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Fatigue test of carbon epoxy composite high pressure hydrogen storage vessel under hydrogen environment

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Abstract: A significant temperature raise within hydrogen vehicle cylinder during the fast filling process will be observed, while the strength and fatigue life of the cylinder will dramatically decrease at high temperature. In order to evaluate the strength and fatigue of composite hydrogen storage vessel, a 70-MPa fatigue test system using hydrogen medium was set up. Experimental study on the fatigue of composite hydrogen storage vessels under real hydrogen environment was performed. The experimental results show that the ultimate strength and fatigue life both decreased obviously compared with the values under hydraulic fatigue test. Furthermore, fatigue property, failure behavior, and safe hydrogen charging/discharging working mode of onboard hydrogen storage vessels were obtained through the fatigue tests.

Key words: Hydrogen storage vessel, Composite, Fatigue test, High pressure, Temperature raise
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1 Introduction

Hydrogen is a relatively clean energy carrier, taking into consideration that only water will remain after burning and there is no pollution to the environment. Hydrogen is of great potential to be an alternative fuel in the future and will be widely used in fuel cells and fuel cell powered vehicles (Akansu *et al.*, 2004; Ross, 2006). Therefore, it is a priority in research related to energy replacement in almost every country. One of the key technologies in hydrogen energy is hydrogen storage and transportation, which is the most expensive and difficult part at present. High pressure hydrogen storage technology has the advantages of low cost, easy operation, and quick charge and discharge in normal temperatures compared with other hydrogen storage techniques. More than 80% of hydrogen at refueling stations and in fuel cell vehicles is stored in high pressure vessels (Utgikar and Thiesen, 2005; Mori and Hirose, 2009). There are many factors which can affect the performance of the onboard high pressure hydrogen storage vessels, for example, fatigue, hydrogen corrosion, impact, fire, etc. The fatigue failure caused by frequent hydrogen charge and discharge is the main failure mode (Camara *et al.*, 2011; Tomioka *et al.*, 2011). To predict the fatigue life of onboard composite vessels, hydrostatic fatigue and burst tests are widely used (Sayman, 2005), which only produce internal pressure to the vessels. However, in practical applications, pressure vessels are directly subjected to the cyclic loading of both high pressure and extreme temperature during hydrogen charging and discharging processes (Ansari *et al.*, 2010). The fast filling of hydrogen can lead to a significant temperature rise within the vessel due to the Joule Thomson effect and the released heat of gas compression (Monde *et al.*, 2012; Zheng *et al.*, 2012). Furthermore, there may be an obvious temperature decline in the process of gas usage routine and exhaustive deflation (Gentilleau *et*

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al., 2011). The significant changes of temperature can lead to serious thermal stress, which is accompanied by internal pressure during numerous charging and discharging processes, and finally result in thermo-mechanical fatigue of the composite vessel. Therefore, the fatigue behavior of onboard composite hydrogen storage vessel is rather complicated, and it is necessary to conduct such fatigue test under real hydrogen environment.

2 Fatigue test system using hydrogen as medium

2.1 Principle of the fatigue test system

To obtain enough driving distance, the normal pressure of onboard high pressure hydrogen storage vessel reached 70 MPa at present. This is the critical pressure for high-pressure hydrogen storage, because it is very difficult to enlarge the hydrogen storage capacity with higher pressure. Thus, the test system is designed at 70 MPa in this study. The schematic is shown in Fig. 1, and its working principle is as follows: 80-MPa high-pressure hydrogen is filled into onboard hydrogen storage vessel (called sample vessel) through pneumatic valve and orifice plate flow-meter. The filling process will stop when the pressure reached the working pressure (70 MPa). Then the pressure release valve of the sample vessel will be opened to release the hydrogen into a low pressure buffer tank, reducing the pressure in the sample vessel below 1 MPa. The low-pressure hydrogen of the buffer tank is then compressed into a 80-MPa high pressure hydrogen storage tank. Thus, the whole cycle is completed and the next fatigue cycle will be done in the same manner. The hydrogen flow route is shown in Fig. 1 with red line (in the web version).

