

THE RESIDUAL STRENGTH OF AUTOMOTIVE HYDROGEN CYLINDERS AFTER EXPOSURE TO FLAMES

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ABSTRACT

Fuel cell vehicles and some compressed natural gas vehicles are equipped with carbon fiber reinforced plastic (CFRP) composite cylinders. Each of the cylinders has a pressure relief device designed to detect heat and release the internal gas to prevent the cylinder from bursting in a vehicle fire accident. Yet in some accident situations, the fire may be extinguished before the pressure relief device is activated, leaving the high-pressure fuel gas inside the fire-damaged cylinder. To handle such a cylinder safely after an accident it is necessary that the cylinder keeps a sufficient post-fire strength against its internal gas pressure, but in most cases it is difficult to accurately determine cylinder strength at the accident site. One way of solving this problem is to predetermine the post-fire burst strengths of cylinders by experiments. In this study, automotive CFRP cylinders having no pressure relief device were exposed to a fire to the verge of bursting; then after the fire was extinguished the residual burst strengths and the overall physical state of the test cylinders were examined. The results indicated that the test cylinders all recorded a residual burst strength at least twice greater than their internal gas pressure.

1.0 INTRODUCTION

Fuel cell vehicles and some compressed natural gas vehicles are equipped with carbon fiber reinforced plastic (CFRP) composite cylinders as fuel containers. The CFRP material consists mainly of carbon fibers and the matrix resin holding the carbon fibers together. The heat resistance of CFRP, dependent on the characteristics of matrix resin, is known to start declining when exposed to temperatures exceeding the glass transition temperature of matrix resin[1,2,3]. When the CFRP cylinder is exposed to heat in a vehicle fire accident, the gas pressure inside the cylinder rises, increasing the internal stress on the cylinder. Consequently CFRP cylinders are fitted with a thermally-activated pressure relief device (TPRD) which detects ambient heat and is activated at approximately 110°C to release the internal gas for preventing the cylinder from bursting. Yet if the fire is extinguished before TPRD is ever activated, the high-pressure gas is left inside the cylinder. For the safe handling of such a cylinder on and off the accident site, it is necessary that despite damage by fire the cylinder retain sufficient strength for withstanding the internal gas pressure.

In our previous study, 35 MPa compressed hydrogen automotive CFRP cylinders each fitted with a TPRD were exposed to flames until the TPRD was activated; then the cylinders were cooled by water or naturally and underwent pressure proof testing to measure their residual burst pressures [4]. The results indicated that the TPRD-activated cylinders retained a burst strength comparable to that of new cylinders provided that the flames had covered the whole, rather than a part, of the cylinder body. In our present study, the previous study was modified in that the TPRD was removed in advance from each test cylinder in order to investigate the residual burst strengths of cylinders in the worst case of the TPRD failing to operate in a vehicle fire accident.

2.0 TEST METHOD

Table 1 summarizes the test cylinder and the test conditions applied in this study. The existing automotive CFRP cylinders can be classified into Type3 with aluminium alloy lining and Type4 with plastic lining. We used 5 variations of test cylinders: 1) Normal Working Pressures(NWP) 20MPa Type3, 2) NWP 20MPa Type Type4, 3) NWP 35MPa Type3, 4) NWP 70MPa Type4, 5)NWP 70MPa Type3. As the filling gas, helium was fed into the test cylinders to their normal working pressures for

Tests #1 through #14,17,18 and to half of their normal working pressures for Tests #15,#16,#19,#20 in order to examine the effect of working pressure levels on cylinder behavior.

