3. Material Considerations when working with Hydrogen

3.1.11 Influence of Hydrogen on Materials

All materials deform under load. The stress which a structural material is able to withstand is conditioned by its ductility. Ductility is the ability to deform permanently prior to fracture, and it is measured in terms of percentage elongation at fracture.

Most materials behave linearly under low loads. A material is elastic if, after being elongated under stress, it returns to its original shape as soon as the stress is removed. Elastic deformation is recoverable and involves both a change of shape and a change of volume.

At a certain strain, when the load exceeds the yield load called ‘yield stress’, the stress strain behaviour becomes non-linear. It departs from linearity meaning that the material will retain a permanent elongation. Behaviour is not reversible, i.e. permanent changes in shape occur, but the volume remains constant. A further increase of the strain eventually reaches the ultimate load called ‘ultimate tensile stress’ beyond which the stress decreases finally leading to rupture.

Ductile materials can accommodate local stress concentrations, they can be greatly bent and reshaped without breaking, i.e. in a ductile material, the molecular bonds gradually break and re-form. In contrast, brittle materials have only a small amount of elongation at fracture, i.e. in a brittle material, all the molecular bonds break suddenly at a certain stress level. The strength of ductile material is approximately the same in tension and compression, whereas that of brittle material is much higher in compression than it is in tension. Brittle materials do not show significant permanent elongation. They fail suddenly and catastrophically when they are exposed to their tensile stress.

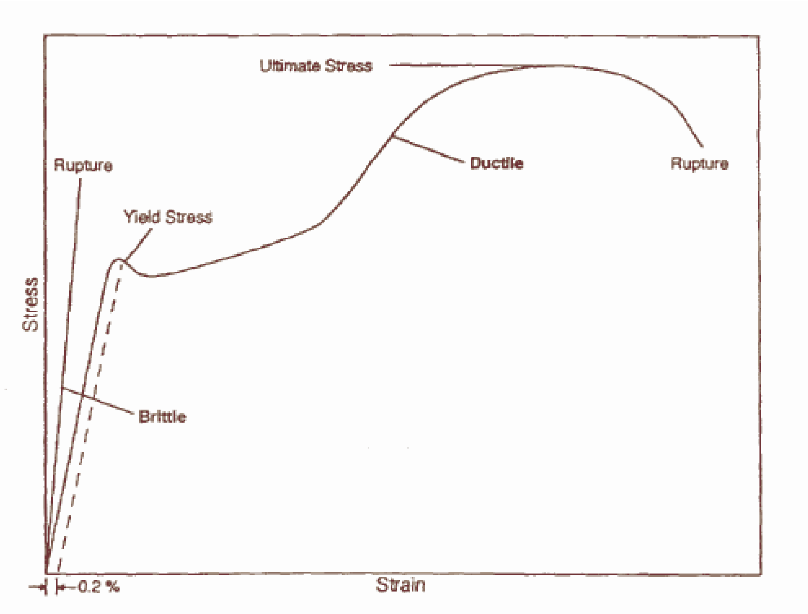

Figure I: Ductile and brittle behaviour (K. Verfondern, 1999 and M. Mohitpuro, C.L. Pierce, P. Graham, 1990)

Hydrogen can have two main effects on materials:

1°- At low temperature for example when it is stored in liquid form it can have an indirect effect called "*cold embrittlement*". This effect is not specific to hydrogen and can occur with all the cryogenic gases if the operating temperature is below the ductile-brittle transition temperature.

Cryogenic temperatures can affect structural materials. With decreasing temperature, there is a decrease in toughness that is very slight in face centred cubic materials, but can be very marked in body centre cubic ones such as ferritic steels. This phenomenon shall be considered for liquid hydrogen storages and associated equipment used at low temperature.

Metals that work successfully at low temperatures include aluminium and its alloys, copper and its alloys, nickel and some of its alloys, as well as stable austenitic stainless steels.

2°- Hydrogen can have a direct effect on the material by degrading its mechanical properties; this effect is called "*hydrogen embrittlement*" and is specific to the action of hydrogen and some other hydrogenated gases.

3.1.11.1. Hydrogen Embrittlement

The effect of hydrogen on material behaviour, on its physical properties, is a fact. Hydrogen may degrade the mechanical behaviour of metallic materials and lead them to failure.

Hydrogen embrittlement affects the three basic systems of any industry that uses hydrogen:

- Production;
- Transport/Storage;
- Use.

In fact, the presence of hydrogen atoms in a solid metal dissolved in the metal grid and accumulated in disturbed lattice regions results in the reduction of its ductility by decreasing the energy of cohesion and consequently in the increase of its probability of brittle fracture.

