Hydrogen in metals

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Abstract

The effects of hydrogen on various metals and the use of metal hydrides for hydrogen storage are discussed. The mechanisms of, and differences between, hydrogen embrittlement and hydrogen attack of ferritic steels are compared, common sources of hydrogen in metals processing and treatment identified, and mechanisms for hydrogen entry into a ferritic surface are discussed. The differences between hydrogen attack of ferritic steels and copper alloys are contrasted, and an unusual case study of hydrogen embrittlement of an alloy steel is presented. © 2001 Published by Elsevier Science Ltd.

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1. Introduction

Hydrogen suffers from a poor public image in general, usually summoning up images of the airship 'Hindenberg' crashing in flames at Lakefield, New Jersey on 6th May 1937. Hydrogen, however, by far the most abundant element in the universe, is a safe and clean fuel gas of high calorific value, available in virtually unlimited quantities by the electrolysis of water. Non-polluting, it produces essentially only the water from which it was originally derived as a combustion product, and from which it may be recovered for re-use.

Another major source of hydrogen-containing fuels are fossil-based hydrocarbons. Whilst much less environmentally-friendly than pure hydrogen, they are much more readily available, being provided by a massive commercial global infrastructure for extraction, refining and distribution. Both natural and synthetic hydrocarbon fuels are widely used and constitute by far the largest source of energy available to mankind today.

Thus the extraction and processing of hydrogen and hydrogen-containing materials is of prime importance to the global economy, and their safe containment during processing presents major challenges to the materials engineer.

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2. Hydrogen

Hydrogen is the lightest element with an atomic structure of one proton and a single electron and is, in its natural state, a di-atomic molecular gas, H_2. In its molecular form, it is too large to diffuse interstitially in most metals, neither can it readily cross the gas/metal interface in the molecular form. If the metal is molten, molecular hydrogen can dissolve readily, but dissociates once in solution and can be retained as a mono-atomic solute on solidification.

If the material is solid, some mechanism to generate mono-atomic hydrogen at the gas/metal interface is necessary, and several known mechanisms will be discussed.

Whilst an interstitial solute, hydrogen remains in the mono-atomic form and is relatively mobile, even at ambient temperatures. However, to maintain such a mobile atom as an interstitial solute presents problems in metals, although crystalline, are far from perfect, and lattice defects present areas where the lattice strain induced by the solute hydrogen atom is reduced, and thus will tend to act as hydrogen traps.

When it is so trapped, the hydrogen atom becomes relatively immobile, but it is thought to remain as a single atom. If the trap site is a vacancy, the presence of a single hydrogen atom will lower the lattice strain due to the vacancy, and the hydrogen atom becomes a substitutional, rather than an interstitial, solute.

If, which is more likely due to their larger size and thus better accommodation, the trap is a line defect, there may well accumulate a string of hydrogen atoms along the defect. The presence of a string of individual hydrogen atoms would not immobilise a dislocation, although it would increase the applied stress needed for movement. However, if two adjacent atoms on a line defect recombine to form molecular hydrogen, the applied stress required to cause movement becomes much greater, effectively pinning the dislocation at that point. Since dislocation movement is the underlying process to plastic flow, the ductility of the material is reduced and the probability of brittle failure increased by the presence of hydrogen. In this context, interfaces such as grain boundaries or second phases should be considered as dislocation arrays, and thus are likely to accumulate solute hydrogen, quite possibly in molecular form, embrittling the interface. In addition to reducing the mobility of dislocations, solute hydrogen can also react, either with the solvent metal to form a hydride, or with some other solute element to form a new phase.

3. Hydrogen entry mechanisms into metals

Molecular hydrogen gas can readily enter a molten metal surface, often added accidentally as water contained in fluxes, mould dressings and alloying additions, dissociating into the mono-atomic form on dissolution, and remaining as a mono-atomic solute on solidification.

The diatomic hydrogen molecule is too large to enter the surface of a solid metal, and must be dissociated into single atoms. Two mechanisms for this are known, electrochemical and chemisorption.

