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Effects of cyclic hydriding–dehydriding reactions of $LaNi_5$ on the thin-wall deformation of metal hydride storage vessels with various configurations

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ABSTRACT

The aim of this study is to investigate the influences of pulverization and expansion of $LaNi_5$ on the deformation of metal hydride storage vessels during cyclic hydriding/dehydriding reactions. Three thin-wall vessel configurations, namely hollow, internal gas tunnel, and multi-chamber, are adopted for comparison. Experimental results show the hoop strains induced on the vessel wall by volumetric expansion of $LaNi_5$ hydrides can not be neglected. Unavoidable pulverization and agglomeration of alloy powders in the hollow vessel result in a greater extent of strain accumulation at a lower position. An internal gas tunnel built in the reaction vessel enhances the hydrogen storage capacity and reduces the expansion deformation in the vessel wall. Built-in separators in the multi-chamber vessel can evenly distribute the alloy powders into various chambers and more effectively lessen densification and agglomeration of alloy powders. Consequently, accumulation of wall strain is significantly reduced in the multi-chamber reaction vessel.

1. Introduction

$LaNi_5$ is commercially available as a hydrogen storage medium because of its attractive characteristics, such as large hydrogen storage capacity at low working temperature and pressure, easy activation, and fast reaction rates [1–3]. The hydrogen storage capacity of $LaNi_5$ varies from 0.89 wt% to 1.40 wt% depending on the method of alloy preparation [3]. $LaNi_5$ alloys are commonly prepared by conventional melt casting and the hydrogen storage capacity can reach 1.40 wt% [3]. Although the hydriding and dehydriding characteristics of $LaNi_5$ have been extensively studied, e.g. in Refs. [4–9], attention should also be paid to the safety, efficiency, and cost for practical applications. To use hydrogen storage alloys in many applications, they need to be stored in a reactor, so called hydride storage vessel, in which hydriding and dehydriding reactions take place. A proper design of hydride storage vessel is important to ensure a good performance and safety for a selected hydrogen storage alloy.

Several issues need to be considered in design of a hydride storage vessel scheme, such as primary configuration, thermal management, hydrogen transfer, and mechanistic strength [10]. Many previous studies were focused on the coupling process of porous flow, heat and mass transfer, and reaction kinetics in hydride storage vessels, e.g. in Refs. [10,11]. Only a few studies investigated the mechanistic strength and structural deformation in hydride storage vessels [12–20]. When a metallic alloy absorbs hydrogen, its volume will expand. The volumetric expansion ratio is around 22.4% when a $LaNi_5$ alloy is transformed from a state of solid solution to saturated hydride [21]. Such a volumetric expansion can induce wall stress and deformation in the metal hydride storage vessel. For an improper vessel design, a large change in the specific volume of a metal hydride during hydriding/dehydriding cycles may result in permanent deformation and/or cracking in the vessel wall. Therefore, it is important to study the expansion characteristics of metal hydrides and their influences on the wall deformation for design of a reliable hydride storage vessel. Previous studies on these issues for $LaNi_5$ and its multiphase alloys [12–18] were focused on the relationship between the hydriding/dehydriding behavior and wall stress or strain in storage vessels with a simple, hollow structure. In particular, the effects of cyclic hydriding/dehydriding reactions, initial packing fraction of alloy powders, and orientation of storage vessel were characterized in those studies [12–18]. However, the influences of pulverization and expansion of $LaNi_5$ hydrides on the thin-wall deformation of storage vessels with various configurations during cyclic hydriding/dehydriding reactions have not been studied yet. If the relationship between the primary configuration and thin-wall deformation is characterized, it will be helpful for design of a reliable $LaNi_5$ hydride reactor. Therefore, the aim of this study is to investigate the expansion

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deformation of storage vessels with various configurations under cyclic hydriding/dehydriding reactions of $LaNi_5$ alloy.

2. Experiment

2.1. Experimental setup

In order to investigate the influence of primary configuration on the wall deformation of reaction vessel for $LaNi_5$ alloy during cyclic hydriding/dehydriding processes, three types of thin-wall vessels, namely hollow, internal gas tunnel, and multi-chamber, were employed in the present study. Geometries and dimensions of these three vertical thin-wall vessels are shown in Fig. 1. Fig. 1(a) shows a hollow, cylindrical vessel, while in Fig. 1(b) an internal, porous gas tunnel is added inside the cylindrical vessel. Fig. 1(c) shows a multi-chamber vessel which has an internal gas tunnel and three chambers to distribute the alloy powders evenly into three reaction zones. The wall of each vessel is made of an AISI 316 stainless steel. The internal porous gas tunnels and separators in Fig. 1(b) and (c) are made of a 7075 aluminum alloy. A 1-μm-grade net filter of AISI 316 stainless steel was used and rolled over the internal porous gas tunnel. The circular holes on the gas tunnel tube have a diameter of 1 mm. Wall strain measurements during cyclic hydriding/dehydriding reactions were taken using the experimental setup shown in Fig. 2. SV1–SV8 are the solenoid valves for controlling the hydrogen flow route. P1–P3 are the pressure transducers for monitoring the discharging hydrogen pressure, input hydrogen pressure, and hydrogen pressure in the hydride storage vessel, respectively. A 0.5-μm-grade tubular filter is placed at the top flange of the hydride storage vessel to prevent $LaNi_5$ alloy powders from being extracted out by the vacuum pump. An auxiliary chamber is attached to the gas pipes to provide a sufficient amount of hydrogen for hydriding reactions in the vessel.

