SAFE STORAGE OF COMPRESSED HYDROGEN AT AMBIENT AND CRYOGENIC TEMPERATURES IN FLEXIBLE GLASS CAPILLARIES

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ABSTRACT

We have demonstrated that the strength of produced flexible quartz capillaries can be high enough to withstand the internal hydrogen pressure up to 233 MPa at normal and cryogenic temperature. According to the experimental results, the cryo-compressed storage of hydrogen in the capillaries at moderate pressure can enable one to reach DOE 2015 aims for the gravimetric and volumetric capacities of vessels for the safe mobile hydrogen storage. Furthermore, flexible capillaries in a bundle can probably serve as a high-pressure pipes for the transportation of gases over long distances. The developed technology of hydrogen storage can be applied to methane and hythane (H_2 - CH_4 mixture) which bridge the gap between conventional fossil fuels and the clean future of a hydrogen economy. It can be also applied to other gases, i.e. air, oxygen and helium-oxygen mixtures widely used in autonomic breathing devices.

1.0 ADVANTAGES AND LIMITATIONS OF GLASS MICRO-VESSELS

The theoretical tensile strength of glass σ is high compared to that of stainless steel, but in practice, it depends strongly upon a glass surface. According to Griffith [1], if there is a nanometer-deep crack on the surface, then the stress tends to concentrate near the defect and the local stress can exceed the rupture limit of glass, even though the average stress stays below the limit. The following number of facts confirmed the Griffith theory. Fresh glass fibers are significantly stronger than those after a few days storage without preventing them from moisture. Surface etching may eliminate deep cracks and increase the tensile strength. As a rule, thinner samples have the better strength due to the lower probability of deep cracks. Since it is impossible to locate the deepest crack in a sample, the actual rupture pressure in the capillaries can vary from sample to sample. The probability of failure $F(\sigma, l)$ at applied stress σ of glass capillaries with length l can be described by the Weibull distribution

$$F(\sigma,l) = 1 - \exp\left[-\frac{l}{l_0}\left(\frac{\sigma}{\sigma_0} \right)^m \right] \qquad (1)$$

Here l_0, σ_0, m are parameters to be derived experimentally. For the samples with a relatively small spread of the distribution, parameter m is large and the Weibull plot has a rapid ascent near the ultimate value of σ. In the past hollow glass, microspheres (HGMS) [2] and closed cylinder microcapsules [3] were suggested as possible medium for compressed hydrogen storage. They are relatively safe compared to conventional steel or composite tanks. Indeed, since both volume and the probability of simultaneous destruction of all microspheres are small, the amount of accidental release of hydrogen is small too. One of the substantial lacks of the microcapsules is that hydrogen can penetrate inside and outside them at an acceptable rate exclusively due to the diffusion through the walls. The rapid diffusion needs the elevated temperature at which hydrogen pressure inside the microspheres increases above the breakage limit. Besides, energy is needed for heating. The strength of HGMS depends upon the ideal spherical shape, but it is very difficult to control the diameter and the form of microspheres during the process of their manufacturing. Due to the above reasons HGMS are not suitable for hydrogen storage, however, there are attempts to find mechanisms other that elevated temperature to govern the process of hydrogen diffusion. Particularly, IR sensible diffusion [4] and microspheres made of porous glass [5] were considered. Alternatively, the capillary arrays, closed at one end, were suggested for the safe hydrogen storage [6,7] and several methods were developed [8, 9] for the rapid injection of hydrogen into the capillary arrays and the release of hydrogen out of the capillaries. In the experiments [10,11] with quartz

capillary arrays we achieved 48g/l volumetric and 10% gravimetric capacity at pressures near 100 MPa. Similar results were obtained in the experiments at BAM [12] with short single capillaries made of various kinds of glass. The capillary arrays had the following advantages over HGMS:
- better control of capillary diameter and shape during their manufacturing,
- better packing ratio, i.e. less unused space between the micro-capsules,
- loading and extraction of hydrogen do not need the diffusion through the glass walls.

