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Experimental formula for estimating porosity in a metal hydride packed bed

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ABSTRACT

An experimental formula for estimating porosity in a metal hydride packed bed is presented. The formula was developed by direct observation of the volume changes of a metal hydride packed bed under free expansion in a vessel. The experimental results showed that the cycles of expansion and contraction were repeated at large porosities above 60% after a rapid state change caused by early particle breakup. The formula for porosity was expressed as a function of the reacted fraction and as a function of the cycle number. The function formula of the reacted fraction can be used to compute different values of porosity for expansion by absorption and for contraction by desorption. The coefficients assuming 100% hydrogen storage based on the experiments with $LaNi_5$ were an expansion ratio of 16.7% and a contraction ratio of 8.4%, on average. This experimental porosity formula is useful for effective thermal conductivity calculations and for numerical simulations of metal hydride packed bed behavior.

1. Introduction

Environmental problems have led to an increase in the use of various renewable energy sources. However, most renewable energy sources cannot supply a steady source of energy. Moreover, power generation operations on the ocean have a problem with the transmission of electrical energy. The ability of such renewable energy sources to supply a steady source of electrical power requires an electricity storage method that is both long-term and effective on a large scale. Hydrogen is a promising candidate for electrical power storage, because it can be obtained by subjecting fresh water to an electrolytic process and can generate electricity by means of a fuel cell, without any carbon dioxide emissions. Thus, hydrogen must play a central role in the future energy cycle [1].

One of the main problems in the usage of hydrogen energy is the storage process [2]. Although hydrogen storage methods have been explored worldwide, an adequate method has yet to be developed. “The hydrogen economy” may be realized sooner by selecting a storage method that is suitable for various needs. In particular, metal hydrides show great promise as a safety-conscious method because they do not easily explode and can absorb hydrogen at a moderate temperature and a relatively low pressure [3]. For practical use, the basic properties of metal hydrides should be studied more closely [4].

Heat transfer in a metal hydride strongly depends on the compound’s properties. Because the hydrogen absorption of a metal hydride is an exothermic reaction and the hydrogen desorption is an endothermic reaction, the rapidity of absorption and desorption decreases in the absence of heat-transfer enhancement [5,6]. Hence, thermal management of metal hydrides is essential to achieve a continuous process. Several numerical and experimental studies have investigated

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methods to increase the heat transfer rate on metal hydride reactors [7–24]. These methods include the use of internal heat exchangers [7,9,11–16] or external active cooling systems such as a circulating coolant or fin [7–11,13,14], integration of a copper wire net structure [17], compaction of the metal hydride powder with an expanded graphite [18,19], insertion of nickel or aluminum foam [20–23], and direct synthesis of a single-walled carbon nanotube [24]. In all cases, metal hydride is used in powder form to increase the reactive area. The heat transfer property of the powder is the effective thermal conductivity of the entire packed bed. For other simple powders, various computational expressions of the effective thermal conductivity have been proposed [25,26]. In these expressions, the significant parameters are the gas thermal conductivity, the solid thermal conductivity, and the porosity. Researchers van Antwerpen et al. [25] reported that the packing structure (porosity, coordination number, and contact angle) has a large effect on the effective thermal conductivity of a packed bed. Porosity is an important parameter. However, the porosity is often assumed to be about 50% and to remain unchanged by hydrogenation. Most research on heat-transfer enhancement has not focused on porosity.

Methods to measure the effective thermal conductivity of a metal hydride packed bed have already been established [27,28]. However, the reasons for the measured values have not been fully explained, and calculations or simulations of the effective thermal conductivity for metal hydrides have been less thoroughly investigated. Hahne and Kallweit [29] observed that the effective thermal conductivity stabilized after five absorption–desorption cycles for pressures greater than 0.01 bar and decreased slightly compared to the delivery state. They explained that the breakup of larger particles brings forth the Smoluchowski effect and causes the reduction in the effective thermal conductivity. Asakuma and co-workers [30,31] analyzed the effective thermal conductivity of a metal hydride bed by the homogenization method. Smith and Fisher [32] presented a multiphysics modeling approach for heat conduction in metal hydride powders, containing particle shape distribution, size distribution, granular packing structure, and effective thermal conductivity. However, these studies did not focus on porosity in detail.