When tensile stresses are applied to a hydrogen embrittled component, it may fail prematurely in an unexpected and sometimes catastrophic way. An externally applied load is not required as the tensile stresses may be due to residual stresses in the material. The threshold stresses to cause cracking are commonly below the yield stress of the material. Thus, catastrophic failure can occur without significant deformation or obvious deterioration of the component.

This form of cracking, which typically changes from transgranular[1] to intergranular[2] with increasing yield strength and other processing variables and which is maximum around room temperature, is normally referred to as '*Hydrogen Embrittlement Cracking*' (HEC).

This phenomenon is different from the so called "*hydrogen attack*" that can lead to failure of steels at temperature above 473 K, being the result of the reaction of hydrogen with the carbon of the steel forming voids in the metals . In this case the solution is to use low alloy steels with addition of Cr, Mo or other elements able to fix the carbon; the Nelson curves give the pressure and temperature regions at which the different steels can safely be used; but again because it is relevant only at temperature higher than 473 K, this is normally not a concern for most of the hydrogen storage systems.

The reasons that cause the embrittlement of materials are still debated in the scientific community. Hydrogen embrittlement detection seems to be one of the most difficult aspects of the problem.

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[1] A transgranular fracture progresses across the grains.
[2] An intergranular fracture follows the grain boundaries.

However, it is known that strain, geometry, the medium and also material influence to which extent metal is degraded by hydrogen.

Purity of hydrogen is important. Some impurities can be used for putting off or avoiding the cracking phenomena due to hydrogen, because hydrogen permeability in metals can be diminished by reaction of the surface of the metal to inhibitors.

Phenomena

Embrittlement involves the ingress of hydrogen into a component, an event that can seriously reduce the ductility and load-bearing capacity, and causes cracking and catastrophic brittle failures at stresses below the yield stress of susceptible materials.

It is understood that hydrogen can cause embrittlement when present in a metal or alloy in its atomic form and not as a molecule. Dissolved hydrogen atoms in metals tend to concentrate in defects of the crystal structure (dislocations, grain boundaries …), imposing a barrier to the movement of dislocations, effectively impeding the plastic flow of the material. As a result, the ductility of the metal decreases and the material becomes brittle.

Furthermore, the concentration of hydrogen at grain boundaries, possibly in molecular form, and the potential of formation of hydrates after the reaction of hydrogen with the metal, are additional mechanisms that may lead to embrittlement.

Atomic hydrogen may enter the metal via several mechanisms: via dissolution during welding, while the metal melts locally dissolving hydrogen from water or other contaminants; via electrochemical processes, such as surface treating (electroplating, acid pickling….) or aqueous corrosion, where molecular hydrogen dissociates into atoms that diffuse into the metal; or via chemisorption, resulting from van der Waals forces between a metal surface and hydrogen molecules also resulting in the dissociation of the hydrogen molecules into atoms.

Mechanisms

Several mechanisms have been proposed which might explain at least partially the degradation of metal by hydrogen embrittlement and which might act simultaneously:

- The formation of hydrides can lead to new hydrogen-related phases which may be brittle and also may have a lower density than the pure metal leading to internal stress.
- The hydrogen distribution in a metal under stress is highly non-uniform which can lead to locally increased hydrogen-enhanced plasticity causing local microscopic deformation and eventually a failure.
- The lattice decohesion effect is presumed to cause embrittlement by a decrease in the atomic bonding strength in the presence of hydrogen. A fracture occurs when the stress exceeds the cohesive stress.
- Molecular hydrogen precipitation forming high pressures and compound formation are other mechanisms identified.

The above ideas help understand the observations that whether or not a metal is susceptible to embrittlement by hydrogen or a hydrogen compound, depends on the metal and also its metallurgical history which affect the migration behaviour of hydrogen within the metal.

The embrittlement is strongly connected with locally high hydrogen concentrations which can be caused by stress-enhanced diffusion rates to lattice defects and reaction sites to initiate cracks. Cracks grow when hydrogen concentrations reach a critical level; crack growth stops when the crack has grown through the H2-enriched region or when the stress factor has decreased sufficiently.

Sources of hydrogen and Embrittlement categories

Sources of hydrogen causing embrittlement have been encountered in the fabrication of steel, in processing parts, in welding, in storage or containment of hydrogen gas, and related to hydrogen as a contaminant in the environment that is often a by-product of general corrosion.

Hydrogen entry, the obvious pre-requisite of embrittlement, can be facilitated in a number of ways summarized below:

- By some manufacturing operations such as welding, electroplating, pickling…

  If a material subject to such operations is susceptible to hydrogen embrittlement then, a final baking heat treatment to force out any hydrogen is employed.

