



Effects of scaling in metal hydride materials for hydrogen storage and compression



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ABSTRACT

For the first time the dependence of thermodynamic parameters of hydrogen desorption process on sample scale (weight) was discovered experimentally for the desorption isotherms of 100 g and 500 g samples of LaFe_{0.1}Mn_{0.3}Ni_{4.8}. The scale effect leads to decreasing of the equilibrium pressure for the larger sample, the pressure difference is $\Delta P^{\text{scale}} = -0.15 \pm 0.03$ MPa at 100 °C, and is in the range $\Delta P^{\text{scale}} = -0.5$ to -0.3 MPa at 150 °C. In our opinion the scale effect is determined by elastic strains due to the mutual influence of particles while phase transition from hydride to solid solution and back in large-scale fine-disperse beds of AB₅-type compounds. Scale effect has no influence on the behaviour of pure hydride phase and is absent for small samples. The value of hydrogen chemical potential change is proposed for the description of scale effect, average values are equal $\Delta\mu_{\text{H}}^{\text{scale}} = -310 \pm 30$ J/mole H for 100 °C and $\Delta\mu_{\text{H}}^{\text{scale}} = -260 \pm 30$ J/mole H for at 150 °C.

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1. Introduction

Metal hydrides are considered as convenient and safe hydrogen storage for PEM fuel cells and large scale metal hydride storage systems are needed for practical applications. An accuracy of data on PCT diagram of a hydrogen absorbing material is crucial to obtain adequate simulation results [1] and thus to a system design. Scaling up from laboratory samples to metal hydride reactors has shown a difference in properties. Changes in capacity and rates of hydrogen sorption and desorption at a system level may include: heat transfer during hydrogen uptake and release, local temperatures within the material test bed, decrepitation and/or agglomeration of the materials, interlocking of grains and resulting forces generated with material expansion, gas channeling effects, special variations in hydrogen content [2].

Investigations of scaling up effects are carried out for magnesium [3], and the measured negative trend is presumably related to undesirable powder compaction. Poor heat exchange is also mentioned [4] as the cause of the negative scaling up effect on the other hand for sodium alanate [5] it is found that scale-up of the system does not have adverse effects on its behaviour and both capacity and speed of charging are in good agreement with data from lab-scale reactors and milligram scale samples. However,

different investigation techniques are always used for small laboratory samples and metal hydride beds of large scale systems, and it is hard to compare results of experiments and obtain information on possible change of properties of metal hydrides due to scaling up effect.

It is well known that the hydrogen absorption is always connected with large unit cell expansion (up to ~25%) due to interstitial occupation of hydrogen atoms [6,7]. This expansion not only leads to the dispersion of materials to powders with average particle size 0–10 μm, but also induces elastic strains in particles as well as in their contact points. In the systems consisting of large number of particles, additional elastic strains may emerge due to the collective elastic particle interactions.

The investigations of the influence of strains on the metal hydrogen interactions began in late 1960s. For example, a response of composition to stress was found for hydrogen in 75% Pd + 25% Ag alloy [8] and the measured values were in close agreement with the response predicted with the theory of the thermodynamics of stressed solids.

Measurable, and reproducible solubility enhancements have been observed for hydrogen in cold-worked palladium [9] due to the lattice defects created by plastic deformation. Such behaviour, typical for other hydride-forming metals, stimulated the appearance of a number of procedures of mechanical and mechanochemical treatment of materials in order to improve their hydrogen sorption properties. However, internal elastic strains can differently influence the hydrogen interactions with intermetallics.

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Kawamura et al. [10] found that in the absence of free volume the strains negatively affected the sorption capacity of LaNi₅ powder interaction with hydrogen, which may decrease in 1.5 times.

Collective elastic particle interactions may cause changes of thermodynamic properties depending on system scale, particularly for phase diagram in the region of the metal hydride phase formation. This hypothesis of new scale effect was discovered in the works of the Hydrogen Energy Technologies Laboratory of JIHT RAS [11]. According to our data, the change of equilibrium pressure values for PCT-isotherms can reach up to 0.1 MPa, which is significant for design of the metal-hydride storage units, especially low-temperature containers.

