UNDERSTANDING HYDROGEN EMBRITTLEMENT:

HARNESSING HYDROGEN SAFELY

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Hydrogen, often heralded as a 'miracle molecule', holds immense promise as a clean energy carrier. As countries worldwide gear up to transition towards a decarbonised future, hydrogen has attracted growing attention. The rapid rise in renewable energies from wind and solar in recent years makes it increasingly feasible to produce hydrogen from renewable sources through electrolysis, and transport it as a fuel.

The uptick in production, storage, transportation and consumption of hydrogen has made it essential to assess and mitigate the associated risks.

MATERIAL DAMAGE BY HYDROGEN

As the smallest of atoms, hydrogen can (under certain circumstances) easily enter materials and alter their properties. The term "Hydrogen Embrittlement" (HE) refers to the deterioration of material properties, in particular the material toughness and ductility, due to the presence of hydrogen. HE is difficult to identify through normal inspection methods and can cause catastrophic incidents by remaining undetected prior to material failure.

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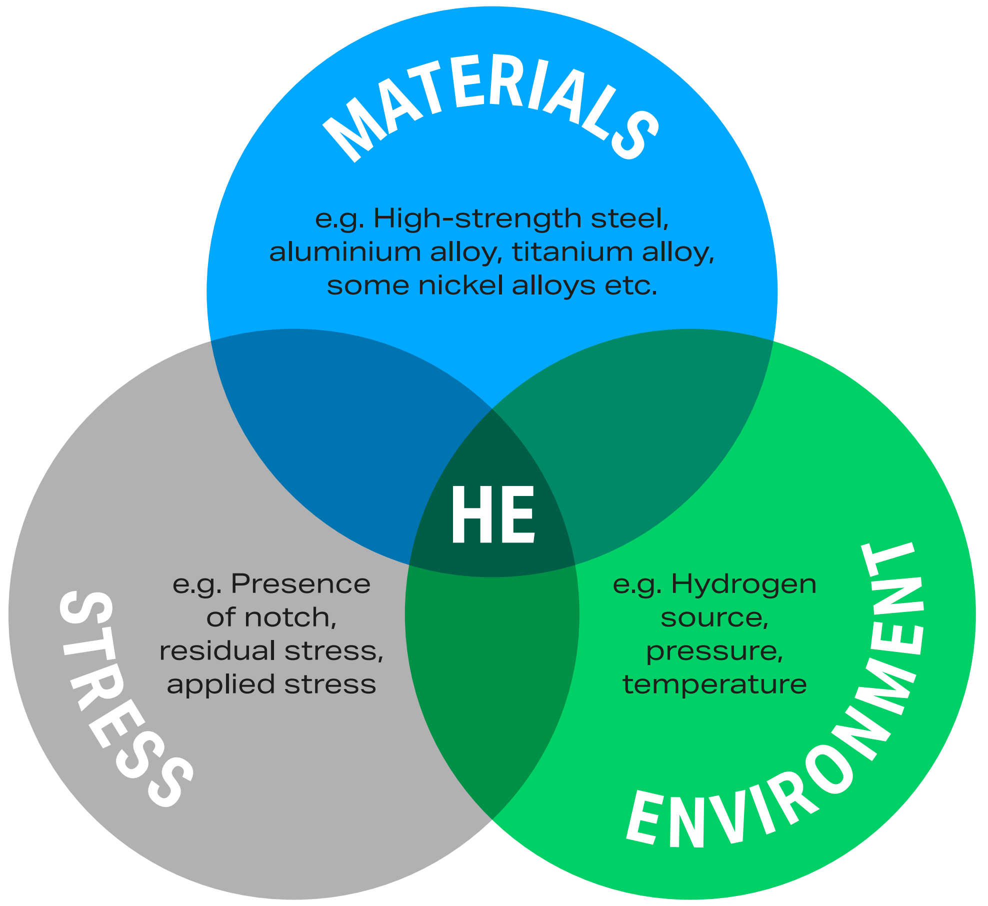

Fig. 1: Factors of Hydrogen Embrittlement

HE is classified into three broad categories:

- Internal hydrogen embrittlement (IHE)
- Hydrogen environment embrittlement (HEE)
- Hydrogen reaction embrittlement (HRE)

IHE is caused by pre-existing hydrogen inside the material, usually from the processing of the material (e.g. welding, cladding or pickling). The internal hydrogen can be removed effectively using heat treatment. The HE generated by exposure to a hydrogen atmosphere is referred to as HEE, the sensitivity of which is highly dependent on hydrogen pressure. HEE is more troublesome than IHE, as the source of the hydrogen may not be removable. It is worth noting that the hydrogen molecule (H_2) cannot directly cause HE without being absorbed and dissolved into the atomic phase. HRE is related to the degradation of certain mechanical properties that occur when hydrogen reacts with the metal matrix itself.

