Article ID: 1003-7837(2005)02,03-0068-06

Metal hydride air conditioner*

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Abstract: The relationship among the hydrogen storage properties, cycling characteristics and thermal parameters of the metal hydride air conditioning systems was investigated. Based on a new alloy selection model, three pairs of hydrogen storage alloys, $LaNi_{4.4}Mn_{0.26}Al_{0.34}$/ $La_{0.6}Nd_{0.4}Ni_{4.8}Mn_{0.2}Cu_{0.1}$, $LaNi_{4.61}Mn_{0.26}Al_{0.13}$/$La_{0.6}Nd_{0.4}Ni_{4.8}Mn_{0.2}Cu_{0.1}$ and $LaNi_{4.61}Mn_{0.26}Al_{0.13}$/$La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$, were selected as the working materials for the metal hydride air conditioning system. Studies on the factors affecting the COP of the system showed that higher COP and available hydrogen content need the proper operating temperature and cycling time, large hydrogen storage capacity, flat plateau and small hysterisis of hydrogen alloys, proper original input hydrogen content and mass ratio of the pair of alloys. It also needs small weight, heat capacity and good heat conductivity of the reaction beds. An experimental metal hydride air-conditioning system was established by using $LaNi_{4.61}Mn_{0.26}Al_{0.13}$/$La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$ alloys as the working materials, which showed that under the operating temperature of 180℃/40℃, a low temperature of 13℃ was reached, with COP = 0.38 and W_{net} = 0.09 kW/kg.

Key words: hydrogen storage alloys; heat pump; metal hydride air conditioner; refrigerating

CLC number: TG139.7; TB657.2 **Document code**: A

1 Introduction

Metal hydrides can be used as the working materials in the field of energy technology and show very promising potentials to contribute to the rational use of energy. One important application of hydrogen energy is the metal hydride heat pump[1-6], which uses the hydrogen reaction enthalpy to generate useful cold or heat, and the metal hydride air conditioner is one important form of it. The correlative reaction processes of metal hydride heat pumps are reversible, high effective, innoxious, non corrosive, steady and low cost. All of these make the metal hydride air conditioner a hot research direction in the area of "green air conditioners" in the world. Metal hydride air conditioner will be a new way to solve the problems of both pollution and energy, compared to the traditional Freon air conditioners. The working principle of a single-stage heat pump is shown in Fig. 1.

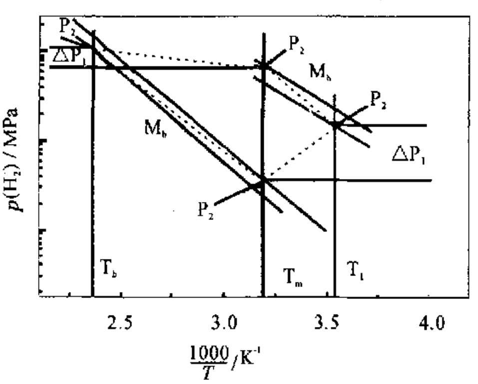

Fig. 1 The working principle of a single-stage heat pump

Received date: 2005-06-06

* Foundation item: The Natural Science Foundation of China (50266063).

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The metal hydride air conditioner shows the following advantages: (1) It can be operated with the waste heat exhausted from industrial plants, low grade heat sources and solar energy. Therefore it is an effective way to recycle low grade heat sources and waste heat to save energy. (2) Compared to other air conditioners, it can be operated only with heat. There is no moving part and the relevant noise in the operating process. Thus it is a quiet heat transfer device. (3) It only utilizes hydrogen as the working medium and has no pollution to environment caused by Freon leak. (4) Since there is only the interaction between gas and solid in the system, there is no corrosion and the abrasion caused by the operation of accessories, which enhances the working safety for it. (5) As hydrogen is the only working medium and can be transferred through pipelines, both the scheme and outline size of it can be flexible to fit the space. (6) It can provide useful cold in summer and useful heat in winter by changing the cycle model. (7) It offers a wide range of operating temperature from −50℃ to 550℃.

2 Selection of the metal hydride pair

Considering the analysis of classical thermodynamics, P. Dantzer[1] proposed a theoretical metal hydrides selection model for the metal hydride air conditioner system, which gave a relationship between the enthalpy ΔH and entropy ΔS of hydrides with the operating temperature. This model can get the proper ΔH and ΔS of metal hydrides when T_h, Tm and T_l are given. Based on this model, the pressure difference of a hydride pair ΔP, the safe pressure and the hysterisis of hydrides were taken into account to develop a new metal hydrides selection model for the metal hydride air conditioner. Three pairs of metal hydrides were selected based on this model and are shown in Table1. This modified model is more practicable than the Danter's model.