4. Electrochemical evolution

The electrochemical evolution of atomic hydrogen is part of the cathode reaction in either a corrosion cell or an electroplating process. In addition, these can include such processes as acid cleaning and cathodic protection systems. As corrosion is essentially an electrochemical mechanism, both are sufficiently similar to be considered identical for the purpose of hydrogen evolution, and take the form:

$$M + H_2O \rightarrow MO + 2H$$
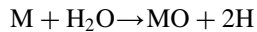
Most of the hydrogen atoms thus formed quickly combine to form diatomic gaseous hydrogen, but a portion of it enter the metal surface and remain as individual atoms in solution.

Chemisorption dissociation of hydrogen (Fig. 1) is a rather different mechanism, and is well described by Christmann [1]. As a hydrogen molecule approaches a metal surface, weak van Der Waal's forces begin to act upon it, drawing it closer.

The molecule reaches an energy well, E_p, at distance Z_p, close to the surface, and very large forces would be required to force it any closer in a molecular form. At this point, however, the dissociation energy for the hydrogen molecule, typically 432 kJ mol^{-1} is exceeded by the chemisorption energy, which varies typically between 500 and 600 kJ mol^{-1}, depending on the metal involved. Thus the hydrogen molecule can be cleaved into two individual atoms, which are individually attracted to the surface by chemisorptive forces. At room temperature, these atoms enter an energy well, E_{ch}, which is closer to the surface than E_p, but are still prevented from reaching the metal surface. At higher temperatures, however, sufficient thermal energy is available to increase the vibrational amplitude of both, the hydrogen atoms and those of the metal surface, and individual hydrogen atoms can reach and enter the metal surface.

5. Case study — a most unusual mechanism

This case study concerns a compressor disc from a gas turbine engine, which failed by hydrogen embrittlement in which the source of hydrogen was unusual, to say the least. The disc was the seventh stage compressor disc, which was of two-part construction, and the failure was of the down-stream half. The turbine, as a result of an accident, caught fire, and was partially burned out, the fire being extinguished after some time by the Fire Department, who used water-based foam extinguishant. The casing of the turbine compressor, made of a magnesium alloy, had burned away, and when examined, some twenty-four hours after the incident, the compressor discs were visible without dismantling, and the seventh stage disc was seen to be cracked. Unfortunately, no photographs were taken at the site, and it was not until the entire unit was transported back to the workshop that the position of cracking was recorded as at the top of the rear half of the disc.
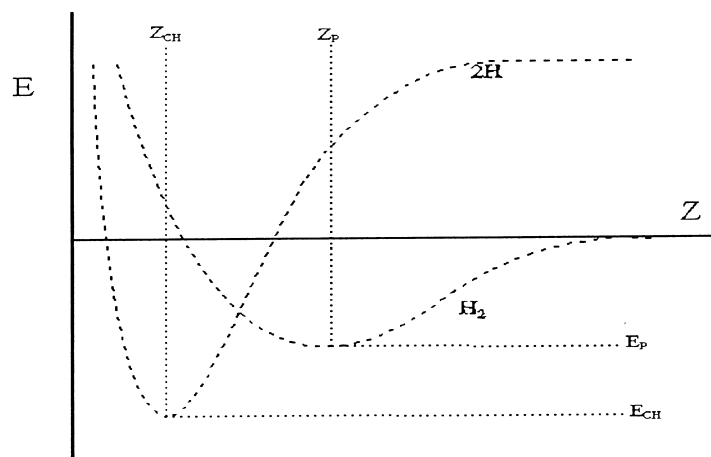

Fig. 1. Chemisorptive dissociation of hydrogen (after Christmann [1]).

Table 1
Composition of the compressor disk in wt%, balance iron

C	Mn	Si	S	Ni	Cr	Mo	V
0.42	0.61	0.35	< 0.001	0.21	3.22	0.83	0.24

After preliminary examination and dismantling by the engineers, the cracked disk was submitted to the Materials Laboratory for investigation, which initially followed conventional lines. The material of construction of the disc was correct, being a medium carbon steel alloyed with chromium, molybdenum and vanadium (Table 1), for creep resistance, typical for a compressor disc operating at elevated temperatures.

The microstructure of the disc was correct as a tempered martensite structure (Fig. 2), indicating that the material was in the hardened and tempered condition, as was specified on the construction drawings, with a hardness, also correct to the specification, of approximately 387 HV30. When the areas of the disc around the crack were examined, a very different picture began to emerge. The microstructure was of untempered martensite (Fig. 3), with a hardness above 660 HV30. In addition, when left alone, the disc continued to crack, with the propagation being audible as a series of 'pings'. When examined using a scanning electron microscope, the fracture surface exhibited a number of features typical of hydrogen embrittlement (Fig. 4).