Table 1. The test cylinder and the test conditions

Test#	Cylinder (Bursting pressure of new cylinder: BP_{new})	Filling pressure	Flame exposure conditions	Cooling condition	Room temperature during fire test
1	20MPa Type3 (91.7MPa)	20MPa	Engulfing fire	Exposed to the flame until the rupture or leak	22°C
2				Cut off fire just before rupture, and immediately cooled with water	21°C
3				Cut off fire just before rupture (Natural cooling)	25°C
4			Localized fire	Exposed to the flame until the rupture or leak	19°C
5				Cut off fire just before rupture, and immediately cooled with water	25°C
6	25MPa Type4 (123.1MPa)	25MPa	Engulfing fire	Exposed to the flame until the rupture or leak	23°C
7				Cut off fire just before rupture, and immediately cooled with water	24°C
8				Cut off fire just before rupture (Natural cooling)	27°C
9	35MPa Type3 (122.8MPa)	35MPa	Engulfing fire	Exposed to the flame until the rupture or leak	21°C
10				Cut off fire just before rupture, and immediately cooled with water	22°C
11				Cut off fire just before rupture (Natural cooling)	24°C
12	70MPa Type4 (186.8MPa)	70MPa	Engulfing fire	Exposed to the flame until the rupture or leak	19°C
13				Cut off fire just before rupture, and immediately cooled with water	20°C
14				Cut off fire just before rupture (Natural cooling)	19°C
15		35MPa	Engulfing fire	Exposed to the flame until the rupture or leak	19°C
16				Cut off fire just before rupture, and immediately cooled with water	19°C
17	70MPa Type3 (226.8MPa)	70MPa	Engulfing fire	Exposed to the flame until the rupture or leak	25°C
18				Cut off fire just before rupture, and immediately cooled with water	25°C
19		35MPa	Engulfing fire	Exposed to the flame until the rupture or leak	27°C
20				Cut off fire just before rupture, and immediately cooled with water	29°C

Figure 1 shows the diagram of the propane burner used in this study. To provide uniform flames along the cylinder body, the burner had many burner ports of silica fiber cloth[5]. Figure 2 shows the test positions of the cylinder and the burner and the points where temperatures were measured. Flame temperature was defined as the temperature measured 25 mm below the horizontally placed cylinder namely at points F1~F3, using K-type sheath thermocouples. The flame intensity was regulated by adjusting the propane flow rate to keep the flame temperatures between 600 and 800°C. To examine the effect of flame range, the range was limited to 50% of the cylinder length in Tests #4~5 (localized flame mode) while the flame covered the entire cylinder length in other Tests (engulfing flame mode).

