The World Future Fuel Summit 2022, 16-17 February 2022

Perspective of Japan's hydrogen Energy and Application of Hydrogen Storage Alloys

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Fellow & Vice President, Int. Assoc. for Hydrogen Energy (IAHE)

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1. ***Japan's Energy Policy***
   Background => Environmental & Radioactive Pollutions
2. ***Active Tackling on Spreading Hydrogen Technologies***
   Japanese Governmental & Industrial Sectors are moving to:
   Cost down of H2 / Power-to-Gas with Renewable Energy
   CO2&C-Recycling / International Standardization
   Implementation of Paris agreement & SDGs by Carbon neutralization
3. ***Renewable Energy Storage/Control by Hydrogen using Nano-Structured FeTi Hydrogen Storage Alloy***
4. ***Application of Waste & Unused Heat & MH to agriculture and fish breeding using Hydrogen Storage Alloys***

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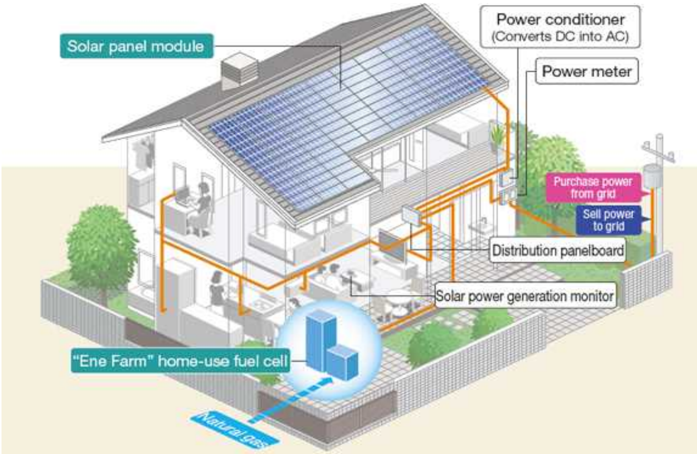
Advancing Hydrogen Technology

Hydrogen Fuel Cell technology
- Stationary and Mobile -

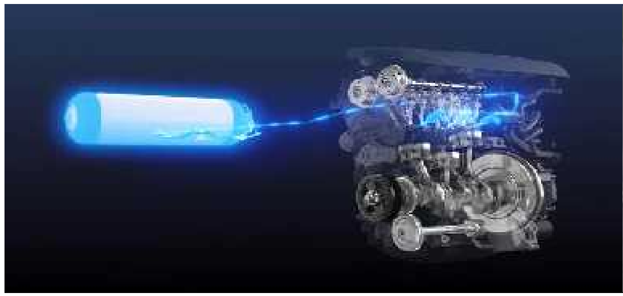


RESIDENTIAL FUEL CELL
ENE·FARM

ENE FARM over 310,000 installed in 2019

FCV

H2 combustion engine 2021



A Toyota hydrogen engine vehicle participated in the Fuji 24h Race June 2021 with high pressure H2 tanks for FCV

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Hydrogen Combustion Engine again ?

MAZDA hydrogen rotary engine with IAHE Award

2000s

FeTi + Mg2Ni Hydrogen storage alloys

Stuttgart
1970s

L-H2 at -253℃

Munich
2000s

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H2 Stationary and Mobile Stations in Japan

166 stations in August 2021

*Plan: 1000 stations by 2030

Data from Kanagawa Prefecture, Japan

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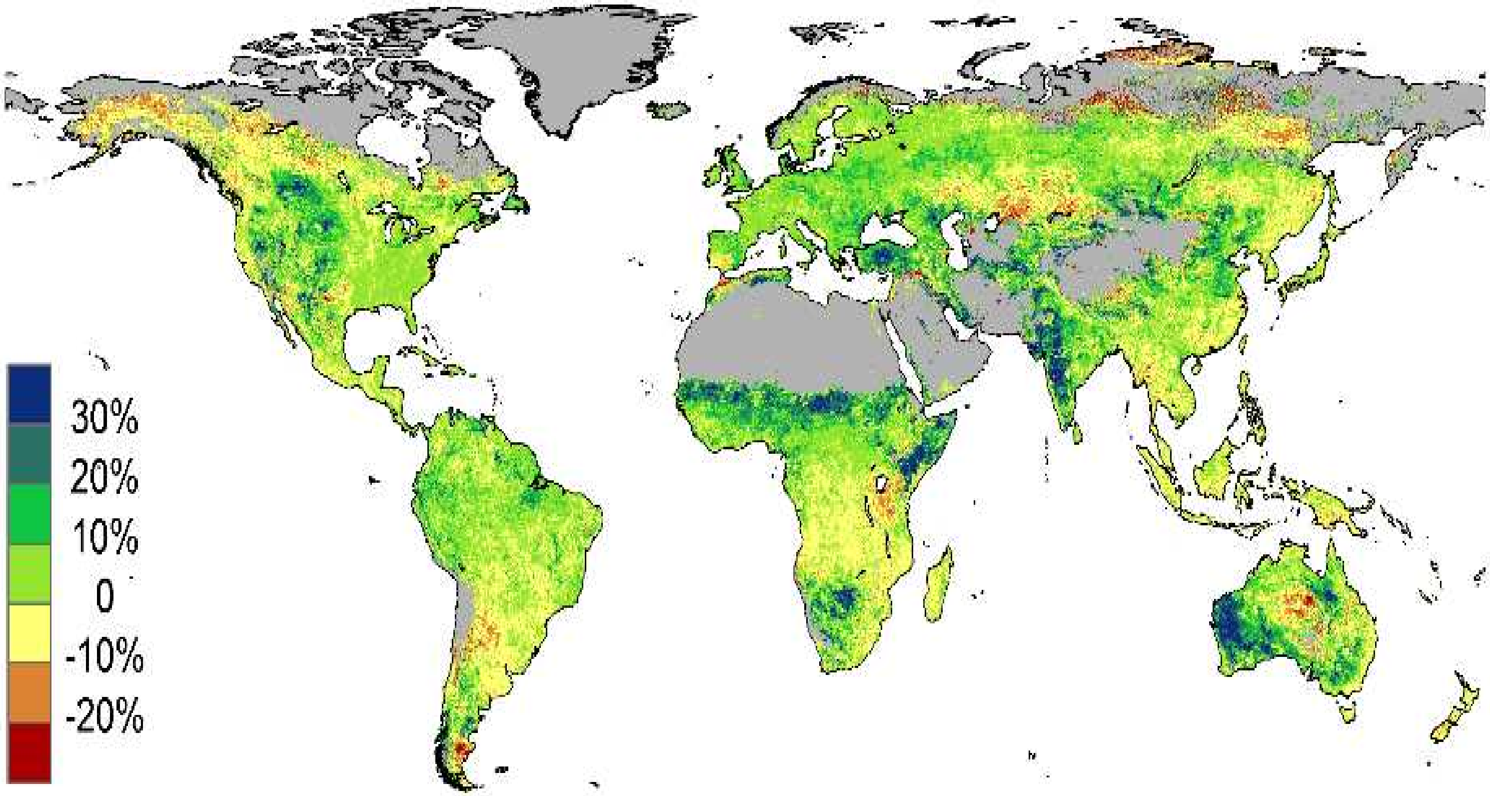
H2 and CO2

Global Greening is Advancing in the last 30 Years by Increasing CO_2 in Air

R.J.Donohue et al, Geographical Research Letters 40(2013)3031



http://www.csiro.au/en/News/News-releases/2013/Deserts-greening-from-rising-CO2

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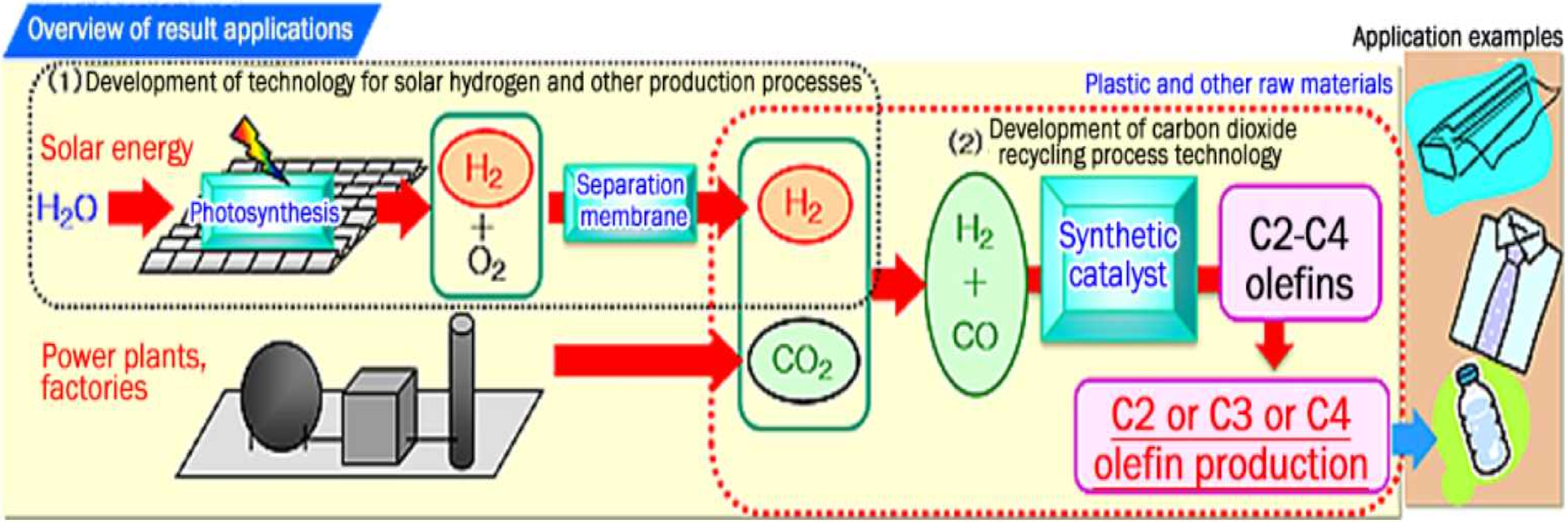
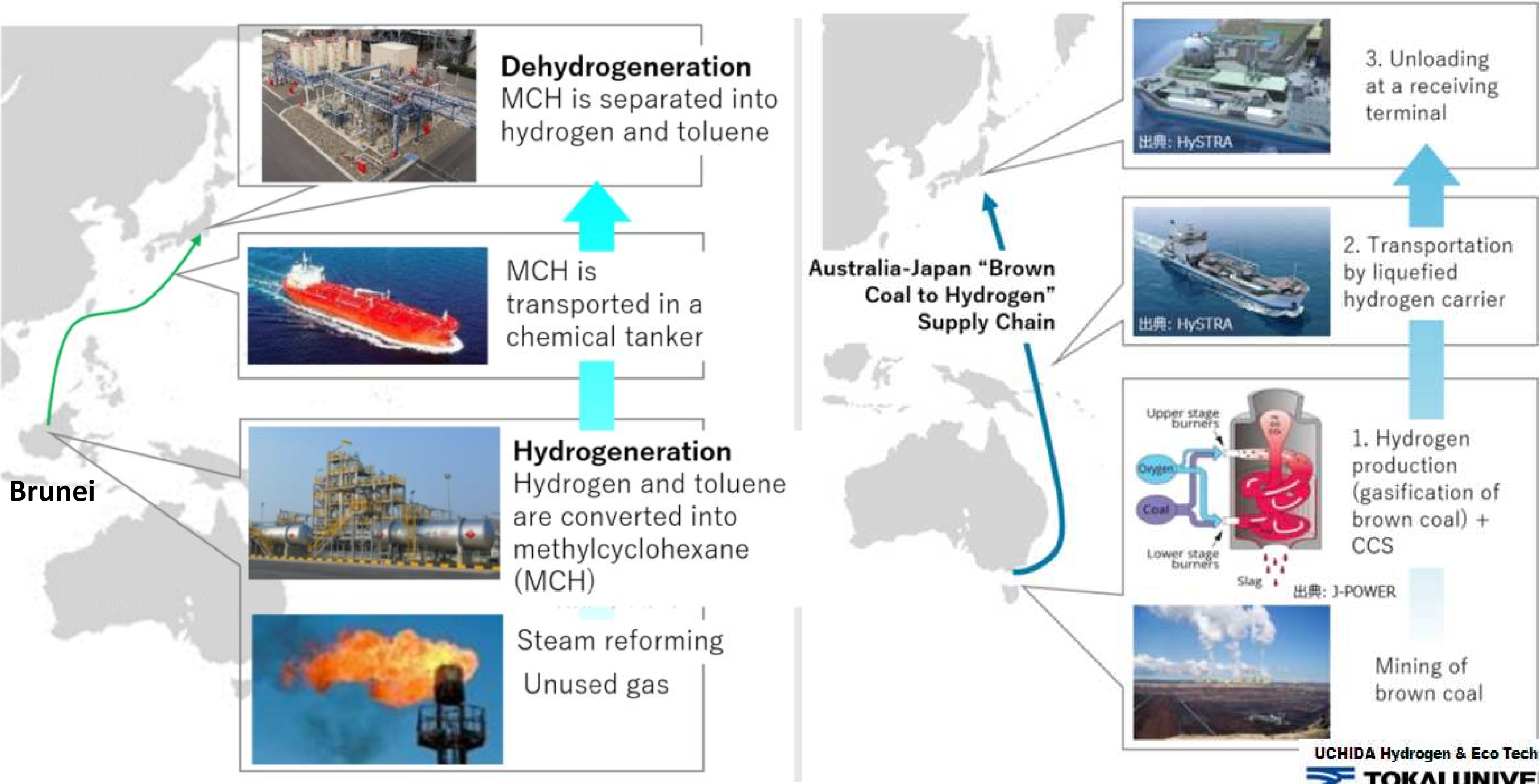
CO2 Recycling with H2 for Materials Production by NEDO



