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Review

Material Challenges and Hydrogen Embrittlement Assessment for Hydrogen Utilisation in Industrial Scale

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Abstract: Hydrogen has been studied extensively as a potential enabler of the energy transition from fossil fuels to renewable sources. It promises a feasible decarbonisation route because it can act as an energy carrier, a heat source, or a chemical reactant in industrial processes. Hydrogen can be produced via renewable energy sources, such as solar, hydro, or geothermic routes, and is a more stable energy carrier than intermittent renewable sources. If hydrogen can be stored efficiently, it could play a crucial role in decarbonising industries. For hydrogen to be successfully implemented in industrial systems, its impact on infrastructure needs to be understood, quantified, and controlled. If hydrogen technology is to be economically feasible, we need to investigate and understand the retrofitting of current industrial infrastructure. Currently, there is a lack of comprehensive knowledge regarding alloys and components performance in long-term hydrogen-containing environments at industrial conditions associated with high-temperature hydrogen processing/production. This review summarises insights into the gaps in hydrogen embrittlement (HE) research that apply to high-temperature, high-pressure systems in industrial processes and applications. It illustrates why it is still important to develop characterisation techniques and methods for hydrogen interaction with metals and surfaces under these conditions. The review also describes the implications of using hydrogen in large-scale industrial processes.

Keywords: hydrogen interaction; industrial processes; mechanical properties

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1. Introduction

The global energy transition from fossil fuel to renewables and hydrogen is driven by both environmental motivation and economic considerations, which have gained international momentum in recent years. One of key challenges which has been identified in development of new technologies dealing with hydrogen production and hydrogen processing is the development of materials capable of sustained operation in the specific operational conditions, including high temperature, high pressure, and atmospheres which include pure hydrogen or hydrogen in mixtures. The risks and challenges of materials processed with hydrogen need further study. This includes varying concentrations of hydrogen–syngas mixtures and their effect on current industrial infrastructure, such as pipeline systems typically used in high-strength applications [1]. Another example is hydrogen embrittlement, an understanding of which is crucial to ensure the safety of structures used in engineering applications. Hydrogen embrittlement is also extremely important in the longevity and robustness of industrial reactors, burners, welds and pipelines [2].

As metals and alloys are used across every aspect of the hydrogen value chain, it is crucial to understand the short- and long-term interactions of hydrogen with metal surfaces. Factors known to influence hydrogen interaction with materials include environmental, mechanical, chemical, and material aspects [3]. A wide range of studies and scientific opinions have been developed to evaluate possible mechanisms and hydrogen interaction models [3–7]. The most commonly agreed-upon factors influencing the longevity of materials in hydrogen environments include the specific microstructure of the material, the origin and introduction method of the hydrogen, the hydrogen volume concentration, the distribution of hydrogen over the material surface, and environmental parameters [6,8–12]. Most of these approaches are evaluated at laboratory scale, and useful conclusions from these need to be translated to scaled-up, industrial processes at highly specific processing conditions. What further commonly complicates matters in industrial processes is that more than one mechanism of hydrogen interaction with surfaces occurs simultaneously [13]. Therefore, developing a comprehensive understanding requires a multidimensional approach, as represented in Figure 1.

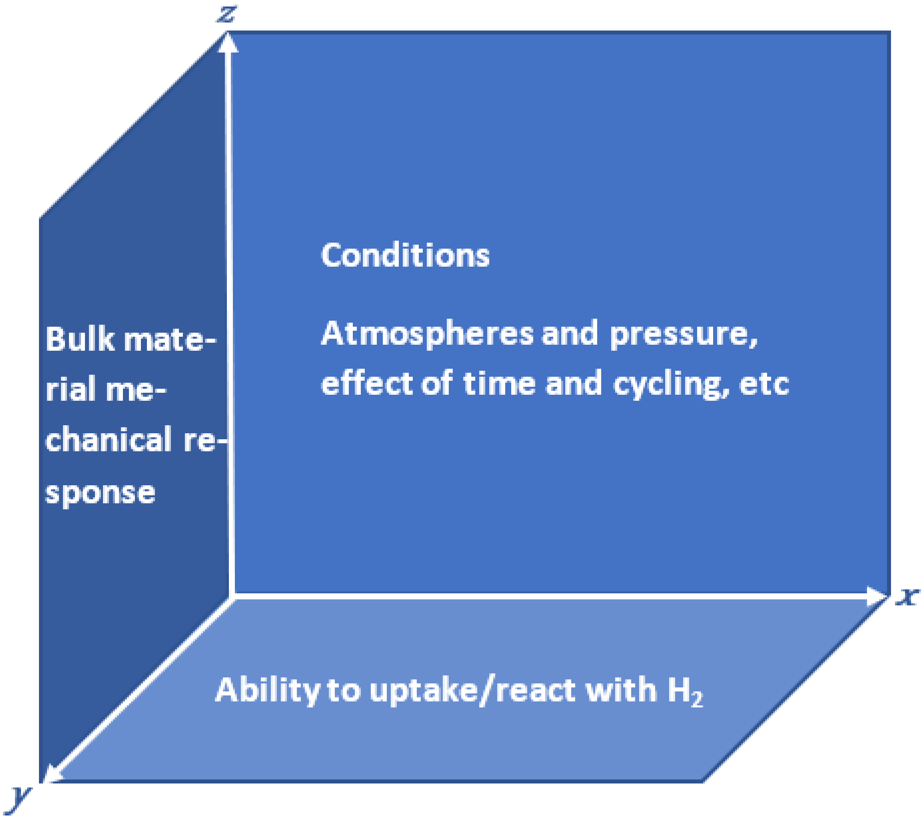

Figure 1. Graphical 3D representation of the main components needed to fully understand and characterise the effect of hydrogen on materials in industrial applications.

The first question to consider is how hydrogen interacts and reacts with metal surfaces and subsequently diffuses through different metal lattices. The second aspect is whether these reactions and interactions occur only on the surface or throughout the bulk of the metal, and which phenomena affect the mechanical properties of the metals. Lastly, what is the impact of industrial processing conditions on these aspects?

The influence of temperature, pressure, continuous long-term use of metals, and start-up/shut-down cycles is generally not related to the first two questions. Many studies focus solely on either of these two questions instead of considering all aspects in a holistic approach. Identifying where these fundamental and applied research areas overlap would inform decision-making and provide a better understanding of technical risk in industrial processes.

To translate our current understanding of hydrogen interactions (e.g., embrittlement and attack) with metals in upscaled processes, we need simple and appropriate testing methods. These should provide easily interpreted results that are representative of the system, process, conditions, and parameters. The interaction of analysis approaches is shown in Figure 2.

