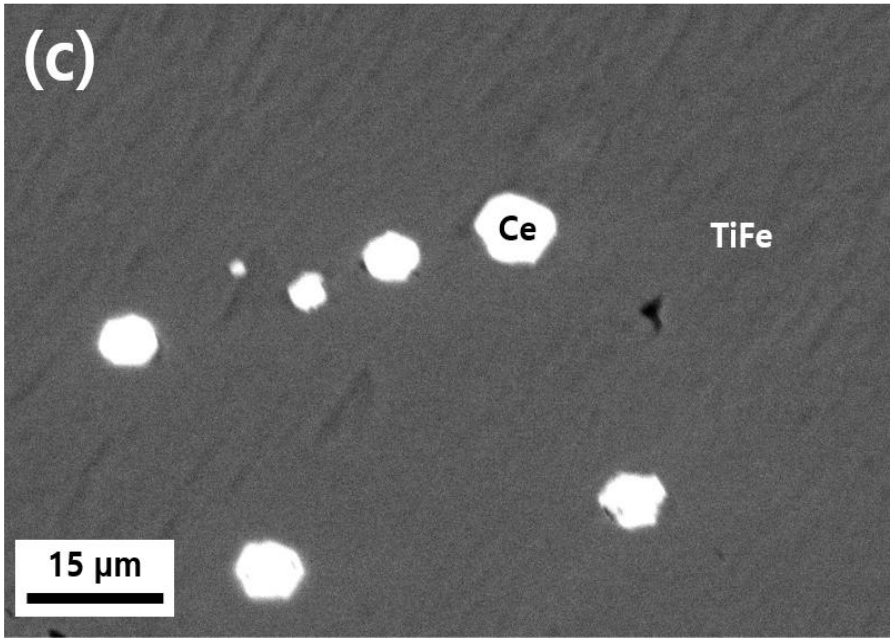
Phase amount from Rietveld refinement of the XRD patterns (wt%)

Alloy	TiFe (B2)	Ti_2Fe (cubic)	γ-Ce	ε-CeH_2
Ce-0	97.6	2.4	-	-
Ce-1	98.5	-	**1.5**	-
Ce-2	96.7	-	**3.3**	-
Ce-2 after hydrogenation	96.7	-	-	**3.3**