Project diagram

Hydrogen Production/Transportation from Brunei and Australia to Japan

JPY120/m3 ➡ JPY20~30/m3 (2050)



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Hydrogen Storage Technologies using Hydrogen Storage Alloys=Metal Hydrides

Typical Hydrogen Storage Alloys

- **A2B** = Mg2Cu, Mg2Ni   (1967~68)

- **AB5** = LaNi5 (1970) → Mm(Ni, Al, Co, Mn)5 for Ni-MH battery
  Easy activation/ high cyclic stability / expensive

- **AB = FeTi** (1974)
  Difficult activation / inexpensive

H density in MH is higher than that in L-H2 in a same volume!

Reversible Simple Hydrogen Reactions of Hydrogen Storage Alloys (HSA)

HYDRIDING / H_2 ABSORPTION

$$M(HSA) + H_2\ (H^+) \Rightarrow\ MH + Q : \text{Exoth.}$$

DEHYDRIDING / H_2 DESORPTION

$$M(HSA) - H_2\ (H^+) \Leftarrow\ MH - Q : \text{Endoth.}$$

H density in MH is higher than that in L-H2 in a same volume!

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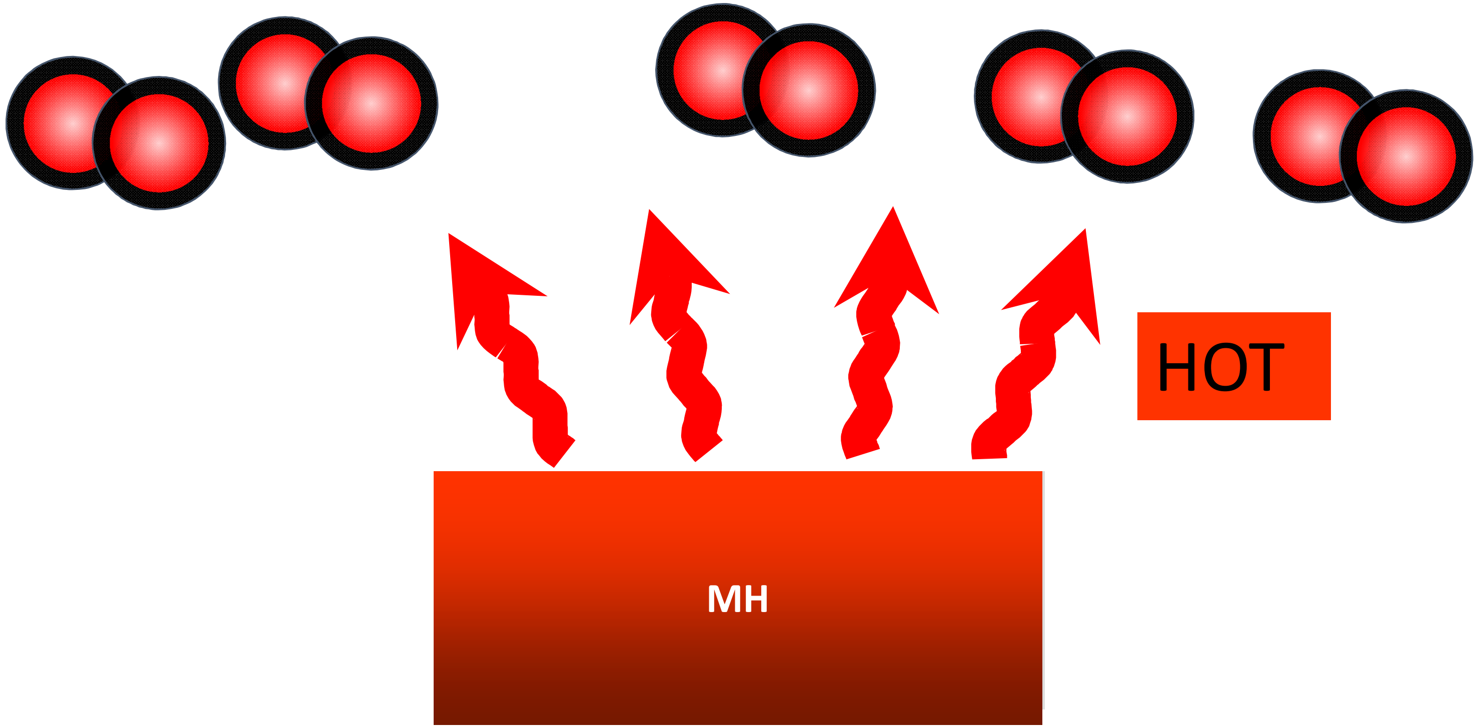
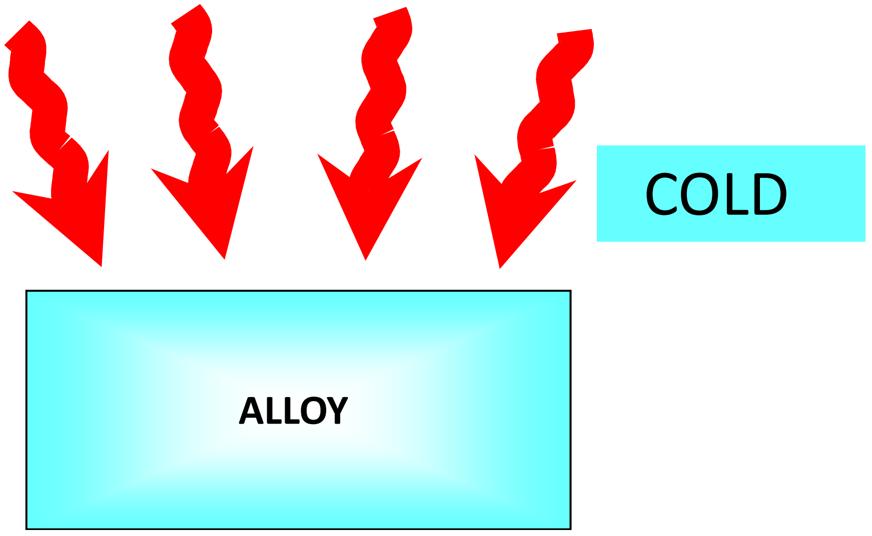
Hydrogen Storage Alloy?

On H_2 absorption (uptake)



Hydrogen Storage Alloy?

On H_2 desorption (relaese)



In June 1988, for the first time, we demonstrated the high performance of a Ni-MH rechargeable battery using hydrogen storage alloys

日経産業新聞 1988年7月8日

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Ni-MH Rechargeable Battery

- Reversible Hydrogen Reactions -

Toyota PRIUS

Hydrogen absorption => Charge

M(HSA Electrode) + H^+ from H_2O => MH

Hydrogen desorption => Discharge

MH => M(HSA Electrode) – H^+ into H_2O

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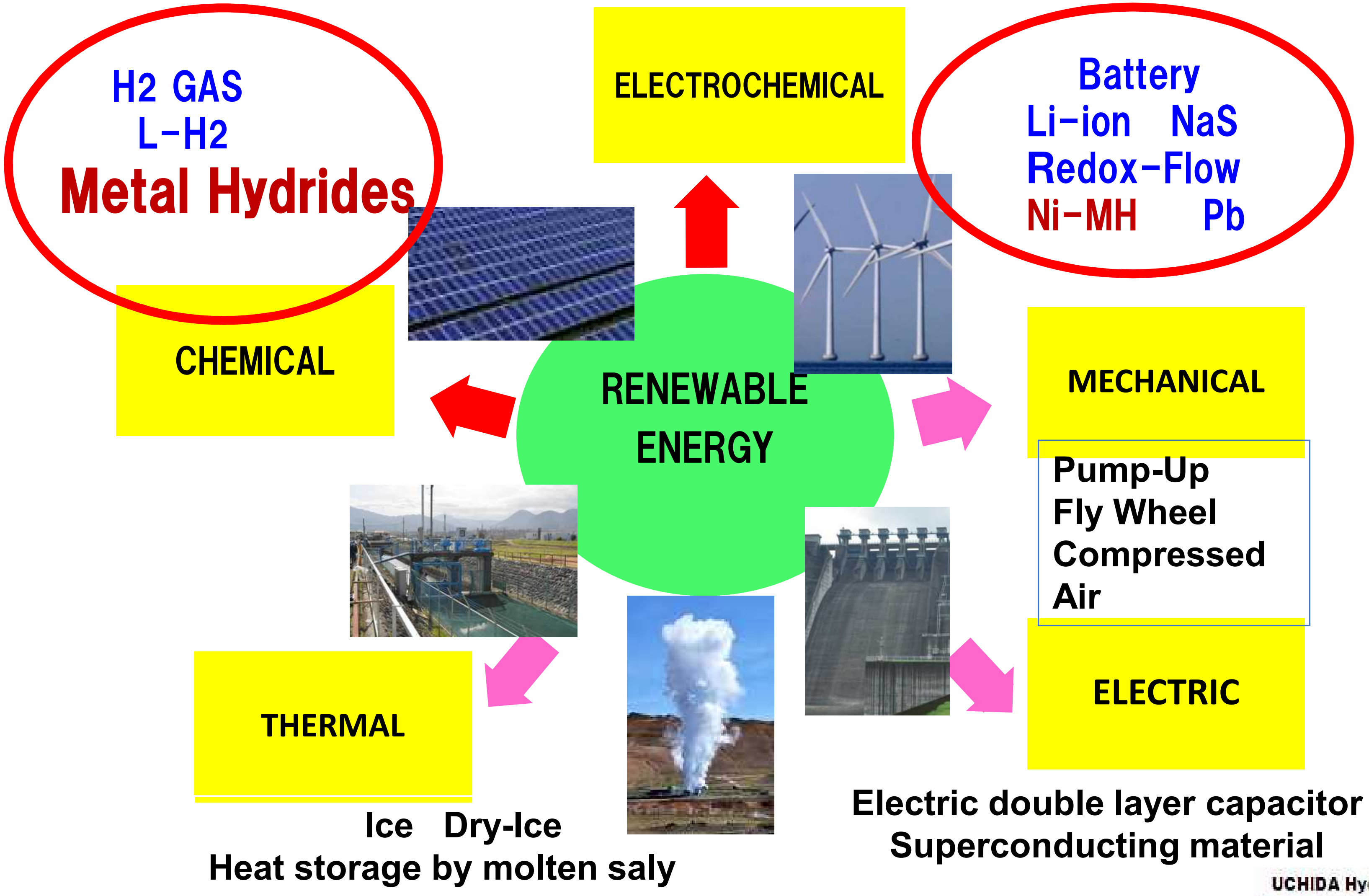
Renewable Energy Storage/Control by Hydrogen/MH