2.2 Technical parameters of the hydrogen environmental fatigue test system

The 70-MPa hydrogen environmental fatigue test system was manufactured according to the design (Fig. 1). The fatigue test system was installed at the Institute of Beijing Aeronautic and Astronautic Testing Technology, China (Fig. 2). The parameters of this test system are described as follows: The high pressure storage tank contains hydrogen under 80 MPa, which can be discharged into onboard hydrogen storage vessels. With this system, five sample vessels

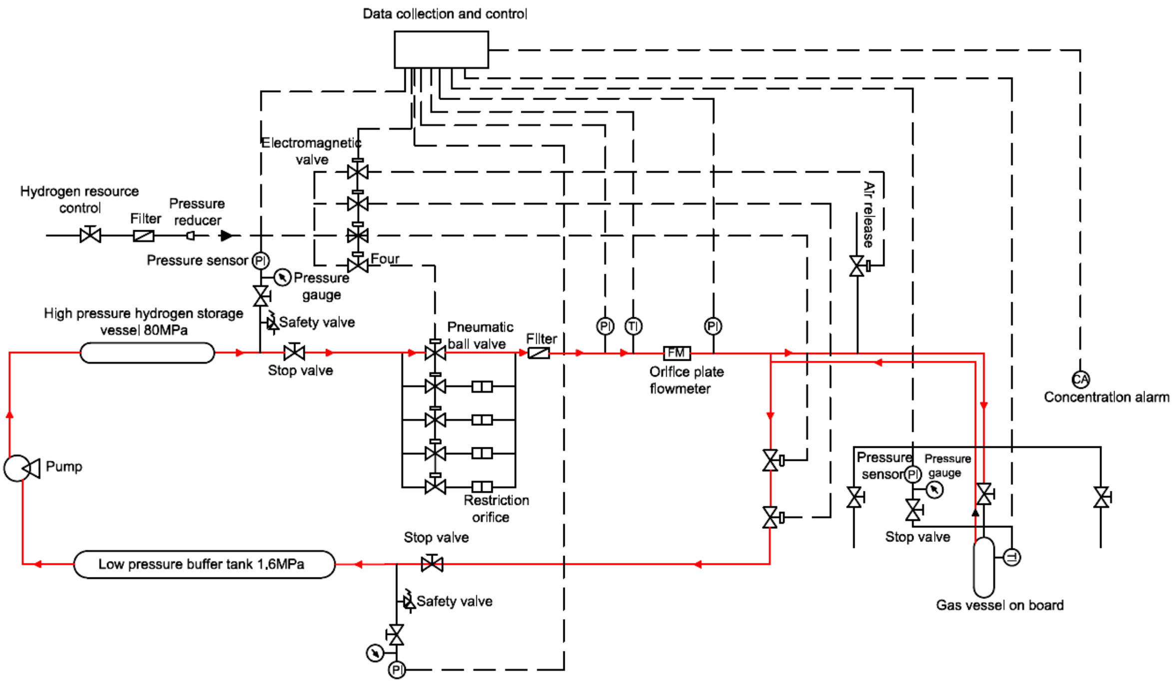

Fig. 1 Schematic diagram of the fatigue test system

Fig. 2 Installation of the fatigue test system

can be tested at the same time as long as the total volume of the cylinders is less than 100 L. The duration of one hydrogen charging and discharging cycle is 10 min. The highest testing pressure of the system is 70 MPa and the greatest hydrogen mass flow rate is 3.24 kg/min. Both automatic and manual controls are set for this fatigue test system. The area containing hydrogen is separated from the operator area by a thick wall, and safety measures are taken to prevent possible explosions in order to protect the workers and facilities.

