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Selection of Alloys in a Metal Hydride Heat Pump- A New Procedure

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ABSTRACT

Metal hydride heat pump (MHHP for short) is a promising candidate among the many sorption heat pumps. To improve its performance, the alloys used in the system should be selected carefully. In this article, a new procedure was proposed for selection of pairing alloys according to the operation conditions of MHHP, which followed a two-step strategy. First several pairs of alloys feasible for working under given conditions were chosen by a deductive method, next some indices such as COP, alloy output, and compatibility of pair were calculated for the pairs to assess corresponding performances, thus the best pair of alloys can be figured out. Finally, an example was presented to show the validity of the procedure.

1. INTRODUCTION

Nowadays increasing energy consumption has been a critical issue on global scale. To alleviate the pressing situation, reasonable use of energy resources is very necessary. As an example, thermally driven sorption heat pumps have shown great potential in using thermal energy efficiently, thus are paid much attention by researchers, see the work of Pons *et al.* (1999a, 1999b). Among these sorption heat pumps, metal hydride heat pump is one that can work under a broad range of conditions and features little environmental side effect, thus is a competitive candidate in many applications. In the MHHP system, heat effect during the reversible reaction between certain kinds of metals/alloys and hydrogen is applied for various uses, such as heat upgrading, heat amplification or refrigeration. The general reaction taking place in MHHP is of the form,



M is the referred metal or alloy, and MH_x is the so-called metal hydride. In the main stage of this solid-gas reaction, which is termed plateau under isothermal conditions, the system is mono-variant. Thus the reaction equilibrium can be described by the Van't Hoff expression:

$$\ln P_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (2)$$

Equation (2) corresponds to straight lines in Clapeyron diagram. For different alloys, ΔH and ΔS take different values, thus the lines can be discriminated by the slope and intercept. If the working alloys and working conditions are given, the thermodynamic cycles of MHHP can be fixed in the diagram. One-stage heat upgrading cycle and refrigeration cycle of MHHP are shown in Fig.1 and Fig.2 respectively, the arrows indicate the directions of hydrogen flow. In each cycle a work process and a regeneration process run alternatively. Take the former one for example, it requires two alloys (hydrides) for operation, a high pressure alloy M^H and a low pressure alloy M^L . Hydrogen is desorbed from M^H by heating at T_M , then is absorbed by M^L , with useful heat at T_H released, thus forms the work process. After hydrogen stored in M^H is exhausted, the regeneration process starts. Hydrogen is desorbed from M^L by heating at T_M , then is absorbed by M^H , with heat released to the environment at T_L . The difference between the equilibrium pressures of the two hydrides makes the flow of hydrogen possible, as is shown in the figures. The refrigeration cycle can be interpreted in much the same way. Moreover, two-stage cycles can be considered to improve the efficiency or flexibility of MHHP, which require three types of alloys for operation.

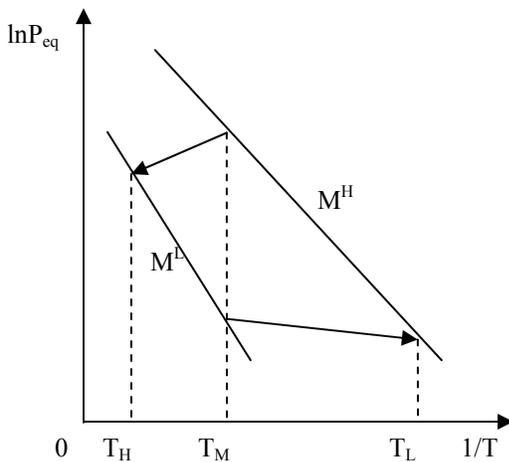


Fig.1 Heat upgrading cycle of MHHP

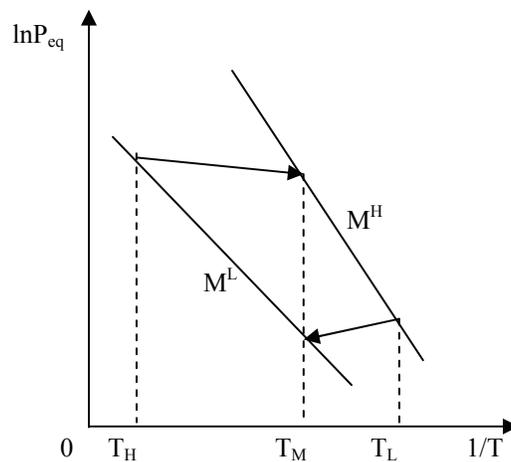


Fig.2 Refrigeration cycle of MHHP

Although MHHP has many advantages, more work is still to be done to improve its performance. The selection of alloys is the first step to construct a realistic MHHP system and shows significance in the performance of MHHP, thus attracts many researchers' attentions.