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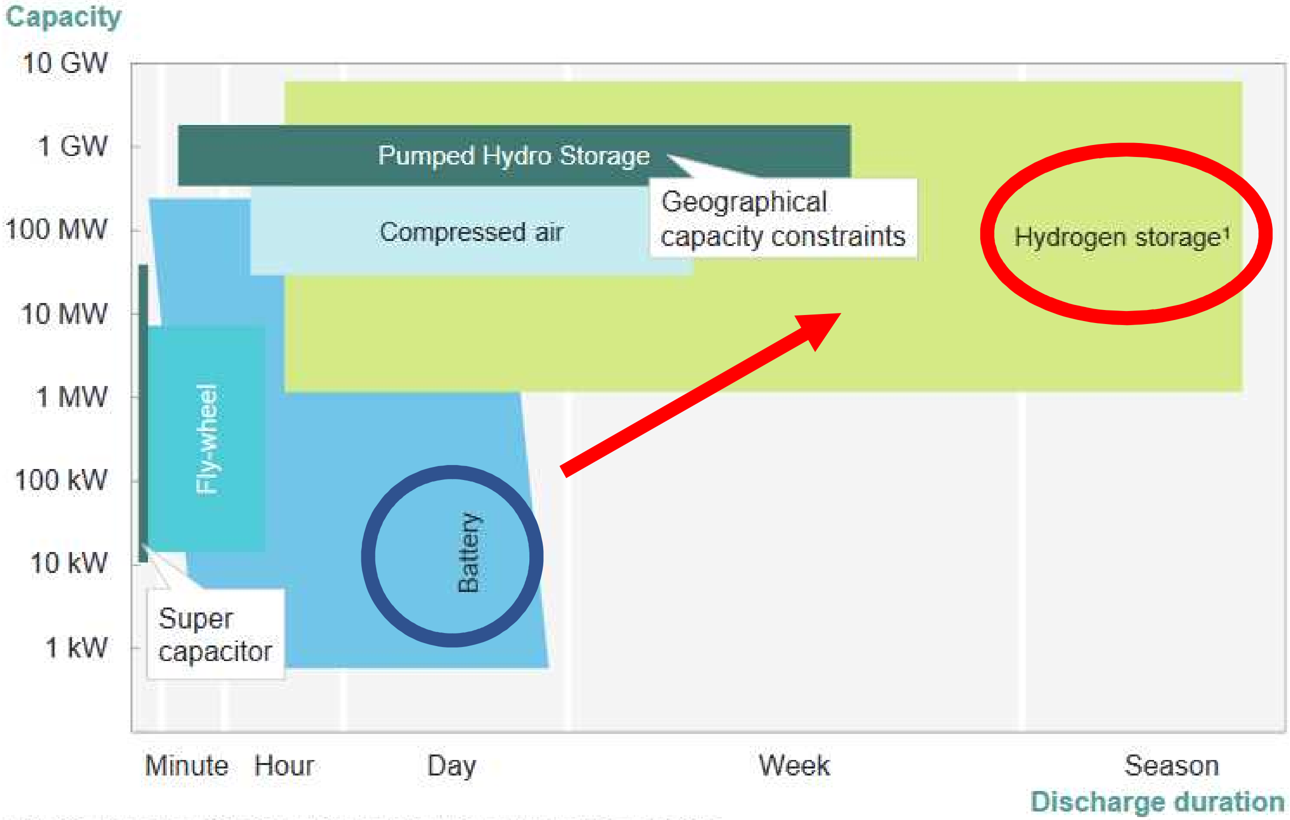
World Economic Forum Annual Meeting

17-20 January 2017
Davos-Klosters, Switzerland

Figure 4: Hydrogen is most promising for long-term carbon-free seasonal storage

Technology overview of carbon-free energy storage technologies

World Economic Forum Davos Conference 2017



1 IEA data updated due to recent developments in building numerous 1MW hydrogen storage tanks

Source: IEA Energy Technology Roadmap Hydrogen and Fuel Cells, JRC Scientific and Policy Report 2013

Hydrogen Council World Economic Forum, Davos, Switzerland

Growing momentum for hydrogen as further multinationals join global coalition on Jan. 2021

3M, AIRBUS, Air Liquide, AIR PRODUCTS, ALSTOM, AngloAmerican, aramco, BMW GROUP, BOSCH, bp, CF

Chemours, CHN ENERGY, CMA CGM, CNH INDUSTRIAL, Cummins, DAIMLER, EDF, ENEOS, ENGIE, equinor, faurecia, gm

Great Wall, HONDA, HYUNDAI, Iwatani, JM Johnson Matthey, Kawasaki, KOGAS, Linde, MICHELIN, Microsoft, MSC, op

sabic, SCHAEFFLER, Shell, SIEMENS energy, SINOPEC, SOLVAY, thyssenkrupp, TOTAL, TOYOTA, uniper, WEICHAI

ACME, AFC Energy, AVL, Baker Hughes, BALLARD, BLACK & VEATCH, BUREAU VERITAS, CHART, Chevron, CLARIANT, Delek, elringklinger, ENBRIDGE, Faber CYLINDERS, FMG Fortescue

galp, GORE, HEXAGON, ILJIN, ITOCHU, LIEBHERR, MAHLE, MANN+HUMMEL, Marubeni, MCDERMOTT, McPhy, Mitsubishi Corporation, MITSUBISHI HEAVY INDUSTRIES, MITSUI & CO.

nel, NGK NTK, NIKOLA, NYK Line, PETRONAS, PLUG POWER, Port of Rotterdam, Power Assets 電能, REFIRE, Reliance Industries Limited, 中自催化 SINOCAT, 亿华通 SinoHytec

中材科技股份有限公司, SMBC, snam, SoCalGas, Sumitomo Corporation, TechnipFMC, TOKYO GAS, TOYOTA TSUSHO, TRUE ZERO, umicore, Vopak, Woodside

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ANTIN, BNP PARIBAS, CRÉDIT AGRICOLE, GIC, John Laing, MUBADALA, NATIXIS BEYOND BANKING, PROVIDENCE ASSET GROUP, SOCIETE GENERALE

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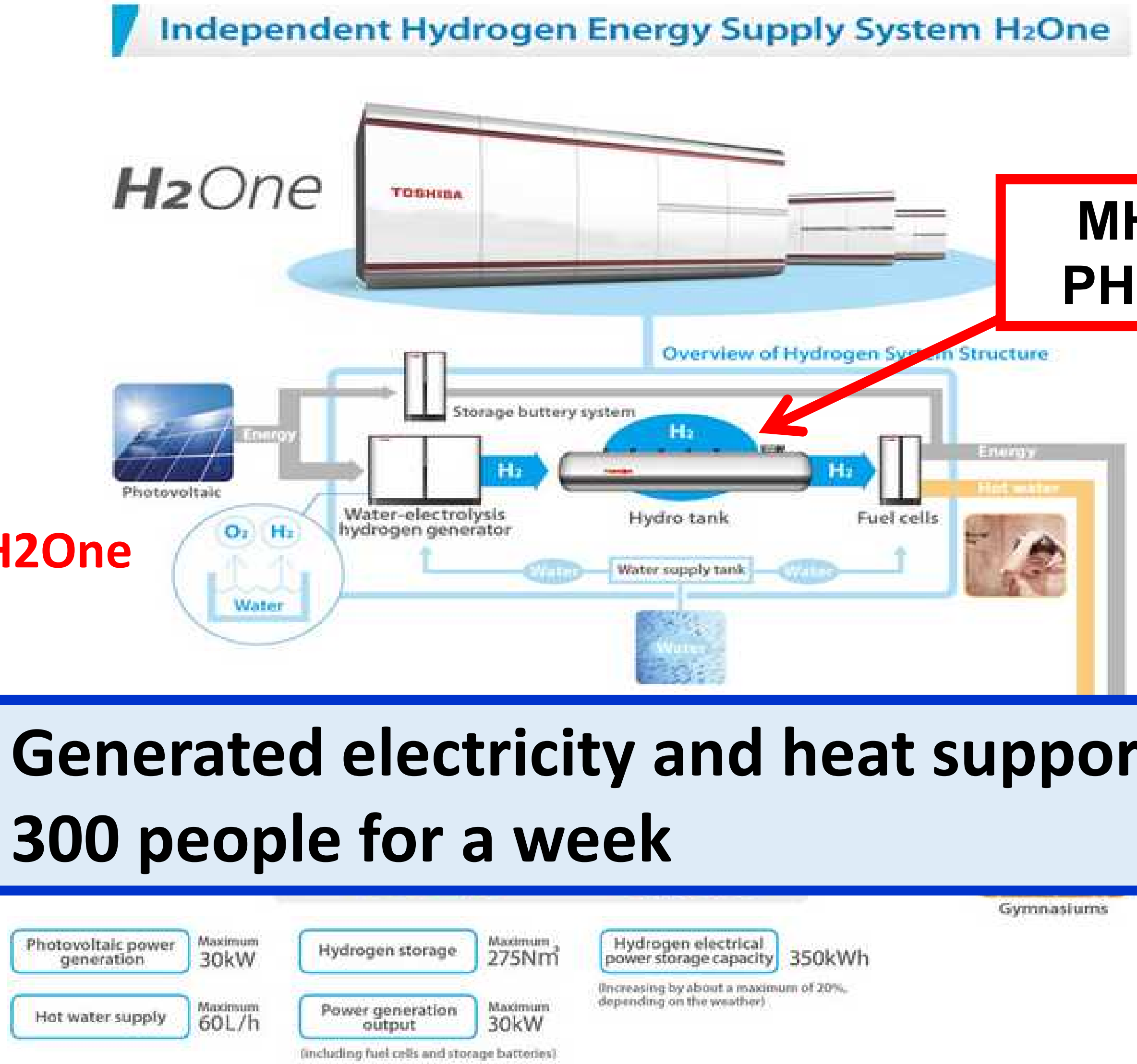
TOSHIBA Stand Alone Hydrogen Energy Supply System

H2One



MH tanks
PH2<1MPa

*) Active use of H2One in Indonesia

Generated electricity and heat support about 300 people for a week

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Toshiba H2One
Stationary and
Mobile use
on rail and road

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In case of Kawasaki City, Kanagawa

Hydrogen Hotel / Waste Plastic / H2

Keihin Industrial Area over Kawasaki and Yokohama, Kanagawa and Tokyo

The World Frist's Hydrogen Hotel operated by *TOSHIBA FC System H2Rex using MH since* 30 May 2018

