A TEMPERATURE CONTROLLED MECHANICAL TEST FACILITY TO ENSURE SAFE MATERIALS PERFORMANCE IN HYDROGEN AT 1000 BAR

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ABSTRACT

Increasingly, car manufacturers are turning to high pressure hydrogen storage for on-board power applications. Many prototypes use costly materials and fabrication methods, such as Type 316L austenitic stainless steel and processes such as TIG (GTA) welding. There is a need to move to less expensive options without compromising safety to assist in developing economic vehicles. It is important that the behaviour of new/modified materials and joints (including those fabricated by new technologies) is understood at anticipated service temperatures and hydrogen pressure as the consequences of poor material choice could be severe. The greatest detrimental effect of gaseous hydrogen on the mechanical properties of metallic materials is commonly observed under conditions of dynamic plastic strain. Under such conditions, an atomically clean surface is produced, where hydrogen molecules will dissociate, and penetrate the material. Thus, static load test methods with hydrogen charging are not reliable for engineering data generation. To meet the need for dynamically straining material in a pressurised hydrogen environment, TWI has developed a facility to load specimens in a high pressure environment for tensile, toughness and fatigue testing. The design of this has involved a number of innovative steps. This paper outlines the requirements and the design and construction issues that were encountered when installing a facility which can not only perform tests at up to 1000bar (100MPa) but also for temperatures between –150°C to +85°C.

1.0 INTRODUCTION

In order for the automotive industry to move towards the hydrogen economy, there is a need to develop affordable vehicles and also the infrastructure for provision of hydrogen to these vehicles. In order to do this safely, the behaviour of the materials used in high pressure hydrogen needs to be understood.

At ambient pressure, the boiling point of hydrogen is 20.3K (-252.7°C). Hydrogen has a triple point of 14.0K at 7.2kPa (0.07atm). The major safety concerns of hydrogen are its combustion and detonation properties. Hydrogen-oxygen mixtures are flammable over a much greater range of compositions than methane, propane or octane, although the auto-ignition temperature is much higher than for petrol/gasoline. When hydrogen burns it has a colourless flame, which can be extremely dangerous. However, the high diffusivity of hydrogen ensures that it disperses more quickly than other fuels; the diffusivity of hydrogen in air is 0.63cm^2s^{-1} compared to 0.2 cm^2s^{-1} for methane [2]. Despite the safety concerns, hydrogen has been used for many decades in the chemical and petrochemical industries, and is therefore relatively well-known in terms of issues of risk mitigation.

Nevertheless, the consequences of a hydrogen leak and subsequent deflagration or detonation could be disastrous. Any containment vessels need to be sufficient to contain hydrogen at the anticipated service conditions: This is especially critical for storage on-board vehicles, on the container would need to resist failures that could lead to hydrogen release in crash situations. As this is not directly an effect of hydrogen embrittlement, crashworthiness of storage vessels is not covered further in this paper.

2.0 STORAGE

2.1 General Considerations

There are a number of options for storage of hydrogen for either static or mobile use. The storage method depends on the application. Currently the most common storage method is as compressed gas. Hydrogen at 180bar is readily available in bottles, and larger static stores of hydrogen typically consist of compressed gas in heavy-wall carbon steel vessels. For applications where mobile storage is required, and the weight of steel cylinders is unacceptable, composite cylinders are under development.

A higher density storage of hydrogen is as a liquid, although the energy density is lower than that of petrol/gasoline. However, there are a number of problems associated with the low temperatures required for liquid storage. The boiling point of hydrogen is 20K, so liquid storage vessels therefore need to be cooled to this temperature which can use a large amount of energy. There is also a problem with boil-off of hydrogen causing the pressure in the liquid container to increase. This pressure is often vented to the atmosphere, which means that there is loss of hydrogen over time. For example at present, in the BMW 7 series which has been developed to run on liquid hydrogen, almost all of the hydrogen has boiled-off and been vented to the atmosphere after three weeks without driving the vehicle. Another problem is that vehicles carrying liquid hydrogen may be prohibited from travelling through long tunnels.

Another promising approach is solid state storage of hydrogen. Hydrogen can be stored in the form of metal hydrides at similar densities to petrol/gasoline. However, at present although a large number of different hydrides are under development, the hydride needs to be heated to in excess of 300°C in order to release the hydrogen. This poses a number of problems especially where mobile applications are considered.

2.2 Why High Pressure?

Hydrogen has only 70% of the energy density of conventional natural gas so will need to be stored at very high pressures if storage volumes for acceptable vehicle ranges are to be kept within reasonable bounds. For compressed hydrogen storage, the current suggested pressure is 875bar. This would allow refuelling of vehicles with on-board storage at 700bar. These pressures are currently under investigation by European automotive companies. The method of hydrogen delivery from the on-site storage to the on-board storage has consequences for materials requirements. For compressed hydrogen it will take a few minutes even if the refuelling station holds hydrogen at 875bar. The tubes, valves etc. required for the refuelling operation need to be resistant to hydrogen-assisted embrittlement mechanisms at temperatures as low as -80°C due to adiabatic expansion of high pressure hydrogen. Currently, there are materials which are suitable for this type of service but their cost for mass production of components is prohibitive. Materials choice is therefore an area of research which needs to be addressed for refuelling stations as well as for on-board storage. One vehicle manufacturer has indicated that each vehicle will be required to have a lifetime of 50,000 refuelling cycles, each of which will involve a pressure cycle. Thus the fatigue life of the components will need to be considered.