2.3 Control system

A pneumatic ball valve is used to control the charging and discharging process in this fatigue test system. Industrial computer system is adopted to collect the data during hydrogen charging and discharging process. A hydrogen concentration probe is applied to monitor the hydrogen leakage. Telecontrolled camera is used to monitor the testing field and acoustic emission sensor to detect the fracture development of the vessels during fatigue tests.

The data required to be collected were: hydrogen temperature within the high pressure hydrogen storage tank; inner gas temperature, liner temperature, and outer wall temperature of the sample vessel; pressure within the high pressure hydrogen storage tank; front and back pressures of the inlet/outlet orifice plate; pressure in the sample vessel. Data collection of the hydrogen concentration probe is also included. Individual collecting and processing devices are adopted for the acoustic emission detection instruments and endoscope. The data measurement control system for test is managed with the aid of the commercial software package LabView as shown in Fig. 3. This control system plays an important role in the hydrogen fast charging and discharging process during the fatigue test. It could be used as part of data measurement control system for hydrogen refueling station after some modifications.

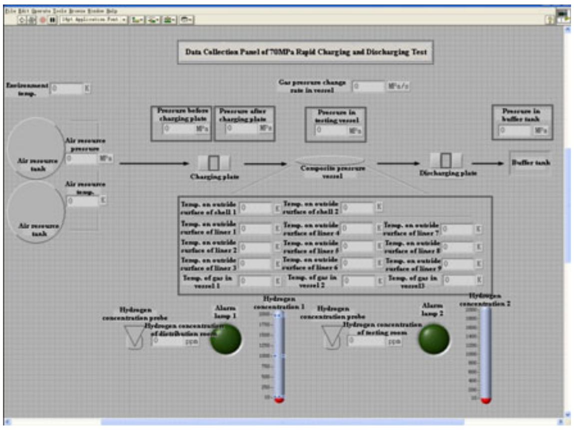

Fig. 3 Window of the control system

3 Fatigue test of carbon epoxy composite hydrogen storage vessel under hydrogen environment

3.1 Effect of the temperature during hydrogen fast charging and discharging

High pressure composite hydrogen storage vessel is one of the most effective solutions for onboard hydrogen storage at present. However, there will be a significant temperature rise during the refueling process of 70-MPa hydrogen vehicle cylinder due to the fast filling of hydrogen (Liu *et al.*, 2010; Galassi *et al.*, 2012; Hosseini *et al.*, 2012). On the contrary, the discharging process is a cooling process for the gas inside the vessel. The temperature changes will seriously affect mechanical properties of the epoxy resin and carbon fibers. The fracture toughness of the epoxy resin matrix will decrease seriously at low temperatures, while the interlaminar shear strength of the composites will dramatically decrease at high temperature. Furthermore, there will be remarkable thermal stresses in the aluminum liner and composite layer of the vessel. Thus, the strength and fatigue life of the composite vessel are seriously affected. In order to ensure that the onboard high pressure composite vessel can be used safely, the temperature must be controlled during the hydrogen charging process.

In general, the temperature should be below 100 °C (An, 2009).

The commonly used composite high pressure vessel with aluminum alloy as liner and epoxy resin solidified high strength carbon fiber as the winding layer was applied in this test. Its working pressure was 70 MPa and the effective volume was 30 L. Its weight and hydrogen capacity were 24 kg and 1.2 kg, respectively. The mass hydrogen storage capacity was 5% (in weight), and the volume hydrogen storage capacity was 40.2 kg/m^3. An onboard high pressure hydrogen storage vessel is shown in Fig. 4 (Zheng and Yang, 2008).

To test the temperature changes during the charging and discharging process, temperature sensors were installed on different places of the sample vessel (Fig. 5). G1–G3 are the gas temperature sensors within the vessel, D1–D6 are the outer surface temperatures of aluminum alloy liner, and W1 and W2 are the outer surface temperature sensors of carbon fiber winding layer. Thus, the thermal condition in different spatial positions of the sample vessel can be obtained during the fatigue test.