- Output= 100 kW covering 30% demand of the hotel
- Heat supply= 60℃ hot water
- Electric power generation use >50%
- Total power utility > 95%
- Start-up < 5min
- H2 supply by a 5 km pipe line from an incinerator (waste plastics for NH_3 and H_2 gas) of Showa Denko => using MH storage by DAIWA HOUSE

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Topics : Waste Plastic => Hydrogen

Plastikmuell => H2

United Nations

MSN

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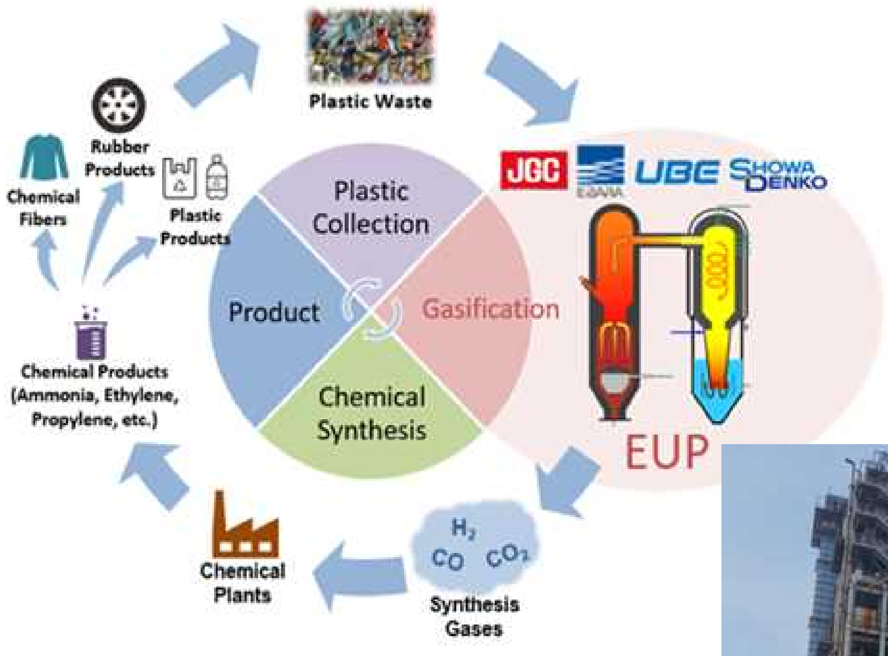
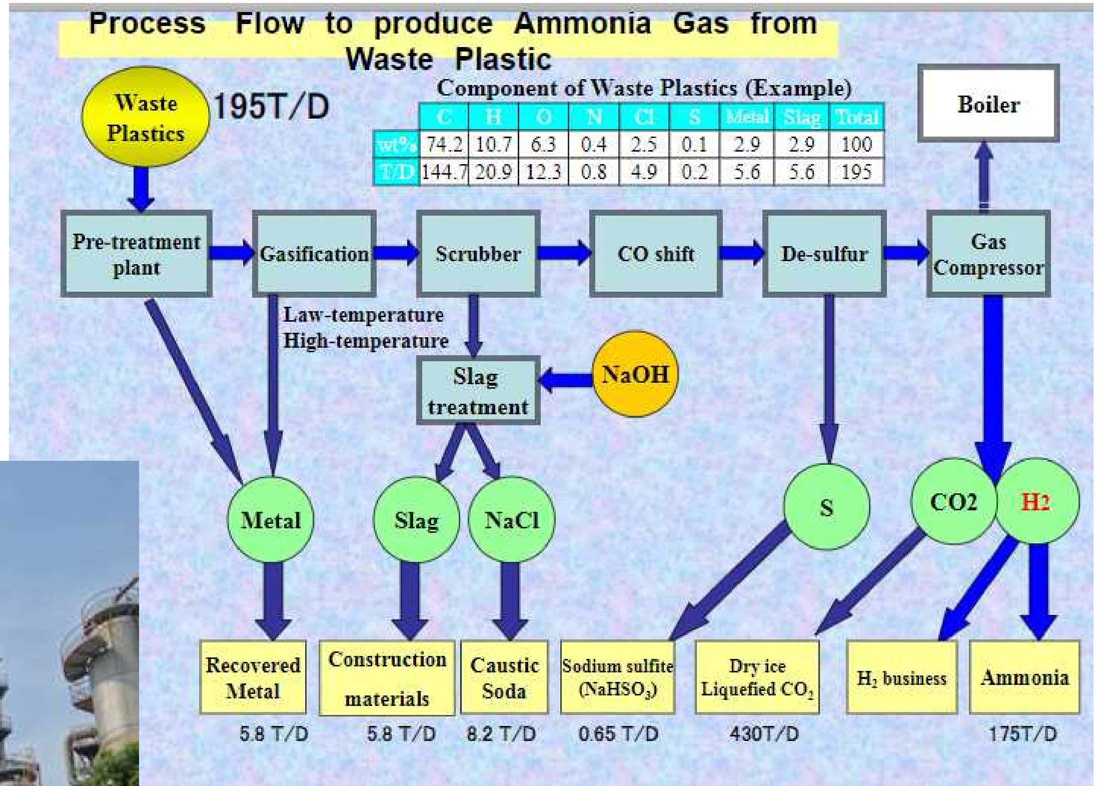
Showa Denko K.K. produces H2 from Waste Plastic at Kawasaki
This is becoming a new business





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Production and Application of Inexpensive Hydrogen Storage Alloys

A New Production Method of HSA

Production & Application of
Nano-structured FeTi Alloy
manufactured by
Mechanical Alloying (MA)

A Ball Milling System for Production of 300kg n-FeTi Alloy

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Ministry of the Environment Japan

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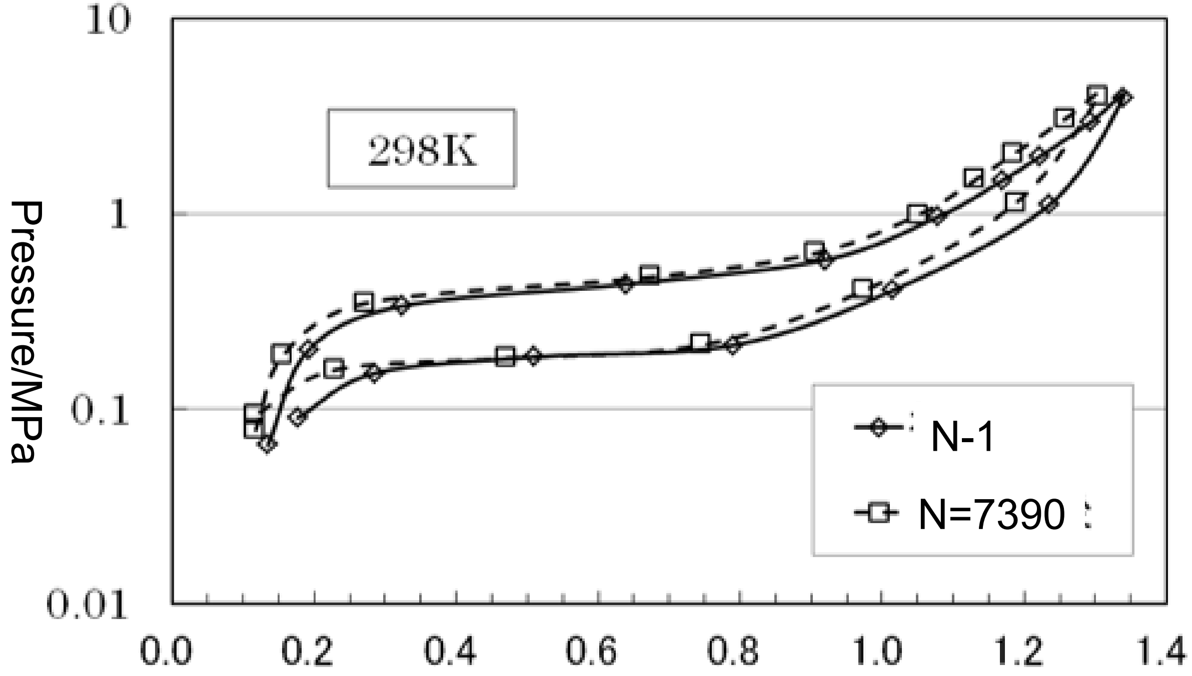
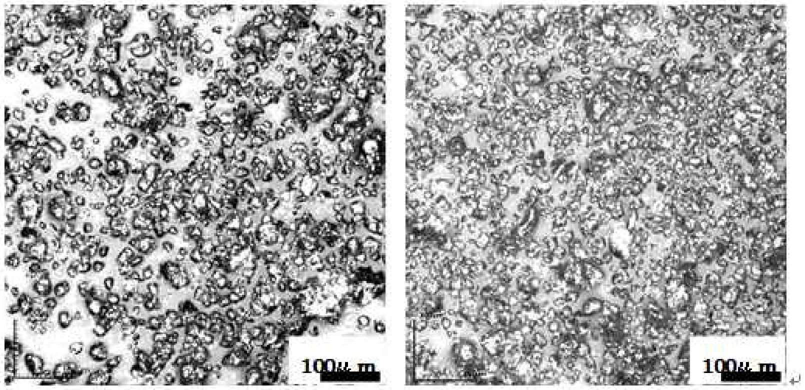
A Ball Milling System for Production of 300kg n-FeTi Alloy

Ministry of the Environment Japan

PCT characteristics of n-FeTi by mass production





Change in alloy particle size after N=7390

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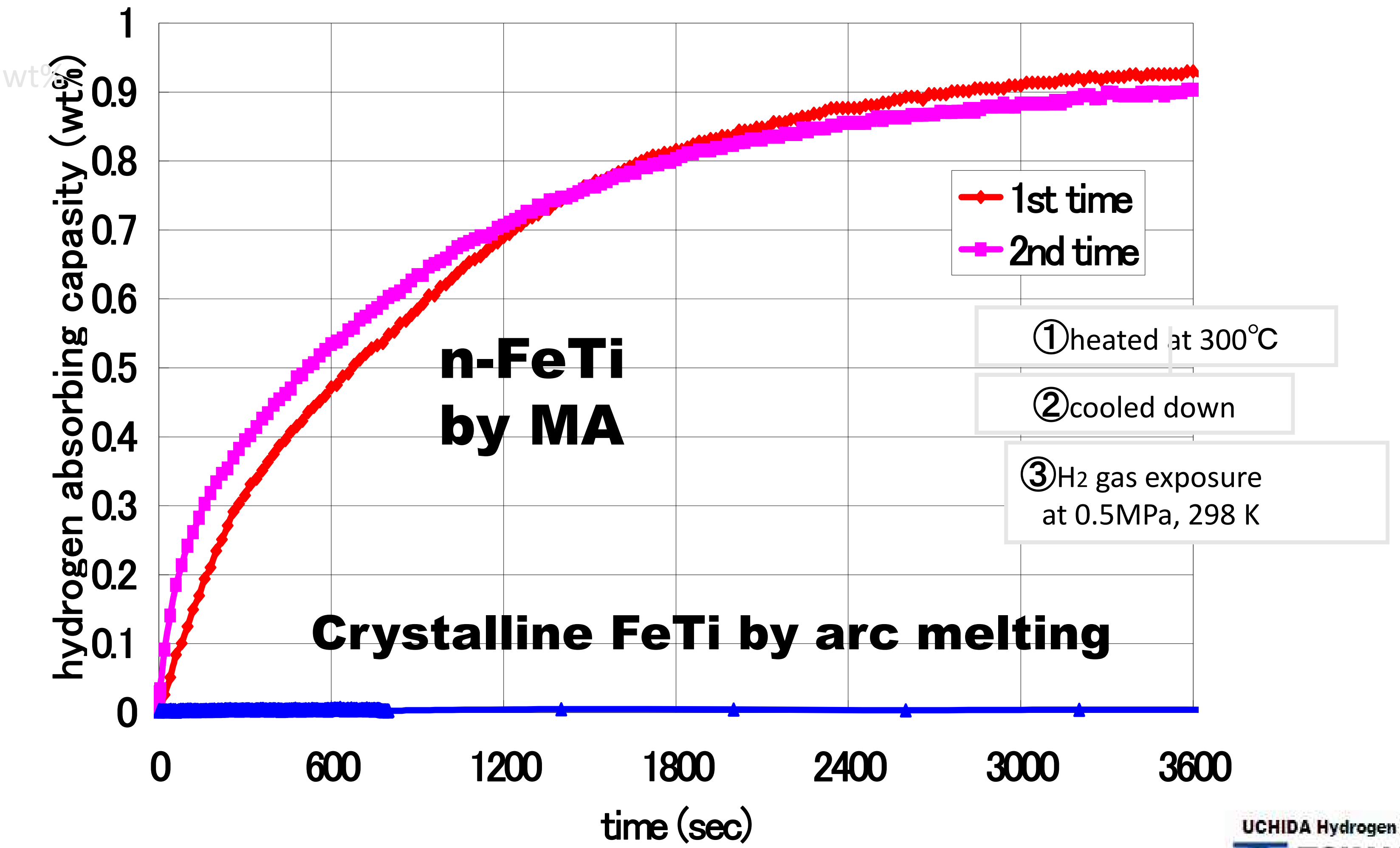
Comparison of the rate of initial activation



