A PROSPECTIVE HYDROGEN STORAGE ALLOY PAIR FOR BUS AIR CONDITIONERS[①]

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ABSTRACT A new hydrogen storage alloy pair $LaNi_{4.45}Cu_{0.3}Al_{0.14}$—$ML_{0.99}Ni_{4.4}Fe_{0.6}$ was studied for a bus hydride air conditioners, in which ML means La-riched mischmetal. The waste heat from exhaust gas of the bus engine was used as the high temperature heat source and the atmosphere was used as the heat sink. $LaNi_{4.45}Cu_{0.3}Al_{0.14}$ was used as hot side alloy, its effective hydrogen capacity, hysteresis factor $f_h(= p_a/p_d)$ and sloping factor $f_s(= d\ln p_d/dn_H)$ are 5.67 mol/kg, 1.16, 0.13, respectively. $ML_{0.99}Ni_{4.4}Fe_{0.6}$ was used as cool side alloy with its three aforesaid properties being 5.68 mol/kg, 1.33, 0.12, respectively. From the theoretic calculations for the new alloy pair the theoretic COP_c(0.55) and E_{out}(1 407.9 kJ/kg·h) were obtained under operating temperatures of 150 ℃/40 ℃/20 ℃ and 6 min cycling time.

Key words hydride hydrogen storage alloy bus heat pump air conditioner

1 INTRODUCTION

The hydride heat pumps and air conditioners have been receiving much attention in the field of hydride applications because of their many advantages including the possible high coefficient of performance (COP), possible utilization of low grade heat and no environmental pollution. Conventionally, a hydride heat pump or air conditioner adopts two kinds of metal hydrides with different characteristics to execute its thermal cycle. Its COP depends mainly on the heat transfer properties of metal hydride beds and the matching properties of hydrogen storage alloy pair. Ron M[1, 2] designed and tested a model hydride bus air conditioner, with the alloy pair of $LaNi_{4.7}Al_{0.3}$ and $MmNi_{4.15}Fe_{0.85}$ (Mm: commonly used Ce-riched mischmetal). Although in his air conditioner, porous metal hydride compacts (PMHC) were adopted to enhance the heat transfer properties, the actual COP_c of the unit reached only 0.22~ 0.35, the poor performance of the unit is probably due to the unsatisfactory matching of the alloy pair. It is difficult to pick out a proper alloy pair with suitable pressure ranges and at the same time with good comprehensive characteristics under the present operating temperatures from the hydrogen storage alloys reported in literatures. So far, no specific investigation on the hydrogen storage alloy pair for a bus air conditioner has been reported. In this work, we are aiming at developing a pair of alloys which are suitable for a bus air conditioner.

2 EXPERIMENTAL

The raw materials used to prepare alloy were as follows: Ce-riched mischmetal (Mm) contained 21% La, 47% Ce, 6% Pr, 17% Nd and 9% other rare earths; La-riched mischmetal (ML) was prepared by Mm and La with different ratio of Mm to La. The purities of La, Cu, Al and Fe were all 99%, and Ni 99.9%. Alloys were prepared in an arc furnace under argon gas protection, and were remelted twice to ensure a better homogeneity.

X-ray powder diffraction results revealed

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that all samples were single phase with the $CaCu_5$ structure. The absorption pressure composition isotherms (p-c-T curves) were determined by the constant volume and pressure difference method, and the desorption p-c-T curves by collecting hydrogen through the displacement of water in a measuring cylinder[3-5]. The hydrogen used was 99.99% pure. Prior to the p-c-T measurements, samples were activated and hydrided/dehydrided several times. All samples were activated easily at room temperature and pressure of 4.0 MPa.

3 RESULTS AND DISCUSSION

The following aspects are probably rather important for hydrogen storage alloys used in a bus hydride air conditioner: the first is that the individual alloy has large effective hydrogen capacity to minimize the amount of alloys needed and subsequently to reduce the mass of the whole conditioner system, has a flat pressure plateau and a small hysteresis to make the best use of the effective hydrogen capacity and proper pressure to make the system operate under a rather low pressure; and the second is that the alloy pair has good matching properties to raise the efficiency of the system.

