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Hydrogen embrittlement in power plant steels

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Abstract. In power plants, several major components such as steam generator tubes, boilers, steam/water pipe lines, water box of condensers and the other auxiliary components like bolts, nuts, screws fasteners and supporting assemblies are commonly fabricated from plain carbon steels, as well as low and high alloy steels. These components often fail catastrophically due to hydrogen embrittlement. A brief overview of our current understanding of the phenomenon of such hydrogen damage in steels is presented in this paper. Case histories of failures of steel components due to hydrogen embrittlement, which are reported in literature, are briefly discussed. A phenomenological assessment of overall process of hydrogen embrittlement and classification of the various damage modes are summarized. Influence of several physical and metallurgical variables on the susceptibility of steels to hydrogen embrittlement, mechanisms of hydrogen embrittlement and current approaches to combat this problem are also presented.

Keywords. Hydrogen embrittlement; cold cracking; steels; power plant components; control of hydrogen embrittlement

1. Introduction

Hydrogen embrittlement is a form of environmentally assisted failure which is caused by the action of hydrogen often in combination with residual or applied stress resulting in the reduction of the load bearing capacity of a component. Many metallic alloys such as those of Fe, Ni, Al, Ti, Zr, Ta, Hf, Nb, V, W, Mo and U are susceptible to hydrogen embrittlement and in fact no structural alloy is totally immune to this type of embrittlement. Generally a small quantity of hydrogen is sufficient to cause failures because it has the ability to magnify its effect by migrating to regions of high triaxial stress. The problem of hydrogen embrittlement in structural alloys has been of great concern in various industries including power plants. Hydrogen embrittlement or hydriding has led to the failures of fuel cladding in nuclear reactors (Caskey *et al* 1962), cracking of fossil fuel boilers tubes (Weiss 1993; Speidel & Atrenes 1984; *Metals handbook* 1987), retaining rings of generator rotors (Speidel & Atrenes 1984), waterside components of condensers (*Metals handbook* 1987) and in many other components where there is a possibility of hydrogen ingress in the material. Hydrogen embrittlement manifests itself in diverse modes of material failures each of which is highly specific to the alloy system. This topic has been of research investigations for more than one and half century. Based on the findings different classifications and theories have been put forward to explain the phenomena. Owing to the vastness of the subject, we have restricted our focus in this article in elucidating the current status of our understanding of these hydrogen embrittlement phenomena in steels mainly used in power plants. In the initial part of this article, the case histories of failures in power plant components due to hydrogen embrittlement, which are hitherto evaluated in the literature, are briefly described. This is followed by phenomenological assessment of overall process of hydrogen embrittlement including a classification of hydrogen damage. Subsequently various mechanisms of hydrogen embrittlement in steel are summarized in a nutshell. Finally the evolution of recent techniques in arresting or preventing hydrogen embrittlement has been analysed.

2. Hydrogen embrittlement failures in power plant components

Plain carbon steels, low and high alloy steels, martensitic and ferritic stainless steels are some examples of steels that are generally used in power plants for fabrication of various components such as steam generators, condensers, water headers, bolts, nuts and fasteners. During their service life, these steels pick up hydrogen from the surrounding environment, which migrates in to the matrix and causes damage. The pick up of hydrogen may be due to corrosion in aqueous medium (including pickling), excessive cathodic protection, electroplating (without baking), welding using damp electrodes, hydrogen gas (if moist) used as coolant in generators etc. Hydrogen can initially be present either externally or internally within the bulk of a structural alloy. Whenever steel surfaces come in to contact with an aqueous environment the following reactions take place:

$$x\mathrm{Fe} + y\mathrm{H_2O} \rightarrow \mathrm{Fe}_x\mathrm{O}_y + 2y\mathrm{H}^+,$$
$$\mathrm{H}^+ + e \rightarrow \mathrm{H}_{(\mathrm{ads})}.$$

The adsorbed hydrogen (in atomic form) migrates further into the metal matrix causing metal–hydrogen interaction. The molecular hydrogen formed on the external surface gets evolved as a gas in the aqueous solution. Hydrogen can also be introduced into steel during the steelmaking process, fabrication or service causing hydrogen embrittlement failures.

A very common failure in fossil boiler tubes is hydrogen damage/attack (Speidel & Atrenes 1984; *Metals handbook* 1987). It results from acid corrosion either due to condenser leaks allowing ingress of chloride or improper rinsing of chemical cleaning solutions. The nascent hydrogen generated by corrosion reactions diffuses into the metal and reacts with carbon present in the iron carbides to form methane bubble. Reduction in carbon content leads to decarburisation. The large methane molecules trapped produce very high localized stress leading to microfissures which link up and form cracks. Sometimes pitting caused by high oxygen level as well as chlorides is also associated with hydrogen damage. This problem can be avoided by controlling condenser leaks, using adequate post cleaning and flushing operations and also by maintaining good oxygen control.