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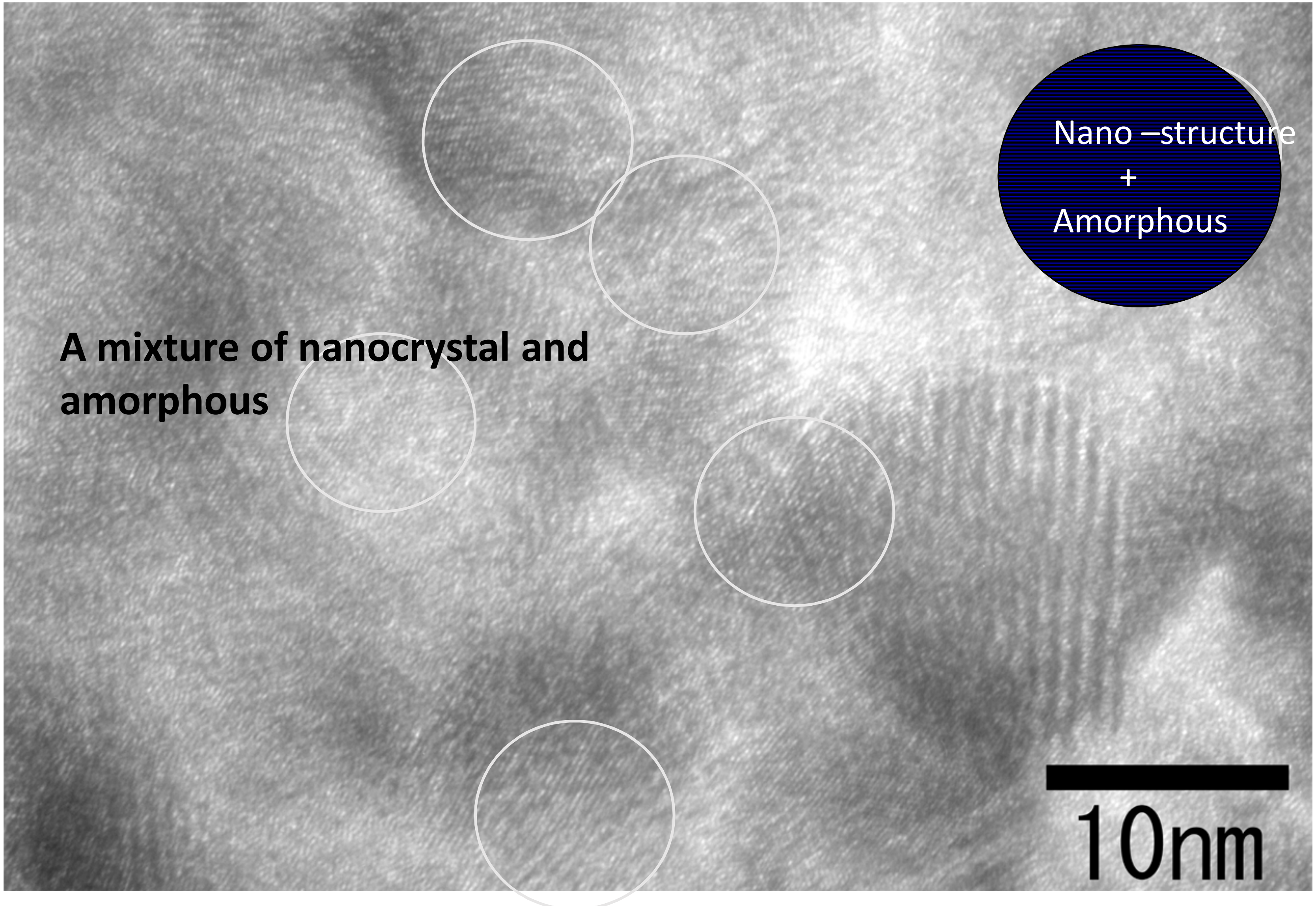

Surface and inside of a n-FeTi alloy particle

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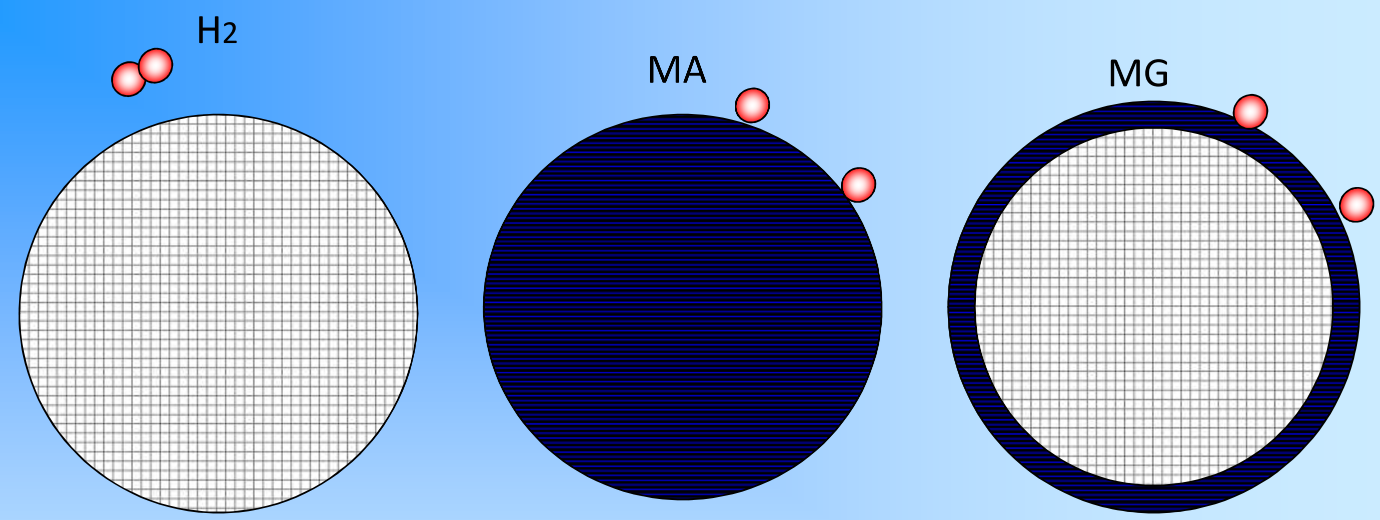
Why nano-structured surface is active with H_2?

Mechanism of H_2 dissociation on surface



FeTi single crystal
with surface oxide layers

No H_2 dissociation

Nano-structured FeTi

Easy H_2 dissociation
but lowered H storage
capacity

Nano-structured
surface layers

Easy H_2 dissociation
with an original
H storage capacity

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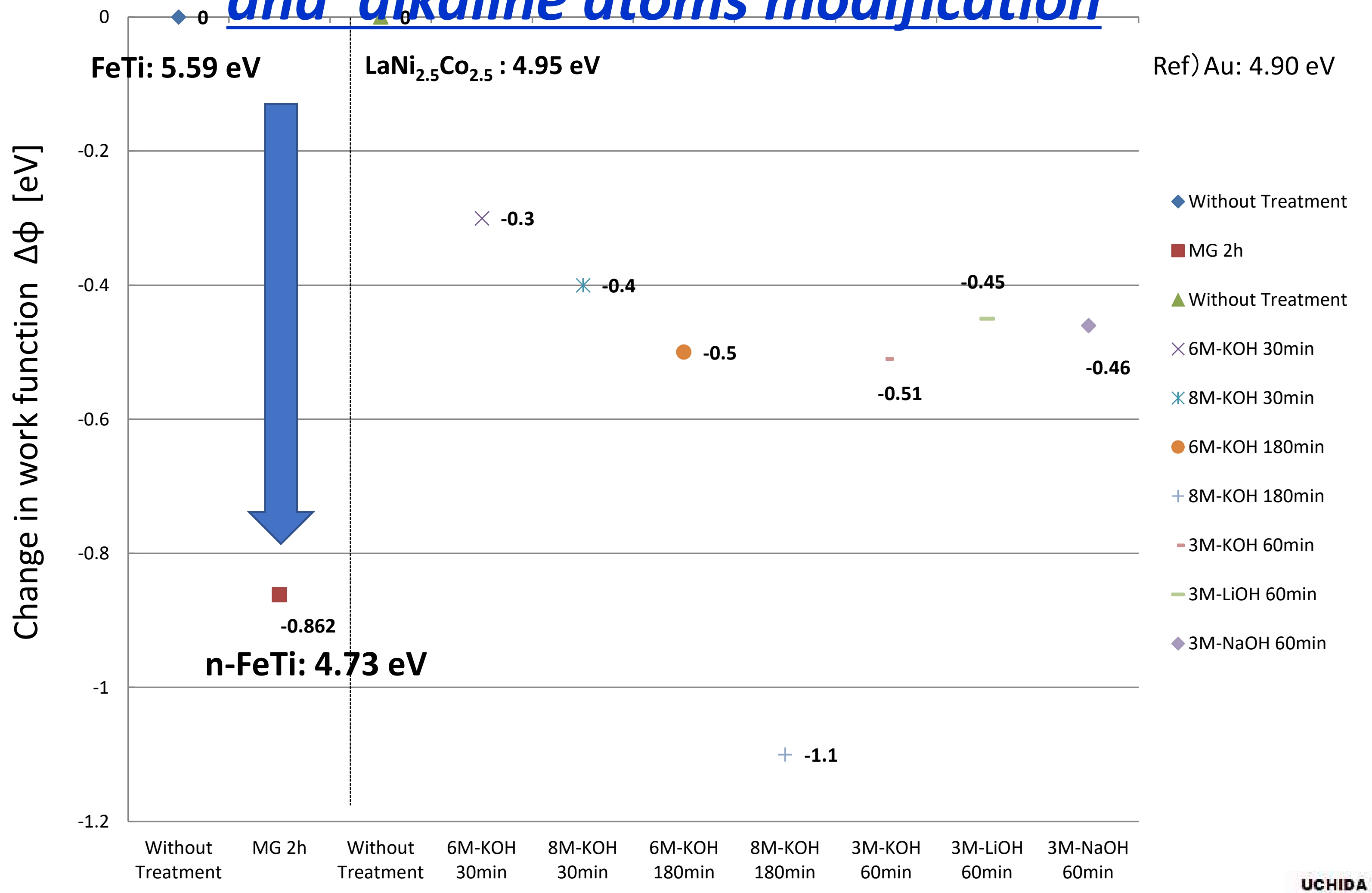
Work function reduction induced by treatments of ***nano-structuring and alkaline atoms modification***