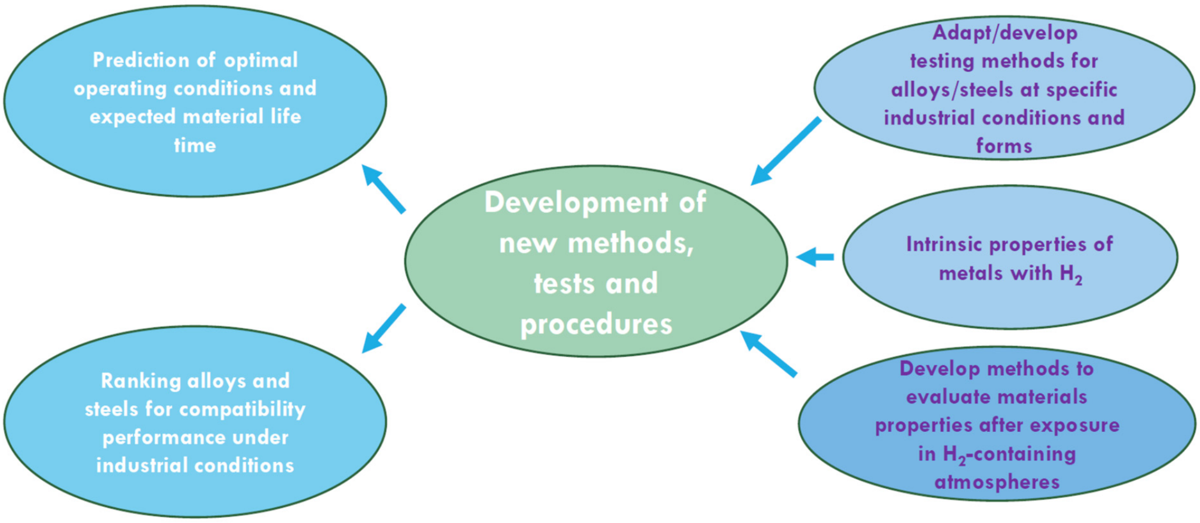

Figure 2. Interactions of the two aims of appropriate testing methods (**left**) and three possible testing method approaches (**right**).

Standard testing methods are often inappropriate for the size or shape of samples in reactor vessels or pipelines and cannot provide conclusive results. These methods should be based on systematic laboratory exposure testing and evaluation of samples that have undergone long-term exposure in typical systems. This creates a big picture from which solid conclusions can be made.

Most hydrogen embrittlement (HE) studies in industrial or large-scale applications focus on practical applications in nuclear reactors, rocket engines, and metals and materials used mainly in chemical, petrochemical, and marine industries [14–16]. However, growing interest in hydrogen production has seen more technologies dealing with high-pressure, high-temperature systems, such as gasification and syngas processing, steam methane reforming, and ammonia production or cracking. Even low-temperature gasification technologies for hydrogen production from different feedstocks operate between 700 and 900 °C [17], which is significantly higher than the temperature range for HE that is traditionally investigated. These technologies and processes rely on various stainless steels and alloys. It is understood that austenitic stainless steels can potentially resist the elevated temperatures and chemical environments associated with hydrogen production [17]. Another important aspect for industrial process considerations is the blending of hydrogen with natural gas and how that affects materials. The use of current infrastructure, such as pipelines and currently used reactors, to be retro-fitted for hydrogen utilisation might be cost-effective in the short term, but it could introduce significant technical risk if the current mechanical state of pipelines is unknown [18–20].

This paper highlights recent advances in the understanding of hydrogen interactions with industrial metals, particularly steels exposed to high-temperature, high-pressure processes. We also provide an overview of techniques currently used in industry and laboratory research to characterise HE/attack and introduce the concept that there is a need for adapting current methods and exploring alternative methods for testing and evaluating hydrogen interaction with metals specifically for long-term use and robustness in industrial processes.

2. Hydrogen Embrittlement

Hydrogen degradation of materials occurs via a series of complex phenomena that influence the material properties of metals and alloys across a range of lengths and timescales. This degradation of materials and associated phenomena are referred to as either HE, or hydrogen attack. Given the ubiquitous nature of H atoms, particularly in the field of energy research, the absorption of hydrogen into a material is difficult to avoid [21]. HE was first documented by Johnson in 1875 [21]. When a material is exposed to hydrogen, subsequent hydrogen absorption can cause cracking and brittle failures at stresses below the previously identified yield stresses of the material. The mechanisms of HE are yet to be completely understood, with several competing mechanisms proposed in the literature and supported by various experimental evidence. HE includes multiple phenomena associated with metal–hydrogen interactions:

- Hydrogen environmental embrittlement represents the conditions where metals are exposed to a high-pressure, gaseous hydrogen environment.
- Internal hydrogen embrittlement is the degradation of a metal's mechanical properties during forming or finishing operations, and results in the unintentional introduction of hydrogen into susceptible metals or alloys (e.g., via electrodeposition).
- Hydrogen reaction embrittlement is the degradation of certain mechanical properties when hydrogen reacts with the metal matrix itself to form metallic compounds, such as metal hydride, at relatively low temperatures [22].

The effect of hydrogen on metals is crucial to understand for any engineering system exposed to hydrogen, particularly for the selection of resistant materials with a long, robust service life. For HE to cause the failure of metals, hydrogen must be present in sufficient amounts and interact for a sufficient time with the metal surface. The hydrogen must interfere with the tensile stress of the metal, and the metal material must be susceptible to hydrogen interaction [23].

Of these possible hydrogen interaction phenomena, hydrogen environmental embrittlement is most often encountered in industrial environments involving high-temperature, high-pressure processing or utilisation. One of the consequences of exposing metals to hydrogen under industrial operating conditions is intensification of atomic hydrogen reactions with constituents or impurities in metals at internal grain boundaries [24]. This increase in reactions is attributed to the elevated temperatures common in industrial processes.

The extent of HE depends on factors such as exposure to hydrogen (electrochemical or otherwise), temperature, time of exposure, pressure of hydrogen, and the type of material and its properties [25].

While discussion on a specific mechanism for HE is ongoing, the following steps of hydrogen interaction with metal materials are generally accepted [26]. Figure 3 shows typical interactions of hydrogen with metal crystal lattices. The first step in HE is the adsorption onto the metal's surface (Figure 3i), followed by the absorption or ingress of hydrogen into the metal (Figure 3ii) [27]. The metal's surface governs the degree of penetration, determined by the amount of hydrogen available. If the surface is well covered by a thick oxide film, penetration will usually be hindered. Oxide films typically reduce the degree of dissociation of H_2 molecules, similar to the effect of decreasing hydrogen pressure. At increased temperatures, more hydrogen will penetrate in less time. The degree of absorption and penetration will increase even further without oxide films and in the presence of other corrosives or surface defects, such as cracks [28].

Once hydrogen is absorbed, it diffuses through a material in different ways depending on the material's microstructure. As hydrogen atoms diffuse through a metal lattice, as shown in Figure 3, they accumulate in interstitial sites such as grain boundaries, vacancies, and other areas with sufficient volume to accommodate newly absorbed hydrogen (Figure 3iii). Hydrogen at such locations is referred to as dissolved or diffusible hydrogen, whereas hydrogen at extraordinary sites is most commonly referred to as trapped hydrogen. Dissolved and trapped hydrogen are generally in local equilibrium. However, as trapped hydrogen has longer residence times than dissolved hydrogen, the concentration of trapped hydrogen is often higher. However, as trapped hydrogen has longer residence times than dissolved hydrogen, the concentration of trapped hydrogen is often higher. These sites act as initiation areas for cracks to form in the material [9]. In Figure 3iv, the first consequence of hydrogen interaction is crack propagation as hydrogen accumulates in the crystal lattice and increases stress—this phenomenon gives rise to HE. The second consequence arises from hydrogen accumulation in the crystal lattice and then reacting and interacting with components of the crystal lattice itself, changing the stress and composition, this is referred to as a hydrogen attack.

