Strain variation on the reaction tank of high hydrogen content during hydrogen absorption-desorption cycles

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Abstract

The strain generated in a reaction tank of hydrogen storage alloys were measured in order to analyze strain variation in different locations during hydrogen absorption-desorption cycles. Strain gauges were set on the various locations of the tank. The change of strain was continuously monitored using the strain analyzer. The results indicate that plastic deformation had occurred during activation period, and it did not become larger in the later hydriding-dehydriding cycles though the tank still had the ability for elastic deformation. The stress induced by alloy swell on the tank was over 8 MPa. Tangential strain was greater than longitudinal strain in each place. There wasn't much more difference in longitudinal at respective points while tangential strain in the middle part was much larger than that in two sides' parts of the tank. The nonuniform packing density lead the deformation tended to occur more serious in tail part than in head part.

1. Introduction

Hydrogen storage alloys have a lot of advantages in hydrogen storage compared to high-pressure hydrogen storage or liquid hydrogen storage, such as more secure, higher volumetric hydrogen storage density, higher purity of hydrogen and longer life. For these reasons, hydrogen storage alloys have great competitiveness as hydrogen storage media in fuel cells area and some of the specific application area (such as submarine, electric forklifts).

Hydrogen storage alloys are often crushed into powder and packed in a reaction tank as hydrogen source. The reaction tanks of metal hydride have been intensively researched for the energy source of proton exchange membrane fuel cell (PEMFC). Toyota has developed the world’s first set of PEMFC combined with metal hydride hydrogen storage tank used for electric car, which has a 60% energy conversion rate, 2~3 times more efficient than gasoline engines [1]. Germany has begun to use metal hydride hydrogen storage device for the source of fuel cell system as conventionally power for AIP type submarines. This type of submarine is already in mass production which has better concealment [2].

Research on the practical use of these systems has always been reported from the perspective of alloy materials, such as hydrogen ab-desorption cycle performance, changes in the lattice expansion [3]. However, repeated hydrogen ab-
desorption cycles cause particles to swell and pulverize [4]. These results lead to the advent of stress generated in the tank. The stress is a kind of unhidden danger in application process of the tank since it can cause deformation and even fracture of the tank [5]. It was reported that alloy packing fraction is needed to be below 0.4 in order to not exceed the elastic limit of the tank during alloy expansion, especially using rare earth series metal hydride even in the case of a horizontal tube reactor [6]. According to F. Qin et al. [7] more than 45 MPa pressure would be exerted on tank inner surfaces by alloy expansion of up to 27% vol during absorbing hydrogen in La0.6Y0.4Ni4.8Mn0.2 hydrogen storage tank. Nasako [3] reported that the stress continued to increase every per cycle even after tanks’ plastic deformation, while T. Satio et al. [8] suggested that the Ti–Fe pellet expand to some extent during activation and remained at a constant volume through subsequent hydride-dehydride cycles. These investigations show that the alloy types, tank dimensions, hydrogen content and some other factors play important roles in the strain on tank surface. The strain seriously restricts the application of the metal hydride hydrogen storage tank.

In this study, we aim at TiFeMn alloy hydrogen storage tank, test the changes of strain at different positions during hydriding-dehydriding processes, analyze the influence factors and proposed programs to improve the security of the storage tank.

2. Experimental details

2.1. Alloy characterization

TiFe is a typical AB-type hydrogen storage alloy. Its hydrogen storage capacity is higher than that of rare earth alloys, and it is more suitable for application of mobile type fuel cell hydrogen source system since the plateau pressure is moderate. However during alloy activation, the activation temperature must reach up to 400 °C–450 °C, and subject to more than ten times hydriding-dehydriding cycles [9]. These difficulties prevent the practical use of this alloy.

So we added a small amount of Mn in the TiFe alloy to improve the activation performance [10] and synthetic TiFeMn alloy for the sample material used in this study. The alloy density is 6.4 g/cm³. Its pressure-composition isotherms (PCI) desorption curve was measured as shown in Fig. 1. Since the fuel cell supported by the hydrogen storage tank works at 65 °C, we explored the PCI curve at this temperature.

2.2. Experimental apparatus

Fig. 2 shows an overview of the experimental apparatus used to induce hydrogen absorption-desorption by the sample material. Sample material was packed in a reaction tank. The packing fraction was 64.18% which had reached the largest ratio since there were circulating water pipes, gas pipes and some other components inside the tank. Hydrogen source (purity 99.999%) was provided by the high-pressure hydrogen bottle through gas pipes. We used a pressure reducing valve to reduce the 13 MPa pressure from the hydrogen bottle since the maximum pressure of the hydrogen charging was 4 MPa.