H. Uchida et al, J. Alloys and Compounds 293-295(1999)751-755.
J. Alloys and Compounds 330-332(2002)622-626.

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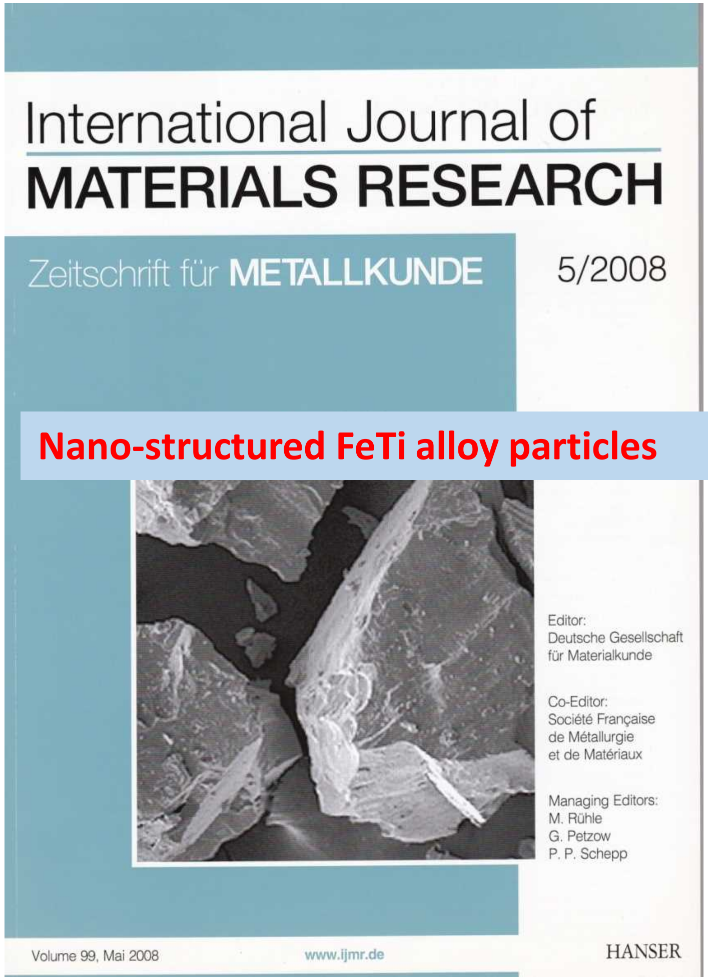
Nano-structured FeTi Hydrogen Storage Alloy :

The commercialized n-HSA for market



Nano-structured FeTi alloy particles

International Journal of
MATERIALS RESEARCH

Zeitschrift für METALLKUNDE

Applied

Takeshi Haraki[b], Keigo Oishi[a], Hirohisa Uchida[a], Yasuo Miyamoto[b], Masatake Abe[c], Takayuki Kokaji[c], Satoshi Uchida[d]

[a] Tokai University, Course of Applied Science, Graduate School of Engineering, Kanagawa, Japan
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[c] NASU DENKI TEKKO Co. Ltd., R&D Department, Tokyo, Japan
[d] Tokyo Metropolitan Industrial Research Institute, Tokyo, Japan

Properties of hydrogen absorption by nano-structured FeTi alloys

Dedicated to Professor Dr. Reiner Kirchheim on the occasion of his 65th birthday

In this study, two different nano-structured samples of the FeTi compound were prepared by mechanical alloying and mechanical grinding. For these samples, kinetics of the initial rate of hydrogen absorption, and the equilibrium hydrogen pressure as a function of hydrogen concentration were measured. Mechanical alloying of Fe and Ti atoms produced the FeTi compound powder samples with microstructures of a mixture of nano-structured FeTi grains and amorphous phases. This sample exhibited a high initial rate of hydrogen absorption even at 298 K, however, a strongly reduced hydrogen storage capacity. Mechanical grinding of the FeTi produced samples of particles with a particular microstructure: surface layers with a mixture of nano-structured FeTi grains and amorphous phases, and a single crystalline phase of FeTi below the surface layers for each particle. This sample exhibited a high initial rate of hydrogen absorption without a significant reduction of the hydrogen storage capacity compared with that of the standard FeTi sample. This mechanical grinding treatment was found to be an effective method of surface modification to improve the initial activation of the FeTi hydrogen storage alloy.

Keywords: FeTi; Nano-structure; Hydrogen storage; Kinetics of hydrogen absorption

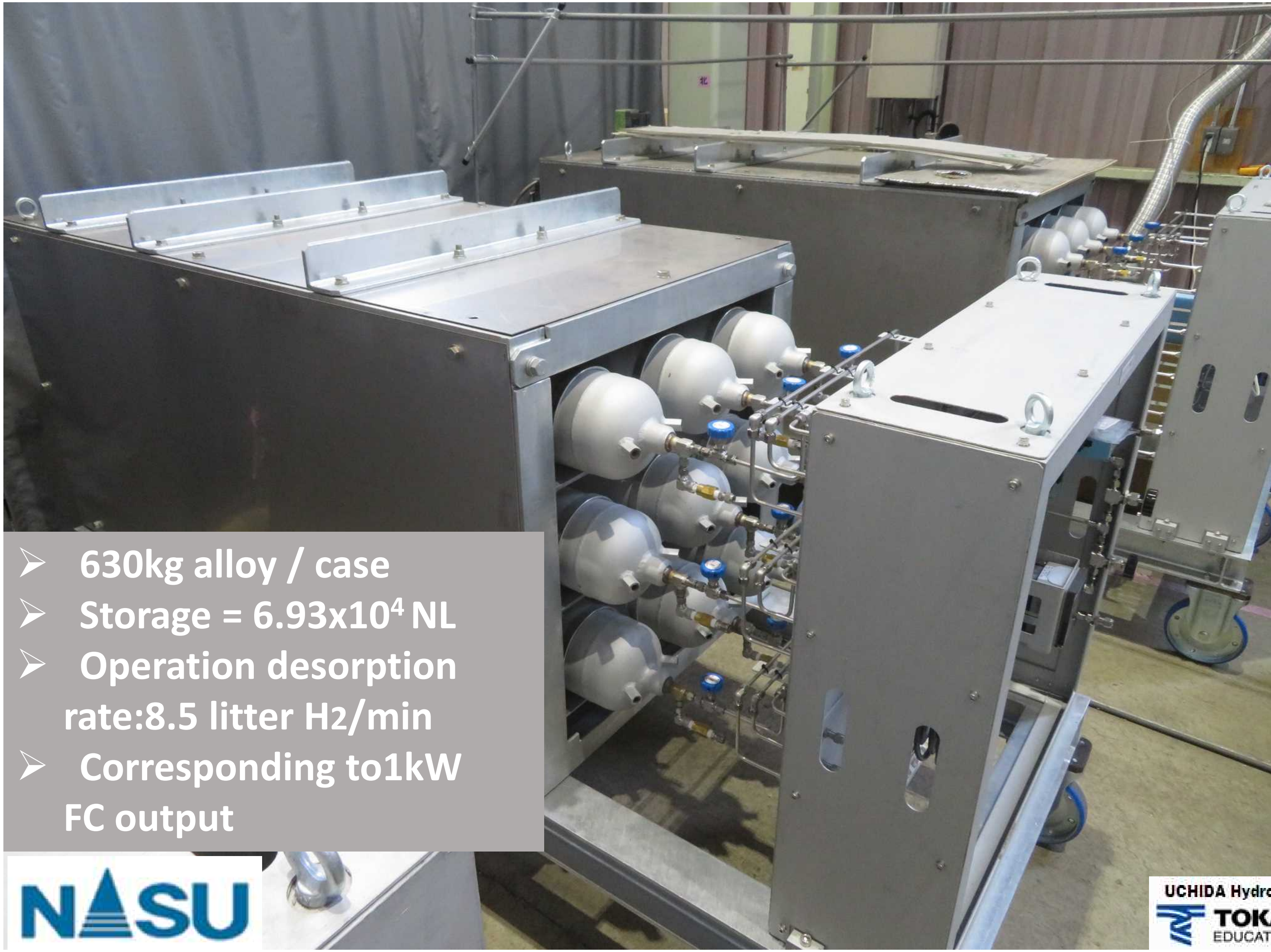
1. Introduction

The FeTi intermetallic compound is one of the most conventional hydrogen storage alloys, and much work has been done since the first finding of this interesting feature of FeTi by Reilly and Wiswall [1]. FeTi is an attractive candidate for practical use as a hydrogen storage material because of its relatively inexpensive material costs and a hydrogen storage capacity around H/FeTi = 1.9.

As is well known, the surface of FeTi exhibits very inactive behaviour on exposure to hydrogen gas. Cyclic hydrogenation–dehydrogenation is needed for the initial activation of FeTi at high temperatures and hydrogen pressures. Attempts to enhance the rate of the initial activation have been made by various methods: the mechanical milling of Mg into FeTi alloys [2]; the partial substitution of the constituent elements by Ni, Mo, Cr [3], Zr [4], Mm [5] or V [6]. Sandrock and Goodell found that the addition of small amounts of oxygen to FeTi enhances the initial rate of hydrogen uptake [7]. Khatamian et al. [8], and Hirata [9, 10] reported that particular oxides at the surface contribute to increasing the initial rate of hydrogen absorption.

Recent studies on the synthesis of intermetallic compounds by mechanical alloying (MA) have been reported [11–13]. The intermetallic hydrogen storage compounds (AB_5, AB, AB_2) prepared by MA showed a significant enhancement in the initial rates of hydrogen absorption [11]. The FeTi alloy forming through MA also tends to exhibit a

Int. J. MATERIAL RESEARCH (Z. Metallkunde) 99(2008)507-512.



- 630kg alloy / case
- Storage = 6.93x10^4 NL
- Operation desorption rate:8.5 litter H_2/min
- Corresponding to1kW FC output

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A typical mobile case of H storage for house/ building energy management

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A Mass Production of n-FeTi Hydrogen Storage Alloy by Mechanical Alloying (MA)

**"R&D Project of
Renewable Energy Storage
by Hydrogen Storage Alloy
Aiming at Effective CO_2 Reduction"**

With CO_2 Reduction Assessment by Life Cycle Assessment

Production Cost < 50% of AB5 (MmNi5)

***Ministry of the Environment, Japan
from 2017 to 2019***

Project of Ministry of the Environment

Since 2018 at Ashikaga University,
Tochigi Prefecture

40 kW wind turbine
10 kW solar cells

Electricity storage and fluctuation response
by n-FeTi hydrogen storage alloy tanks
are being tested.