Orgaz and Dantzer(1986, 1987) conducted the studies early for refrigeration type MHHP. The same equilibrium pressures for the two hydrides were assumed in the work or regeneration process with T_M fixed, thus T_L and T_H could be obtained for given pair of alloys. Since T_L and T_H are generally in a certain range for real applications, the results can be used for evaluating the feasibility of the alloys, in this way the pairs of alloys available were reduced. Next the coefficient of performance (COP), the mass ratio of alloys and estimated power for remaining candidates were calculated and compared, and the pair of superior performance could be figured out finally. Later the selection of alloys in heat upgrading type MHHP was discussed by Sun(1992, 1995), with some realistic factors such as hysteresis, pressure difference and sensible heat considered. He introduced three indices, namely actual COP, alloy output and temperature output to assess the performance of different pairs, while the feasibility of pairs was guaranteed by adjusting the alloy composition. Recently Ni *et al.*(2005) and Qin *et al.*(2006, 2007a, 2007b) have carried out research on MHHP as automobile air conditioner, and the pair of alloys was also chosen carefully. First the compositions of the alloys were adjusted to obtain required thermodynamic properties, which is necessary for the operation under given conditions. Then the theoretical COP was applied for evaluation of the performance of the pairing alloys.

Obviously, a general two-step strategy can be recognized in these studies, first the alloys should be proved viable for operation, then certain performance indices are used for further selection. The strategy is effective, yet there is still

margin for the improvement of its implementation details, such as flexibility, accuracy and clarity. The paper is dedicated to this purpose.

2. SELECTION PROCEDURE

Follow the strategy described above, we discuss the selection procedure step by step, with operation temperatures provided.

2.1 First Step

With hysteresis, the slope of the plateau and the pressure difference taken into account, a deduction method is introduced to choose the pairs of alloys that can meet the requirement of operating under certain conditions. First one-stage cycles of MHHP are considered, which need two types of alloys. After analyzing the results, we may insert a third alloy to form two-stage cycles for better efficiency or flexibility.

The principle of deduction is based on the driving force of reaction, namely the pressure difference between two alloys in the work or regeneration processes. If the pressure difference concerned is larger than zero, the corresponding process will be theoretically possible.

The details of the deduction is given as,

1. The alloy with lowest operation pressure is fixed first to guarantee positive gauge pressure in the whole system, for one-stage heat-upgrading cycle it is the high pressure alloy at T_L .
2. A second alloy can then be tested whether is proper to form a pair with the first one. This is carried out by calculating the pressure differences in the work and regeneration processes. Obviously, a one-stage cycle can be realized by the pair if both pressure differences are larger than zero.
3. If the pressure difference for the work process is larger than zero while the one for the regeneration process is not, a third alloy may be inserted to form two new regeneration processes with the two alloys, yet the work process is kept the same. Thus a two-stage cycle (1 work + 2 regeneration) is constructed.
4. If the pressure difference for the work process of a feasible one-stage cycle is very large, a third alloy may be inserted to form two new work processes with the two alloys, while the regeneration process is kept the same. In this way a different two-stage cycle (2 work + 1 regeneration) can be constructed.

Of course, in procedure 3 or 4 the requirements of pressure differences should still be fulfilled in the new work or regeneration processes.

2.2 Second Step

The performances of the feasible pairs of alloys are evaluated to pick out one good to use. The indices of the performance adopted are respectively defined below.

Coefficient of performance (COP): The index is often used in the assessment of heat pump efficiency. COP can be simply defined as output/input, however, in the specific studies of a MHHP system it may take different forms. Here a basic thermodynamic formulation is adopted with the internal heat recovery and the thermal mass considered. For a one-stage heat upgrading cycle, the COP of a MHHP is written as,

$$COP = \frac{m_{H_2} \Delta H^L - (1-\eta) \sum C_R^L (T_H - T_M)}{m_{H_2} (\Delta H^H + \Delta H^L) + (1-\eta) \sum C_R^H (T_M - T_L) - (1-\eta) \sum C_R^L (T_H - T_M)} \quad (3)$$

Alloy output: It is an index specially adopted in studying the MHHP performance, which is defined as the ratio of the effective output capacity to the total mass of the alloys used in the system. For a one-stage heat upgrading cycle, the alloy output qm is derived,

$$qm = \frac{n(m_{H_2} \Delta H^L - (1-\eta) \sum C^L (T_H - T_M))}{2(W^L + W^H)} \quad (4)$$

Obviously, large qm implies compact design of the system and low cost, thus favors the application of a MHHP.