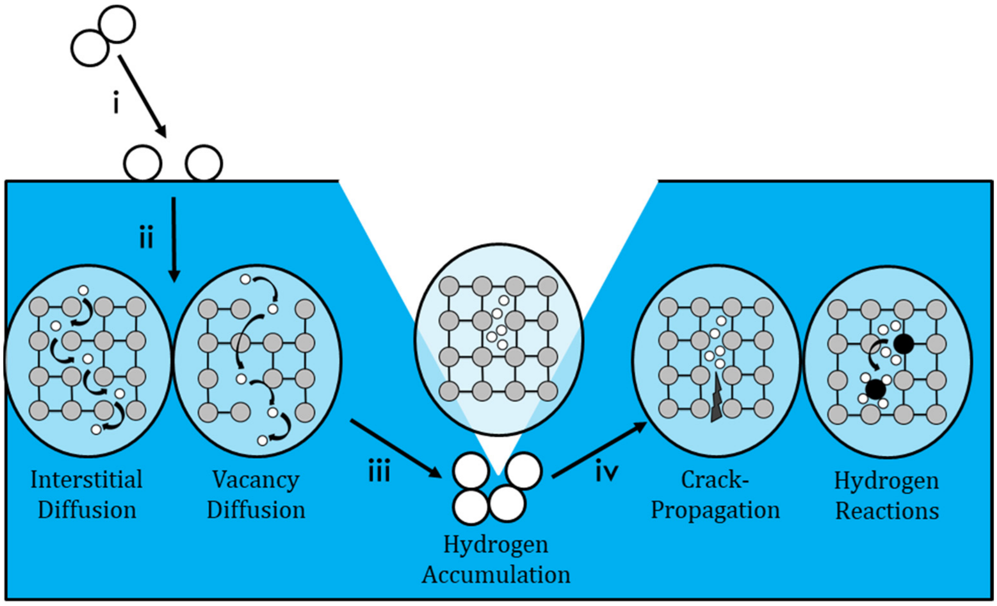

Figure 3. Schematic illustration of hydrogen atoms interacting with metal crystal lattice.

From the range of various factors affecting HE discussed above, it is clear that the mechanism/influence of HE in metals, particularly steels, are still a matter of significant academic and industrial discussion and interest.

The existing standards for HE testing consider these two categories of testing conditions and are focused on mechanical properties such as ductility, strength, toughness, and hardness. Testing of mechanical properties is accompanied by microstructural analysis to identify any structural changes, such as cracks or corrosion. This can be performed using optical and scanning electron microscopy or energy-dispersive X-ray spectroscopy.

3. Testing Methods for Hydrogen Embrittlement

HE often occurs after metal materials have been in operation for some time and manifests as intergranular fracture surfaces [28]. Degradation of mechanical properties and plasticity are common effects of HE [29]. As HE or attack proceeds during increased operation time, the first effect observed is an increase in tensile strength. Hydrogen interaction causes a solid-solution strengthening effect similar to that of carbon or nitrogen. This introduces resistance to the gliding or movement of dislocations [30]. Hydrogen damage manifests as hydrogen-induced blistering, cracking due to precipitation of hydrogen in the internal lattice, hydrogen attacking, and cracking due to hydride formation [28].

Therefore, one sensible testing route should be mechanical testing. The susceptibility of structural materials to hydrogen-assisted fracture in hydrogen gas can be evaluated by mechanical testing in two broad categories of environmental conditions: (1) testing in high-pressure hydrogen gas (applying stress concurrent with hydrogen gas exposure) or (2) testing in air subsequent to pre-charging with hydrogen (applying stress following hydrogen gas exposure) [31]. Testing methods include electrochemical testing with hydrogen charging to introduce hydrogen into the metal's structure; this can be further combined in situ with mechanical testing such as tensile or fracture testing. Additionally, relating charging via electrochemical methods to gaseous hydrogen pressure has been explored and reported in the literature [3,26,32,33]. More often than not, these standard tests are inconclusive for large-scale samples that have been exposed to hydrogen due to their shape and size. Hydrogen charging also has repeatability constraints, and results can vary significantly with an experimental design. For example, pre-charging and in-situ charging of hydrogen can produce significantly different results due to different surface concentrations of hydrogen [34]. This section highlights these issues and explains the need for adapted or new methods of testing.

3.1. Mechanical Testing

Tensile testing, or slow strain rate (SSR) tensile testing, is widely used for HE and is considered one of the most reliable testing methods. As the geometry of specimens directly influences fatigue life, it is of critical importance when comparing results; notched samples are typically used [35]. While SSRT is a displacement-controlled test method, the linearly increasing stress test (LIST) can also be used. In LIST, smooth tensile specimens are exposed to the environment with an applied tensile load, which increases linearly at a controlled rate [36]. If the applied stress exceeds the threshold limit, stress corrosion cracking begins, and when the crack reaches a critical length, rapid brittle fracture occurs.

Many mechanical properties can be assessed from tensile tests. These include yield strength, ultimate strength, total elongation, and reduction in cross-sectional area. A common specimen dimension may affect the total impact of hydrogen-induced surface crack formation and subcritical propagation on a metal's tensile properties [37].

Mechanical testing such as tensile and three-point bending can be adapted for the shapes and geometries that can be obtained from the walls of different reactors exposed to high temperatures and pressures for relatively long periods in hydrogen-containing atmospheres [38]. Schematic methods of three-point bending and tensile testing for standard shapes and curved shapes, such as reactor tubes, are shown in Figure 4.

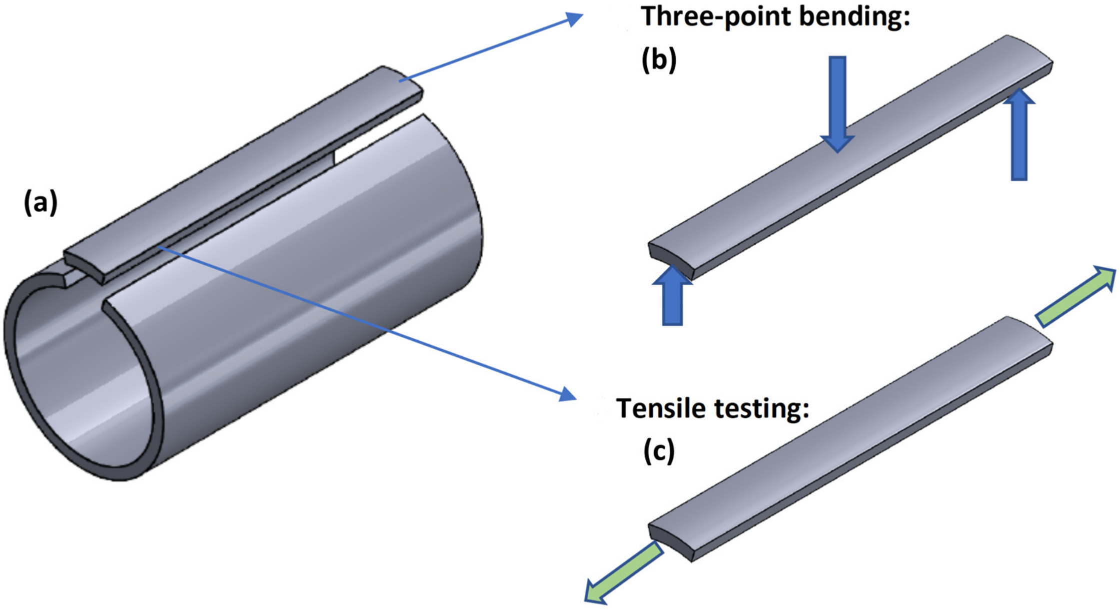

Figure 4. Metal sample geometry (**a**) and directions of forces in three-point bending (**b**) and tensile testing (**c**). Arrows indicate the applied forces.

