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# Development of Metal Hydride Heat Pump

Chan-Kyo Park*, Tae-Hwan Cho* and Seijirau Suda**

*Department of Industrial Chemistry, DanKook University
San-29 Anseu-dong, Chunan, Chungnam, Korea
**Department of Chemical Engineering, Kogakuin University,
Nakano-Machi 2665-1, Hachioji-shi, Tokyo, Japan

## 요 약

금속수소화물은 열에너지 및 수소저장 또는 에너지변환장치 등에 많은 응용이 기대되고 있다. 특히 금속수소화물을 이용한 최근의 에너지 변환기술은 기술적으로 뿐만 아니라 경제성면에서도 그 가능성이 한층 높아지고 있다. 본문에서는 이와 같은 열변환장치의 하나인 열펌프의 제작에 필요한 동적특성을 P-C-T, 열 및 물질전달, 흡·탈착반응속도 그리고 성능 등의 관계에서 그 발전과정을 살펴보고, 그밖에 실용화에 따른 문제성도 논의하였다.

## 1. INTRODUCTION

The relatively high enthalpies of formation of reversible metal hydride led to the proposal that these materials could be used to store heat. This concept was then extended to the various applications, one of which was the use of pairs of metal hydride in a heat pump[1,2]. The feasibility study utilizing pairs of metal hydride beds as chemical heat pump was first demonstrated by a series of research known as HYCSOS[3-6].

In recent years, efficient and cost-competiv metal hydride chemical heat pump and energy conversion system by solar, waste heat from various chemical plants and other low grade heat source have reached more practical stages[7-8]. The technological aspects inherent to the use of hydride, whose physicochemical properties are not well known, are not sufficient enough to optimize the functioning of the heat engines. The operational characteristics and efficiency of these ststems are strictly dependent

on the hydride properties, especially on the amount of hydrogen gas transferred through hydriding and dehydriding reactions between two metal hydrides. The need is to improve the performance in the cyclic applications of hydride reactions for any future significance of using hydrogen as a chemical engine. This can be achieved by improving the hydride properties and the heat and mass transfer characteristics of the metal hydride bed. The availability of hydrogen gas in a coupled hydride system depends on the P-T-C property mainly as well as hysteresis, plateau slopes, sorption kinetics and etc. Besides the packing density of hydride bed and reactor characteristics are also the factors which control the total amount of hydrogen transferred in a coupled metal hydride[9].

Hydrogen sorpiton is a dynamic chemical process during which equilibrium states are not achieved. Many experimental and numerical studies have been carried out on the dynamics of hydrogen transfer in a metal hydride. A number of excellent reviews of metal hydride and their applications have been published in recent years[10-13]. This paper aims to review the development of hydride technolgy especially in the field of heat pump experimentally as well as analytically over the last ten years, and reports the typical problems in current attempts to establish a generalized procedure at the designing energy conversion devices.

## 2. CYCLIC APPLICATIONS OF HYDROGEN SORPTION PROCESS

Energy conversion using the metal hydride is a physical procedure which is driven by a heat source utilizing the absorption/desorption reactions between an absorbent-refrigerant pair in order to achieve one of the three objectives like as temperature boosting, heat upgrading, and refrigeration. Hydrogen gas is the refrigerant and is bounded differently to the metal hydride absorbents in the absorber and desorber. Heat of reaction and rapid kinetics of metal hydride have been applied for developing the energy conversion devices such as thermal and hydrogen storage units[14-19], chemical engines[20-22], air conditioning, heat pump and etc.

To establish a generalized procedure for the designing energy conversion devices, P-C-T characteristics for the designing of thermodynamic cycle, heat and mass transfer inside the reaction bed, chemical kinetics and equilibrium properties, and dynamic behaviour of hydrogen transfer should be evaluated exactly.

### 2.1 P-C-T characteristics

Static P-C isotherms are obtained from the measurements with stepwise absorption or desorption of hydrogen in a metal sample for a given temperature under thermal equilibrium conditions. These static conditions differ from the operational coriditions in a thermal machine. In order to begin calculations on the hydriding and dehydriding process of a metal hydride in engineering applications, e.g. for a hydrogen storage system or for an absorption heat pump, one must have reliable informations on the

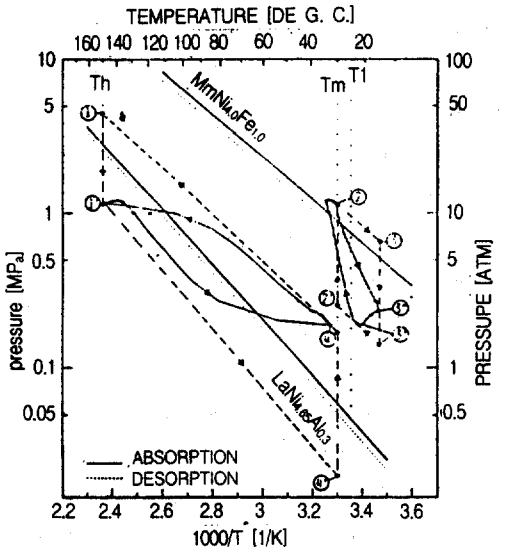


Fig. 1 Dynamic P-T relations of the paired metal hydrides $MmNi_{4.0}Fe_{1.0}$ and $LaNi_{4.65}Al_{0.3}$ for standard conditions of Mode I operation.