Microstructure of as-prepared Ti-Fe-V-Ce alloys

SEM-BSE images of the (a) Ce-0 (0 at% Ce) and (c) Ce-2 (3 at% Ce) alloy samples

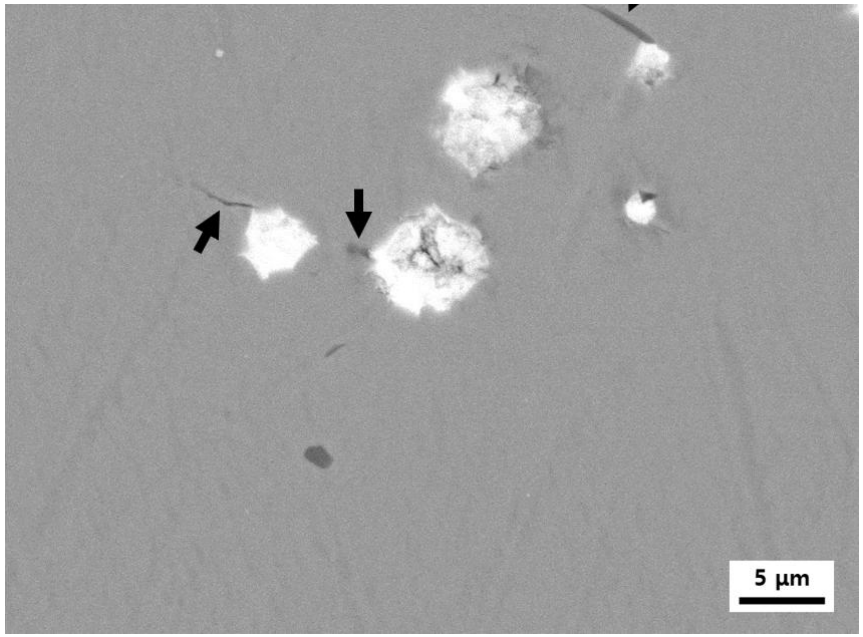


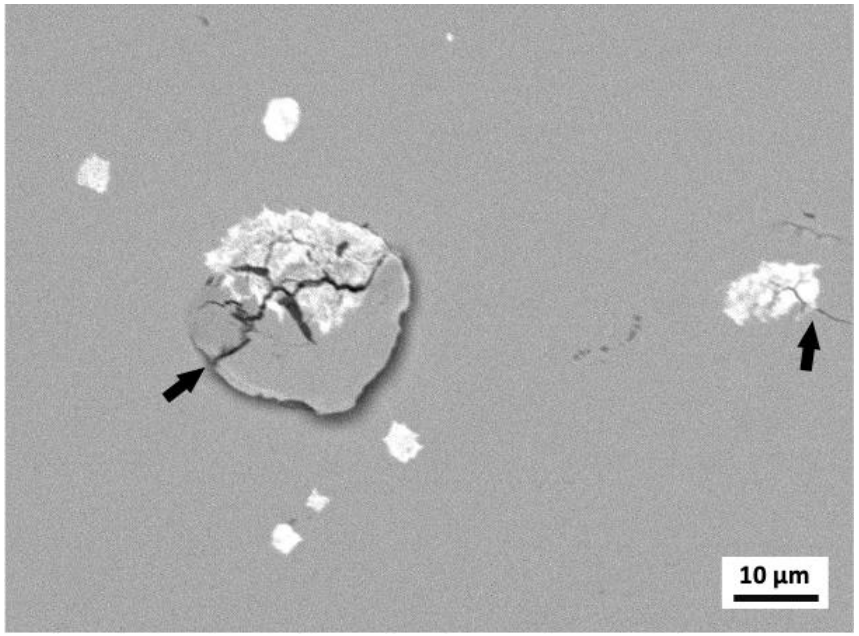


- Ti_2Fe occasionally observed in the Ce-0 alloy sample
- Ce with a high atomic number is bright in a BSE image
- White Ce-rich particles (~10 μm) uniformly dispersed in the TiFe matrix in the Ce-2 alloy sample containing 3 at% Ce

Microstructure after initial hydrogenation for 1.5 h

SEM-BSE images of Ce-2 alloy sample hydrogenated at 30 bar H_2 and 30 °C for 1.5 h



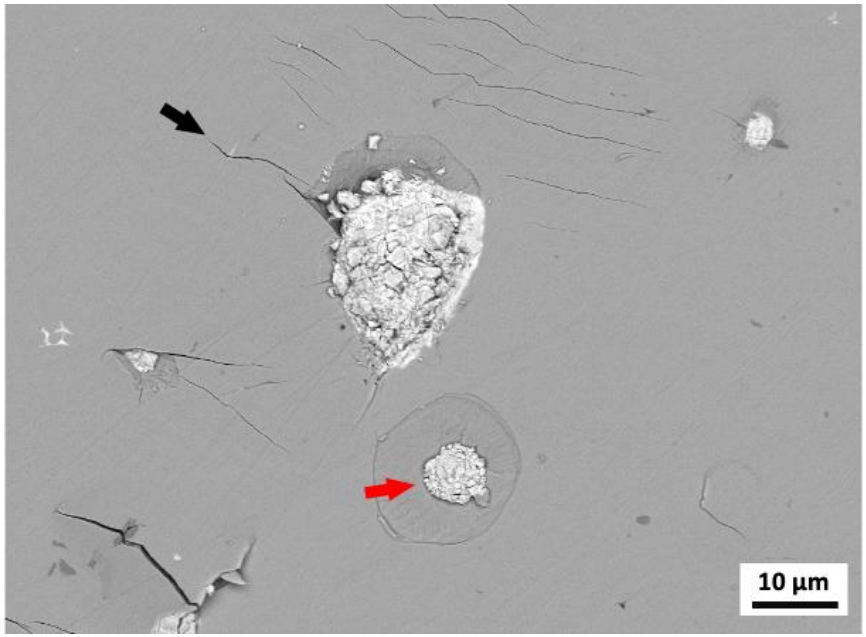


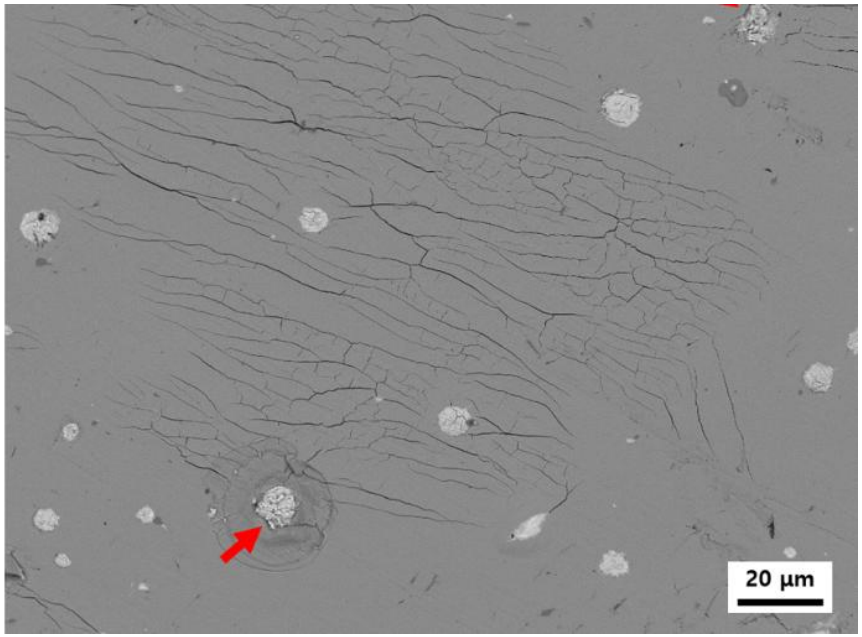
- Small cracks observed around white Ce particles (even inside the particles)
- The crack formation can be attributed to the volume expansion-induced stress for CeH_2 formation
- Volume expansion expected with the reaction $Ce + H_2 \rightarrow CeH_2$ ($\Delta V = 17$ %)
- Do the cracks contribute to the enhancement of the initial hydrogenation?