Table 1 Pairs of alloys used for metal hydride air conditioner

Alloy pairs	T_h/℃	T_m/℃	T_l/℃	COP
$LaNi_{4.61}Mn_{0.26}Al_{0.13}/La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$	180	40	10	0.40
$LaNi_{4.4}Mn_{0.26}Al_{0.34}/La_{0.6}Nd_{0.4}Ni_{4.8}Mn_{0.2}Cu_{0.1}$	180	60	0	0.43
$LaNi_{4.61}Mn_{0.26}Al_{0.13}/La_{0.6}Nd_{0.4}Ni_{4.8}Mn_{0.2}Cu_{0.1}$	150	60	10	0.49

3 Improvement of hydrogen storage property of metal hydrides by alloying

The existing hydrogen storage alloys do not always meet the requirement. For example, large plateau slope and hysteresis of metal hydrides will lead to a decrease of COP for a metal hydride air conditioning system. Alloying is one of the most effective ways to improve the hydrogen storage properties of metal hydrides. In this work, the low temperature alloys were modified by alloying with Cu and substitution of Nd and Y for La. The P-C isotherms of $La_xM_{1-x}Ni_{4.8}Mn_{0.2}$ (M=Y, Nd) alloys are shown in Fig. 2. It can be seen that the substitution of Y for La leads to increases of the plateau pressure and hydrogen storage capacity, but decreases of hysteresis, slope of plateau and hydrogen absorption kinetics. The lower effect of atomic size factor and larger average difference of electronegativity make the enthalpy of hydride formation more negative and the hydride more stable, thus substitution of Y for La leads to an increase of the plateau pressure[8-10]. $La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$ alloy was modified by alloying with Cu and substitution of Nd for La. Nd is effective on lowering the plateau pressure, improving the hysteresis (from 0.301 to 0.247) and sloping characteristics (from 0.187 to 0.046), in addition to increasing the hydrogen storage capacity. However, the Nd substitution dramatically decreases the hydrogen absorption kinetics, as shown in Fig. 2, which is adverse to the power output of a metal hydride air conditioning system. Alloying with a little amount of Cu improves hydrogen absorption kinetics without changing hydrogen storage capacity of $La_{0.6}Nd_{0.4}Ni_{4.8}$

$Mn_{0.2}$ alloy. The P-C isotherms of $La_{0.6}Nd_{0.4}Ni_{4.8}Mn_{0.2}Cu_x$ ($x=0-0.4$) alloys at 40℃ are shown in Fig. 3. It can be seen that Cu is effective on increasing the plateau pressure and modifying the hysteresis (from 0.29 to 0.09). In addition, a small amount of Cu ($x=0-0.2$) addition can also improve the hydrogen absorption kinetics dramatically. For AB_5 type alloys, the increase of amount of elements on B side probably leads to the formation of free Ni and Mn atoms which disperse in the alloy and contribute to the improvement of the hydrogen absorption and desorption kinetics. However, more addition of Cu ($x=0.3-0.4$) obviously decreases the hydrogen storage capacity, and worsens the sloping characteristic and the hydrogen absorption kinetics for the appearance of second phase Nd_2Ni_7.

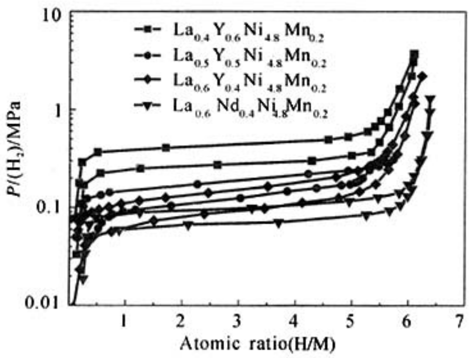

Fig. 2 Hydrogen absorption and desorption isotherms of $La_xM_{1-x}Ni_{4.8}Mn_{0.2}$ ($M=Y$, Nd) alloys at 273K

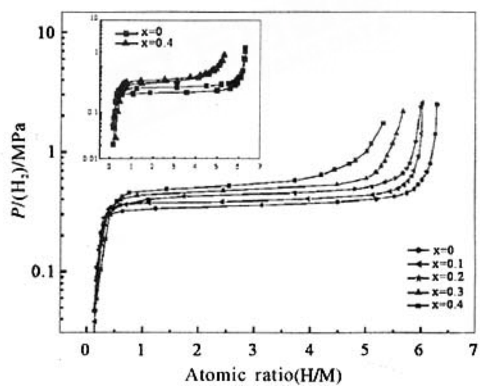

Fig. 3 Hydrogen absorption and desorption isotherms of $La_{0.6}Nd_{0.4}Ni_{4.8}Mn_{0.2}Cu_x$ alloys at 313K

