Dynamic Behavior and Refrigeration Performance in a Heat Driven Type Compact Metal Hydride Refrigeration System

Sangchul Bae
Saga University

Masataka Kosaka
Saga University

Masanori Monde
Saga University

Masafumi Katsuta
Waseda University

Dynamic Behavior and Refrigeration Performance in a Heat Driven Type Compact Metal Hydride Refrigeration System

Sangchul BAE[1]*, Masataka KOSAKA[2], Masanori MONDE[3], Masafumi KATSUTA[4]

[1]Institute of Ocean Energy, Saga University,
Saga, Saga, Japan
(Phone +81-952-28-8879, Fax+81-952-28-8595, E-mail bae@ioes.saga-u.ac.jp)

[2]Institute of Ocean Energy, Saga University,
Saga, Saga, Japan
(Phone +81-952-28-8879, Fax+81-952-28-8595, E-mail kosaka@ioes.saga-u.ac.jp)

[3]Institute of Ocean Energy, Saga University,
Saga, Saga, Japan
(Phone +81-952-28-8806, Fax+81-952-28-8595, E-mail monde@me.saga-u.ac.jp)

[4]Graduate School of Science and Eng., Major in Environment and Energy Eng., Waseda University,
Shinjuku-ku, Tokyo, Japan
(Phone+81-03-5286-3251, Fax+81-03-5286-3251, E-mail katsuta@waseda.jp)

ABSTRACT

In the refrigeration field, the research on the refrigerator using waste heat and natural energy attracts attention. Heat driven type metal hydride refrigeration system is one of the candidates. The dynamic behavior of pressure, temperature is strongly related to the metal hydride heat exchanger characteristics, such as the heat transfer mechanism and the geometrical configuration of the metal hydride heat exchanger. And, the resulting heat transfer along with the hydrogen transfer between two connected heat exchanger is the predominant factor in designing in this system. Then, in the present study, an experimental study has been carried out to investigate dynamic behavior and refrigeration performance in coupled metal hydride heat exchangers. And, the amount of hydrogen gas transferable between the paired metal hydrides is measured and the optimum value of the charged initial hydrogen amount, charged metal hydrides mass ratio, volume of gas part and cycle time is found for the maximum hydrogen transfer.

1. INTRODUCTION

By restricting freon, the necessity for non-freon refrigerator technology using natural energy or exhaust heat is becoming large. One of the solutions of this problem is heat driven type metal hydride (briefly MH) refrigerator. This refrigerator is composed of two kinds of MH that for heat source and for cooling. Refrigeration is generated by endothermic reaction of MH for cooling. MH refrigerator offer many advantages over conventional system. They are compact, environmentally safe, utilize low-grade energy sources and offer wide operating temperature ranges. Based on MH technology, some refrigeration system have been built and tested. According to these research results, it is necessary the optimization of design parameters and operation condition based on heat and mass transfer characteristics of the coupled heat exchangers. In this study, an experimental study has been carried out to investigate dynamic behavior and refrigeration performance in coupled metal hydride heat exchangers. And, the amount of hydrogen gas transferable between the paired metal hydrides is measured and the optimum value of the charged initial hydrogen amount, charged MH mass ratio, gas part volume of system and cycle time is found for the maximum hydrogen transfer.

