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HYDROGEN COMPRESSOR UTILIZING OF METAL HYDRIDE

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Abstract: After low pressure hydrogen production by electrolysis of water, compression is required to increase the storage pressure in the final containers. The use of metal hydride materials seems to be a very effective way to increase the pressure of stored hydrogen. Heating these alloys significant increase the hydrogen pressure. The article describes the design of the compressor for using the generated heat at absorption process of the hydrogen into metal alloy during compression process. The equilibrium pressure, by which the absorption process occurs, is highly dependent at temperature of alloy. Difference in equilibrium pressures of MH materials at acceptable temperature change led to the effort to create a hydrogen compressor. The article describes the basic characteristic of hydrogen compressor and its actual state of development.

1 Introduction

Hydrogen is a chemical element with indication H and atom number 1. Hydrogen is non-toxic, without colour, taste and odor at standard temperature and pressure. Nevertheless, its properties are unique and important. Hydrogen is most numerous chemical substances in the space especially in the stars and gas packets of the planets. It is found on the Earth in the form of hydrocarbons and water [1].

Hydrogen is non occurring in the molecular unbound form. The most often the hydrogen produces by partial oxidation of natural gas, steam reforming and electrolysis of water.

In the case that hydrogen is not consumed right after production, is the necessary its storage. The majority of the storage methods require the using of the compressor which will increase the pressure to the desired level. The increase of the pressure is necessary due to the low density of hydrogen.

Hydrogen can be stored in high pressure vessels, in cryogenic containers and using adsorption and absorption materials.

Perspective hydrogen storage materials are metal hydride (MH) alloys that absorb hydrogen in the intimate space of its crystalline grid. These materials are characterized by a considerable pressure gradient, depending on the changing temperature. This knowledge can be used to compress hydrogen using MH trays [2].

2 Storage of hydrogen in the solid phase

In general, fuel tanks that are exposed to high loads must store high density energy, resist external mechanical effects, high pressure and temperature differences.

Hydrogen may be stored on the surface of the solids by adsorption, but also within the solids by absorption. In adsorption (Figure 1a), hydrogen is bonded to the surface of the material, either by hydrogen molecules or by hydrogen atoms. When hydrogen is absorbed (Figure 1b, c), the hydrogen molecule is dissociated and the atoms are then diffused into the metal lattice. This method allows storage of hydrogen at ambient temperature and pressure. Finally, hydrogen may be bound by a strong chemical reaction in molecular structures such as chemical compounds containing hydrogen atoms (Figure 1d) [3].

Metal hydrides offer several advantages over pressure storage or cryogenic storage:

- SAFETY: The safety limits for hydrogen storage in metal hydride are negligible compared to liquid or compressed hydrogen.
- SHUTDOWN: In the standby mode of the metal hydride reservoir, hydrogen is not released into the environment due to evaporation, as is the case with cryogenic storage.
- LOW PRESSURE: The metallic reservoir operates at a pressure range of between 8 and 30 bars (which corresponds to the electrolyser output pressure in the production of hydrogen by electrolysis and thus often does not require the use of compressors).

- PERFORMANCE: Selected metal hydrides have fast kinetics and achieve fast charging and discharging rates, as well as the high volumetric density of stored hydrogen.
- SIMPLIFIED USE: Metal hydride storage systems can be easily transported and installed. Additionally, the end of the metal hydride life cycle does not pose a danger to the environment [4].

Atom of hydrogen

Molecula of hydrogen

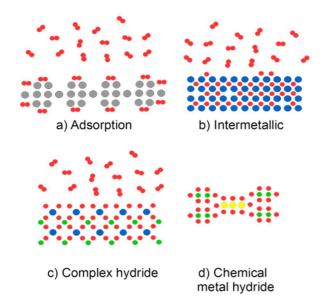


Figure 1 Possibilities of storage of hydrogen in the solid phase [3]

3 Storage of hydrogen in the metal hydrides

The metal hydride is formation by the metal and hydrogen atoms. Metal and hydrogen form two different types of the hydride. Alpha phase is if the metal absorbs only one part of hydrogen and the beta phase if the metal is completely saturated with hydrogen. Metals differ in their ability to catalytically dissociate hydrogen, which ability is dependent on surface structure, morphology and metal purity.