However, the pressure needed for high enough volumetric and gravimetric capacity of the capillaries was too close to the burst pressure while the safe pressure needs to be at least 2.25 times lower. Secondly, since the walls of the capillaries are very thin, the leakage rate of hydrogen through the walls can be unacceptable for the long-time storage. To solve the existing problems it was proposed [13] to use long flexible capillaries cooled with liquid nitrogen or other coolant. Flexible capillaries can be produced using the optical fiber technology. It is known that optical fibers have tensile strength close to 5 MPa at 10 km length and fiber diameter can be controlled with good precision. A glass fiber is drawn out of the preform. A preform usually measures 10 to 25 mm in diameter and up to 1 m in length. The preform first passes through a furnace, where it is heated to the softening point of glass. As the fiber is pulled from the preform at speed around 10 m/s, measuring devices monitor its diameter and its concentricity, while another device applies a protective coating. The fiber then passes through a curing furnace and another measuring device that monitors diameter, before being wound on a spool. The structure of the fiber repeats the structure of the preform. For example, if the preform is a capillary array, the fiber will be a flexible multi-capillary. To slow the glass erosion, moisture-resistant polymeric coatings, such as UV curable silicone, polyimide or silane compounds, are applied. The polymer also connects both sides of the cracks preventing them from growing.

Low storage temperature, besides the evident increase of hydrogen density, has the additional advantages. As demonstrated before by many investigators, the strength of glass filament and filament-resin composites can be significantly (up to 2 times) enhanced at cryogenic temperatures. For example, at 77K tensile strength of S-glass fibers was 8275 MPa compared to 4585 MPa at room temperature. The strength of S-2 glass fibers with 12.7 mm length and 10 μm diameter could reach 11600 MPa at 77K at [14]. Besides, at low temperatures the permeation of hydrogen through thin capillary walls can be significantly (many decimal orders) reduced.

In the present report we discuss the main factors influenced the strength of the capillaries and their failure modes under the internal hydrogen pressure, calculate the volumetric and gravimetric capacity of capillary vessels and compare the theoretical predictions with the results of the experiments with quartz flexible capillaries at room and liquid nitrogen temperatures.

2.0 THEORETICAL ESTIMATES

The capillary vessel design is schematically shown in Figure1.

Figure 1. Schematic view of capillary vessel for hydrogen storage

A number of flexible capillaries with the internal radius r and wall thickness h, small compared to r, are tightly winded around a spool with radius R and their ends are glued into the holes in the spool body. Hydrogen flow can be controlled with the rotating disc with a single hole that works as a micro-valve for many capillaries. The packing factor of the loops of the tightly winded capillary is 0.907. The inter-loop space can be used for purposes other than hydrogen storage. For example, to increase the strength of the capillary vessel it can be filled with epoxy resin. In this case UV or thermal curing should be applied after the capillaries being wound on a spool. The spool is not subjected to high pressures and can be made of thin and light material. To be used at low temperature, it should be placed in a dewar with a coolant. The capillaries in the vessel are supposed to be long enough, so the spool volume is negligible compared to the total volume of the capillaries. The probability of catastrophic accidental release of hydrogen can be reduced, if a large number of spatially separated capillaries are used in the vessel. According to the theory of toroidal pressure vessels [15], the maximum tangential stress σ_t takes place at the internal surface of a capillary and is determined by the following expression

$$\sigma_t = \frac{p[r^2 + (r+h)^2]}{(r+h)^2 - r^2} \tag{2}$$

The radial stress $\sigma_r = -p$ is compressive and always less than the tangential stress. It should be taken into account that the compressive strength of glass is much higher that the tensile strength. We obtain the following expression of the rupture pressure

$$p_{\text{rup}} = \sigma \frac{(r+h)^2 - r^2}{[r^2 + (r+h)^2]} \tag{3}$$

Here σ denotes the actual tensile strength of glass. For a thin-wall ($h<<r$) capillary we may rewrite Eq. 2 as $p_{\text{rup}} = \sigma/A$, where $A = r/h$ is the so-called aspect ratio of a capillary. We determine the gravimetric capacity of the capillaries G_c as the ratio of the weight of stored hydrogen to the total weight of a capillary (filled with hydrogen). The volumetric capacity V_c is determined as the ratio of the hydrogen weight to the volume of the capillary. In the calculations of G_c and V_c as a function of hydrogen pressure and temperature we used the equation of state (EOS) [16]. The accuracy of the equation is better than 0.2% within the ranges of pressure and temperature applied in our experiments. The gravimetric and volumetric capacity of the capillaries can be expressed in terms of hydrogen density and the measured parameters of a capillary

$$G_c = \frac{\rho S}{\rho S + w}, \quad V_c = \frac{k\rho d^2}{D_2^2} \tag{4}$$

Here $\rho = \rho(p,T)$ denotes the hydrogen density at pressure p and temperature T, d is the internal diameter of a capillary, $S=\pi d^2/4$ is the cross-section of the internal space of a capillary, D_2 is the external diameter of a coated capillary, w is the actual weight of a capillary per unit length, $k \approx 0.907$ is the packing factor of the capillary loops.