3.1 Optimum design of hydrogen storage alloy pair

Among the alloy pairs developed so far, most hot side alloys are La-Ni-Al family[6]. When transitional elements were used as the substitutional elements for Ni, Al is very effective on adjusting the plateau pressure and diminishing the hysteresis, however, when the substitution amount of Al is greater than 0.3 mole atom, it will lead to the much steeper plateaus and also remarkably reduce the effective hydrogen capacity. While Cu is one of the best elements to maintain a flat plateau, but its effect of adjusting the plateau pressure and diminishing the hysteresis is much lower than Al[7]. The investigation of nonstoichiometry alloy AB_x (x = 4.9~5.5) revealed that when x is less than 5.0, the plateau pressure decreases and the hydrogen storage capacity increases[8]. On the basis of the above analyses, we used both Al and Cu as the substitutional elements and investigated the hydrogen storage properties of $LaNi_{4.9-x-y}Al_xCu_y$ nonstoichiometry alloy family, in which x varied from 0 to 0.25, y from 0 to 0.5. In consideration of the factors including the plateau pressure (p), the effective hydrogen capacity (C_{eff}), the slope factor (f_s) and the hysteresis factor (f_h), the alloy $LaNi_{4.45}Cu_{0.3}Al_{0.14}$ was chosen as the hot side alloy. Its p-c-T curves are shown in Fig. 1. The thermodynamic parameters were determined by van't Hoff equation: $\ln p = \Delta H/(RT) - \Delta S/R$ and its main properties are tabulated in Table 1.

Because of its low cost and suitable pressure range Mm-Ni-Fe family is the commonly used cool side alloy. Large hysteresis is the remarkable demerit for $MmNi_5$ alloy, Fe is one of the most effective elements to suppress the hysteresis. However, when the substitution amount of Fe for Ni is high in cool side alloy, such as $MmNi_{4.15}Fe_{0.85}$ and $MmNi_4Fe$, many disadvantages are induced, such as the reduction in hydrogen storage capacity, the steep slope of pressure plateau etc. Our previous work indicated that the increment of La/Ce ratio in mischmetal can also diminish the hysteresis[5, 9]. Therefore, by means of increasing the La/Ce ratio and

Table 1 Main properties of $LaNi_{4.45}Cu_{0.3}Al_{0.14}$ and $ML_{0.99}Ni_{4.4}Fe_{0.6}$ alloys

	C_{eff}/ mol·kg^{-1}	f_s	f_h	ΔH_a/ kJ·mol^{-1}	ΔH_d/ kJ·mol^{-1}	ΔS_a/ J·mol^{-1}·K^{-1}	ΔS_d/ J·mol^{-1}·K^{-1}
Hot side alloy $LaNi_{4.45}Cu_{0.3}Al_{0.14}$	5.67	0.13	1.16	30.8	32.5	101	103.8
Cool side alloy $ML_{0.99}Ni_{4.4}Fe_{0.6}$	5.68	0.12	1.33	27.1	27.7	107	107.6

decreasing the substitution amount of Fe we can also obtain an alloy with small hysteresis. The properties of $MLNi_{5-y}Fe_y$ (among ML, La/Ce from 0.45 to 1.9; y = 0.2~ 0.8) were studied. The results revealed that $ML_{0.99}Ni_{4.4}Fe_{0.6}$ is a good cool side alloy and can match the hot side alloy well. Its main properties are superior to that of $MmNi_{4.15}Fe_{0.85}$ and $MmNi_4Fe$[10, 11]. Fig. 2 shows its p-c-T plots. Its main properties are also listed in Table 1.

3.2 Cycling properties of selected alloy pair

In Fig. 3, the van' t Hoff plots of the $LaNi_{4.45}Cu_{0.3}Al_{0.14}$—$ML_{0.99}Ni_{4.4}Fe_{0.6}$ hydride pair for a refrigeration cycle are presented. By using the formulae for calculating the maximum working hydrogen capacity reported in literature [12], ΔC_{hmax} and ΔC_{lmax} were calculated and