Another mechanical test is a disc pressure or rupture test, which consists of a thin, disc-shaped sealed sample being pressurised on one side until it ruptures. Burst pressure measured using hydrogen gas is compared with burst pressure measured using an inert gas to determine the embrittlement index of the disc's material. The disc pressure test is simple and can be applied to materials exposed to a pressurised hydrogen-containing system from one side and atmospheric pressure from the other side, as shown in Figure 5.

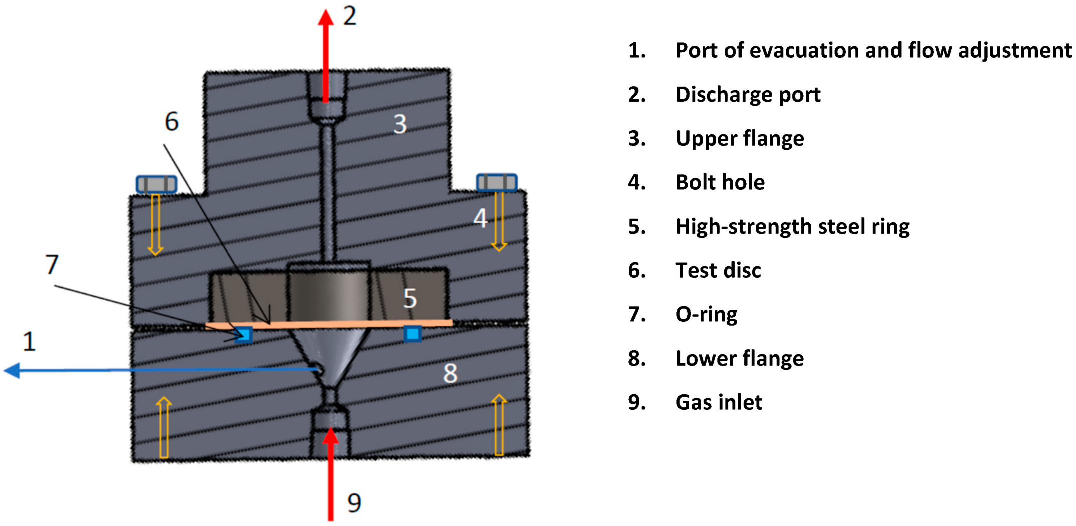

Figure 5. Direction of disc rupture testing, with the direction of force indicated.

Fracture mechanics techniques can also be used to assess the effect of hydrogen on steel properties. For example, standard single-edge notch bend specimens were used to determine the fracture toughness of a component made from C-Mn steel in the hydrogen-charged condition [39]. Out-of-plane displacement measurements were used to analyze the crack propagation under high pressure of gaseous hydrogen in martensitic stainless steels [40].

3.2. Hydrogen Charging during Testing

Investigating the effect of HE on a metal's strength, ductility, and toughness requires methods of controlling the exposure of test samples to hydrogen environments. These methods can be referred to as hydrogen charging techniques. Charging materials with hydrogen involves the forced interaction of hydrogen with the material to accelerate the effect of HE.

Samples can be either pre-charged with hydrogen ex situ or charged in situ, depending on the available equipment and scale of the samples to be analysed.

3.2.1. Pre-Charging at Elevated Temperature/Pressure (Ex Situ)

Installation and testing of materials with hydrogen pre-charging can be expensive [26]. However, it can be relatively simple and performed at a higher throughput than in situ techniques. For pre-charging, samples are placed in a hydrogen environment, allowing hydrogen to adsorb and diffuse into the material. The rate is dependent on the applied temperature and pressure, which can result in the need for more complicated systems to address safety risks. Additionally, it can be difficult to expose samples to adequate concentrations of hydrogen given that sorption and diffusion can be slow in the absence of high temperatures and pressures [30].

Other considerations for charging techniques are the properties of the material being analysed. Metals such as ferrous steels have a high hydrogen diffusion coefficient [16]. Therefore, hydrogen pre-charging is often unsuitable for HE testing due to rapid hydrogen loss between charging and testing stages. Mechanical testing with in situ hydrogen charging can be used for such materials [26].

3.2.2. Hydrogen Charging In Situ

In situ charging can be achieved via a range of different techniques that are mechanically comparable. Cathodic charging can result in an apparent loss in tensile strength relative to other charging techniques, but this loss is small compared with the loss in ductility and fracture toughness as a result of HE [30].

3.2.3. Electrochemical Charging (Ex Situ/In Situ)/Hydrogen Charging in Acid Aqueous Medium (In Situ)

Electrochemical charging is commonly used to introduce a reliable concentration of hydrogen into a material sample for analysis. Electrochemical cell tests are simple to set up and can be performed safely. To undertake electrochemical hydrogen charging, the sample is used as a cathode. At the correct applied potential/current, hydrogen is generated at the cathode surface, where it can adsorb and then diffuse into the sample.

When low current densities are applied to the sample, hydrogen adsorbs onto the metal as a function of current density, allowing only the depth of diffusivity to be calculated [30]. Harsh electrochemical charging, however, may decrease tensile strength due to the induction of subsurface and surface cracking during the charging process. High hydrogen concentration gradients that arise at high current densities result in internal stress, which in turn increases embrittlement and loss of strength. To reduce these effects, low current densities can be used for longer charging times [30]. Additionally, when using acidic aqueous media to facilitate the generation of hydrogen at the cathode/sample surface, the presence of H_2S can result in the precipitation of hydrogen bubbles within cracks. H_2S can also cause hydrogen-induced cracking and blistering in the sample [25].

When undertaking mechanical testing, evaluation of changes in mechanical properties and microstructures should be supported by measurements of the hydrogen content in the sample. An electrochemical permeation test (measurement of hydrogen flow through the material and evaluation of the amount of hydrogen trapped in the material) is also required. Such information is critical, as it provides a link between the bulk properties of the material and the intrinsic properties observed during testing.

4. ASTM Standards Assessing Hydrogen Embrittlement

Table 1 lists some American Society for Testing of Materials (ASTM) standards relating to the assessment of HE in materials. These standards are particularly relevant to the assessment of HE in materials that have been exposed to elevated temperatures and pressures typical of industrial conditions. Each standard is described further below.

Table 1. American Society for Testing of Materials (ASTM) standards for hydrogen embrittlement.

