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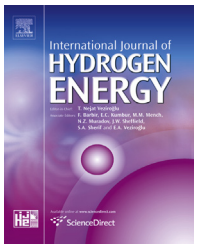

A novel capacitive device for the study of volumetric expansion of hydride powders

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ARTICLE INFO

Article history:
Received 20 June 2015
Received in revised form
22 August 2015
Accepted 22 August 2015
Available online 9 October 2015

Keywords:
Hydrogen storage
$LaNi_5$
Metal hydride
Hydride bed swelling
Capacitive experimental device

ABSTRACT

A new experimental device was developed to assist in the study of materials with potential for hydrogen storage with energy applications. Through measurements of electrical resistance and capacitance in AC, we can evaluate the alterations in porosity and volumetric expansion of very small amounts of material (~ 0.1 g) as functions of hydrogen concentration. Observations of global sample resistivity permit the qualitative evaluation of changes of powder packing and grain mobility. To obtain the physical parameters of the materials, we propose an equivalent circuit with a complex impedance function developed from the internal geometry of the device. The circuit has been calibrated with three different conductive metallic alloys and tested successfully in the hydride of $LaNi_5$ on samples free of stresses. We measured an increase of the volume expansion of the hydride bed on hydrogen cycling, evolving from below to above the crystallographic volume expansion.

Introduction

Concerns with the Environment and decarbonization of the economy are driving the development of hydrogen related technologies for energy storage, present in ever more sectors, such as substituting conventional batteries in portable devices [1], in automotive applications [2], or coupled to micro-generation or large-scale energy production plants. Lowering carbon dioxide emissions in transportation motivate the present large research effort in the application of hydrogen fuel cells in electric motor driven vehicles [3,4]. One of the great challenges in this market remains the storage of hydrogen [5]. New lighter and efficient materials have to be developed and studied, and adequate tanks fabricated and tested to compete with fossil fuel tanks [6]. Renewable sources of energy, like solar and wind plants, have normally an intermittent production due to their dependency of climate conditions. Being able to store produced energy for later use is thus a strong drive for development in the energy industry [7,8]. Size and weight of storage facilities are not a problem in such stationary applications, although many issues remain to be solved regarding cost optimization, operability, performance and above all, safety [9]. The optimization of storage in solid materials requires the study of their properties and behaviour upon absorption of hydrogen [10]. One issue in the optimization of metal hydride storage tanks is related to the need of a thermal control, as heat is released in the hydriding and absorbed in the dehydriding processes, and the charge/discharge kinetics are dependent of the working temperature

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http://dx.doi.org/10.1016/j.ijhydene.2015.08.063

[11–13]. Another important issue regarding absorption of hydrogen by solid materials is the expansion of the crystalline lattice $\Delta V/V_0$, which can reach values of the order of 30% in intermetallic hydrides [14] leading to considerable periodic changes of the macroscopic volume occupied by the hydride bed when cycling.

The changes of the crystalline lattice parameters are responsible for the brittleness of the material leading to its degradation and consequently to the reduction of the size of the grains constituting the hydride bed. The process of fragmentation of grains in irregular forms accompanied by the increase of their packing density enhances the contact and thus the thermal conduction between grains [15], but the volumetric changes of the material may result in the application of considerable stress on the walls of the reservoir that may compromise its structural integrity. The stress is related to the shape and size of particles and their distribution within the tank. Nasako et al. [16] describe the process of increasing tensions in two steps: The agglomeration of particles, mainly in the bottom of the reservoir, and the pulverization of particles with the cycling process. Okumura et al. [17] verified experimentally a non-uniform distribution of particles within a reservoir, with higher packing densities resulting in a larger deformation of the walls at the bottom of the reservoir. The control of the void space above the sample (dead volume) is fundamental to reduce the stress on the walls of a hydride reservoir. Qin et al. [18] verified experimentally with thin wall tanks that the stress on the walls is directly linked to the degree of packing of the used alloy (AB5 type) and related with the pulverization effect of the material as it is cycled.

Various techniques have been employed to characterize the volumetric changes, compaction and porosity of a metallic hydride bed in situ as the hydrogen concentration varies. Neutron irradiation (radiography and tomography) of a chamber with a hydride reveal the changes of volume, porosity and density along the process of charge and discharge with hydrogen [19–21]. Charlas et al. [22] present an experimental apparatus for the study of the macroscopic volumetric changes of the hydride of a Ti–Cr–V + Zr–Ni alloy. This apparatus has rigid cylindrical walls and the sample is confined and slightly compressed by a spring attached to a vertically moving piston that allows the measurement of the volume occupied by the sample. As the cycles progress, they observed a decrease of the volume and porosity. The volumetric expansion is further reduced with a higher compression of the spring, generating a stress on the walls of the chamber [23]. Matsushita et al. [24] studied the porosity of the system $LaNi_5$–H_2 by direct observations of the height occupied by the hydride on a transparent chamber without induced compression. The porosity decreases during a charge of hydrogen and increases back to a higher value in the following discharge. The height of the sample increases rapidly in the first charge and decreases in the next discharge but not returning to the initial value, the rate of increase becoming lower in the following cycles. Herbrig et al. [21] found the same effect.

The development of materials with efficient storage capacity and the design of appropriate tanks meeting the criteria of each application are, as outlined above, important challenges to the competitiveness of hydrogen in the energy market. Regarding materials, the study of porosity, agglomeration and volumetric expansion is of great importance due to the implications with structural integrity and lifetime of the tanks. In this context, we here propose a new instrument to characterize those properties in materials with potential utility for hydrogen storage. The new instrument explores a different approach in the analysis of volume and porosity changes of conductive powder beds upon hydrogen absorption, by correlating those macroscopic properties with A.C. electrical measurements of resistance and capacitance. The measurements are made in parallel with hydrogen concentration measurements along the processes of hydrogen absorption and desorption, and the calculation of the volume of the powder bed is based on a model of an equivalent electric circuit for the chamber and the sample and on calibration measurements with samples of known volume. The geometry of the capacitor core and sample space of this instrument, manufactured with high-precision machining tools, result in a very high sensitivity to volume changes, and thus to porosity changes, while maintaining a very good stability along lengthy assays. This allows the study of smaller quantities of material than reported for a visual method [24]. Additionally, by avoiding the compressing springs used in other devices [21–23], it allows the study of powder beds in the loosest state possible for small quantities. Like other laboratory bench instruments, it does not have the high costs of the use of high-scale facilities like those needed for neutron irradiation [19–21]. Finally, the measurement of a global resistivity, although of much poorer resolution than that of the capacitance, allows a qualitative appreciation of dynamic changes of the electrical contacts between the grains of the powder, thus indicating when they are moving amidst the bed.

Experimental apparatus and methods

The new experimental apparatus was developed with the purpose of better characterizing the changes of volume and associated parameters during hydrogen charge and discharge cycles of intermetallic hydrides. It consists of a high-pressure chamber, leak-free to at least 50 bar of helium, with a sample holder designed with a coaxial capacitor geometry. The primary measurements of electrical capacitance and resistance are converted into values of volume, porosity and resistivity of the hydride sample, whose hydrogen concentration is evaluated in parallel by a volumetric method.

In this section, we describe the details of the chamber and sample holder and the basic experimental procedures when using the apparatus.

Pressure chamber and capacitive sample holder

Fig. 1 shows a detailed sectional drawing and perspective view of the high-pressure chamber with the sample holder mounted in its working position. The chamber was manufactured in AISI 316 stainless steel.

The internal space where the sample holder sits has a height of 76.27 mm and a diameter of 30.42 mm. The large area of the internal surfaces is polished to minimize the