Influence of geometrical non-uniformities of LaNi₅ metal hydride bed on its structure and heat and mass transfer at hydrogen absorption

D V Blinov¹, D O Dunikov¹,², A N Kazakov¹ and I A Romanov¹

¹ Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 bld. 2, Moscow, 125412 Russia
² National Research University «Moscow Power Engineering Institute», Krasnokazarmennaya 14, Moscow, 111250 Russia

Abstract. We perform cycling of a 500 g bed of La₀.₉Ce₀.₁Ni₅ intermetallic compound in vertical and horizontal orientations with measurements of PCT isotherms, and further XRD and SEM investigation of bed structure. Significant decrease in equilibrium absorption pressure is observed in vertical orientation of the bed from 1.58 to 1.36 MPa at 333 K, and from 2.68 to 2.51 MPa at 353K, accompanied by evident particle segregation by the bed height and densification at a bottom with formation of a robust agglomerate of small particles (< 10 μm) jointed with big particles of the size 100-200 μm, while particle size distribution in upper parts is more uniform with mean size about 10-20 μm. Fill density increases by 15% from the top to the bottom from 3.26 g/cm³ to 3.86 g/cm³, while structural properties of particles remain the same with X-ray density 8.31 g/cm³. Investigations of heat and mass transfer inside a vertical metal hydride reactor RSP-8 with 1 kg of La₀.₉Ce₀.₁Ni₅ also show considerable non-uniformity of pressure inside the bed. If the reactor is charged from the top the hydrogen pressure at the bottom is lower on 0.2-0.3 MPa, which results in earlier occurrence of heat and mass transfer crisis.

1. Introduction

The development of efficient hydrogen storage systems first of all depends on the efficiency of heat and mass transfer for the heat evacuation or supply during hydrogen absorption or desorption. Activated hydrogen absorbing material in metal hydride devices is usually a fine dispersed bed of powder with particles in the range of 1-10 μm and low effective thermal conductivity (0.1-1 W/m K), which depends on the pressure of the filling gas and on the concentration of hydrogen absorbed in the particles.

Pulverization of hydrides due to significant lattice expansion up to 20–25 % at hydrogen absorption is well known [1]. A phenomenon of spontaneous separation of a granular system (granular segregation) is observed when the system composed of several particle species differing in size or material properties is exposed to an energy source, and this separation may be complete or partial and may occur vertically or horizontally, depending on the system parameters [2]. Metal-hydrogen interaction can provide enough energy to drive the granular separation inside a metal hydride bed and aspect ratio of height and width of the bed should have influence on the particle separation.

Non-uniform particle distribution is one of the main features of hydrogenation/dehydrogenation cycles. The aggregate formation tends to occur easily due to the increase of cohesion and friction in the metal hydride powder during cycling [3]. Experiments [4] revealed that the resulting agglomeration regions had a packing ratio of about 0.6 and more, hydrogen packing caused agglomeration regions to form over a wider area. The change of the dense packed particle size at desorption and absorption of hydrogen results in
internal stresses in metal hydride beds [5]. Alloys are pulverized by repeated absorption and desorption and concentrate in the lower parts of the vessel and particularly strong stress was generated, causing deformation [4]. Experiments show that the agglomeration could degrade the hydrogen storage capacity of a hydride reaction vessel [6]. External mechanical pressure-tensions can significantly influence the degree of sorption of hydrogen [7].

Our previous experimental investigations of metal hydride beds of various scales show that hydrogen sorption properties of IMC depend on the size of the metal hydride bed [8]. The similar effect is discussed in [9] and attributed to compositional inhomogeneities arising inside the bed due to temperature non-uniformities connected with released heat of absorption reaction. From our point of view since the variation of porosity caused by granular separation and densification can significantly change metal hydride bed permeability and effective thermal conductivity, it should have direct influence on the sorption properties of the bed and the performance of metal hydride reactors.

The goal of the present study is to investigate influence of non-uniformities caused by repeated cycles of hydrogenation of a metal hydride bed in horizontal and vertical orientations on performance related characteristics of the bed. We measure PCT isotherms by Sieverts method and investigate properties of a 500 g sample of an AB5-type intermetallic compound La0.9Ce0.1Ni5 by SEM imaging and X-ray diffraction, as well as heat and mass transfer for a vertical metal hydride reactor filled with 1 kg of the IMC in order to determine heat and mass transfer crisis during absorption.

2. Experimental details

Sieverts measurements were performed at 333 and 353 K using US-150 test facility [8], the working autoclave was a stainless steel cylinder of 180 mm height and 45 mm diameter, which allows an arbitrary variation of orientation due to a flexible hydrogen inlet line (figure 1).