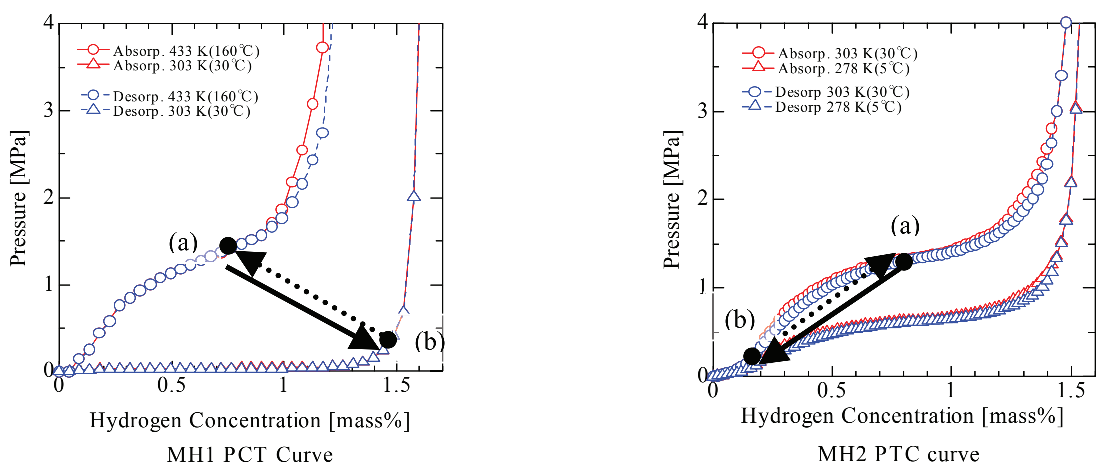
2. OPERATION PRINCIPLE OF HEAT DRINVEN TYPE MH REFRIGERATOR

In this paper, we only use the one-coupled heat exchangers for system performance estimation. Figure 2 expresses the operation principle of heat driven type MH refrigerator using its Pressure-Concentration-Temperature curve(briefly, PCT curve). Two sort of MH heat exchanger are connecting in such way that hydrogen can flow freely between them. MH1 heat exchanger is used for heat source and MH2 heat exchanger is used for cooling. Our system is driven by changing the temperature of MH1 without valve.

(1) Initial condition: Initially, after both heat exchangers are vacuum, the MH1 heat exchanger is set to a heat source temperature, 160℃ and the MH2 heat exchanger is set to an atmosphere temperature, 30℃. Afterwards, the hydrogen of certain initial supplying pressure is supplied to this system. At that time, MH1 and MH2 generate heat by hydrogen absorbing. Therefore, we wait until exothermic reaction finishes. Finally, MH1 and MH2 become an (a) state of Figure 1.

(2) Refrigeration process: This process is started by lowering the MH1's temperature to 30℃ of heat sink temperature. As shown in Figure 1(1), hydrogen adsorbing of MH1 is started by this temperature changing of MH1. And, it triggers the hydrogen discharging of MH2. The refrigeration effect is yielded by this hydrogen discharging of MH2. Finally, MH1 and MH 2 become a condition (b) of Figure 1. An arrow of solid line of the Figure 1 shows the MH state change during refrigeration process.

(3) Regeneration process: In order to obtain the continuous cooling effect, the regeneration process in which MH1 and MH2 are returned to (a) state is necessary. The regeneration process starts by raising the temperature of MH1 to 160℃ of the heat source temperature. As shown in Figure 1(1), by raising the MH1's temperature, MH1 discharges the hydrogen. Then, MH2 adsorbs this discharged hydrogen. MH1 and MH2 return to (a) state of Figure 1. An arrow of dotted line of the Figure 1 shows the MH state change during regeneration process.



(1) State change of MH1 (2) State change of MH2

Figure 1: Operation principle of heat driven type MH refrigerator

3. EXPERIMENTAL METHOD

Figure 2 shows the experimental apparatus. It consists of gas supply system, heat exchangers of MH1 and MH2, thermal constant bath, measurement part and vacuum pump. Pressure is measured by strain gage (accuracy ±0.2 %) and degree of vacuum is measured by pirani gauge (accuracy ±3 %). Hydrogen is supplied to the system by compressed high-pressure gas (purity >99.9999 %). A powerful vacuum pump, which pressure can be as low as 0.13 Pa, has been installed into the experiment system to make sure the hydrogen concentration of MH is essentially 0 before experiment starts. And all thermocouples have been calibrated by a set of ±0.1 K standard thermometers. A thermal constant bath with ±0.1 K accuracy provided a stable thermal environment. To measure the discharged hydrogen amount of MH during the refrigeration process and the regeneration process, hydrogen mass flow meter of maximum 15NL/min is set up into the piping between both heat exchangers. Every experimental condition has been tested at least three times to make sure the reproducibility.