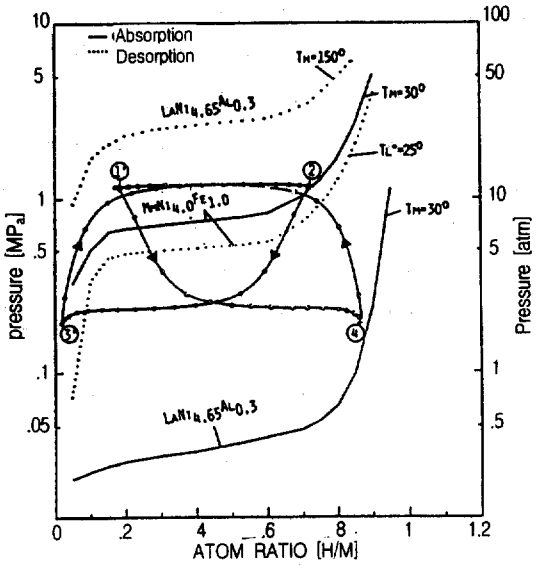


Fig. 2 Dynamic P-C relations of the paired hydrides (···) $MmNi_{4.0}Fe_{1.0}$ and (···) $LaNi_{4.65}Al_{0.3}$ during cooling and heat recovery processes under standard conditions.

P-T-C behavior of paired metal hydrides. Operational characteristics of metal hydride heat pump are strongly dependent on the P-T-C behavior of the paired metal hydrides. Rate of hydrogen transfer is not dependent on the equilibrium pressure determined between the paired hydrides but on the dynamic pressure relations of the given system[23-25]. The amount of hydrogen transferred was correlated with actual behaviour of each metal hydride together with the static P-T-C behaviour to analyse heat pump operations under dynamic conditions[24]. In Fig. 1 and 2, actual behaviour is far from the static equilibrium conditions and there a large deviation from static P-T-C relations is shown.

Dynamic P-T-C behaviours were first suggested by Goodell and Sandrock[25] for a single hydride system, and observed as onset over pressure, and then hydride overpressure[26]. Nagel[27] named this simply as dynamic pressure. A semi-empirical equation with six constants was proposed to obtain a single curve for the relations beween the isothermal hydrogen concentration(H/M) and equilibrium pressure [$RT\ln(P/P_{ref})$] based on the free energy function of gas-solid solution by Suda et al.[28]. Comparison of the calculated results with experimental data of $LaNi_{4.79}Al_{0.21}$ hydride showed excellent agreement with average accuracy of less than a few % error. Tuscher et al.[29,30] studied the dynamic behaviour of single and dual hydride bed devices, trying to estimate their influence on the prospective operation of simple metal hydride heat pump. Ron and Jos-

ephy[31,32] investigated the dynamic characteristics upon desorption for the PMH compacts (production of compacted metal hydride) of $MnNi_{4.15}Fe_{0.85}H_x$ with an 18wt.% Al matrix and found a linear reationship between $lnP_{dyn}$ and the reciprocal absolute temperature of the hydride. Groll et al.[33] used for their measurements a specially designed reactor, and showed hydrogen sorption process under dynamic condition with a finite hydrogen flow rate was accompanied by a distinct increase in absorption-desorption hysteresis and also plateau slope even under close to isothermal conditions. Recently Yoshida et al.[34] reported P-C isotherm in $LaNi_5$-$H_2$ system had two plateau regions above 343K and hydrogen storage capacity declined in comparison with the initial storage.

The P-C isotherms are sensitive to the thermal history and affected by the maximum operating temperature. The reaction on metal hydrides and the hydrogen sorption process are concerned with equilibrium properties. On the other hand thermodynamic machines based on the metal-hydride reaction produce a thermal output depending on a hydrogen flow and therefore function in non-equilibrium, dynamic conditions. From the design point it is necessary to establish the quantitative relation between dynamic P-T-C and reaction kinetics to simul ate the dynamic behavior of a paired hydride system.

## 2.2 Design of metal hydride heat pump reactor : Heat and mass transfer

Metal hydride reactor for sorption process is simultaneously a pressure vessel and a heat exchanger. So its design is fundamentally different from that of a ordinary heat exchanger in some phases. One of the main differences is that in the designing considerations metal hydride bed has the finite amount of heat of formation and dissociation depending on the operational conditions. Many studies for the heat and mass transfer of metal hydride beds have been done on recent years and most of works have been concentrated on measurements of the effective thermal conductivity($K_e$) of metal hydride beds as well as on improving their heat transfer characteristics and the design of suitable heat storage exchangers. Suda et al.[35-37] have carried out model calculations for the thermal conductivity, comparing with the experimental data of $TiMn_{1.5}$ obtained by a steady method and $Mg_2Ni$ by a nonsteady method, and heat transmission studies inside the metal hydride bed to predict temperature profile. The effective thermal conductivity of $Mg_2NiH_4$ and $MmNi_4FeH_{5.2}$ was measured under steady state conditions as a function of the hydrogen pressure and the temperature by Suissa et al.[38] and the similar experiment was carried on the $K_e$ of tightly packed powder of $LaNi_5$ and FeTi in a thin-disc configuration by Goodell[39]. The theoretical model for calcuation the $K_e$ was presented by Sun and Deng[40].

