

MEASUREMENT OF HYDROGEN STORAGE CAPACITY IN $\text{Ca}_{72}\text{Mg}_{28}$ ALLOY

Tomáš Brestovič¹, Natália Jasminská¹, Marián Lázár¹, Karel Saks², Ľubica Bednárová¹,
Michaela Šulíková², Mária Čarnogurská¹

¹ Department of Power Engineering, Technical University of Košice, Letná 9, 040 01 Košice, Slovakia, e-mail: tomas.brestovic@tuke.sk; natalia.jasminska@tuke.sk; marian.lazar@tuke.sk; lubica.bednarova@tuke.sk; maria.carnogurska@tuke.sk

² Slovak Academy of Sciences in Košice, Watsonova 47, 040 01 Košice, Slovakia, e-mail: ksaksl@imr.saske.sk; msulikova@imr.saske.sk

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ABSTRACT

This article discusses the measurement of hydrogen storage capacity in $\text{Ca}_{72}\text{Mg}_{28}$ alloy that has been produced by melt spinning. The alloy has an amorphous structure in which there is an assumption of hydrogen storage of acceptable concentration. The research is to analyse the possibility of desorption of the gas without recrystallization of the alloy. Subsequently, the problem of reversible hydrogen storage is examined at temperatures between 410–450 °C in the pressure range 0 to 3.5 MPa. This paper deals with the indirect determination of the amount of heat generated in the absorption of hydrogen by using the calorimetric method. In the conclusion there is a comparison of the storage capacity of hydrogen in the amorphous and crystalline structure of the alloy.

Keywords: metalhydrid, hydrogen, hydrogen storage, storage capacity of hydrogen

INTRODUCTION

The use of hydrogen in power and mobile applications has a high potential in a view of the zero emissions from combustion with oxygen. The widespread use of the gas is linked to the need to resolve energy-efficient storage at high density. Standard pressure and cryogenic storage methods require the use of high pressures (up to 75 MPa), or low temperatures (under 20.39 K) [1]. To increase the storage capacity of hydrogen, research is focused primarily on the development of adsorptive and absorbent materials, upon which high demands are placed. These are mainly low mass, high concentration by mass of stored hydrogen, low cost and easy production [8].

Metal hydrides based on magnesium are constantly the object of research precisely because of their low cost, light weight, heat resistance, reversibility and cyclic stability. Magnesium

hydride MgH_2 has the highest energy density (9 MJ·kg⁻¹) of all reversible hydrides [2]. This compound combines the advantages of a high mass content of hydrogen (7.66 wt.% H₂), low price of magnesium and reversibility.

For its wider practical use, it is necessary to add catalysts to the Mg such as Pd, Ni, Ge, Ti, and various oxides of V, Cr, Fe and Ti. This is due to high temperature during desorption of hydrogen from Mg and slow kinetics of the process.

The disadvantage of the given hydride is the high desorption temperature, slow desorption kinetics, and its high reactivity with oxygen. A critical factor in the use of metals for forming metal hydride is their surfaces, which must allow the dissociation of hydrogen molecules and their subsequent diffusion into the metal. In Table 1 are some types of magnesium hydrides, together with their properties.

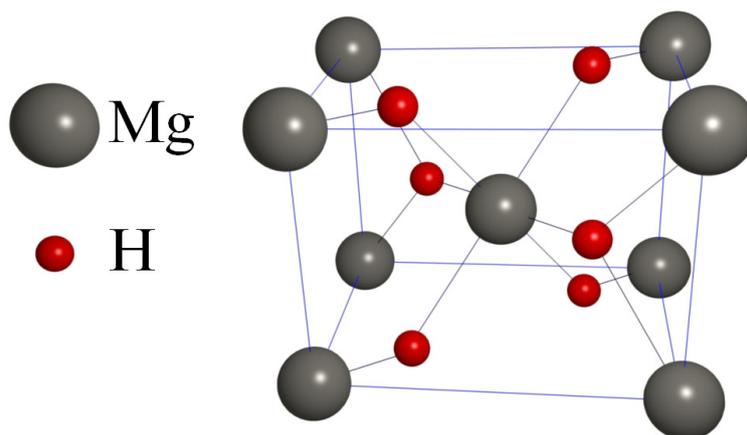


Fig. 1. Crystalline lattice of MgH₂

Table 1. Properties of selected magnesium hydrides [4]

