

11. Task 1 1 Development of Hydrogen Storage Materials

11.1 R&D Goals

In fiscal year 2001, the following three activities were performed :

- (1) Research and development for promising alloys and technologies with WE-NET target performance
 - Effective hydrogen storage capacity : more than 3 mass%
 - Temperature for hydrogen desorption : 100 or below
 - Durability : hydrogen storage capacity more than 90 % of the initial capacity after 5,000-cycle use
- (2) Investigation and inspection of new carbon materials and others

11.2 Achievement of research and development in fiscal year 2001

In the fiscal 2001, following three items were conducted: improvement of capacity and endurance of V-base and Ti-Cr base alloys developed in the previous year, research for next generation alloys with more than 5 mass% capacity, start of research for chemicals and carbonaceous materials

11.2.1 Metal Hydride

11.2.1.1 Improvement of capacity and endurance of developed alloys

(1) V base alloys

Practical properties of the novel alloys of V-10 at%Ti-12.5 at%Cr-3 at% Mn alloy and V-10 at%Ti-11 at%Cr-2 at%Mn-1.5 at% Ni with a very large effective hydrogen capacity were investigated. These alloys showed neither pyrophoricity nor ignitability while conventional practical hydrogen storage alloys of AB₅ and AB₂ types are dangerous substance, and a good durability for 1,000 charge/discharge cycling. Although the hydrogen capacity was decreased by oxidizing gas such as O₂, CO and CO₂, it was recovered by flashing treatment with pure hydrogen gas. The hydrogen reservoirs using these both alloys were demonstrated to have larger hydrogen volume- and mass-capacity than using conventional best alloy.

(2) TiCrMo alloys

In this year, the hydrogenation property of Ti-Cr alloys was improved by changing producing condition and added element. Floating zone (FZ) method is greatly effective on improving the capacity of developed Ti-Cr alloys and we can expect to reach the goal of 3 mass% or more effective hydrogen storage amount

(3) Durability Tests for Hydrogen Storage Alloys

In this work, some hydrogen storage alloys developed in WE-NET have been investigated on durability thereof. All tests were carried out at temperatures

between 293 and 353 K and at H₂ pressures between vacuum (less than 1 hPa) and 4.5 MPa. Every alloy is examined its degradation of characteristics during 1,000 cycles of absorption and desorption.

11.2.1.2 Research for next generation alloys with 5 mass% (provisional) capacity

(1) Enlargement of plateau of V base alloys

In FY2000, new alloys of V-Cu-Ni and V-Cu that have a monohydride and dissociate hydrogen at 140 °C around 0.1 MPa were found in WE-NET. In FY2001, we searched for alloys that formed monohydride and dihydride and can dissociate hydrogen at lower than 140 °C around 0.1 MPa from both hydrides. However such alloys were not found. The alloys which formed dihydride were found not to have monohydride which dissociated hydrogen at lower than 140 °C.

We succeeded in producing nano order thin foil laminates by cold rolling method. The hydrogen storage properties of this super-laminate of V-15 at%Pd were similar to that of casted V-15 at%Pd instead of vanadium. However, the super laminates of V-25 at%Pd had a two-step plateau on the PCT curves and the monohydride dissociated at 140 °C around 0.1 MPa.

(2) CaMg₂ alloys with nano size composite structure

New alloy with fine composite structure of CaMgNi₄(1.0 mass%, hydrogen desorption temperature: 70 °C) and CaMg₂ (5.4 mass%, 350 °C) was produced by ball-milling method. This composite material showed hydrogen desorption, which was not observed in single phase of CaMgNi₄ or CaMg₂ and this composite method is expected to be a new method for improving the hydrogen desorption rate of Ca-Mg system.

(3) New alloys of Ca-Mg system

An alloy, which contains CaMg₂ phase that is one of Mg-Ca-Ni system, has been investigated to improve the absorption/desorption property with some additives. In this research, the (Ca_{1-x} A_x)Mg₂C_z alloy that can absorb 4 to 5 mass% at 25 °C was found. This alloy did not disproportionate after hydrogen absorption.