Although the hydriding/dehydriding reactions generally possess very fast intrinsic reaction kinetics, it's usually limited by the internal and external resistance of heat transfer around reactor. Mass transfer characteristics of

hydrogen in a paired metal hydride system are strongly dependent on the heat transfer characteristics of heat exchanger, particularly on overall heat transfer coefficient[41]. The rate of hydrogen transfer furthermore is not regulated by the equilibrium pressure difference but is governed by the dynamic pressure relationships between the two kinds of hydride which are governed by the heat transfer characteristics of metal hydride layer in the heat exchanger[27].

In order to achieve short reaction time which is conformed to the cycle number of metal hydride heat pump, considerable effort has been directed to improve the heat and mass transfer characteristics of metal hydride beds on recent years. There are several methods to improve the heat and mass transfer which may be classified into as follows, depending on the structure of metal hydride bed :

(a) inserting the metal matrices such as porous aluminium foam ;
(b) compacting the metal hydride bed ;
(c) improving the design of metal hydride powder bed ;
(d) attaching fin.

Since the Argonne multi-tube hydride heat exchanger which used a tubular design hydride bed with the alloys contained in the interstices of open pore aluminium foam for enhanced heat transfer[4,6], metal matrices types have been employed in many experimental researches. Finite element computer model was developed to simulate the thermal process of metal hydride heat pump and hydride exchanger by Rohy et al.[42]. The optimized tubular reactor design was the one with internal or external copper fin as shown in Fig. 3. Great improvement of the effective thermal conductivity($K_e$) of metal hydride powder had been obtained when metal

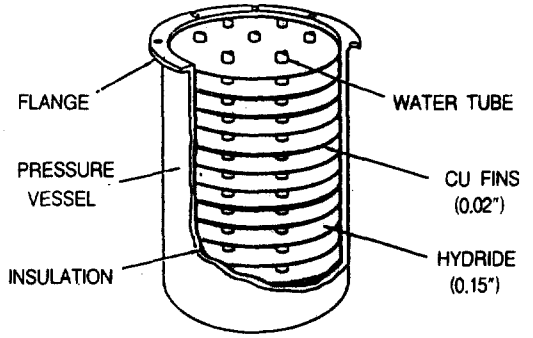


Fig. 3 Finned tube hydride heat exchanger package.

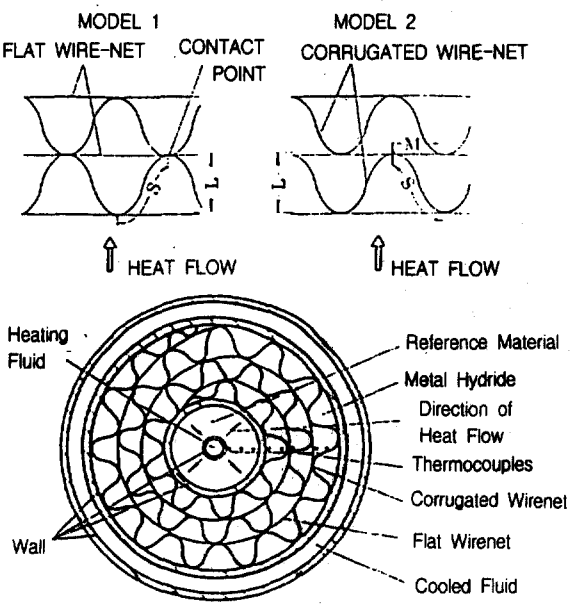


Fig. 4 Structure model of a copper wire matrix to imprive $K_e$.

matrices with aluminium foams and copper nets were inserted by Suda et al.[43], giving a $K_e$ value for $MnNi_{4.46}Al_{0.54}$ ranging 5 to 7 $Wm^{-1}K^{-1}$, but their high cost and poor commercial availability made alternative methods like as a corrugated copper wire matrix necessary[44]. A schematic diagram of this structure is shown in Fig. 4. Groll et al.[45-47] reported that tubular reactor with two stainless steel screen arteries placed into two axial grooves cut opposite each other along the outside of the aluminium foam could be effected to the heat and mass transfer greatly. It could be seen that the 90% reaction time( $\tau_{0.9}$) was about 3.6~4.2 times shorter for the reaction bed with arteries and about a factor of 2.24~3 faster only for the porous aluminium foam bed.

