5. Task 5 Development of Hydrogen Fuel Tank System

5.1 Target of Research and Development

The target of research and development for the task 5, “Development of Hydrogen Fuel Tank System”, in the WE-NET phase II program was “to develop element technologies for hydrogen fuel system of hydrogen fuel cell vehicles taking into account hydrogen supply from the hydrogen refueling station and to verify its facility combining with hydrogen refueling stations”. To achieve the above target, we developed rapid hydrogen filling method and carried out safety evaluation for hydrogen absorbing alloy tank in fiscal 2001.

5.2 Results of Research and Development in Fiscal 2001

5.2.1 Development of rapid hydrogen filling method

(1) Design and trial manufacture of hydrogen absorbing alloy tanks

Based upon the result of rapid filling test for mini-sized MH (Metal Hydride) tanks performed in fiscal 2000, we designed the divided chamber type tank and plate-fin type tank of full size and manufactured experimentally one tank for each type . The effective storage capacity of full size tanks (defined as difference in hydrogen absorbing capacity between at 1.1 MPa and at 0.1 MPa (atmospheric pressure)) was set for 31.25 Nm^3 in this trial manufacture. A rare earth group AB_5 alloy was selected as the MH to be filled in full size tank from the viewpoint of its stability and poisoning tolerance during absorption/desorption cycles. As for the desorption characteristics, the desorption plateau pressure at 60℃ was set for 0.55 MPa. Based upon the rapid filling test performed in the preceding fiscal year, the hydrogen absorption condition was determined so that 80 % of the effective storage capacity for the full size tank, i.e. 25 Nm^3, should be filled within 10 minutes at the coolant flow rate of 125 L/min., coolant temperature of 25℃ and hydrogen supply pressure of 0.8 MPaG.

We designed a new structure for the divided chamber type of tank of full size, which was easy to manufacture and had the similar advantage in heat conduction performance as the tank structure manufactured experimentally in the preceding fiscal year. Namely, the average distance between MH and cold heat source was reduced by arranging a coolant pathway at the intersection of container wall and separators. Heat conduction plates were arranged radially at the center of sintered pipe filters in the MH filling part for equalizing its temperature distribution. The thickness of container wall was increased for ensuring the strength during extrusion process of the manufacture. There was no problem in this new sectional shape, because the simulation result showed that the hydrogen filling speed for this structure was higher than that for the structure used in preceding fiscal year and higher enough than the target. It was found that the temperature distribution for the new sectional shape during hydrogen filling showed better uniformity than the structure in the preceding fiscal year. We manufactured a small tank (an effective storage capacity of 1.95 Nm^3) which is about 1.6 times larger than the mini-sized MH tank (an effective storage capacity of 1.25 Nm^3) manufactured in the preceding fiscal year. A hydrogen storage capacity of 31.25 Nm^3 was attained by arranging 8 small tanks in the upper half and 8 small tanks in the down half in parallel. We contained a tank body and pipes for hydrogen and coolant of the full size tank in a box. Joints for pipe of hydrogen and those for supply and return of coolant were equipped on the same side of the box. For the plate fin type MH tank, we manufactured a small tank which was about 8.4 times larger than the mini-sized MH tank (an effective storage capacity of 1.25 Nm^3) manufactured in the preceding fiscal year. A hydrogen storage capacity of 31.25 Nm^3 was attained by arranging 3 small tanks in parallel. We contained a tank body and pipes of hydrogen and coolant for the full size tank in a box, covering tank body and pipes with lagging. We designed that the small size tanks had the same heat exchange performance per unit alloy quantity as mini-sized MH tanks. Consequently, the basic structure for the small size tank was the same as the mini-sized MH tanks, though the number of alloy layers and coolant layers were increased from 4 to 7, and from 5 to 8. The width and length of the small tank was about 2.85 times larger and 1.81 times longer than the mini-sized tank.

Because there was difference in the effective MH storage capacity between for the divided chamber type tank and for the plate fin type tank due to difference in their AB_5 alloy composition, MH quantity filled in the former was smaller than that the latter. As the plate fin type tank had a structure attaching importance to heat conduction performance, it had larger heat conduction areas for both coolant side and MH side than the divided chamber type tank. Thus, an overall tank weight and volume for the divided chamber type tank was smaller than that for the plate fin type tank.

(2) Evaluation of performance of hydrogen absorbing alloy tanks

We carried out evaluation of the tank performance by means of hydrogen rapid filling tests in order to verify that the full size tank in this trial manufactured satisfied the basic design specifications and that the performance of the mini-sized MH tank was secured for the tank. For an evaluation of the performance of the tank itself, the test was performed without the coupler to be used in a hydrogen refueling station.

It was showed that the divided chamber type of full size tanks satisfied the design specification, as it took 7 minutes to fill hydrogen of 25 Nm^3 under the above hydrogen absorption conditions. The performance was found to be similar to that of the mini-sized MH tank, because it took 6.5 minutes for filling hydrogen of 25 Nm^3.