Test	Conditions	Parameters
ASTM G142-98: Standard test method for determination of susceptibility of metals to embrittlement in hydrogen-containing environments at high pressure, high temperature, or both [41]	In H_2/air, high temperature, high pressure	Load-displacement curve Plastic elongation Ultimate tensile strength Notched tensile strength
ASTM G129-00: Standard practice for slow strain rate testing to evaluate the susceptibility of metallic materials to environmentally assisted cracking [42]	Any with H_2 versus control environment	Applying different extension rates: monitoring applied load and crosshead displacement, recorded corrosion potential
ASTM F1459-06: Standard test method for determination of the susceptibility of metallic materials to hydrogen gas embrittlement (HGE) [43]	In H_2/He, room temperature, high pressure	P_{He}/P_{H2}
ASTM F1624-12: Standard test method for measurement of hydrogen embrittlement threshold in steel by the incremental step loading technique [44]	In air or controlled environment	Threshold stress by four-point bending
ASTM E1681-03: Standard test method for determining the threshold stress intensity factor for environment-assisted cracking of metallic materials [45]	Controlled environment	Stress intensity factor threshold for environmentally assisted cracking, K_{EAC}

4.1. ASTM G142-98 and G129-00

The test procedures and specimen preparations outlined in ASTM G-129 [42] and ASTM G-142 [41] are commonly applied as material screening methods for HE susceptibility under slow strain rate (SSR) testing. These test methods can also be used to assess the effects of the material's composition, processing parameters, and heat treatment when the materials are exposed to specific hydrogen pressure and temperature conditions [46].

4.2. ASTM F1459-06

This disc-rupture technique is applied to quantify the level of susceptibility between different metals and alloys to HE by exposing samples to high-pressure gaseous hydrogen. Rupture pressure is applied to thin sample discs in hydrogen (P_{H_2}) and is referenced against an inert gas such as helium (P_{He}). Ratios of P_{He}/P_{H_2} greater than 1 indicate that the material is possibly susceptible to HE; for a ratio between 1 and 2, HE is likely to occur after long exposure to hydrogen. Ratios higher than 2 indicate high susceptibility to HE. The standard indicates the relative severity of the degradation of mechanical properties expected in gaseous hydrogen [43].

As the experimental set-up is relatively simple, ASTM F1459-06 is suitable for assessing a range of metals and alloys to be used in a high-pressure system. However, it is designed for a room-temperature test. Therefore, the effect of temperature must be evaluated separately, or the standard should be adapted for high-temperature testing.

4.3. ASTM G142-98

This standard reliably estimates a material's susceptibility to the loss of strength and ductility caused by exposure to a hydrogen environment. In contrast to ASTM F1459-06, ASTM G142-98 is designed for a comparative test that exposes smooth or notched specimens to a gaseous, H_2-containing environment at high pressure and/or high temperature while being pulled to failure in uniaxial tension. The same conditions are applied to test samples in non-hydrogen atmospheres as a control. Standard mechanical properties, such as yield strength, ultimate tensile strength, and reduction in area or elongation, are compared for samples under each test condition. The experimental set-up for this standard is more complex than for ASTM F1459-06 and includes a high-temperature/pressure autoclave equipped with a metal test cell [41].

While the outcomes of these tests can be used to evaluate the effects of material composition, environment, and processing parameters (temperature, pressure), the results may not apply to samples exposed to practical industrial operating conditions. When this standard is used to assess high-temperature HE/attack in steels, a suitable exposure time under test conditions is required before testing to allow internal blistering, decarbonisation and cracking to develop.

4.4. ASTM G129-00

This standard includes accelerated testing of the resistance of metallic materials to environmentally assisted cracking (EAC) under various environmental processing conditions.

EAC initiation is accelerated by applying a dynamic strain at a sample's notch tip or crack tip. This method also includes a testing cell placed in an autoclave with a controlled atmosphere and temperature at atmospheric pressure. The test compares materials exposed to a control environment that is not susceptible to EAC with materials in an environment in which the resistance to EAC is being determined. In both environments, SSR is applied as a slowly increasing strain imposed by an external means on the gauge section or notch tip of a uniaxial tension specimen or the crack tip of a fatigue pre-cracked specimen.

Due to the accelerated nature of this test, it is not intended to represent service performance under industrial conditions. Its main purpose is to comparatively evaluate the effects of metallurgical and environmental variables on sensitivity to known environmental cracking problems and to detect environmental interactions with a material. The SSR test and derived data should also be used in combination with service experience, long-term EAC data, or both, obtained through literature sources or additional testing using other testing methods.

4.5. ASTM F1624-12

This standard can be used to rapidly assess the effects of residual hydrogen caused by processing or to quantify the relative susceptibility of a material under a fixed set of hydrogen-charging conditions. The method measures the load enough to initiate a subcritical crack in the steel for specimens of different geometry in different environmental conditions. The threshold stress can be determined by progressively decreasing loading rates.

ASTM F1624-12 is performed in air to measure the effect of residual hydrogen in the steel because of processing (internal hydrogen embrittlement) or in a controlled environment to evaluate the effect of hydrogen introduced into the steel from external sources. Therefore, it is only likely to be used to assess materials after long-term exposure to industrial hydrogen-containing atmospheres or to evaluate hydrogen interaction with other materials if test conditions can reproduce industrial conditions.

4.6. ASTM E1681-03

Similar to ASTM G129-00, this method characterises a material's resistance to crack growth with a sharp crack in specific environments under loading conditions. The method introduces the environment-assisted cracking (EAC), and threshold intensity factor parameters (K_{IEAC} and K_{EAC}), defined as the highest value of stress intensity factor at which neither failure nor crack growth occurs. The measured K_{EAC} or K_{IEAC} value can be used to estimate the relationship between failure stress and defect size for a material under a service condition where crack-like defects are expected. Some level of uncertainty is inherent in the concept of a true threshold for EAC in metallic materials.

4.7. Adapting Standards to Industrial Settings

Owing to the simplicity and accelerated nature of these tests, the results are not necessarily designed to represent a true hydrogen-service environment for long-term exposure but rather to provide a basis for material screening [46].

At present, there are no HE-specific standards that can be applied for materials behaviour under specific high-temperature/pressure, thermochemical processing conditions in the presence of hydrogen-containing gases. However, existing HE ASTM standards can be adapted to the conditions relevant to specific industrial processes. For instance, ASTM F1459 testing conditions can be adapted to high temperatures to evaluate metals and alloys used in high-temperature/pressure reactors, particularly those using cyclic pressurising and/or heating.

The F1459 standard is also known as the disc pressure test (DPT) method and was originally developed for hydrogen gas embrittlement [47]. It was later modified to test hydrogen environment embrittlement by comparing materials under non-embrittlement and embrittlement conditions, such as temperature (−196 to 450 °C), H_2 pressure (up to 1600 bar), H_2 purity, and the pressure increase rates [48]. In that study, delayed failure experiments on 252-ksi H-11 250 maraging steel and several other martensitic steels were also conducted.

