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 $\Delta P^{scale} = -0.15 \pm 0.03$ MPa at 100 °C, and is in the range $\Delta P^{scale} = -0.5$ 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 AB_5-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 $\Delta\mu_H^{scale} = -310 \pm 30$ J/mole H for 100 °C and $\Delta\mu_H^{scale} = -260 \pm 30$ 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 o 1–10 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 LaNi$_5$ 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 thermophysical 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:

$$\mu_H = \frac{1}{2}\mu_{H_2}^{gas} \qquad (1)$$

Considering hydrogen as the ideal gas phase:

$$\mu_{H_2}^{gas} = \mu_{H_2}^0 + RT \ln\left(\frac{p_{H_2}}{p_0}\right) \qquad (2)$$

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

$$\mu_H = \mu_H^0 + RT \ln\left(\frac{n}{1-n}\right) \qquad (3)$$

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 $n = H/Me$ 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 $\Delta\mu_H^{strain}$:

$$\mu_H = \mu_H^0 + RT \ln\left(\frac{n}{1-n}\right) + \Delta\mu_H^{strain} \qquad (4)$$

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

$$\mu_H^0 + RT \ln\left(\frac{n}{1-n}\right) + \Delta\mu_H^{strain} = \frac{1}{2}\mu_{H_2}^0 + \frac{1}{2}RT \ln\left(\frac{p_{H_2}}{p_0}\right) \qquad (5)$$

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:

$$\Delta\mu_H^{scale} = \Delta\mu_{H_2}^{strain}(m_2) - \Delta\mu_{H_2}^{strain}(m_1) = \frac{1}{2}RT \ln\left(\frac{p_{H_2}(m_2)}{p_{H_2}(m_1)}\right). \qquad (6)$$

Analysis of the chemical potential change $\Delta\mu_H^{scale}$ 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
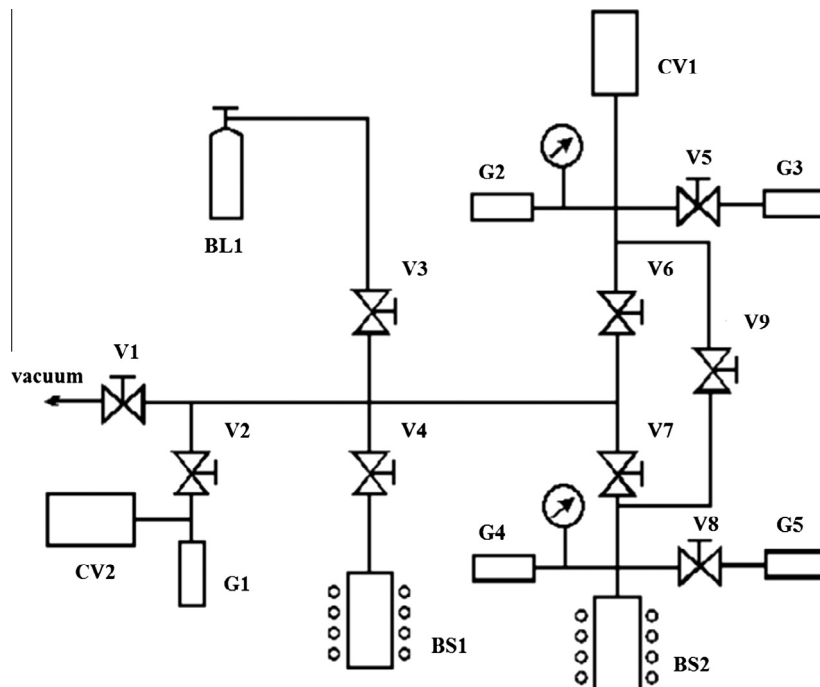
Fig. 1. Scheme of the US150 setup for measuring of the PCT – isotherms: BL1 – vessel with hydrogen; V1–V9 – valves; BS1 – accumulator of hydrogen (filled with LaNi$_5$); BS2 – working autoclave; CV1 – buffer autoclave; CV2 – low pressure vessel; G1 – gauge for measuring absolute pressure (0–0.1 MPa); G2, G4 – gauges for measuring excess pressure (1–15 MPa); G3, G5 – gauges for measuring excess pressure (0.1–1 MPa).