The result was obtained that hydrogen of 25 Nm^3 was filled in 2.6 minutes for the plate fin type tank of full size under the above hydrogen absorption conditions. As it took 2.3 minutes for filling hydrogen of 25 Nm^3 for the mini-sized MH tank, it was found that the performance of the plate fin type tank of full size was similar to that of mini-sized tank.

(3) Rapid filling test in combination with hydrogen refueling stations

We carried out rapid filling tests at the natural gas reforming type hydrogen refueling station in Osaka with the divided chamber type tank and at the PEM electrolysis type hydrogen refueling station in Takamatsu with the plate fin type tank. The hydrogen stored in the MH type storage unit was filled in the MH tank via a dispenser. After completion of hydrogen filling, the hydrogen filled in the tank was desorbed by warming the tank with heated brine supplied from a desorption unit provided by another WE-NET task. Though the hydrogen supply pressure had been controlled both in the rapid filling test for a mini-sized MH tank performed in fiscal 2000 and in the evaluation test of the performance for a full size tank, the hydrogen supply flow rate was controlled in the rapid filling test at the hydrogen refueling station. The fill of hydrogen increased linearly with time, as the hydrogen flow rate was controlled for constant.

As the result of test for the divided chamber type tank of full size under the following conditions as coolant temperature of 5℃, coolant flow rate of 125 L/min, hydrogen supply flow rate of 2.83 Nm^3/min, it was ascertained that we can fill hydrogen of 25 Nm^3, 80 % of the effective storage capacity of the tank, within 10 minutes as the target. It took 9.3 minutes for filling hydrogen of 25 Nm^3.

As the result of test for the plate fin type tank of full size under the following conditions as coolant temperature of 5℃, coolant flow rate of 125 L/min, hydrogen supply flow rate of 2.83 Nm^3/min, it was ascertained that we can fill hydrogen of 25 Nm^3, 80 % of the effective storage capacity of the tank, within 10 minutes as the target. It took 9.1 minutes for filling hydrogen of 25 Nm^3.

5.2.2 Safety evaluation for hydrogen absorbing alloy tanks

(1) Fire-resistance evaluation for hydrogen absorbing alloy tanks

In the fire-resistance evaluation conducted in fiscal 2000, the test was performed for MH tanks equipped with a spring type relief valve to prevent destruction of the tank caused by rise of pressure. As the pressure had not been entirely released even by opening the relief valve, the temperature rose under nearly the set pressure for the relief valve. Because the strength of Al alloy used as the tank material decrease suddenly around 150℃, withstanding pressure of the tank decreased and the tank was destroyed at last. Therefore, in this fiscal year, we learned the situation in the test for the MH tank with a fusible plug, which released the internal pressure entirely by melting as temperature increased. We also studied effects of operating temperature of fusible plug and tank materials upon its destruction. Furthermore, the fire-resistance test was conducted for a tank unit composed of a number of full size tanks.

As for the operating temperature of the fusible plug, we used a 105℃ type and 177℃type fusible plug, the former was the same kind as those mounted on valves for high pressure gas containers in general, and the latter was used for comparison. The test was conducted by fixing the hydrogen absorbing alloy container on a test jig and by igniting methanol filled in a stainless steel vessel, which was installed at the bottom of tank. The quantity for methanol was selected to be 18 Litter corresponding with about 50 minutes of combustion. The relief pressure of spring type relief valve was precedently set on 1.4 MPa.

Under the condition where hydrogen quantity had been fully charged (H/M = 1.0), the spring type relief valve operated in less than 2 minutes. Under the condition where hydrogen quantity had been nearly empty (H/M = 0.2), it took 3 to 4 minutes till the spring type relief valve operated. On the other hand, it took a longer time till the fusible plug operated, when the hydrogen storage was high. It was due to that it became more difficult for tank temperature to rise, as the process of desorption of hydrogen from the alloy was endothermic reaction. The higher the set temperature of fusible plug, the longer was the time for operation of fusible plug. Taking a sudden decrease of Al-alloy strength above 150℃ into consideration, we considered that an 105℃ fusible plug widely used for high pressure gas applications was appropriate. From the result of experiment, it was proved that the burst of tank could be prevented when the fusible plug operated and the residual tank pressure reduced down to atmospheric pressure. At the completion of test, no burst or deformation of the tank was observed.

In case of using SUS as the tank material, no burst occurred even without mounting the fusible plug in the test.

