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Hydrogen Embrittlement

Mechanisms of Material Failure ACEA7010

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Abstract

This report investigates hydrogen absorption and embrittlement in metals, with a specific focus on their implications for welding and hydrogen transport pipelines. It provides a concise overview of hydrogen's origins—both in its natural state and combined forms—and details the structural changes that occur in metals upon hydrogen absorption in both liquid and solid states. Metallographic examinations via optical and electron microscopy reveal microstructural modifications and hydrogen trapping phenomena, while the effects on mechanical properties of ferrous metals are evaluated.

Additionally, the report highlights how hydrogen absorption adversely impacts fabrication processes such as welding. Complementary computational models are discussed to predict weld structural integrity under hydrogen exposure. Overall, the study addresses critical aspects of hydrogen-induced fracture, fatigue, creep, and environmental degradation, aligning with the objectives to examine underlying mechanisms and apply analytical techniques to predict material behavior.

1. Background

Natural hydrogen has been extensively studied in the recent decades, notably after the discovery of hydrogen-rich fluids at midocean ridges (Wang et al., 2023). But way back in the early 1500s the alchemist Paracelsus noted that the bubbles given off when iron filings were added to sulfuric acid were flammable. In 1671 Robert Boyle made the same observation. Neither followed up their discovery of hydrogen, and so Henry Cavendish gets the credit. In 1766 he collected the bubbles and showed that they were different from other gases. He later showed that when hydrogen burns it forms water, thereby ending the belief that water was an element. The gas was given its name *hydro-gen*, meaning water-former, by Antoine Lavoisier (Royal Society of Chemistry, 2011).

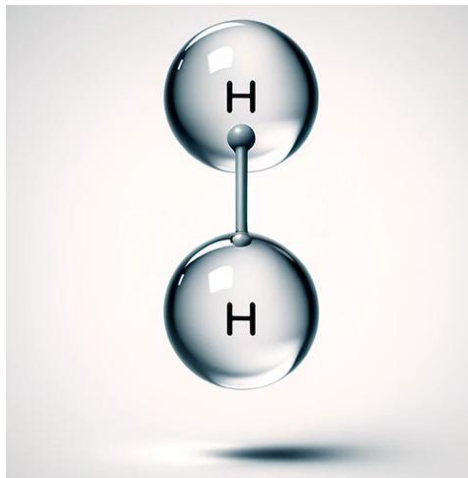


Figure 1 Visual Representation of a Hydrogen Molecule (IMECHE, 2024)

From its initial discovery, hydrogen found several early applications. One of the most notable was its use in ballooning, pioneered by the Montgolfier brothers in the late 18th century. This era marked the beginning of hydrogen's journey as a versatile element, transcending from mere scientific curiosity to a practical component in transportation. Its unique properties, such as lightness and flammability, made it an intriguing subject for further exploration and use in various fields (IMECHE, 2024).

Natural hydrogen has not only played a vital role in our historical and technological narrative but also occurs naturally through various processes on Earth. Beyond its early scientific observations and practical applications such as ballooning, hydrogen is continuously generated in nature. Its formation, as illustrated in Figure 2, involves both biological processes—such as the decomposition of organic matter and fermentative activities—and

abiotic processes including radiolysis and direct water reduction. Among these, serpentinization stands out as the most significant abiotic mechanism, occurring when water interacts with ultramafic rocks. These low-silica rocks, rich in reduced metals, predominantly consist of iron and magnesium minerals, with olivine (a solid solution of fayalite, Fe_2SiO_4 , and forsterite, MgSiO_4) serving as a principal constituent, alongside other minerals like pyroxene.

