

RESEARCH PAPER

MEASUREMENT OF THE ABSORPTION-BASED HYDROGEN STORAGE CAPACITY OF $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{0.8}\text{Mn}_{0.8}\text{V}_{0.2}\text{Ni}_{0.2}$ ALLOYTomáš Brestovič¹, Natália Jasminská¹, Marián Lázár¹, Ľubica Bednárová^{1*}, Romana Dobáková¹¹Technical University of Košice, Faculty of Mechanical Engineering, Letná 9, 042 00 Košice, Slovakia

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ABSTRACT

The article describes potential application of the BCC alloy $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{0.8}\text{Mn}_{0.8}\text{V}_{0.2}\text{Ni}_{0.2}$ in the hydrogen absorption process. It deals with the measurements of the PCI (Pressure Concentration Isotherm) characteristics applying the volumetric method. With regard to the fact that it is an indirect measurement method, the thermodynamic description was analysed in details and subsequently used to identify the weight capacity of the stored hydrogen. The article presents a detailed description of the procedure for measuring the free volume of the measuring equipment using helium which is able to penetrate into pores and apertures with the size of only a few nanometres but does not participate in the absorption into the intermetallic structure of the alloy. The hydrogen absorption into the tested alloy was initiated by repeatedly performed activation of the alloy surface. The final section of the article presents the examination of the cyclic stability of the absorption-desorption cycle within the repeated monitoring of the maximum weight capacity of the stored hydrogen.

Keywords: hydrogen storage, alloy, absorption, PCI, activation

INTRODUCTION

The complete implementation of the use of hydrogen as an energy carrier requires efficient, safe, and cheap storage thereof [1-3]. Compared to gaseous and liquid storage systems, storage of hydrogen in metal hydrides (MH) exhibits several advantages [4-8]. The most important ones include mainly high volumetric density and low operating pressure; this represents significant improvement of the safety of applications thereof in the transportation segment, in various industries, or in households [9, 10]. The development of novel MH materials requires the identification of their PCI (Pressure Concentration Isotherms) curves indicating the changes in the pressure depending on hydrogen concentration at a constant temperature [11-13]. The PCI curve shows the hydrogen absorption at the equilibrium pressure until the alloy is fully saturated, as indicated by a sharp pressure increase at the maximum concentration.

The kinetics of alloy activation and storage capacity are also affected by the chemical composition of the alloy [14-16]. The impact of elementary composition on the hydrogenation characteristics of the BCC alloys was subjected to multiple investigations. As for the $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{Cr}_{0.8}\text{Mn}_{0.8}\text{V}_{0.2}\text{Ni}_{0.2}$ alloy, the addition of Zr and Ni has a significant effect on the activation process. Without these components, the activation was required, at the temperatures of 300 to 750 °C. After the addition of the above mentioned elements, there is no need for the thermal activation of the alloy, unless it was exposed to oxygen; therefore, it may be assumed that the hydride surface will not be covered with the layer of oxides. The alloy with a similar composition was also investigated by Yu et al. [17].

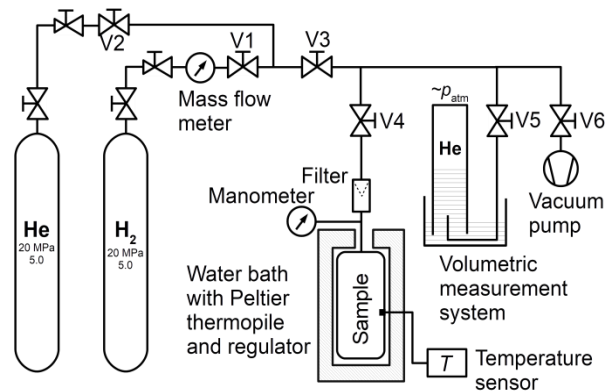
DESCRIPTION OF THE SPECIMEN PREPARATION AND THE MEASURING SYSTEM ASSEMBLY

For the purpose of the PCI measurements, 6.177 g of the alloy were produced applying the arc welding method. In order to ensure higher homogeneity of the specimen, it was subjected to three cycles of melting and cooling to the ambient temperature. The resulting powder product was ground in the inert argon atmosphere and subsequently subjected to the X-ray diffraction. The results of the final chemical composition of the specimen are listed in Table 1.

