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Investigation on a three-stage hydrogen thermal compressor based on metal hydrides

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Abstract. In this paper we report our recent investigation about a three-stage hydrogen thermal compressor based on metal hydrides (HTC) in order to reach an overall compression ratio 28:1. The research was focused to: (i) elaborate hydride alloys with good storage capacity and higher thermodynamic characteristics acquired by tailoring of their properties; (ii) develop new technical solutions based on advanced materials, and fast mass and heat transfer for a hydrogen storage-compression reactor; (iii) build up a prototype of the HTC. Cyclic performance of the hydrogen compressor is studied following up the operating parameters: supply pressure, storage volumes, cold and hot fluid temperatures, cycle duration. The experiments show that the HTC can attain a high overall compression ratio 28:1, it will raise the hydrogen pressure from 2 bars to 56 bars, using three hydride compression stages working between 20 and 80°C. Cycling the compressor at a short absorption-desorption cycle, about 2 minutes, a satisfactory hydrogen flow rate was obtained, 10 l/cycle, which ensures a hydrogen flow rate about 300 l/hour using a small quantity of hydride alloy, about 360 g. To improve the efficiency and economics of compression process, HTC prototype based on metal hydrides must operate in conjunction with advanced hydrogen production technologies from renewable resources.

1. Introduction

Hydrogen as an economically energy alternative, in the context of continuous decrease of fossil energy resources, environmental concerns related to release of gases responsible for the greenhouses effect and public health issues, must be considered a serious candidate over a time frame of decades. The vision of the hydrogen economy is based on two expectations: that hydrogen can be produced from domestic energy sources in a manner that is affordable and environmentally benign, and that applications using hydrogen (for example fuel cell vehicles) can gain market share in competition with the alternatives [1].

In Hydrogen Economy an important element of large scale hydrogen production, storage and utilization infrastructure is hydrogen compression. Considering that the future of hydrogen fuel cells become closer, energetic efficient compression technologies can contribute to hydrogen pipelines transport to the point of use and to distribute hydrogen by refuelling stations.

In order to use hydrogen in practice, besides production it must be efficiently stored and pressurized to increase the energy density. The most promising hydrogen storage methods are: absorption, compression, liquefaction and chemical binding [2]. Metal hydrides as absorbents for hydrogen absorption, offer some main advantages like high volumetric density and reversible absorption/desorption carried out at low pressure and low temperatures. Hydrogen compression based
on the reversible hydrogen absorption/desorption ability of metal hydrides is investigated as a reliable process to compress hydrogen at high pressure, without contamination and at low energy costs [3-5].

In this paper we report the development of a novel thermal hydrogen compressor (HTC) that may offer advantages for compressing hydrogen produced from renewable resources using advanced production techniques. Our three-stage thermal compressor is an absorption based system that uses the properties of reversible metal hydride alloys in a cyclical manner: hydrogen is absorbed into an alloy bed at ambient temperature and is desorbed at elevated pressure when the bed is heated with hot water.

Our research was focused on three main directions in order to: (i) elaborate hydride alloys with high storage capacity, resistant to poisoning, and higher thermodynamic characteristics acquired by the modeling of their properties; (ii) elaborate new technical solutions based on advanced materials, and fast mass and heat transfer for a hydrogen storage-compression reactor; (iii) develop a functional model of a thermal hydrogen compressor.

2. Principle of operation
Usage of the metal hydrides to hydrogen thermal compression, is based on the equilibrium pressure $P_{eq}$ variation with temperature $T$, described by van’t Hoff equation:

$$\ln P_{eq} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

where: $\Delta H$ is the enthalpy variation and $\Delta S$ is the entropy variation associated to absorption process (exothermal) or desorption (endothermic) of the metal hydride and $R$ is the ideal gas constant. As shown in figure 1 the operation of a one-stage hydride compressor consists of four processes namely: DA – hydrogen absorption at low temperature ($T_L$) and low pressure ($P_L$); AB - sensible heating and compression from cold fluid temperature ($T_L$) to hot fluid temperature ($T_H$); BC - desorption of compressed hydrogen at hot fluid temperature ($T_H$) and high pressure ($P_H$); CD - sensible cooling from $T_H$ to $T_L$. Compressor starts to discharge hydrogen when the hydride equilibrium pressure exceeds the preset value of the delivery pressure. In this case, the storage pressure is constant at the preset value of the delivery pressure.

![Figure 1. Principle of operation of a single stage hydrogen MHx compressor.](image)

According to equation (1), the pressure increases exponentially with increasing temperature, and large pressure values can be obtained by moderate temperature changes. The metal hydride based hydrogen compressor can be tailored to cover a wide range of operating pressures and pressure ratios by selecting suitable alloys.

To have a high outlet pressure, more hydride units can be serial connected, each unit with a different alloy and successive higher operating pressure. The most important properties of an alloy suitable for hydrogen compression are good hydrogen absorption - desorption rate, smaller process
enthalpy, fast reaction kinetics, great structural stability during the cycles. For compression, metal hydrides with large pressure to temperature gradients are desired, especially in the range of low temperatures. The efficiency of a single stage hydrogen metal hydride compressor is given by:

$$\eta = \frac{m(R_T \ln P_H - RT_L P_L)}{mC_p(T_H - T_L) + \Delta H}$$

(2)

where: $m$ is the mass of metal hydride, $C_p$ is the specific heat of metal hydride, $P_L$ is the equilibrium pressure at absorption temperature $T_L$, $P_H$ is the equilibrium pressure at desorption temperature $T_H$, $\Delta H$ is the enthalpy variation of metal hydride and $R$ is the ideal gas constant.