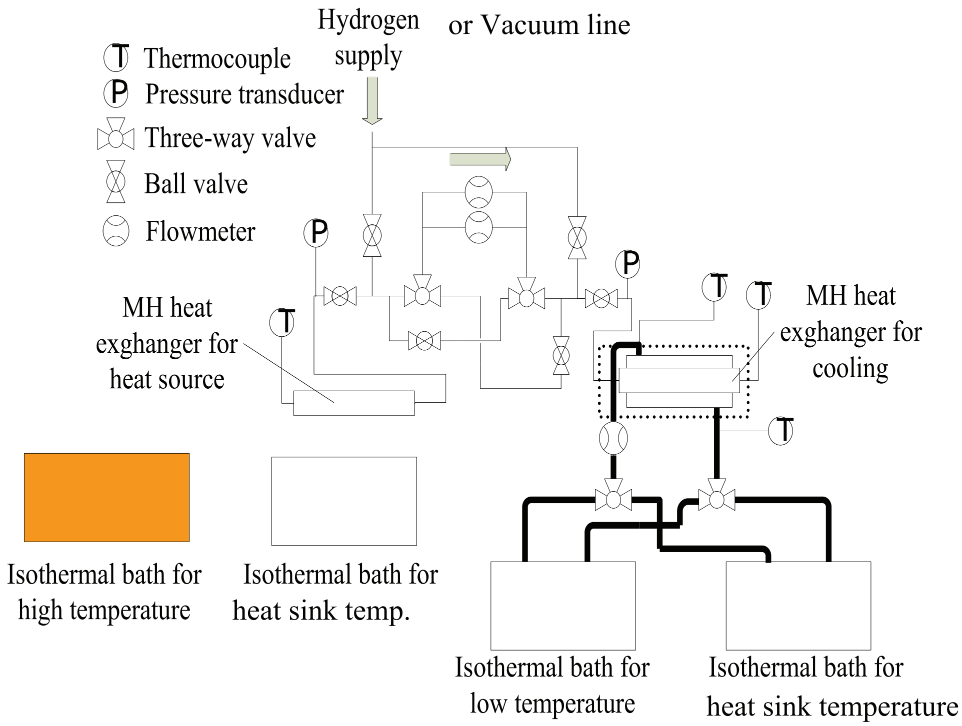


Figure 2 : Experimental apparatus

Figure 3 shows the heat exchanger of MH1. This is made of outer diameter, 19.1 mm copper tube (thickness 1 mm) and has a 300 mm length. MH1 particle and brush type carbon fiber (2 mass% of MH mass) is filled into the tube. The MH2 heat exchanger of Figure 4 is a double tube type heat exchanger that composed of outer diameter, 25.4 mm (wall thickness 2 mm) copper tube and outer diameter, 17.05 mm (wall thickness 1 mm) copper one. And, the length of these tubes is 300 mm. MH particle and brush type carbon fiber(2 mass% of MH mass) is filled in the inner part tube, and the heat exchange medium is streamed between inner part tube and outer part tube. To measure MH particle bed center temperature of both heat exchangers, mineral insulated thermo-couple (K type) of outer diameter, 1mm is installed individually. The silicon holder that has 4 legs is used to make sure the head of mineral insulated thermocouple is in the center of the tube. Moreover, K type mineral insulated thermo-couple is set up at the heat exchange medium inlet and outlet of the MH2 heat exchanger. Inner pressure of two heat exchangers is measured by strain gage (accuracy ±0.2 %). By these temperature and pressure measurement of MH particle bed, we can also estimate the discharged hydrogen amount of MH from PCT curve.

Generally, in order to evaluate the refrigeration performance of refrigeration system, the cooling load and the system COP (Coefficient of performance) are used. But, because the MH2 amount, 150 g of our system is too small, endothermic heat of MH2 during the refrigeration process is not much than the heat capacity of the heat exchanger, carbon fiber and MH particle. Moreover, because there is the heat loss of system, we cannot estimate the cooling load from our system heat balance. Therefore, in this study, we measure and estimate the discharged hydrogen amount of MH2 during the refrigeration process and use it for evaluating the system COP. When we obtain the maximum discharged hydrogen amount of MH2 during the refrigeration process, it means a dehydriding ability of MH2 is fully used and an endothermic heat of MH2 is the maximum. And that time, system COP is also the maximum. An endothermic heat of MH2 during the refrigeration process is given by

$$Q_{MH2\_H_2} = m_{MH2\_H_2} \cdot \Delta H \tag{1}$$

where ΔH is the enthalpy of MH2 and m_{MH2_H2} is the discharged hydrogen amount of MH2 during the refrigeration process.