Table 1 Composition of the resulting specimen

Element	Desired alloy composition [wt. %]	Achieved alloy composition [wt. %]
Ti	28.88	28.57
V	6.46	6.77
Cr	26.41	25.94
Mn	27.91	28.09
Ni	7.45	7.58
Zr	2.89	2.78

The measurements of the desorption PCI curve were carried out applying the volumetric method based on the principle of the gradual release of hydrogen into a volumetric cylinder [18-20]. After releasing a small amount of hydrogen, it was necessary to stabilise the pressure in the storage system. Subsequently, the amount of the released hydrogen was monitored and calculated for normal conditions with concurrent monitoring of the pressure in the hermetically sealed equipment and the hydrogen temperature. The scheme of the measuring apparatus is shown in Fig. 1.

**Fig. 1** Scheme of the measurement apparatus

A substantial part of the system is a hermetically sealed chamber containing the alloy specimen; the chamber is located upstream the V4 valve. The specimen was immersed in the water bath where it was possible to measure and regulate the temperature within the range from 0 to 60 °C. The system facilitated independent supplies of helium and hydrogen at the maximum pressure of 7 MPa. Gases were removed from the system using the Edwards E2M1.5 two-stage oil vacuum pump. The pressure measurements were carried out using the BD SENSORS DX9-DMP 331i pressure sensor with the pressure range from 0 to 6 MPa. The temperature was measured using the ALMEMO FPA32P1 temperature sensor. The sensors were attached to the ALMEMO 2890-9 datalogger by the ALMEMO ZA 9020-FS connector. The assembled apparatus contained the BOSS-ML6-05 spherical valves. The measured data were indirectly used to calculate the weight capacity of the stored hydrogen; it was necessary to apply the mathematical procedure described below.

The amount of hydrogen absorbed in the alloy specimen was identified using the following formula:

$$V_{\text{abs},n,i} = V_{\text{tot},i} - V_{\text{FV},n,i} - V_{\text{VMS},n,i} \quad (1.)$$

where: $V_{\text{abs},n,i}$ [m³] – volume of hydrogen absorbed in the alloy at the i^{th} measurement;
 $V_{\text{tot},i}$ [m³] – total volume measured applying the volumetric method;
 $V_{\text{FV},n,i}$ [m³] – volume of hydrogen in the free space between the alloy grains, including the supply pipeline;
 $V_{\text{VMS},n,i}$ [m³] – volume of hydrogen measured in the volumetric measurement system.

All parameters in formula (1.) were calculated for normal conditions (101,325 Pa and 273.15 K). The volume of hydrogen in the free space of the apparatus, relative to normal conditions at the i^{th} measurement, may be calculated using the following formula:

$$V_{\text{FV},n,i} = \frac{T_n}{T} \cdot \frac{p_i}{p_n} \cdot \frac{z_n}{z_i} \cdot V_{\text{FV}} \quad (2.)$$

where: T_n [K] – normal temperature (273.15 K);
 T [K] – average temperature in the storage volumetric system;
 p_i [Pa] – absolute hydrogen pressure;
 p_n [Pa] – normal pressure (101,325 Pa);
 z_n [1] – compressibility factor of hydrogen in normal conditions ($z_n = 1$);
 z_i [1] – compressibility factor at the average temperature and absolute hydrogen pressure;
 V_{FV} [m³] – free volume of the hermetically sealed system.

The free volume represents the space between the grains of the powder material, including the distribution pipeline between the pressure tank containing the specimen and the first closing valve V4. The volume of hydrogen released into the volumetric system $V_{\text{VMS},n,i}$, as calculated for normal conditions, is defined by the following formula:

$$V_{\text{VMS},n,i} = V_{\text{VMS},i} \cdot \frac{p_{\text{VMS},i}}{p_n} \cdot \frac{T_n}{T_{\text{VMS},i}} \quad (3.)$$

where: $V_{\text{VMS},i}$ [m³] – volume of the released hydrogen in operating conditions;
 $p_{\text{VMS},i}$ [Pa] – absolute pressure in the volumetric system;
 $T_{\text{VMS},i}$ [K] – thermodynamic temperature in the volumetric system.