In this connection, a fundamental problem arises, namely to investigate the peculiarities of sorption characteristics and thermo-physical properties of fine-disperse metal hydride beds, determined by scale effects in metal hydride storage and purification systems.

Our experimental procedure does not suggest an artificial deformation of a bed or the absence of free volume in order to design hydrogen storage and purification reactors of various shapes. We use Sievert's method, which is a quasi-equilibrium method describing a state of a solid phase by measuring hydrogen pressure and temperature in the gaseous phase on the base of an assumption that the chemical potentials of hydrogen in solid and gaseous phases are equal in equilibrium state. Thus, the chemical potential of atomic hydrogen in solid phase is equal:

$$\mu_{\text{H}} = \frac{1}{2} \mu_{\text{H}_2}^{\text{gas}} \quad (1)$$

Considering hydrogen as the ideal gas phase:

$$\mu_{\text{H}_2}^{\text{gas}} = \mu_{\text{H}_2}^0 + RT \ln \left(\frac{p_{\text{H}_2}}{p_0} \right) \quad (2)$$

the chemical potential for hydrogen in a metal is [7]:

$$\mu_{\text{H}} = \mu_{\text{H}}^0 + RT \ln \left(\frac{n}{1-n} \right) \quad (3)$$

where μ_{H}^0 is the standard potential of hydrogen in metal, second right-hand term – configuration term, corresponding to ideal distribution of hydrogen atoms in octahedral sites and $n = \text{H}/\text{Me}$ is the number of atoms ratio.

The conditions of phase equilibrium substantially change when external nonuniform fields lead to appearance of mass forces having different effect on the phases [12]. For the quantitative evaluation of the scale effect one should separate out in Eq. (2) the change of hydrogen chemical potential, caused by strains inside and between particles $\Delta\mu_{\text{H}}^{\text{strain}}$:

$$\mu_{\text{H}} = \mu_{\text{H}}^0 + RT \ln \left(\frac{n}{1-n} \right) + \Delta\mu_{\text{H}}^{\text{strain}} \quad (4)$$

Combining Eqs. (2) and (4) we get:

$$\mu_{\text{H}}^0 + RT \ln \left(\frac{n}{1-n} \right) + \Delta\mu_{\text{H}}^{\text{strain}} = \frac{1}{2} \mu_{\text{H}_2}^0 + \frac{1}{2} RT \ln \left(\frac{p_{\text{H}_2}}{p_0} \right) \quad (5)$$

Considering two samples of a hydrogen storage material with different mass m_1 and m_2 in equal conditions and equal n one should expect that additional strains in the metal hydride beds would result in a change of pressure of the gas phase:

$$\Delta\mu_{\text{H}}^{\text{scale}} = \Delta\mu_{\text{H}_2}^{\text{strain}}(m_2) - \Delta\mu_{\text{H}_2}^{\text{strain}}(m_1) = \frac{1}{2} RT \ln \left(\frac{p_{\text{H}_2}(m_2)}{p_{\text{H}_2}(m_1)} \right). \quad (6)$$

Analysis of the chemical potential change $\Delta\mu_{\text{H}}^{\text{scale}}$ for different conditions is the way to determine mechanisms of origination and regularities of scale effect and gives a possibility to evaluate an input of scale effect in ΔH and ΔS values of hydrogen absorption and desorption reactions.

2. Experimental details

In the present work, PCT isotherms of the intermetallic compound LaFe_{0.1}Mn_{0.3}-Ni_{4.8} are measured by a Sievert's method modified to enable the investigation of large samples. A scheme of JIHT RAS US150 experimental setup is shown in Fig. 1. The purpose of US150 is to measure the sorption/desorption isotherms for