The DPT method was also used to study HE in 21-6-9 stainless steel and medium carbon steel at different experimental conditions, including various gas atmospheres (air, N_2, H_2), different pressures, and different times of pre-loading [49]. The authors determined that 21-6-9 stainless steel (SS) was likely insensitive to hydrogen, although there was still a slight degradation in ductility properties in hydrogen when samples were exposed for a long time (more than 1000 h). The degradation of quenched medium carbon steel in hydrogen was more significant, and the rupture pressure was significantly lower in a hydrogen-containing atmosphere than in air.

Disc-rupture tests performed on different ferrous and non-ferrous alloys in helium and hydrogen atmospheres demonstrated no HE for 316SS, copper, aluminium, and titanium alloys at room temperature [50]. The DPT results agreed with those obtained after cathodic charging.

Some studies have evaluated the method and results of the DPT test. A nonlinear, finite element model of a specimen was used to accurately evaluate stress and strain as a function of applied pressure [51]. The model was used to interpret test results and allowed for a more general understanding of the ability of DPT to assess the mechanical properties of metals exposed to hydrogen. The threshold concentrations given by DPT were lower than the critical concentrations obtained by electrochemical measurements, possibly due to the influence of stress/strain state on material fracture.

A highly non-linear, finite element simulation of DPT has been developed to predict failure pressure under hydrogen for different materials and thicknesses [52]. The simulations include a large range of pressure conditions, which is useful knowledge for high-pressure hydrogen storage.

There are a number of ASTM fracture toughness testing standards conducted in air and room temperature that do not consider hydrogen atmosphere. These include ASTM E399 (Standard Test Method for Linear-Elastic Plane-Strain Fracture Toughness of Metallic Materials) [53], ASTM E740 (Standard Practice for Fracture Testing with Surface-Crack Tension Specimens) [54], ASTM E1820 (Standard Test Method for Measurement of Fracture Toughness) [55], and ASTM E2899 (Standard Test Method for Measurement of Initiation Toughness in Surface Cracks Under Tension and Bending) [56]. These standard tests can also be used to evaluate the mechanical properties of materials exposed to hydrogen or hydrogen-containing atmospheres. However, commonly used specimen geometries for fracture toughness testing have to be modified to be relevant to the original material shapes for correct interpretation of the results.

5. Hydrogen in Industrial Materials

Hydrogen susceptibility is controlled by the concentration of hydrogen and hydrogen kinetics. In turn, this depends on characteristics and parameters such as microstructure, hydrogen introduction methods, temperature, and the kinetics of deformation [25]. Some characteristics inherent to metals that are typically used in industrial applications make them susceptible to HE. These include steel composition and alloying, microstructure, grain size, displacement rate, and tempering temperature [26]. The following sections look at typical metals used in industrial applications and how hydrogen interaction differs due to these characteristics. We discuss HE in pipeline steels, high-pressure hydrogen storage tanks, and ammonia processing systems; metal hydride formation; and HE in alloys at elevated temperatures.

5.1. Hydrogen in Pipeline Steels

To minimise the risk of HE, hydrogen gas transmission pipelines are made of low- or medium-strength ferritic-pearlitic steels. The possibility of injecting hydrogen into existing natural gas transport pipelines has been reported [57]. Typical natural gas transmission pipelines are made of low-carbon and high-strength steel. These higher-grade pipeline steels show high HE susceptibility [58,59]. Mechanical loads on pipe steel and simultaneous hydrogen exposure may cause various problems related to hydrogen effects.

Another factor that has to be considered is the gas chemistry in hydrogen-blended pipelines. The effect of CH_4 as the main component of the hydrogen-blended natural gas pipeline and natural gas impurities such as CO, O_2, H_2S, H_2O, and SO_2 should be considered in the HE of pipelines. For instance, CO addition to H_2 gas inhibits the accelerated fatigue crack growth in pure iron and low-carbon steel [60,61]. CH_4 and especially CO compete with H_2 for dissociative adsorption sites on an iron surface and inhibit the HE of X80 steel [62]. Even the addition of 0.1 vol.% CO provided good HE protection. Both CO_2 and H_2S promote hydrogen permeation in the X80 pipeline steel; however, promotion by CO_2 is far weaker than H_2S [63].

Recent studies suggest that mixing hydrogen with natural gas up to 20% per volume does not escalate the risk of pipeline failure [64]. For example, Britain's gas grid operators plan to start accepting a blend of up to 20% hydrogen in 2023 as part of the UK's effort to decarbonise its infrastructure [65].

Hydrogen can either be weakly absorbed in pipeline steels, known as diffusible hydrogen, or strongly associated with the steel structure, also called solution hydrogen. The interaction of hydrogen with steel, and therefore its effect on steel structure, is governed by alloying elements in the steel, lattice defects, and crystal structure [35].

Hydrogen uptake in pipeline steels can occur via H_2 physisorption, H_2 dissociative chemisorption, H absorption, and H diffusion, which are typical for other metals and alloys described in 'Hydrogen embrittlement' section.

Hydrogen absorption in pipeline steels increases as cathodic potential is applied to inhibit corrosion or due to H_2S present in the gaseous transport medium. As pipeline systems have completely different charging environments, especially over long-term use, hydrogen molecules dissociate into hydrogen atoms that interact with the steel surface [66]. A partial pressure difference is thus created between the bulk and the steel surface. It is at this equilibrium concentration that hydrogen diffuses into the steel bulk. Electrochemical charging forces hydrogen into the bulk by forcing ions into traps due to a potential difference mechanism. Therefore, electrochemical charging can overestimate hydrogen adsorption and diffusion [66].

The routine fluctuations in pressure along hydrogen pipelines stress the steel, which increases both hydrogen diffusion and hydrogen-induced damage. The main mechanism of hydrogen degradation in pipeline steels is thought to be hydrogen-assisted fatigue crack growth, which takes place under cyclic loading, combined with the metal's resistance to crack growth, which decreases the durability of the pipeline system [67].

To characterise the fracture-resistant properties of pipeline steel, a fracture toughness test can be applied. The test design uses a fatigue pre-cracked specimen placed to a slowly rising displacement or a slowly rising (dynamic) load. The fracture resistance is determined by calculating the intensity factor K_{Ic} [67].

Several research projects are currently investigating the relationship between the parameters causing HE [68,69].

5.2. H_2 in High-Pressure Hydrogen Storage Tanks

In gaseous form, H_2 is typically stored by compression in high-pressure gas cylinders with a maximum operating pressure of 20 MPa [70]. Four different types of typical H_2 pressure vessels are currently used (Table 2).

Table 2. Types of high-pressure hydrogen storage tanks [71].

	Cylinder	**Liner**	**P_{max}, MPa**
Type I	metal	metal	20–30
Type II	Metal with wrapped grass/carbon fibre	metal	Not limited
Type III	fibre resin composite	metal	45
Type IV	fibre resin composite	polymer	100

Type I is a metallic pressure vessel, mostly used for industrial applications, with a pressure of 20–30 MPa and a capacity of about 1 wt.% of H_2. Type II is also a metallic vessel, with the cylindrical section wrapped in fibre resin composite. Type III and Type IV are fully composite, materials-based pressure vessels made of plastic or carbon fibres embedded in a polymer matrix. The maximum pressure for Type III is 45 MPa, and for Type IV it is 100 MPa. These types can store up to 4.8 wt.% of H_2 [71].