Such irreversible hydrogen attack has been reported in several high pressure steam pipes which were in service for as long as 25 years (figures 1 and 2) (Antonio 1993). In these cases, initially thick internal corrosion deposits were formed on the walls. The hydrogen and hydroxyl ion concentrations built up on these deposits caused active corrosion and atomic hydrogen generated from such corrosion reactions led to hydrogen attack. Rupture of refinery boiler tubes by a similar mechanism has also been reported (Islam 1993). Water-wall tube failures in a coal-and oil-fired boiler in service for 12 years have been caused by localized corrosion and hydrogen damage (Hahn 1993). In this case copper in the corrosion deposit was detected which accelerated corrosion through the galvanic effect and promoted hydrogen damage by generating more hydrogen at the tube/water interface. A rear-wall tube section of a boiler that had been in service for 38 years also failed due to decarburisation and methane formation similar to the one described above (Weiss 1993). The boiler experienced a pH depression during operation and hydrogen generated led to the failure as shown in the figures 3 and 4.

Hydrogen embrittlement of retaining rings has been observed in many generator rotors which are cooled with gaseous hydrogen (Speidel & Atrenes 1984). The retaining rings made from 18Mn–4Cr steel are resistant to hydrogen embrittlement in dry hydrogen gas but show cracking in water or moist hydrogen medium. These rings – have improved performance and use of dry hydrogen gas is generally recommended to avoid such failures.

Hydrogen embrittlement cracking has been identified as a problem on the water side of ferritic stainless steel tubes in several condensers fitted with cathodic protection system (*Metals handbook* 1987). An excessive cathodic protection current generated hydrogen on the surface of the tubes which promoted slow crack growth and fracture at the end of the tubes. The tube ends were particularly susceptible to hydrogen embrittlement cracking as the roller expansion during fabrication introduced higher level of residual stress. Such failures can be avoided by selection of proper cathodic protection parameters and eliminating or reducing the residual stresses in the tubes.

The damage in the form of hydrogen induced cracking (HIC) is the most common cracking problem encountered during the fabrication of welded steel structures used in power plants. It is also known as cold cracking or delayed cracking. This occurs due to the combined presence of tensile residual stresses and hydrogen absorbed during welding. The most important sources of hydrogen in the weld joints are absorbed moisture, organic materials in the electrode coating, flux, flux-cored wires, water vapour in air and shielding gas, hydrogen in filler and corrosion products. In general, higher the strength of the weld, lower is the resistance to HIC and the tougher a microstructure, greater is its resistance to HIC (Dolby 1977; Bailey *et al* 1989). Steels containing Cr and Mo are extensively used in power plants as steam generator tubes in heat exchangers. The microstructure of both weld metal and heat affected zone (HAZ) of these steels are of high hardness in the as-welded condition and hence they are quite susceptible to HIC. For instance, 9Cr–1Mo steel which is a candidate material for steam generator tube of fast reactors has been found to be highly susceptible to HIC in the as-welded condition without post weld heat treatment (PWHT) at the heat affected zone/base metal interface (Parvathavarthini *et al* 1995). The same zone has been reported to be sensitized and hence susceptible to intergranular corrosion. Hence, if proper PWHT is not performed after welding, corrosion generated hydrogen is likely to cause failure as shown in figure 5. By pre or post-weld heat treatment and by using non-cellulosic electrodes with proper baking, HIC can be minimized.

In addition to the above mentioned components, there are many other vital metallic parts made of steels in the power plant system where hydrogen embrittlement problems are encountered. For example cadmium plated carbon steel socket head cap screws generally used in valve assemblies failed as shown in figure 6 (Tanner 1993) during service due to the absorption of hydrogen during plating process and the subsequent insufficient baking of cap screws. Similarly, self-drilling tapping screw made of type 410 martensitic stainless steel which is used in the structural steel frames in the buildings failed in re-torquing test due to the hydrogen

Figure 1. High pressure steam pipe containing blow out window fracture (Antonio 1993).

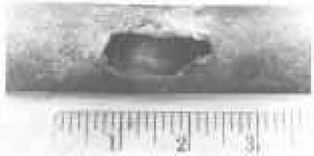

Figure 2. Close-up view of the window (Antonio 1993).