3.0 EXPERIMENTAL LAYOUT

Quartz capillaries were produced using fiber-optics technology described above. They were around 500 m long and had various geometrical parameters, such as the internal radius and wall thickness, and were coated with epoxy resin. Their parameters were verified with scanning electron and digital optical microscopes. The SEM image of the typical quartz capillary, without a striped coating, is presented in Figure 2. The actual weight per unit length of the capillaries was measured with precision 0.1%. The tensile strength σ of short (0.5 m) capillaries was estimated with a stress rupture machine, as the ratio of the breaking tensile force to the cross-section of the quartz core of a capillary. Then 30 cm to 100 m long capillaries were subjected to the internal hydraulic pressure supplied by the two-stage hydraulic booster.

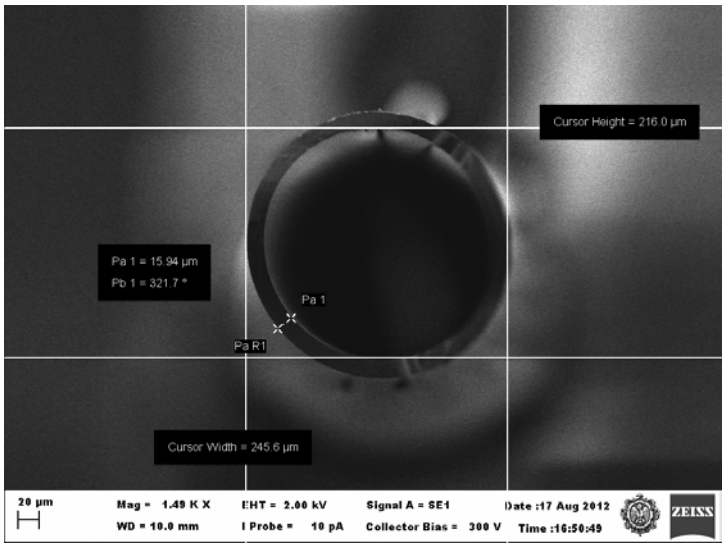

Figure 2. SEM image of the uncoated quartz capillary

The experiments with the injection of the pressurized hydrogen into the capillaries were performed using the high-pressure installation. Pressurized up to 250 MPa hydrogen was generated in the hydride compressor due to the disintegration of vanadium hydride inside the closed vessel when it was heated. Before hydrogen injection into the capillaries, they were vacuumed with the pump. The capillaries could be cooled down to 77K in the Dewar vessel with liquid nitrogen. All real-time data from the pressure and thermal sensors were written to the computer hard drive and can displayed both numerically and graphically on a PC screen. The capillary near their tips were stripped off the polymer coating using acetone and then glued into the stainless steel clutch served for the conjunction of quartz capillaries with the steel pipeline of the hydride compressor (Figure 3). Alternatively, when the single inlet was used, another one was closed with the metal stopper. The stopper was formed when the melted alloy (Wood's or In52Sn) was pumped into the capillary and then solidified inside.