Fig. 4 Onboard 70 MPa composite hydrogen storage vessel

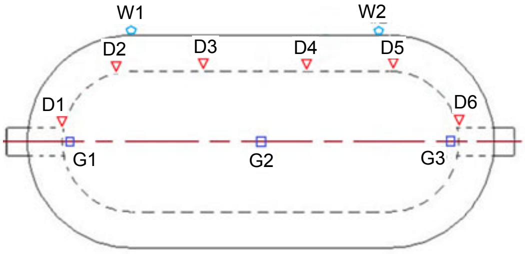

Fig. 5 Positions of the installed temperature sensors on the sample vessel

After conducting a large number of tests and measurements, we found that the shortest time of one hydrogen charging and discharging cycle in this fatigue test is 600 s: the hydrogen charging time is 100 s; the time waiting for cooling-down is 225 s; the hydrogen discharging time is 105 s; and the time waiting for heating-up is 170 s. Thus, it is able to ensure that the temperature in the vessel is limited within 100 °C throughout the test, and the onboard high pressure vessel can be used safely.

The temperatures at different positions of the sample vessel are shown in Fig. 6. During the fatigue test, the temperatures of the gas and vessel varied remarkably with the pressure, indicating that the vessel was under thermo-mechanical cyclic loadings.

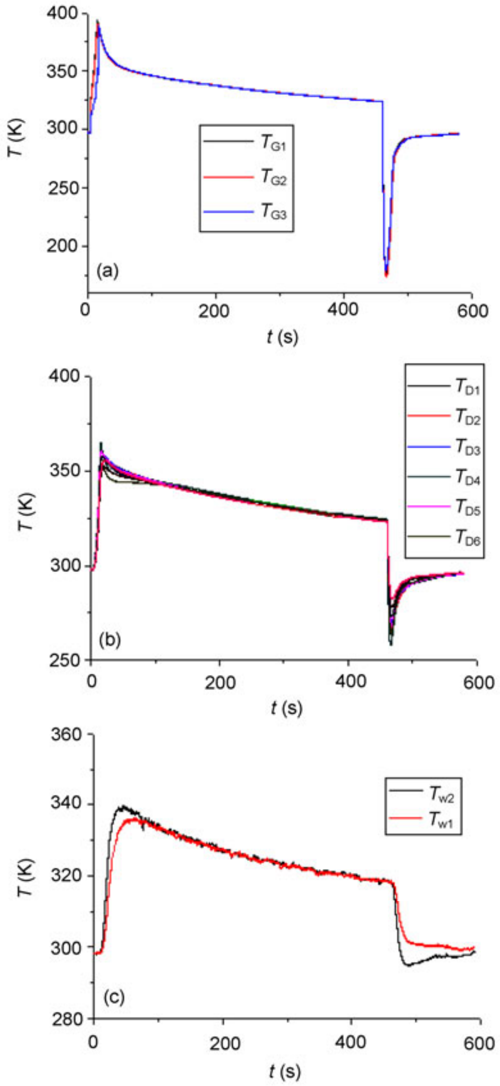

Fig. 6 Temperature within the vessel (a), on outer surface of the aluminum alloy liner (b), and on outer surface of the carbon fiber winding layer (c) using different color lines

Note: for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article

There is a remarkable temperature increase/decrease in the hydrogen charging/discharging stage, while slow temperature changes in the cooling-down or heating-up process. Due to the small thermal conductivity of composite and the effect of heat convection, the temperature change of carbon fiber winding layer is much smaller than that of hydrogen, and has a significant time delay during the process.

3.2 Fatigue test cycle

The 70-MPa fatigue test was carried out with hydrogen environmental fatigue test system as shown in Fig. 7. Considering the longer time needed in the fatigue test and the allowable temperature limit 100 °C, one fatigue test cycle was set as 10 min, namely, the test frequency was 6 times per hour, as shown in Fig. 8, where T_B is the gas temperature (blue line) and P_B is the gas pressure within the vessel (black line). Thus, we can conduct this fatigue test within a relatively short time and respect the temperature limit throughout the test. However, the discharging time of hydrogen in this test is much shorter than that in the real working condition, which may lead to serious temperature loads and a significant decrease in fatigue life of the sample vessel. So the results obtained from the fatigue test are relatively conservative.