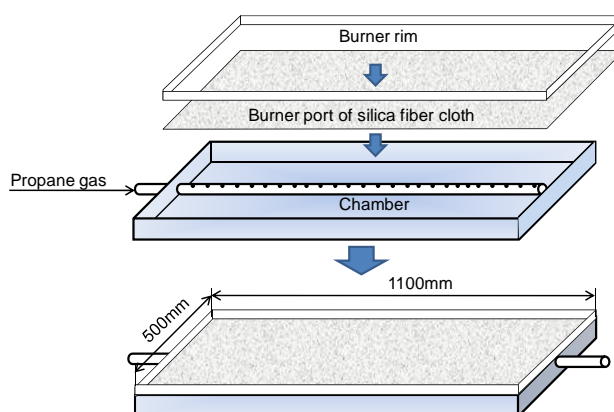


Figure 1. Propane burner

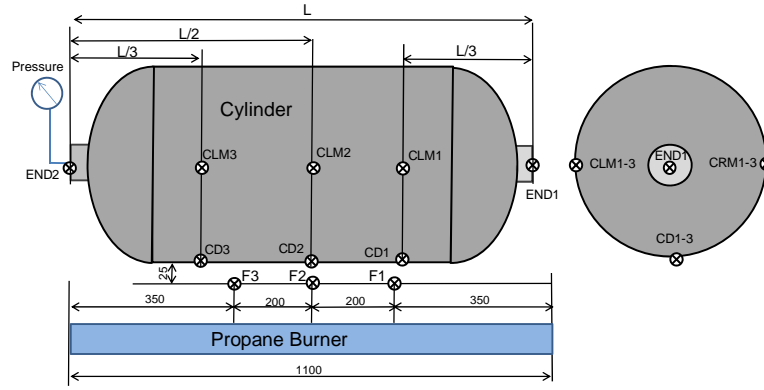
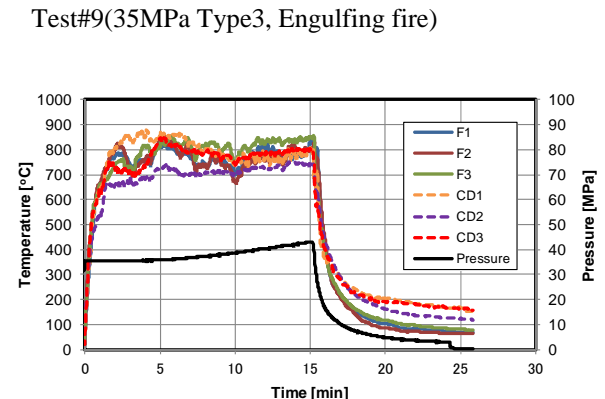
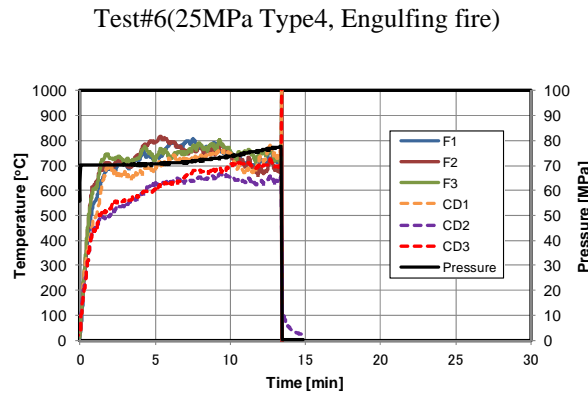
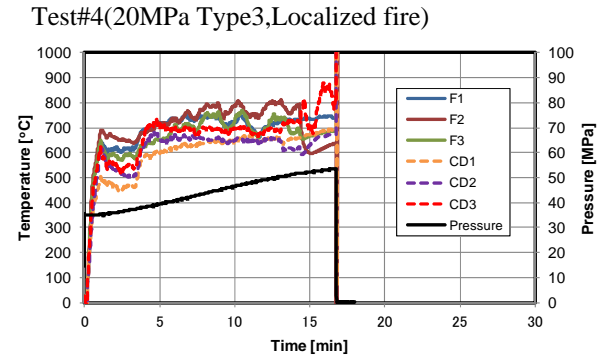
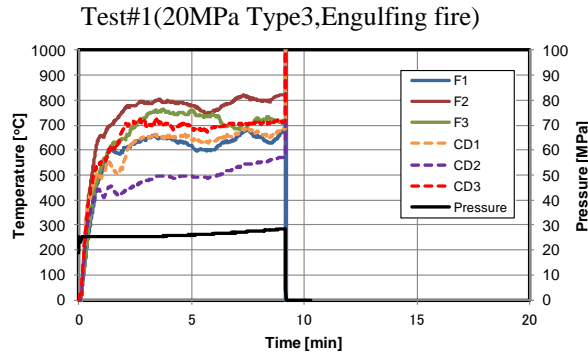
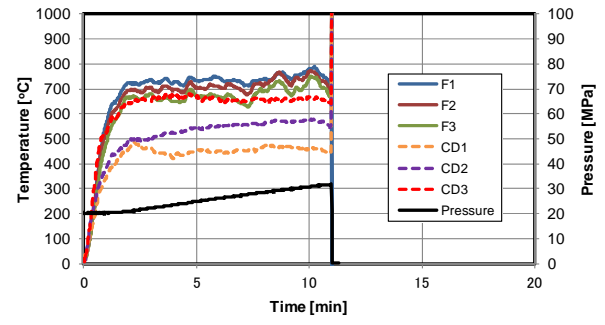
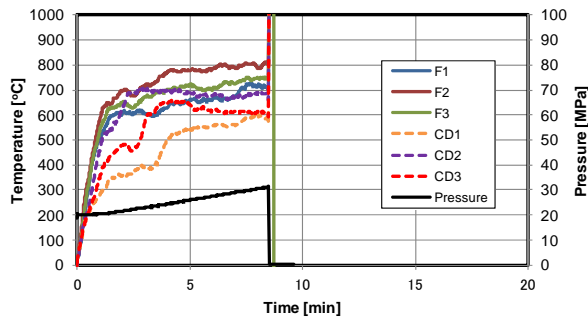