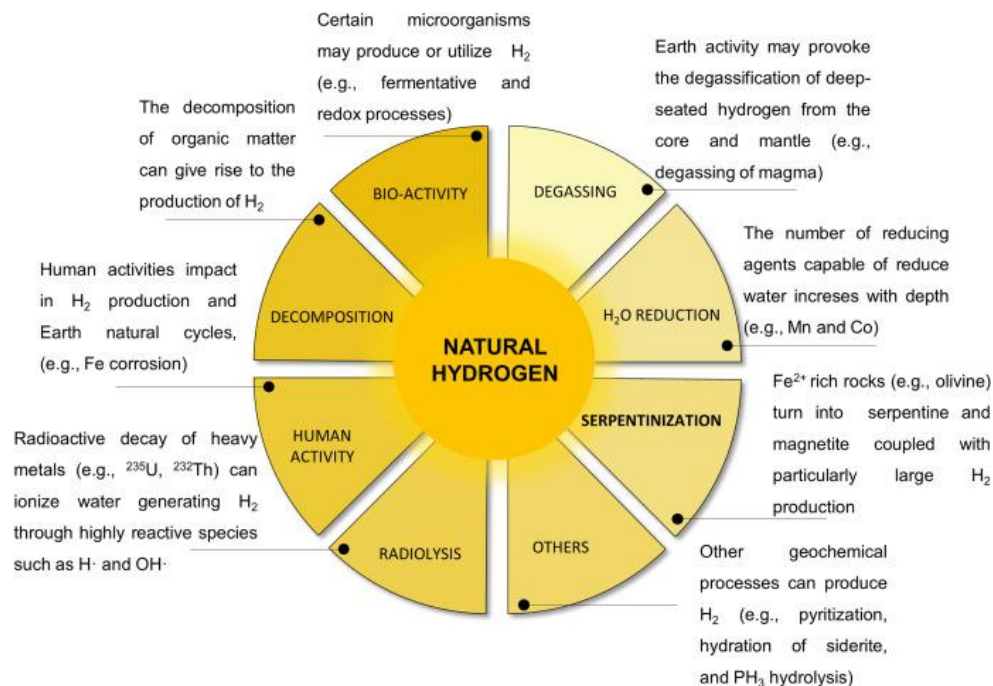


Figure 2 Different hypotheses about the origin of natural hydrogen deposits. Although the formation of natural hydrogen seems to have a primarily abiotic origin, other theories about its genesis are being considered.

Now days hydrogen has emerges as a key player in the energy sector, particularly with the development of fuel cells in the mid-20th century. These cells, which convert the chemical energy of hydrogen into electricity, revolutionized our approach to clean energy. Their applications range from powering vehicles to providing electricity in remote locations, underscoring hydrogen ´s potential as an alternative to fossil fuels (IMECHE, 2024).

But even looking at the history of hydrogen there are many uses for hydrogen as: fuel, a source of energy, an energy carries, reducing agent, and many more but there is an small sector which hydrogen is not well accepted and is when HE happens or Hydrogen embrittlement occurs which is a type of stress corrosion cracking that occurs when hydrogen atoms are absorbed into a metal, causing it to become brittle and fracture (Office of Energy Efficiency & Renewable Energy, 2024).

2. Hydrogen Absorption

2.1 Impact of Hydrogen Embrittlement: Cases & Possible Causes

Now days hydrogen has become in the industry of metals in both liquid and solid states, “The silent Killer”. The deterioration of metals due to hydrogen infiltration is not a recent discovery—it was first documented in 1875, more than a century ago. However, the potential hazards associated with hydrogen embrittlement, particularly in mechanical fasteners or other type of metals, still require much more thorough scrutiny (www.bossard.com, 2024).

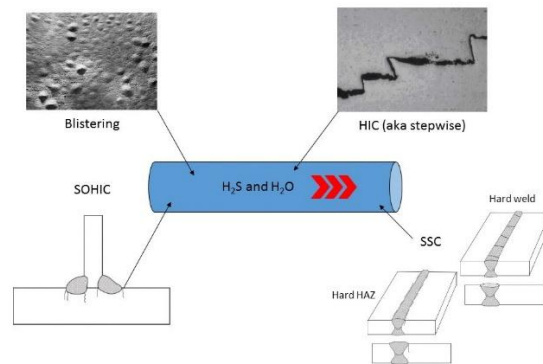


Figure 3 Types of defects due to hydrogen embrittlement (Frend, 2016)

Atomic hydrogen, is known as the smallest atom in then periodic table and as such it is small enough to diffuse readily through a metallic structure, mentioned before. When the crystal lattice is in contact or is saturated with atomic hydrogen, the mechanical properties of many metals and alloys are diminished (Roberge, 2008).

