

Journal of Alloys and Compounds 293-295 (1999) 915-918

# A multi-hydride thermal wave device for simultaneous heating and cooling

E. Willers\*, M. Wanner, M. Groll

Institut für Kernenergetik und Energiesysteme (IKE), University of Stuttgart Pfaffenwaldring 31, D-70569 Stuttgart, Germany

### Abstract

A multi-hydride thermal wave device for simultaneous heating and cooling has been built and investigated. Seven different metal hydrides have been implemented on the high temperature side and two on the low temperature side. First experimental results with a hydrogen load of about 60% of the maximum hydrogen inventory showed the feasibility of the concept. The performance values are in the range of the predicted data, i.e. during the cooling period, a coefficient of performance (COP) of 0.60 has been obtained at cooling temperatures between 0°C and 10°C, while the average cooling power was about 360 W. With nominal hydrogen load, higher values can be expected. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Solid sorption; Refrigeration; Metal hydrides; Heat pump

## 1. Introduction

In the recent years, various thermally driven solid sorption systems using different working pairs have been investigated with respect to heating, cooling and heat transformation applications. The goal is to make it competitive with the highly developed conventional vapour compression devices and also with commercially available liquid sorption devices. It is obvious, that multi-effect or multi-stage systems with high efficiencies are needed in order to be attractive concerning environmental and/or economical aspects.

Compared with common solid sorption machine schemes (single-stage, double-stage and double-effect), both multi-sorbent systems (ammonia-salts, hydrogen-metals) [1,2] and thermal wave systems (zeolite-water, activated carbon-ammonia, activated carbon-methanol) [3–5] are promising because of their relatively simple machine schemes and good performance.

Both types of systems are multi-effect systems as long as a part of the heat gained in the absorbing high temperature reaction bed reduces the required amount of driving heat for high temperature desorption, which has to be provided by an external heat source. Reactors must allow the propagation of thermal and reaction waves, i.e. the heat and mass transfer to/from the reaction bed and within must be good. Additionally, a high number of transfer units (NTU) is essential for efficient operation.

The multi-effect is achieved by positioning several

suitable sorbents in series in one reactor and/or by inducing a thermal front to a reactor containing a sorbent having a large equilibrium temperature difference at a given pressure between completely charged or completely discharged states. A device employing multi-hydride reactors can be considered as a multi-hydride-thermal-wave system, due to the non perfect phase-change characteristics of metal hydrides.

## 2. Design of the combined heating/cooling device

The basic operational principle has been described elsewhere in detail [2,6]. Fig. 1 shows a schematic Van't Hoff plot of the device containing the machine scheme with the design pressures and temperatures.

The prototype consists basically of two heat transfer fluid (HTF) loops with oil as HTF in the high temperature loop I, and water in the low temperature loop II. Loop I contains two high temperature reactors HT1/2 and loop II two low temperature reactors LT1/2. Each loop needs a counter or cross current heat exchanger for heat input (I: HE1, II: HE4) and for heat output (I: HE2, II: HE3). The HTFs are pumped by a reversible two-channel proportionating pump. The machine does not need valves for operation, however, a bypass valve V in loop II (Fig. 1) can improve the performance of the device due to an improved internal heat recovery in loop I.

Each reaction bed has a diameter of 30 mm and a length of 880 mm with an annular channel for the HTF of 0.5 mm around it. The reactors HT1/2 contain 7 hydrides H1-H7

\*Corresponding author.

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PII: S0925-8388(99)00440-5



Fig. 1. Van't Hoff plot of the process, design pressures and temperatures are indicated.

and the reactors LT1/2 two hydrides H8, H9, arranged in series. The equilibrium temperature differences at uniform pressure from one hydride to the next in each reaction bed are about 15 to 25 K (see Table 1). The hydrogen is axially distributed via a sintered filter tube.

Each hydride section has an anisotropic thermal conductivity caused by a multitude of axially arranged aluminium foam cylinders (length:  $\approx 20$  mm, porosity: 92%, pore size: 1 mm, thermal conductivity: 8 W/mK) with hydride powder (thermal conductivity: 1 W/mK) in their pores and in the gaps between the cylinders. Due to the low thermal conductivity of the hydride in the gaps, the overall axial conductivity is 1 W/mK, while the radial conductivity is about 8 W/mK. The relatively high porosity, the axial filter tube and the heat transfer matrix contribute to a good heat and mass transfer in the reaction bed.

