Hydrogen failures without Hydrogen?

The shift towards a hydrogen economy brings about many challenges, not least the well-known, but often poorly understood, threat it poses to the integrity of pipework and vessels on hydrogen duty.

On the macro-scale, these mechanisms manifest themselves as three low temperature mechanisms (hydrogen embrittlement, hydrogen induced cracking, and hydrogen stress cracking) and are often observed in the material as step-wise cracking (Figure 1). Providing the right materials are used, hydrogen pipework / vessels generally operate without issue, however, hydrogen failures can still occur on site and pose a risk to asset integrity, often when there is no direct exposure to hydrogen.

High strength steels are most commonly affected by hydrogen however certain types of stainless steel or cold worked stainless steel can be affected, as can some nickel alloys as well as cast iron and exotic metals that form hydrides such as titanium.

Hydrogen enters metals in the form of nascent (atomic) hydrogen, which is always present to some degree in gaseous hydrogen, and is small enough to enter between the crystal structure interstices. Molecular hydrogen cannot enter as this is much larger than the space between interstices, Molecular hydrogen having a diameter of 124 pm compared to ~75 pm for the interstices of BCC iron, and 13 pm for nascent hydrogen. Corrosion evolves relatively significant amounts of nascent hydrogen which can enter and damage material even when hydrogen is nowhere near to be found. This tends to be the most common cause of hydrogen failures seen.

Figure 1: Step-wise cracking which is characteristic of low temperature hydrogen failures.

Despite regular and well documented inspection regimes for non-return valves, hydrogen induced cracking failures are still seen in high strength steel springs in these items (Figure 2). These failures occur due to corrosive product coming into contact with the bare metal of the spring, due to paint degradation typically as a result of its poor application. Failure of relief valve (RV) springs could the valve to consequently fail to lift and potentially having much larger consequences.

High strength lifting chains also typically experience hydrogen induced cracking due to the evolution of hydrogen due to corrosion when used in acidic or alkali environments, such as chimney stacks and wash bays, there is even HSE guidance note PM39 advising against the use of grade 8 chains in these locations yet failures still occur. A failure of a lifting chain could easily result mechanical damage to nearby assets, large spills, or even a casualty.

Figure 2: Corrosion in a high strength steel RV spring which failed due to hydrogen embrittlement.

Another common hydrogen failure is the embrittlement and cracking of zinc coated high strength steel bolts. These become charged with hydrogen during manufacture when they are acid cleaned before galvanising and lead to early failures once used on site. The failure of bolts on a flange for example could lead to leaks and if being used for hydrogen duty could have much greater consequences.

In summary, the majority of hydrogen related failures do not occur on hydrogen duty, particularly when equipment has been designed for hydrogen service, but arise from the introduction of atomic hydrogen to a susceptible material where hydrogen damage mechanisms may not be anticipated. Hydrogen failures require a susceptible material, most often it is high strength steels, particularly if they are galvanised, and a source of atomic hydrogen, most commonly being corrosion or damp welding rods. This is due to the fact that molecular hydrogen is too large to enter the material while atomic hydrogen is small enough to pass through the interstitial spaces of metallic crystals. Once hydrogen has entered the material, however, the underlying theoretical mechanisms are not fully understood.

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http://www.axiom-ltd.com
Steve Woodward BSc CEng FIMMM
Principal Materials Engineer, AXIOM
E: steve.woodward@axiom-ltd.com