Material	Temperature (°C)	Pressure (MPa)	Kinetics (min)	Cyclical stability	wt.% H ₂
MgCoH ₅	T _{abs} = 450–550	p _{abs} = 1.7–2.5	No data	1000 cycles	4.48
MgH ₂ -5 wt.% V	T _{ats} = T _{des} = 300	p _{abs} = p _{des} = 0.1–0.3	t _{abs} = 2, t _{des} = 10	2000 cycles	5.00
Mg/MgH ₂ -5wt.% Ni	T _{abs} = 230 – 370	p _{abs} a p _{des} = 0.4–0.04	t _{abs} = 90	800 cycles	6.00
MgH ₂ -0.2mol%Cr ₂ O ₃	T _{ats} = T _{des} = 300	p _{abs} a p _{des} = 0.1–0.2	t _{abs} = 6	1000 cycles	6.4

EXPERIMENTAL DETAILS OF ABSORPTION PROCESS

Ribbon specimens with the cross section of 0.033 m² were prepared directly from powder mixture of Ca (99.5 at.%) and Mg (99.9 at.%) metals by a melt spinning technique. A jet of molten material formed by ejecting the melt under pressure of purified argon through an orifice impinged on the surface of a cooper wheel rotated with a surface velocity of 31.4 m·s⁻¹ [4, 6]. The final chemical composition of the so-prepared ribbons was examined by energy dispersive X-ray microanalysis [11]. The ribbon was later powdered in a swing mill and placed in the pressure vessel for later hydrogen test.

The stated sample with the mass of 6.1172 g was placed in the reaction pressure container in an inert helium atmosphere and subsequently connected to the measuring system (Fig. 2). It consists of a pressure vessel with a reducing valve, which allows the regulation of hydrogen pressure up to 10 MPa, mass flow meter, pressure sensor, wire filter for possible prevention of penetration of the fine fractions of the alloy into pressure pipelines, pumps to extract gas from the system and apparatus for accurate volumetric determination the amount of hydrogen released. After sealing, the

measuring system was vacuumed for 10 minutes with subsequent increase in hydrogen pressure to 1 MPa. Flushing system with vacuuming was repeated three times to ensure the removal of unwanted gases from the measuring system [3, 7, 9].

A temperature sensor with a datalogger was placed on the surface of the reaction vessel, the vessel was then heat-insulated (insulation thickness 10 mm, thermal conductivity 0.04 W·m⁻¹·K⁻¹). The insulation of the container enables the deter-

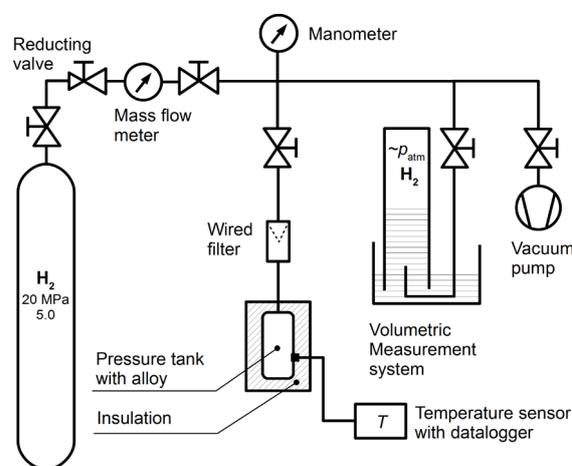


Fig. 2. Schema of the measuring device for determining the absorption of hydrogen

mination of the approximate amount of heat released in the absorption of hydrogen. With the gradual increase of the hydrogen pressure in the reaction vessel to 7 MPa there was a discernible temperature increase (Fig. 3), caused by absorption of hydrogen.

