Resistant Cast Iron for a 50% Efficient Hydrogen Engine

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Abstract.
Regarding CO2 reduction on commercial vehicles, hydrogen engine is becoming a strong complementary solution, especially for high load profiles. In addition, costs and durability make internal combustion engine a very attractive and effective solution based on current powertrain layouts. The first generation of hydrogen engines follows spark ignited engine combustion processes, which are operated lean with intake manifold or low-pressure direct injection. These concepts have some limitations on the achievable efficiencies and power densities. To achieve significant increase in efficiency, an alternative combustion process close to diesel combustion is required. That demands hydrogen to be injected under high pressure near top dead center. The available or necessary approaches to initiate the diffusion combustion of the hydrogen are also discussed to show path to the target of 50% BTE.

Different engine technologies will expose Hydrogen in different levels, which can create concern of embrittlement. Hydrogen embrittlement is caused by two main mechanisms: high pressure and temperature exposure or high corrosion. In a Hydrogen combustion engine, the key mechanism is high pressure exposure. Hydrogen penetration mechanisms are related to voids and soft materials where it positions on the grain boundaries. Cast irons are favorable to resist embrittlement due to the high number of graphites, serving as an accommodation to hydrogen, delaying embrittlement effect. The shape of graphites and different alloy elements will play an important role on embrittlement resistance combined to the mechanical and fatigue resistance, also necessary on such highly efficient engines. Bench tests and measurements in parallel to dyno evaluations are presented to support the alloy development.

Keywords: H2ICE, Embrittlement, Cast Iron

1 H2 ICE and Embrittlement

1.1 Concepts on H2 ICE

GHG and CO2 targets by 2050 are linked to carbon neutral transport solutions. On commercial vehicles three main propulsion systems are in a strong position: battery-electric, fuel cell and hydrogen internal combustion engine (H2ICE). Once battery and fuel cell production are dependent on critical minerals intensive on energy to be produced, H2 ICE is becoming a strong complementary solution, especially for high load profiles [1, 2, 3]. Lower costs and much higher durability position internal combustion engine as a very attractive solution.

The first generation of hydrogen engines for commercial vehicles follow spark ignited engine combustion processes, which are operated lean with intake manifold or low-pressure direct injection [2, 3, 4, 5]. Although these engine concepts are characterized by low injection pressures which means advantages regarding the necessary hydrogen storage concepts, the achievable efficiencies and power densities are limited due to the combustion process. That demands an engine design with higher volumetric displacement to achieve the required power level and transient performance [6].

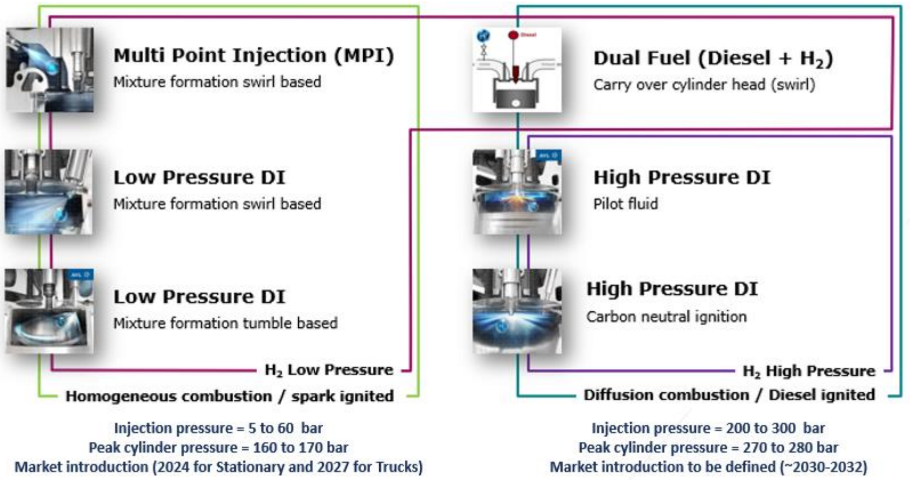

Fig. 1. Different injection strategies for H2 internal combustion engines. Adapted from [2].

To achieve significant increase in efficiency, an alternative combustion process is required that comes close to Diesel engine combustion. To accomplish this, the hydrogen must be injected under high pressure near to top dead center, which is enabled by high pressure direct injection systems [7, 8], such as Westport's HPDI^{TM} product. As shown in Figure 1, the combination of hydrogen with hydrocarbon as ignition fuel is a possibility to have a robust system. In the same way for zero emission option, Diesel can be substituted by HVO. On low carbon strategies, the hydrogen combustion in a Diesel cycle is possible by two main ways: Hydrocarbon pilot (minimum pilot fluid content to support mixture ignition) or other hot source like a glow plug. The use of Diesel cycle to burn hydrogen can enable efficiency in a combustion engine exceeding 50% BTE [6].