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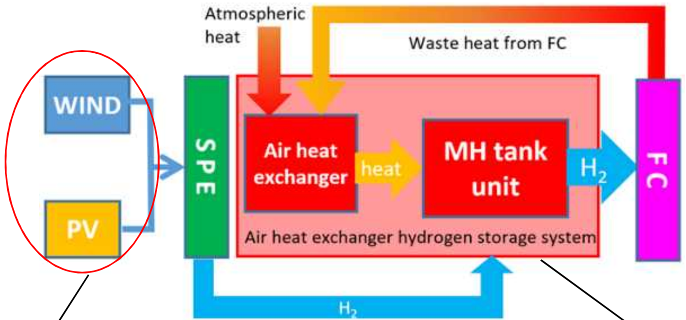
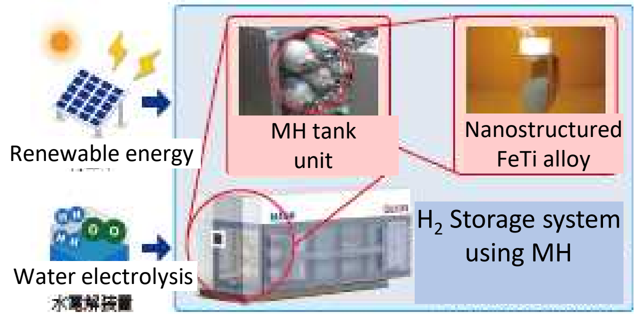
Dynamic Field Experiment of Solar-Wind-FC System using MH

Ministry of the Environment Japan





One MH tank unit:
9 x 70kg FeTi alloy

Two units : 1260 kg alloy

Wind 40kW　　Solar 20kW

An MH system
$72Nm^3(H_2) \times 2$ units

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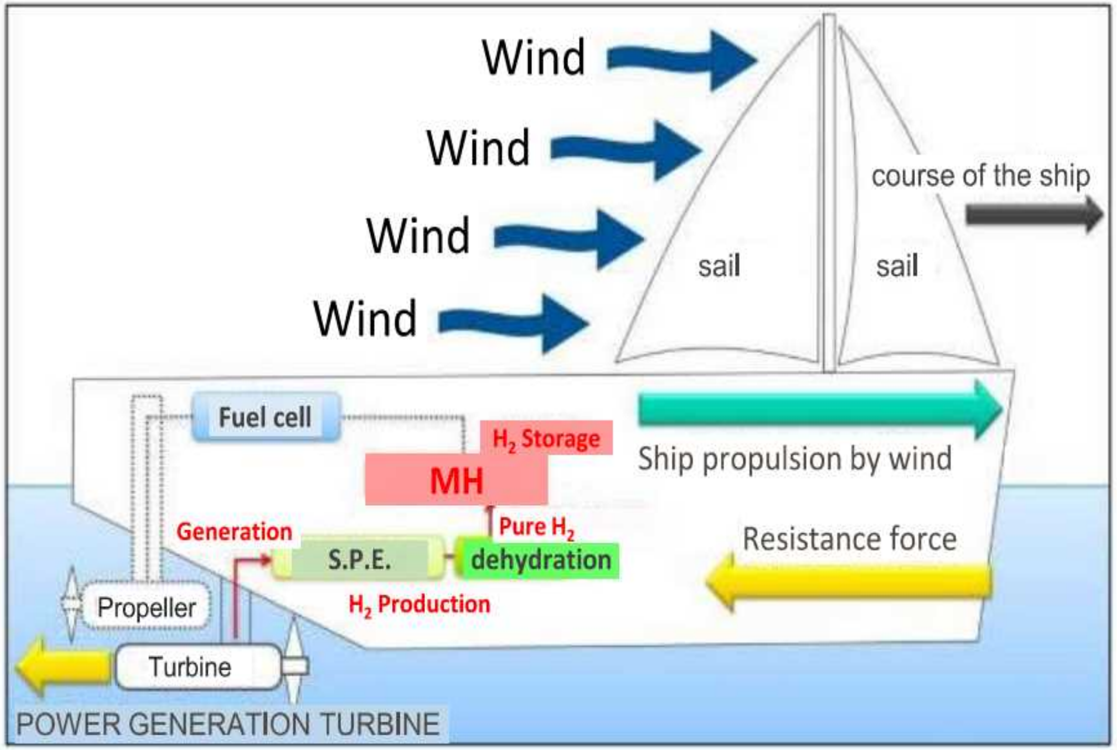
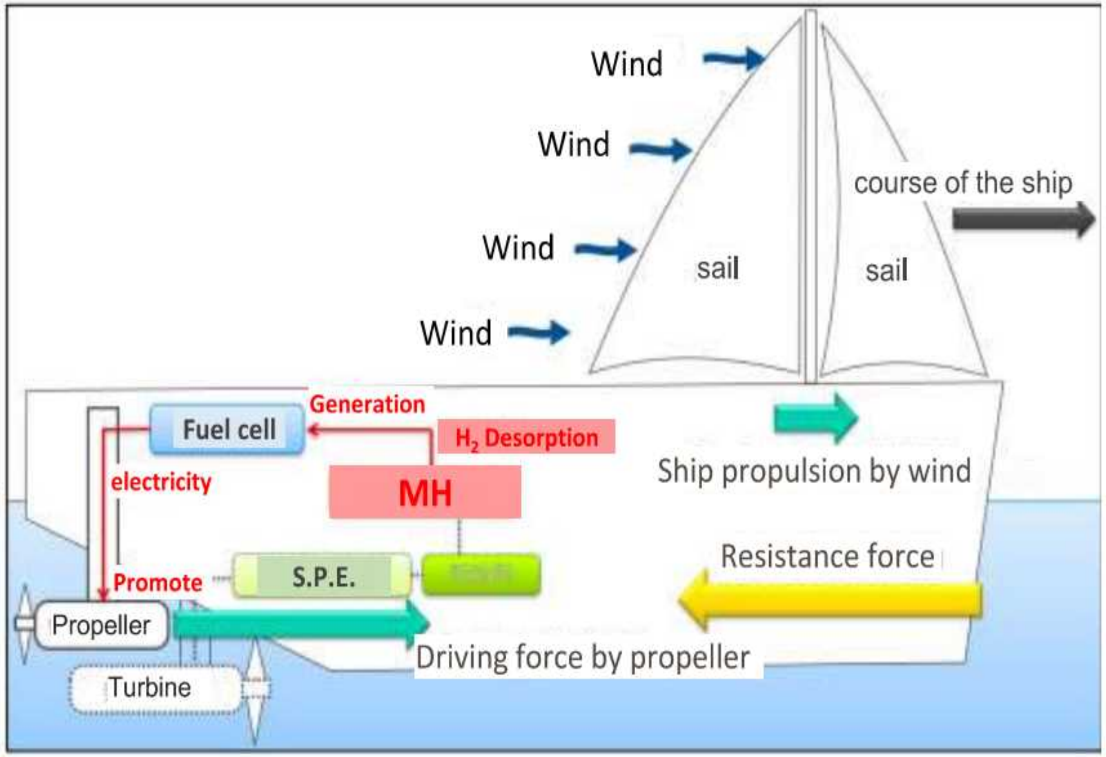
Ongoing Project :MH+FC for Ship Propulsion by Wind
MITSUI O.S.K. Lines + NASU Denki Tekko





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Applications of MH
Utilization of Industrial Waste Heat for Cold Water Production :
Hydrogen Strawberry Cultivation & Fish Breeding

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Reversible Simple Hydrogen Reactions of Hydrogen Storage Alloys (HSA)

HYDRIDING / H_2 ABSORPTION

$M(HSA) + H_2\ (H^+) \Rightarrow MH + Q$: Exoth.

DEHYDRIDING / H_2 DESORPTION

$M(HSA) - H_2\ (H^+) \Leftarrow MH - Q$: Endoth.

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Reversible Simple Hydrogen Reactions of Hydrogen Storage Alloys and Reversible Heat Reactions of HSA

HYDRIDING / H_2 ABSORPTION

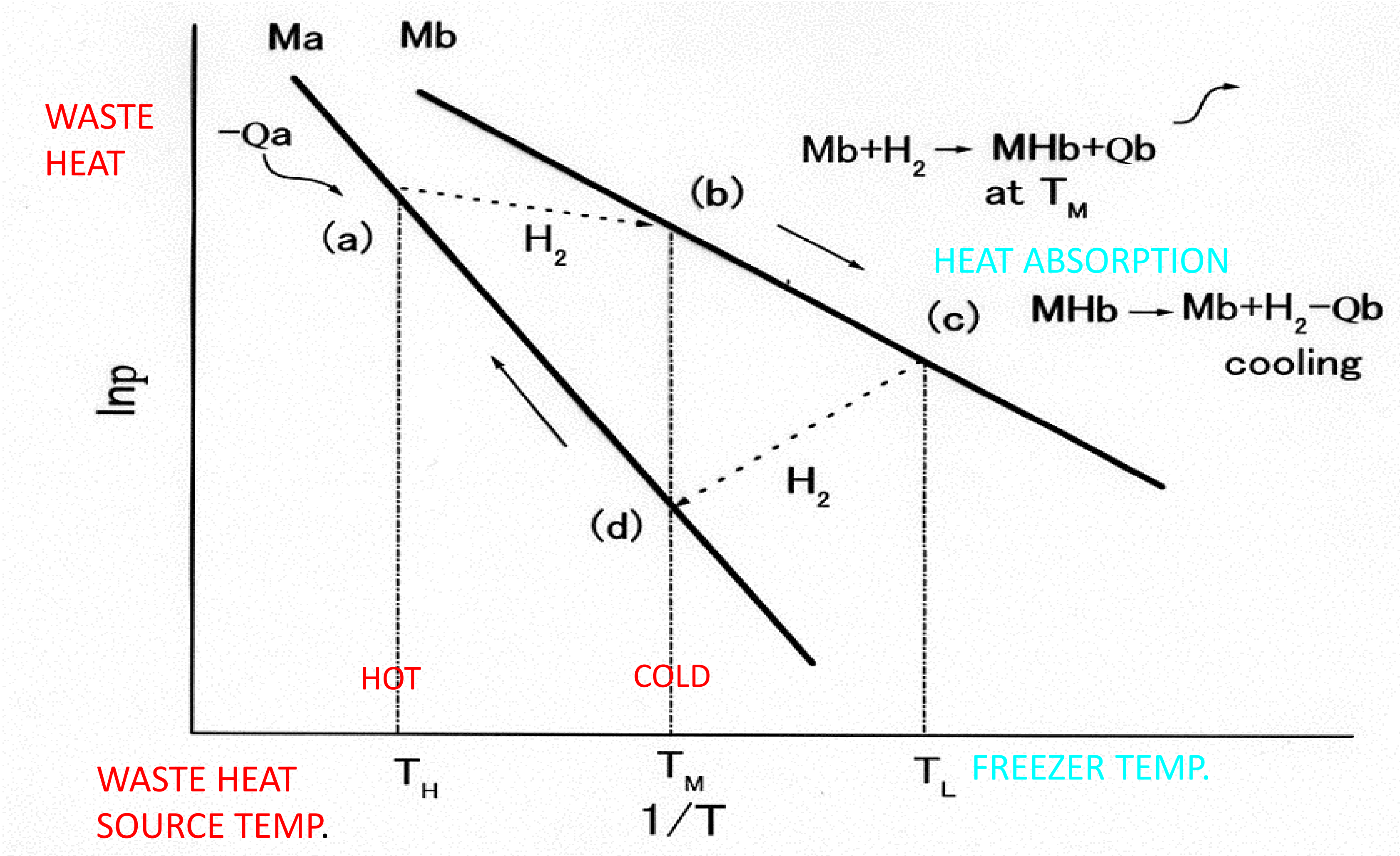
$M(HSA) + H_2\ (H^+) \Rightarrow MH + Q$: Exoth.

Heating

DEHYDRIDING / H_2 DESORPTION

$M(HSA) - H_2\ (H^+) \Leftarrow MH - Q$: Endoth.