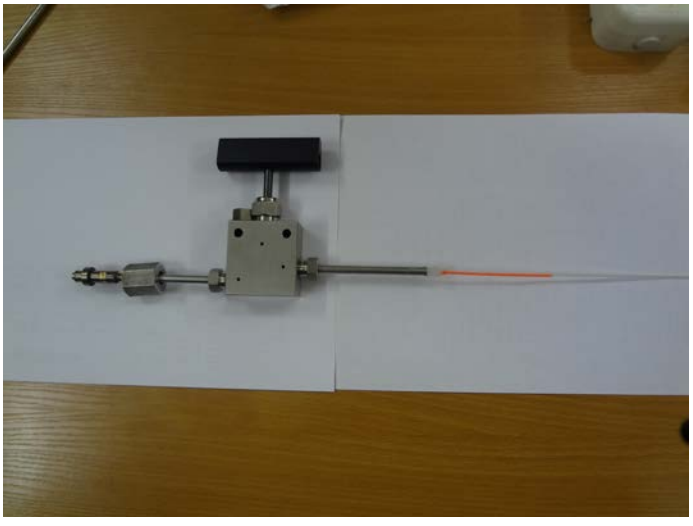

Figure 3. Conjunction of the capillary with compressor fittings

Figure 4. View inside the safety chamber of the high-pressure installation

The experimental arrangement inside the safety chamber of the high-pressure installation is shown in Figure 4. The capillary, 41.8 m long and with 0.63 cm³ storage volume, was placed inside the dewar with liquid nitrogen. A short part (≃50 cm) of the capillary between the dewar and the clutch had the temperature different either from room or liquid nitrogen. It was placed in a plastic tube for the better visibility during handling.

4.0 EXPERIMENTAL RESULTS

The main results obtained for three different types of quartz capillaries are summarized in Table 1.

Table 1. Capillary parameters.

Capillary type	1	2	3
Mean internal diameter d, μm	134	224	200
Mean external diameter D_1, μm	220	272	225
Mean diameter with polymer coating D_2, μm	286	389	310
Aspect ratio $A = d/(D_1 - d)$	1.57	4.68	8. 0

Weight per unit length w, mg/m	73.1	118	55.5
Estimated maximum tensile strength σ, MPa	2030	1300	2640
Hydraulic rupture pressure p_h, MPa	130 - 250	100 - 250	160 - 230
Hydrogen rupture pressure p_{rup}, MPa	184@77K, >233@293K	74.5@77K	85.0@77K

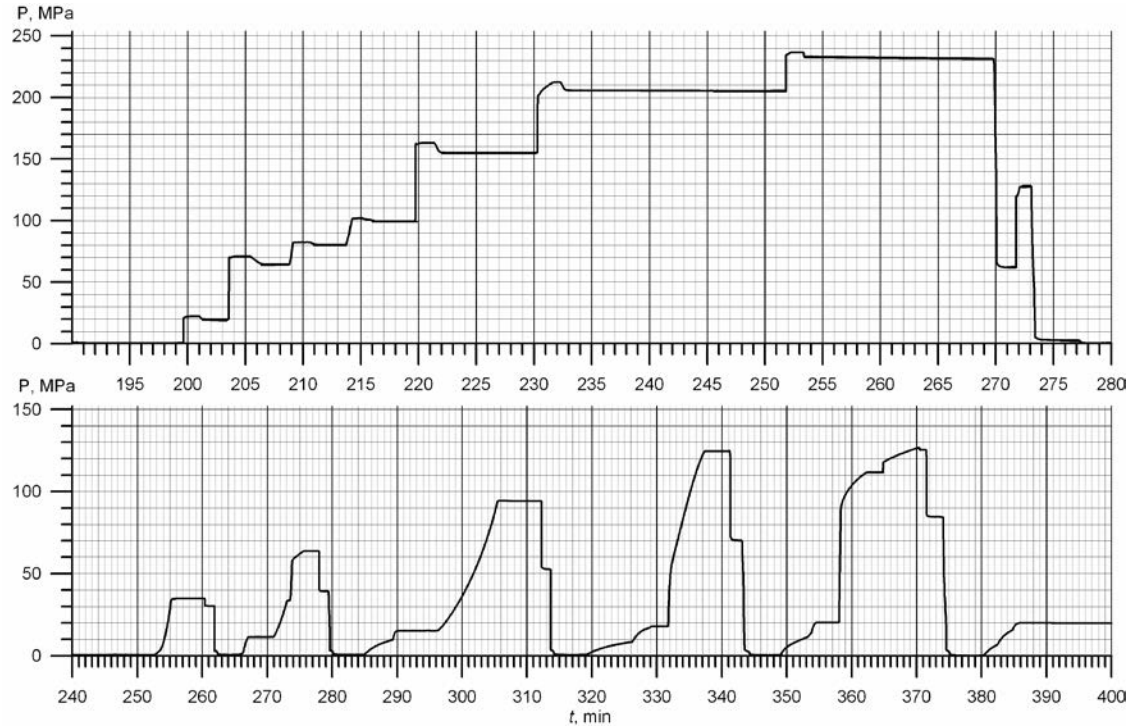

Figure 5. Pressure vs time in capillary type 1 (top) and 3 (bottom).

