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Swelling response behavior of palladium during hydrogen absorption and discharge

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ABSTRACT

Swelling characteristics of hydrogen storage alloy (HSA) with hydrogen content change were experimentally determined. Its kinetic behavior is important for an HSA actuator which is driven by the volume change of the HSA in a hydrogen atmosphere. Although hydrogen absorption characteristics of the alloy are expected to be strongly related to the actuator performance, it is difficult to clarify the relationship using the previous HSA actuators which consist of plural materials. In this paper, the authors investigated the swelling ratio and the response time of palladium powder in a hydrogen atmosphere. As a result, the swelling ratio increased with hydrogen absorption amount. The response time increased with hydrogen pressure during pressurization, while it was independent of pressure. It was revealed from reaction kinetics that a rate-limiting step was diffusion and interfacial reaction during the pressurization and the evacuation, respectively. Thus, the swelling property of palladium is determined from its hydrogen absorption behavior, which suggests the HSA actuator can be designed based on hydrogen storage characteristics.

Introduction

A hydrogen storage alloy (HSA) increases its volume by absorbing hydrogen into its lattice with an increase in its surrounding hydrogen pressure. Actuators using the volume change as their driving forces have been developed as one of the technologies to control hydrogen gas in a so-called hydrogen society that uses hydrogen as a major source of power [1,2]. The HSA actuators are operated by the change in hydrogen pressure, therefore, they are anticipated to be used in specific environments such as in hydrogen atmosphere and in space [3].

Two types of the HSA actuators have ever been proposed, i.e., unimorph-shape and capsule-shape. The unimorph actuator [4–7] has a two-layer structure made of an HSA foil and a non-hydrogen-storage substrate. The bending or twisting motion is induced by the swelling of the HSA foil in a hydrogen atmosphere. In the capsule actuator [8,9], an HSA foil is placed on the inner wall of a hollow capsule. The

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swelling of the foil is converted into the deformation of the capsule.

Performance of an HSA actuator is influenced by hydrogen absorption characteristics of a hydrogen storage alloy because it is deformed by hydrogen absorption and discharge of the alloy. For example, Kagawa et al. [4] compared the deformation behavior of HSA unimorph actuators using Pd-11 at%Ni and Pd-13 at%Ni as HSA foils. They found the deformation rate of the actuator with Pd-13 at%Ni is more than twice as that of the actuator with Pd-11 at%Ni, which is considered to be based on their hydrogen absorption rates. Thus, the performance of HSA actuators changes with the hydrogen storage alloy used. It is important to select an appropriate alloy according to the usage environment. It is, however, difficult to evaluate a relationship between hydrogen absorption ability and actuator's characteristics using the previous HSA actuators which are the composite materials made of hydrogen storage alloys and non-hydrogen-storage materials.

The macroscopic volume change of HSA powder has been investigated to reveal the effect of the swelling on a hydrogen tank. Some studies [10–14] measured the strain of a sample holder containing HSA powder and revealed that the swelling of the alloy during hydrogenation was large enough to deform the holder. Matsushita et al. [15,16] observed the volume change of $LaNi_5$ powder directly with a transparent cylinder and an optical camera. Electrical measurements of the volume and porosity were performed with a capacitive sample holder by E.S. Ribeiro [17,18]. B. Charlas et al. [19] investigated the cyclic volume change of the HSA powder during hydrogen absorption/discharge with an apparatus in which a piston displaces with the change in the sample volume. These studies focused on the measurements of the static swelling behavior, that is, the volume change before and after hydrogenation. For HSA actuators, however, the information on its kinetic behavior such as response time and its mechanism is also important.

In this work, the kinetic swelling behavior of HSA powder was evaluated in addition to the static characteristics. A technique to measure the macroscopic swelling behavior of hydrogen storage alloys in hydrogen atmosphere was established using palladium powder as a sample. Palladium has a good hydrogen storage ability and a high reactivity with hydrogen such that it is used for a hydrogen permeation membrane [20], the capsule-shape HSA actuator [9], etc.

Experiment

Experimental apparatus and sample

Fig. 1 shows schematics of an apparatus for the measurement of the displacement in a hydrogen atmosphere. A cylindrical sample holder was put into a pressure chamber (Fig. 1a). The pressure chamber was connected to a hydrogen tank and a vacuum pump, and hydrogen was changed inside the chamber. Therefore, there was no pressure difference between inside and outside the sample holder. The sample holder consists of a cylinder, a piston, and a spring. The cylinder has an inner diameter of 13 mm with a hole of 2 mm in diameter at its bottom (Fig. 1b). The clearance between the cylinder and the piston is below 50 μm. The contact surface of the piston was greased with HIVAC-C (Shin-Etsu Chemical Co., Ltd.) to decrease the friction. A restoring force was generated by the spring. The inner bottom surface of the cylinder was covered by a gas permeable membrane (Opulent, Mitsui Chemicals Tohcello, Inc.) to prevent the powder scattering. Displacement of the top surface of the piston, u was measured with a laser displacement sensor (LK-G85, Keyence Co.) through a viewing window of the pressure chamber. The purity of hydrogen gas (Taiyo Nippon Sanyo Co.) was 99.999% or more.

The Palladium powder (AY-406, Tanaka Kikinzoku Kogyo K.K.) was packed in the sample holder. The particles were spherical before and after the experiment as shown in Fig. 2. It is noted that the particles plastically deformed only near the wall of the holder (Fig. 2c). No pulverization was observed through the experiment. The sizes of 680 and 628 particles were measured before and after the experiment, respectively, using the SEM images and the image processing software, ImageJ [21]. The size distribution is shown in Fig. 2d. The average diameter increased 0.07 μm after the experiment. The mean volume diameter, d_V was calculated using Eq. (1).

$$d_V = \frac{\sum_i V_i d_i}{\sum_i V_i} = \frac{\sum_i d_i^4}{\sum_i d_i^3} \quad (1)$$

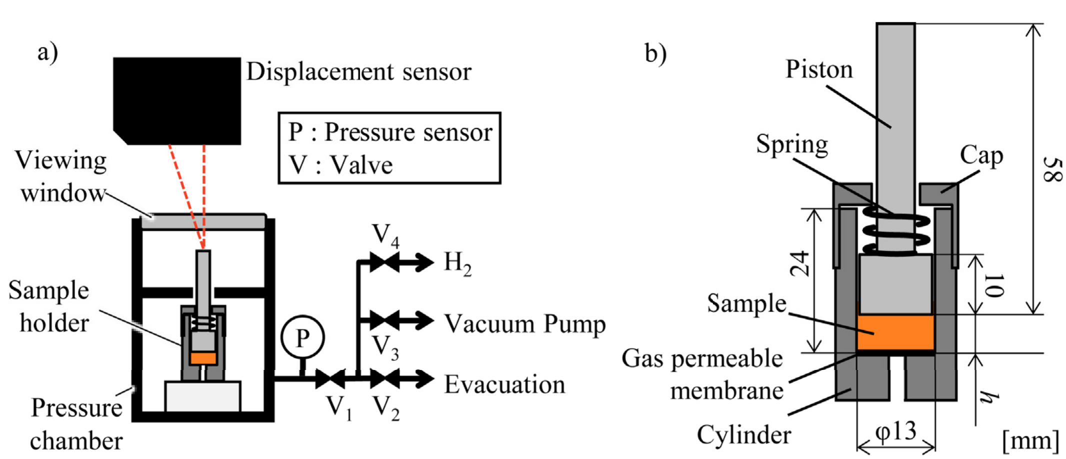

Fig. 1 – Schematics of a) apparatus and b) sample holder.

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