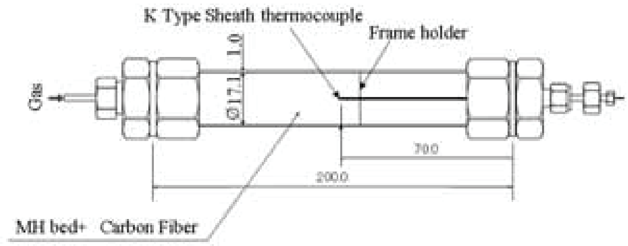


Figure 3 : Heat exchanger of MH1

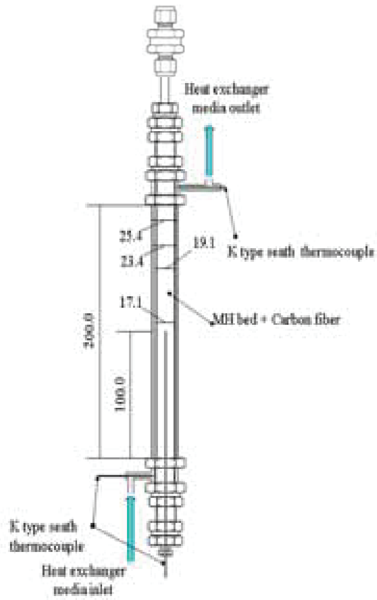


Figure 4 : Heat exchanger of MH2

Table 1 : Basic Experimental conditions

Heat source temperature	160 ℃
Heat sink temperature	30 ℃
Brush type Carbon Fiber mixing ratio	2.0 mass%

Table 2 : Experimental parameter for refrigeration performance estimation

Process time	500,1000,1500,2000 s	
Initial supplying hydrogen pressure	0.2, 0.8, 1.0,1.2,1.3,1.4,1.5,1.6,1.7 MPa	
MH1:MH2 mass ratio	150g : 150g,	300g : 150g
Gas part volume (Total Internal Volume-Volume of (MH particle + Carbon Fiber))/(Total Internal Volume)	78%, 88%	82 %, 92 %

Next, experimental conditions are shown in Table 1 and 2. As shown in Table 1, the heat source temperature of system is set to 160 ℃, and the heat sink temperature of system is set to 30 ℃ that is an atmosphere temperature. In order to find the optimum design and driving conditions, the influence of process time, MH mass ratio, initial supplying hydrogen pressure and gas part volume is estimated in this study.

4. EXPERIMENTAL RESULT AND CONSIDERATION

Generally, the cycle time of heat drive type MH refrigerator is expressed by adding the regeneration process time to the refrigeration process time. But, the refrigeration process time and the regeneration process time of this refrigerator are not the same. Therefore, we double the longer process time between them and define it as the cycle time in this study. Figure 5 and Figure 6 show the influence of the process time on the discharged hydrogen amount during the regeneration process and the refrigeration process. As shown in Figure 5, the discharged hydrogen amount of regeneration process time, 500 seconds and 1000 seconds is only 70 % and 90 % than that of regeneration process time 1500 seconds. And, it shows that 1500 seconds are enough to saturate the accumulated hydrogen transfer amount of the regeneration process. As understand in Figure 6, the hydrogen transfer of refrigeration process is almost finished within 500 seconds. And, the discharged hydrogen amount of the refrigeration process is controlled by the discharged hydrogen amount of the regeneration process. Thus, the cycle time is depends mainly on the regeneration process time. Namely, the optimum hydrogen transfer amount can be obtained by giving the cycle time of 3000 seconds. We estimate the reason of the slow reaction rate of regeneration process is the initial state of MH. As shown in Figure 1, the initial states of MH1 and MH2 on the refrigeration process are the α+β state (solid solution + metal hydride), but the initial states of MH1 and MH2 on the regeneration process are the metal hydride state (briefly, β state) and the solid solution state (briefly, α state), individually. Even if the small pressure and temperature change, reaction rate of α+β state is faster than that of the β state and the α state. Hence, the reaction rate of refrigeration process is faster than that of regeneration process.