HE is a complex phenomenon influenced by three major factors (see Fig. 1). Crystal structure, microstructure, hydrogen solubility and diffusion coefficient, and internal defects are essential characteristics of materials. HE is especially problematic in high-strength steels with an ultimate tensile strength of > 1,000 MPa or hardness > HRC 32. From a stress perspective, hydrogen atoms tend to accumulate at areas of concentrated stress, either residual stress as a result of processing or stress applied in service. Environmental factors include hydrogen source, temperature etc.

MITIGATION OF HYDROGEN EMBRITTLEMENT RISKS

The risks of hydrogen embrittlement to hydrogen storage and transportation cannot be overstated, as the infrastructure for these processes often involves materials susceptible to HE. Mitigating HE risks requires a multifaceted approach: material selection, surface modification and design optimisation. Also, appropriate testing should be conducted to evaluate a material's resistance to HE.

MATERIAL SELECTION

Material selection involves choosing alloys resistant to embrittlement. In general, alloys with a face-centred cubic (FCC) crystal structure are more resistant to HE than those with a body-centred cubic (BCC) crystal structure, due to their higher hydrogen solubility and lower hydrogen diffusion coefficient in hydrogen environments. The HE of steels is dependent on their microstructures: the martensitic structure shows the highest HE susceptibility, followed by bainite, pearlite and austenite. Therefore, most hydrogen-resistant alloys are austenitic alloys with an FCC crystal structure, such as austenitic stainless steels or iron-nickel-based alloys.

The advent of composite materials offers promising opportunities. For example, hydrogen storage tanks that employ a plastic liner for gas containment and a carbon fibre composite for strength, have shown good resistance to embrittlement while meeting demanding performance and safety requirements.

SURFACE MODIFICATION

When a metal surface is coated with a protective film, hydrogen entry into the alloy is suppressed and it exhibits high HE resistance. For example, a surface coated with Ni, Cd, Al and Al-Ni complex film can effectively suppress hydrogen infusion and reduce HE susceptibility. Surface nitriding and carbonisation and peening treatments are also promising approaches for enhancing HE resistance.

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DESIGN OPTIMISATION

In the design phase, reducing stress concentrators and applying low-stress design principles can help to limit the opportunities for crack initiation. However, this can be constrained by the intended design window. For example, the typical pressure of a compressed hydrogen storage tank is 35-70 MPa.

To determine the suitability of a material for hydrogen storage and transportation, its susceptibility to HE can be evaluated by standard tests, such as 'ASTM G142-98(2022) Standard Test Method for Determination of Susceptibility of Metals to Embrittlement in Hydrogen Containing Environments at High Pressure, High Temperature or Both'.

Appropriate Testing		
Material Selection	Surface Modification	Design Optimisation

Fig.2: Mitigating HE Risks

The HE sensitivity of materials can be measured using various parameters. For example, the HE sensitivity of materials can be quantitatively represented by the relative reduction of area (RRA) obtained via slow strain rate tensile tests in the presence of hydrogen (or after hydrogen charging) versus that in the air (or an inert gas). If a material is more susceptible to HE, its reduction of area in the presence of hydrogen will be much smaller than that it is in air (i.e. more brittle).

There are two types of testing method: pre-charging hydrogen experiments (internal hydrogen) and environmental hydrogen experiments (external hydrogen). The latter is more relevant for hydrogen storage and transportation facilities. Those interested in a detailed comparison of HEE among various metals and alloys, should refer to the technical document 'NASA/TM-2016-218602 Hydrogen Embrittlement' prepared by the National Aeronautics and Space Administration (NASA).

Despite the challenges, hydrogen embrittlement should not be seen as an insurmountable barrier to the hydrogen economy. Instead, it is a problem that needs to be managed and mitigated. If we can rise to this challenge, hydrogen's full potential as a clean, abundant and efficient energy carrier can be realised, providing a significant step forward towards a sustainable energy future.