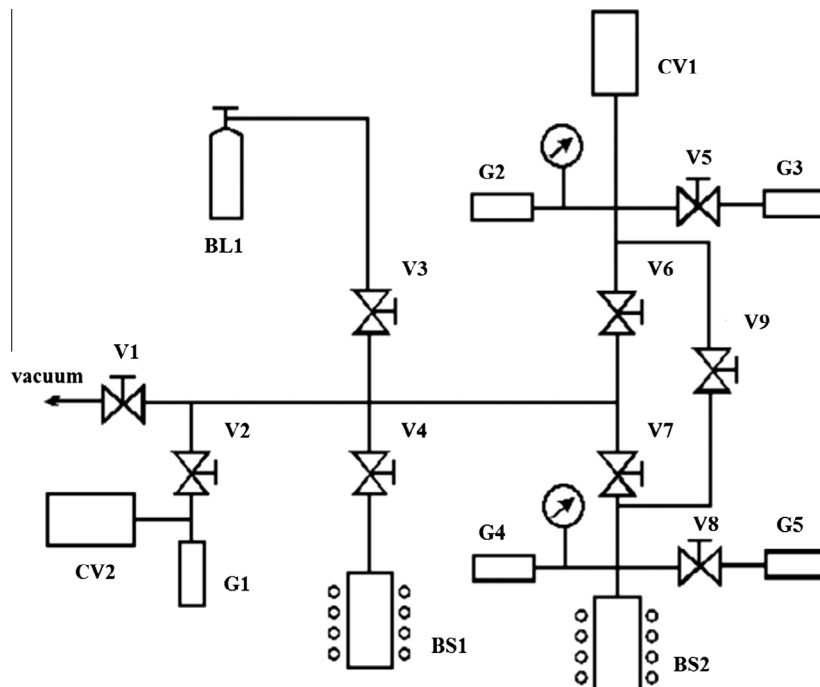


Fig. 1. Scheme of the US150 setup for measuring of the PCT – isotherms: BL1 – vessel with hydrogen; V1–V9 – valves; BS1 – accumulator of hydrogen (filled with LaNi₅); BS2 – working autoclave; CV1 – buffer autoclave; CV2 – low pressure vessel; G1 – gauge for measuring absolute pressure (0–0.1 MPa); G2, G4 – gauges for measuring excess pressure (1–15 MPa); G3, G5 – gauges for measuring excess pressure (0.1–1 MPa).

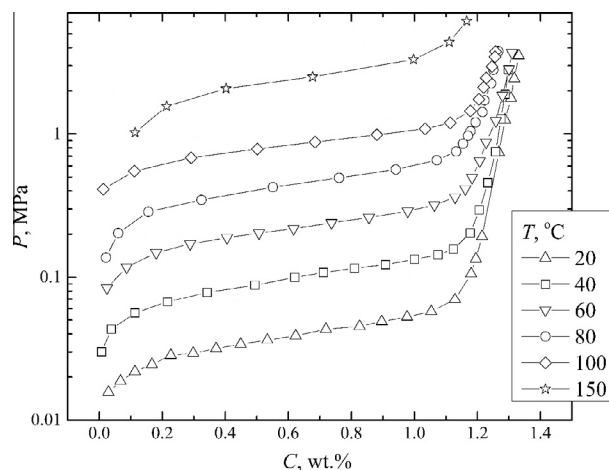


Fig. 2. Isotherms of hydrogen desorption for the 100 g sample of $\text{LaFe}_{0.1}\text{Mn}_{0.3}\text{Ni}_{4.8}$ alloy.

Table 1
Hydrogen sorption properties of 100 g sample.

Temperature		$C_{\text{max}}^{\text{H}}$ (wt.%)	P_{eq} (MPa)	$\Delta H_{\text{o}}^{\text{des}}$ (kJ/mole)	$\Delta S_{\text{o}}^{\text{des}}$ (J/mole K)
°C	K				
20	293	1.3	0.038	34.0 ± 0.3	108 ± 2
40	313	1.3	0.097		
60	333	1.3	0.214		
80	353	1.3	0.432		
100	373	1.3	0.828		
150	423	1.2	2.87		

Table 2
Hydrogen sorption properties of 500 g sample.

Temperature		$C_{\text{max}}^{\text{H}}$ (wt.%)	P_{eq} (MPa)	$\Delta H_{\text{o}}^{\text{des}}$ (kJ/mole)	$\Delta S_{\text{o}}^{\text{des}}$ (J/mole K)
°C	K				
100	373	1.2	0.685	31.0 ± 0.3	99.4 ± 2
150	423	1.2	2.38		

samples with a weight from 10 to 800 g at temperatures from 243 to 673 K and excess pressures of hydrogen up to 15 MPa. The construction of the setup gives the opportunity to change the volume of the working autoclave with the aid of inert inserts of different volumes. The working autoclave BS2 with activated samples can be thoroughly evacuated by a turbo molecular vacuum pump to a residual pressure of 0.1 Pa. A liquid thermostat in a range from 243 to 373 K controls the temperature in the autoclave; for measuring the isotherms in the range from 373 to 673 K an independent heater is used.