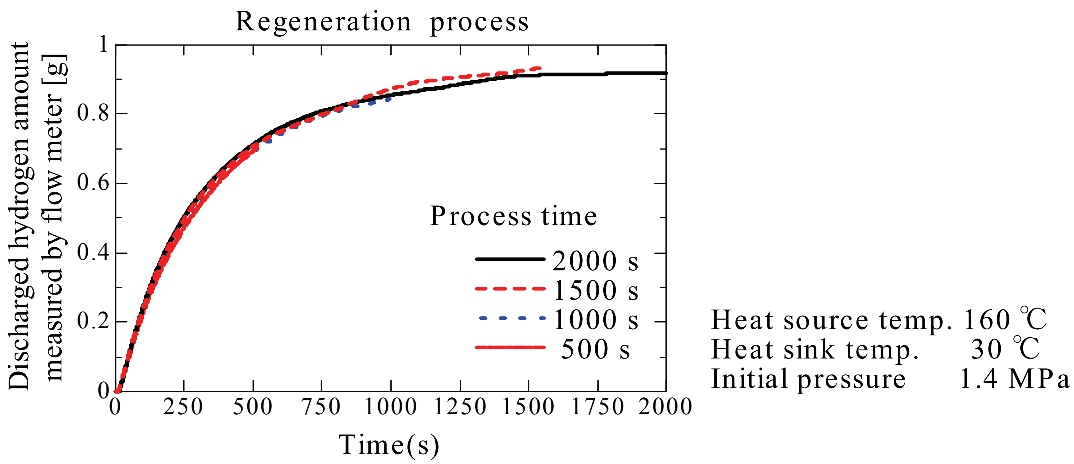


Figure 5 : Influence of regeneration process time on the discharged hydrogen amount of MH2

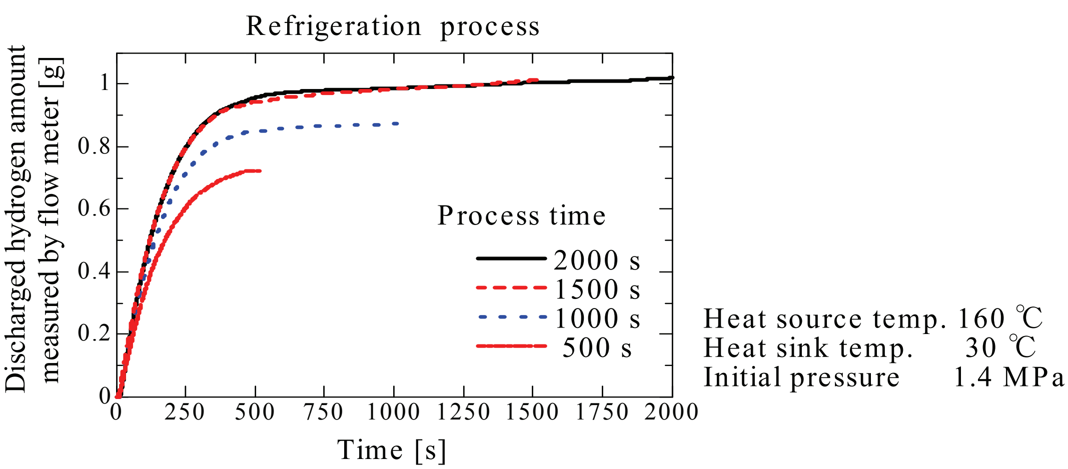


Figure 6 : Influence of refrigeration process time on the discharged hydrogen amount of MH2

And as shown in Figure 1, hydrogen storage ability of MH1 is smaller than that of MH2 under the operating condition. Therefore, we think that the discharging hydrogen amount of MH2 during the refrigeration process is increased by the increasing of MH1 mass charging ratio. In this study, in order to estimate the influence of MH mass ratio, the discharged hydrogen amount of MH2 during refrigeration process is compared at the two MH mass ratio conditions, and is shown in Figure 7. The discharged hydrogen amount of the MH mass ratio, 2:1 is about 1.5 times larger than that of the MH mass ratio, 1:1.