(4) Ti base alloy designed with the space factor principle

We utilize a space factor as a guiding principle for searching new hydrogen storage materials. The space factor is defined as an average space size per atom in a compound. We found that the average space size of several hydrogen storage alloys ranges from 0.013 nm³ to 0.015 nm³, and has a correlation with the hydrogen pressure and capacity. We can succeed in increasing hydrogen pressure of a Ti-V binary alloy by reducing the space factor to 0.01552 nm³ by Al and Ni addition (Ti_{0.44}V_{0.39}Al_{0.07}Ni_{0.10}). Consequently, we ascertained that the adjustment of the space factor corresponding to the above criterion is effective to obtain a new hydrogen alloy

with the capacity beyond 5 mass%.

(5) New Mg alloys

Mg-Ti system alloys were investigated in order to create new alloys that have a possibility of achievement of 5 mass% capacity. Until now, the BCC structure Mg-Ti alloy does not exist. However Mg-Ti alloy with BCC structure and α -Ti solid solution consisted of Mg and Ti were successfully synthesized by ball milling of Mg and Ti powders for 7.2×10^5 s under argon atmosphere. The composition of the BCC phase and α -Ti solid solution were $Mg_{1-x}Ti_x$ ($x=0.34-0.62$) and $Ti_{1-y}Mg_y$ ($y<0.2$), respectively. This BCC alloy is expected to absorb hydrogen in large amount because the alloy consisted of light-weight hydrogen absorbing elements.

(6) Ternary R-Mg-Ni alloy

Recently, it has been reported that pseudobinary $MgNi_2$ - YNi_2 and $NgNi_2$ - $CaNi_2$ alloys take the C15b structure and can absorb-desorb hydrogen reversibly. In the present work, $MgRNi_4$ ($R=Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm$ and Yb) alloys were prepared and structures of these alloys before and after hydrogenation were identified. It was found that these ternary C15 Laves phases with the atomic radius ratio larger than 1.37 can keep their crystal structure and less than 1.37 amorphize by hydrogenation. The hydrogen content increased with increasing the lattice constant of $MgRNi_4$ alloys. Therefore the atomic radius ratio plays the important role and alloys of $R=Y$ or Tb with relatively small lattice constant is expectable for absorbing hydrogen.

(7) Improvement of hydrogen desorbing kinetics of Mg alloys

The $Mg_{85}Ni_{10}Nd_5$ alloy that can readily absorb about 5 mass% hydrogen at 373-573 K and can fully desorb it with a moderate speed at 453-573 K in vacuum has been developed. This alloy has a composite-phase structure in which Mg_2Ni and Nd-hydride particles, ~ 1 nm and ~ 30 nm in diameter, respectively, are precipitated uniformly in the Mg matrix phase with nano-grains of ~ 5 nm. This refined microstructure, coupled with a catalytic action of Nd-hydrides, strongly enhances the absorption/desorption kinetics. However application of this alloy to hydrogen reservoir is difficult because of its low adsorbing pressure.

(8) New magnesium intermetallic compounds including Ge

New intermetallic compounds including group 14 elements which bond with hydrogen covalently, such as Mg_2Ge , were synthesized by mechanical alloying. The mechanically alloyed Mg_2Ge absorbs and desorbs hydrogen reversibly at moderate temperature, though the amount of hydrogen was small. The amount of hydrogen released from the compound was enhanced by addition of nickel. The tendency was

remarkable at the composition of $\text{Mg}_2\text{Ge}_{0.8}\text{Ni}_{0.2}$ (the composite of Mg_2Ge and Mg_2Ni).