The gauges G2 and G4 are used for measuring the pressure in the interval from 1 to 15 MPa. To increase the accuracy of measurements in the region of pressures from 0.1 to 1 MPa, gauges G3 and G5 are used. The error of pressure measurement by gauges G2–G5 is 0.05%. For measurements of pressures below 0.1 MPa, gauge G1 is used. The error of measurements of gauge G1 is 0.5%. The temperatures in the working autoclave, vacuum tank, and pipes are measured using K-type thermocouples with thermally stabilized cold junctions. A platinum resistance thermometer measures the temperature of the buffer vessel. The error of the temperature measurements is ± 0.05 K. Calculations of the molar volume of the released hydrogen are performed with the use of the modified van der Waals equation suggested by Hemmes et al. [13], the values of the molar volumes obtained by this equation differ from the literature data [14] less than 0.1% for pressures up to 15 MPa and temperatures from 250 to 500 K.

3. Results and discussion

Using modified Sievert's method, the isotherms for $\text{LaFe}_{0.1}\text{Mn}_{0.3}\text{Ni}_{4.8}$ alloy samples with the weight $m_1 = 100$ g (Fig. 2) and $m_2 = 500$ g are measured. Precise sample weights are 100.029 g

and 499.954 g respectively. Detailed description of the experimental procedure and calculation of thermodynamic parameters of its interaction with hydrogen can be found in [15]. The reaction autoclave is a cylinder with inner diameter 45 mm and depth 180 mm. Since the bulk density of the alloy is approximately 3.5 g/cm^3 the samples have heights 18 mm and 90 mm for 100 g and 500 g respectively.

Considering the hydrogen desorption process as a phase transition, the plateau of desorption isotherms must be strictly parallel to concentration axis. However, this plateau is often has some slope (see Fig. 2), the desorption plateau can be approximated by linear dependence of equilibrium pressure on concentration (quadratic reliability factor $R^2 = 0.99$). To estimate an influence of plateau slope on the values of enthalpy and entropy of desorption we calculate ΔH and ΔS for van't Hoff equation for several values of the hydrogen concentration on the plateau (0.2%, 0.4%, 0.6%, 0.8%, 1% weight). In spite of the inclination of the plateau, the ΔH and ΔS values remain constant for all these concentrations. Hydrogen sorption properties of $\text{LaFe}_{0.1}\text{Mn}_{0.3}\text{Ni}_{4.8}$ alloy samples are in Tables 1 and 2.

Fig. 3 shows the comparison of desorption isotherms at 100 °C for both samples. For the 500 g sample, two isotherms are presented with different times of retention interval in each data point (24 h and 48 h). Such prolonged static experiments and the absence of noticeable difference between isotherms with different retention intervals ensure the equilibrium for each data point and the measured scale effect is not caused by the effect of dynamic PCT measurements described in [2]. Similar behaviour (Fig. 4) demonstrate the desorption isotherms at 150 °C for 100 g sample (4 h and 8 h per point) and for 500 g sample. The isotherms for both samples almost coincide in the region of saturated hydride while in solid solution–hydride transition region there is a significant difference, which is shown in Fig. 5, the pressure difference is $\Delta P^{\text{scale}} = -0.15 \pm 0.03$ MPa at 100 °C, and is in the range $\Delta P^{\text{scale}} = -0.5 \dots -0.3$ MPa at 150 °C. Data in Tables 1 and 2 show the presence of the scale effect for equilibrium thermodynamic parameters of hydrogen desorption reaction. Appearance of elastic strains leads to 10% decrease of ΔH and ΔS values, which is considerably higher than the determination error for these values using our experimental procedure.