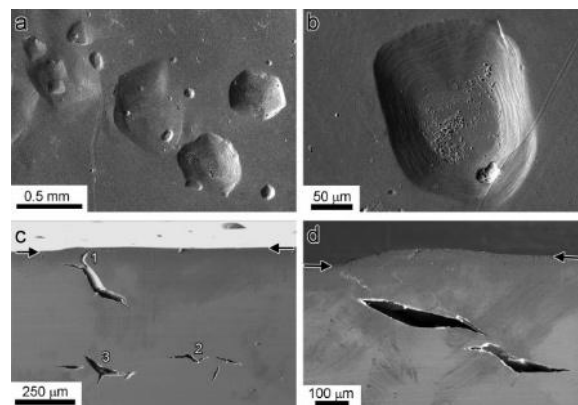
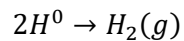


Figure 4 Scanning Electron Mycroscopy micrographs showing blisters and crack morphologies. (a) Low magnification view of blisters on sample surface. (b) Higher magnification of a large blister on the sample surface (Tiegel et al., 2016).

According to Pierre R. Robert stating in the book of corrosion engineering, principles and practices, Nascent atomic hydrogen can be produced as a cathodic reaction, either during natural corrosion processes or forced by cathodic protection, when certain chemical species are present which act as negative catalysts (i.e., poisons) for the recombination of atomic to molecular hydrogen as shown in Eq. (1).



When the formation of molecular hydrogen is suppressed, freshly generated atomic hydrogen may instead migrate into the tiny gaps within the metal rather than being released harmlessly as a gaseous byproduct. Various chemical species can inhibit this recombination process—for example, cyanides, arsenic, antimony, or selenium compounds. However, the most frequently encountered inhibitor is hydrogen sulfide (H_2S), which is generated during many natural decomposition processes and in numerous petrochemical operations. Environments or processes that involve wet hydrogen sulfide (commonly referred to as sour services) and a high incidence of sulfide-induced hydrogen induced cracking (HIC) can result in sulfide stress cracking (SSC).

This issue has consistently posed challenges during the exploration and exploitation of oil and gas fields and is addressed by many international standards. Similar problems occur in any context where wet hydrogen sulfide is present, such as in acid gas scrubbing systems, heavy water plants, and wastewater treatment facilities.



Figure 5 Tank Joint Welding - Oil Storage Tanks (Casagrande Júnior, 2025)

Field failures have been reported when storage tank roofs, saturated with hydrogen due to corrosion, experienced a sudden pressure surge, leading to the brittle failure of circumferential welds. On rare occasions, even materials like copper and Monel 400 (N04400) have suffered from HIC (Roberge, 2008). Even hydrogen can pose a severe problem with welds by the diffusion of hydrogen to the highly stressed, hardened of the weldment, most of the hydrogen cracks are to be found in the parent metal and the types found in welds are the ones shown in figure 3.

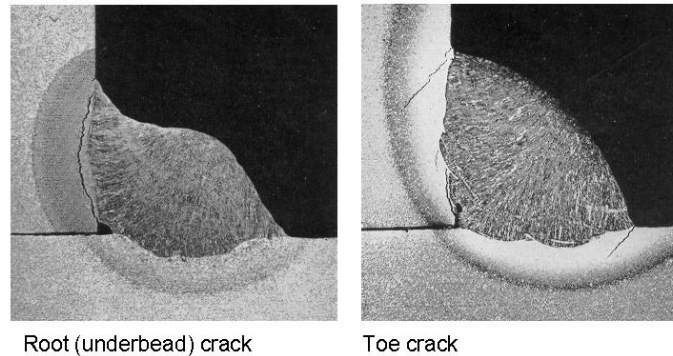


Figure 6 Hydrogen Induced Crack types (The Piping Engineering World, n.d.)

From the previous example of the brittle failure of circumferential welds or in the grain-coarsened region of the HAZ, and known as cold cracking, delayed cracking or under-bead / toe cracking, the combination of four factors is necessary to cause hydrogen cracking:

1. Hydrogen level above 15ml/100 g of weld metal deposited
2. Stress over 0.5 of the yield stress
3. Temperature below 300 Degree Celsius
4. Susceptible micro-structure above 400 HV hardness

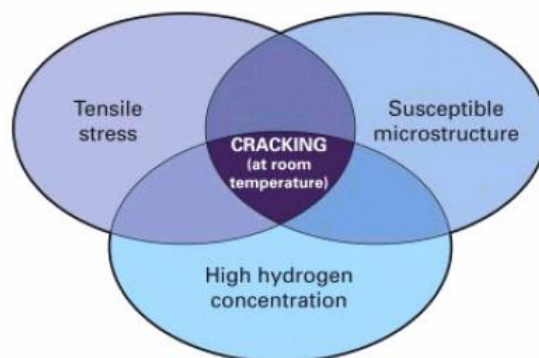


Figure 7 Factor for Hydrogen Induced Cracks (The Piping Engineering World, n.d.)