This particular reaction bed design allows the propaga-

Table 1Properties of the hydrides used

Hydride	No.	Equilibrium temperature [°C]			
		at 20 bar		at 5 bar	
		Abs.	Des.	Abs.	Des.
LaNi <sub>4 3</sub> Al <sub>0 4</sub> Mn <sub>0 3</sub>	1	212	222	152	161
$LaNi_{44}Al_{034}Mn_{026}$	2	196	205	139	147
$LaNi_{45}Al_{029}Mn_{021}$	3	172	181	125	134
LaNi <sub>4.7</sub> Sn <sub>0.3</sub>	4	154	163	107	115
LaNi <sub>4 75</sub> Al <sub>0 25</sub>	5	126	136	81	90
LaNi <sub>4.85</sub> Al <sub>0.15</sub>	6	113	122	66	75
LaNi <sub>5</sub>	7	95	105	47	55
La <sub>0.555</sub> Co <sub>0.03</sub> Pr <sub>0.12</sub> Nd <sub>0.295</sub> Ni <sub>5</sub>	8	60	66	18	25
Ti <sub>0.98</sub>	9	35	44	-3	4

tion of a sharp thermal and reaction front along the length of each hydride section of a reaction bed. The heat transfer coefficients between reaction bed and heat transfer fluid are about 3000 W/(m<sup>2</sup>K) for water and about 650 W/(m<sup>2</sup>K) for oil. The temperature change of the HTF while passing the reaction bed is great due to the different hydride equilibrium temperatures at uniform pressure, i.e. the number of transfer units (NTU) is high.

Due to the slowly propagating reaction waves in the multi-hydride-thermal-wave system, the half cycle time is relatively long, viz. about 20 min for the reaction beds used in the prototype. However, the half cycle time is a function of the reaction bed geometry and the overall heat transfer coefficients; it can be substantially reduced, e.g. 5 to 10 min are possible, if capillary tube bundle reactors are used [7].

The operation is comprised of two half cycles. With a half cycle time of 20 min and the measured properties of the selected low-temperature hydrides, a LT-module needs four desorbing low-temperature reaction beds to obtain a cooling power of 0.5 kW. In total, four modules (HT1, HT2, LT1, LT2), each containing four reaction beds, are needed for a quasi-continuous generation of cold.

For the cycle analysis we consider the temperatures at the nominal pressures of 5 bar (cooling half cycle) and 20 bar (regeneration half cycle) (Fig. 1). We start with heat exchanger HE3.  $Q_{\text{Heat,II}}$  is rejected in HE3 by cooling down the fluid from  $T_{\text{Heat,II,max}}$  (60°C) to  $T_{\text{Heat,II,min}}$  (40°C) While passing through reaction bed LT2, the fluid provides heat to the hydrides H8 and H9, causing desorption at low pressure  $P_{\text{L}}$  (5 bar), and is cooled down in two steps from 40°C to the cooling temperature  $T_{\text{Cool,min}}$  (4°C). In HE4 low temperature heat (useful cold)  $Q_{\text{Cool}}$  is taken up by the HTF. In LT1 the fluid is heated up from  $T_{\text{Cool,max}}$  (e.g. 20°C) to  $T_{\text{Heat,II,max}}$  (60°C) by heat from the hydrides H9/H8, where absorption takes place at high pressure  $P_{\text{H}}$  (20bar) After entering HE3, loop II is closed. The same functional principle holds in loop I. In the desorbing reaction bed HT1 (coupled with LT1) there is a temperature decrease in seven steps from 240°C down to 95°C. Useful heat  $Q_{\text{Heat,I}}$  is released in HE2 by cooling down the fluid from  $T_{\text{Heat,I,max}}$  (95°C) to  $T_{\text{Heat,I,min}}(40^{\circ}\text{C})$ . During hydrogen absorption in HT2, the HTF is heated up to  $T_{\text{Drive,min}}(152^{\circ}\text{C})$ . In HE1 the fluid is heated up by  $Q_{\text{Drive}}$  to  $T_{\text{Drive,max}}(240^{\circ}\text{C})$ .

When the exchange of hydrogen is finished, the pumping direction is reversed and internal heat recovery (in loop I) takes place. During internal heat recovery the bypass valve V in loop II is opened and the mass flow of the water through loop II becomes zero.

After the internal heat recovery the second half cycle begins. In this period, hydrogen is absorbed in HT1/LT2 and desorbed from LT1/HT2. A quasi-continuous power output both for heating and air-conditioning is obtained. A 'multi-effect' is given as long as the HTF temperature at the outlet of the absorbing HT-reactor ( $T_{\text{Drive,min}}$ ) is higher than at the outlet of the desorbing HT-reactor ( $T_{\text{Heat,I,max}}$ ).

The basis for the selection of the nine hydrides was – apart from their position in the Van't Hoff diagram – the plateau slope and the hysteresis. Both aspects have a great influence on the performance of the machine, however, the negative influence of the plateau slope is partly eliminated by the thermal wave passing through the respective hydride section. The influence of the hysteresis, however; cannot be eliminated.

Design operating temperatures and hystereses of the selected hydrides are shown in Table 1. The hysteresis between absorption and desorption is in a range of 6 to 10 K, which is an acceptable value. However, if the machine is operated with hysteresis-free hydrides, the COP for cooling will increase by up to 50%.