Fig. 7 Fatigue test of composite hydrogen storage vessel

One sample vessel was tested in this 70-MPa fatigue test system, with the number of fatigue test cycle 500 times, which was not large enough to lead to failure of the vessel. After 500 times fatigue test under hydrogen environment, the performance of the sample vessel was checked by the Zhejiang Special Equipment Inspection and Research Institute, China. Results show that the vessel was still strong enough to load 70-MPa pressure and there are no apparent defects after hydrostatic test with the water pressure of 87.5 MPa. To further clarify bursting characteristics of the vessel under thermo-mechanical fatigue cycling, the test pressure was further increased until its explosion. The bursting pressure was 119 MPa. The ultimate strength decreased by 15% compared with the original design pressure of 140 MPa. The test vessel after bursting is shown in Fig. 9.

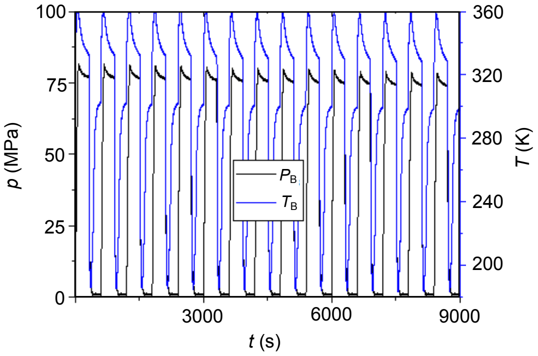

Fig. 8 Frequency of the fatigue test

Note: for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article

Fig. 9 Sample vessel (a) and vessel fragments (b) after bursting

An additional sample vessel was tested in this 70-MPa fatigue test system until failure. The failure is characterised by hydrogen leakage in form of soap foam appearing on outer surface of the vessel

(Fig. 10). The pressure in vessel cannot be constant, thus the vessel is considered to be under failure. Its fatigue cycle number is 5122 times, which is much smaller than the value under hydraulic fatigue test. After the test, there are no obvious defects on the outer surface of the vessel. Finally, the leak points were determined by X-ray photos (Fig. 11).

Fig. 10 Failure after fatigue test

Fig. 11 X-ray photography of the leak points after fatigue failure

3.3 Analysis of the experiment results

In this study, due to the lack of research data, long test period, and high cost, only two composite hydrogen storage vessels were used in the fatigue test under hydrogen environment. The strength test was carried out for one sample vessel after 500 times fatigue test cycle. The ultimate strength of the vessel decreased obviously, nearly 15% compared with the design pressure. Song *et al*. (2012) showed this decline is 9.6%, and Onder *et al*. (2009) also reported that the burst pressure can be depressed at high temperature due to the thermal stress and the reduced mechanical strength.

The fatigue test of another sample vessel under hydrogen environment was performed till its failure. The fatigue life is 5122 times which is much shorter than that of hydraulic test because of the serious temperature changes during the hydrogen charging and discharging process. Comond *et al*. (2009) showed that the normal fatigue life under hydraulic is no less than 12000 times for onboard composite vessels. Henaff-Gardin and Lafarie (2002) also revealed that failure in composite vessels occurs more easily under thermal cycling than in mechanical fatigue process.

The experimental results show that the ultimate strength and fatigue life both decreased obviously compared with the values under hydraulic fatigue test. The main reason is that the violent changes of temperature will decrease the mechanical properties of composites and cause thermal stress due to the mismatch in the coefficient of thermal expansion of adjacent plies with different fiber orientations (Bechel *et al*., 2002). These thermal stresses, when added to the stresses caused by internal pressure, can lead to significant laminate damages in the form of micro cracks in the resin which further result to composite failure (Mallick *et al*., 2003).