However, disintegration of the storage material into a very fine powder and swelling of the powder by the hydrogen absorbed have hindered the practical employment of such systems widely[48]. The permeability characteristics of a hydride powder $Mg_2Ni$ in heat storage system were examined experimentally by Kawamura et al.[49]. Ron et al.[5] suggested that porous metallic matrix hydrides(PMH) supported by a thin metal matrix of Cu, Al, etc. greatly improved thermal conductivity and were able to withstand repeated cycling without disintegrating. Metal hydride powder which was mixed with 5~10wt.% of an inactive material and compressed under high pressure(10~20ton $cm^{-1}$) was applied to the hydrogen storage for motor vehicle by Toepler et al.[17]. The mechanical stability and gas permeability of PMH compacts was studied by Bershadsky et al.[50]. They determined the permeability as a function of aluminium matrix fraction and found that PMH compacts were very stable upon a number of 22000 and 33000 sorption cycles for the $LaNi_5H_x$ and $MmNi_{4.15}Fe_{0.85}H_x$.

The design of hydride container in compacted form and the preparation and properties as well as their behaviour of porous metal hydride compacts ware described in detail by Tuscher et al.(see Fig. 5[51]). Compacting the hydrogen

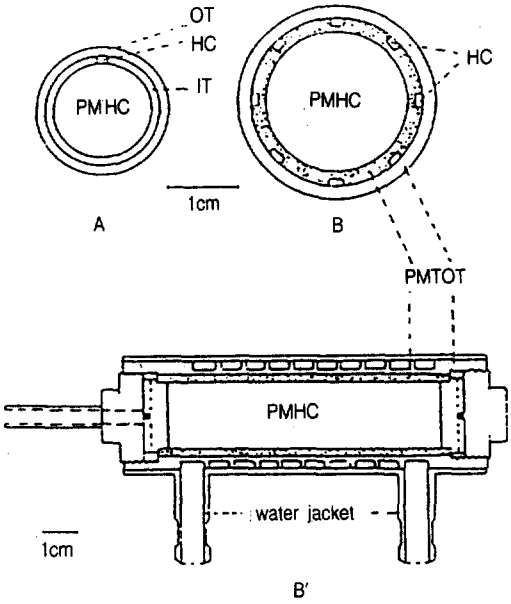


Fig. 5 Cylindrical containers for PMHCs. Type A : The crosssection shows the PMHC surrounded by a side-slit Al cylinder (IT). The slit serves as hydrogen channel (HC). The outer tube(OT) encloses the unit. Type B, B' : Radial and longitudinal cross-sections of another PMHC container using a porous metal tube(PMT) for hydrogen exchange. Eight hydrogen flow channels(HC) are provided.

storage materials together with flakes or particles of high thermal conductivity includes a number of advantageous features compared with usual powder hydride bed :

(a) easy to handle large amounts of fine powder ;
(b) prevent from hydride powder swelling and sometimes cracking upon repeated cycling ;
(c) make much better contact with the tubes, reducing the thermal contacting resistance ;
(d) increase the thermal conductivity which may be effected to improve the sorption kinetics.

Experimental results showed that the heat conduction of such material gives so much improved value ranging from 17 to 20$Wm^{-1}K^{-1}$ i.e. 20~30 times larger than a corresponding powder bed[52]. Recently the micro-encapsulation of finely powdered alloys by coating the surfaces with a thin porous layer of metallic copper, using a chemical plating method was suggested[53]. Extensive experiments were carried out to determine the reactor characterization and sample conductivity with the tightly packed powder of the hydride container whose hydrogen storage materials were used in compacted form[29,30,54], tube coil[4,55], and capsule[6,56]. Table 1 shows an illustration of the effective thermal conductivity of metal hydride beds, depending on their morphologies and packings.

Besides Yonezu et al.[57] suggested new metal hydride container with heat pipes which were able to transfer heat rapidly. El-Osery[58] studied two alternatives for the configuration of hydrogen reaction in metal hydride beds. The

Table 1 Comparison of effective thermal conductivity

| Bed morphology | Metal hydride | $K_e$ | Ref. |
|---|---|---|---|
| Powder | $Mg_2Ni$ 0.5 | [15] | |
| | TiMn1.5 | 0.3-1 | [35, 36] |
| | $Mg_2NiH_4$ | 0.83 | [38] |
| | $MnNi_4FeH_{5.2}$ | 1.05 | [38] |
| Loosely pressed TiFe | | 0.5-1 | [17] |
| Compressed | TiFe(5wt.% Al) | 3 | [17] |
| | TiFe(10wt.% Al) | 7-9 | [17] |
| Powder with foam | $MmNi_{4.5}Al_{0.5}$ | 5-7 | [44] |
| | $LaNi_{4.7}Al_{0.3}$/ $MnNi_{0.5}Al_{0.5}$ | 1-4 | [43] |
| P.M.H. | $LaNi_5$(20wt.%Al) | 32.5 | [5] |
| | $MmNi_{4.15}Fe_{0.85}$ (18wt.%Al) | 17-20 | [31,32] |
| | $LaNi_{4.6}Al_{0.4}H_x$ (Cu powder) | 4.3 | [29] |
| | $LaNi_{4.6}Al_{0.4}H_x$ (Al powder) | 3.6 | [29] |

P.M.H.=porous metallic-matrix hydride; $K_e$=effective thermal conductivity($Wm^{-1}K^{-1}$)

results showed that the design of metal hydride bed on the basis of out-in cell configuration is better than in-out cell. Recently Yanoma et al.[59] investigated the performance of metal hydride heat pump system in heat upgrading cycle whose heat output is 174kW and reported that hydrogen mass transfer was far more improved than an ordinary type with piping between two exchangers when used a single-shell type heat exchanger, where two metal hydrides were contained in one shell and were separated by center plate for the purpose of easier mass transfer(see Fig. 6).