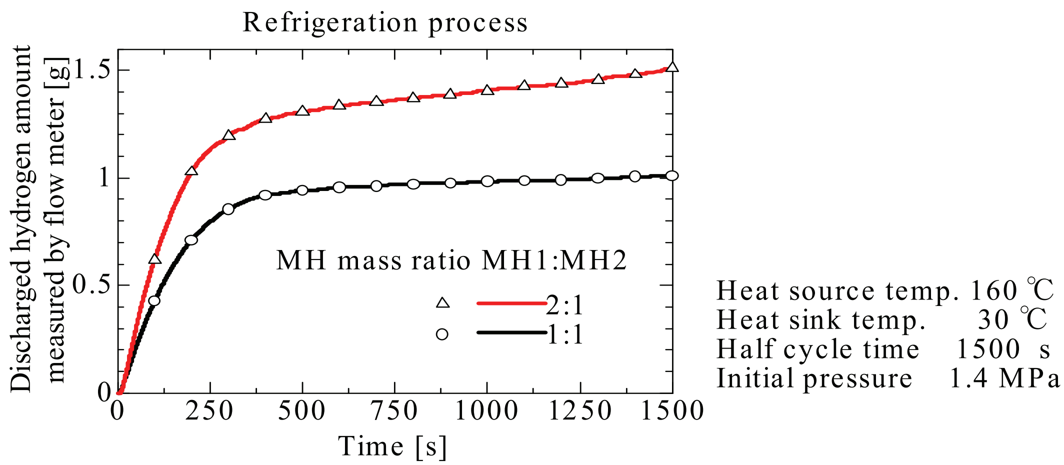


Figure 7 : Discharged hydrogen amount of MH2 at different MH mass ratio

Figure 8 shows the change history of heat exchanger inner pressure and MH2 particle bed center part temperature at different MH mass ratio. The minimum decrease temperature is 13℃ at the MH mass ratio, 1:1 while the one is 3℃ at the MH mass ratio, 2:1. This result means that an endothermic heat of MH mass ratio 2:1 is large, and the refrigeration performance is also high. In both conditions, the time that reaches the minimum decrease temperature is 250 seconds and a rapid pressure change with time is finished at almost 250 seconds. That is, 80% hydrogen transfer of the refrigeration process finishes during initial 250 seconds as known in Figure 7 and 8. And, from Figure 8, we can find that system inner pressure during the process is changed under the initial hydrogen supplying pressure. It means that the initial hydrogen supplying pressure is able to use as the pressure design standards of this system.

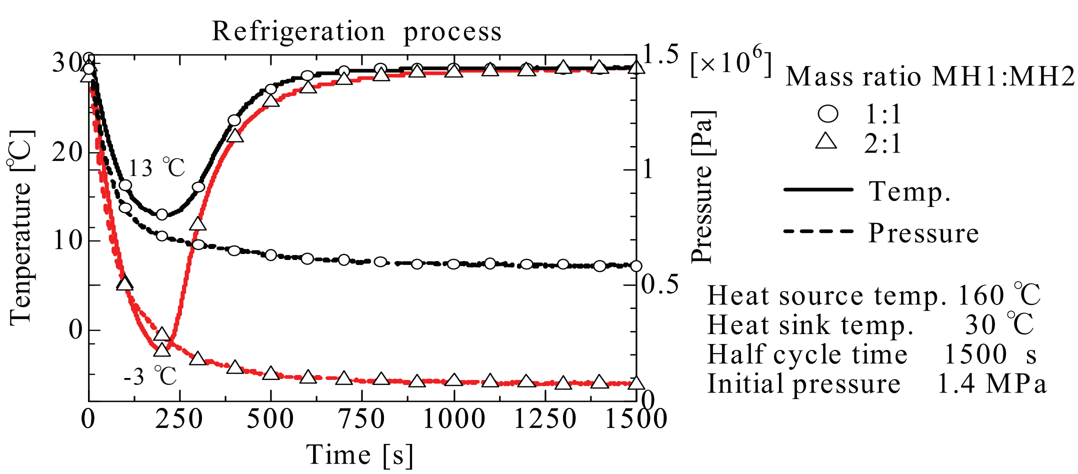
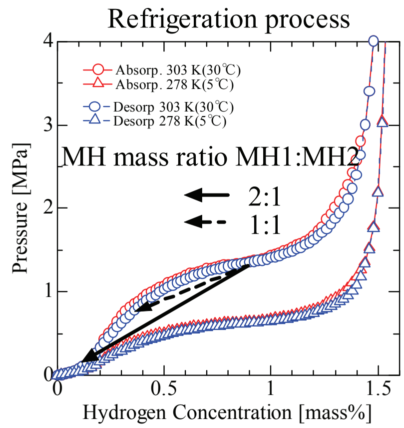