The total volume released into the measuring cylinder calculated for normal conditions was identical to the calculation made using formula (3.); however, it corresponded to the last (n^{th}) measurement.

$$V_{\text{tot},n} = V_{\text{VMS},n,i} \Big|_{i=n} \quad (4.)$$

The resulting mass concentration of the stored hydrogen for the i^{th} measurement was identified as follows:

$$c_i = \frac{\rho_{\text{H}_2,n} \cdot V_{\text{abs},n,i}}{m_{\text{alloy}}} \quad (5.)$$

where: m_{alloy} [kg] – mass of the alloy specimen;
 $\rho_{\text{H}_2,n}$ [kg/m³] – hydrogen density in normal conditions.

During the measurements of different specimens, the free volume of the hermetically sealed system V_{FV} was changing due to changes in the porosity and the amount of the powder alloy. It was therefore necessary to identify this parameter prior to the measurement of the next specimen. For this purpose, the secondary gas, helium, was used prior to hydrogen absorption. The system was vacuumed, using a vacuum pump, to the absolute pressure of 5 Pa and then filled with helium with which absorption into the alloy structure does not occur; this facilitated measuring the amount of the gas released into the volumetric measurement system in order to identify the free volume between the grains and use such data to make a simple calculation of the missing parameter V_{FV} . The calculation was based on the differential form of the equation of state; a pressure decrease in the hermetic chamber was adequate to the amount of the released hydrogen:

$$dp_{\text{He}} \cdot V_{\text{FV}} = dm_{\text{He}} \cdot r_{\text{He}} \cdot \bar{T} \cdot \bar{z}_{\text{He}} \quad (6.)$$

where: dp_{He} [Pa] – elementary change in the pressure in the closed chamber during the release of helium;
 dm_{He} [kg] – elementary change in the mass of helium released from the system;
 r_{He} [J/(kg·K)] – specific gas constant of helium;
 \bar{z}_{He} [1] – average value of the compressibility factor.

By subsequent solving of the equation, it was possible to calculate the ratio of the free volume and the average temperature; the ratio was identical to that observed during the measurements with hydrogen and helium (while maintaining the same thermal field of the tank). Therefore, it was possible to substitute the ratio of the free volume to the average temperature directly to formula (2.) obtaining the following formula:

$$\frac{V_{\text{FV}}}{T} = \frac{\Delta m_{\text{He}}}{\Delta p_{\text{He}}} \cdot r_{\text{He}} \cdot \bar{z}_{\text{He}} \quad (7.)$$

A change in the mass of hydrogen was identified using the equation of state for hydrogen released from the volumetric measurement system:

$$\Delta m_{\text{H}_2} = \frac{p_{\text{VMS,He}} \cdot V_{\text{VMS,He}}}{r_{\text{He}} \cdot T_{\text{VMS,He}}} \quad (8.)$$

where: $p_{\text{VMS,He}}$ [Pa] – pressure in the measuring cylinder;
 $V_{\text{VMS,He}}$ [m³] – hydrogen volume in the measuring cylinder;
 $T_{\text{VMS,He}}$ [K] – hydrogen temperature in the measuring cylinder.

SPECIMEN ACTIVATION

The specimen of the Ti_{0.95}Zr_{0.05}Cr_{0.8}Mn_{0.8}V_{0.2}Ni_{0.2} alloy was activated in order to eliminate the oxidation layer which might generate during the production of and manipulation with the specimen. The specimen was exposed to three cycles of heating and cooling at the temperatures from 3 to 100 °C and at the pressures from 0 to 4.3 MPa. The specimen was first heated to 100 °C at the absolute pressure below 5 Pa and then left in these conditions for the period of 30 minutes. Subsequently, the pressure tank of the hermetically sealed system was cooled to the temperature of 3 °C and the system was filled with hydrogen to the pressure of 4.3 MPa and then left in these conditions for the period of 5 hours. During

hydrogen absorption, the pressure in the chamber slowly decreased (Fig. 2); this facilitated the calculation of the increase in the mass concentration of the stored hydrogen over time.