Another example of this problem is seen in fasteners where hydrogen-induced cracking does not occur immediately after assembly but is delayed—manifesting hours, days, or even weeks later. This delayed failure makes it extremely challenging to detect hydrogen embrittlement during in-process inspections or final quality checks. More often than not, products have already been assembled and shipped by the time the issue becomes evident, leading to costly product recalls and potentially devastating damage to brand reputation (www.bossard.com, 2024).

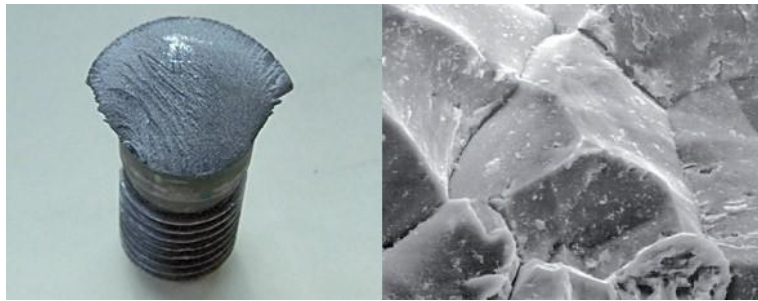


Figure 8 Hydrogen Embrittlement in fasteners (AYA, 2024)

Several commonly techniques for detecting hydrogen embrittlement include:

1. Slow strain test: In this method, the specimen is initially deformed to a predetermined strain level at room temperature. It is then further loaded at a slow rate to determine if a fracture occurs. Materials suffering from hydrogen embrittlement are more likely to fracture at these reduced strain rates.

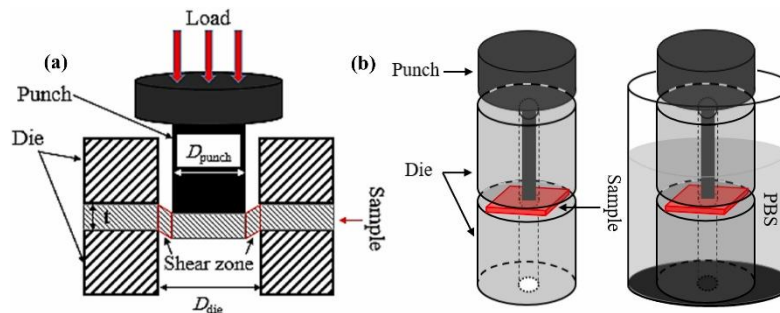


Figure 9 (a) Schematic illustration of SPT setup and (b) SPT die-punch-sample set in the air and inside the PBS (Faraji et al., 2022)

2. Barcol hardness test: By applying a load on the sample and then measuring the hardness, observe whether there are abnormal hardness values. Hydrogen embrittlement usually results in an abnormal increase in hardness.



Figure 10 Field Hardness Tester for GRP and FRP Composites (Moisturemeters.co.uk, 2025)

3. Hydrogen transmission test: Immerse the sample in an acidic medium and observe whether hydrogen gas is released. Hydrogen embrittlement materials release hydrogen gas in acidic environments.

2.2 Atomic Dislocation related with Hydrogen Absorption

Atomic dislocations play a critical role in modulating hydrogen uptake and diffusion within metals. By serving as effective traps for hydrogen atoms, the dislocation networks—particularly those formed during cold rolling (CR)—can enhance resistance to hydrogen embrittlement without altering the grain size. This section elucidates how variations in dislocation density, induced by CR, influence hydrogen permeation behavior.

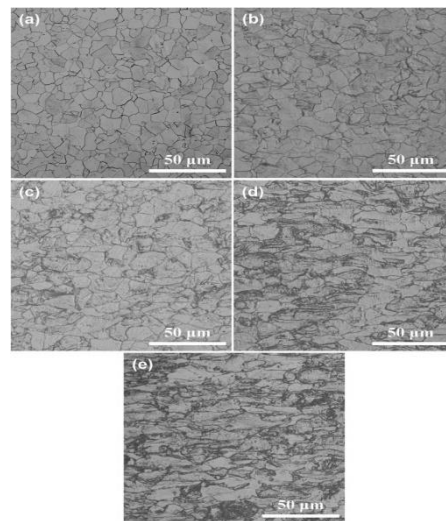


Figure 11 The grain size and morphology of the samples with CR (Cold Rolling) deformation amounts of 0%, 30%, 50%, 70% and 80% (Chen et al., 2020).

