

# MSc Motorsport Engineering

## Hydrogen Embrittlement

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## Introduction

With a global push towards renewable sources of energy and a net zero carbon energy policy, hydrogen has emerged a leading contender for an alternative source of energy. However, hydrogen is known to be difficult to store and transport, in part due to damage caused by hydrogen embrittlement. In this assignment, the damage caused by this phenomenon will be investigated with regards to the structural damage caused, and the effects on the properties of ferrous and non-ferrous metals. The effect of hydrogen ingress during welding and casting will also be investigated, as well as the methods of examination used to assess the extent of damage caused by hydrogen sorption, including optical and electron microscopy. The origins of hydrogen both in it's natural state and in it's combined forms will also be explored.

## 1: Origins of Hydrogen

Hydrogen in its natural state occurs diatomically bonded as  $H_2$ . It is the most abundant element in the universe and was formed directly after the Big Bang when the universe was extremely hot and dense, due to its elemental makeup being a single proton (Harvard Center of Astrophysics, n.d.). Neutral hydrogen atoms formed roughly 370,000 years afterwards, after the universe cooled enough to allow electrons and protons to combine. On earth, hydrogen in its pure form is less abundant, only making up 0.5-1.0ppm of Earth's atmosphere, as hydrogen that enters the Earth's atmosphere quickly escapes the planet's gravity due to its lightness. This rarity is however contrasted by hydrogen's abundance in its combined forms, primarily in water, hydrocarbons, and biomass (Royal Society of Chemistry, 2025).

Therefore, in industrial applications, hydrogen is often manufactured on site (U.S. Department of Energy, n.d.), partly due to its abundance in combined forms and partly due to the difficulty of storing and transporting pure hydrogen gas. This allows for energy to be produced using this stored hydrogen. This energy production comes from a myriad of techniques that range in environmental sustainability. The electrolysis of water is among the most sustainable, given water's abundance and the fact that negligible carbon is emitted. Biomass, on the other hand, can be burned to release hydrogen, which, while renewable, is polluting. Hydrocarbons can also be burned to release hydrogen (U.S. Energy Information Administration, 2023), which is naturally significantly less sustainable.

An example of this is where hydrogen is sourced from natural gas, where it is reacted with high temperature steam to form synthesis gas. This is the cheapest, most efficient, and therefore most common method for hydrogen synthesis (U.S. Department of Energy, n.d.), and is the most common method for hydrogen production in the USA, for example. Hydrogen gas can also be produced in a process called gasification, where coal or biomass is reacted with high temperature pressurised steam and oxygen, which produces hydrogen and carbon monoxide, that can be reacted further to separate the hydrogen. These processes however, while cheap, do consume fossil fuels and thus should be moved away from in the long term in order to achieve a net zero carbon future. However, they serve a purpose in reducing the cost of obtaining hydrogen for early adoption of this technology.

## 2: Structural changes due to hydrogen absorption

Structural changes occur in metals when hydrogen is absorbed. Hydrogen is of an extremely small atomic size and so can easily penetrate a metal's lattice structure. This damage occurs in a variety of ways that are often all referred to as hydrogen embrittlement.

Hydrogen embrittlement itself occurs when atomic hydrogen interacts with a metal already under mechanical stress and induces crack growth. One hydrogen-induced method of weakening metals is high temperature hydrogen attack (HTHA), which occurs in steels above 204°C (Ali, Ul-Hamid, Alhems, & Saeed, 2020). This involves the formation of methane gas pockets within the metal, resulting in discontinuities in the metal lattice structure. Other hydrogen induced structural damage includes metal hydride formation, which doesn't occur in steel but primarily affects alloys of group five metals (Turnbull, 2020). This is where hydrogen forms brittle hydrides with the parent metal in the region of stress concentration at the crack tip, significantly weakening the metal.

When hydrogen affects the metal in the liquid state, hydrogen can occupy space within the metal lattice structure, and diffuse out once the metal has cooled, resulting in the formation of voids and discontinuities that weaken the metal. This is referred to as blistering and reduces the ductility and tensile strength of the affected metal (Martin & Sofronis, 2022). It can occur due to damp welding rods or malpractice in the installation of electroplating, however it has also been suggested that it is the same phenomenon as hydrogen induced cracking, given their similarity and that they are often found together (Martin & Sofronis, 2022).

In relation to moving towards a net-zero energy policy, hydrogen has been proposed as one of the primary energy solutions. This presents the difficult problem of storing hydrogen, which, given its gaseous nature at atmospheric temperature and pressure, requires holding it in pressurised tanks or cryogenically (Moradi & Groth, 2019). Even still, hydrogen still leaks through most materials due to its small molecular size, and is able to damage the material it is stored in. Due to the high pressure storage, this presents a safety issue for the storage of hydrogen, which is sometimes solved by using materials such as carbon fibre in hydrogen tank manufacture (Hyfindr, 2024).

### **3: Metallographic Examination**

Metals have to be examined to assess the effects of structural damage, to ensure that the structures and components manufactured remain fit for purpose. This remains true for metals affected by hydrogen damage, and microscopy is often used to assess for this damage.