In terms of material development, spark ignition H2 ICE would demand solutions to reduce weight and size. Once higher volumetric displacement is necessary to deliver similar power and torque, packaging can become an issue. Mechanical and thermal loads are below Diesel levels, which indicate an easy carry over of materials. On the other hand, the HPDI design is also more demanding on mechanical and thermal perspectives, e.g. peak firing pressure can be 75% higher than LPDI design and injection pressure can be 15 times higher. This brings the material selection in high focus for HPDI design. There are techniques being evaluated on combustion side to minimize the embrittlement risk. The HPDI^{TM} system with diffusion flame combustion has H2 combusted as maximum possible before it hits the engine components. The aim is that only the fuel system is constantly exposed for H2.

Both designs will be operating on the chance to create hydrogen embrittlement on the parts of the combustion chamber, which can affect durability and is discussed in detail ahead.

1.2 Introduction to embrittlement

Internal combustion engines are known to have a long life to a minimum of 1.5 million km. There are even engines, already in series, designed to resist 2.0 million km. Such long term durability is a strong differentiation to other technologies considered to zero emission. Fuel cells and batteries are expected to be replaced 3 to 5 times during the life of an internal combustion engine. Besides the inconvenience, it is also an economical and environmental problem due to the energy necessary to build the materials based on critical minerals. In [9], an estimation is giving on the additional cost that each new technology will have in 2030, when it was estimated 60% reduction for batteries and 50% cost reduction to fuel cells, while only 20% cost reduction of hydrogen tanks. For a drive range of 600km, the additional cost compared to a Diesel in 2030 will be lower for hydrogen internal combustion engine powertrains compared to Fuel Cell (70% higher) and Batteries (230% higher). Notice that such estimation of cost reduction of the existent solutions is already doubtful in 2022: battery costs have increased, not reduced.

Such superior durability performance of H2ICE needs to be carefully taken. On system operating with hydrogen, it is a known effect of hydrogen contamination to cause embrittlement on metals. Hydrogen embrittlement is caused by two main mechanisms: high pressure and temperature exposure or high corrosion. In a hydrogen combustion engine, the key mechanism in consideration is high pressure and temperature exposure [9]. Solutions on combustion strategy are being considering to reduce the exposure time of hydrogen during injection for the combustion chamber components. Besides that, material design is critical to assure high durability to H2ICE. Figure 2 illustrates the hydrogen contamination and its possible effect due to hydrogen embrittlement.

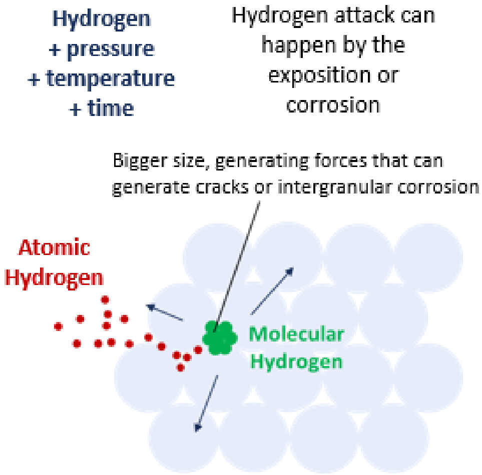

Fig. 2. Illustration of the hydrogen contamination.

High density metals like forging steel are known to present low resistance to hydrogen embrittlement. However, cast irons present much higher levels of resistance to hydrogen embrittlement once graphites actuate as areas to accommodate hydrogen in its grain boundaries delaying any risk of embrittlement [10, 11, 12]. In a similar approach, steel devices exposed to hydrogen can use carbon steel as an incremental alternative, while stainless steel is preferred due to its protective layer preventing the entrance of hydrogen to the core.

Examining the combustion chamber, the key parts at risk of hydrogen embrittlement are:

- Piston
- Cylinder head
- Valves
- Valve seat
- Liner
- Top piston ring

One important effect to be better studied is the effect of lubrication, which can serve as a barrier to hydrogen to enter the metal parts. Once combustion chamber area tends to have less lubrication the role of lubrication is to be better understood once hydrogen exposure is closer to top dead center in many combustion strategies.

Bench tests are presented to explore the risk of hydrogen embrittlement on H2ICE and its development routes to support materials with high resistance.

2 Test assessment

2.1 H2 accumulation

One important characteristic to be explored is the dynamic of hydrogen to enter and exit the metal. Due to the reciprocating behavior of internal combustion engine, it is expected that for a moment hydrogen injected will be exposed to the metal parts from the combustion chamber at high pressure and high temperature for a short period of time, while after it is free of pressure, hydrogen is able to get out of the metal. The question is to understand how fast the hydrogen is released.