Figure 2. Cylinder/burner positions and temperature measurement points

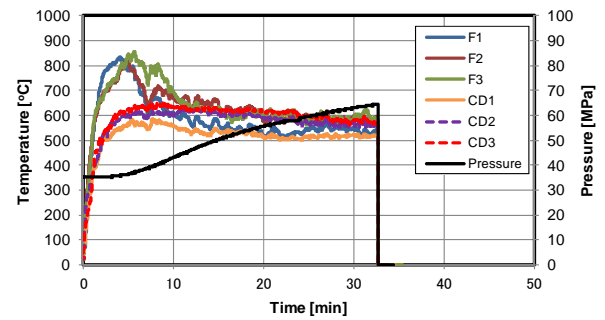
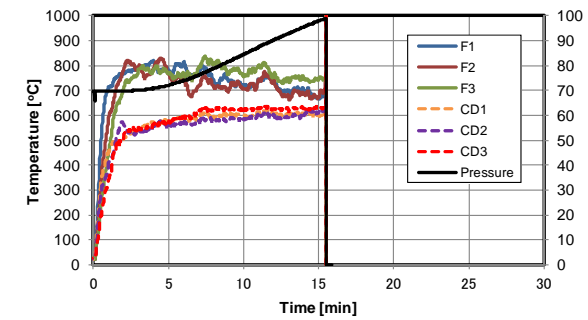
In Tests #1, 4, 6, 9, 12,15,17 and 19, the test cylinders were heated to rupture or leak at which their internal pressures (“burst or leak pressures BP_{df} ”) and the burst time from heating start (BT_{df}) were recorded. Leak was defined as escape of gas from a melt-down opening in cylinder lining. After the bursting test, another set of cylinders of the same type were heated just to the verge of bursting or leaking; then cooled down in order to obtain intact samples for determining their residual strengths. Two cooling modes were applied: a. cooling by water assuming the water spray by fire fighters (Tests #2, 5, 7, 10, 13, 16,18,20), b. natural cooling in ambient air (Tests #3, 8, 11, 14). In the water cooling mode, after the burner was turned off, water was sprayed to the whole areas of the cylinder from above, while in the natural cooling mode the cylinder was simply left to cool down to normal temperature. The starting time of cooling was slightly delayed so that the peak internal pressure would equal the burst pressure of the test cylinder. In some cases where shear noises of the carbon fibers were heard, cooling was immediately started assuming that the cylinder was about to burst.

3.0 RESULTS AND DISCUSSION

In Tests #1, 4, 6, 9, 12,15,17 and 19, the CFRP cylinders were exposed to flames until rupture or leak at which burst pressure, temperature, and the time from heating start were recorded. Figures 3 show the graphs of measured flame temperatures at points F1~F3, cylinder temperatures at its lower-side points CD1~CD3, and cylinder internal pressure in time sequence from heating start to rupture or leak. Table 2 shows the numerical values of measured filling pressures, burst or leak pressures, and their ratios.



Test#12(70MPa Type4, Engulfing fire, 70MPa filling) Test#15(70MPa Type4, Engulfing fire, 35MPa filling)



Test#17(70MPa Type3, Engulfing fire, 70MPa filling) Test#19(70MPa Type3, Engulfing fire, 35MPa filling)

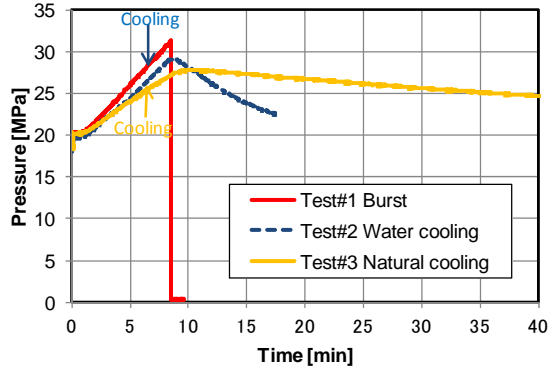
Figure 3. Flame and cylinder lower-side temperatures and internal pressures of the cylinder until the rupture or leak by flame exposure

Table 2. Filling pressure, burst/leak pressures after fire exposure and burst/leak time

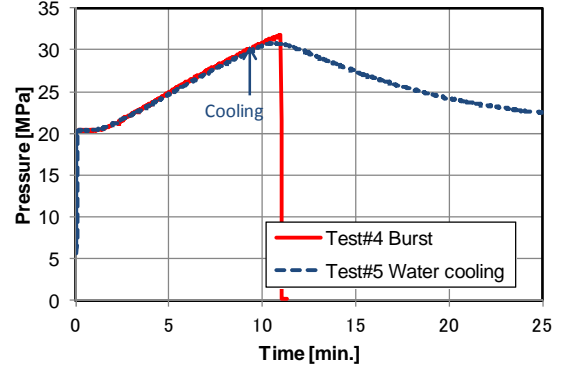
Test#	Cylinder	Filling Pressure P_{fill}	Burst (leak) pressure after flame exposure BP_{df}	Burst (leak) time BT_{df}	BP_{df}/P_{fill}
1	20MPa Type3	20MPa	31.2MPa(Burst)	8min 29s	1.56
4			31.8MPa(Burst)	10min 59s	1.59
6	25MPa Type4	25MPa	28.4MPa(Burst)	9min 10s	1.14
9	35MPa Type3	25MPa	53.5MPa(Burst)	16min 46s	1.53
12	70MPa Type4	70MPa	77.7MPa(Burst)	13min 25s	1.11
15		35MPa	43.1MPa(leak)	15min 6s	1.23
17	70MPa Type3	70MPa	98.9MPa(Burst)	15min 29s	1.41
19		35MPa	64.5MPa(Burst)	32min 39s	1.84