### 2.3 Hydride and dehydride reaction kinetics

The study of hydriding and dehydriding

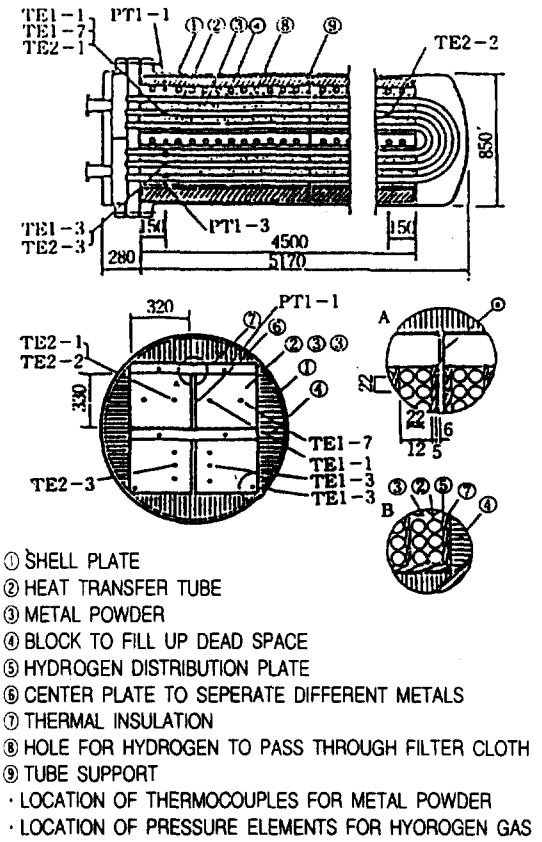


Fig. 6 Schematic drawing of heat exchanger.

kinetics in metal hydride bed is an example of simultaneous heat and mass transfer with reaction occuring, although certain properties like as the thermal conductivity or the heat transfer coefficient also change, depending on the structure of metal hydride bed and metallic alloy involved. Once the hydride bed has reached thermal equilibrium, it is difficult to distinguish that anyone of a number of factors may be rate determining such as the chemisorption of hydrogen molecule, the surface diffusion of hydrogen atom or else.

So many ideas for defining the rate controlling step related to the reaction kinetics of metal hydride bed have been proposed[60-62]. But we will not be further described here as it's not the purpose for our review. Instead of that it may be rather profitable to introduce an excellent review published recently[63].

## 3. PERFORMANCE OF METAL HYDRIDE HEAT PUMP

A high temperature heat pump process utilizing metal hydrogen reactions was proposed by Alefeld[2] as a topping cycle for thermal power stations. After the work based on the pioneer research on the HYCSOS system by Gruen et al.[3,4], many extensive studies of hydride system and chemical heat pump have been reported in terms of system design parameters and several hydride properties[64,65]. The bulk of the previous works on the metal hydride heat pump seems to have been directed toward the experimental investigations utilizing laboratory scale apparatus[66-68].

Nagel et al.[69] investigated the performance of a metal hydride heat pump system in refrigeration cycle, whose cooling output is 1.28kW, the optimum cycle time of the system 13 min. and so on. In a typical heat pump operation, the temperature profiles and the amount of hydrogen transferred are shown in Fig. 7 and 8. Maximum COP as a relation of histersis factor, slope factor, and average hydrogen transfer rates for typical hydride quantitatively was reported to be 20~30% lower

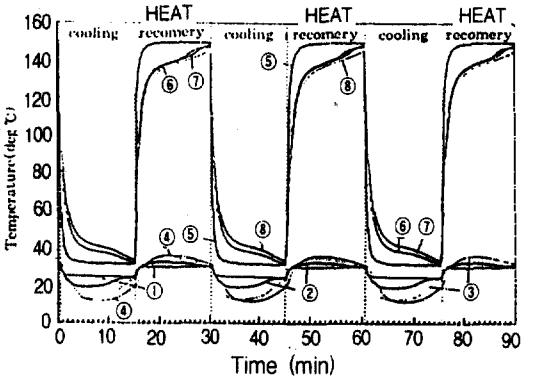


Fig. 7 Temperature profiles obtained in $MmNi_{4.0}Fe_{1.0}$(curve 1, inlet; curve 2, T(inside); curve 3, T(outside); curve 4, outlet)and $LaNi_{4.65}Al_{0.3}$(curve 5, inlet; curve 6, T(inside); curve 7, T(outside); curve 8, outlet).