According to the article (Chen et al., 2020), Figure 10 shows the consistency which confirms that any observed changes in hydrogen permeation behavior are predominantly due to the increased dislocation density rather than alterations in the grain boundary structure.

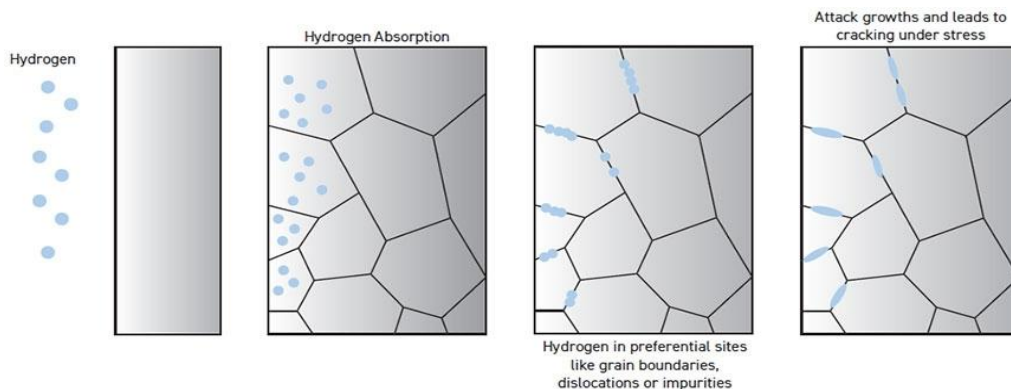


Figure 12 Hydrogen atoms in grain boundaries or impurities (Hannifin, 2015)

Finally, the increased CR delays the breakthrough time (t_b) and reduces the diffusion coefficient (D) of hydrogen under constant grain size conditions, underscoring the effective trapping of hydrogen by dislocations. Additionally, it was observed that D is positively correlated with the amount of hydrogen ion adsorption on the surface. These findings highlight that the enhanced dislocation density resulting from CR significantly alters hydrogen permeation behavior, offering valuable insights into strategies for mitigating hydrogen embrittlement.

2.3 Metallographic Examination

To comprehensively examine the effects of hydrogen absorption on metals, a dual approach was adopted using both optical and electron microscopy. Optical microscopy provides an initial, broader view of microstructural changes—such as variations in phase boundaries, hydrogen trapping, and diffusion patterns—in materials like duplex stainless steel compared to their lean-duplex counterparts. In contrast, electron microscopy offers a higher resolution analysis, capturing nanoscale phenomena that are critical to understanding hydrogen-induced modifications. Together, these complementary techniques enable a thorough characterization of hydrogen embrittlement from both the mesoscale to the nanoscale, laying the groundwork for deeper insights into the underlying mechanisms and their implications for material performance.

Optical Microscopy

In examining hydrogen absorption and diffusion using optical microscopy, it has been observed that duplex stainless steel weld metal features a reduced distance between its austenite–ferrite phase boundaries. The smaller distance between the austenite–ferrite phase boundaries exists and not only increases the hydrogen trapping tendency. Essentially, the total hydrogen concentration in the material is largely determined by the hydrogen trapped within the austenite and at these austenite–ferrite interfaces. Consequently, within the temperature range of 650 °C to 900 °C, the duplex stainless steel weld metal exhibits a higher amount of hydrogen effusion (1.4462) compared to the lean-duplex stainless steel weld metal (1.4162) (Brauser and Kannengiesser, 2010).