3. Selection of alloys

To operate at low heat source temperatures and low hydrogen pressure inlet, the desorption set point of 80°C was chosen while the absorption temperature is 20°C. Metal hydride materials available for these conditions are Ti-Fe, AB$_2$ and AB$_5$ alloys. The AB$_5$ alloys were selected because they combine good thermodynamic properties and high reaction rates over a large range of plateau pressures, easy activation and long term stability [6].

To reach the desired compression ratio, the metal hydrides used for our three-stage hydrogen thermal compression system are: stage 1 -LaNi$_{4.85}$Al$_{0.15}$, stage 2 -LaNi$_{4.9}$Cu$_{0.1}$, stage 3 -MmNi$_{4.05}$Fe$_{0.95}$. These alloys were prepared by arc melting technique and their pressure composition isotherms measured by a house-built volumetric Sievert installation, are shown in figure 2.

![Figure 2. Pressure composition isotherms of selected alloys for a three stage hydrogen thermal compressor.](image)

Table 1 presents the characteristics, pressure limit for absorption and desorption and the maximum reversible sorption capacity for selected alloy.

<table>
<thead>
<tr>
<th>Metal alloy</th>
<th>Absorption Pressure at 20°C (bar)</th>
<th>Desorption Pressure at 80°C (bar)</th>
<th>Storage capacity (H-wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi$<em>{4.85}$Al$</em>{0.15}$</td>
<td>2</td>
<td>12</td>
<td>1.25</td>
</tr>
<tr>
<td>LaNi$<em>{4.9}$Cu$</em>{0.1}$</td>
<td>10</td>
<td>24</td>
<td>1.22</td>
</tr>
<tr>
<td>MmNi$<em>{4.05}$Fe$</em>{0.95}$</td>
<td>20</td>
<td>60</td>
<td>1.18</td>
</tr>
</tbody>
</table>

4. Prototype development

The prototype of the three-stage hydrogen thermal compressor (HTC) is designed to operate by cycling between two temperatures assured by thermostatic water baths. The schematic design of HTC and van’t Hoff plots for a three-stage hydrogen compressor are shown in figure 3.
The HTC consists of three fast metal hydride reactors (FMHR) able to provide fast hydrogen absorption-desorption cycle and to process reasonable hydrogen flow rates. FMHR combine the effective increase of the thermal conductivity, optimized solutions to dissipate more effectively the heat of reaction and good permeability to hydrogen gas; each reactor is filled with 120 g of hydride alloy powder of starting grain size ~0.4 mm. Gas connections are built with Swagelok connectors with 6 mm pipes and hydrogen pressure inlet and outlet of each reactor are measured by four pressure transducers. Five needle valves and four one-way valves manage the hydrogen path through compressor and a mass flow meter measures the hydrogen flow rate. The hydrogen is delivered in a 3 l volume storage tank. Cold and hot water provided by two circulating baths are swapped between metal hydride reactors, depending on their absorption/desorption status. The experimental setup for the testing of the HTC is equipped with an Omni Logic Data logger for data acquisition regarding hydrogen pressure and flow rate, the cold and hot water temperature.

![Figure 3. Three-stage thermal hydrogen compressor: a) schematic design; b) van’t Hoff plots.](image)

5. Experimental
Thermal cycling experiments on the prototype shown in figure 4 were focused on the parameters which affect the performances of each stage of hydrogen thermal compressor: temperature and flow rate of cold and hot water, hydrogen inlet pressure and cycle duration.

![Figure 4. Prototype of the three-stage hydrogen thermal compressor based on metal hydrides.](image)

The temperatures for cold and hot water necessary for thermal cycling are 20°C and 80°C respectively, and the inlet hydrogen pressure is below 2 bars. While the hydrogen transfer rate between two FMHR is driven by pressure difference between the desorption plateau of an alloy and the absorption plateau of the one that occupies the next compressor stage, the heat of reaction tends to reduce the pressure gradient by changing the equilibrium conditions and the reaction slows down.
The absorption-desorption times were chosen to allow almost complete reaction, near 1 H-wt % in the hydrides alloys. Using FMHR the duration of a absorption-desorption cycle can be reduced down to 120 s, providing a good hydrogen absorption capacity of 0.85% H-weight, and a satisfactory flow rate. Thermal cycling behaviour of each stage of the compressor was studied measuring the absorption/desorption pressures and the flow rate of hydrogen inlet/outlet.

6. Results and discussion

The results obtained after the thermal cycling experiments on the prototype shows that for each stage of the compressor a fairly good compression ratio can be reached for a reduced duration of absorption-desorption cycle, t = 120 s. Figure 5 shows the evolution of pressure variation for each stage of the thermal compressor. It can seen that for the stage I, at an absorption pressure under 2 bars, after some cycles, the delivery pressure of first metal hydride reactor amounts to 10 bar, which correspond to a compression ratio 5:1. For the second stage, the compression ratio is 2:1, and for the third stage is 2.8:1, corresponding to an outlet pressure about 56 bars.

Figure 5. Pressure variation plots of the compressor’s metal hydride reactors for a 120 sec recurrent absorption desorption cycle.

For an inlet pressure P_L=2 bars, the compressor can deliver hydrogen at the pressure P_H=56 bars, corresponding to an overall compression ratio 28:1, in the conditions of a reduced cycle duration t=120 s. This allows to obtain a satisfactory hydrogen flow rate q=10 l/cycle which ensures a hydrogen flow rate Q=300 l/hour using a small quantity of hydride alloys, about 360 g, with small energy input.

7. Conclusions

An analysis of a three-stage hydrogen thermal compressor performance tests shows that: (i) the alloys selected and developed bring out suitable properties for hydrogen storage and compression; (ii) technical solutions built in HTC prototype design offer promising conditions to develop efficiently novel compressors that operates in conjunction with advanced hydrogen production technologies and improves the efficiency and economics of the compression process.

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References