In addition to pipeline materials, the metal parts of vessels and particular steels are also affected by HE. This leads to the consequent degradation of mechanical properties and the formation of cracks, such as stress corrosion cracking. Several studies have focused on this problem by investigating HE mechanisms, developing appropriate mechanical testing, and improving alloy manufacturing and component assembly [71,72].

The optimal materials for a high-pressure cylinder should have a very high tensile strength (not necessarily isotropic), a low density, and be nonreactive with hydrogen (or allow hydrogen to diffuse into them) [73]. Most pressure cylinders used are manufactured from austenitic stainless steel (316SS and 304SS) and Cr-Mo alloys [74]. These are widely accepted as they are relatively resistant to hydrogen effects at ambient temperatures. However, these materials also show signs of HE and deterioration of mechanical properties if exposed to high-pressure hydrogen for a long time. For example, with increasing hydrogen pressure, the threshold stress intensity factor for hydrogen-assisted cracking of 4130X steel decreases [75]. In a 92 MPa hydrogen environment, the fatigue-crack growth (FCGR) of 4130X steel was 30–50 times larger than that in air [76]. In terms of ductility, the elongation fracture (EL) and reduction area (RA) of Cr-Mo steel exposed to a 115 MPa hydrogen gas atmosphere decrease significantly [77].

In austenitic steels, it was found that microstructural characteristics such as grain size and grain boundaries affect HE [78]. The presence of martensite in the composition of steels in hydrogen storage materials increases the probability of HE [79], as martensite is more sensitive to HE than austenite. Hydrogen also accumulates at the boundary between austenite and martensite, leading to crack initiation along the boundaries [80].

In the last two decades, extensive research on hydrogen embrittlement degradation mechanisms has been conducted to address the long-term performance needs of hydrogen storage tanks [74,81].

HE susceptibility of austenitic steels can be reduced by changing the chemical compositions of the steels. For example, the tensile test of 304 austenitic stainless steel demonstrated that the influence of hydrogen on ultimate tensile strength (UTS), elongations, and reduction of area decreased with increasing Ni content [82]. HE resistance of austenite can be enhanced by adding other stable chemical elements, such as Mn and Co [78].

5.3. Hydrogen Embrittlement in Ammonia Processing Systems

Cui et al. (2010) analysed a brittle fracture explosion accident concerning a thick-walled steel pipe connecting the outlet of an ammonia separator and the inlet of a cold exchanger in an ammonia synthesis unit of a chemical fertiliser plant [83]. They concluded that the decrease in toughness of the pipe steel was due to strain-ageing embrittlement, not low-temperature temper embrittlement.

Another microstructural and microhardness analysis looked at a catalyst holder in an ammonia converter vessel that had been in use for five years. The study demonstrated embrittlement of cold-worked wire mesh made of 347 austenitic stainless steel [84].

5.4. Metal Hydride Formation

Certain metals (such as Mg, Li, Ti, Zr) easily absorb and desorb hydrogen reversibly and are commonly used in hydrogen storage and hydrogen compression systems. Metal hydrides are also formed in some intermetallic compounds such as binary alloys ($LaNi_5$, Nb_3Sn, Mg_2Ni, TiFe, $TiMn_2$), ternary alloys ($MgAlNi_4$, $MgLaNi_4$, $LaMg_2Ni_9$, LaNiSn), and metal solid solutions (such as CrVTi) [85]. Hydrogen absorption and desorption rates can be manipulated in these materials by changing the metallic composition. Specifically, the presence of Ni in the crystal lattice of materials can influence the desorption and diffusion of hydrogen through materials and therefore prevent or promote HE [35].

As the metal alloys absorb hydrogen, they expand. This places an upper limit on the safe filling capacity of vessels containing metal hydrides. As these vessels are filled and emptied, the metal hydrides break down into a fine powder. From a kinetic perspective, the smaller particle size of powders can be an advantage. However, heat transfer is limited, as fine powdered beds have poor thermal conductivity due to their porosity and interparticle contact resistance. As a result of poor thermal conductivity, the observed reaction kinetics for absorption and desorption of hydrogen are dominated by heat flow [86].

One possible solution to heat transfer issues is to combine metal hydride powders in structures with components of high thermal conductivity, such as expanded natural graphite. As a result, metal hydride composite materials have attracted great interest [87,88].

Materials issues and challenges associated with hydrogen in metal hydrides have been studied and well-reviewed in the last few years [87,89,90].

5.5. HE in Alloys at Elevated Temperatures

Ni–Cr–Fe alloys, which are widely used in pressurised-water nuclear reactors, demonstrate a hydrogen-enhanced fracture mechanism. This is attributed to the simple cubic crustal (SCC) of nickel-based alloys at elevated temperatures [91]. In that study, alloy X-750 was severely embrittled in high-pressure hydrogen gas at 260–338 °C.

The environmentally induced static-load cracking performance of AISI type 4340 steel exposed to dry hydrogen and hydrogen sulfide gas has been evaluated [92]. Temperature (up to 100 °C) and pressure (up to 100 psig) had a significant effect on cracking performance measured in dry hydrogen gas. However, in H_2S gas, neither temperature nor pressure had a significant effect on the corresponding crack growth rate.

Alloy 718, solution-annealed at 950–1050 °C and aged, was investigated for its tensile properties and fatigue crack growth in high-pressure hydrogen of 1.1–19.7 MPa at temperatures up to 500 °C [93]. HE was still observed at 500 °C and increased as the testing temperature fell and the d phase increased. Corrosion-induced HE of alloy 718 was also studied at 80 and 300 °C by applying SSR tensile tests in an autoclave after exposure at 300 °C in a primary water environment [94]. The effect of hydrogen at 300 °C was attributed to the presence of metallurgical traps that were still active at this temperature.

Chêne et al. (2004) studied the effect of temperature and strain rate on hydrogen-induced intergranular rupture of tensile specimens of alloy 600 [95]. A predominant influence of hydrogen transport by mobile dislocations on hydrogen-induced intergranular rupture in alloy was seen at temperatures up to 230 °C.

High-strength, low-alloy, low-carbon 2.25Cr–1Mo–0.25 V steel, which is widely used in hydrogenation reactors, was tested for HE at high temperatures (660 °C) by tensile testing [96]. In high-temperature deformed specimens, hydrogen significantly increased the formation of cracks. This was attributed to hydrogen trapping at both carbides and dislocations.

The effects of hydrogen and high temperatures on austenitic stainless steel properties have also been studied [17]. Surprisingly, the results do not support the common hypothesis that the effects of HE decrease as test temperatures rise above 230 °C. The authors suggest that an alternative mechanism of HE may occur at high temperatures that has not previously been explored.

Steel and alloy components that are used in applications such as high-temperature fuel cells and electrolysers, pipelines and containers in hydrogen synthesis plants, and hydrogen purification in pressure swing adsorption plants and storage are likely to experience hydrogen embrittlement [97].

6. Key Areas to Address Hydrogen Embrittlement in Industrial Environment and the Challenges

In this section, we discuss a range of approaches that may address the issue of HE. These include the choice of materials for engineering and industrial applications, retrofitting plants in heavy industries, iron ore pelletising, alumina calcination, and clinker production.