The turbine had been fuelled by conventional kerosine-base fuel, and not by gaseous hydrogen, and in any case, the compressor discs are upstream from the combustors where the fuel is burned. The affected component had operated at a temperature of several hundreds of degree centigrade, far above the temperatures at which hydrogen picked up electrochemically is driven off in de-embrittling heat treatment, and where any water vapour in the air will be present as superheated, dry steam. Thus two questions arose. Where had the hydrogen come from, and where and how did it enter the disc material?
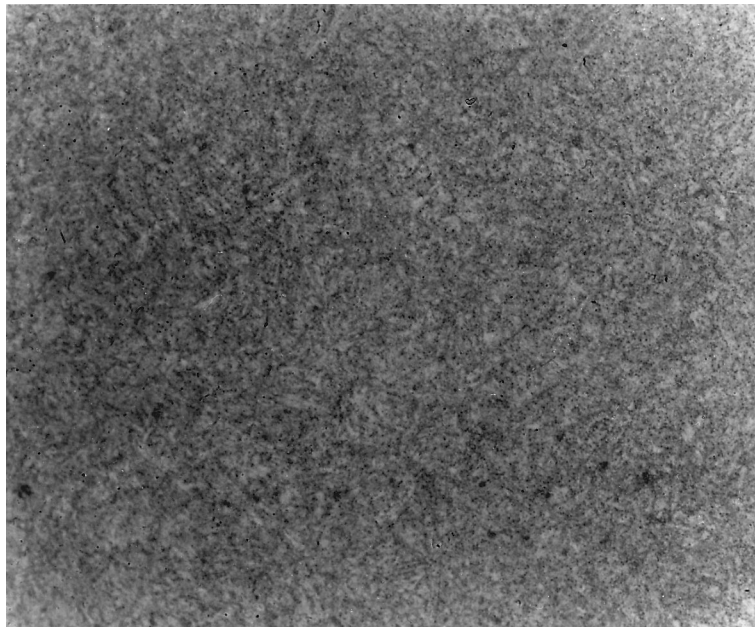

Fig. 2. Hardened and tempered microstructure of disc.

Eventually, it was deduced that the hydrogen had been generated when the Fire Crew extinguished the burning turbine compressor casing. Magnesium is highly reactive, sufficiently so to strip oxygen from water to maintain combustion. Thus a simple chain of events leading to failure of the disc emerges. The disc, locally heated at the top in the fire, was temporarily austenitised. At the same time, the water-based foam in contact with fiercely burning magnesium was stripped of oxygen to maintain combustion, but was denied access to atmospheric oxygen to combust the hydrogen left. Some of this hydrogen was absorbed by the hot disc material, which was promptly quenched by the Fire Crew's foam spray, retaining the hydrogen. This lead to the classic hydrogen embrittlement scenario, in which a high strength, low ductility material, subjected to residual stresses from quenching, was embrittled by hydrogen, leading to delayed cracking.

Incidentally, the failure of the turbine, not due to hydrogen cracking failure of the compressor disc which occurred after the event, was eventually attributed to the ingestion of foreign material.

6. Metal hydrides and the 'hydrogen battery'

Hydrogen does have some beneficial effects when dissolved in metals. With the push towards ecologically-friendly motor vehicles, the safe storage of hydrogen gas in a light weight, compact form has been extensively researched.

