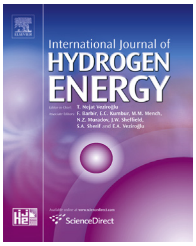
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 19361–19368

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Experimental investigations and a simple balance model of a metal hydride reactor

Dmitry V. Blinov, Vasily I. Borzenko, Dmitry O. Dunikov[*]*,*
Ivan A. Romanov

Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 bld. 2, 125412 Moscow, Russia

ARTICLE INFO

Article history:
Received 9 June 2014
Received in revised form
10 July 2014
Accepted 11 July 2014
Available online 4 August 2014

Keywords:
Hydrogen
Metal hydride
Hydrogen storage
Modeling

ABSTRACT

The metal hydride reactor filled with 5 kg of the AB_5-type ($LaFe_{0.5}Mn_{0.3}Ni_{4.8}$) alloy was investigated with respect to the hydrogen discharge rates classified using C-rate value, which is discharge of the maximum hydrogen capacity 750 st L within 1 h. The reactor cannot be fully discharged with a constant flow rate, for each temperature of hot water and flow rate there exists a moment of crisis at which the hydrogen flow drops under the constant value. The nominal capacity of the reactor reaches 80% of maximum capacity if sufficient heat transfer is provided. The simple balance model of a metal hydride reactor is developed based on the assumption of uniform temperature and pressure inside a metal hydride bed. The model permits to predict behavior of the metal hydride reactor in different operation regimes, quantitative agreement is obtained for low C-rates (less than 4) and sub-critical modes.

Introduction

Hydrogen energy storage systems are perspective way for the load management especially at kW level of renewable energy power production. The use of solid-state reversible hydrogen storage in metal hydrides is of considerable practical interest for this technology [1,2].

Typical metal - hydrogen reaction isotherm can be divided into three areas as hydrogen pressure grows [3]: hydrogen solution in metal (α-phase); co-existence of saturated hydrogen solution and hydride ($\alpha + \beta$ phase); hydrogen in hydride (β-phase). In two-phase area a “plateau” exists, where the pressure change is small and hydrogen absorption and desorption can be considered to take place at constant pressure and temperature, as a first approximation. This feature is useful for application in hydrogen storage devices. If the inlet pressure in metal hydride reactor is higher than equilibrium at corresponding temperature for the hydrogen absorbing alloy, hydrogen is absorbed with heat release, if lower than desorption with heat consumption takes place.

In metal hydride devices hydrogen absorbing material is usually a fine dispersed powder. Technical problems of the development of efficient hydrogen storage systems are connected above all with the necessity to arrange efficient heat and mass transfer for the reliable absorption and desorption reaction heat supply or removal. In the charge or discharge process of metal hydride reactor two main stages could be detected with transition between the stages accompanied by heat and mass transfer crisis inside the bed [4,5]: in sub-

---

[*] *Corresponding author*. Tel.: +7 495 362 55 58.
E-mail addresses: ddo@mail.ru, d.dunikov@gmail.com, h2lab@mail.ru (D.O. Dunikov).

http://dx.doi.org/10.1016/j.ijhydene.2014.07.048
0360-3199/

critical mode the process is limited by hydrogen flow to particles of hydrogen absorbing material at absorption or from particles at desorption (hydrogen filtration or valve capacity) and in super-critical mode by intensity of heat transfer from the bed to the walls of the reactor. Crisis is accompanied by rapid decrease of absorption or desorption in metal hydride devices and one should be able to predict the crisis occurrence for the avoidance of super-critical mode.

The task of detailed calculation of metal hydride device operation is a complicated scientific problem since the system of unstationary heat and mass transfer equations system should be solved for the porous medium with respect to chemical reactions. This task very often cannot be solved reliably because the data on reaction kinetics of hydrogen–metal interaction, thermodynamic, physical and chemical properties of hydrogen absorbing material must be involved, which in most cases, are not available with sufficient precision. As it was shown in Ref. [6] the activation energy, thermal conductivity and heat of reaction are the most important parameters affecting the modeling of the charging and discharging.

Together with this, for engineering means at development of metal hydride devices design and their integration into bigger systems, simplified mathematical models can be used for the optimization of reactors design and evaluation of their efficiency. The aim of this work is to build a simplified, experimentally verified, balance mathematical model of the processes in metal hydride hydrogen storage reactor giving the main operational features of the device for the engineering purposes and permitting to avoid complicated task of heat and mass transfer calculation in fine dispersed bed of hydrogen absorbing material.