As the CFRP cylinders were heated by flames, their internal pressures increased until burst or leak. Ratio of filling pressure to burst pressure after flame exposure (BP_{df}/P_{fill}) proved to 1.11~1.84 times greater than their NWP's (or filling pressures in this study). On the other hand the cylinders filled up to half their NWP (Test #15) leaked instead of bursting.

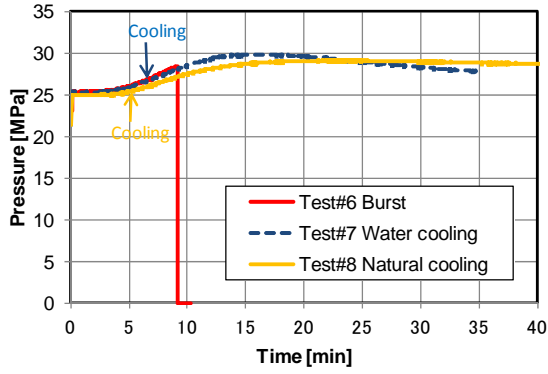
Taking account of the heating temperature and time leading to rupture or leak in Tests #1, 4, 6, 9, 12, 15, 17 and 19, a non-burst cooling version of tests was conducted, using another set of same-type cylinders. These cylinders were heated just to the verge of rupture or leak and then were cooled down in order to produce flame-exposed but intact cylinders. Figures 4 show their internal pressures in time sequence in relation to cooling modes and in reference to their previously measured burst pressures. The arrows inside the graphs indicate the time at which cooling was started.



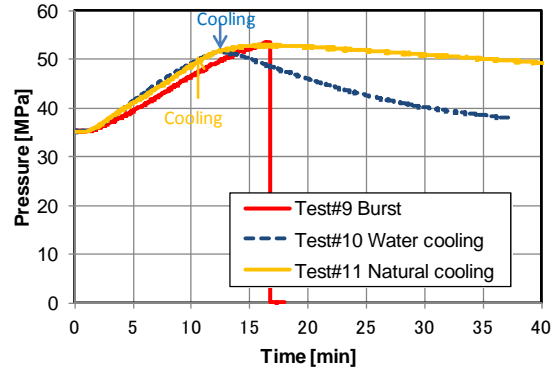
20MPa Type3, P_{fill} 20MPa, Engulfing fire, Test#1, 2, 3



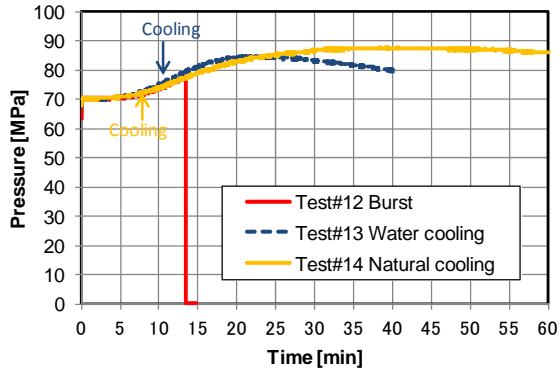
20MPa Type3, P_{fill} 20MPa, Localized fire, Test#3, 4



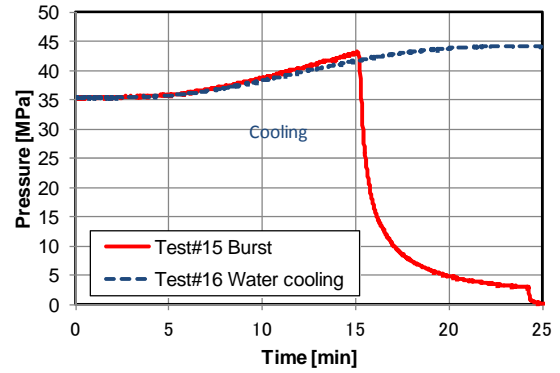
25MPa Type4, P_{fill} 25MPa, Engulfing fire, Test#6, 7, 8