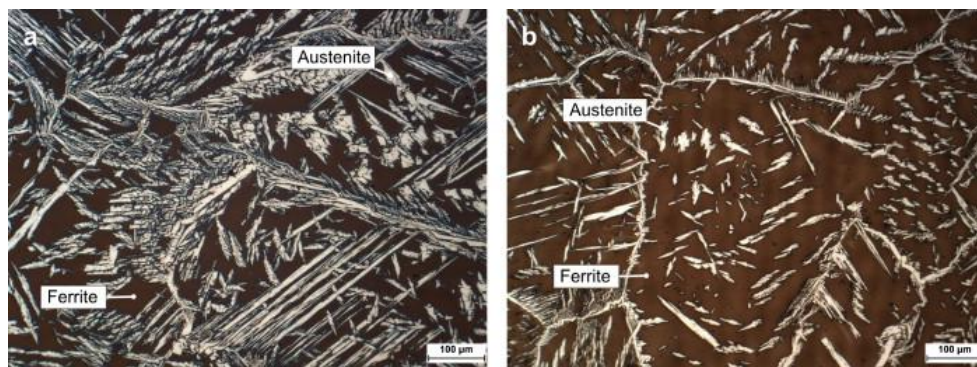


Figure 13 Microstructure of a) duplex stainless steel weld metal (1.4462) and b) lean-duplex stainless steel weld metal (1.4162), with austenite (white) on grain boundaries and inside the ferrite grains; lean-duplex stainless steel (1.4162) weld metal shows less (Brauser and Kannengiesser, 2010)

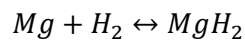
This analysis underscores the importance of examining hydrogen absorption in duplex stainless steel weld metals for future studies on failure detection and maintenance. The varying levels of hydrogen absorption in these materials provide early indicators of potential performance issues, which can guide material selection and predict outcomes for different service conditions.

Electron Microscopy

In the next phase of the metallographic examination, electron microscopy is employed to further investigate and confirm the presence of hydrogen embrittlement. This approach provides a higher resolution view of the microstructural changes, allowing for the identification of features such as fine microcracks, localized phase transformations, and other nanoscale phenomena that are indicative of hydrogen-induced damage. By correlating these detailed observations with those obtained via optical microscopy, the aim is to build a more comprehensive understanding of how hydrogen interacts with the weld metals and potentially compromises their integrity in service. The following example is taken from *Electron Microscope Investigation on Hydrogen Storage Materials* (Ma et al., 2020).

The use of metal hydrides in the Mg–H system is considered among the metallic storage media options. Magnesium is regarded as a promising candidate due to its hydrogen storage capacity of up to 7.6 wt%, which, in simple terms, means it can store hydrogen equivalent to 7.6% of its own weight.

The hydrogenation of metals or alloys can be represented by the following reaction:



Furthermore, Nanostructured forms of magnesium—such as nanofibers (NF), nanoparticles (NP), and particles confined on nanostructured substrates—are artificial constructs compared with bulk Mg metal. In the case of one-dimensional Mg nanostructures, Chen et al. reported the growth of Mg nanowires with diameters ranging from 30 nm to 170 nm via a vapor-transport method. After 10 hydriding/dehydriding cycles, the nanowire morphology of sample 1 collapsed into nanoparticles. Notably, sample 1 demonstrates the fastest hydrogen absorption–desorption rates across different temperatures when compared with samples 2 and 3. The thinner the nanowires, the lower the desorption energy, suggesting that the kinetics and thermodynamics could be further optimized when the diameters are reduced below 30 nm.

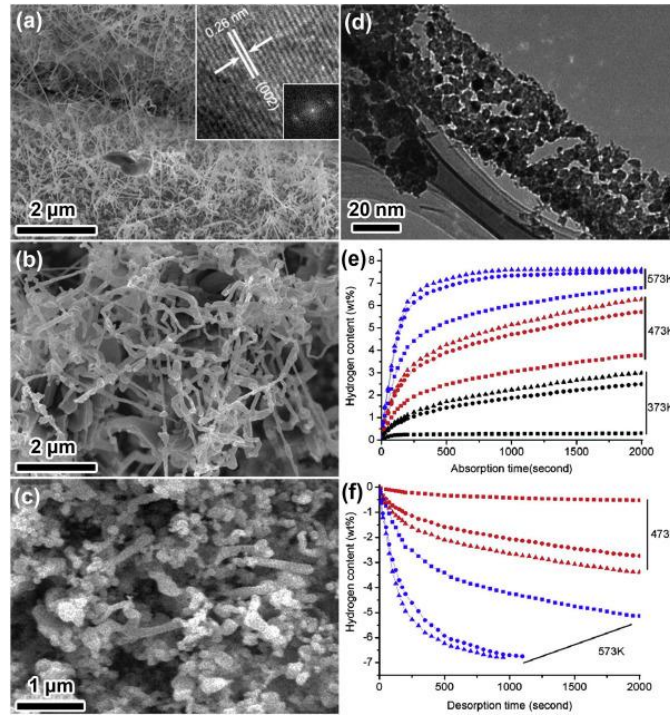


Figure 14 SEM images of Mg nanowires: sample 1 to 3 and (a) to (c); TEM images of Mg nanowires after dehydrogenation(d); Hydrogen absorption (e) and desorption properties (f) of Mg nanowires at different temperatures (sample 1, triangle; sample 2, circle; and sample 3, square) (Ma et al., 2020).