The alloy behaviour somewhat differs from the behaviour in case of the absence of free volume [10], the increase of sample weight and consequently influence of elastic strains do not lead

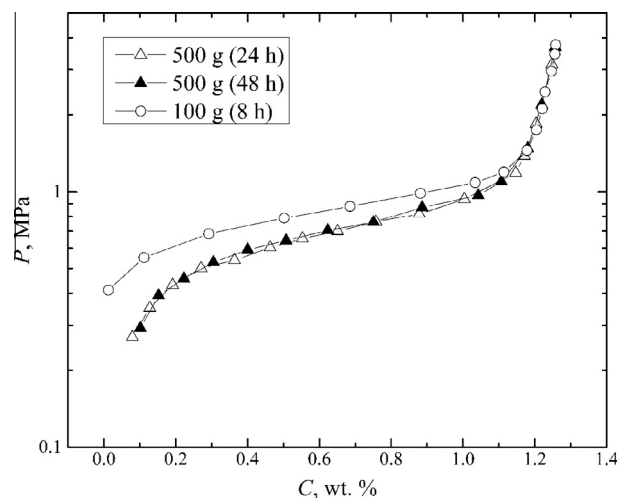


Fig. 3. Scale effect in the desorption isotherms of $\text{LaFe}_{0.1}\text{Mn}_{0.3}\text{Ni}_{4.8}$ alloy at 100 °C for 100 g and 500 g samples with different equilibration times per point.

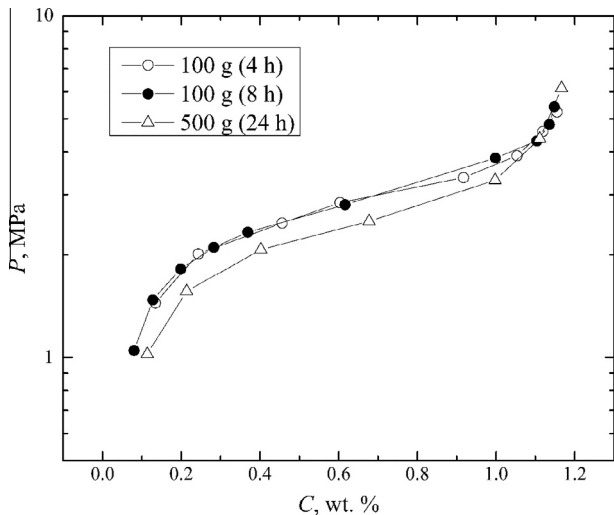


Fig. 4. Scale effect in the desorption isotherms of $\text{LaFe}_{0.1}\text{Mn}_{0.3}\text{Ni}_{4.8}$ alloy at $150\text{ }^{\circ}\text{C}$ for 100 g and 500 g samples with different equilibration times per point.

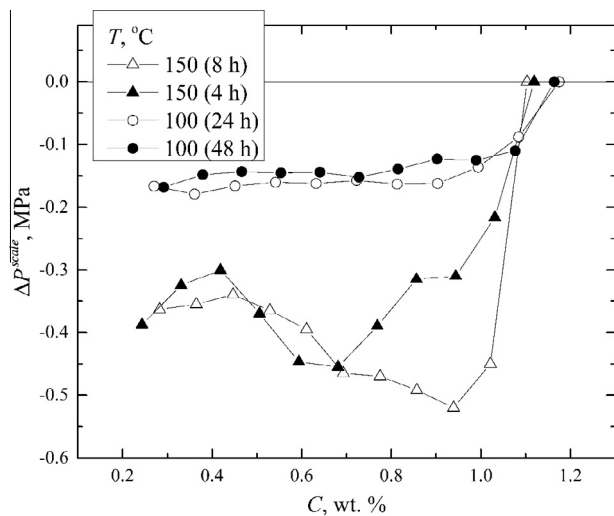


Fig. 5. Pressure difference between the desorption isotherms for 500 g and 100 g samples at $100\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$.

to considerable decrease of absorption capacity. However, for both temperatures the decrease of equilibrium pressure with increase of sample weight was obtained. Such decrease was already found in investigations of the influence of elastic strains on solid solution of hydrogen in palladium [16].