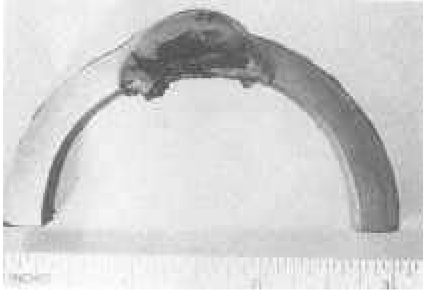

Figure 3. Cross-section of the boiler showing the damage due to hydrogen (Weiss 1993).

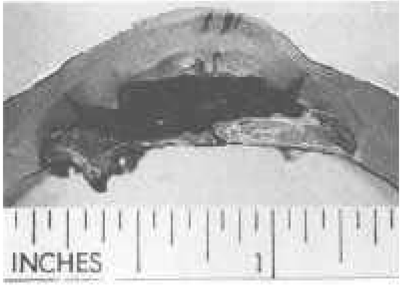

Figure 4. Close-up view of the bulge (Weiss 1993).

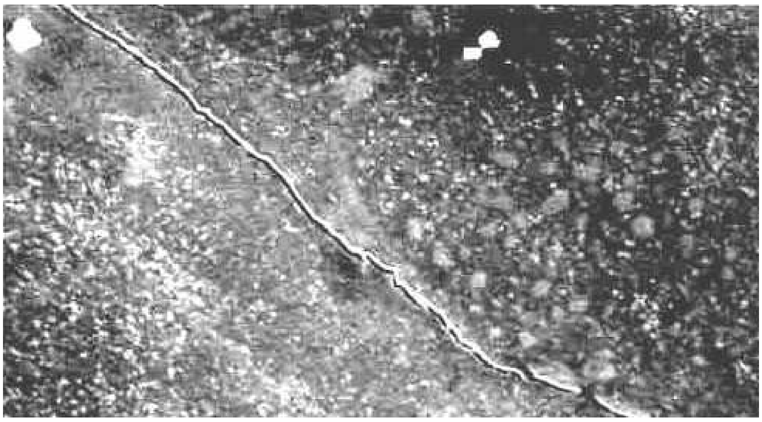

Figure 5. Hydrogen-induced cracking in 9Cr–1Mo steel at HAZ / base metal boundary due to repair welding without PWHT (Parvathavarthini 1995).

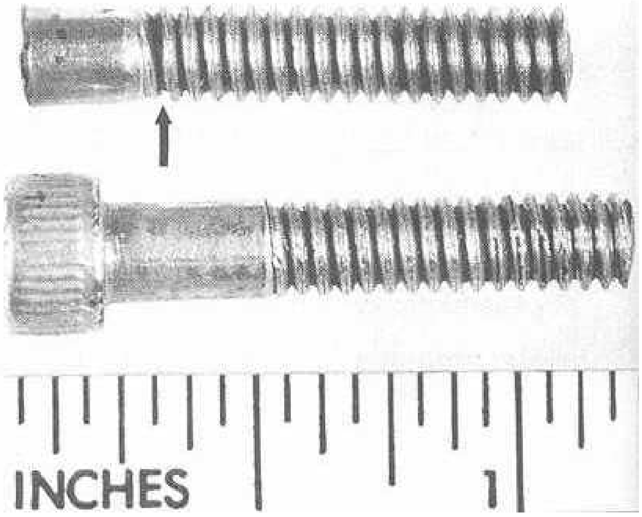

Figure 6. Hydrogen embrittlement failure of socket head cap screws due to hydrogen absorbed during cadmium plating (Tanner 1993).

introduced during corrosion in aqueous service environment and high hardness of the steel (figures 7 and 8) (Chakrapani 1993). Welding-related hydrogen embrittlement failure is also reported on the steel gusset plates used in building construction (Jones 1993).

3. Hydrogen effects in steels

Among the environmental effects on metals, hydrogen embrittlement can be considered the one which is the most influenced by the microstructure. A universal mechanism for this degradation does not exist. Embrittlement is more probably a combination of several elementary actions of hydrogen like surface adsorption, transport through the structure, accumulation (trapping), and decohesion. In the case of steels, particularly, the transport of hydrogen and its trapping behaviour are important aspects, that lead to embrittlement.