The control of the device can be characterized as follows:

The pressure evolution in the system is a function of hydrogen absorption ( $H_2$  sinks) and hydrogen desorption ( $H_2$  sources). If the sources provide more hydrogen than

the sinks take up, the pressure rises and vice versa. The temperatures of each single hydride are related to this pressure. Therefore the pressure can be controlled by inducing temperatures. A reduction of the equilibrium pressure between two coupled reaction beds can be achieved by increasing the mass flow of the proportionated HTF through the absorbing bed, thus taking up more absorption heat and increasing the hydrogen sink. Vice versa, a pressure rise is induced by increasing the mass flow through the desorbing reaction bed and thus strengthening the hydrogen source. Due to the temperature changes in the hydrides, the system will rapidly approach a balanced state at a pressure level characteristic for the respective mass flows and temperatures. Using this strategy, the device can provide a wide useful temperature and/or power range.

## 3. Experimental results with 60% hydrogen inventory

The device has been successfully operated. The working principle has been proved and first test runs have been performed. Due to a leakage problem, one reaction bed was taken out of operation, so each of the four units is operated with three reaction beds, and the nominal cooling power output is about 375 W. In the first test phase, the machine was operated with reduced hydrogen loads, beginning with 20%, 30%, etc.. The actual hydrogen inventory is 60% of the maximum hydrogen load. 20% of the hydrogen load are just sufficient to move the thermal masses, i.e. no hydrogen is left to produce cold after reaching the nominal pressures.

The proportionating pump has been manually controlled in this phase. It is possible to control outlet temperatures and power output by variation of the mass flow relation of the two HTF mass flows. The mass flow variation is achieved by changing the parameters of the peristaltic pump. In the next test phase, it will be controlled via a bypass valve as indicated in Fig. 1.

A set of measurements for one half cycle with a driving temperature of 235°C, a maximum cooling temperature of 18°C and a heat sink temperature of 33°C is shown in Fig.



Fig. 2. Measured pressure and mass flow evolutions over 1500 s.

2a and b. The overall time is 1500 s. The pressure evolution is shown in Fig. 2a. It can be observed, that the pressures can be held constant during the cold generation at 4 bar at the low pressure side and at 20 bar on the high pressure side. The constant pressure evolution is achieved by variation of the mass flow relation. Both mass flows are shown in Fig. 2b. During the intermediate phase, which is a partial recovery of the sensible heat of the HT-reaction beds, loop II is decoupled from the pump, i.e. no heat is transported to and from the low-temperature reaction beds. Due to the heat provided to the high temperature reaction bed, the pressure increases and hydrogen is desorbed from the seven hydrides. The hydrogen is flowing to the low temperature reaction beds, which are heated up by the absorption heat. After reaching the design pressures corresponding to the boundary conditions, loop II is taken into operation. Immediately, the pressure increase is stopped, because the absorption heat in the low temperature hydride is taken up by the HTF. Under normal conditions, this is the case, when the mass flows are in a well-defined relation.

This control has been performed manually at the pump, in order to keep the pressures constant. It can also be performed with the goal of keeping the temperature level of the useful cold constant.

The temperature measured in the reaction bed outlet section is 125°C ( $\Delta T=8$  K) for the high temperature reaction bed and 1°C ( $\Delta T=1.5$  K) for the low temperature reaction bed. The temperature difference  $\Delta T$  between the reaction bed and the heat transfer fluid is directly correlated with the respective heat transfer coefficients mentioned above.

The cooling power of the modules with three reaction beds is in the range of 230 W (outlet temperature  $10^{\circ}$ C) to 500 W (outlet temperature  $0^{\circ}$ C) with an average of 360 W. This is in good agreement with the design data (four beds per module providing 500 W), however, at the beginning of a cycle, the performance is better than towards its end, because the outlet temperatures from the low temperature reaction beds increase slowly. The COP during the cold generation period (550 s) was about 0.60 for cooling and 0.33 for the complete cycle. Both values will be improved by running the machine with higher hydrogen inventory. Then the overall COP will approach to the COP during the cold generation. The COP for heating has been measured to be about 1.4 for heating at levels of 45 to 60°C (about 40% of the total released heat) and 100°C (about 60%) during cooling operation and of about 1.1 for the complete cycle. This relatively low heat pump performance is closely related to several points: (a) the reduced hydrogen inventory, (b) convective and radiative losses to the environment, (c) the specific heat capacity of the oil, which differs by about 20% between the driving temperature and the useful heat temperature and (d) the hysteresis between the absorption and the desorption of the metal hydrides.

### Acknowledgements

This work has been partly supported by the European Commission, Brussels, in the frame of the EU-Contract JOU2-CT94-0445 and the Deutsche Forschungsgemeinschaft (DFG) in the frame of Sonderforschungsbereich (SFB) 270, "Hydrogen as an energy carrier".

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