Figure 8 : Temperature and pressure change history at different MH mass ratio

As shown in Figure 9, the state change of MH2 is expressed on the PCT curve based on pressure and temperature change of Figure 8. The hydrogen concentration change of MH2 during the refrigeration process is increased by MH1 mass ratio increasing. It means the discharged hydrogen amount of MH2 is able to estimate from measuring of temperature and pressure change history. But, because the final pressure of the refrigeration process at MH mass ratio 2:1 is almost the same as the atmosphere pressure, even if the mass of the MH1 is increased more than the twice of MH2 mass, it is not able to increase the discharged hydrogen amount of MH2.



MH2 PTC curve

Figure 9 : Condition change of MH2 at different MH mass ratio

Figure 10 shows the discharged hydrogen amount of MH2 during the refrigeration process at individual initial hydrogen supplying pressure condition. As shown in this figure, ratio conditions, the highest discharged hydrogen amount of MH2 during the refrigeration process is obtained at the initial hydrogen supplying pressure 1.4MPa. The reason of these results is explained by the MH state of the process.

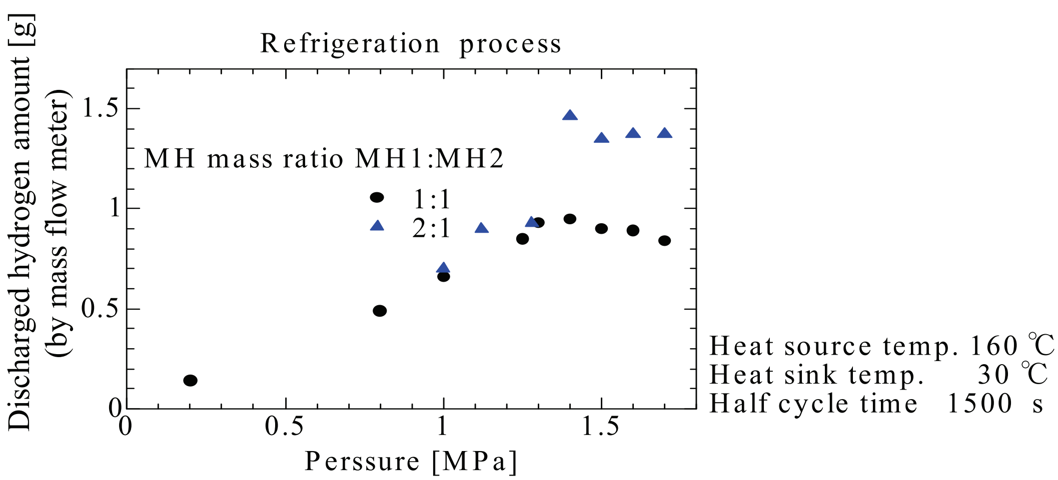
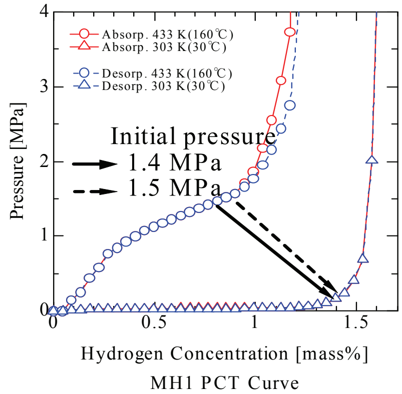
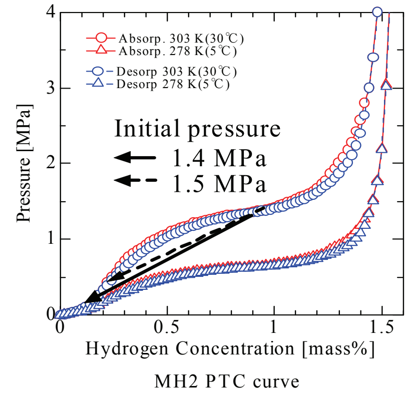