4 Improvement of hydrogen storage property of metal hydrides by annealing

The slope factor of isotherms is affected by the homogeneity of alloys. The slope factor of the alloy has been effectively decreased by annealing, as shown in Fig. 4. The decrease of slope factor of isotherms is favorable for improving the COP of metal hydride air conditioners.

5 Main factors affecting the COP of metal hydride air conditioning systems

Coefficient of performance (COP) for a metal hydride air conditioner can be evaluated through the following equation[11]:

$$\mathrm{COP}=\frac{(\Delta X_2 n_2 (W_2/M_2)/2)\Delta H_2-(W_2C_2+W_{R2}C_{R2})(T_m-T_l)(1-\lambda)}{(\Delta X_1 n_1 (W_1/M_1)/2)\Delta H_1+(W_1C_1+W_{R1}Cp_{R1})(T_h-T_m)(1-\lambda)} \tag{1}$$

Where ΔH (kJ/mol) is the reaction enthalpy, n is the number of cycles per hour, W (kg) is the weight of alloys, W_R is the weight of reaction beds, ΔX is the cycling hydrogen content, M is the molecular weight, C (kJ/kg·K) is the specific heat capacity of alloys, λ is the thermal conductivity of metal hydride air conditioner and C_R is the specific heat capacity of reaction beds.

Cycling hydrogen content has a great effect on the COP of a metal hydride air conditioner. Higher COP and available hydrogen content need the alloys to have large hydrogen storage capacity, flat plateau and small hysterisis. For effective using of the alloys, the mass ratio of a pair of alloys should be close to

$$\frac{W_1}{W_2}=\frac{n_2 M_1 \Delta X_2}{n_1 M_2 \Delta X_1}, \tag{2}$$

The original input hydrogen content should be close to

$$N = n_1 \frac{W_1}{M_1}\frac{x_{1h}}{2} + n_2 \frac{W_2}{M_2}\frac{x_{2l}}{2} \tag{3}$$

And the reaction bed should have small weight, heat capacity and good heat conductivity. It also needs the proper operating temperature and cycle time.

It can be found from Equation (1) that the COP of a metal hydride air conditioner is directly affected by the operating temperature. As the high temperature T_h increases, there is an optimum temperature T_{h0} which gives the maximum COP. When the temperature is higher than T_{h0}, cycling hydrogen content increases monotonically and is saturated but the COP decreases. The reason why COP decreases at temperatures higher than T_{h0} is that the thermal losses of both the alloys and the reaction beds increase while cycling hydrogen content is saturated. The weight, specific heat capacity and thermal conductivity of reaction beds also have influences on the COP. Increasing the weight and specific heat capacity of reaction beds leads to a decrease of the COP for higher thermal loss. Increase of the thermal conductivity contributes to improve the COP. Thus, it is important to select the materials for the reaction beds. Cycle time is based on not only the hydrogen absorption/desorption kinetics of the alloys but also the thermal conductivity of the system. Longer cycle time increases the cycling hydrogen content, but decreases the cycle number per hour and useful cold or heat. Therefore, there is an optimal cycling time.

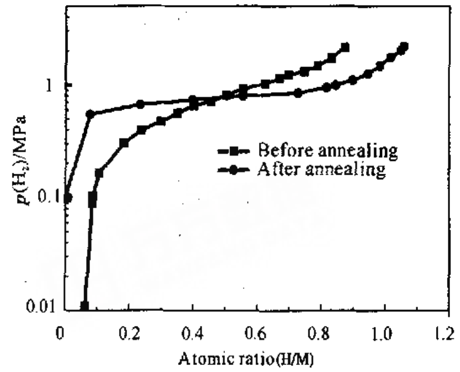

Fig. 4 Hydrogen absorption isotherms of $La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$ alloy at 293K before and after annealing

It is found that higher COP and available hydrogen content need the proper operating temperature and cycling time, large hydrogen storage capacity, flat plateau and small hysterisis of hydrogen alloys, proper original input hydrogen content and mass ratio of the pair of alloys. It also needs small weight, heat capacity and good heat conductivity of the reaction beds.