Temperature controller controlled the temperature of the circulating water which provides appropriate temperature through circulating water pipes. Hydrogen flow rate and total flow were controlled by the flow controller. Hydrogen pressure inside the tank was measured by a pressure gauge installed in the piping, with a range of 0–6 MPa.

Fig. 3 illustrates the details on the distribution of strain gauge on the tank surface. The reaction tank, consisted of three parts welded together, made of stainless steel 304, was 1060 mm in length, 219 mm in outer diameter and 6 mm in wall thickness. A 1 µm pore size sintered filter was placed in the head part of the tank to prevent the pulverized alloy from flowing out. The tank was installed horizontally. Ten pieces of biaxial, 90° stacked high precision strain gauge that can measure strains ε in the longitudinal and tangential directions were adhered to the tank surface. Five were on the top surface and another five were on the undersurface. The measurement range of the strain gauges was –20000 µε ~ 20000 µε. In order to eliminate the influence of temperature on the strain, we put a temperature compensator on the tank surface. All of the strain gauges and the temperature compensator were connected to the strain analyzer.

2.3. Experimental procedure

In order to make the alloy achieve maximum hydrogen absorption capacity, we used the following procedures to activate the alloy: First, we provided 90 °C circulating water to the tank through pipes inside the tank, and vacuum-pumped the tank for 10 h to decrease the pressure below 10 pa in this constant temperature condition. Then, we continually maintained the circulating water 90 °C for 10 h while maintaining the hydrogen pressure inside the tank at 4 MPa. Finally we provided 20 °C circulating water for 10 h to cool the tank. We repeated the activation cycle for ten times until a stable hydrogen absorption capacity was achieved.

After activation, we did hydrogen ab-desorption cycle for ten times. During hydrogen absorption process, we maintained the circulating water at 20 °C for 10 h and kept the
hydrogen pressure inside the tank for 4 MPa. In order to match a set of fuel cell which will use this tank for energy source, the desorption temperature was maintained at 65 °C for 5 h.

3. Results and discussion

Due to residual stress exists during ab-desorption cycles, it is difficult to calculate the actual surface stress especially if there is deformation on the tank. Therefore, we directly adopted strain instead of stress in this paper to illustrate the change of the tank during reaction.

3.1. Effect of cycle numbers on strain

Fig. 4 shows the relationship between the numbers of hydrogen ab-desorption cycles and the reaction tank surface strain of TiFeMn alloy. Picture a and b show the tangential strain and longitudinal strain of the undersurface, respectively. Picture c and d show the tangential strain and longitudinal strain of the top surface, respectively. The elastic limit strain $\varepsilon_m$ of stainless steel 304 can be calculated by using Hooke’s law, represented by Eq. (1) [11]

$$\sigma_m = E \cdot \varepsilon_m$$  

Where $\sigma_m$ and $E$ are the stress at yield and Young’s modulus of stainless steel 304, respectively. By substituting $\sigma_m = 210$ MPa and $E = 2 \times 10^5$ MPa into Eq. (1), we obtained $\varepsilon_m = 1050 \mu \varepsilon$. The strain in many of the points had been greater than $\varepsilon_m$ after activation process and changed within a certain range in the following ab-desorption cycles. This shows that plastic deformation had occurred since activation which can be also confirmed by the fact that the strain never returned to the initial level of “0”. As hydrogen desorption and absorption reaction had reached equilibrium, the alloy stopped swelling in the following process since the strain curves fluctuated in a small range and didn’t significantly improve. The strain in some of the points was neither greater than $\varepsilon_m$ nor returned to the initial level at hydrogen desorption. This is maybe due to the residual stress. Although we can not determine whether plastic deformation had occurred, we can be sure that alloy did swell in these points.

The stress on the tank in hydrogen absorbing process can be calculated with Eq. (2):

$$pr = \sigma \delta$$  

$$r = \frac{d}{2} - \delta$$  

Where $\delta = 6$ mm and $d = 219$ mm are the wall thickness and outer diameter of the tank. The largest strain was over the stress at yield of the tank, so $\sigma > 205$ MPa, by calculating the equation above, it can be found that the whole stress put on the tank was over 12 MPa. Since the stress was caused by alloy swell and gas pressure, the stress induced by alloy swell was over 8 MPa beside of the hydrogen charging pressure 4 MPa.