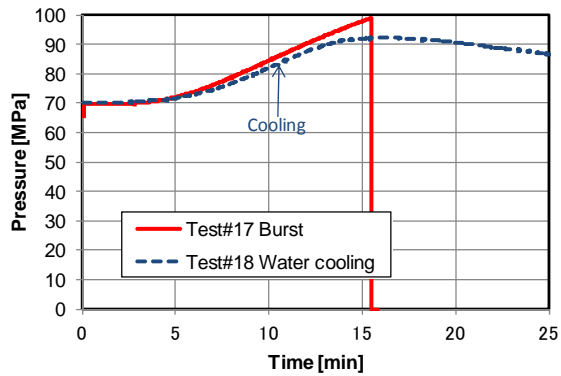
35MPa Type3, P_{fill} 35MPa, Engulfing fire, Test#9, 10, 11



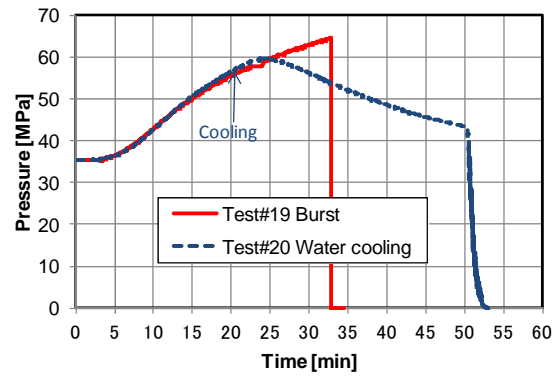
70MPa Type4, P_{fill} 70MPa, Engulfing fire, Test#12, 13, 14



70MPa Type4, P_{fill} 35MPa, Engulfing fire, Test#15, 16



70MPa Type3, P_{fill} 70MPa, Engulfing fire, Test#17, 18



70MPa Type3, P_{fill} 35MPa, Engulfing fire, Test#19, 20

Figure 4. Internal pressure during flame exposure

Even after the flames of the burner had been extinguished and the cooling started, the cylinder's internal pressure increased for some time. The reason for this is as follows.

Figure 5 shows the change in temperature of the CFRP layer (from the outermost surface of 0 mm to the depth of 10 mm) at near the bottom center (CD 2 in figure 2) of a cylinder (20MPa Type3) when a cylinder was exposed to flames under the same conditions as Test #2. Sheath thermocouples with a diameter of 0.2 mm were used for this temperature measurement.

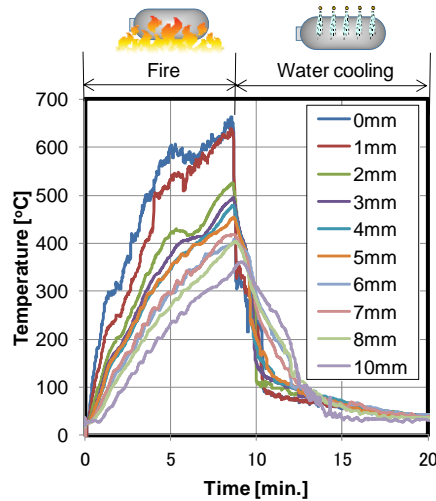
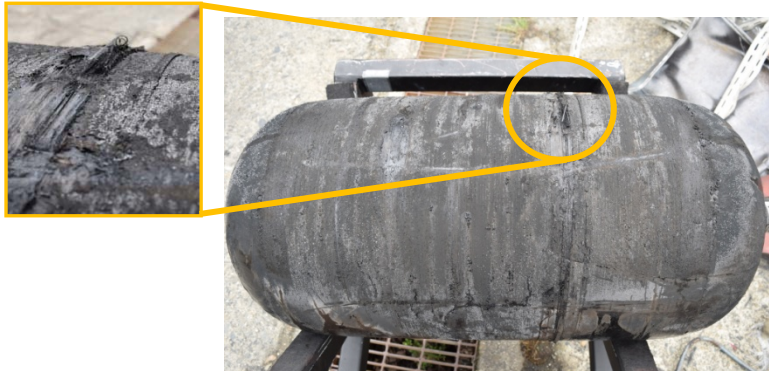


Figure 5. Temperature of the CFRP layer during flame exposure to cooling (depth of 10 mm from the cylinder surface) at near the bottom center of a cylinder under the same conditions as Test # 2.

The temperature of the CFRP layer of the cylinder during flame exposure was lower as layer depth increased. Cooling starts from the outermost surface of the CFRP layer, so the temperature in the deeper layers hardly decreases in the deep part, in other words the inside the cylinder, hardly decrease. Therefore, even after the cooling starts, the cylinder's internal pressure increased for some time.