After the experiments dense particle agglomerations with the size up to 10 mm were found in the 500 g sample. They easily disintegrated under thumb pressing. These agglomerations are most probably caused by compaction occurring in the metal hydride bed due to increased pressure and particle enlargement during hydrogen absorption. Similar compactations were not found in 100 g sample. In our opinion these are the evidences that the change of thermodynamic parameters of desorption reaction is connected with elastic strains, which occur during transition from hydride to solid solution and back for the 500 g sample.

Values for scale effect for the chemical potential are calculated by (6) and presented in Fig. 6, average scale effect is equal $\Delta\mu_{\text{H}}^{\text{scale}} = -310 \pm 30\text{ J/mole H}$ for $100\text{ }^{\circ}\text{C}$ and $\Delta\mu_{\text{H}}^{\text{scale}} = -260 \pm 30\text{ J/mole H}$ for at $150\text{ }^{\circ}\text{C}$. The scale effect for the chemical potential is less dependent on temperature than the pressure change

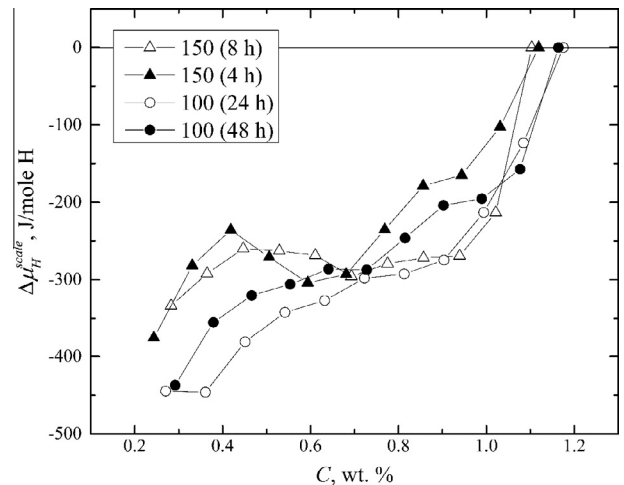


Fig. 6. Scale effect for chemical potential.

ΔP^{scale} . At this stage of research there is not enough data to draw conclusions about the nature of dependence of $\Delta\mu_{\text{H}}^{\text{scale}}$ on temperature and equilibrium pressure and additional experiments are needed with samples with various weights in a broad range of conditions including absorption.

4. Conclusions

For the first time the dependence of thermodynamic parameters of hydrogen desorption process on sample scale (weight) was discovered experimentally for the desorption isotherms of 100 g and 500 g samples of $\text{LaFe}_{0.1}\text{Mn}_{0.3}\text{Ni}_{4.8}$. In our opinion the scale effect is determined by elastic strains due to the mutual influence of particles while phase transition from hydride to solid solution and back in large-scale fine-disperse beds of AB_5 -type compounds. Scale effect has no influence on the behaviour of pure hydride phase and is absent for small samples. Analysis of literature data on mutual influence of internal elastic strains and hydrogen sorption properties of metal hydrides proves the suggested hypothesis.

The scale effect leads to decreasing of the equilibrium pressure for the larger sample, the pressure difference is $\Delta P^{\text{scale}} = -0.15 \pm 0.03\text{ MPa}$ at $100\text{ }^{\circ}\text{C}$, and is in the range $\Delta P^{\text{scale}} = -0.5 \pm -0.3\text{ MPa}$ at $150\text{ }^{\circ}\text{C}$. In addition the sample weight change from 100 g to 500 g leads to 10% decrease of hydrogen desorption reaction enthalpy and entropy. The value of hydrogen chemical potential change is proposed for the description of scale effect, average values are equal $\Delta\mu_{\text{H}}^{\text{scale}} = -310 \pm 30\text{ J/mole H}$ for $100\text{ }^{\circ}\text{C}$ and $\Delta\mu_{\text{H}}^{\text{scale}} = -260 \pm 30\text{ J/mole H}$ for at $150\text{ }^{\circ}\text{C}$.

The problem of determination of the dependence of chemical potential on reaction conditions (equilibrium pressure, temperature and hydrogen concentration in solid phase) and on scale and geometry of intermetallic-hydrogen system is essential for design of hydrogen storage and purification systems and needs further research.

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