3.1 *Transport of hydrogen*

The transport of hydrogen from its original form and location to another form and location within the alloy where degradation can occur is probably the most complex aspect of the hydrogen embrittlement process. Hydrogen transport is made up of a large number of reaction

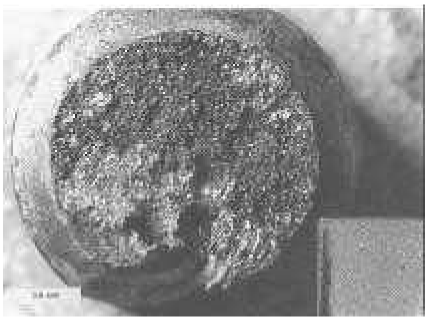

Figure 7. Fractured screw (cadmium-coated type 410SS self-drilling tapping screw) showing brittle failure due to hydrogen absorbed from aqueous service environment (Chakrapani 1993).

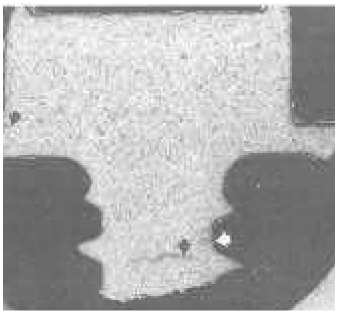

Figure 8. Cross-section of the screw showing primary fracture and several secondary cracks (Chakrapani 1993).

steps which are shown in figure 9 (Nelson 1983). When hydrogen is present in the bulk of the alloy, its transport is a simple process and most often controlled by lattice diffusion under the influence of stress gradient. From an external environment, hydrogen transport can be controlled by any one of individual reaction steps indicated in figure 9. The movement of hydrogen in steel occurs by the migration of atoms through the lattice. Hydrogen molecules are relatively large and only the smaller atomic form of hydrogen can diffuse effectively through the lattice. The driving force for the diffusion of hydrogen is a gradient in the chemical potential that results either from a gradient in the lattice hydrogen concentration or from a gradient in the hydrostatic component of an elastic stress field (Oriani 1967) or gradient in electric field or temperature (Manning 1973).

Hydrogen diffuses away from a region of high chemical potential to a region of low chemical potential until uniformity is reached. The rate of diffusion is related to the gradient in the hydrogen concentration and lattice diffusivity. Locally this force may be opposed by a gradient in stress. The driving forces provided by gradients in concentration or stress act independently. The localization of hydrogen at triaxially stressed regions is known to be an important factor in the delayed failure of steels. Hydrogen diffuses towards an elastic stress field that is tensile in character. Thus, stress gradients such as those produced by notches, by other sharp defects (inclusions or cracks), by bending moments or by elastic stress field of a dislocation can provide a driving force for diffusion. In a region of triaxiality, the energy of the interstitial hydrogen is lower resulting in net flow of hydrogen into this region of locally increased solubility. When tensile stress is applied, solubility increases and the amount of hydrogen that

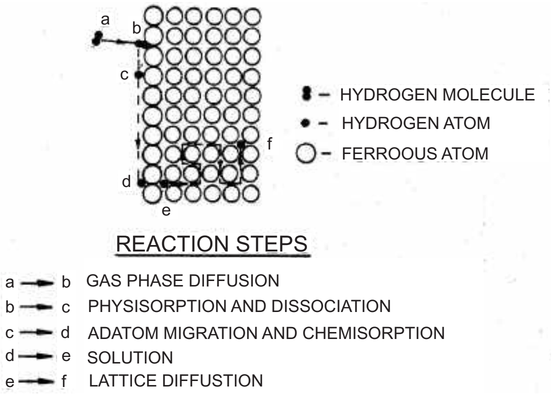

Figure 9. Schematic of possible reaction steps involved in the embrittlement of a structural alloy by external molecular hydrogen environment (Nelson 1983).

diffuses will is proportional to the triaxial component of the stress. At temperatures below about 200°C, the diffusion is hindered by the 'traps' (sites in metal matrix) which capture and delay migrating hydrogen atoms.

3.2 *Location of critical hydrogen interaction*

There are several specific locations in a material where the presence of hydrogen may be critical to the fracture behaviour. These include the lattice itself (hydrogen in solution) as well as grain boundaries, incoherent and coherent precipitates, voids and dislocations as shown in figure 10 (Thompson & Bernstein 1980). The figure indicates the way in which hydrogen from a variety of sources transported by dislocations or lattice diffusion can accumulate at any one or jointly with other sites (traps) in the metal matrix. These traps are classified as 'irreversible' if they act purely as hydrogen sinks or reversible if they accept hydrogen under some circumstances but act as a hydrogen source otherwise. The so-called irreversible traps liberate hydrogen at a sufficiently elevated temperature which depends on the trap energy (Davidson 1995). The local hydrogen concentration at a potential crack site must reach a critical level for a given stress intensity factor (K_I) before the initiation of cracking. The hydrogen traps influence the likelihood of cracking by controlling the availability of hydrogen to the critical cracking locations. The effect of hydrogen trapping on the diffusivity of hydrogen is shown in figure 11 (Yurioka & Sazuki 1990) where the apparent diffusion coefficient is shown as a function of temperature. An increase in temperature decreases the trap energy, thus decreasing their tendency to hinder hydrogen diffusion. Above about 400°C, the apparent diffusion coefficient is close to the diffusion coefficient of hydrogen by lattice diffusion while below this temperature the diffusion coefficient is affected by hydrogen trapping. The number of reversible traps is strongly affected by the transformation products formed on cooling. For example a tempered martensite has more trapping sites than a pearlite. This is due to the increased surface area of the finer carbides in the martensite.