The IMC was prepared by arc melting, ingots were crushed manually into 2 mm particles and a sample of weight 500.517 g was placed into the autoclave. The size of the sample was chosen to fill a half of the inner space. The activation was conducted by 10 cycles of hydrogen sorption during 8 hours at pressure of 9 MPa and temperature 373 K and 8 hours of desorption by turbo-molecular vacuum pump. Since it was expected that the vertical orientation of the bed would lead to a higher degree of agglomeration near the bottom of the autoclave, the isotherms for horizontal orientation were measured at first. Pure hydrogen for experiments was provided from 2 kg LaNi5 accumulator BS1. In order to measure PCT isotherms portions of hydrogen were added (absorption) from the buffer autoclave CV1 to the working autoclave or removed (desorption) into the low pressure vessel CV2. To ensure thermal equilibrium each point was equilibrated at least 3 hours and data were collected after the pressure is constant for at least 0.5 hour. The highest uncertainty in the PCT calculations comes from estimation of the density of IMC particles and due to accumulation of errors from point-to-point isotherm measurement. We estimate the maximum accumulated error for hydrogen concentration in the sample at the last point of the isotherm as 0.01 % wt.

In order to determine structural parameters 4 samples of the IMC were collected: inactivated “as cast” sample and three samples of powder after experiments in vertical orientation from 10 mm, 45 mm and 80 mm of the bottom of the bed. Measurements were conducted at room temperature by X-ray diffraction (XRD) using D8 Advance (Bruker) diffractometer with Cu Kα radiation. Samples for X-ray analysis were prepared by mechanical grinding to a powder. The step was 0.02 and the exposition time was 60.8 s by step. The 29 angles were from 10° to 120°. Processing of diffraction patterns was performed using Jana2006 and Xpowder12 software. The obtained data on X-ray density of the IMC were used for PCT isotherms calculations. SEM images of the samples were obtained by scanning electron microscope Jeol 6380 LA in BSE mode and their fill densities were measured with the aid of surface area analyzer NOVA Quantachrome 1200e.

Heat and mass transfer during absorption was investigated in a RSP-8 metal hydride reactor (figure 2) [10]. The reactor has tubular design, inner and outer tubes form two liquid heat exchangers with an annular reaction chamber between them, which filled with 1 kg of La0.9Ce0.1Ni5, maximum H2 capacity is 140 st.L, nominal operating capacity is 110 st.L.

Hydrogen from the gas ramp was fed to RSP-8 from the top at constant rates 10 and 20 st.L/min with pressure 0.55 MPa, the reactor was cooled by tap water at 9°C and 8°C at 0.214 g/s (equilibrium IMC pressure 0.2 MPa). Measurements: Bronkhorst EL-Flow mass flow meter/controller, Aplisens pressure...
transmitters model PC28, thin film platinum sensors Heraeus M422, 1 kΩ, the experiments were controlled using LabView software, with discretization of 1 Hz.

![Figure 1](image1.png)

**Figure 1.** The working autoclave: 1 – inner space, 2 – casing, 3 – gasket, 4 – cover with 6 mm thermocouple pipe; 5 – spacer; 6 – flange; 7 – hydrogen inlet. Photo of the dense and robust particle agglomeration from the bottom of the autoclave and SEM images of the bed samples from the three levels of the autoclave.

![Figure 2](image2.png)

**Figure 2.** The RSP-8 reactor and the scheme of experiments: P – pressure gauge; FR – flow meter/controller; V – valve.

### 3. Experimental results

PCT-isotherms for horizontal and vertical orientations are shown in figure 3 for 333 K and 353 K. The results show evidently that the orientation of the bed has influence on the PCT diagram.

For desorption in the vertical orientation a non-considerable decrease of the mass content of hydrogen in hydride (about 0.01 - 0.02 wt.%) is observed, and equilibrium desorption pressure also slightly decreases
from 0.985 to 0.964 MPa at 333 K and from 1.83 to 1.78 MPa at 353 K, and apparent values of enthalpy rise from 30.4 to 30.9 kJ/mole and entropy from 110 to 112 J/mole·K. Changes in reaction enthalpy and entropy is slightly higher than calculation uncertainty while pressure difference is significantly higher than measurement error.

For absorption the effect is much more considerable, in the vertical orientation equilibrium pressure decreases from 1.58 to 1.36 MPa at 333K and from 2.68 to 2.51 MPa at 353K. Apparent values of reaction enthalpies and entropies for vertical orientation also rise from 26.3 to 29.6 kJ/mole and from 102 to 111 J/mole·K respectively.

![Figure 3. PCT isotherms for La$_{0.9}$Ce$_{0.1}$Ni$_5$ in the different configurations of the bed.](image)

After measurements in the vertical orientation the autoclave was shaken intensively and even stricken with a hammer in attempt to restore horizontal orientation of the metal hydride bed, which was unsuccessful as it was found from unchanged PCT isotherm and bed inspection after the opening. As it was found the bed have failed to restore its horizontal form and the powder has not spread across the autoclave. The bed appeared to be considerably non-uniform with different degrees of particle agglomeration by height (see figure 4). At the top the bed loose lusterless flammable powder was observed, and in the middle some agglomerations, which easily crumbled at slight pressing, appeared. At the bottom the bed was pressed into a dense and robust compact with the height about 25 mm, which kept its shape and had to be split in fragments to be removed. This part had inclusion of big particles with metallic luster.