2.3 Liquid

BMW has launched a limited number of hybrid vehicles which can use either liquid hydrogen or petrol in their internal combustion engine

(http://www.alternative-energy-news.info/bmw-hydrogen-7-production/).

The storage vessel is 316 austenitic stainless steel and is TIG welded. If this technology is to go to mass market, a cheaper material and fabrication method will be required. The materials challenges are significant given the cryogenic temperatures in addition to the presence of hydrogen in both the storage tank and associated components.

2.4 Solid hydrogen storage

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It is not clear at the moment which technologies will become the market leaders: gaseous or liquid hydrogen or metal hydrides with fuel cells or internal combustion engines.

3.0 MATERIALS BEHAVIOUR IN HIGH PRESSURE HYDROGEN

There are various ways in which hydrogen can affect a material's performance. Although hydrogen within a material can macroscopically damage or embrittle it, exposure to gaseous hydrogen at temperatures below about 100°C does not generally result in sufficient accumulation of hydrogen within the material to have such an effect. This is why hydrogen can currently be stored and transported in steel cylinders at about 200 bar with out any problems. The primary concern with regard to operation in high pressure gaseous hydrogen is "hydrogen environmental embrittlement" (HEE) in which hydrogen molecules dissociate, typically on an atomically clean, plastically strained surface and influence the local fracture behaviour. Embrittlement may occur under either nominally static (typically slow rising load) conditions, or under cyclic loading conditions (fatigue). As such, the 50,000 refuelling cycles anticipated for hydrogen vehicles are of concern, as in a low cycle fatigue regime, expected life can be reduced significantly by the presence of hydrogen.

Measurement of the effect of HEE on a material must be carried out in a representative hydrogen environment. This immediately poses problems concerning experimental methods. Much of the available data on nominally static loading has been measured by first loading a material and then placing it in a hydrogen environment. However, HEE relies on formation of new surface by straining of the material in the presence of hydrogen. It is therefore likely that test results will vary depending on whether specimens are loaded prior to or during exposure to hydrogen. Strain rate is another important factor, with greater HEE generally observed at lower strain rates. Finally, temperature is also an important factor. Many austenitic stainless steels show a drop in HEE resistance at around 50°C. During automotive service, it is anticipated that temperatures lower than this will be seen due to adiabatic expansion of the compressed hydrogen.

The draft standard BS ISO 11114-4 [1] contains three types of standardised testing. Type C tests involves pre-loaded fatigue pre-cracked specimens being placed in hydrogen. After exposure, specimens are examined for any sign of crack growth. Types A and B involve straining material in the hydrogen. The latter involves incrementally increasing the load in a fracture mechanics type test until the specimen fails. Test Type A involves loading a disk in hydrogen by increasing the hydrogen pressure until the disk ruptures. The problem with this type of test is that the loading is not independent of the hydrogen pressure and a number of studies have shown that the HEE effect is pressure dependent. An example of such a study is West et al. [3] who demonstrated that for at least one type of austenitic steel, the susceptibility to HEE increases between the pressures of 690 to 1725bar. Thus Type A tests need to be treated with caution. Results may give a useful comparison between materials, but do not necessarily give a true quantitative measure of the effect of hydrogen on material properties.

4.0 DESIGN ON TEST FACILITY

4.1 General Considerations

Currently, TWI is able to load specimens in tension and fatigue in hydrogen at pressures of up to 450bar and temperatures from ambient to 85°C. TWI is building a further facility to test specimens at up to 1000bar at temperatures between -150°C and 85°C. This new facility, along with the current one, will be capable of carrying out tensile, bend and fatigue testing in high pressure hydrogen and so is ideally suited to investigate the effect of HEE in a wide range of materials.

The building and operation of a test facility of this nature has safety implications in its own right, and TWI has been acutely aware that over and above the usual responsibilities for ensuring a safe work place, any significant incident in a research context could have an adverse effect on public confidence in the hydrogen economy. There have been four principal strands to the project, namely equipment design, physical protection, system design and operating procedures.

4.2 Equipment Design

The centrepiece of the equipment is a simple pressure vessel, and this has been designed conservatively within national codes. Materials have been selected from those which are known to be resistant to high pressure hydrogen, and the design ensures that they are not operating under highly stressed conditions.

4.3 Physical Protection

The test vessel is housed in a separate room ("test cell") which is divided from the control room by heavy steel doors. The walls of the test cell are reinforced, and the roof is a single sheet of corrugated Plexiglas, to provide easy release of blast pressure in the event of unplanned pressure release or explosion. Such measures are, however, very much a last resort. Within the test cell, the equipment is intrinsically safe, with, for example, pneumatically operated valves, and any items which, in principal, could generate static electricity (such as hydraulic hoses) are earthed. There are hydrogen sensors in the test cell, and also the control room and adjacent to the gas pressure booster, which have a minimum detection limit of about 10 ppm.