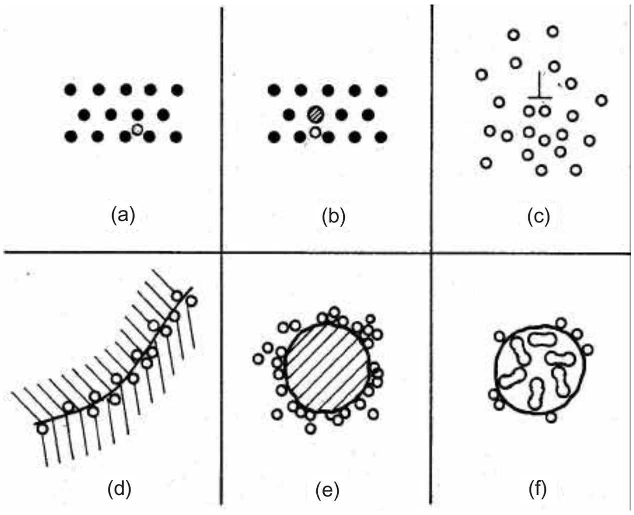

Figure 10. Schematic view of destinations for hydrogen in a metal microstructure: **(a)** solid solution; **(b)** solute–hydrogen pair; **(c)** dislocation atmosphere; **(d)** grain boundary accumulation; **(e)** particle-matrix interface accumulation; **(f)** void containing recombined hydrogen (Thompson & Bernstein 1980).

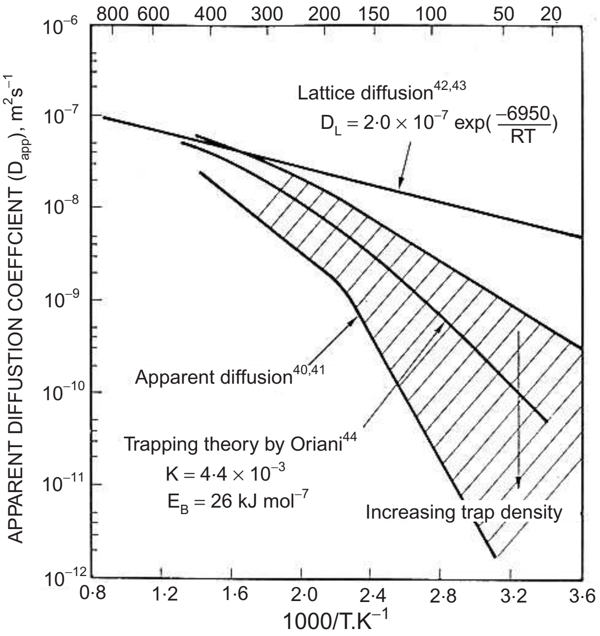

Figure 11. Apparent diffusivity of hydrogen as a function of temperature in ferritic steel (Yurioka & Sazuki 1990).

4. Classification of hydrogen damage in steel

Hydrogen damage can be classified into three major forms, viz., (1) creation of internal flaws, (2) hydride formation and (3) hydrogen embrittlement (Namboodhiri 1999). Since the scope of this article is to address hydrogen damage encountered in power plant steels, the embrittlement due to hydride formation which is the failure mechanism in Ti and Zr base alloys is not included in the following discussion. Both α (ferrite) and γ (austenite) phases of iron form only solid solutions with hydrogen and no evidence of hydride has been observed. The other two forms are discussed in detail below.

4.1 *Creation of internal flaws*

When present in sufficient quantity, hydrogen can produce several internal defects in steel like blisters, shatter cracks, flakes, fish-eyes and porosity.