Hydrogen absorption is noticeable especially with a fall of its pressure. The progress of pressure over time is shown in Fig. 4.

The measurement of the absorbed amount of hydrogen was completed in 5760 s, when the pressure drop and temperature is minimal.

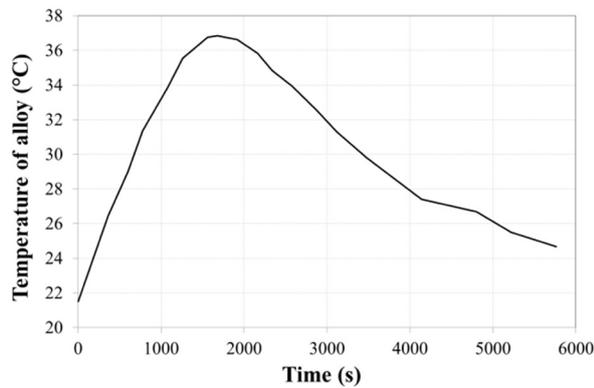


Fig. 3. Course of temperature in pressurizing $\text{Ca}_{72}\text{Mg}_{28}$ alloy to an initial pressure of 7 MPa

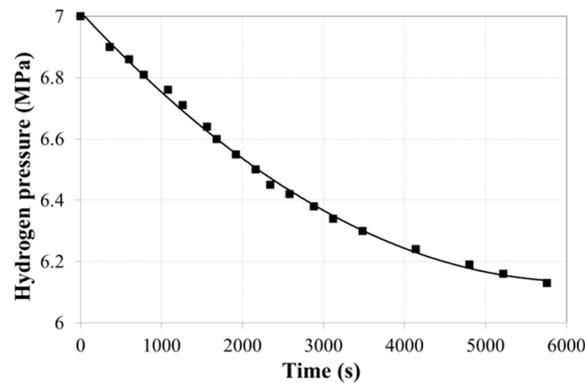


Fig. 4 Progress of relative pressure of hydrogen in the measuring system

Given that the volume of the storage apparatus is known, it is possible to use the pressure drop to calculate the amount of absorbed hydrogen.

By applying the equation of state, at known temperatures and pressures, the amount of hydrogen absorbed Δm_{H_2} were determined by the indirect method as:

$$\Delta m_{\text{H}_2} = \frac{p_1 \cdot V}{r \cdot T_1 \cdot z_1} - \frac{p_2 \cdot V}{r \cdot T_2 \cdot z_2} \quad (1)$$

where: p is absolute pressure (Pa),
 V – volume of storage system (m^3),
 r – individual gas constant for hydrogen ($\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$),
 T – thermodynamic temperature of system (K),
 z – compressibility factor.

Index 1 is for index values at the beginning of the measurement at time 0 and index 2 is for values at the end of the measurement time 5760 s. The mass of hydrogen absorbed in the alloy $\text{Ca}_{72}\text{Mg}_{28}$ of amorphous structure was $5.868 \cdot 10^{-5}$ kg, which represents $6.53 \cdot 10^{-4}$ m^3 . From the calculated mass it follows that the alloy is capable of binding to the structure, 0.96 wt.% of hydrogen.