Electron microscopy, as illustrated in the example from Ma et al. (2020), reveals detailed insights into hydrogen absorption at the nanoscale. The images demonstrate how nanostructured forms of magnesium, particularly the nanowires, evolve under repeated hydriding/dehydriding cycles—highlighting critical changes in morphology and hydrogen desorption rates. Although such high-resolution techniques are not typically employed for routine inspection in industrial settings (such as in pipelines, storage tanks, or fasteners) due to their complexity and cost, they provide invaluable information. This advanced approach deepens the understanding of hydrogen trapping and diffusion mechanisms, offering a powerful tool for investigating hydrogen embrittlement and informing strategies for material design and failure prevention.

2.4 Utilizing Computational Power to Predict Weld Structural Integrity

This section explore how computational methods can predict weld structural integrity in hydrogen transport pipelines, building on the experimental insights gained from metallographic examinations. A study by Mandal et al. is highlighted, where welding process modelling is integrated with deformation-diffusion-fracture simulations to forecast seam weld failure under hydrogen exposure. These computational predictions complement earlier findings on hydrogen absorption and embrittlement, offering a robust framework to assess and enhance the safety of hydrogen transport infrastructures based on both experimental and simulation data.

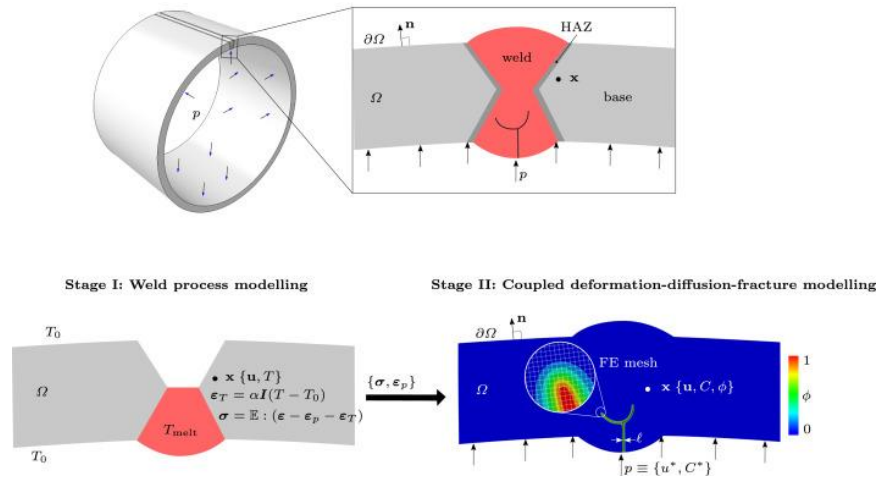


Figure 15 Schematic representation of the finite element modelling framework (Mandal et al., 2024).

In Figure 12 illustrates a two-stage finite element modeling framework designed to predict hydrogen-assisted failures in welded pipeline joints under internal pressure (p). In the first stage, the welding process is simulated, beginning with the formation of a weld bead at its initial melting temperature (T_{melt}). This stage captures key phenomena such as temperature distribution and the development of residual stresses, which are critical in determining the material's microstructural susceptibility to hydrogen absorption.

In the second stage, a coupled multiphysics phase field formulation is used to simulate the nucleation and growth of cracks, accounting for the effects of hydrogen diffusion and mechanical stresses. Together, these stages offer a comprehensive approach to predict how

hydrogen promotes crack initiation and propagation in weld joints, providing valuable insights for ensuring the structural integrity of pipelines in hydrogen-rich environments (Mandal et al., 2024).