On the other hand, in some cylinders the internal pressure exceeded the recorded burst pressure, thus attesting that the test procedure of this study had provided the cylinders with the maximum possible exposure to flames. Since the increase patterns of internal pressure proved similar between burst/leaked cylinders and intact cylinders, the two groups of cylinders were considered to have received an equal amount of heat reception from flames per time unit.

Figures 6 show the appearances of cylinders just before rupture and after cooling. In both cylinders the surface had lost its gloss due to carbonization, and revealed broken carbon fibers. In Test #11, for example, the carbon fibers broke several times during the first 10 minutes of natural cooling, then stopped breaking as the cylinder's internal pressure finally began to decline.



35MPa Type3, P_{fill} 35MPa, Engulfing fire, Water cooling Test#10



35MPa Type3, P_{fill} 35MPa, Engulfing fire, Natural cooling Test#11

Figure 6. Appearance of a cylinder just before rupture

Figure 7 shows the cross section of the cylinder after the flames were extinguished in Test #15. Indicated in the cross-sectional views are the peeling of the outer CFRP layers that had been most intensely exposed to flames when the matrix resin underwent thermal decomposition. Since the amount of heat transfer decreases with the depth of layers, the cross-sectional views reveal separation between undamaged inner layers and the outer layers that were damaged by heat decomposition of matrix resin[6].

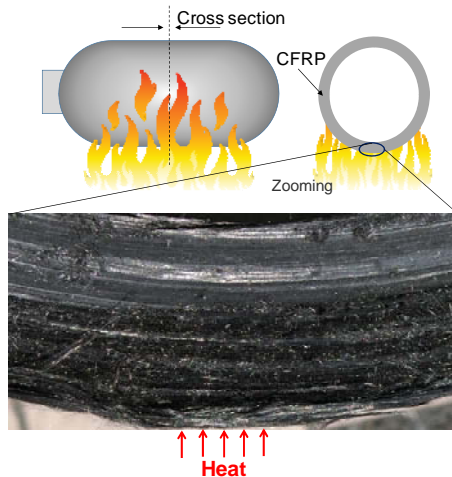


Figure 7. CFRP cross section after exposure to flames (Test #15)

In the next step, pressure proof testing was conducted to measure the residual burst pressures of the burned but intact cylinders. Table 3 shows their measured burst pressures after fire exposure BP_{af} , ratios of burst pressured to filling pressure (BP_{af}/BP_{fill}), and the ratios of the intact cylinder's burst pressure to the new cylinder's burst pressure (BP_{af}/BP_{new}). As exceptional cases, the end boss of the

cylinder broke away at approximately 84 MPa in Tests #2 and #3, indicating that these two cylinders had a residual burst pressure of 84 MPa at least.

Table 3. Burst pressures after fire exposure and comparison with new cylinders

Test#	Cylinder	Flame exposure conditions	Cooling condition	BP_{af}	BP_{af}/P_{fill}	BP_{af}/P_{new}
2	20MPa Type3	Engulfing fire	Water cooling	more 84.2MPa	more 4.21	0.92
3			Natural cooling	more 84.7MPa	more 4.24	0.92
5		Localized fire	Water cooling	82.7MPa	4.14	0.89
7	25MPa Type4	Engulfing fire	Water cooling	77.5MPa	3.1	0.63
8			Natural cooling	79.8MPa	3.19	0.65
10	35MPa Type3		Water cooling	111.1MPa	3.17	0.90
11			Natural cooling	73.3MPa	2.09	0.60
13	70MPa Type4		Water cooling	188.4MPa	2.69	1.00
14			Natural cooling	187.9MPa	2.68	1.00
16			Water cooling	173.4MPa	4.95	0.94
18	70MPa Type3		Water cooling	197.5MPa	2.82	0.87
20			Water cooling	193.0MPa	5.51	0.85

The results indicated that, firstly, the residual strengths of flame-exposed intact cylinders were 60~100% of those of their new counterparts. Secondly, the burst pressures of flame-exposed cylinders more than doubled their initial filling pressures, indicating that their residual strengths were more than twice their filling pressures, provided that the cylinders had not burst or leaked and that their temperatures had returned to normal levels after fire extinguishment. Thirdly, burst pressures of the cylinders proved greater after fire extinguishment than during exposure to flames. In addition, cooling tests for of TEST # 7, #8, #13, #14 and #16, as shown in Figure 4, did not rupture, despite reaching a pressure higher than the burst pressure during fire.