The fire-resistance test for the tank unit composed of 5 full size tanks was conducted outdoors. As the safety valve, we used a spring type relief valve and a fusible plug of 105℃ specification. The test was performed with the tank unit fixed on a test jig and with gasoline filled in a stainless steel vessel installed at the bottom of tank. The gasoline quantity was so controlled as to combust for about 20 minutes that was sufficient time for operating the safety valve. We conducted the tests twice, changing the number of fuel bats and their locations. In the test No.1, the flame attacked the fusible plug area directly when the entire hydrogen absorbing alloy tank was in the flame. In the test No.2, no flame attacked the fusible plug area directly, using two fuel vats. In the test No.1, the rise of the tank pressure stopped at about 0.8 MPa and then the tank pressure was decreased down to atmospheric pressure. This was due to that the fusible plug had operated before the pressure reached the set pressure of spring type relief valve. On the contrary, in the test No.2, the tank pressure reached up to 1.4 MPa and the fusible plug operated after the spring type relief valve had operated, because we arranged this test so as to prevent the flame attacking the fusible plug.

In both tests, hydrogen emitted through either the spring type relief valve or the fusible plug was ignited. It was confirmed in the test of the previous fiscal year that as the hydrogen desorption reaction was endothermic, it took a long time for hydrogen to discharge from hydrogen absorbing alloy, while gas was lost in a short time in case of high pressure gas storage. Also in the test for this time, the combustion continued till the end of test, even though the flame size became smaller. Attention must be paid to that the desorption of hydrogen continued corresponding to the rise in temperature of the hydrogen absorbing alloy, as long as the fire continues. We verified that hydrogen absorbing alloy tank itself showed no deformation of container after completion of the test and it was ascertained that we could prevent an abnormal rise in pressure of the tank, deformation and burst of the container by using a spring type relief valve and a fusible plug together.

(2) Deformation test for mini-scaled tank

As various factors have effects on the deformation of hydrogen absorbing alloy tank due to repetition of absorption and desorption cycle, it is important to clarify a causal relationship between the deformation and various factors. Therefore, we paid attention to the structural factor, and tried to clarify degree of effects of various factors on deformation using mini-scaled tanks, in this fiscal year.

From the viewpoint of weight saving, we adopted aluminum alloy as the material of tanks. Two kinds of filter structure were used. One is a plate filter which is cheap and easy to manufacture, and the other is a tube filter used for the full size tank. In order to investigate the effects of honeycomb structure adopted for the full size tank promoting heat transfer and separation plates equalizing filling rates of alloy in the tank, we manufactured various kinds of tanks combining these structure with the above filters. Further, we changed wall thicknesses of tank with the tube filter structure according to three levels of 2, 3 and 4 mm in order to investigate the influence to tank strength. As alloy material, we adopted AB_5 ($Mm(Ce = 0.5) Ni_5$) and BCC ($Ti_{20}Zr_5V_{35}Cr_{40}$) having volume expansion rate on hydrogen absorption of 20 % and 40 %. Regarding that stress occurred in MH tank by expansion of alloy, we manufactured AB_5 tanks with filling rates of 40, 45 and 50 %, and BCC tanks with those of 35, 40 and 45 % (considering its higher expansion rate), as limit values obtained from our experience.

The strain increased as alloy filling rate increased. At the filling rate of 50 %, the maximum strain of 1354 (strain in scale of 10^{-6}) was generated at the cover side of the tank with wall thickness of 2 mm. The strain tends to be reduced in general, though there was some variations in data, as wall thickness increased, consequently, the strength of tank improved. Strain was especially large for the case of the specification of wall thickness of 2 mm and high filling rates. All data on BBC resulted in much smaller strain value compared with those on AB_5. It is considered that this was resulted from the difference of bulk density.

For plate filter, it was found that the repeated absorption/desorption induced the advance of deformation at the bottom part. Then, it was proved that the tank with the structure having separation plates and honeycomb combined with plate filter had smaller strain than the tank without it, and no advance of strain was observed at some measuring points. For tanks with the plate filters, however, cracks occurred at 70 cycles for both case of wall thickness of 2 mm and 3 mm. But, no crack was found in tanks with tube filters.

5.3 Future Subject in Research and Development

5.3.1 Development of rapid filling method

Following the work in this fiscal year, rapid filling tests will be conducted under various different supply conditions of hydrogen and coolant, in the hydrogen refueling station. In the rapid filling tests conducted in this fiscal year, we filled an MH tank from empty to 80% of the effective storage capacity. As there remains some hydrogen in MH tanks when actual filling, it is necessary to investigate the influence of residual quantity on filling time.

5.3.2 Safety evaluation of hydrogen absorption alloy tank

Based upon the result obtained in this fiscal year, the following evaluations will be made:

(1) Fire resistance test for hydrogen absorbing alloy tank

Verification of sealing property of spring type relief valve to hydrogen and investigation of the location of safety valve for tank unit of practical scale for real vehicle.

(2) Evaluation of deformation in tank by hydrogen absorption/desorption

The estimation technology for stress occurred by alloy expansion will be required for the design of strength of tank.