Hydrogen-induced blistering is generally observed in low strength ferritic steels and highly tempered martensitic steel (tensile strength below 480–550 MPa). This does not require externally applied stress but the presence of internal defects such as voids, laminations, inclusions and micro-cracks are essential pre-requisites for blistering. Atomic hydrogen generated on the metallic surface enters the steel, gets collected at any internal defect where it combines and forms molecular hydrogen. Since molecular hydrogen is large in size, it cannot diffuse through the steel matrix. At these local sites, it thus builds up pressure as atomic hydrogen continues to diffuse in, ultimately forming blisters which grow and finally rupture. As the cause of blistering is well-known, handling and finishing techniques have been developed to minimize this form of damage. Vacuum melting and degassing minimize the quantity of hydrogen in the steels. Acid pickling and other such processes that may introduce hydrogen are avoided when practical, and possible moisture sources, such as the coatings of welding electrodes, are properly taken care of before use. The concentration of hydrogen within the blisters depends upon inclusion and alloying elements. In the presence of hydrogen recombination poisons such as sulphide, cyanide, arsenic, selenium and antimony ions, hydrogen entry and hence blistering is greatly enhanced. Processing techniques to minimize blistering in steels can control inclusions and other defect sites.

In steel-making practices, the presence of hydrogen in heavy sections may lead to various types of internal defects that are known as (snow) flakes, hairline cracks, white spots and shatter cracks. These are due to the hydrogen picked up during the melting operation and occur primarily as a result of hydrogen segregation and precipitation in voids and discontinuities such as micro shrinkage cavities or gas holes during cooling of the solidified steel. The usual source of hydrogen is water vapour reacting with molten steel. Hydrogen solubility is more in austenite (γ) than in ferrite (α) phase. During solidification process the hydrogen precipitates in molecular form in the iron lattices because its solubility decreases with decrease in temperature. This causes very high gas evolution pressure resulting in the flakes formation. The hydrogen flaking can be prevented by limiting hydrogen absorption to the maximum extent possible which can be accomplished by having all additives as dry as possible and preferably red hot in the steel making process. Melting and casting in vacuum can remove the hydrogen absorbed by liquid steel. In solid state, extended annealing can be utilized for the outward diffusion of hydrogen.

The accumulation of hydrogen around the inclusions affects the void nucleation, via internal hydrogen gas pressurisation and hydrogen-induced reduction in critical interfacial strength. During loading, the hydrogen released by interfaces can cause internal cracks around inclusions to grow in a brittle manner resulting in fish eyes on fracture surface (Kwon & Asaro 1990). Strnadel has developed a model to predict the fish-eye crack size at the fracture surface as a function of temperature (Strnadel 1998). He has assumed that the initiation of microcracks is caused by local increase in hydrogen concentration at inclusions. The propagation at these microcracks results in fish-eye formation and is controlled by local stress intensity factor and fracture resistance of the matrix.

Microperforation is another type of damage experienced by steel structures such as compressors which are subjected to extremely high hydrogen pressures of the order of 200–850 MPa at ambient temperature. Small fissures are formed that make the steel permeable to gases and liquids.

Formation of porosity in steel results from liberation of hydrogen gas during the cooling process of liquid metals which contain large quantities of hydrogen. This hydrogen porosity depends on hydrogen content of the melt, its cooling rate, external pressure and equilibrium partial pressure of hydrogen (Namboodhiri 1999).

When steel structures are exposed to high pressure hydrogen at high temperatures, hydrogen molecules dissociate on the steel surface to form atomic hydrogen which readily diffuses into the steel. In some boilers or steam pipes, which are used at elevated temperatures for prolonged durations, corrosion products are formed. In the aqueous medium between the steel wall and scale, hydrogen and hydroxyl ions accumulate, leading to the discharge of atomic hydrogen in large quantities. Atomic hydrogen reacts with iron carbide present in steel resulting in the formation of methane within the steel sections. These bubbles may expand and join to form fissures. Such reactions take place mainly along grain boundaries. Hydrogen attack causes decarburization and dissolution of carbides leading to weakening of the steel structures. This is potentially a serious problem in refinery equipment in the presence of hydrogen. Also this has also been the cause of the failure of several steam carrying pipes and boilers as described in the previous section.

4.2 *Hydrogen embrittlement*

The energy absorption ability of steel is markedly diminished in the presence of hydrogen. The presence of hydrogen in steel reduces tensile ductility and causes premature failure under static load that depends on the stress and time. This phenomenon is known as hydrogen embrittlement.