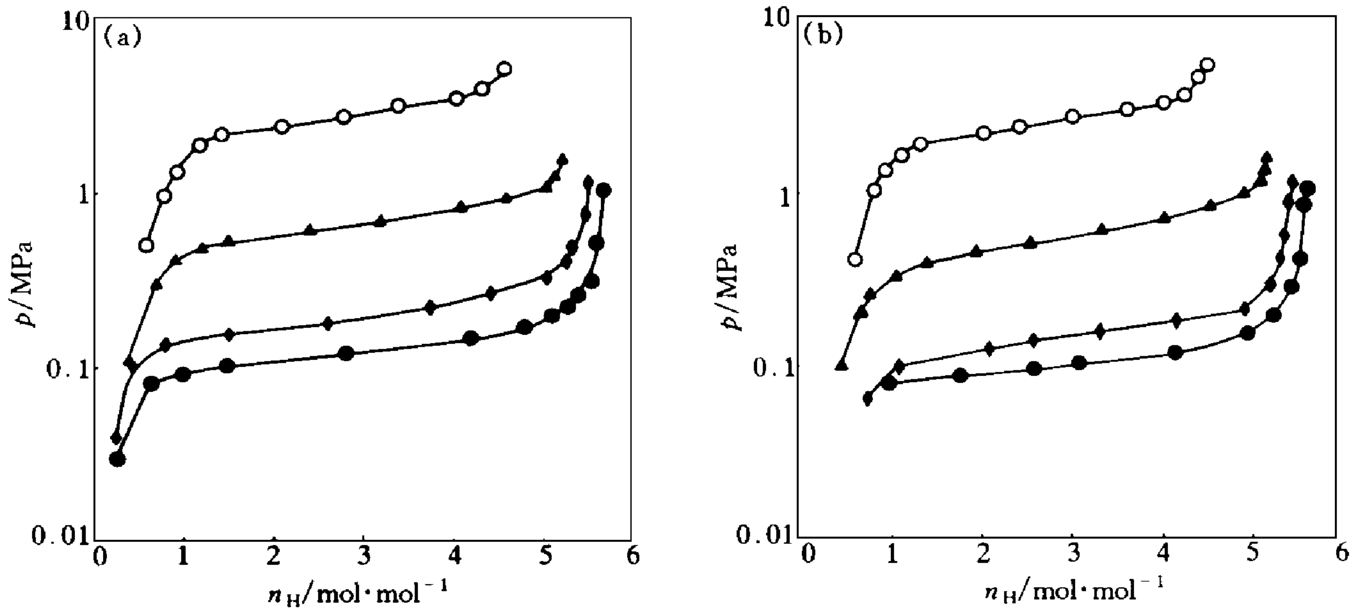

Fig. 1 p-c-T **curves for** $LaNi_{4.45}Cu_{0.3}Al_{0.14}$**—H system**

(a) —absorption; (b) —desorption

● —40 ℃; ◆—50 ℃; ▲ —90 ℃; ○—150 ℃

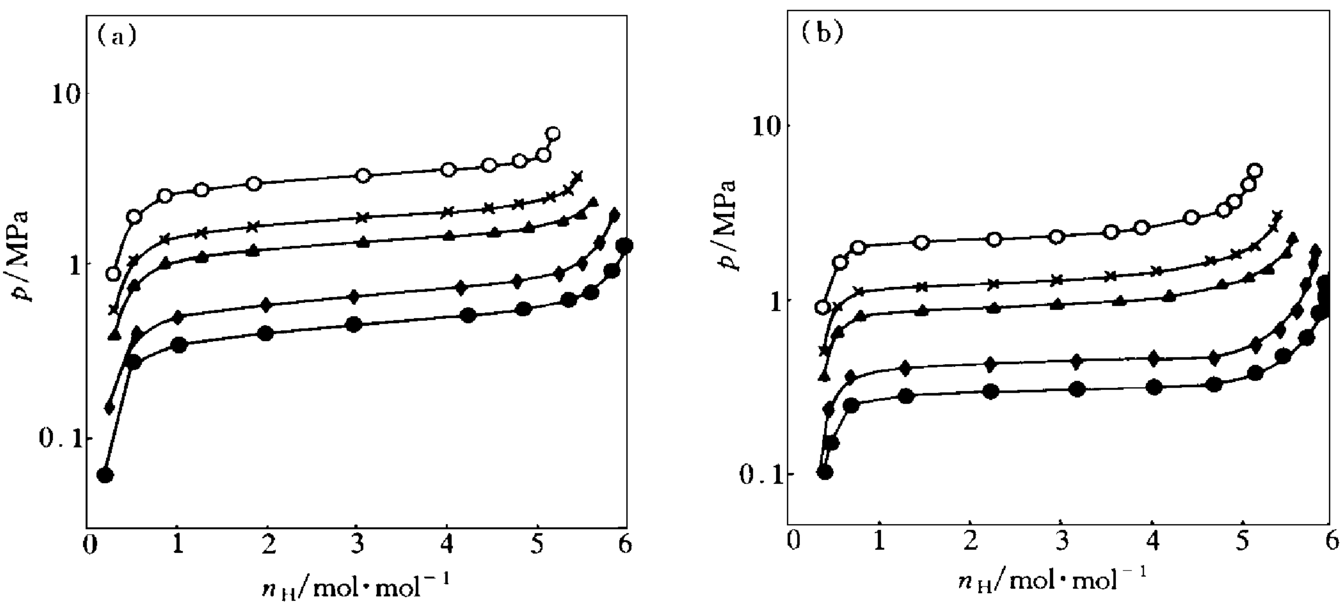

Fig. 2 p-c-T **plots for** $ML_{0.99}Ni_{4.4}Fe_{0.6}$**—H system**

(a) —absorption; (b) —desorption

● —10 ℃; ◆—20 ℃; ▲ —40 ℃; × —50 ℃; ○—70 ℃

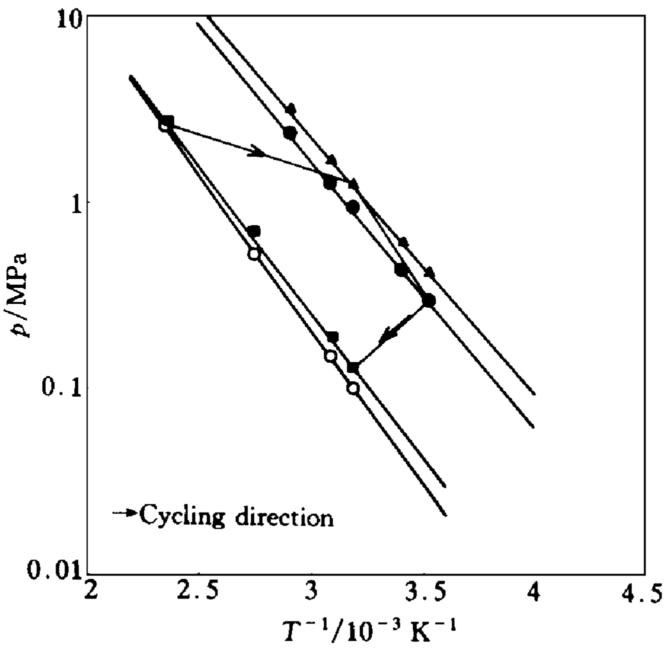

Fig. 3 van' t Hoff plots of $LaNi_{4.45}Cu_{0.3}Al_{0.14}$—$ML_{0.99}Ni_{4.4}Fe_{0.6}$ for a refrigeration cycle

(alloy 1: $LaNi_{4.45}Cu_{0.3}Al_{0.14}$; alloy 2: $ML_{0.99}Ni_{4.4}Fe_{0.6}$)

○—alloy 1, desorption;
■—alloy 1, absorption;
●—alloy 2, desorption;
▲—alloy 2, absorption

tabulated in Table 2.

COP_c and overall thermal output capacity E_{out} were calculated from the following equations with the heat loss being neglected.

$$COP_c = \frac{(\Delta H_{d2})(\Delta C_{max}) - C_{p2}(T_m - T_l)}{(\Delta H_{d1})(\Delta C_{max}) + C_{p1}(T_h - T_m)}$$

$$E_{out} = \Delta H_{d1} \Delta C_{max} \cdot m \cdot n$$