4.4 System Design

Management of purging and pressurisation of the test vessel is via a programmable logic controller (PLC), so that the operator is not responsible for ensuring that (for example) the vessel has been purged of air before hydrogen is introduced, or remembering the correct sequence of valve operations. Clearly it is possible to re-program details such as the set test pressure, but the operator is not able to interfere with the basic operating sequence for purging and pressurisation.

The draft standard [1] requires test vessels to be evacuated at least once prior to filling with hydrogen. This, however, places demands on pressure seals, which are easier to design to either contain or resist pressure rather than both, and is in fact less effective than purging by multiple pressurisation and dilution. In the first place, the TWI system is pressurised to about 10 bar with nitrogen twice. Simple dilution calculations show that this results in <2.5% air. Thus, the air in hydrogen on first pressurisation with hydrogen (also to about 10 bar) will be an order of magnitude below the flammable limit of 25% air in hydrogen. A total of eight 10 bar pressurisations with hydrogen ensures a purity of ~0.000001% contaminant in the test gas. This is not a safety issue, but before the vessel is opened, hydrogen needs to be flushed out with nitrogen, by a similar procedure, this time to achieve less than the flammable limit of 4% hydrogen in air. Five 10 bar nitrogen pressurisations ensure that about 0.15% is achieved. As indicated above, these purging sequences are pre-set, and are not under the control of the operator.

The system design incorporates several interlocks, which ensure that the vessel is not pressurised unless it is safe to do so, and cause pressurisation to be stopped and/or the vessel to be vented if certain problems arise. The full details of the interactions between control items (test cell door switches, hydrogen gas detectors, pressure and temperature monitors, fire detectors and emergency stop buttons) and the equipment (PLC, gas booster and valves) are complex, but the principals are as follows.

In the first place, the PLC controller will not operate unless the door switches indicate that the door is closed, and there is a manual valve on the test vessel supply, which is linked to the air supply for operating the pneumatic valve system. Thus, with the door open and this valve closed, the operator can work on and in the vessel with complete confidence that hydrogen cannot be supplied to it. In the second place, various events will result in automatic shut-down of the gas pressure booster, and venting and purging of the test vessel. Hydrogen levels at the sensors of 1000ppm or more (2.5% of the lower flammable limit of hydrogen in air) or a fire alarm or operation of the Emergency-stop button, cause shut down by interaction with the PLC controller. They also cause the supply of hydrogen from bottles to be cut by closing solenoid valves. The pneumatic valves depend on a supply of compressed air, and the supply lines for this are plastic, and are deliberately routed around the laboratory so that they would rapidly burn through in the event of a fire. The selection of valves (normally closed or normally open) is such that consequent loss of air pressure would result in shut off of supply of hydrogen, venting of the vessel, and purging with nitrogen. A power cut would shut off solenoid valves, and also disable the gas pressure booster and thus prevent the supply of any further hydrogen to the vessel, but the system would be kept running by a back-up “uninterruptible power supply” (UPS) and the vessel would not be vented. Similarly over temperature would result in heating being shut down, and over pressure would result in the gas booster being shut off, but the vessel would not be vented.

In addition to automatic shut down systems, there are audible and visible alarms, and the hydrogen detection system sets off an alarm at 400ppm (1% of the lower flammable limit of hydrogen in air), without initiating any shut down procedures. Fire alarms, hydrogen alarms, power cuts or over pressure or over temperature all activate an automatic telephone dialling system to alert operators if they are not present.

It is important to recognise that this test facility incorporates a hydraulically operated load train as well as a pressure vessel. Care has been taken in the design of the loan train to ensure that breakage in this or malfunction of the hydraulics cannot result in, for example, pull rods being ejected from the vessel under pressure.

4.5 Operating Procedures

From the above it is evident that considerable care has been taken to ensure that the test facility as a whole is as safe to use as possible. Nevertheless, the importance of good operating procedures and operator training cannot be over-emphasised. Operators need to be skilled in the basic operations required for handling compressed gasses and operating servo-hydraulic test equipment, but also need to be aware of the properties of the materials they are handling (in this case hydrogen) and the special features of the laboratory they are working in. When performing routine testing, a check list of operations is followed, and if anything out of the ordinary is undertaken (for example during maintenance) a formal risk assessment is carried out first.

5.0 CONCLUSIONS

Amongst the EU aims for a hydrogen economy, is a plan that vehicles should be ready for mass production by 2015 and that by the year 2020 between 0.4 million and 1.8 million vehicle units should be manufactured per year. If these aims are to be achieved, there is a significant amount of research and development required to ensure that suitable, safe, economical materials and fabrication methods for on-board hydrogen storage, refuelling stations and the infrastructure required to support these are available.

Test equipment has been developed at TWI to enable safe and reliable mechanical testing, including tensile, fracture mechanics and fatigue testing, in hydrogen at up to 1000 bar pressure, within the temperature range 150 to +85°C to support these needs.

6.0 REFERENCES

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