4.2a *Hydrogen induced cracking (HIC) in steel weldments:* During welding process hydrogen is absorbed into the molten weld pool. As the weld metal solidifies, solubility of hydrogen decreases because of decrease in temperature and hydrogen present in the weld metal becomes supersaturated and diffuses away from the weld fusion zone to the heat-affected zone (HAZ) where hydrogen concentration is lower. In the HAZ, due to heating and cooling cycles, transformation products of high hardness are produced. This region of high hardness and low ductility is subjected to a relatively high tensile load imposed by the contracting weld fusion zone resulting in cracking in the presence of hydrogen (HIC) within a few hours of completion of welding operation. For hydrogen cracking, three primary independent conditions are necessary to be fulfilled: a high hydrogen level, susceptible microstructure and tensile stress acting on the weld. These conditions are schematically shown in figure 12 (Timmins 1997). All arc welding processes introduce hydrogen into the weld to some extent. Hydrogen can originate from moisture that exists in electrode coatings or from the surrounding humid atmosphere. Hydrogen can also originate from hydrocarbons, grease, rust, or other organic contaminants. In general, only hard HAZ microstructures are susceptible to HIC. The risk of hydrogen cracking in the HAZ increases with hardness. Such microstructures are promoted by steel that has high carbon equivalent as proposed by Yurioka (Yurioka *et al* 1987).

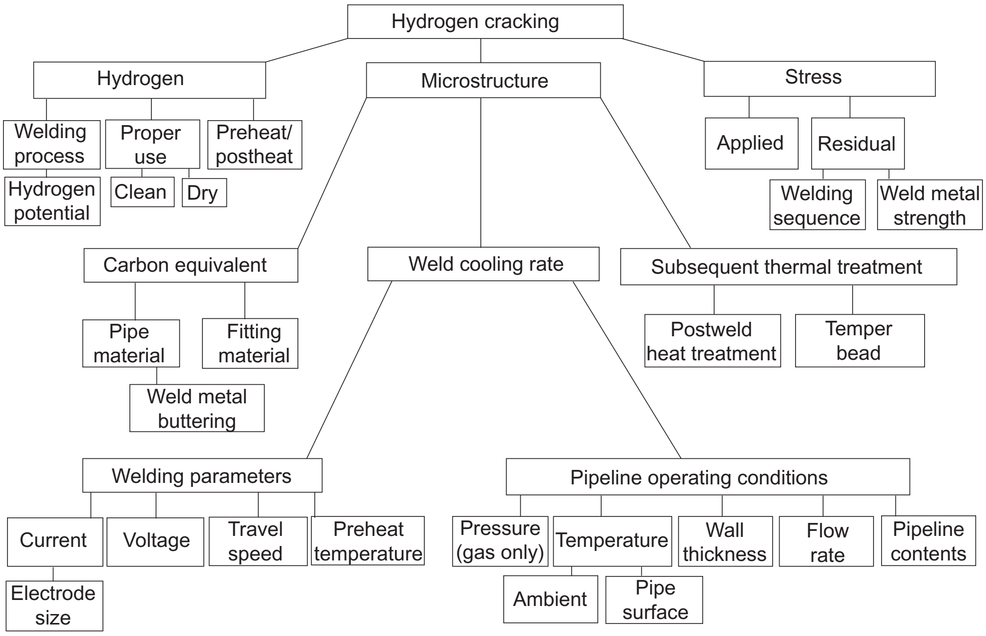

Figure 12. Factors influencing HIC in weldments (Timmins 1997).

In a multipass weld, hydrogen concentration builds up in successive layers of a weld pass. After a pass is deposited, hydrogen continuously diffuses from the weld. If another pass is deposited immediately over the first, then the diffusion distance increases and removal of hydrogen is restricted. This increases the HIC susceptibility. Allowing some waiting period between passes can reduce hydrogen build up.

Several factors affect the susceptibility of the material to HIC such as strength, microstructure and alloy composition. However, it is difficult to separate the effects individually because the three factors are interrelated. For example, if weld metal microstructure is changed from acicular ferrite to martensite by increasing the alloy content or the cooling rate, then the strength will be increased. At the same time, the time available for the removal of hydrogen from the weld decreases and HIC susceptibility increases. Optimum weld metal toughness is achieved by fine grained acicular ferrite while martensite, proeutectoid ferrite and bainites are detrimental to toughness. Although martensite microstructure is most susceptible to HIC, if hydrogen content and residual stresses are high, even an ideal microstructure such as acicular ferrite may fail by HIC.