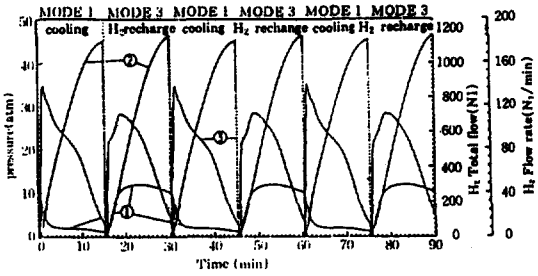


Fig. 8 Dependence of hydrogen gas pressure (unit A) (curve 1), total amount of hydrogen cycled (curve 2) and hydrogen flow rate (curve 3) on time.

than Carnot cycle in heating mode and 60~70% lower in the cooling mode[70,71]. Prototype of a metal hydride heat pump for use as an air conditioner to run on waste heat recovered from the exhaust gas of the diesel engine was designed by Ron[52]. According to his report heat pump can produce the lowest air temperature of -2C from about 400C exhaust gas. However the hydrogen pressure reaches up to the maximum value of about 9.8 KPa in the refrigeration cycle.

A low heat transfer rate has been recognized as the major factor limiting the hydrogen flow rates and thus the thermal power output. The very low thermal conductivity of powder hydride beds has been found to play a dominant role in the poor heat transfer of hydride container[30]. In order to increase the thermal conductivity of hydride beds and to eliminate the burden of handling, the production of compacted solid[5,29,31,51,52], multitube hydride exchanger[6] and metal hydride composite structure[37,44] has been suggested. Anevi et al.[28] also has studied several types of hydride reactor to increase the thermal conductivity and reported that the best is a flat-bed type in which the hydride bed and its heat exchanger are thermally separated from the pressure vessel and the average heat transfer coefficient from hydride bed to water is greater than $1kWm^{-2}K^{-1}$.

The dynamic characteristics of the hydrogen sorption process by rechargeable metal hydride are great importance as a basic point of view. In recent years a number of studies related to the dynamic behavior of hydride beds have been published. However only a few reports exist on the dynamics of hydrogen transfer in a chemical absorption heat pump, utilizing two reactors cooperatively. The effects of operational parameters on the performance for a full cycle of successive heat pumping and regeneration process have been studied and analysed in terms of deviation from equilibria between

hydrogen and hydride by Suda et al.[24,27,43]. A number of factors affecting the specific power output were considered to optimize a single stage heat pump, including the morphology and packing of metal hydride as well as dynamic pressure defferential by Ron and Josephy[65]. Tuscher et al.[29,30,54] have also investigated heat pump cycles using so-called dynamic P-C-T relations and tested $LaNi_{4.6}Al_{0.4}$ as well as $MnNi_{4.5}Al_{0.5}$, $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$ storage units with regard to their dynamic behaviour, in order to combine them into a scheme simulating laboratory heat pump. A major obstacle in investigating the dynamic characteristics (Pdyn-T-C) arises from the fact that strict isothermal conditions are difficult or even impossible to achieve whenever an appreciable hydrogen flow exists[31,32].

Several experimental and numerical studies have been carried out on the dynamics of charging hydrogen into or discharging it to a hydrogen storage unit based on metal hydride. Nishizaki et al.[72] studied the effect of sensible heat exchange between the two reactors containing same hydride to increase the COP and presented an equation for calculating the COP of the $LaNi_{4.77}Al_{0.23}/LaNi_5$ system. The results of numerical calculation showed that highly efficient sensible heat exchange is essential to the achievement of a high coefficient of performance. Nagel et al.[27] presented a similar investigation using paired metal hydrides of $LaNi_{4.65}Al_{0.3}$ and $MnNi_{4.0}Fe_{1.0}$ and analysed the effect of various operational parameters which influence the system characteristics. Adding a second reactor modifies the problem significantly because the charging of hydrogen does not proceed under the same boundary conditions. The effects of operational parameters on the performance of heat pump were analysed experimentally and theoretically by Bjurstrom and Suda[73]. They found that heat transfer determined the hydrogen transfer rate and introduced lumped parameter on the basical idea that all resistance to the heat transfer can be lumped into a single overall heat transfer coefficient, U.

Many prototypes of metal hydride heat pump have been reported in the literature until now but commercially available ones are limited at present. Operating perfermance of a large scale metal hydride heat pump whose design is optimized by computer simulation program was reported[59]. Yoneta et al.[74] also researched the operating performance of metal hydride heat pump in upgrading mode which utilizes a hydrogen compressor. They adopted the shell and tube type heat exchanger which has middle fin tubes made of copper to enhance the heat transfer and accomplished the design output 15000 kcal/hr when COP equaled about six.