To study this behavior, an experimental test was proposed. In a pressurized vessel, specimens of cast iron grades were tested with hydrogen. Cube-shaped specimen with a border length of 5mm were charged for 7 days at 300°C in an atmosphere of 20% H2 and 80% N2 at 150 bar. After the charging, hydrogen content in the metal was analyzed by Carrier Hot-gas extraction. The analysis was performed immediately after finishing the charging and 1, 24 and 72 hours after charging, respectively to support the degasification dynamics evaluation after exposure. Table 1 presents the main information of the tested materials. Figure 3 presents the main results regarding the hydrogen concentration analysis.

Table 1. Tested cast iron materials.

Name	Description
FC300	Standard gray iron alloy
CGI450	Standard vermicular iron alloy
CGI500HT	Higher strength and thermal conductivity vermicular iron alloy

All 3 materials presented similar concentration curves. The test included an increase in the hydrogen concentration by 1.5 and 2.0 ppm. This increase of hydrogen concentration is not maintained after 72 hours being reduced by half. That indicates that some hydrogen is encapsulated with time, which is the principle for embrittlement effect.

Notice in Figure 3 that the hydrogen release is not immediate, while the measurement 24h after hydrogen exposition does show a significant decrease in hydrogen concentration. That can indicate that in reciprocating movement inside the engine, the hydrogen tends to increase in concentration and release is only to be observed after the engine shut down.

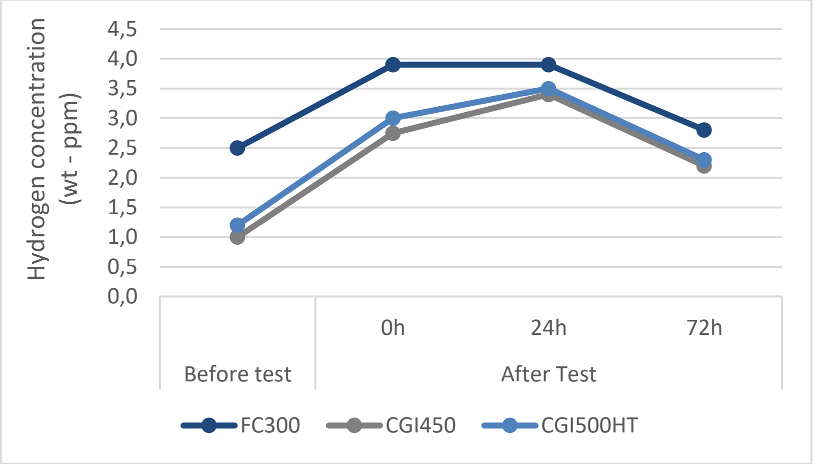

Fig. 3. Hydrogen concentration before and after exposition test at 20%-H2 and 80%-N2 in a vessel at 150 bar and 300 °C for 168h.

2.2 Effect on mechanical characteristics

Round Tensile Specimen of 5 mm diameter of the four cast iron grades were Hydrogen charged in the same way as the cube specimen. After charging the specimen were tested by slow strain rate tensile testing with a strain rate below 5x10-6 1/s. In order to prevent hydrogen diffusion and outgassing from the metal, the specimen were frozen in liquid nitrogen in the time between charging and testing. Slow strain rate tensile tests are capable to detect hydrogen effects. In case of hydrogen effects, the tensile properties will degrade, especially tensile strength (only for severe hydrogen effects), elongation at fracture and reduction of area. Table 2 summarizes the results.

Table 2. Tensile stress analysis on reference and loaded parts.

Materials	Hydrogen concentration (wt-ppm)		Traction Resistance (MPa)		Elongation (%)	
	Reference	H-charged	Reference	H-charged	Reference	H-charged
FC300	2.4 ± 0.3	4.0 ± 0.2	256 ± 24	268 ± 28	0.60 ± 0.17	0.58 ± 0.12
CGI450	1.0 ± 0.2	2.7 ± 0.3	384 ± 3	385 ± 18	1.60 ± 0.07	1.51 ± 0.22
CGI500HT	1.3 ± 0.2	3.0 ± 0.3	449 ± 6	425 ± 6	2.31 ± 0.19	2.21 ± 0.23

As results from Table 2 indicate, the level of hydrogen concentration was not enough to represent a differentiation on mechanical performance of materials. The level of hydrogen concentration found in these tests showed to be not sensitive to mechanical properties from cast iron alloys. However, as evaluated in [10], high strength steels can already face embrittlement issues at this level of hydrogen concentration as seen in Figure 4.