- As a by-product of a corrosion reaction such as in circumstances when the hydrogen production reaction results from a cathodic reaction since some of the hydrogen produced may enter the metal in atomic form rather than evolving as a gas into the surrounding environment.

  In this situation, cracking failures can often be thought of as a type of stress corrosion cracking. If the presence of hydrogen sulphide causes entry of hydrogen into the component, the cracking phenomenon is often termed '*Sulphide Stress Cracking*' (SSC).

- The use of cathodic protection for corrosion protection if the process is not properly controlled.

These ways lead to the definition of three different categories of the phenomena:

- Environmental Hydrogen Embrittlement

  Occurs when the material is being subjected to a hydrogen atmosphere, e.g., storage tanks. Absorbed and/or adsorbed hydrogen modifies the mechanical response of the material without necessarily forming a second phase. The effect strongly depends on the stress imposed on the metal. It also maximizes at around room temperature.

- Internal Reversible Hydrogen Embrittlement

  Takes place when hydrogen enters the metal during its processing. It is a phenomenon that may lead to the structural failure of material that never has been exposed to hydrogen before. Internal cracks are initiated showing a discontinuous growth. Not more than 0.1 - 10 ppm hydrogen in the average are involved. The effect is observed in the temperature range between 173 and 373 K and is most severe near room temperature.

- Hydrogen Reaction Embrittlement

  It is a phenomenon in which the hydrogen chemically reacts with a constituent of the metal to form a new microstructural element or phase such as a hydride or to generate gas bubbles -'blistering'-. These reactions usually occur at higher temperatures. They result in the formation of blisters or expansions from which cracks may start to weaken the metal.

  Thus, this phenomenon leads to the formation of internal hydrogen blisters or blister-like cracks at internal delaminations or at sites of non-metallic inclusions in low strength materials. These internal cracks may propagate by a process called '*Hydrogen-Induced Cracking*' (HIC) or hydrogen blistering.

This embrittlement category is also responsible for failures in hydrogen-related process plants, a phenomenon known as '*Hydrogen attack*'. Hydrogen attack has been reported in plain carbon steel, low alloy steels and even some stainless steels operating above 473 K. It is one of the major causes of problems in refineries, where hydrogen and hydrocarbon streams are handled under conditions of up to 20 MPa and 773 K. In this context, failure is the result of the formation of intermetallic phases from the host metal and hydrogen dissolved in the metallic matrix via chemisorption and electrochemical reactions, changing the properties of the material, degrading its mechanical properties and forming methane gas that accumulates in the grain boundaries of metallic components leading to failure caused by void growth and assisted by creep.

The case of hydride formation presents a different nature and that of titanium alloys is a typical one. The microstructure of these alloys consists usually of two phases (α and β) with different hydrogen solubilities and diffusivities. Hydrogen enters the alloy via grain boundaries or other easy paths as β phase forming hydrides that precipitate in the α phase. The mechanism of embrittlement is related in these alloys to this localized hydride precipitation.

Materials

Material suitability for hydrogen service should be evaluated carefully before it is used. A material should not be used unless data are available to prove that it is suitable for the planned service conditions. In case of any doubt the material can be subjected to hydrogen embrittlement susceptibility testing (e.g. ISO 11114-4).

According to the information included in the *ISO/TR 15916:2004 Basic considerations for the safety of hydrogen systems /Technical Report* most of the metallic materials present a certain degree of sensitivity to hydrogen embrittlement. However, there are some that can be used without any specific precautions as for example brass and most of the copper alloys or aluminium and its alloys. On the other hand, nickel and high nickel alloys or titanium and its alloys are known to be sensitive to hydrogen embrittlement. For steels the sensitivity may depend on several factors as the exact chemical composition, heat or mechanical treatment, microstructure, impurities and strength. Concerning non-metallic materials, ISO/TR 15916:2004 also provides information as far as the suitability of some selected materials.

Fortunately many materials can be safely used under controlled conditions (e.g. limited stress, absence of stress raisers such as surface defects….).

3.1.12 Knowledge gaps and recent progress

The main knowledge gaps on this matter are concentrated on the reasons that cause the embrittlement of materials. As it was said in the previous subchapter, these reasons are still debated in the scientific community. Currently this phenomenon is not completely understood and hydrogen embrittlement detection, in particular, seems to be one of the most difficult aspects of the problem. Now, a materials test equipment has been developed in Japan within the WE-NET (World Energy NETwork) project to investigate the environmental hydrogen embrittlement under particular conditions (high pressure hydrogen up to 10MPa, and temperatures between 20-1500K).

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