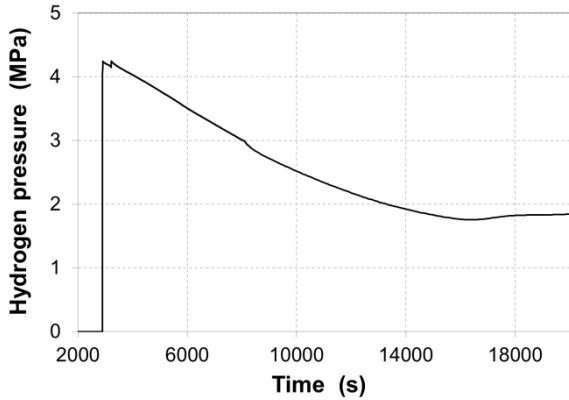


Fig. 2 Pressure decrease in the tank during the first activation

An increase in the mass concentration may be defined as the ratio of the change in the mass concentration of the stored hydrogen per time unit in the initial linear area of the pressure decrease (between 4,000 and 8,000 s) using the following formula:

$$\psi_1 = \frac{\Delta c}{\Delta \tau} = \frac{\Delta m_{H_2}}{\Delta \tau \cdot m_{\text{alloy}}} = - \frac{\Delta p_{H_2} \cdot V_{FV}}{\Delta \tau \cdot m_{\text{alloy}} \cdot r_{H_2} \cdot T} \quad (9.)$$

where: ψ_1 [s^{-1}] – increase in the mass concentration over time;
 Δc [1] – change in the mass concentration of the stored hydrogen;
 Δm_{H_2} [kg] – change in the mass of the absorbed hydrogen;
 Δp_{H_2} [Pa] – decrease in hydrogen pressure in the pressure tank;
 r_{H_2} [J/(kg·K)] – specific gas constant of hydrogen.

During the first activation cycle, the absorption kinetics were very slow and reached the value $\psi_1 = 4.93 \cdot 10^{-7} s^{-1}$. This value represented an increase in the mass concentration in $4.93 \cdot 10^{-5} \%$ per second.

The second activation cycle was carried out in identical conditions, but the kinetics of the process of the initial absorption was as much as 117 times faster ($\psi_2 = 5.8 \cdot 10^{-5} s^{-1}$). The curve of the pressure in the hermetic chamber during the second activation of the alloy is shown in Fig. 3.

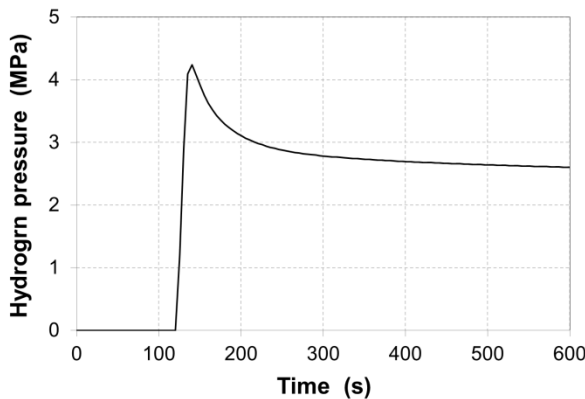


Fig. 3 Decrease in the pressure in the tank during the second activation

During the third activation, the value of the increase in the mass concentration ψ_3 was $1.66 \cdot 10^{-5} s^{-1}$.

DISCUSSION

The measurements of the decrease in the pressure in the hermetically sealed measurement chamber during the activation indicate that the initiation of hydrogen absorption into the alloy structure requires at least three consecutive cycles of the activation process. This will initiate the process of hydrogen storage with acceptable process kinetics. Following the alloy activation and the measurement of the free volume of the hermetically sealed system, the system was vacuumed using a vacuum pump; this resulted in an increase in hydrogen pressure to 5 MPa. Through the gradual release of hydrogen into the volumetric measurement system and a subsequent calculation, as described in the mathematical apparatus, the PCI characteristics of the alloy were identified (Fig. 4).