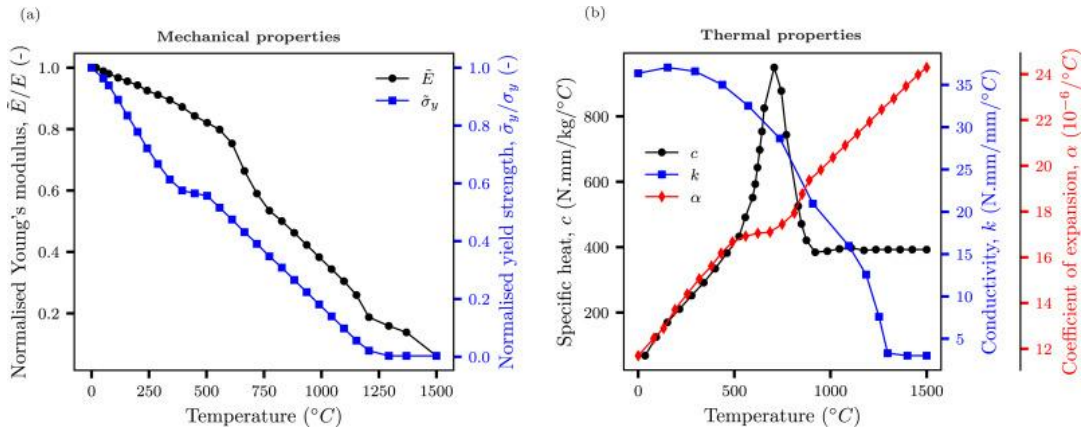


Figure 16 Temperature-dependence of the material properties of carbon steel SA-516 Grade 70 (Mandal et al., 2024)

Figure 13 displays the temperature-dependent properties of carbon steel SA-516 Grade 70. In panel (a), the normalized mechanical properties, Young's modulus (E) and yield strength (σ_y), are presented relative to their room temperature values, with Celcius representing the temperature-dependent parameter.

This normalization illustrates how the material's stiffness and strength change as temperature increases. In panel (b), the thermal properties, including specific heat (c), thermal conductivity (k), and the coefficient of thermal expansion (α), are depicted as functions of temperature, providing insight into how the material's ability to store and transfer heat, as well as expand, evolves with temperature (Mandal et al., 2024).

Understanding these temperature-dependent properties is crucial for hydrogen absorption because they directly affect the material's behavior under thermal loads, such as those encountered during welding. Variations in mechanical properties influence the development of residual stresses and microstructural defects, which in turn can act as trapping sites for hydrogen atoms. Similarly, thermal properties govern the distribution of heat during welding, where rapid cooling or non-uniform temperature gradients can lead to microcracking and additional stress concentrations.

3. Conclusion

This investigation critically examined the causes, effects, and mechanisms of hydrogen-induced degradation in metals, with particular emphasis on fracture, fatigue, and creep phenomena associated with hydrogen embrittlement. The study traced the origins of hydrogen—from its natural occurrence in both elemental and combined forms—to its role in altering microstructures during absorption. Detailed metallographic analyses using both optical and electron microscopy revealed subtle yet significant changes in the microstructure and mechanical properties of ferrous metals, while complementary computational models provided insight into welding process dynamics under hydrogen exposure, capturing thermal effects, residual stresses, and crack propagation mechanisms.

Beyond the core findings, awareness must rise to potential preventive measures against hydrogen embrittlement. The observed degradation mechanisms suggest that cracking and subsequent failure might be mitigated through controlled processing parameters. Strategies such as preheating, maintaining specific inter-pass temperatures, and applying post-weld heat treatments can reduce cooling rates, facilitate hydrogen effusion, and minimize residual stresses. Moreover, optimizing welding processes—by selecting appropriate consumables, employing multi-run or hot pass techniques, using austenitic or nickel fillers, and utilizing dry shielding gases—can further diminish the susceptibility to embrittlement. These approaches, although not directly addressed in the primary investigation, are crucial for developing robust prevention mechanisms in future applications.

Collectively, the findings of this report underscore the importance of integrating experimental observations with advanced computational modeling to predict material behavior in hydrogen-rich environments. By critically examining the underlying degradation mechanisms and considering additional strategies for controlling hydrogen uptake—such as optimizing thermal management and welding parameters—a comprehensive framework is established. This framework not only enhances the fundamental understanding of hydrogen embrittlement but also lays the groundwork for developing effective preventive measures, thereby ensuring the durability and safety of critical infrastructures in the pursuit of a net zero energy policy.

Word Count: 3,180

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