Figure 10 : Initial hydrogen supplying pressure vs. discharged hydrogen amount of MH2

As shown in Figure 11, the state changes of MH1 and MH2 on the PCT curve can be estimated by the experimental results of pressure and temperature change. As shown in Figure 11(1), the hydrogen concentration change of MH1 of the initial hydrogen supplying pressure 1.4 MPa is 0.1mass% larger than that of the initial hydrogen supplying pressure 1.5 MPa during the refrigeration process. The hydrogen concentration change of MH2 at the initial hydrogen supplying pressure 1.4 MPa is increased by this hydrogen concentration change increasing of MH1. And, it means the discharged hydrogen amount increasing of MH2. The reason why the discharged hydrogen amount of initial hydrogen supplying pressure 1.4 MPa is larger than that of other initial hydrogen supplying pressure is explained by the process initial state of MH1. As shown in Figure 11(1), the initial state of MH1 at the pressure 1.4 MPa is α+β state, but the one of MH1 at the pressure 1.5 MPa is β state.





(1) Condition change of MH1 (2) Condition change of MH2

Figure 11 : Condition change at different initial hydrogen supplying pressure

Table 3 shows the influence of the gas part volume of the system on the discharged hydrogen amount of MH2 during the refrigeration process. As shown in this table, when the gas part volume of the system is smaller, the discharged hydrogen amount is increased.

Table 3 : Influence of gas part volume on the refrigeration performance

MH mass ratio MH1: MH2	300 g : 150 g		150 g : 150 g	
Gas part volume ratio	78 %	88 %	82 %	91 %
Discharged hydrogen amount (at refrigeration process)	1.45 g	1.24 g	0.94 g	0.83 g
Minimum temp. of MH2 particle bed	-3 ℃	0 ℃	13 ℃	14 ℃

5. CONCLUSIONS

The optimum design and driving condition for the heat drive type MH refrigeration is obtained as follows.

- The optimum cycle time of this system is 3000 s.
- When the MH1 mass is increased until the twice of MH2 mass, the discharged hydrogen amount of this system is increased.
- It has been able to estimate the hydrogen concentration change of MH by measuring pressure and temperature change during the process, and to use it for the discharged hydrogen amount estimation of MH.
- The best initial supplying hydrogen pressure is 1.4 MPa and when the system is driven by temperature control without valve, system pressure during the process changes under initial hydrogen supplying pressure, then the initial hydrogen supplying pressure is able to use as the pressure design standards of this system.
- The gas part volume of this system must be suppressed as much as possible.

REFERENCE

Gruen, D. M., Mendelssohn, M. H., Sheft,I., and Lamitch, G., 1978, Materials and performance characteristics of the HYCOS chemical heat pump and energy conversion system, *Hydrogen Energy systems, Proc. 2nd Word Hydrogen Energy Conf.,* in T.N. Veziroglu and W. Seifritz(eds): p.1931-1946

Nagel, M., Komazaki, Y., Uchida, M., and Suda, S., 1984, Operating characteristics of metal hydride heat pump for generating cooled air. *J. Less-common Met.* Vol. 104: p.307-314

Suda, S., 1984, Experimental evaluation of heat pump performance in connection with metal hydride properties. *J. less-common Met.* Vol. 104: p.211-222

ACKNOWLEDGEMENT

This research is supported financially by Ministry of the Environment, Government of Japan.