The optimal properties of the materials for hydrogen storage are: the high sorption capacity of hydrogen to the unit weight and volume, the low energetic difficulty (low generation of thermal during absorption), the low dissociative temperature, the medium dissociative pressure, the low temperature during production of the metal hydride, the minimum needed energy for desorption of hydrogen, the reversibilitation, the fast kinetic of the absorption-desorption cycle, high stability and oxy resistance (high service life), low recycling costs and high safety.

4 Basic characteristic of the hydrogen compressor

The compressor for compressing hydrogen, which is driven by the interaction of the hydride formation in the metal or in the intermetallic compound with hydrogen to the metal hydride, is considered to be a promising application for the hydrogen energy system. The advantage of a hydrogen compressor lies in its simplicity in design, compactness, safety, reliability, and absence of moving parts and the possibility of consuming waste heat instead of electricity.

Hydrogenation of the metal, respectively, alloys can be described by the following equation:

$$M(s) + \frac{x}{2}H_2(g) \leftarrow absorption/desorption \rightarrow MH_x(s) + Q$$
 (1)

where:

M - metal or alloy,

- s solid faze,
- g gas faze,
- Q generated thermos during absorption (J).

Process of produce of metal hydride by absorption of hydrogen into to alloy is accompanied by heat release Q. In desorption process, during decomposition, the alloy consumes approximately to the same quantity of heat.

Absorption and desorption process is strongly dependent to own characteristic of the reaction (1) including their thermodynamic and kinetic characteristics which include very important process of the heat and mass transfer. Also, important aspects include the composition, structure and morphology of the fixed phase involved in the process. These properties are related to basic aspects of the studied metal hydride material, mainly.

Using of the metal hydride for thermal compression of the hydrogen is founded on the equilibrium pressure and temperature described by van Hoff's equation (2) [5,6]:

$$\ln p_{\rm eq} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{2}$$

where:

- ΔH Enthalpy change (J·mol-1),
- ΔS Entropy change associated with absorption or desorption in a metal hydride (J·K-1).

As shown in figure (Fig. 2), single-stage compressor operation consists of 4 processes:

- DA Absorption of hydrogen in low temperature (TL) and low pressure (PL),
- AB Adequate heating and compression at change from temperature TL to temperature TH,
- BC Desorption of the compressed hydrogen at temperature TH and at increased pressure PHA,
- CD Adequately cooling from TH to TL.



The compressor is starting to perform desorption of the hydrogen if the equilibrium pressure of the hydride exceeds a set pressure value discharge In this case the pressure of the storage is constant with set value of the discharge pressure. The principle of operating the single-stage hydrogen compressor is shown in figure 2.

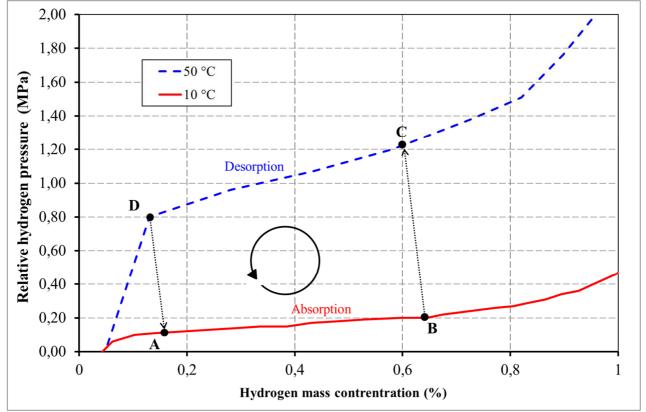


Figure 2 The principle of operation of the single-stage hydrogen compressor MHx [6]

Within the solution of the design hydrogen compressor was drawn up the scheme of the involvement (Fig. 3), which contains three metal hydride tanks and pipeline network for hydrogen with valves (V1 until V6). They will serve to regulate the filling and emptying of metal hydride tanks (MH1 until MH3). Each of the MH tanks will be equipped with temperature sensors t_1 , t_2 and t_3 . The diagram includes pressure sensors for each hopper and hydrogen output (p1 until p4). In scheme are shown threeway zone valves (TZ₁ until TZ₄), which will be regulate the circulation of the cooling or, respectively, heating water. VT_1 and VT_2 are heat exchangers that are part of the heat pump HP. The heat pump allows the collection of heat from the storage tank where the heat is absorbed and supplied to the pressure-increasing tank. The chiller (Ch) is also part of the assembly, which will, if necessary, help to cool the metal hydride tanks.