6 Performance of $LaNi_{4.61}Mn_{0.26}Al_{0.13}$/$La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$ alloys pair

A metal hydride air conditioner using two different types of metal hydrides, $LaNi_{4.61}Mn_{0.26}Al_{0.13}$/$La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$, was investigated. The alloys were crushed after the annealing and ground into powders of about 500 μm size. The mass ratio of the pair of alloys was close to Equation (2). The weight of the high temperature alloy, $LaNi_{4.61}Mn_{0.26}Al_{0.13}$, was 68.5 g and the low temperature alloy, $La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$, 70g. The two alloys were hydrided/dehydrided for ten times to ensure that they were fully activated. The original input hydrogen content was close to Equation (3), 0.5 mol high pure hydrogen. The cycling experiments were carried out to obtain steady cooling output by changing T_h and T_l when T_m = 40℃. The experiment result and the theoretical result are presented in Fig. 5 and Table 2. It can be seen that the practical result of COP is lower than the theoretical one. The main reason of

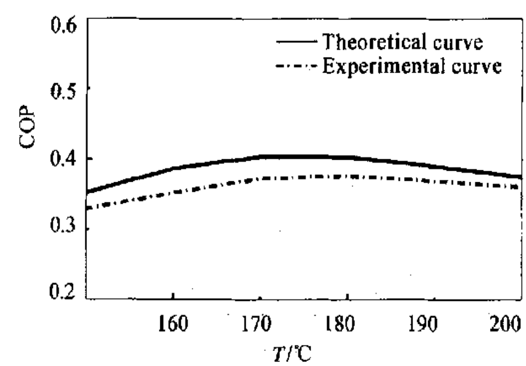

Fig. 5 Comparison between the results of theoretical and experimental COP

this phenomenon is that the real cycling performance is dynamic, both the hydrogen pressure difference of alloys and the cycling hydrogen content are lower than the theoretic ones, and there exists thermal loss as well. However, the experimental and theoretical results have the same changing trend and optimal operating temperature, which illuminates that the COP of refrigerating cycles of the alloys pair well fits with the result of the calculation model. The calculation model of COP plays an important role in design of the metal hydride air conditioner.

Table 2 Cycling parameters of the metal hydride air conditioner system at 40℃

T_h/℃	T_l/℃	Q_{in}/kJ	Q_{out}/kJ	COP theoretic	COP experimental	E_{out} /(kW·kg^{-1})
150	18	4.56	1.50	0.35	0.33	0.07
160	16	4.60	1.62	0.39	0.35	0.08
170	14	4.71	1.75	0.40	0.37	0.08
180	13	4.92	1.85	0.40	0.38	0.09
190	13	5.15	1.90	0.39	0.37	0.09
200	12	5.41	1.95	0.37	0.36	0.09

7 Conclusions

(1) A way of selecting proper alloys for metal hydride air conditioning systems is proposed. Three pairs of alloys, $LaNi_{4.4}Mn_{0.26}Al_{0.34}/La_{0.6}Nd_{0.4}Ni_{4.8}Mn_{0.2}Cu_{0.1}$, $LaNi_{4.61}Mn_{0.26}Al_{0.13}/La_{0.6}Nd_{0.4}Ni_{4.8}Mn_{0.2}Cu_{0.1}$, $LaNi_{4.61}Mn_{0.26}Al_{0.13}/La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$, are selected as the working materials of metal hydride air conditioners.

(2) A study on the effect of alloying on hydrogen storage properties and matching properties of metal hydrides shows that the substitution of Y for La leads to an increase of the plateau pressure, and Nd is effective on lowering the plateau pressure and improving the hysteresis and sloping characteristics, in addition to increasing the hydrogen storage capacity. Small amount of Cu ($x=0-0.2$) addition increases the plateau pressure and improves the hydrogen absorption kinetics dramatically.

(3) Higher COP and available hydrogen content need the proper operating temperature and cycling time, large hydrogen storage capacity, flat plateau and small hysterisis of hydrogen alloys, proper original input hydrogen content and mass ratio of the pair of alloys. It also needs small weight, heat capacity and good heat conductivity of the reaction beds.

(4) An experimental metal hydride air-conditioning system was established by using $LaNi_{4.61}Mn_{0.26}Al_{0.13}/La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}$ alloys as the working materials, which showed that under the operating temperature of 180℃/40℃, a low temperature of 13℃ was reached, with COP $=0.38$ and $W_{net}=0.09$ kW/kg. The COP of refrigerating cycles of the alloy pair well fits in with the results of the calculation model.

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