Many of the hydrogen-powered motor vehicles developed so far utilise the ability of some metals and alloys to react reversibly with hydrogen to form metal hydrides, enabling a low-pressure, but high storage density, 'hydrogen battery'. It is possible [2], by careful selection of the metallic components of the hydride, to store a slightly greater volume of hydrogen as an hydride than as liquid hydrogen, and about an order of magnitude more than as compressed gas. If measured in terms of energy density, these figures are improved still further. This method of storage almost completely eliminates the dangers
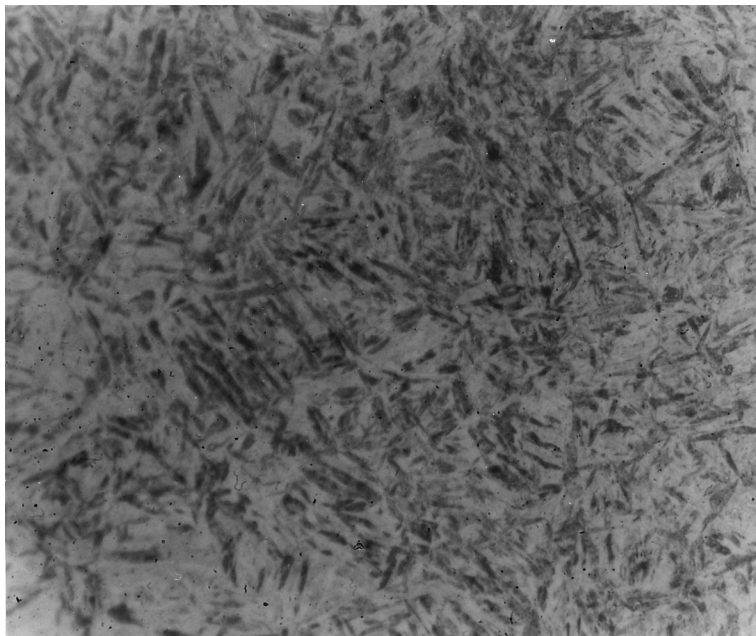

Fig. 3. Untempered martensite adjacent to cracking.

of high pressure hydrogen gas storage, and its obvious problems of heavy containment vessels, as well as the probability of fire or explosion if the containment integrity is violated in an accident. Metal hydride hydrogen storage systems release the gas content relatively slowly, and, even if punctured, render unlikely the ignition of the escaping gas by discharge of the static electrical charge generated by escaping high pressure gas.

Apart from utilising metal hydrides as a storage medium, almost without exception, any other combination of metals and hydrogen is likely to prove problematic, with hydrogen degrading, and ultimately destroying the mechanical properties of the material which it attacks. Even the metals used for hydride batteries slowly disintegrate into powder by the repeated formation and dissolution of hydrides within their microstructures, becoming unusable after a time.

7. Hydrogen attack of copper and copper alloys

A lesser-known hydrogen attack mechanism is that on copper. Largely eliminated by the introduction of oxygen-free copper materials, hydrogen attack nevertheless still rears its ugly head from time to time when oxygen-containing copper and copper alloys are exposed to hydrogen at even moderately elevated temperatures.

The residual dissolved oxygen in copper from air injection during the refining process usually manifests as a fine dispersion of inclusions of copper oxide Cu_2O in the microstructure, either at grain boundaries when as-cast, or as dispersed stringers after hot working. Removal of dissolved oxygen by the addition of phosphorus significantly reduces the conductivity, and is therefore undesirable in many applications.

In contact with hydrogen at elevated temperatures, hydrogen enters the material and reduces the oxide inclusions:
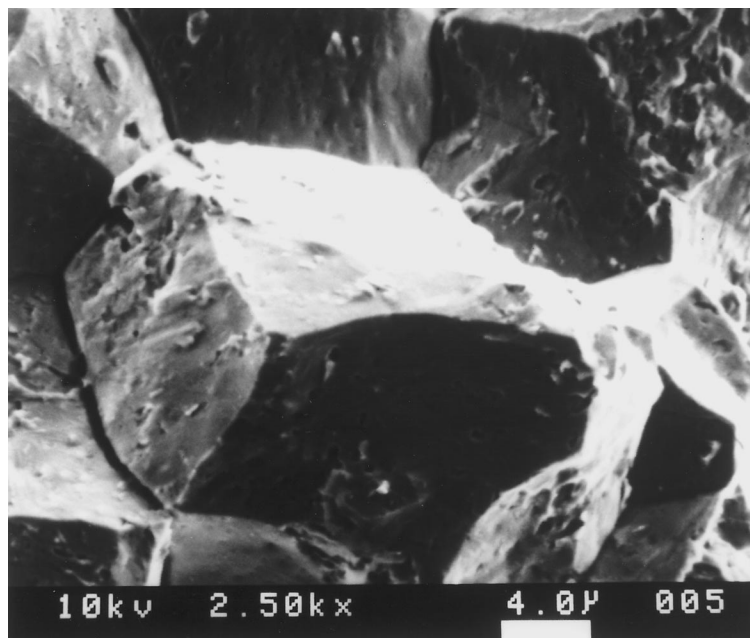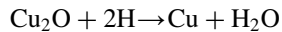

Fig. 4. SEM image of the fracture surface.

$$Cu_2O + 2H \rightarrow Cu + H_2O$$

producing steam at high pressures, sufficient to form small voids in the microstructure, similar to creep voids, and with the same deleterious effect on the mechanical properties. As may be surmised, the process is irreversible and the damage permanent.