NUMERICAL SIMULATION OF HEAT LOSSES AT ABSORPTION PROCESS

The amount of heat that is released in the absorption of hydrogen by the alloy can be determined by the analysis of the heat flow passing through the insulation, brass feed line and the amount of heat stored in parts of the reaction vessel at the end of the measurement. Due to three-dimensional heat conduction in combination with convection and radiation, a numerical calculation of heat transfer was performed in the ANSYS CFX software. The calculation mesh of the reaction vessel with the feed pipe is shown in Fig. 5. The steel reaction vessel is connected to 3/8" UNC threaded to a brass holder, while to

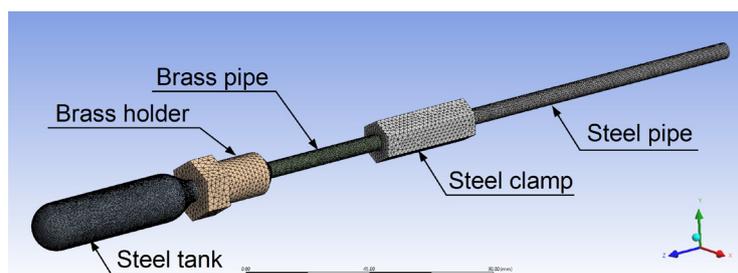


Fig. 5 Depiction of calculation mesh of reaction vessel with feed pipe

prevent the leakage of hydrogen an aluminium seal is used. The $\text{Ø}6 \times 1$ mm brass tube is connected to a stainless steel tube of the same size using steel couplings.

To simplify the model, insulation was substituted by a boundary condition on the surface of the container with a set value of overall heat transfer coefficient including the resistance of the thermal insulation. As mentioned above, the heat flux also passes through the feed pipe, which acts as a rib, thus increasing heat loss to the surroundings (Fig. 6).

The numerical calculation was performed as time dependent with a total time of 5760 s and a step of 10 s. Between the boundary conditions it

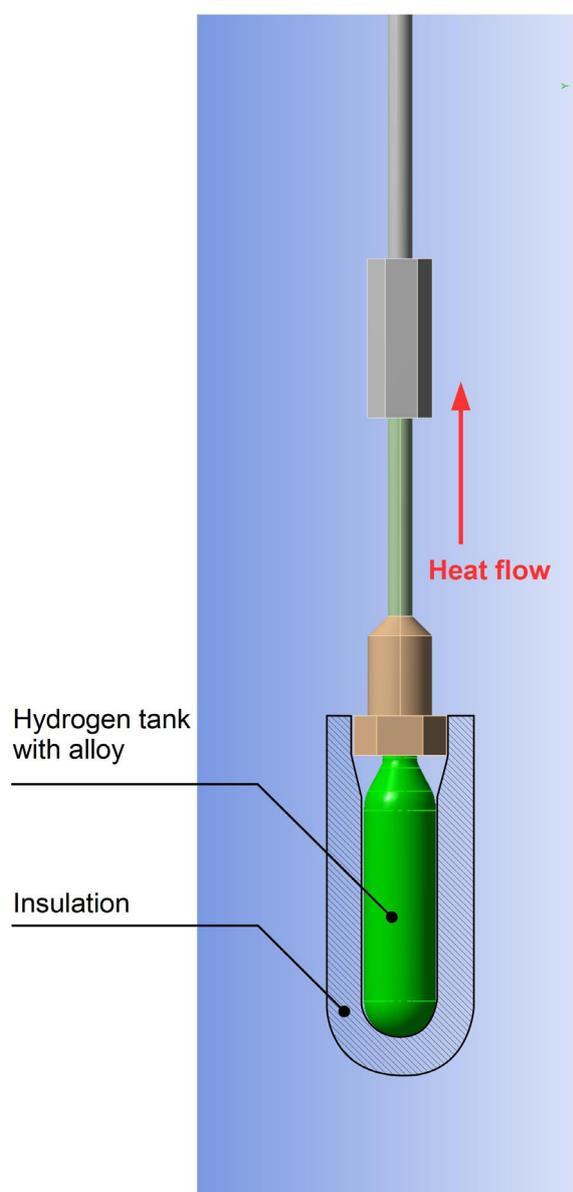


Fig. 6. Detailed depiction of insulation and direction of heat flow along the feed pipe to the environment

is possible to determine the temperature inside the reaction vessel based the measured data (fig. 3) and the heat transfer coefficient between the surface of the equipment and the environment, which has been specified as a temperature-dependent. It was determined from the criterion equations according to the literature [8]. The resulting temperature field at the maximum temperature of the tank at time 1680 s is shown in Fig. 7.