6.1. Choice of Materials for Engineering Applications

Materials must be tested in precise environments for each engineering application, taking pipeline conditions into account [2]. Different grades of steel/materials and their microstructure can provide useful information about the susceptibility of these materials. Different types of HE should be explored to obtain quantitative values for crack growth rate, corrosion rate, and others to predict damage evolution [23].

6.2. Choice of Barrier Coatings for Prevention of Hydrogen Permeation

Steels with low alloy content are much less expensive than high-alloyed steels but more susceptible to hydrogen embrittlement. In order to utilise these steels in industrial applications, another approach to material selection is to develop barrier layers/coatings in low-alloyed steels to prevent their hydrogen uptake. Various coating techniques were recently reviewed with respect to their ability to produce layers (oxides, nitrides, and carbides) with suitable quality and their ability to scale up for industrial applications [97].

6.3. Choice of Testing Methods for Industrial Applications

As mentioned, the lack of methods to test metals and alloys relevant to specific industrial conditions provides a driving force for the development of proper testing procedures. One approach is to modify existing standard mechanical tests that deal with any form of hydrogen interaction (e.g., hydrogen environmental embrittlement, internal hydrogen embrittlement, and hydrogen reaction embrittlement). For instance, conducting the F1459-06 test in hydrogen-containing syngas at elevated temperatures realistically evaluates a gasifier's downstream material resistance to any reactions associated with hydrogen. If a test is conducted in H_2 mixtures with N_2 and ammonia, the reactor material's performance can be assessed in relation to exposure to ammonia synthesis or ammonia-cracking processes.

Another approach is to apply standard mechanical tests to metals exposed to industrial conditions in the shape specific to a particular component, such as joints, reactor walls or piping. One study tested different welded and non-welded parts of a used kiln shell using the standard test method for measurement of fatigue crack growth rates (ASTM E647-08) [98]. The measured crack growth rates under a constant-amplitude load in welded, longitudinal, and circumferential parts were compared. The results were used to predict the fatigue crack growth of a rotary kiln structure.

Such an approach can be applied to standard tensile tests for the wall materials of reactors exposed to a hydrogen-containing atmosphere.

ASTM A370 [99] is one of the most broadly recognised and encompassing standards for measuring the tensile stress of metals and is conducted on a wide variety of steel products and specimen geometries (e.g., bar, tube, fasteners, round wire). Therefore, this method can be adapted to new shapes and geometries that can be obtained from exposed reactor walls. Recently, we used this approach by cutting longitudinal strips from an exposed reactor wall (316SS), and then testing new and exposed samples by tensile stress and three-point bending [38]. The results of the tests were consistent and clearly demonstrated the difference in tensile stresses of new and exposed reactor materials.

6.4. Retrofitting of Plants in Heavy Industries

The gradual replacement of natural gas with increasing amounts of hydrogen presents unknown risks to heavy industrial processes. These include aspects of material compatibility and impacts on process chemistry and performance.

6.4.1. Iron Ore Pelletising

When using hydrogen in industrial systems, especially when retrofitting, pipeline systems must be able to handle appropriate hydrogen pressures and be resistant to embrittlement and attack. Hydrogen is used as a source of heat in these applications. Therefore, the hydrogen burner or an adapted traditional natural gas burner process and material are important to consider. The choice of materials to deliver and store hydrogen is critical, and they must have a microstructure resistant to hydrogen interdiffusion. Of the common metals used in industrial applications, austenitic stainless steels and aluminium alloys are most resistant to hydrogen crystal lattice interactions.

6.4.2. Alumina Calcination

Gradually replacing natural gas with hydrogen for gibbsite calcination has various possible benefits. Here, hydrogen could be used as a heat source, which would decrease carbon emissions while also making use of steam-rich calciner off-gas for heating in upstream processes. Again, materials in these systems will be exposed to hydrogen and steam. Therefore, material choice and embrittlement risk are of concern and should be carefully evaluated and mitigated.

6.4.3. Clinker Production

In current kiln furnaces used for clinker production, fossil fuels such as oil, coal, or natural gas are combusted to heat the kiln. Supplying hydrogen to the kiln burner system may result in some potential problems with burner operation and material issues in burner and kiln refractories.

The use of hydrogen in a kiln furnace burner results in higher flame speeds and firing temperatures. To facilitate the incorporation of hydrogen into the fuel stream, changes in burner construction materials and burner types will be required [100].

Some steels used in traditional burner construction can undergo HE and attack at elevated temperatures, causing premature failure of the burner [101]. Addressing this issue may require additional evaluation of steels and alloys relevant to kiln furnace operating conditions (e.g., temperatures, pressures, atmospheres, and impurities) and revision of standards for burner materials.

7. Conclusions and Outlook

Despite extensive studies of various phenomena in metals and alloys that interact with hydrogen, there is still much to understand about the likely behaviour of these materials at elevated temperatures and pressures in a hydrogen-containing atmosphere, specifically for upscaled industrial processes. Even though hydrogen embrittlement and attack mechanisms are well researched and documented, the effect thereof at specific operating conditions and hydrogen content in blends pose significant technical risks to decarbonisation by the utilisation of hydrogen. The behaviour of materials and metals in current industrial infrastructure such as pipelines and reactors is still hard to predict, and methods to evaluate and characterise possible lifetimes and robustness of such systems for the introduction of hydrogen still need understanding and development.

One challenge is knowing how to apply existing knowledge of HE, hydrogen attack, mechanisms of reactions with H_2, and intrinsic properties of metals and steels that interact with hydrogen (physisorption, dissociative chemisorption, absorption, diffusion, and interactions with dislocations) to very complex conditions, which include various atmospheres, temperatures, pressures, and gradients of these.

In this review we have tried to observe the big picture by addressing the current state-of art in materials, evaluation methods and relevant industrial experience. The knowledge gaps we have identified are the result of three main factors:

1. Limitations of laboratory assessment methods: these are more likely ‘two-dimensional’, trying to link the ability of a material to uptake/react with hydrogen with its intrinsic properties or resulting mechanical (bulk) properties.
2. Applicability of ASTM standards for materials testing for industrial use: test conditions differ from industrial tests, and shapes, sizes, and forms are standardised and often differ from those used in industrial processes.
3. Limited industrial samples: little data are available for materials exposed to hydrogen-containing atmospheres.

To address these challenges in industries where the transition from fossil fuel to hydrogen may occur, we need to properly assess materials in terms of their use in specific industries, predict the lifetime of industrial components, and assess the compatibility of materials in industrial systems if modified. All of these goals require further development of existing test methods, procedures, and techniques.

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Nomenclature

ASTM	American Society for Testing and Materials
DPT	disc pressure test
FCGR	fatigue-crack growth
EAC	environmentally assisted cracking
EL	elongation fracture
HE	hydrogen embrittlement
HGE	hydrogen gas embrittlement
K_{EAC}	Stress intensity factor threshold for environmentally assisted cracking
K_{Ic}	intensity factor for fracture resistance determination
LIST	linearly increasing stress test
P_{He}/P_{H2}	Rupture pressure ratio
RA	reduction area
SSR	slow strain rate
SSRT	slow strain rate tensile
UTS	ultimate tensile strength

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