8. The effects of hydrogen on ferritic steels

Iron does not, at normal pressures and temperatures, form hydrides. It has been reported [3] that at very high pressures, of the order of several GPa, and at elevated temperatures, iron hydride FeH_2 is formed. Having a hexagonal close-packed structure, this phase will be completely incoherent with the bc-cubic α-Fe lattice. At atmospheric pressure and temperatures ≥ 153 K, it decomposes to bc-cubic α-Fe and, reportedly, molecular hydrogen. However, it is probable that the hydrogen is initially mono-atomic, and only combines to form molecular hydrogen if it is not retained within the microstructure, and is released to atmosphere, or into a void within the material.

If the dissolved hydrogen migrates to lattice defects, the overall internal lattice strain within the system decreases, but the ability of the material to accommodate plastic deformation, which relies upon the movement of line defects decreases. This occurs through the dislocation locking effect of the trapped hydrogen, either as single atoms or as di-atomic molecules, and the material exhibits decreased ductility.

Hydrogen attacks ferritic steels by two distinct and different mechanisms, one at ambient temperature, known as 'hydrogen embrittlement', the other is a high temperature phenomenon, known as 'hydrogen attack'.

9. Hydrogen embrittlement

Hydrogen embrittlement occurs when solute hydrogen gas accumulates on lattice defects, usually dislocations and interfaces between the metal and a second phase, or grain boundaries, the latter two of which features can be considered to be complex dislocation arrays, restricting ductility and promoting brittle behaviour. Two common forms of hydrogen embrittlement exist, differentiated by the method by which hydrogen is introduced into the material, welding and surface electrochemical processes and reactions.

10. Welding

Hydrogen pick-up during fusion welding operations is a relatively straight-forward mechanism in which hydrogen, dissociated from water present as a contaminant either in welding consumables, filler materials, fluxes or shield gases, enters the molten weld pool. Alternatively, hydrogen from surface contamination of water or hydrocarbon oils or greases on the faying surfaces is absorbed into the molten weld pool and remains trapped on solidification. While the weld area remains hot from the welding process, this hydrogen diffuses away from the weld fusion zone and into the adjacent parent material. This area of parent material is the zone affected by the welding heat and is known as the heat affected zone (HAZ), and is the area in which transformation of the microstructure will occur due to the heating and cooling of the weld cycle. Harder transformation products are produced, and additionally the stresses generated by the contraction of the solidifying weld pool must also be accommodated. Thus there exists a region which is high in hardness, due to the metallurgical transformations resulting from

the weld heat cycle, and which is subjected to a relatively high tensile load imposed by the contracting weld fusion zone, Also the ductility is locally impaired by the presence of hydrogen. The result is inevitable, and cracking occurs, usually withing a few hours of the completion of the welding operation. Most welding codes insist that non-destructive testing of welded fabrications is delayed by at least 72 hours to allow hydrogen cracking to develop and so not go un-detected.

Fortunately, in a well designed welded joint all three factors can be eliminated. Undesirable transformations of the parent material in the HAZ to unwanted hard structures are controlled by suitable pre-heat and controlled post-weld cooling, and any remaining unwanted transformed structures are further modified to an acceptable form by post weld heat treatment. The very presence of hydrogen is eliminated, as far as possible by elimination of hydrogen-containing water or hydrocarbons from the joint and the weld consumables, and the stresses imposed by solidification contraction are removed by post-weld stress relief. Any remaining hydrogen is also eliminated by the post-weld stress relief heat treatment.

In spite of the ease with which hydrogen cracking can be eliminated, and the high degree of understanding of the mechanisms responsible, it remains a major cause of weld failure.