(9) Formation of unstable hydrides by electrochemical charging

Previous works on preparing non-stable hydrides (hydrides with high dissociation pressures) by electrochemical charging were reviewed and extensive studies were carried out on some iron alloys. Some iron alloys that were strongly distorted by coherent nitride particles were electrochemically charged in a similar way employing a KOH electrolyte and the formation of their hydrides were tested. The particle-dispersed iron absorbed hydrogen, however the amount was small. It was suggested that the characteristics of electrolyte is very important for the formation of unstable hydrides (FeH).

(10) High-pressure Synthesis Novel Hydrides in Mg-M Systems

New hydrides in Mg-M (M = Ca, Y, Mn) systems have been prepared at GPa order high- pressure by using a cubic-anvil-type apparatus.

In MgH_2 -x% CaH_2 system, $\text{Mg}_{1-x}\text{Ca}_x\text{H}_2$ (x=0.4-0.6) was synthesized at 1,223 K, 5 GPa. The decomposition temperature of the new hydride was 646 K.

In MgH_2 -x% YH_3 system, new hydride of a FCC-type structure was synthesized nearby x = 67 (MgY_2H_x) at 3 GPa or higher.

The Mg_3MnH_x phase exhibited a different crystal structure from Mg_3MnH_7 that has been synthesized at 1,073 K for 2 h under 2 GPa. The decomposition temperature of the hydride was 620 K. And its hydrogen content was found to be 3.69 mass%, corresponding to $\text{Mg}_3\text{MnH}_{4.86}$.

(11) Hydriding properties induced by the interaction between inter- and intra-nanostructured grains

Nanostructured vanadium-hydrides were prepared by mechanical milling under hydrogen atmosphere. The hydrogen concentration in the grains x_G decreases with decreasing grain size from $x_G = 0.82$ in 80 nm grains to 0.72 in 10 nm grains. The hydrogen concentration in the intergrains, x_{IG} 0.5-0.6, is smaller than in the grains, and nearly independent of the grain size. The hydrogen diffusivity in the intergrain regions measured by NMR is substantially higher than inside the grains. The exchange of hydrogen atoms between the grains and the intergrain regions occurs very slowly.

(12) Nano-composite Mg thin film

The nano-composite Pd-Mg multi-layer film that absorbed 4.4 mass% of hydrogen for Mg and all the hydrogen desorbed at temperature lower than 120 have been reported. Using an in-situ system, the Pd(50nm)/Mg(200nm)/Pd(50nm), Pd(10nm)/Mg(200nm)/Pd(10nm) films were prepared and hydriding properties of them were

examined. Hydrogen can be desorbed at temperature lower than 150 °C even after 10 times hydriding-dehydriding reaction.

(13) Be₂Ti alloy

Be is categorized as a specified chemical and regulated legally. However Be is very stable metal chemically and really generates toxic substances. In the case of vehicle part materials, some risks might be assumed but we could take measures to meet them.

Be₂Ti alloy can be produced by melting-heat treating-pulverizing process. In the materials prepared this time, metallic Ti exists and it spoils the hydrogen absorbing properties of the alloy. Some improving of production conditions may be required in next trial. In hydrogenation at 200 °C, 10 MPa (these are not the best conditions), these samples absorbed 1.4-1.5 mass% hydrogen, which is less than the amount of 4.4 mass% reported in the paper.

11.2.2 Chemicals for hydrogen storage

In WE-NET two kinds of chemicals, hydrogen complex compound and naphthenes, are studied as 5-8 mass% hydrogen storage materials that can be used repeatedly.

11.2.2.1 Hydrogen complex compound

(1) NaAlH₄ for hydrogen storage material

The kinetics of the reverse hydrogenation reaction have been determined over a range of temperatures and H₂ pressures and acceptable charging capacities rates at temperatures as low as 100 °C under 10 MPa of H₂ have been observed. From the thermodynamical analysis it becomes clear that the kinetics of hydriding of doped mixtures Na₃AlH₆ and Al to NaAlH₄ are limited by the micro-reverse, of the fundamental, Al-H bond breaking process. Some useful technology for rehydriding might be developed from this viewpoint. A long duration hydrogen cycling study of the hydrogenation reaction and its reverse are also conducted. To date 3.0 mass% hydrogen has been discharged and re-charged in 24 cycles with no loss of capacity.