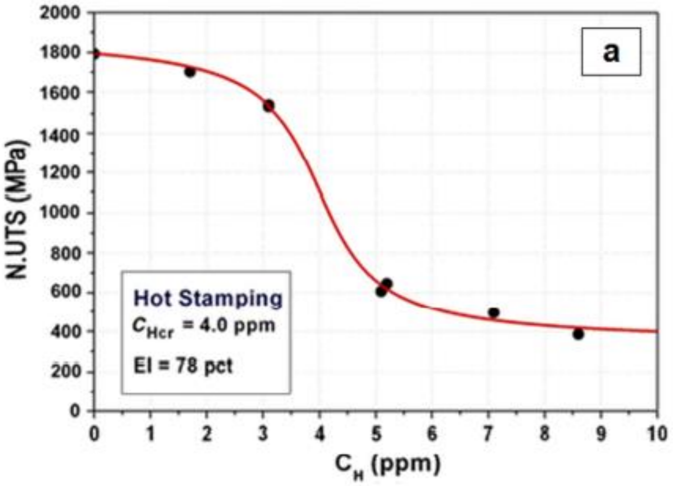

Fig. 4. Hydrogen embrittlement curve for high strength steel – extracted from [10].

Similar results are found in [11] with critical hydrogen concentration of 1-2 wt-ppm for Ultra-High-Strength Steel. In [12], different alloys of nodular cast iron were evaluated on different hydrogen concentration from 10 to 60 wt-ppm. Such variation of hydrogen absorption was given by different graphite diameters. Tensile strength indicated that in the same material, relevant tensile strength influence was found starting with 30 wt-ppm of hydrogen concentration, which is much higher than high strength steel and much higher than the levels found in the test assessment in Table 2.

2.3 Future tests for higher hydrogen contamination

Once the previous tests were not enough to create embrittlement, it is necessary to redesign tests to bring materials to this level. Two main routes are to be evaluated: cathodic charge and vessel with higher pressure, and higher hydrogen concentration for longer exposure time.

The cathodic charge will allow the achievement of very high levels of hydrogen concentration making sure to get significant tensile strength modification even for cast iron alloys. This is important to allow the verification of different behavior between different cast iron alloys, which can support the alloy design most recommended for high durability H2ICE. As mentioned at [12], graphite size plays an important role in hydrogen concentration, once graphite boundaries act like a hydrogen repository, delaying any embrittlement effect. Following the same rationale, the number of graphite particles and their shape are also important to define the best design to the application of parts on H2ICE. Temperature influence tends to facilitate the hydrogen entrance into the metal. However, variations are not expected to be strongly found on different engine operating condition. Thermal conductivity of the materials could be engineered to maximize the benefit between control the hydrogen penetration and facilitate the hydrogen to be released.

The vessel tests on harsh conditions will give also important results to identify potential limits of hydrogen concentration and its effect on metals to be found in H2ICE. Using the experience of labs working in the oil and gas industry, a preliminary vessel test was able to be performed with cast iron parts at 300bar with 100% Hydrogen gas maintained at 350 ºC for 341 hours. In this preliminary test, CGI450 material after hydrogen contamination showed certain mechanical properties variation compared to reference specimens from the same batch:

- 5% lower Yield Strength
- 10% lower Traction Resistance
- 25% lower Elongation

There is a high chance that a certain level of embrittlement was achieved due to significant reduction in elongation. More tests comparing other cast iron alloys as well as forged steel as a reference will be tested in similar conditions and different exposure time.

3 Conclusions and next steps

H2ICE is a promising carbon neutral solution for commercial vehicle transportation. Its high performance at full load conditions combined with lower cost and much higher durability are factors for a significant advantage to other carbon neutral solutions.

To assure the same durability for H2ICE as for Diesel ICE, hydrogen embrittlement must be assessed. From literature, it is known to be critical for high strength steels and better for cast iron alloys. An assessment with different cast iron alloys on vessel exposure with 20% hydrogen showed an increase in hydrogen content and even after 72 hours evaluation not all hydrogen was released after the test. The mechanical tests showed no significant influence of hydrogen contamination on the cast iron alloys. This is a promising result for current development of low pressure direct or indirect injection H2ICE alternatives.

Regarding high pressure direct injection, further evaluations are planned to achieve the limits of cast iron alloys to best define the most resistant solution for H2ICE applications. Bench tests with cathodic charge will address the comparison of alloys after embrittlement is achieved. As well high pressure and longer exposure tests on vessels will be performed as well to assess limits of the same mechanism identified for H2ICE. That will enable the design for specific alloys dedicated to H2ICE durability at the same level as Diesel.

A demonstrator H2 HPDI engine is running with the target to achieve more than 50% BTE. This will support further tests on actual application environment enabling direct comparison with stressed bench tests indicated before.

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