Cooling



The operating principle of a MH freezer

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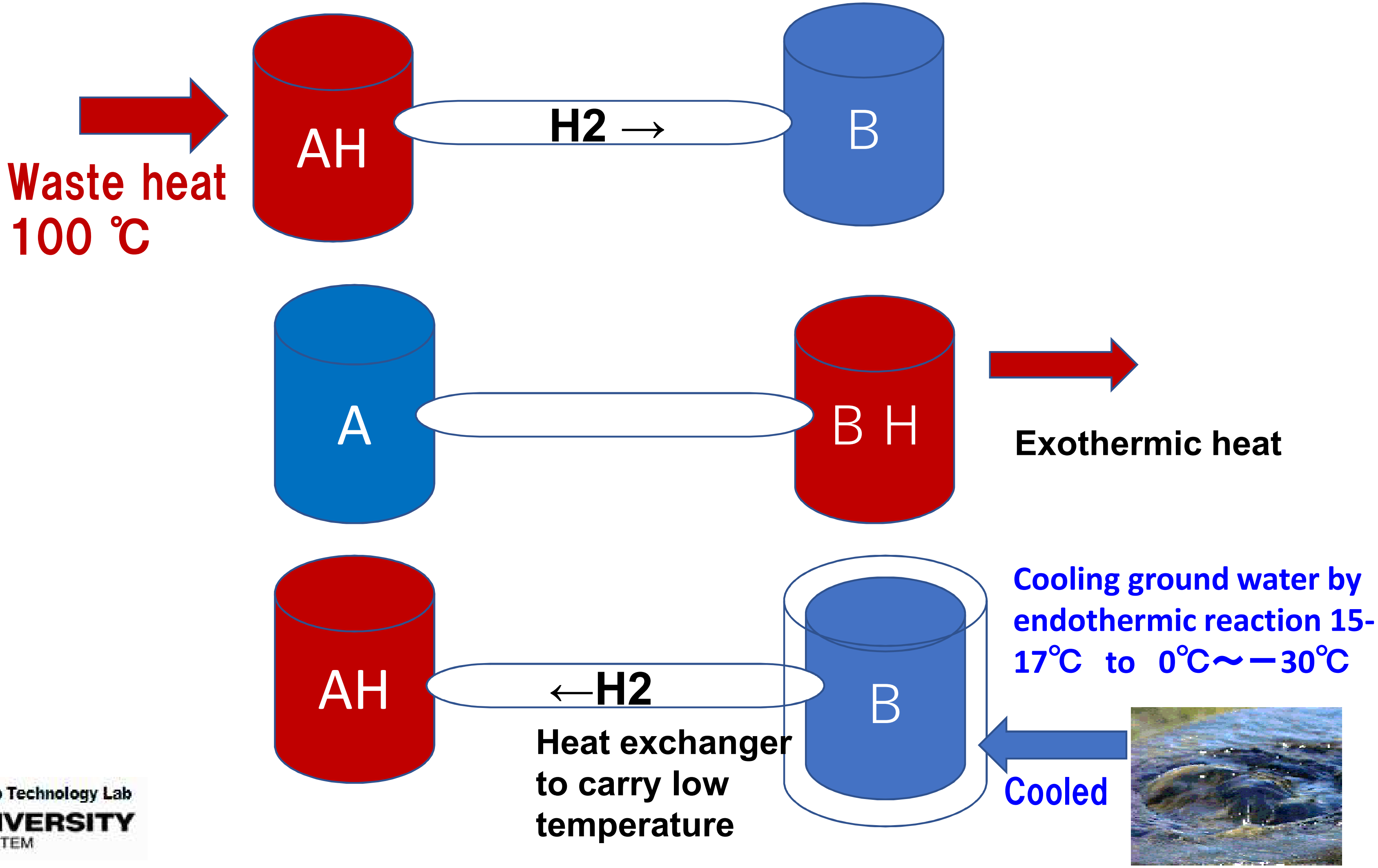
MH Refrigerator System using Waste Heat



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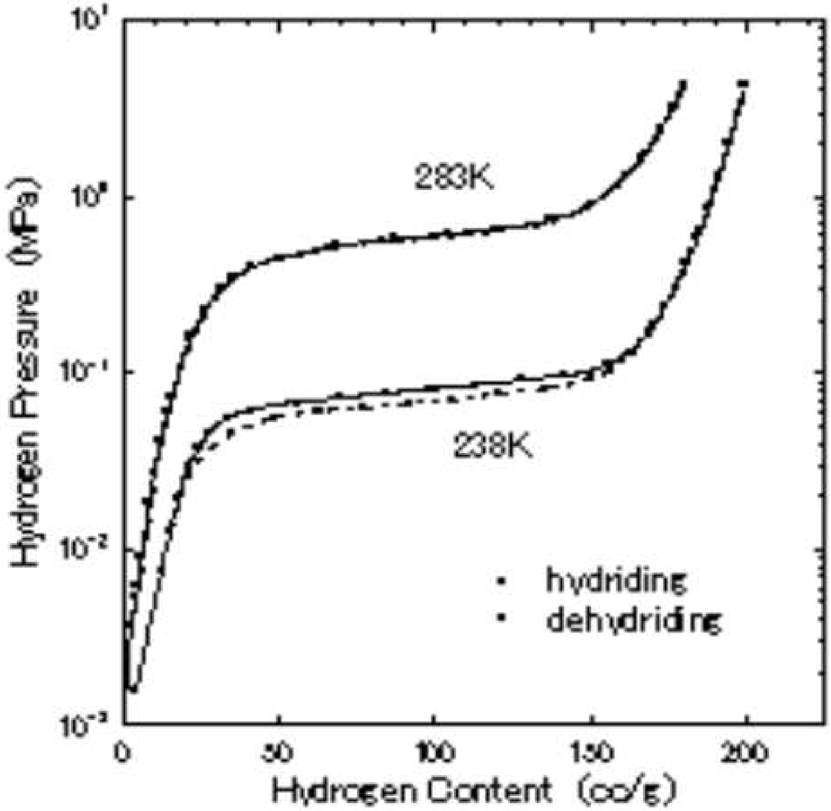

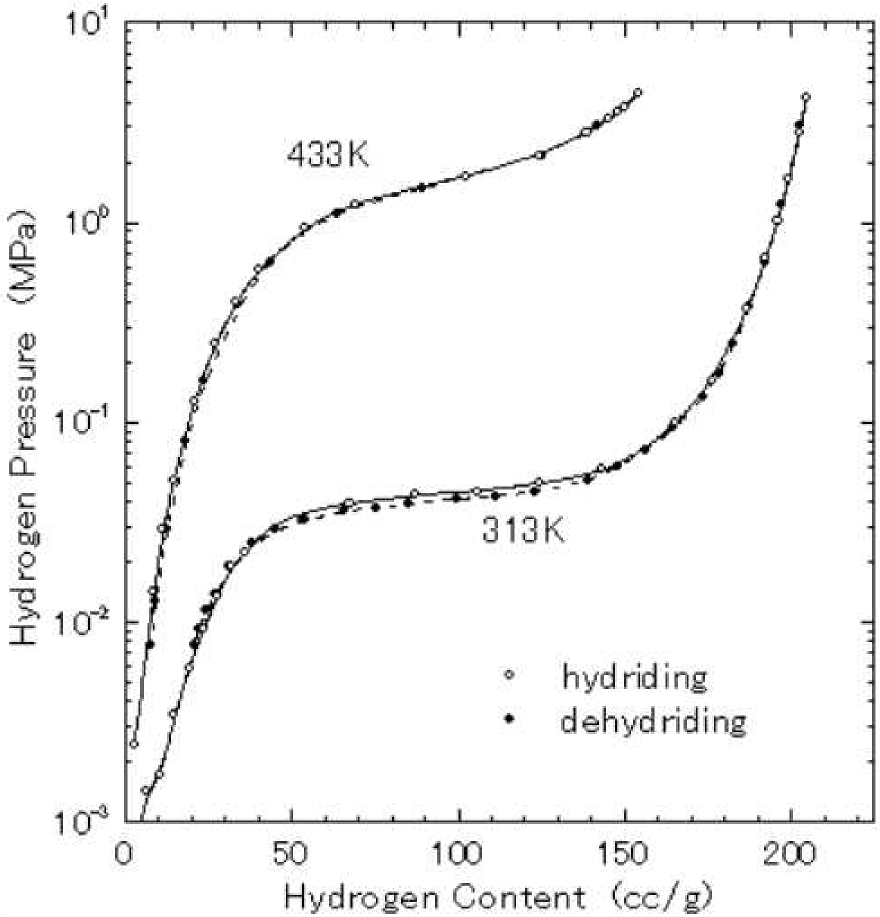

LOW TEMP. ALLOY Mb

Pressure-composition isotherms of a Ti-Zr-Cr-Fe-Ni-Mn-Cu alloy Japan Steel Works

HIGH TEMP. ALLOY Ma

Pressure-composition isotherms of a Ti-Zr-Mn-V-Fe alloy Japan Steel Works

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Saijo's first MH freezer system supported by METI

2001

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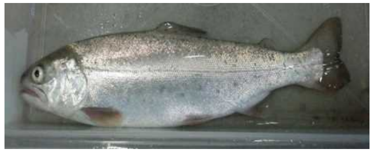
Fish Cultivation

<Left> An on-land fish cultivation facility with a area of 144 m^2
with 4 x 5 tons water tanks at 5 ℃.

<Right> A 5 ton water tank for on-land fish cultivation. Controlled ±1 deg.



40cm

Hydrogen SATSUKI Trout

Additional 3 freezers(3x1.2 USRT) are being operated to produce cold water in Saijo using waste heats from industrial factories.

Metal Hydride Freezer systems（JSW）

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MH Freezer Systems
highly energy saving and effective CO2 reducton

- **Compared with conventional cooling using electric chillers, an MH cooling system saves energy and CO2 reduction**

  more than 80%

  because the MH cooling system uses waste heat from the primary energy to absorb heat and to produce cold water by chemical hydrogen reactions of metal hydrides.

Concluding Remarks

- **Hydrogen utilization technology is not limited to FC, but is extremely diverse.**

- **Waste heat from industrial sectors can be applied to produce freezer or cold water, i.e., for agriculture/fish breeding.**

- **Waste heat utilization using hydrogen storage alloys has high energy saving and CO_2 reduction effects.**

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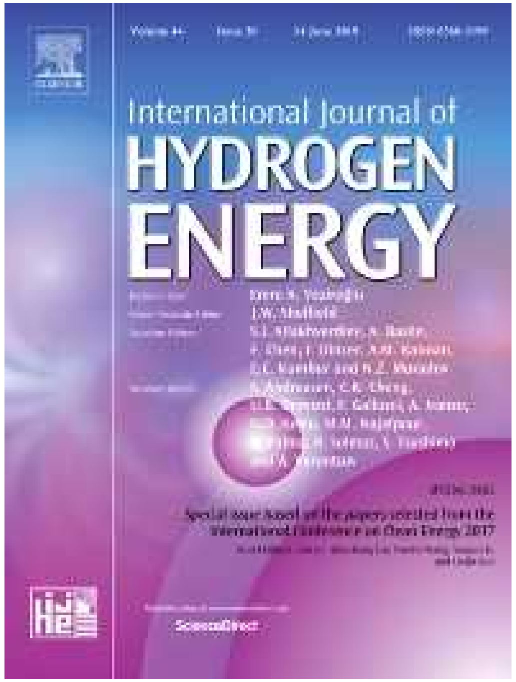
Thank you for your attention!

We IAHE hold WHEC 2022 in Istanbul.
The 23rd World Hydrogen Energy Conference,
26-30 June 2022 – Istanbul, Turkey



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