Figure 8 shows the image diagram of temperature and stress change in cylinders during and after exposure to flames.

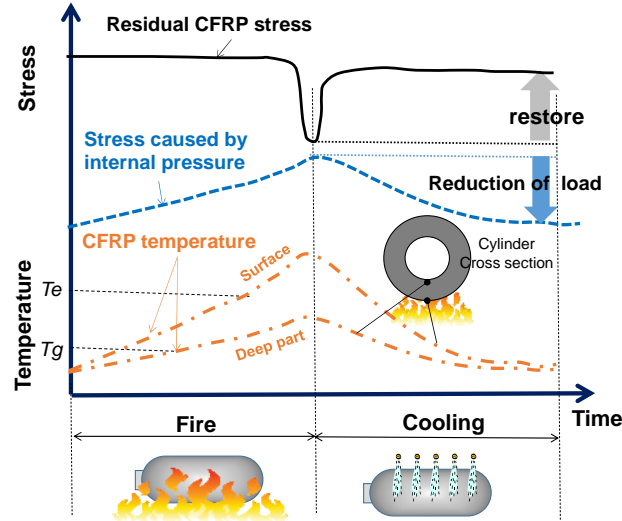


Figure 8. Image diagram of temperature and stress change in cylinders during and after exposure to flames

Sumida et al.[7,8,9] compared the strength of CFRP between heating period and cooling period under the test conditions identical to those of this study. The test cylinders varied in carbon fiber shapes and matrix resins including epoxy and inorganic resins. Sumida et al. reported that the strengths of the test cylinders proved greater in the cooling period than in the heating period. According to the results of their tensile testing, the tensile strengths of new cylinders steadily declined to half the pre-heating level at 250~300°C temperatures, but the tensile strengths and elastic moduli of previously heated then cooled cylinders declined only slightly in the temperature range up to 250~300°C and recovered practically to preheating levels during cool-down. As explanation of this phenomenon, Sumida et al. cited the following factors:

Once CFRP temperature exceeds the glass transition temperature during exposure to flames, CFRP strength steadily declines with the rise of temperature; however, the strength of the CFRP that has been heated and then cooled down to normal temperature depends on the reduction rate of matrix resin[1]. The temperature T_e at which the quantity of matrix resin start decreasing is higher than the glass transition temperature. As shown in Figure 7, the amount of heat transfer from flames diminishes in the inner CFRP layers so that some of the inner layers remain below T_e , leaving a large amount of matrix resin undamaged. As these layers are cooled down to normal temperature, their strength is recovered[8] and is conceivably increased above their previous strength measured during exposure to flames.

Explanation of this phenomena is as follows: When a CFRP cylinder is exposed to flames, gas temperature and gas pressure both increase inside the cylinder, intensifying the stress on CFRP. Once the cylinder is cooled, however, the internal pressure declines, reducing the stress on CFRP to even less than the stress level of the heating period. Therefore, due to the recovered strength of CFRP itself and also due to a decline of internal gas pressure during cool-down, the CFRP cylinder can be considered to become stronger during and after cool-down than during exposure to flames.

Therefore, since burned cylinders through bringing back to normal temperature, have sufficient strength, there is little fear of rupture. Also, in the case of a fire, it is important to shut down the fire source and cool down the cylinders by discharging water.

4.0 CONCLUSIONS

Automotive CFRP cylinders are fitted with a thermally-activated pressure relief device which detects ambient heat and is activated in a vehicle fire accident, releasing the gas from inside and preventing the cylinder from bursting. Nevertheless, if the fire is extinguished before the pressure relief device is ever activated, the high-pressure gas is left inside the cylinder. For the safe handling of such a cylinder, it is necessary that despite damage by fire the cylinder retain sufficient strength for withstanding the internal gas pressure. In this study, the pressure relief devices were removed from the test cylinders in advance to heat them to the point of rupture or leak under internal gas pressure and to measure the residual strengths of the cylinders heated to verge of rupture/leak and then cooled down intact. The results indicated that these cylinders had a residual strength at least twice their internal gas pressures.

Therefore, even if the TPRD fails, burying damaged cylinders through bringing back to normal temperature, are not subject to the risk of rupture by cooling sufficiently, there is no need to urgently degass out of cylinders. Also, in case of fire, it is important to shut down the fire source and cool down the cylinders by discharging water.

ACKNOWLEDGEMENT

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