3.2. Effect of strain gauge directions, locations and packing nonuniformity on strain

Fig. 5 reveals the largest strain in tangential and longitudinal directions during the ten cycles in every point. Since the strain in each point had fluctuated in a certain range, it would be relatively accurate and safe if we chose the largest one to explain the following issues. Comparison of strain in the two
directions in each point shows that tangential strain was greater than longitudinal strain especially in the middle position of the tank where tangential strain had reached about 17000 με. When hydrogen is charged to an empty tank in the same dimension, the strain in tangential and longitudinal directions can be determined from stress on the tank using Eq. (4) and Eq. (5), respectively. The relationship between stress σ and strain ε is showed as Eq. (6). Since the wall thickness is very small compared to the inner radius, we used the inner radius \( r_i \) for the arithmetic mean of the inner and outer radii \( r_m \) as Eq. (7) shows.

\[
\begin{align*}
  p r_m &= \sigma_1 \delta \\
  p r_m^2 &= \sigma_1 \cdot 2 \pi r_i \delta \\
  \sigma &= E \cdot \varepsilon \\
  r_m &= r_i 
\end{align*}
\]

Where \( \delta \), \( p \) are the wall thickness of the tank, the internal pressure in the tank, respectively.

By calculating these equations we can find that tangential strain \( \varepsilon_t = \frac{p r_m}{6E} \) is twice as longitudinal strain \( \varepsilon_l = \frac{p r_m}{2E} \). However, tank packed with alloy made this situation very different. The mechanical seal covers in both sides of the tank provided a pulling force to reduce the tangential strain causing it in two sides much less than that in middle places where the stress generated by alloy expansion had all exerted on the tank surface. As seen in Fig. 5, longitudinal strain didn't
change much along the tank. This is considered to be due to the fact that each point had the same environment for longitudinal force. A small gap had been left after installing filter in the tank head, so that the alloy had expansion space in the longitudinal direction. This also helped release some of the internal stress to achieve consistency in the longitudinal direction.

Though the alloy was packed uniform in the tank before test, the small gap in the tank head part made the packing fraction there much less than that in central and tail areas. As Fig. 5 shows, tangential strain in point 1, 2, 3, 4 were much larger than that in point 9, 10, 7, 8, respectively. This asymmetry could be attributed to nonuniform packing density. Although the alloy was uniformly mixed when packed into the tank, the small gap left by filter provided space when the alloy expansion happened. It can be assumed that this situation helped release the strain from other places to the head place in longitudinal direction of the tank and even cause compression in the head position.

### 3.3 Effect of the hydrogen desorption percentage

During the hydrogen desorption process, we found the strain no matter in tangential or longitudinal with the change of the total amount of hydrogen desorption were just like the curve showed in Fig. 6. The strain had a linearly decline before hydrogen desorption achieved 34%. Then the tank didn’t shrink significantly in the flowing desorption process.

As we know, hydrogen atoms would occupy the interstitial sites when they get into the crystal lattice of the metal hydride, and interact with the metal atom, resulting in significant expansion of the metal lattice. Lattice volume increases linearly with the increase of hydrogen concentration, regardless of the hydride phase state [12]. After released 34% hydrogen, the metal hydride still shrank while the tank stopped change, this proved once again that plastic deformation on the tank had occurred and it still had the ability for elastic deformation.

**Fig. 6** – Strain change with the hydrogen desorption percentage.

### 4. Conclusion

In this study, experimental investigations had been carried out in a hydrogen storage tank packed TiFeMn alloy. Ten strain gauges were distributed on the tank surface. We repeatedly performed hydrogen ab-desorption operations for ten times in order to measure the strain to analyze the mechanical deformation behavior. Our findings can be summarized as follows: Plastic deformation had occurred during activation process and it did not become larger during the following ab-desorption cycles though the tank still had the ability for elastic deformation. It is necessary to search for a kind of cushion material to ease the large 8 MPa stress put on the tank caused by alloy swell. The largest deformation occurred in the middle of bottom place and tangential strain was greater than longitudinal strain in each place. There wasn’t much more difference in Longitudinal at respective points while tangential strain in the middle part was much larger than that in two sides’ parts of the tank. The nonuniform packing density lead the deformation tended to occur more serious in tail part than in head part.

### References