#### **3.1: Optical Microscopy**

Optical microscopy can be used to assess damage caused by hydrogen sorption. For example, scattering scanning near-field optical microscopy (s-SNOM) can be used to investigate hydrogen sorption in magnesium nanostructures (Linnenbank, Sterl, Steinle, Morz, & Giessen, 2017). This technique is used to its high resolution, and the effect of hydrogen absorption on the scattering properties of the nanostructure can be observed clearly. In this case, magnesium is being investigated as a method of storing hydrogen, where it can be hydrogenated into  $\text{MgH}_2$  for easier storage, and dehydrogenated again when necessary. This is one of the solutions proposed to increase hydrogen's viability as an alternative energy source as industries strive towards net zero carbon emissions.

#### **3.2: Electron Microscopy**

Electron microscopy is also used to monitor hydrogen absorption. For example, transmission electron microscopy (TEM) is can be used to create high-resolution images of the internal structure of materials, allowing the study of a material's molecular structure including any discontinuities caused by hydrogen absorption (Decamps, Joubert, Cerny, & Percheron-Guegan, 2005). In the Decamps study, this analysis is done on dislocations caused by the cyclic absorption and desorption of hydrogen stored in containers mainly made up of  $\text{LaNi}_5$ .

## 4: Effect on Properties of Ferrous Metals

Hydrogen tends to negatively affect the structural properties of ferrous metals. The extent of hydrogen absorption has been shown to be dependent on the nature of the crystal structure of the steel. This is manifested in that the extent of hydrogen diffusion in austenitic steels is roughly four times smaller than that in ferritic and martensitic steels (Murukami & Matsunaga, 2006).

One way in which hydrogen can be absorbed in steels is that hydrogen atoms can become lodged at the core of a screw dislocation, which increases its potential for worsening (Hirth, 1980), (Berthier, Longa, Creuze, & Legrand, 2024). This dislocation results in the metal softening even at room temperature, weakening it. Hydrogen also accelerates the growth of cracks generated via fatigue (Chen, et al., 2024). These cracks propagate further and lead to sudden catastrophic failure of the affected part if gone unnoticed by NDT techniques. Hydrogen affects these areas by absorbing into the metal due to its atomic size, and while the exact mechanisms are not yet fully understood, it can be observed that hydrogen plays a crucial role in crack propagation in the early stages of the crack growth process (Murukami & Matsunaga, 2006). However, as mentioned above, the extent of the effect of hydrogen is dependent on the nature of the steel.

Hydrogen's affects on steel alloys are not always detrimental however, as hydrogen exposure can result in increased yield strength and ductility, facilitating some resistance to fracture. This has been observed particularly in materials with higher hydrogen solubility, such as face-centred cubic (FCC) iron and steels. In this case, hydrogen exposure was shown to reduce the effects of ductile dimple rupture, showing ductile fracture (Chen, et al., 2024).

## 5: Effect on Material Processing

Hydrogen can also negatively affect the mechanical properties of metals if absorbed during the casting process, particularly in aluminium casting. When hydrogen dissolves into the liquid metal, it can cause porosity when the metal cools to a solid, leaving voids where the hydrogen occupied space in the liquid metal (Yaktiti, et al., 2023). This reduces the component's tensile strength and also reduces its ductility (Du Plessis, Yadroitsava, & Yadroitsev, 2020).

Hydrogen absorption can also affect metals during the welding process. Hydrogen can be absorbed during the welding process in numerous ways, however typically it occurs in the form of moisture, H<sub>2</sub>O. This can come in the form of atmospheric humidity, simple dampness or wetness, or in the form of greases, oils, paints, and other coatings (Hobart Brothers, 2024). Hydrogen is able to escape from the weld while it is hot in its liquid form, however once the weld has cooled it is more difficult for it to escape. When hydrogen collects in these areas over time, it can cause cracking in the base metal or in the weld itself, which naturally leaves the weld and part weakened (Hobart Brothers, 2024). This increased risk is due to the weld creating microstructural inconsistencies and dislocations within the metal, which provides greater opportunity for hydrogen damage (Zhou, Ren, Yokagawa, Xue, & Li, 2024). Metals with higher carbon or alloy levels are at greater risk of hydrogen-induced cracking, and this is due to the presence of martensite, a particularly brittle and therefore more crack sensitive metal microstructure. This structure may occur during the formation of steel, but it can also form during the weld, especially if the weld cools too rapidly (Hobart Brothers, 2024). Furthermore, hydrogen atoms tend to accumulate at the phase boundary of the metal, which leads to further hydrogen-induced crack propagation (Zhou, Ren, Yokagawa, Xue, & Li, 2024).

## Conclusion

In conclusion, hydrogen is a promising renewable source of energy that can be used to help move industry towards a net zero carbon energy policy, especially given its abundance in combined forms, where it may be extracted primarily through the electrolysis of water. However, the storage and transport of hydrogen present difficulties due to the small size of monoatomic hydrogen. This can be mitigated by producing it in situ, however hydrogen still diffuses into metals and causes damage at all stages of production and use. This usually weakens the metal, reducing tensile strength and ductility, and promoting crack formation and propagation, resulting in eventual failure. Hydrogen absorption can also accelerate crack growth in welds, and increase porosity in metal castings, particularly in cast aluminium. Therefore, care must be taken to mitigate these problems presented by the handling of hydrogen in order to increase its viability as an alternative source of energy, and further research should be undertaken to better understand the full extent of the effects of hydrogen sorption on metals and materials common in industry.

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