(2) Novel complex-type hydrogen storage material

A vibrating-milling technique for 1 hour was used to prepare titanium (III) chloride (TiCl₃ 1/3AlCl₃)-doped LiAlH₄ powder nanocrystallites. This mixture started to release hydrogen from 100 °C on the first heating process in hydrogen atmosphere at a pressure of 4 MPa. On the following cooling process, an exothermic thermal effect that indicates hydrogenation of the decomposed material on the heating process, LiH, to Li₃AlH₆ was appeared. Further study on reversible dehydrogenation of LiAlH₄ through optimization of preparation process and investigation of reaction mechanism would contribute to development of a lighter hydrogen storage system.

(3) Safety dealing with NaAlH₄ and disposal condition

The objectives of this study are clarifying the properties of NaAlH₄ and collection of the data to design hydrogen storage tank. NaAlH₄ is highly flammable solid and reacts violently with water or other oxidizer. The results of reactivity test with some liquid material, i-propanol showed relatively mild reaction and silicone oil showed no reaction with Ti-doped NaAlH₄. Safety manual dealing with NaAlH₄ and disposal condition were established.

(4) NaAlH₄ System for Hydrogen Storage

Design and fabrication of the equipment, which has 10 g reactor and 100 g reactor, for investigation of dehydriding/hydriding properties were performed. The result of the investigation with 10g reactor in first stage of hydrogen release shows very low reaction rate for ordinary Ti-doped NaAlH₄ at 100 °C. Hydrogen transfer remains only 63% of theoretical value, however deterioration with cycle was not observed. These results show the possibility of NaAlH₄ application for hydrogen storage tank.

11.2.2.2 Hydrogen transport and storage using naphthenes

Naphthenes like cyclohexane are very promising as chemical carriers for transporting and storing hydrogen because their hydrogen contents are exceeding 7 mass% and they are in liquid state at room temperature like gasoline.

(1) Research for hydrogen transport and storage system of cyclohexane

The major technical problem involving this system is how the hydrogen can effectively be taken out of naphthenes in the dehydrogenation process, which is limited by thermodynamic equilibrium. First, the type of membrane reactor is discussed from the viewpoint of obtaining an equilibrium shift as well as pure hydrogen. For such a purpose, it is found that a membrane reactor using palladium membrane is the most suitable. Next, selection of a better operation manner of the palladium membrane reactor is made. The reaction should be carried out under an elevated pressure so as to keep the partial pressure of hydrogen higher than the pressure on the perm-side. Then experiments with cyclohexane dehydrogenation at 0.1-0.3 MPa are carried out to establish the rate of reaction, which is needed for the reactor modeling.

(2) Phase behavior for solid-liquid equilibrium of naphtene system

At first, some physical properties of the pure compounds were cited. However, there is no report for other two systems at all except the data for benzene + cyclohexane system. Thermodynamic model was applied to predict the solid-liquid equilibria. In case of assuming the ideal solution, the predicted eutectic temperature is lower than the reported one for benzene + cyclohexane system. In case of assuming non-ideal solution the solid-liquid equilibria of benzene + cyclohexane system was well

predicted.

(3) Quantum chemical molecular dynamics study on the permeation process of hydrogen in palladium membrane

The permeation process of hydrogen in palladium membrane was studied by the theoretical approach, in order to perform a screening of new non-palladium materials for hydrogen separation. The simulation on the hydrogen adsorption on the palladium membrane was performed using our accelerated quantum chemical molecular dynamics program "Colors". From this simulation, it was found that the electron transfer from the palladium atoms to the hydrogen molecule promotes the dissociation of the hydrogen molecule. In order to investigate the equilibrium state of the hydrogen absorption in Pd-Ag alloys, we succeeded in the development of new Monte-Carlo simulation program "MONTA", which enables us to simulate the dissociative absorption of the hydrogen molecules in transition metals and their alloys.