Additionally, stress generated in the metal hydride reactor by alloy expansion may lead to deformation and crushing. Therefore, stress is an important factor to consider when designing and using the metal hydride reactor [33–36]. Porosity is also important for the stress generated in the metal hydride reactor. Ao et al. [34] measured the packing state by industrial computed tomography (ICT). Okumura et al. [36] measured the local packing ratio by slicing a frozen packed bed. However, the best and quickest way to evaluate porosity is to make a measurement by direct observation of the volume change.

In summary, porosity is important for the heat transfer and the stress of metal hydride packed beds, and it needs to be properly evaluated with respect to expansion, contraction, and breakup. However, few studies have directly observed the expansion and contraction of such a bed. Therefore, we have investigated the volume change of a metal hydride packed bed by direct observation [37–39]. The purpose of this paper is to show the experimental results and porosity formula for effective thermal conductivity calculations and for numerical simulations of a metal hydride packed bed. The direct observation of volume changes of a metal hydride packed bed was carried out under free expansion in a vessel. The formula was developed on the basis of the direct observation results. The porosity formula was expressed as a function of the reacted fraction and as a function of cycle number. The function formula of the reacted fraction can be used to compute different values for expansion by absorption and for contraction by desorption.

2. Experimental apparatus and methods

The investigation material was the metal hydride $LaNi_5$ (Japan Metals & Chemicals Co., Ltd., Japan). The characteristics of $LaNi_5$ and of $LaNi_5H_6$, which is a hydrogenated product of $LaNi_5$, are presented in Table 1. The maximum hydrogen storage of $LaNi_5$ is 1.4% by wt.

2.1. *Experimental apparatus*

The experimental apparatus used in this study consisted of a hydrogen supply system, a pressure chamber, and a circulating water system, as shown in Fig. 1. Hydrogen was supplied from the secondary tank (304L-HDF4-1000; -500; -300, Swagelok, USA) to calculate the amount of hydrogen storage. The test chamber was put into the acrylic tank with circulating water. The test section temperature was kept uniform by circulating water (hot water: TRL-750H, THOMAS KAGAKU Co., Ltd., Japan; cold water: NCB-2500, Tokyo Rikakikai Co., Ltd., Japan). Fig. 2 shows the appearance of the test section, the observation pressure chamber, and the glass bottle of metal hydride. The observation pressure chamber is a transparent reaction vessel and is made of polycarbonate pipe and flanges and stainless-steel flanges. The observation chamber withstands a pressure of about 1.0 MPa [37]. Metal hydride was put into the internal glass bottle, as shown in Fig. 2(c), because the observation chamber is not likely to withstand the expansion stress. The internal glass bottle is cylindrical in shape with an inside diameter of 27 mm.

The pressures of the secondary tank (P_1) and of the test chamber (P_2) were measured using absolute manometers (P_1: NS100A-5MPA; P_2: NS100A-2MPA, Minebea Co., Ltd., Japan). The temperatures of the secondary tank (T_1), the test chamber (T_2), the metal hydride packed bed (T_3), the acrylic tank water (T_4), and the circulating water (T_5) were measured using K-

Table 1 – Characteristics of $LaNi_5$ and $LaNi_5H_6$.

Name	$LaNi_5$	$LaNi_5H_6$
Lattice constant		
a_0	5.017 Å	5.440 Å
c_0	3.982 Å	4.310 Å
Volume	86.8 Å^3	110.5 Å^3
Volume ratio	1	1.273
Mass	432.4 u	438.4 u
Mass ratio	1	1.014
Real density	8272 kg/m^3	6588 kg/m^3