4 Conclusions

In this paper, a 70-MPa fatigue test system using hydrogen medium was set up, which has considered real hydrogen environment, and the effect of fierce temperature changes during the hydrogen charging and discharging process. Through the fatigue tests, the fatigue property, failure behavior, and safe hydrogen charging/discharging working mode of onboard composite hydrogen storage vessels are obtained. All these properties cannot be simulated by the traditional hydraulic fatigue test.

During the fatigue test cycles, there is a remarkable temperature increase/decrease in the hydrogen charging/discharging stage. The serious temperature changes have a great influence on mechanical properties of the composite vessels. In order to keep the temperature within the limit of 100 °C throughout the test, the shortest time of one fatigue test cycle is set as 10 min. Through a series of tests of the first sample vessel, it can be concluded that the hydrogen environment fatigue affects the ultimate strength of the composite vessels: nearly 15% drop off after 500 times fatigue test cycles. The fatigue life of another test sample is 5122 times which is much shorter than that under hydraulic fatigue test (about 12000 times). The failure is characterised by hydrogen leakage in form of soap foam appearing on outer surface of the vessel, and there is no burst or obvious defects during the test.

The experimental results show that the thermomechanical behavior of vessels in hydrogen fatigue test is extremely complex. The pressure vessels are directly subjected to the cyclic loading of both high pressure and extreme temperature, which can seriously influence mechanical properties of the epoxy resin and carbon fiber/epoxy composites. Thus, the performances of the composite vessel are affected, and finally lead to a significant decrease in the ultimate strength and fatigue life of the vessel. However, results obtained from this fatigue test are relatively conservative, due to the shorter discharge time of the vessel.

This paper can provide guidance for fatigue analysis and life prediction of onboard 70-MPa composite hydrogen storage vessels. However, results obtained from the fatigue test cannot be taken as universal due to the small number of specimens used in this experiment, and further experimental research should be performed to support these conclusions.

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Recommended paper related to this topic

Investigation of low-cycle fatigue behavior of austenitic stainless steel for cold-stretched pressure vessels

Authors: Cun-jian Miao, Jin-yang Zheng, Xiao-zhe Gao, Ze Huang, A-bin Guo, Du-yi Ye, Li Ma
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Abstract: Cold-stretched pressure vessels from austenitic stainless steels (ASS) are widely used for storage and transportation of liquefied gases, and have such advantages as thin wall and light weight. Fatigue is an important concern in these pressure vessels, which are subjected to alternative loads. Even though several codes and standards have guidelines on these pressure vessels, there are no relevant design methods on fatigue failure. To understand the fatigue properties of ASS 1.4301 (equivalents include UNS S30400 and AISI 304) in solution-annealed (SA) and cold-stretched conditions (9% strain level) and the response of fatigue properties to cold stretching (CS), low-cycle fatigue (LCF) tests were performed at room temperature, with total strain amplitudes ranging from ±0.4% to ±0.8%. Martensite transformations were measured during the tests. Comparisons on cyclic stress response, cyclic stress-strain behavior, and fatigue life were carried out between SA and CS materials. Results show that CS reduces the initial hardening stage, but prolongs the softening period in the cyclic stress response. Martensite transformation helps form a stable regime and subsequent secondary hardening. The stresses of monotonic and cyclic stress-strain curves are improved by CS, which leads to a lower plastic strain and a much higher elastic strain. The fatigue resistance of the CS material is better than that of the SA material, which is approximately 1×10^3 to 2×10^4 cycles. The S-N curve of the ASME standard for ASS is compared with the fatigue data and is justified to be suitable for the fatigue design of cold-stretched pressure vessels. However, considering the CS material has a better fatigue resistance, the S-N curve will be more conservative. The present study would be helpful in making full use of the advantages of CS to develop a new S-N curve for fatigue design of cold-stretched pressure vessels.