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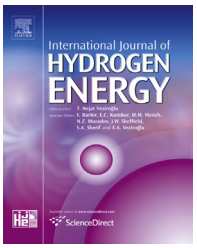

Pulverization mechanism of hydrogen storage alloys on microscale packing structure

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ABSTRACT

In-situ and transient visualizations of the packing structure of a hydrogen storage alloy bed are carried out using an X-ray computed tomography (CT) system. The packing structure is clearly observed on the microscale using the CT system. When the alloy bed is subjected to hydrogen absorption–desorption cycles, the pulverization progresses from the lower to the upper regions of the bed. After several hydrogen absorption–desorption cycles, the packing structure in the lower region of the bed changes and the microstructural void decreases slightly. Based on these results, we propose a pulverization mechanism of the packed bed in which the friction between particles affects the pulverization process.

1. Introduction

Hydrogen storage alloys are promising materials for hydrogen storage. The alloys are capable of storing large quantities of hydrogen, and they undergo hydrogenation under relatively mild conditions at ordinary temperature and pressure.

When these alloys absorb hydrogen, their lattice expands, causing swelling and pulverization of the structure. Therefore, reaction vessels in which these reactions are carried out are subjected to stress in hydrogen absorption reactions and the stress can damage the vessels. Several studies have focused on the investigation of methods for preventing this damage. Although Wang et al., Ao et al., and McKillip et al. [1–3] reported that the use of an additional substance (such as silicone oil) and the preparing appreciable free space inside the vessel above the packed bed are effective methods, their results are applicable only to similar cases to their experiments, and the scope is limited. Thus, a quantitative prediction of the phenomena that takes place in theinside a vessel is required.

In previous studies, the phenomena that occur in a reaction vessel have been investigated by strain measurements on the vessel surface. Kawamura et al. [4] investigated the stress change during one hydrogen absorption–desorption cycle. They suggested that particle rearrangement and pulverization occurred in the vessel during the hydrogen absorption or desorption process. McKillip et al. [3] investigated the wall stress distribution of a vessel, which is set horizontally. They suggested that the stress distribution depends on the alloy powder distribution and the particle size distribution in the bed. Nasako et al. [5] reported that the stress gradually increases with every hydrogen absorption–desorption cycle.

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They proposed that the local packing fraction increases gradually in a downward direction as a result of the downward movement of pulverized particles. These investigations were performed by measuring only the observed stress and the internal phenomena in the vessel were not considered.

Qin et al. [6,7] measured the strain and observed the vessel packing state opening the vessel. They revealed that after several absorption–desorption cycles, the alloy bed was separated into an agglomerated state and a loosened state, and the agglomeration size increased with an increase in the initial packing fraction. However, they were not able to perform *in-situ* visualization of those phenomena and of the changes in the vessel packing state with hydrogen absorption–desorption cycles, because the vessel material is a metal must be able to withstand high-pressure and a pure hydrogen atmosphere. In addition, in a vessel made of a transparent material such as glass or acrylic resin, only the surface of the alloys could be observed. Although use of a transparent vessel might enable evaluation of the transitive surface packing state, it cannot be used to observe the internal packing.

The methods mentioned above are not suitable for *in-situ* visualization of the microstructural changes that occur in the vessel. Thus, a non-destructive and *in-situ* observation method is required. Computed tomography (CT) scan is such a method. There are two main CT techniques: neutron CT and X-ray CT.

Jacobson et al. [8] and Gondek et al. [9] investigated the transient and steady-state hydrogen distributions in an alloy bed using the neutron CT imaging method. They were able to observe transient phenomena by tracing hydrogen. In these studies, the mean diameter of the pulverized alloy particles was about 10–20 μm, and a high resolution level was required to observe the packing structure. However, because the maximum resolution of the neutron CT imaging method is about 50 μm, it was difficult to observe the packing structure of the alloy bed.

On the other hand, an X-ray CT system with high resolution (0.4 μm) has recently been developed. The high resolution enables the X-ray CT system to observe the packing structure. An additional advantage is that the time required for capturing an X-ray CT image (a few minutes) is much shorter than that for capturing a neutron CT image (several hours). Furthermore, X-ray CT observation does not make the sample radioactive, unlike neutron CT. Therefore, using the X-ray CT system, we can clearly visualize changes in the vessel packing state with hydrogen absorption–desorption cycles.

In this study, microstructural changes in the packed bed are investigated with *in-situ* and transient visualization. In addition, we propose a mechanism for the progress of pulverization in the bed.

2. Materials and methods

Fig. 1 shows an experimental flowchart. Hydrogen storage alloy particles are packed in a reaction vessel. Following an activation treatment, the alloys are made to repeatedly absorb and desorb hydrogen and their X-ray images are taken.

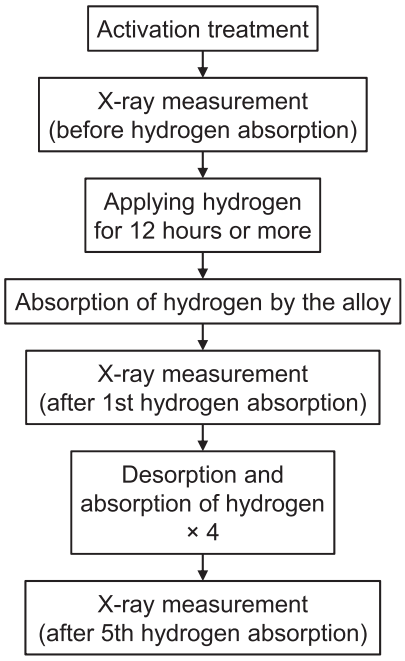

Fig. 1 – Flowchart of the experimental procedure.

2.1. Samples

Fig. 2 shows the schematic diagram of a pencil-type reaction vessel (1 mm inner diameter, 1 mm wall thickness). The vessel is made up of aluminum, is conical in shape, and has a burr caused by the metal work. We did not use commercially available vessels because they are not able to transmit X-rays.

The hydrogen storage alloys used are AB5-type ($MmNi_{4.12}Co_{0.60}Mn_{0.23}Al_{0.05}$) with a density of 8030 kg/m^3. The pressure–composition isotherms (PCT) are shown in Fig. 3 [10]. The volumetric expansion rate of the alloy is 24.7% at (mol H)/(mol M) = 1.1 [11]. Alloy particles filtered through a 40–60 mesh are initially packed to a height of 51 mm in the vessel. A valve is attached to the vessel for pressurizing it with hydrogen. Furthermore, a detachable plate is attached to the vessel only during scanning.

In this study, we analyze the images of the entire vessel as well as of three specific regions (0.0–1.0, 7.5–8.5, and 15.0–16.0 mm from the bottom).

2.2. X-ray CT system

We used two X-ray CT systems: a typical X-ray CT system (inspeXio SMX-225CT-SV3, Shimadzu Corporation) and a recently developed X-ray CT system (SMX-160CTS, Shimadzu Corporation). The typical system is used to capture the image of the entire alloy bed and the recently developed system (Fig. 4) is used to capture three-dimensional and cross-sectional images in each region.

The typical system has a resolution >4 μm and the recently developed system has a resolution >0.4 μm. The typical system can take a transmission image of the entire packed bed because it has a large viewing area. However, it cannot