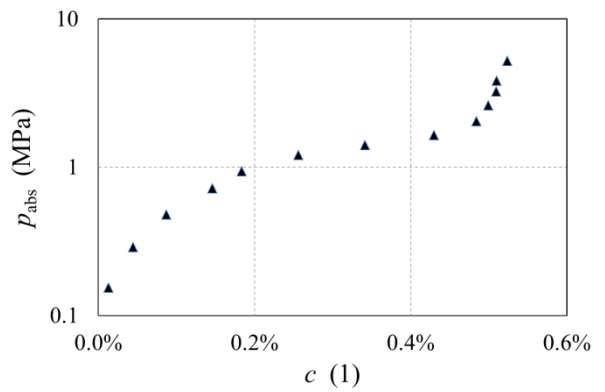


Fig. 4 PCI characteristics of the $Ti_{0.95}Zr_{0.05}Cr_{0.8}Mn_{0.8}V_{0.2}Ni_{0.2}$ alloy during hydrogen desorption

Hydrogen absorption into the alloy begins already at the pressure of 0.2 MPa. The relevant curve indicates that the plateau pressure for the tested alloy was 1.4 MPa and after the peak mass concentration of 0.52 % was achieved, the pressure sharply increased. This was caused by the alloy saturation and further supplies of hydrogen into the storage system caused the gas accumulation in the free volume V_{FV} . In order to confirm the measurement accuracy and determine the cyclic stability, the measurements of the PCI characteristics were repeated 6 times while maintaining the same thermodynamic conditions. Fig. 5 shows the curve of the peak mass concentrations of the stored hydrogen at individual measurements.

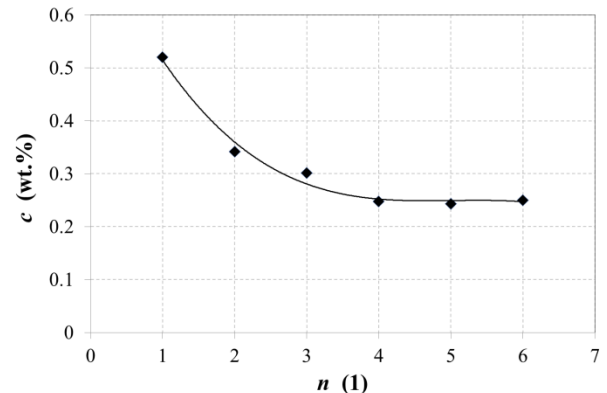


Fig. 5 Curve of the peak weight capacity of the alloy under the periodic load

A stable value of the mass concentration, i.e., 0.25 wt. %, was reached after the third absorption-desorption cycle. From cycle 4 onwards, the alloy appeared to be stable for further hydrogen storage.

CONCLUSION

Certain disadvantages of the pressure and cryogenic storage of hydrogen urge the necessity to search for alternative methods of storing this gas [21]. An option that seems to be appropriate is the use of metal hydride alloys which facilitate the storage of hydrogen in crystal lattices of metals. In the case of the tested alloy $Ti_{0.95}Zr_{0.05}Cr_{0.8}Mn_{0.8}V_{0.2}Ni_{0.2}$, hydrogen was stored in the cubic lattice. This alloy may be used for hydrogen storage, but the use thereof requires multiple activation of its surface. The measurements of the PCI characteristics were made applying the volumetric method which is, compared to the high-pressure thermogravimetric analysis, more cost-effective, provided that the obtained results are comparable. The problem associated with the practical application of the tested alloy in hydrogen storage is insufficient cyclic stability with a 50 % decrease in the maximum value of the mass concentration after three consequent storage processes. After the mass concentration stabilises, its value is only 0.25 wt. %, representing 27.8 litres of the stored hydrogen (in normal conditions: 101,325 Pa; 273.15 K) in 1 kg of the alloy. The measurements of the PCI characteristics clearly show that this alloy exhibits low absorption pressure of 1.4 MPa; it is therefore suitable for the direct absorption of hydrogen produced through the electrolysis of water in high-pressure electrolyzers which achieve the pressures of up to 2 MPa. This eliminates the necessity of using a compressor.

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