SEM images of the samples from the bottom, middle and top of the bed are presented in figure 4. The sample from the bottom (about 10 mm from the bottom) shows maximum inhomogeneity of particle sizes and includes fine fraction with particle sizes smaller than 10 μm joint with big particles of the size 100-200 μm, these particles have a lot of cracks as seen on image, but they have not fall apart, the sample from the middle (about 45 mm) is the most homogenous with particle sizes around 10 μm and the sample from the top (about 80 mm) contains particles with the size around 20 μm. Fill density decreases from the bottom to the top: 3.86 g/cm$^3$ (at 10 mm), 3.47 g/cm$^3$ (at 45 mm), 3.26 g/cm$^3$ (at 80 mm), thus the fill density changes in 15% along the bed.

The XRD measurements were performed for 3 samples: nonactivated “as cast” sample, and activated samples from the top (80 mm) and the bottom (10 mm) of the metal hydride bed. Cycling has led to significant decrease of diffraction peaks intensity due to IMC amorphization and distortion of crystal lattice, also there was a difference in peak intensities for the samples from the top and the bottom. Nevertheless, difference between calculated elementary cell parameters is lower than 0.3% and there are no peaks of a new phase in activated sample diffractograms. The structure of IMC belongs to CaCu$_5$ type. The elementary cell parameters calculated by Jana 2006 software are quite close for all the samples: \(a = 5.003 \text{Å}, c = 3.99 \text{Å}, V = 86.4 \text{Å}^3,\) X-ray density is \(d = 8.31 \pm 0.01 \text{g/cm}^3\).

Results for RSP-8 charge with pure hydrogen are shown in figure 4. Each charge started with the flow jump, when the controller tried to support constant flow rate, which was unsuccessful for the 20 st.L/min regime, heat and mass transfer crisis [11] was observed from the start and the reactor could not take
hydrogen at the constant rate. The crisis in both cases occurred at the moment when pressure $p_1$ at the top of the bed became close to pressure $p_{in}$ in the supply line. Totally 137 st.L was charged at the flow set point 10 st.L/min and 140 st.L at 20 st.L/min, to SoC 100% (110 st.L) the reactor was charged in 9.7 min and 6.6 min respectively. It can be stated, that hydrogen absorption is accompanied by substantial non-uniformities along the bed, which lead to non-linear flow regimes inside the bed. Bed permeability can be estimated as ratio of gas flow to pressure difference (see figure 4), for Darcy’s flow it should be constant, but this condition was fulfilled only for the subcritical part of the 10 st.L/min experiment.

![Figure 4. RSP-8 charge with pure hydrogen for 10 st.L/min (left) and 20 st.L/min (middle) flow regimes and apparent bed permeability (right). Pressures: $p_{in}$ - supply line, $p_1$ - top, $p_2$ - bottom; $q$ - flow; SoC - state of charge (100% is nominal capacity 110 st.L).](image)

4. Conclusion

Influence of geometrical non-uniformities of the La$_{0.9}$Ce$_{0.1}$Ni$_5$ metal hydride bed on its structure and heat and mass transfer at hydrogen absorption were investigated by PCT measurements and analysis of structure of the 500 g sample in the cylindrical autoclave of height 180 mm and diameter 45 mm and by experiments on hydrogen absorption in the vertical metal hydride reactor RSP-8 of height 420 and diameter 48 mm filled with 1 kg of the IMC.

Metal-hydrogen interaction during cycling provides enough energy to drive the granular separation inside the metal hydride bed. The bed after the cycling in vertical orientation appeared to be considerably non-uniform with different degrees of particle agglomeration by height and at the bottom the bed was pressed into the dense and robust compact of particles smaller than 10 μm, which had inclusion of big 100-200 μm particles with metallic luster. Fill density decreases from the bottom to the top: 3.86 g/cm$^3$ (at 10 mm), 3.47 g/cm$^3$ (at 45 mm), 3.26 g/cm$^3$ (at 80 mm), while structural properties of particles remain the same with X-ray density 8.31 g/cm$^3$.

During the charge of the RSP-8 reactor with constant flow rates 10 and 20 st.L/min the considerable non-uniformity of pressure inside the bed was observed. The heat and mass transfer crisis occurred at the moment when the pressure at the top of the bed became close to the pressure in the supply line, while the pressure at the bottom was lower on 0.2-0.3 MPa, thus the crisis occurred earlier than in the case of uniform pressure in the bed. For the inlet set point 20 st.L/min the crisis was observed from the start and the reactor could not take hydrogen at the constant rate. Totally 137 st.L was charged at the flow set point 10 st.L/min and 140 st.L at 20 st.L/min, to SoC 100% (110 st.L) the reactor was charged in 9.7 min and 6.6 min respectively. Estimation of the bed permeability has shown that non-linear flow regimes were inside the bed at supercritical regimes, since for Darcy’s flow with constant ratio of gas flow to pressure difference was fulfilled only for the subcritical part of the 10 st.L/min experiment.
We conclude that geometrical non-uniformities of metal hydride beds have influence on its structure and performance related characteristics of the bed, as well as on heat and mass transfer, and should be taken into account in design of metal hydride devices.

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