On the basis of the numerical calculation of non-stationary heat transfer it is possible to determine the heat flow P_h supplied to the system during the absorption of hydrogen (Fig. 8).

It is calculated by integrating the heat flux q across the whole heated surface of the tank A and by the relationship to the expression:

$$P_h = \int_A q \, dA \quad (2)$$

The total heat released in the absorption is the sum of the loss energy E_o and the stored energy in individual systems E_{acu} according to the following relationship:

$$E_o = \int_0^{5760} P_h \, d\tau = 1413 \, \text{J} \quad (3)$$

$$E_{acu} = \sum \left[\int_V \rho \cdot c \cdot (T - T_a) \, dV \right] = 161 \, \text{J} \quad (4)$$

where: τ is the time (s),

ρ – density of material (kg m^{-3}),

c – specific heat capacity ($\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$),

T – thermodynamic temperature of element of reaction vessel and pipe (K),

T_a – ambient temperature (K). The energy released in absorption of hydrogen into $\text{Ca}_{72}\text{Mg}_{28}$ alloy with amorphous structure, related to the volume of absorbed hydrogen, in the relationship (5) is $26.8 \, \text{MJ kg}^{-1}$ ($2.4 \, \text{MJ m}^{-3}$, $54 \, \text{kJ mol}^{-1}$).

$$q_{\text{Ca}_{72}\text{Mg}_{28}} = \frac{E_o + E_{acu}}{\Delta m_{\text{H}_2}} \quad (5)$$

EXPERIMENTAL DETAIL OF DESORPTION PROCESS

After cooling the samples and again increasing the pressure to 7 MPa there was no increase in temperature, from which it can be concluded that the alloy is unable to absorb a greater amount