11. Surface electrochemical processes and reactions

Hydrogen is evolved in a mono-atomic form as part of the cathode reaction of almost any electrochemical reaction, several of which are commonly applied to ferrous surfaces. Common examples are processes such as electroplating and acid pickling, both of which are almost notorious causes of post-processing failure through hydrogen embrittlement.

Another, less obvious, electrochemical mechanism is almost any aqueous corrosion process. In most instances, the level of hydrogen generated is insufficient to give problems, and the affected layer is removed by the corrosion process itself before any damage be done by the hydrogen evolved, but the ability of corrosion to utilise hydrogen in its destructive workings should never be underestimated.

It is widely believed that hydrogen plays a major role in the mechanism of stress corrosion cracking, which is a well-known destroyer of chemical process plant and other metallic structures. SCC is also known as 'Hydrogen Stress-Sorption Cracking', which emphasises the part played by hydrogen in the mechanism.

Another, perhaps better understood mechanism is that of hydrogen embrittlement resulting from the imposition of electrical cathodic protection systems to steel structures either buried in the ground or immersed in water. The cathodic protection technique utilises externally applied electrical charges to force the surface to protected to become cathodic to either an inert or consumable anode, thus protecting the surface from metal loss through corrosion. Unfortunately, the cathodic reaction includes the evolution of hydrogen which is, initially at least, in the mono-atomic form in which it can readily enter the metal surface.

12. Hydrogen attack

Hydrogen attack, unlike hydrogen embrittlement, involves the formation of a second phase by the solute hydrogen, and, unlike the previous mechanisms, is an elevated temperature phenomenon. Hydrogen solubility in α-Fe is negligible. Similarly, the solubility of carbon in α-Fe is extremely small. However, if the two are present they can react together, at a suitable elevated temperature, to form methane.

$$C + 2H_2 \rightarrow CH_4$$
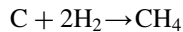
The items of equipment with which hydrogen attack is normally associated are usually items of hydrocarbon processing plant, which spend substantial periods of time, years rather than hours, at high temperatures and in contact with hydrogen. Thus they can be considered to operate in equilibrium conditions from microstructural and metallurgical thermodynamics aspects.

While in contact with hydrogen containing process streams in such plants, the hydrogen is normally either molecular or combined with carbon, and the electrochemical processes responsible for the mono-atomic hydrogen causing hydrogen embrittlement are absent because of the lack of water in the process stream. However, the previously discussed chemisorption mechanism can provide a source of individual hydrogen atoms at a metal surface in the absence of an aqueous electrochemical mechanism.

When the chemisorbed hydrogen enters the structure, it reacts with the solute carbon in the α-Fe structure and destroys the equilibrium of the α-Fe phase with carbon. As the system is operating under essentially equilibrium conditions, more non-solute carbon, in the form of metal carbides will dissociate, and redissolve in the α-Fe phase to restore the equilibrium altered by the reaction. Thus the material appears at a macro-scale to become decarburised, and this is the initial indication of hydrogen attack when normal macro scale examination techniques are employed. The rate of supply of carbon to restore the equilibrium solute carbon concentration will depend upon a number of factors. The dissociation of carbides is an Arrhenius-rate controlled process, and is consequently dependant upon the temperature. In addition, the binding energy of the specific carbide will be a factor, with the more stable carbides releasing carbon more slowly and at higher temperatures.

As the supply of hydrogen continues, an increasing amount of methane is formed, consuming more and more carbon. The methane molecule is large, and is immobile in the lattice, and voids are formed in the microstructure. It is believed that these voids grow initially by the diffusion of iron atoms away from the void, that is essentially a vacancy condensation mechanism. After reaching a critical size, growth is by power-law creep driven by the increasing methane pressure within the void.

The pressure of methane within the voids can reach very high values, at which the behaviour of methane as a non-ideal gas becomes very relevant, and the difference between methane pressure and methane fugacity becomes a major consideration in the prediction of void growth by creep.

The behaviour of the more common engineering steels in a hydrogen environment has been summarised by Nelson [4], who examined data from many operating hydrocarbon processing plants around the world, and produced a family of curves [5], known as the 'Nelson Curves'. These delineate the attack/safe boundary in terms of temperature and hydrogen partial pressure for the more commonly used alloys for hydrogen plant service. These curves have been updated as new data becomes available, and form the basis for material selection for hydrogen service.

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