Compatibility of pair: This is a newly-introduced index. Meaning of the compatibility of pair is less straightforward, but some analysis may help in understanding it. After the pairing alloys are chosen, they should be packed in different reactors of the system, which were reviewed by Yang *et al.*(2008). If the volumes and heat effects of the alloys show little difference, a virtually symmetrical configuration can be utilized, thus the design and assembly of the MHHP system are greatly simplified. In the two factors, heat effect is more important, which affects the heat transfer area, the flow rate of medium, etc. Thus the index is defined as,

$$CP = \frac{Q_{\min}}{Q_{\max}} \quad (5)$$

Here Q is mainly determined by the reaction, thus Q_{\min}/Q_{\max} can be replaced by $\Delta H_{\min}/\Delta H_{\max}$ for certain quantity of transferred hydrogen. A pair with good compatibility gives a CP close to 1.

3. EXAMPLE

Before the selection starts, a database of the physical properties of alloys should be built. The data were taken from the records of SNL through website: <http://hydpark.ca.sandia.gov/> and 8 alloys often applied in MHHP were considered. The physical properties of these alloys were listed in Table1.

Table 1 Physical properties of the candidated alloys

alloy	ΔH	ΔS	c_L	c_H	$d(\ln P_d)/dc$	$\ln(P_a/P_d)$	M
LaNi ₅	30.8	0.108	0.07	1	0.13	0.13	432.456
MmNi _{4.15} Fe _{0.85}	25.3	0.105	0.1	0.75	0.36	0.17	431.373
V	40.1	0.1407	1	2	0.15	0.45	50.942
(V _{0.9} Ti _{0.1}) _{0.95} Fe _{0.05}	43.2	0.1396	1	1.95	0.45	0.8	50.898
CaNi ₅	31.9	0.101	0.2	0.75	0.19	0.16	333.63
LaNi _{4.7} Al _{0.3}	34	0.1068	0.03	0.8	0.48	0.05	422.938
LaNi _{4.8} Sn _{0.2}	32.8	0.105	0.03	0.95	0.22	0.19	444.452
TiFe _{0.8} Ni _{0.2}	41.2	0.119	0.1	0.5	0.36	0.05	104.32

In table 1, $d(\ln P_d)/dc$ and $\ln(P_a/P_d)$ are respectively used to describe the slope and hysteresis of the plateau for an alloy, and they provide the detailed information about the plateau together with ΔH , ΔS , c_L and c_H . The selection course was programmed by MATLAB 7.0, and the performance indices were calculated for every feasible pair based on the following assumptions:

1. The maximum amount of hydrogen that can be transferred matches for the pairing alloys.
2. All the hydrogen is transferred in 10 minutes' cycle time.
3. The specific heat capacity of the alloys and the hydrides are based on the Dulong-Petit rule and Neumann-Kopp rule as adopted by Nakagawa *et al.*(2000).
4. The reactor vessel is made of stainless steel and its weight is twice as much as that of the alloy packed in it.
5. The heat loss and temperature difference for heat exchange is not considered.
6. Internal heat recovery is conducted and an efficiency of 50% is achieved.

Suppose a case of heat upgrading: Waste heat at 80°C is utilized to obtain useful heat at 110°C, and the ambient temperature is set to be 30°C. Under this situation, 15 pairs of alloys including LaNi₅-CaNi₅ were found viable for application and corresponding indices were listed in Table 2.

Table 2 Performance indices for the feasible pairs in a heat upgrading application

No.	pairing alloys	COP	qm	CP
1	LaNi ₅ -CaNi ₅	0.425	0.0631	0.966
2	LaNi ₅ -LaNi _{4.7} Al _{0.3}	0.450	0.0738	0.906
3	MmNi _{4.15} Fe _{0.85} -LaNi ₅ -V	0.259	0.0476	0.768
4	LaNi ₅ -TiFe _{0.8} Ni _{0.2} -CaNi ₅	0.314	0.0472	0.748
5	LaNi ₅ -TiFe _{0.8} Ni _{0.2} -LaNi _{4.8} Sn _{0.2}	0.317	0.0505	0.748
6	LaNi ₅ -TiFe _{0.8} Ni _{0.2} -LaNi _{4.7} Al _{0.3}	0.311	0.0487	0.748
7	V-CaNi ₅ -LaNi ₅	0.249	0.0491	0.795
8	V-CaNi ₅ -(V _{0.9} Ti _{0.1}) _{0.95} Fe _{0.05}	0.225	0.0548	0.738
9	V-LaNi _{4.7} Al _{0.3} -LaNi ₅	0.269	0.0567	0.848
10	V-LaNi _{4.7} Al _{0.3} -(V _{0.9} Ti _{0.1}) _{0.95} Fe _{0.05}	0.243	0.0636	0.787
11	V-LaNi _{4.8} Sn _{0.2} -LaNi ₅	0.264	0.0583	0.818
12	V-LaNi _{4.8} Sn _{0.2} -(V _{0.9} Ti _{0.1}) _{0.95} Fe _{0.05}	0.239	0.0658	0.759
13	(V _{0.9} Ti _{0.1}) _{0.95} Fe _{0.05} -TiFe _{0.8} Ni _{0.2} -CaNi ₅	0.284	0.0511	0.774
14	(V _{0.9} Ti _{0.1}) _{0.95} Fe _{0.05} -TiFe _{0.8} Ni _{0.2} -LaNi _{4.7} Al _{0.3}	0.282	0.0529	0.825
15	(V _{0.9} Ti _{0.1}) _{0.95} Fe _{0.05} -TiFe _{0.8} Ni _{0.2} -LaNi _{4.8} Sn _{0.2}	0.287	0.0551	0.796