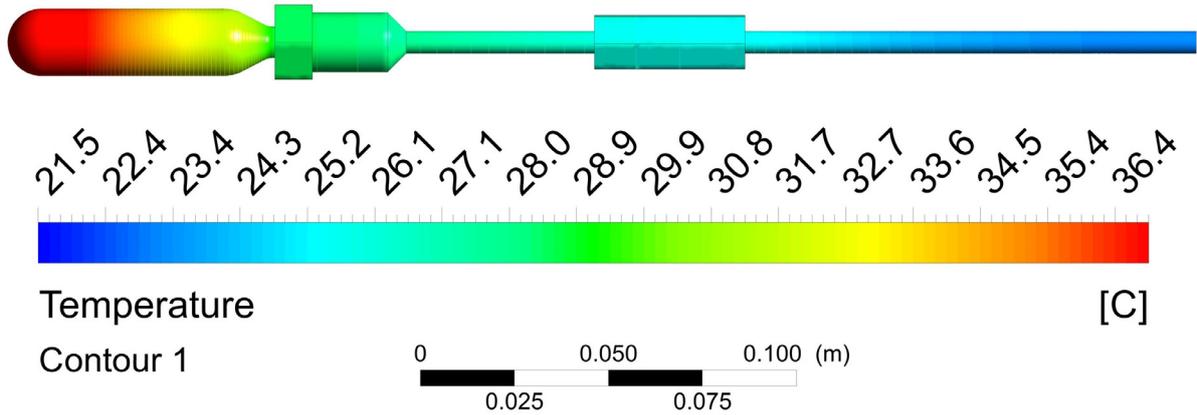


Fig. 7. Temperature fields on the surface of the reaction vessel at 1680 s

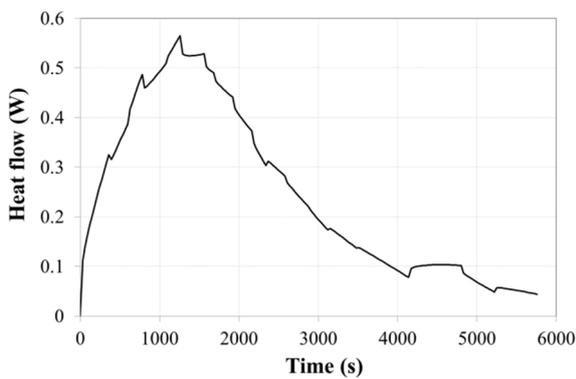


Fig. 8. Heat flow in absorption of hydrogen

of hydrogen. After heating the sample to 180 °C (using an electric resistance furnace at an absolute pressure of 0.1 MPa) there was no release of hydrogen, therefore, the sample was cooled to 21 °C, vacuumed out and then heated under vacuum to 330 °C without hydrogen desorption. At 330 °C, the first recrystallization of the alloy was observed. From this part of the experiment it can be concluded that the alloy is not capable of desorbing hydrogen from the amorphous structure even under vacuuming of the system.

Given the unsuccessful attempts to desorb hydrogen from the amorphous structure, hydrogen from the storage chamber is vacuumed off by vacuum pump; the opened reaction vessel was heated by electric resistance furnace at a rate of 3.3 K min⁻¹ up to recrystallization temperature. The liberated hydrogen was taken in by the vacuum pump into a graduated cylinder filled with deionised water (Fig. 9) up to the measured temperature and the outside atmospheric pressure. Subsequently, the volume was recalculated to the standard condition (0 °C, 101325 Pa).

After exceeding the temperature of 390 °C, where there is an expectation of crystalline alloy

structure, there was a gradual release of hydrogen, with the largest increase in the volume of gas released at temperature between 410–450 °C (Fig. 10).

During desorption 350·10⁻⁶ m³ of hydrogen was released. Subsequently, the sample was left in the furnace, where it slowly cooled to ambient temperature with continuous vacuuming of the system. This ensured the creation of a uniform crystal structure suitable for the reversible storage of hydrogen. The progress of temperature of the alloy with respect to time is shown in Fig. 11.

Given that the ability of the alloy to desorb hydrogen in the range 410 to 450 °C has been demonstrated, the following measurements were performed of PCI (Pressure Concentration Isotherms) curves at temperatures of 410, 430 a 450 °C.

The progress of indirect measurement of pressure concentration isotherms involves the gradual discharge of hydrogen into the measuring cylin-

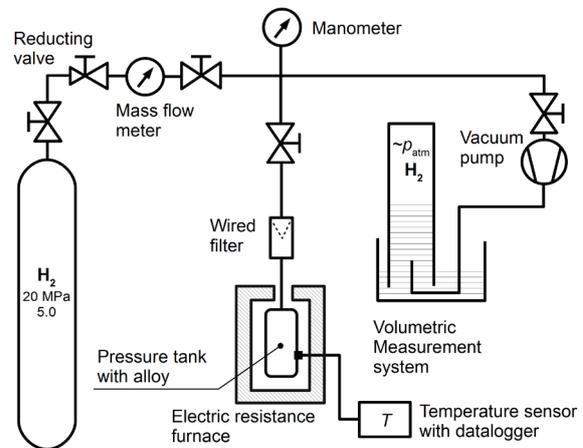


Fig. 9. Schema of measuring equipment for determining the volume of desorbed hydrogen in vacuuming