Besides a hydride heat pump system for application to an integrated energy system for community[75], viehcle[52], and industrial use[2,64,68] were reported. Bogdanovic et al.[76] proposed magnesium hydride system which could not be used for heat storage reactors due to its lack of reactivity can be used as a heat transformer as well as a heat storage system[78]. On the other hand, in order to increase the performance of

hydrogen sorption process a new ternary hydride system was introduced, which has high temperature gain and efficiency through the cascade reactions between three metal hydrides by werner et al.[93,94], and extensive studies also have been performed by Suda et al.[71,77] on the operational performance of double stage heat pump with the different capacities(7.72kw and 77kw), using three different kind of metal hydrides; $LaNi_{4.57}Al_{0.46}Fe_{0.05}$ / $MmNi_{4.57}Al_{0.46}Fe_{0.05}$/ $MmNi_{3.98}Fe_{1.04}$. General treatment for optimizing the choice of alloys in single and multistage modes based on the classical thermodymanics was studied comparing the characteristics of selected ternary heat pump[78,79], and its experimental result was presented to compare the performance of heat engines according to the selected alloys[80]. Recently new type of metal hydride heat pump combined with hydrogen compressor which consists of two different stages of enforced and natural stage was reported by Park et al[97,98]. A model for calculating the coefficient of performance was also presented and compared with the experimental results. A concept of adiabatic compression work also was introduced in a model on the basis of the Carnot reversible cycle and the dependence of COP on the various operational parameters. Very important investigations were carried out by Libowitz et al.[81] on the COP of the heat pump using the general formula $[V_{1-x}Ti_x]_{1-y}Fe_y$. They found that the COP can be enhanced comparing with that of pumps employed intermetallic compounds and because of the unusual thermodynamic properties of the Vanadium-based alloy hydrides, heat pump can be designed with $H_{lowtem.}/H_{hightem.}>1$

Table 2 Characteristics of metal hydride heat pump

| Stage | Mode | System condition | Ref. |
|---|---|---|---|
| Single | Heating | $La_{0.87}Mn_{0.14}Ni_{5.32}Al_{0.11}$<br>$T_h$=353, $T_m$=333, $T_l$=313<br>$\alpha$=5-10, COP=6, $\eta$=174 | [74]*<br>[54,30,56] |
| | | Cooling $MnNi_{4.0}Fe_{1.0}/LaNi_{4.65}Al_0$<br>Th=423, Tm=303, Tl=298<br>$\alpha$=10-20, COP=0.32, $\eta$=12.78 | [69]*<br>[9,41,42, 52,66,67] |
| | Heat transformer | $LaNi_{4.7}Al_{0.3}/MmNi_{4.15}Fe_{0.85}$<br>$T_h$=453, $T_m$=323, $T_l$=268<br>COP=1.2-1.4, $\eta$=8 | [45]* |
| Double | Heating | $LaNi_{4.88}Al_{0.23}/MmNi_{4.57}Al_{0.46}$-<br>$Fe_{0.05}/MmNi_{3.98}Fe_{1.04}$<br>$T_h$=393, $T_m$=353, $T_l$=293<br>$\alpha$=7.5, COP=0.21, $\eta$=7.72 | [77]* |

System condition from Ref.[ ]*.
$T_h$=high temperature(K); $T_m$=medium temperature(K); $T_l$=low temperature(K); $\alpha$=cycle time(min.); COP=coefficient of performance ; $\eta$=output(kW).

Many experimental performances for the hydriding/dehydriding reaction of metal hydride heat pump have been carried out until now. Table 2 summarizes these results which have been published over the last decade for comparison purpose.

## 4. THEORETICAL CONSIDERATION

A reactor for metal hydride heat storage system is required to have good heat transfer properties and small heat capacities as possible because the heat produced during the metal-hydrogen reaction is finite and its loss must be minimized. Besides the repetitions of hydriding and dehydriding reactions make the metal

hydride bed as a fine particle packed bed. Therefore to get quantitative understanding in the characterization of metal hydride bed is important as the guide line of the heat pump designs.

Fisher and Watson[82] have developed the equilibrium model to predict the performance of metal hydride beds for hydrogen storage, but it was inadequate for quantitative prediction of the response of the storage systems because they didn't take the effects of chimical kinetics and hysteresis into account in the model. Mathematical model of a hydride bed has been developed to describe its dynamic behaviors such as heat & mass transfer[40], chemical kinetics and equilibrium[83], and effective thermal conductivity with the analysis of the heat transfer mechanisms under the hydriding and dehydriding condition[18]. The effect of heat transfer, especially the influence of effective thermal conductivity on the overall reaction kinetics by solving the differential heat balence equation was studied by Suda et al.[37]. A study on the role of heat transfer on the hydriding kinetics, assuming non-isothermal conditions for an open system under constant pressure by Danzer and Orgaz[84], and similar investitigation by Heung[85] was carried out. The dynamic characteristics of heat storage system were investigated by Kawamura and Ono[86]. Their model showed that temperature gain of the heat transfer medium depends strongly on the flow rate of heat transfer medium, heat transfer area and heat transfer coefficient. Commercially available reactor, rather than one of ideal situation was simulated from the heat transfer characteristics and the diffusion properties of metal alloys by Lucas and Richards[87]. Besides a numerical model for two dimensional transient heat and mass transfer including the effect of effective thermal conductivity in the metal hydride beds was developed, in which the numerical solution based on finite difference approximations showed to be applied to the all kinds of coordinates at different boundary conditions by Sun and Deng[40, 88].