T. Ha et al., "Crucial role of Ce particles during initial hydrogen absorption of AB-type hydrogen storage alloys", Nano Energy **112**, 108483 (2023)

Microstructure after further hydrogenation for 12 h

SEM-BSE images of Ce-2 alloy sample hydrogenated at 30 bar H_2 and 30 °C for 12 h

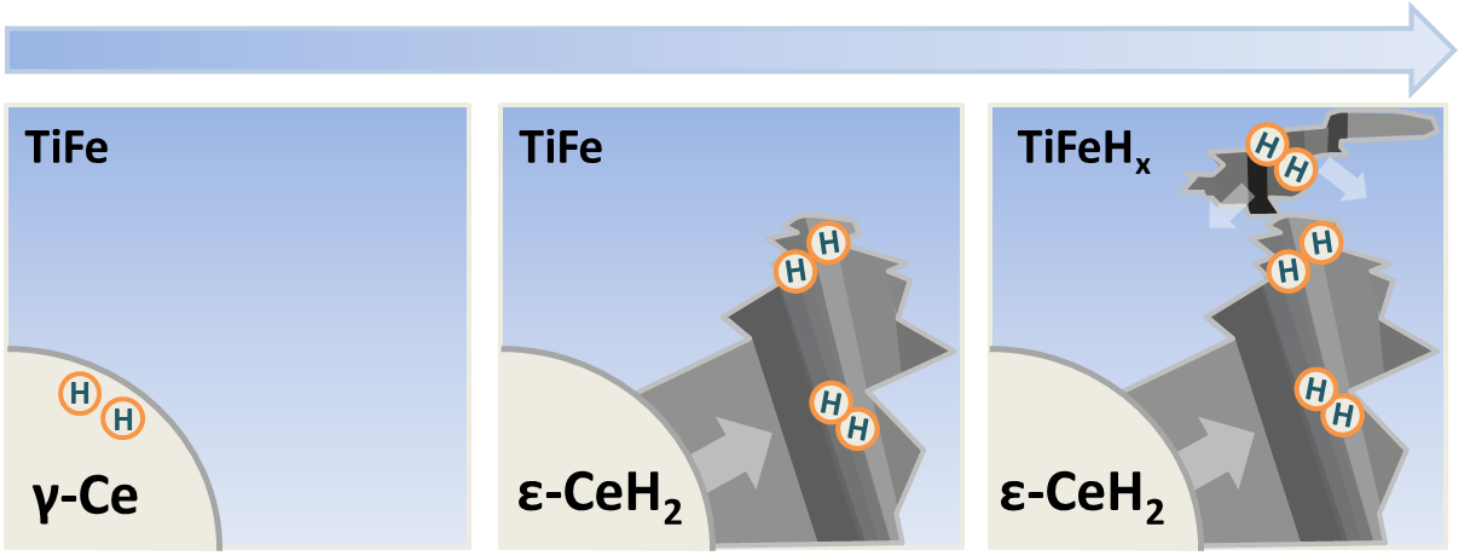




- More cracks observed around the particles and even in the TiFe matrix far from the particles
- Cracks around the particles → fresh TiFe surfaces formation → hydrogenation of TiFe matrix → volume expansion-induced stress (ΔV = 17 % for $TiFeH_2$) → fresh TiFe surfaces formation → further hydrogenation of TiFe
- Crack propagation continues due to the further matrix hydrogenation
- In conclusion, Ce particles obviously act as starting sites of the initial hydrogenation of the alloys thanks to the volume expansion effect for CeH_2 formation

Mechanism for the enhanced initial hydrogenation

Role of Ce particles during initial hydrogenation of Ti-Fe-V-Ce alloys



$Ce + H_2 \rightarrow CeH_2$
$\Delta V = 17\ \%$

$TiFe + 0.5\ H_2 \rightarrow TiFeH$ $\Delta V = 12\ \%$
$TiFeH + 0.5\ H_2 \rightarrow TiFeH_2$ $\Delta V = 5\ \%$

I. Hydrogenation of Ce particles

II. Volume of expansion due to CeH_2 formation

→ Appearance of fresh surfaces of TiFe matrix

→ Hydrogenation of TiFe matrix

III. Crack propagation due to further hydrogenation of TiFe matrix with the exposure of fresh surfaces

T. Ha et al., "Crucial role of Ce particles during initial hydrogen absorption of AB-type hydrogen storage alloys", Nano Energy **112**, 108483 (2023).

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