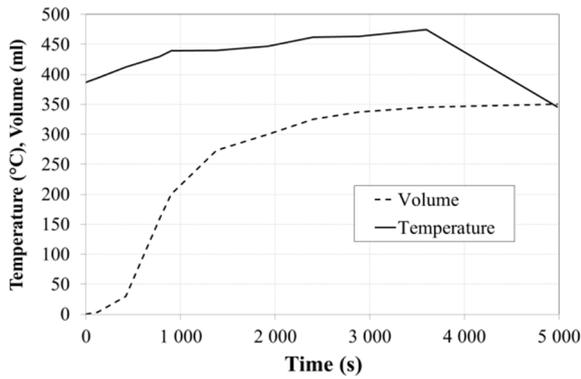


Fig. 10 Desorption of hydrogen from crystalline $\text{Ca}_{72}\text{Mg}_{28}$

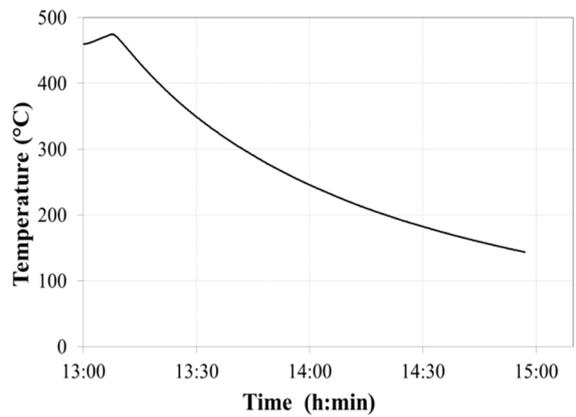


Fig. 11 Cooling the sample of alloy

der under isothermal reduction of the pressure in the reaction vessel in which the sample alloy is placed (Fig. 12).

In measuring, it is necessary to determine the mass of stored hydrogen in an empty reaction vessel (without the alloy and pressure of hydrogen at isothermal conditions). Comparison of the storage capacity of the empty reaction vessel and the reaction vessel with the alloy allows the determination of the density of hydrogen stored (Fig. 13).

The maximum density of crystalline alloy $\text{Ca}_{72}\text{Mg}_{28}$ was measured at temperature 430 °C, where it reached a value of 0.37 wt.%. The equilibrium pressure at temperature 430 °C is 1.1 MPa.

RESULTS AND DISCUSSION

Absorption and desorption process

At hydrogen absorption into the $\text{Ca}_{72}\text{Mg}_{28}$ alloy with amorphous structure, manufactured while applying the melt spinning technology, the alloy is capable of absorbing hydrogen at the temperature of 20 °C, once the pressure is increased up to 7 MPa. The decrease in the pressure in the reaction storage vessel was used to calculate, while applying the state equation of the real gas, the amount of the absorbed hydrogen. The measurements indicated that the alloy is capable of absorbing 0.96 vol% of hydrogen. Hydrogen desorption at the absolute pressure of 0.1 MPa within the temperature range from 21 to 180 °C was not proved, the sample was thus repeatedly deaerated within the temperature range from 21 to 330 °C, again without evident hydrogen release. We can therefore state that hydrogen cannot be desorbed from the $\text{Ca}_{72}\text{Mg}_{28}$ alloy with amorphous structure without

recrystallization that occurs at the temperature of 330 °C. At subsequent gradual increasing of the temperature of the $\text{Ca}_{72}\text{Mg}_{28}$ alloy with crystalline structure, hydrogen release started at the temperature of 390 °C. During the experiment, hydrogen desorption process was terminated once the temperature of 470 °C was achieved at second 3600. With regard to the aforesaid, Pressure