11.2.3 Carbonaceous materials for hydrogen storage

Following in the wake of last year's accomplishment of this working group, in which we had established accurate measurement techniques (balance method and Sievert's method), we investigated hydrogen storage capacity in several carbon materials.

11.2.3.1 Hydrogen uptake of single-walled carbon nanotubes(SWNT) synthesized in China

At first, a new setup used for synthesis of SWNTs by the hydrogen arc discharge method with a designed yield of one kilogram of SWNTs per year was established. Secondly, a multi-step purification and pretreatment process was developed. Ultrasonic sonication, hydrothermal treatment, acid washing, bromination, air oxidation, and high temperature vacuum treatment were involved in these processes. Thirdly, the pretreated SWNTs were used for volumetric hydrogen storage measurements. In order to calibrate the measurement apparatus, the standard sample among WE-NET Group, Maxsorb, was used. The H₂ storage capacities we obtained for different SWNT samples were between 0.9 to 4.3 mass%, depending upon the sample states.

11.2.3.2 Structure-controlled carbon nanotubes

The structure-controlled carbon nanotubes have special wall structure that consists of ultrafine graphite plane fragment with very large specific surface area. The property of the hydrogen storage of this material was 3.1 mass% at 10 MPa. The Temperature Programmed Desorption (TPD) measurement showed that this material had more than two types of adsorption site and the particular structure. It was also suggested that this new carbon material differed from the other carbon materials on

the structure and the adsorption mechanism.

11.2.3.3 Carbon nanohorn

Carbon nanohorn was synthesized by laser vaporization method without metal catalyst. Synthesized material consists a single wall structure. The mean length of a horn is 30-50 nm and the mean diameter of born-like tube is 2-3 nm.

Hydrogen absorbing amount of carbon nanohorn at 303K is 0.23 mass% at 10 MPa. This amount is very low considering the expected value as hydrogen storage. Pretreatment of oxidization at various temperatures and washing in nitric acid or alkali were tried. The caps at the both end of a horn were removed by oxidization at elevated temperature and the amount of hydrogen absorbed at 10 MPa increased to more than twice, even though it was only 0.52 mass%. The effect of noble metal element was not clear. Therefore it was suggested that a carbon nanohorn does not possess enough absorbing ability as hydrogen storage material. The results of this research demonstrate that increasing the amount of specific surface area and micropore volume is very important to develop high storage capacity carbonaceous materials.

11.2.3.4 Effect of local electronic structure on desorption from nanostructured graphite

Nanostructured hexagonal (h)-BN was prepared by mechanical milling under hydrogen atmosphere. The hydrogen concentration reaches up to 2.6 mass% after milling for 80 h, and this value corresponds to ca. 35% of that of nanostructured graphite as was previously reported. In addition to the hydrogen desorption starting at about 570 K, nitrogen desorption was also detected at about 700 K. There was no recrystallization phenomenon at least below 1,173 K. The dissimilarities on the (de-)hydriding properties between nanostructured h-BN and graphite might be due to the different local electronic structure near the specific defects.

11.2.3.5 Study of adsorbed hydrogen properties by NMR measurement

The mechanism of hydrogen storage in carbonaceous adsorbents has been evaluated by means of ^1H -NMR relaxation measurement. These results indicate that the characteristics of surface structure of carbon strongly affect the hydrogen adsorption properties. It has become apparent that the amount of hydrogen adsorbed on the activate carbon is independent of conventional pore characters such as specific surface area and total pore volume. Thus, in-situ measurement of the change in the properties of adsorbed hydrogen, which is difficult to evaluate using conventional techniques such as gravimetric analysis, has become possible using ^1H -NMR relaxation technique. The results obtained in this study clearly demonstrate the

advantage of ^1H -NMR relaxation measurement for the evaluation of hydrogen adsorbed on carbonaceous materials.