Adding a second reactor modefies the problem significantly as the hydrogen transfer between paired reactor is always in the state of dynamic condition. In spite of its fundamental importance, only a few studies have been devoted to a specific modelling of a hydride chemical heat pump. Coefficient of permance in a metal hydride energy conversion system was correlated with several hydride properties by Suda and Kobayashi[70]. Furthermore the effects of operational parameters on the performance of a heat pump were studied by Nagel et al.[69] and presented a similar investigation, using so-called dynamic relation for the hydride-hydrogen system by Tuscher et al.[30] and Ron[52].

Several theoretical studies have been carried out on the dynamics of hydriding and dehydriding between paired reactors in a metal hydride heat pump. Model for calculating the coefficient of performance was presented for a chemical heat pump which contains two metal hydrides and which consists of four reactors[72]. The results of numerical calculation showed that sufficiently flat plateau, low reactor capacity and

highly efficient sensible heat exchange are essential to achieve a high COP of about 0.8. Mathematical model for transient heat and mass transfer was developed to investigate the behaviour of single and coupled reaction bed operated in a heat pump mode and showed the calculated COP could be reached 1.2~1.4 with a appropriate design condition[45,89]. But Kang and Kuznetsov[95] investigated the transient transport process of hydrogen and heat transfer between two reactor modules through their thermal modeling and analysis, and showed the cooling water had a negiligible effect on the COP but a strong effect on the cooling capacity. Dantzer et al.[78,90] studied the efficiencies of hydride chemical heat pump and the thermochemical behaviour based on a classical thermodynamic analysis, and proposed a way to analyse the various types of engine configuration, single and multi-stage. For the proposed analysis, more realistic efficiencies can be calculated with that model than with a Carnot analysis, without coupling between the system and heat exchangers. Lumped parameter model was presented to describe the hydrogen transfer between paired reactors in a metal hydride heat pump[73]. The numerical results provide a description of the hydrogen transfer without requiring the information about the geometry of the heat exchanger. Recently Gopal and Murthy[96] said even though the lumped parameter model showed good agreement between their experimental and predicted values, the assumption was not appropriate as the effectivs thermal conductivity of hydride beds was extremely small. They simulated the metal hydride reactor for a pair $ZrMnFe/MmNi_{4.5}Al_{0.5}$ and found the effective thermal conductivity increases with bed thickness and influences the cycle time and the specific output of the system. Gambini[91] showed a theoretical procedure for the evaluation of the performance of metal hydride heat pumps under dynamic operational condition. The developed procedure based on the single hydride bed allows one to evaluate the performance of the coupled metal hydride beds operating in a heat pump mode and make the heat pump system to be set at the most suitable initial condition for a wide range of working parameters such as the necessary time for the development of the several stages of the cycle, the amount of hydrogen to be charged into the hydrides, the thermodynamic parameters under dynamic conditions, and also the effective thermal power output and the efficiency, and was tested to be in good agreement with the experimental results.

One of the fundamental factors in the construction of a heat transformer system is the selection of a metal hydride with characteristics appropriate for the operating condition. The formation of metal hydrides was investigated theoretically by the use of ternary thermodynamics including ternary phase diagrams[92]. It has been found that only a few elements lead to the hydrogenation properties which may be useful for hydrogen storage material.

## 5. TECHNICAL AND ENGINEERING PROBLEMS

Recently metal hydride energy conversion systems have reached on a commercial stage, even though further improvements are necessary for heat transfer elements, metal hydride themselves and etc. Metal hydride heat pumps offer the great possibility of increased efficiency in the use of energy resources, especially in the field of waste energy of various kinds of factory, and provide the possiblity of performing work over much wider temperature range than the classical heat engines. The immediate objectives of operating such a system are to carry out the optimum design for the scaling up and cost studies that demonstrate the commercial potential of the proposed system, compared with competing one. Major technical problem to the realization of metal hydride energy conversion system can be summarized as follows.

(1) A suitable pair of metal hydride need to be selected for constructing the efficient and cost-competive energy conversion system although the metal hydride themselves should be developed. Namely broad and flat plateau, low hysteresis, the quantity of hydrogen absorbed per mole of metal, long-term chemical stability and susceptibility to posisoning should be considered when selecting the appropriate alloys for a metal hydride heat pump.

(2) Light-weight heat exchangers with high heat transfer performance and working materials with high gas absorption capacity(available hydrogen content), small molecular weight and high density are desirable for minimum sensible heat losses and high COP's.

(3) After repeating cycles of hydriding and dehydriding, the efficient heat transfer within alloy becomes very poor as the alloy reduces its size into very fine powder. Formed metals with high thermal conductive material or compression of a mixture of metal hydride seem to be a promissing solution, there by volumetric expansion associated with the sorption process can also be handled.

(4) General method for optimizing the dynamic performance in a paired hydriding/dehydriding reaction need to be established.

(5) The improvements on the design of metal hydride heat pump, for exemple the combination of more than two stage of cycle or enforced stage of hydrogen transported by mechanical work, need to be considered to raise the performance and operating stability of metal hydride heat pump because the system performance based on the second thermodynamics law is very poor.

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