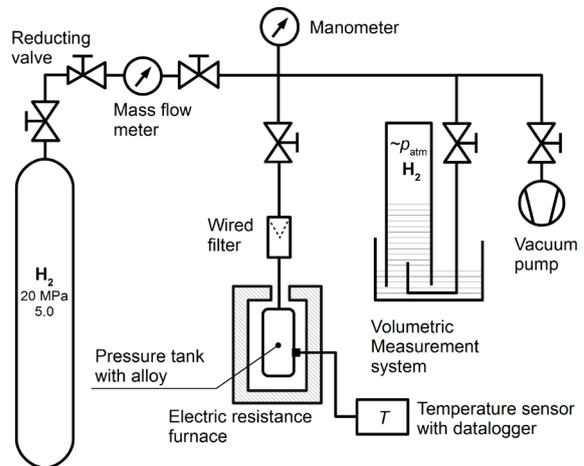


Fig. 12. Schema of measuring equipment for determining PCI curves

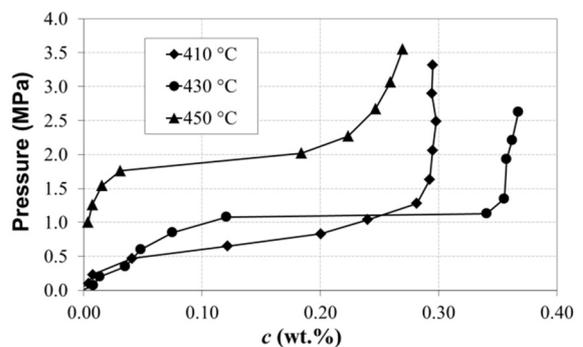


Fig. 13. Pressure concentration isotherms

Concentration Isotherms were measured at constant temperatures of 410, 430, and 450 °C, which proved also the reversibility of the ability to store hydrogen in the crystalline structure of the alloy. The maximum mass concentration of the stored hydrogen, which can be reversibly stored, is 0.37 wt% at the temperature of 430 °C and at the pressure of 1.1 MPa.

On the basis of the results of the experimental measurements it can be concluded that hydrogen desorption from the $\text{Ca}_{72}\text{Mg}_{28}$ alloy with amorphous structure is not possible. Hydrogen may only be reversibly stored in the $\text{Ca}_{72}\text{Mg}_{28}$ alloy if the material's structure is crystalline.

Numerical simulation

Hydrogen absorption into the $\text{Ca}_{72}\text{Mg}_{28}$ alloy with amorphous structure resulted in the release of thermal energy consisting of the heat passing through the insulation of the reaction pressure vessel, the heat distributed into the surrounding environment through the supply pipeline, and the heat accumulated in metal parts of the measurement system. Determination of thermal flows was carried out by an indirect method, using a numerical calculation, while applying the finite volume method, in the ANSYS CFX software. We applied the marginal condition of the known sample temperature during the experiment, ambient temperature, and the value of the heat transfer coefficient calculated using the criteria equations. Connecting the measured data and a numerical calculation with the subsequent analytical calculation resulted in obtaining the value of the total heat released during hydrogen absorption into the $\text{Ca}_{72}\text{Mg}_{28}$ alloy with amorphous structure, amounting to $54 \text{ kJ} \cdot \text{mol}^{-1}$.

CONCLUSIONS

The present article indicates the potential of using the $\text{Ca}_{72}\text{Mg}_{28}$ alloy with amorphous and crystalline structure for hydrogen storage purpose. Operating parameters of hydrogen absorption and desorption were obtained; they can be used when designing storage systems. Inability to desorb hydrogen in the case of amorphous structure resulted in alloy recrystallization; this contributed to achieving the reversible hydrogen storage ability. PCI curves of the alloy were determined within the temperature range from 410 to 450 °C.

The $\text{Ca}_{72}\text{Mg}_{28}$ alloy with amorphous structure shows the mass concentration of 0.96 wt %, whereas the mass concentration of hydrogen stored in the alloy with crystalline structure shows the maximum of 0.37 wt %.

The difference in the storage capacity between the alloy with the amorphous and the crystalline structure is probably attributable to the rigid coupling of hydrogen in a form of calcium hydride (CaH_2) which allows for hydrogen to be desorbed within the temperature range of 600–1,000 °C.

The article also presents a numerical simulation using the measured values of the reaction vessel surface temperature for determining the total released energy for hydrogen absorption into the amorphous structure, amounting to $54 \text{ kJ} \cdot \text{mol}^{-1}$.

A numerical calculation was used to identify the total heat loss of the measuring apparatus at non-stationary heat transfer which were then used to calculate, while applying an indirect method, the value of the heat generated during hydrogen absorption.

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