Experiments and methods

Experiment

For experimental verification of the model we use the RSP-3 reactor [5,7]. The reactor is presented in Fig. 1 and consists of seven water cooled cartridges filled with 5 kg of $LaFe_{0.5}Mn_{0.3}Ni_{4.8}$ alloy, which was activated in 10 charge/discharge cycles. For the temperature range from 0 to 100°C the maximum hydrogen capacity is $C_{\max} = 1.35 \pm 0.01\%$ mass and the maximum reactor capacity is 750 st L H_2. State of charge (SOC) and depth of discharge (DOD) of the reactor are determined as:

$$SOC = 1 - DOD = X = \frac{C}{C_{\max}} \tag{1}$$

where X is dimensionless fraction of transformed solid phase in the gas–solid chemical reaction.

The RSP-3 reactor is installed in an experimental test bench 12-04 JIHT RAS and provided with connection to a gas supply (hydrogen, nitrogen), a hot and cold water supply (from 10 to 95 °C and from 0.05 to 0.3 kg/s), a vacuum system and an automatic control system. Before each experiment the reactor is fully discharged and evacuated. During experiments the reactor is charged with pure hydrogen from a standard 40 L gas cylinder (15 MPa max pressure) or from a PEM electrolyzer HPAC 10 (ITM POWER).

The gas flow at the inlet/outlet valve of the reactor is controlled and measured by a Bronkhorst EL-FLOW Select mass flow meter/controller F-202AC-RAA-55-V, the pressure inside the reactor and the gas supply is measured by Aplisens pressure transmitters model PC28, the water temperature is measured by thin film platinum sensors Heraeus M422, 1 kΩ. The experiments was controlled using LabView software, discretization 1 Hz.

Two discharge techniques are used. The first one is a “hot start”: the reactor is charged, preheated by hot water and discharged (the outlet valve to atmosphere is opened) from a point of thermal equilibrium and constant pressure inside the reactor. The second technique is a “cold start”: the reactor is charged, cooled by water at near ambient temperature until thermal equilibrium and constant pressure are reached and discharged by simultaneous opening of outlet hydrogen valve and inlet valve for hot water.

Discharge rates are classified using C-rate method similarly to batteries, the C-rate equal to 1 corresponds to discharge of the maximum hydrogen capacity 750 st L within 1 h or 12.5 st L per minute. Results for several C-rates are presented in Fig. 2 and Table 1. The reactor cannot be fully discharged with a constant flow rate, for each temperature of hot water and C-rate there exists a moment of crisis at which the hydrogen flow drops under the constant value. Thus nominal capacity is less than maximum value and depends on temperature of heating water. On the other hand the discharge rate is practically independent from the flow rate of water in the reactor's heat exchanger and from the “hot or

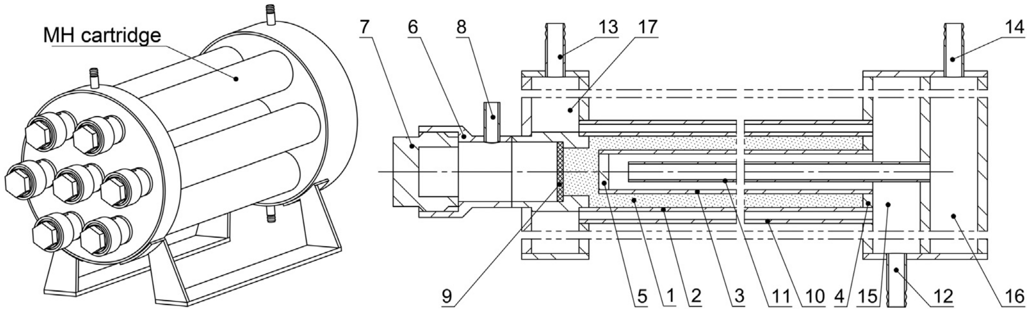


Fig. 1 – The RSP-3 metal hydride reactor. 1 – metal hydride bed; 2 – reaction chamber outer tube; 3 – reaction chamber inner tube; 4,5 – bungs; 6 – cartridge neck; 7 – plug; 8 – hydrogen inlet; 9 – filter; 10 – cartridge shell; 11 - internal heat exchanger inner tube; 12, 13, 14 – water nozzles; 15, 16, 17 – water collectors.