The capillaries type 1 and 3 were made of quartz produced with CVD method while the capillaries type 2 were made of less expensive fused quartz. The pressure inside the capillaries increased step by step according to Figure 5. Increasing pressure in the capillary, we determined the value 184 MPa of the rupture pressure that totally destroyed the capillary and caused spilling of liquid nitrogen. We noticed a relatively broad hole in the plastic covering caused by the jet of hydrogen from the origin of the crack. We suppose that the reason for the total destruction was a rarefaction wave propagating along the capillary. At lower pressure 30 MPa the destruction did not propagate far from the place of capillary failure. The gravimetric and volumetric capacities of the tested capillaries are presented in Figure 6 by the solid curves. The marks at the curves correspond to the capillary type and the dots on the curves indicate the values of the pressure applied. The gravimetric capacity of the thick-wall capillary type 1 is below 2%, and its volumetric capacity is below 20 g/l, even at the cryogenic temperature and relatively high pressure. The capillaries 2 and 3 with the higher aspect ratio have much better performance. We reached over 9% and 32g /l volumetric and gravimetric capacities at relatively moderate pressure 70 MPa with type 3 capillaries. Furthermore, the values could be even higher, if the thickness of the polymer coating of the capillaries can be reduced from 42 μm to 10 μm. Possible enhancements are illustrated by the dashed curves.

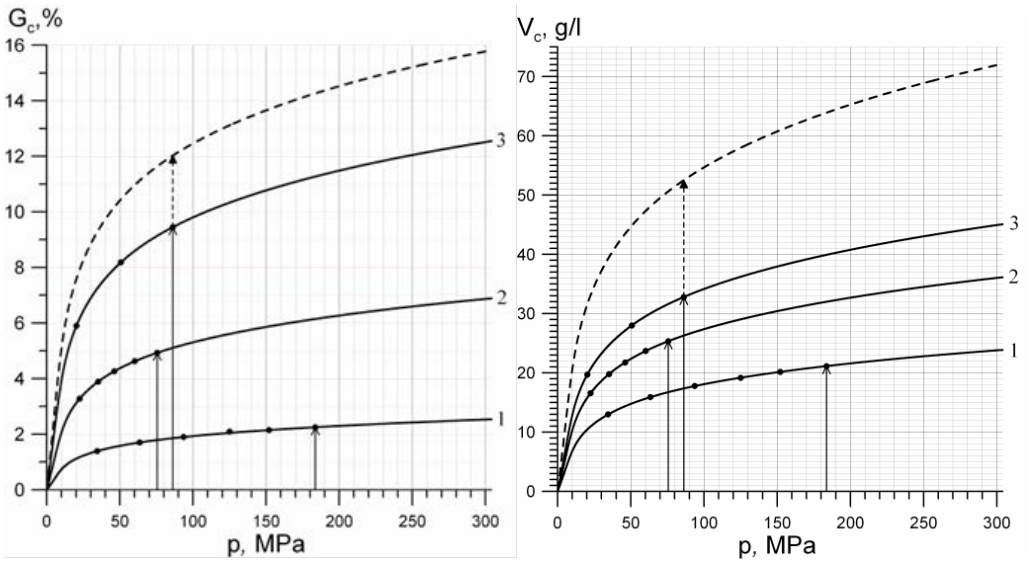

Figure 6. Gravimetric (left) and volumetric (right) capacities of quartz capillaries at 77K vs. hydrogen pressure.

5.0 CONCLUSIONS

Due to the rapidly decreasing compressibility of hydrogen at pressure higher than 40 MPa it is unreasonable to store hydrogen at higher pressures and cryogenic temperature. Unfortunately, the produced capillaries had lower tensile strength than typical optical fibers. The measured rupture pressure values are even lower than it follows from the values of tensile strength of relatively short samples obtained with a stress rupture machine (Table 1) and Eq.3. It was impossible to control the wall thickness, concentricity and the surface quality along the total length of the capillaries using the existing optical fiber technology. On the other hand, it follows from Eq.1 that the actual tensile strength depends on the capillary length. The loss of the concentricity or wall thickness may be the reasons for decreasing strength of long capillaries under the internal hydrogen pressure. Nevertheless, at 35 MPa and liquid nitrogen temperature we obtained 7% and 25g /l capacities, at safety factor 2.3, despite of the reduced tensile strength and the excessive thickness of the polymer layer. We hope that if the technological problems will be solved, the performance of the flexible capillaries may be much close to the optimistic theoretical estimates.

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