Apparently, two pairs (1 and 2) are feasible for one-stage cycle, while 13 pairs can also be candidates with two-stage cycle (1 work + 2 regeneration) considered, thus the procedure proposed in the paper adds to the flexibility of selection. This is great advantage for some extreme working conditions.

By comparison of the indices, it is found that the one-stage cycle will generally obtain larger COP and alloy output than the two-stage cycle (1 work + 2 regeneration), which is straightforward to understand. Similarly, the two-stage cycle (2 work + 1 regeneration) can even achieve better performance than the one-stage cycle. Thus it is suggested that the pair of alloys should be searched in a category of the superior performance first, which shows that more than one category of pairs are viable. Nevertheless, in a realistic application performance is not the single concern, and the pairs in other categories may be adopted, too.

Finally we come to the last question, how to compare the performances of the pairs in the same category? We need to assess them in a whole sense, and the multi-element valued method is applied here. As an example we analyze the performances for pair 4~8. Firstly the indices for these pairs are normalized and then used to form a matrix G, in which every column stands for the performance of a specific pair:

$$G = \begin{vmatrix} 0.987 & 1 & 0.974 & 0.704 & 0.6 \\ 0.6 & 0.774 & 0.679 & 0.7 & 1 \\ 0.670 & 0.670 & 0.670 & 1 & 0.6 \end{vmatrix}$$

Secondly the indices are weighted by their importance, and this is done by the well known AHP (analytic hierarchy process). For a MHHP system, cost is critical for the application, then the efficiency and convenience, thus the importance of indices can be recognized: alloy output > COP > compatibility of pair. This is reflected in the comparison matrix B:

$$B = \begin{vmatrix} 1 & 1/3 & 5 \\ 3 & 1 & 7 \\ 1/5 & 1/7 & 1 \end{vmatrix}$$

Follow the procedure of AHP, the weight vector of indices was obtained as:

$$w = [0.279 \quad 0.649 \quad 0.072]$$

Then the integrated performance of j-th pair d_j can be calculated as follows:

$$d_j = \sum_{i=1}^3 w_i G_{ij} \quad (6)$$

The results were listed in Table 3 and the performance of the pair 8 was found to be the best.

No.	4	5	6	7	8
d_j	0.713	0.829	0.761	0.723	0.860
Comparison	8>5>6>7>4				

As is shown in the example, given the required properties of candidates, a reasonable selection of the pairing alloys for MHHP application can be realized by the procedure introduced in the paper, which is meaningful in the engineering practice.

4. CONCLUSIONS

The following conclusions can be drawn from the study:

- The new procedure shows flexibility and clarity in selection of the pairing alloys.
- The performances for different categories of pairs can be roughly determined as two-stage cycle (2 work + 1 regeneration) > one stage cycle > two-stage cycle (1 work + 2 regeneration), thus the selection should be considered firstly in the category with better performance.
- The several performance indices for a pair can be integrated by multi-element valued method, and then a definite result of a comparison among the pairs is obtained.

NOMENCLATURE

c	hydrogen concentration	($molH / mol$)	Subscripts
C	thermal capacity	(J / K)	a adsorption
ΔS	reaction heat	($J / (mol \cdot K)$)	d desorption
ΔH	reaction heat	(J / mol)	eq equilibrium
m_{H_2}	hydrogen transferred	(mol)	H high
M	molar mass	(kg / mol)	L low
n	cycle frequency	($1 / s$)	max maximum
P	pressure	($bar = 10^5 Pa$)	min minimum
Q	heat	(J)	M middle
R	universal gas constant	($J / (mol \cdot K)$)	R reactor
T	temperature	(K)	Superscripts
W	mass	(kg)	H high pressure alloy
η	efficiency of heat recovery	(—)	L low pressure alloy

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