The hydrogen storage is ongoing in closed thermodynamic cycle at low temperatures. In the figure 3 is showed filling operation of the MH_1 tank where it occurs the hydrogen molecules are dissociated and subsequent the diffusion of atoms into the intermetallic structure of the alloy. During this reaction the heat is generated. The blue darts represent cooling water circuit. This circuit

withdraws the generated heat and with the help of the heat pump the transports the thermal energy into the tank MH₂.

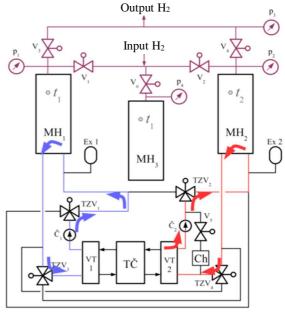


Figure 3 Scheme of the operation of the hydrogen compressor when filling the MH1 tank



We consider, the alloy in tank MH_2 is already saturated. By feeding the heat generated by tank MH_1 the pressure in the MH_2 tank increases. Subsequently, hydrogen can be desorbed from the alloy to the next stage of the compressor. Thus, the capacity of the MH_2 container is again reduced to its original state and the cycle can be switched to the opposite mode to ensure continuous operation of the hydrogen compressor.

Compressor uses absorption of the hydrogen into the two MH tanks arranged tandem. For transport of heat between tanks is used heat pump. The valve V_1 is open during hydrogen absorption into MH₁, while valve V_3 is closed. Heat is generated during this reaction. This heat removes the cooling circuit (highlighted by blue colour) connected to the heat pump evaporator (VT₁). In the tank MH₂ there is an increase in pressure the due to heat transfer by heating circuit (highlighted by red colour) from heat pump capacitor (VT₂). When the required pressure in the MH₂ tank is reached, the valve V₄ opens while the valve V₂ remains closed. Therefore, hydrogen is released to a higher degree of compression. After the MH₂ tank is emptied, valve V₄ and V₁ are closed.

5 Concurrency state of the hydrogen compressor

At the Department of Energy Technology, within the framework of the APVV project and in cooperation with

the company TATRANAT – water heaters, s.r.o. was designed heat pump (Fig. 4) water-water.



Figure 4 Heat pump water-water

The heat output of this heat pump is 1.5 kW with a cooling output of 1.2 kW. The R134a refrigerant with a weight of 900g is used in the heat pump. Measurements are currently taking place to optimize the amount of refrigerant to ensure continuous cooling and heating. For measurements, the heat pump was connected according to the following diagram (Fig. 5).

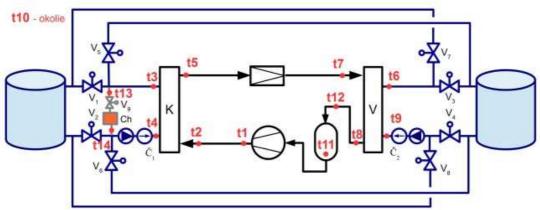


Figure 5 Connection of heat pump

Instead of the MH tanks were used in the measurement the water tanks, the amount of which corresponded to the heat capacity of two MH alloys with La, Ni and Ce alloys. The measurements were carried out in a temperature range of 10 to 50 °C. When the heat pump is operating, the heat output is still greater than the cooling, so the cooler is also included in the experimental set, which is cooled down to 50 °C if the chilled tank has not yet reached the temperature of 10 °C.

During the measurement, the compressor is switched off after several cycles. This emergency shutdown caused an increase in pressure over 2.3 MPa on the safety pressure switch. This pressure increase caused a sharp change in temperature in the condenser and evaporator. Subsequently, the amount of refrigerant from the original 900 g was adjusted to 700 g.

6 Conclusion

The development of a hydrogen compressor has a great potential for innovative social and economic needs in the development and application of hydrogen technologies in the automotive industry and transport, especially in the context of the Slovak and European innovation strategy.



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