where C_p is the heat capacity of the hydride, taking roughly as 0.627 kJ/kg·K. T_h, T_m, T_l stand for high temperature, intermediate temperature and low temperature, respectively. ΔC_{max} is the smaller one of the ΔC_{hmax} and ΔC_{lmax}, the subscripts, 1 and 2, denote the hot side alloy and the cool side alloy respectively. m is the mass of alloy and n stands for the cycles per hour. The results are also listed in Table 2.

Table 2 Theoretic cycling properties of hydride pair

t/℃	ΔC_{hmax} /mol·kg^{-1}	ΔC_{lmax} /mol·kg^{-1}	COP_c	E_{out}/kJ·kg^{-1}·h^{-1} $n=6$	E_{out}/kJ·kg^{-1}·h^{-1} $n=10$
150/40/20	5.20	5.67	0.55	844.7	1407.9
150/50/20	4.40	4.52	0.50	715.5	1192.4

4 CONCLUSION

The $LaNi_{4.45}Cu_{0.3}Al_{0.14}$—$ML_{0.99}Ni_{4.4}Fe_{0.6}$ hydride pair has good hydrogen storage properties and is prospective for bus hydride air conditioners which use the waste latent heat from the exhaust gas of the bus engine as the high temperature heat source. In a refrigeration operation, the maximum theoretic COP_c value attains 0.55, and the theoretic overall output thermal capacity is 1 407.9 kJ/kg·h with the cycle time of 6 min uder operating temperatures of 150 ℃/ 40 ℃/20 ℃.

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