In order to measure the wall deformation in the vertical hydride reactors during cyclic hydriding/dehydriding reactions, strain gages were adhered on the exterior surface of each cylindrical vessel. The hoop strain was expected to be the maximum principal strain in the vessel wall. Therefore, strain gages were employed to measure the hoop strains at locations of 1/10, 3/10, and 5/10 height from the bottom of the vessel, for the vessel configurations shown in Fig. 1(a) and (b). For the multi-chamber vessel (Fig. 1(c)), strain gages were adhered at 1/10 height of each chamber. All the cyclic hydriding/dehydriding reaction steps were controlled by a programmable logic controller (PLC). The wall strain and hydrogen pressure data during cyclic hydriding/dehydriding reactions were monitored and recorded through a data acquisition system (strainmeter) and a personal computer (PC).

2.2. Material and cyclic hydriding/dehydriding processes

The hydrogen storage alloy $LaNi_5$ was supplied by the vendor in a form of ingot. The alloy ingot was then ground into powders and sieved with a 100-mesh sieve. The particle size corresponding to 100 mesh is less than 149 μm. An amount of 56 g of $LaNi_5$ alloy powders, corresponding to about 70 vol% of the interior space in the hollow vessel, were filled into each type of vessel. In each test, the vessel containing alloy powders was firstly evacuated by a vacuum pump for 120 min, followed by 80 cycles of hydriding/dehydriding reactions. The cyclic hydriding/dehydriding processes were carried out in a way that the $LaNi_5$ alloy powders were charged with 3.2-MPa hydrogen for 80 min and then evacuated by a vacuum pump for 60 min at room temperature in each cycle. Due to easy activation for $LaNi_5$, the first five cycles were performed as an activation process. In the present study, the strain values read at the end of the absorption and desorption steps in each cycle are taken as the data points to show the variation of strain with cycle number. Size and morphology of the $LaNi_5$ powders before the activation process and during the cyclic hydriding/dehydriding test were analyzed using scanning electron microscopy (SEM).

3. Results and discussion

3.1. Strain variation at various vessel positions

Fig. 3 shows the variations of hoop strain at 1/10, 3/10, and 5/10 height from the bottom of the vertical, hollow reaction vessel. The solid and open symbols represent the strains at the end of the absorption and desorption steps in each cycle, respectively. As shown in Fig. 3, the absorption-step strain at 1/10 height increases with cycle number from the beginning of the cyclic hydriding/

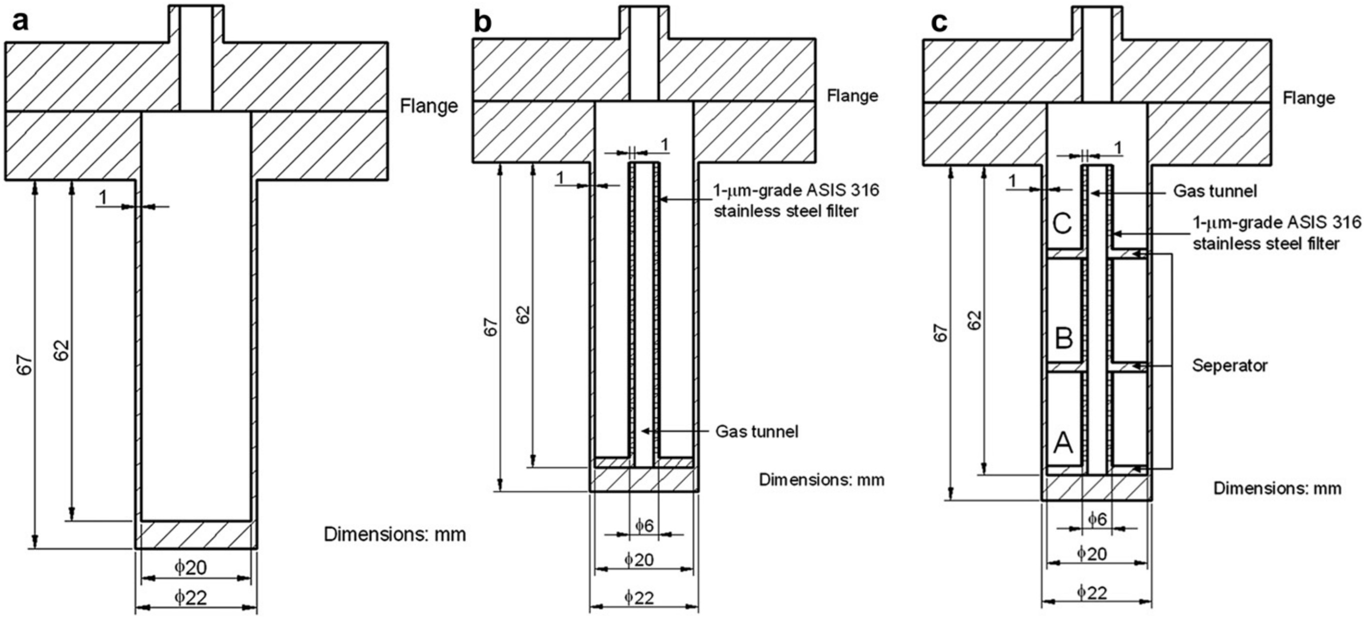

Fig. 1. Cross-sectional views of $LaNi_5$ hydride storage vessels tested: (a) hollow; (b) internal gas tunnel; (c) multi-camber.