In the case of Cr–Mo steels, because of the high alloy content and hardenability, the microstructure of both weld metal and HAZ are bainitic or martensitic in the as-welded condition and hence they are highly susceptible to HIC. Systematic investigations were carried out (Albert *et al* 1993,1996,1997) to determine whether the diffusible hydrogen content (H_D) in the welds can be correlated to HIC susceptibility for these ferritic steels using UT modified hydrogen sensitivity tests. It was found that as the vol.% of hydrogen in the shielding gas increases, H_D also increases and is a strong function of alloy content. As the hydrogen in the shielding gas increases, critical preheat temperature also increases. Under identical testing conditions, H_D is minimum and susceptibility is maximum for 9Cr–1Mo steel as shown in figure 13 (Albert *et al* 1997). From the electrochemical permeation studies carried out for 2·25Cr–1Mo steel and 9Cr–1Mo steel (Albert *et al* 1997; Parvathavarthini *et al* 1999, 2001), it is seen that when the alloy content is higher, solubility of hydrogen in the reversible traps is higher. Therefore susceptibility to HIC can be correlated to hydrogen present in the reversible traps.

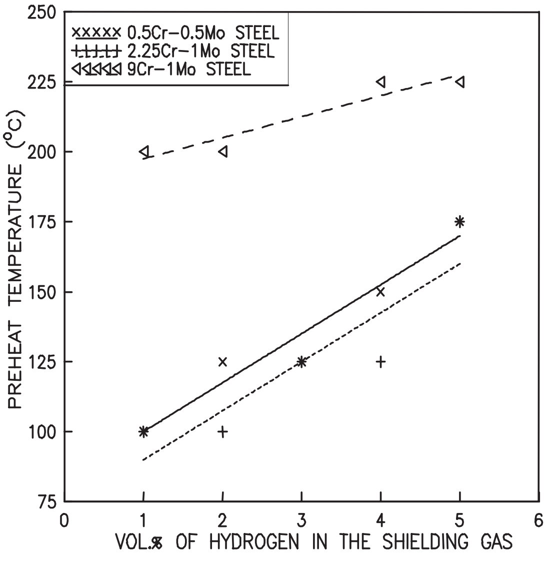

Figure 13. Variation of preheat temperature with volume % of hydrogen in the shielding gas (Albert *et al* 1997).

5. Effect of various factors on hydrogen embrittlement

5.1 *Stress intensity factor*

Hydrogen-induced slow crack growth rates in gaseous and aqueous environment show a three-stage dependence on applied K_I (stress intensity factor) as in the case of stress corrosion cracking (SCC) (figure 14). In this case the threshold stress intensity factor is termed as K_I. At threshold and in stage I, a mechanical fracture process governs the crack growth rate and there is sufficient time for generation, transport and accumulation of hydrogen to achieve critical hydrogen concentration. In this stage, the plastic zone is very small (less than a grain in diameter) and thus the elastic stress distribution predominantly controls diffusion and crack growth rates. In stage II, it is mainly the plastic process which controls crack growth because the plastic zone size is several times larger than grain diameter and crack tip blunts. So triaxial hydrostatic stress gradient is independent of K_{IHE} in stage II and hence is the crack growth rate. Stage III refers to overload failure. Since most useful life occurs before crack growth has begun, K_{IHE} is of engineering importance.

5.2 *Effect of temperature and strain rate*

Generally as temperature increases, K_{IHE} also increases. But at higher temperatures, K_{IHE} is material dependent (Moody & Robinson 1990). Fracture mode is intergranular at low temperatures whereas at high temperatures it is ductile. Susceptibility to hydrogen embrittlement is maximum at ambient temperature and vanishes at elevated temperature. A study of effect of temperature on peak crack growth for 18Ni (250) maraging steel showed three distinct regions of temperature dependency as illustrated in figures 15a and b (Gangloff & Wei 1977). In the very low temperature region, crack growth rate is thermally activated and hence increases with increase in temperature. In this region, K_{IHE} increases only slightly with temperature. In an intermediate temperature range, crack growth rate shows a maxima and then decreases at higher temperatures. As the strain rate increases, the amount of hydrogen transported per unit strain decreases. This dependence coupled with dislocation transport mode explains decrease in hydrogen embrittlement as strain rate increases.

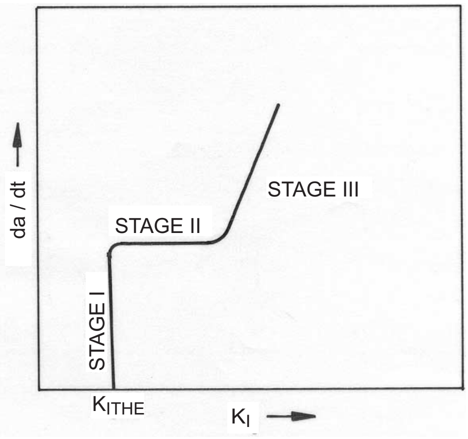

Figure 14. Crack growth rate as a function of K_I

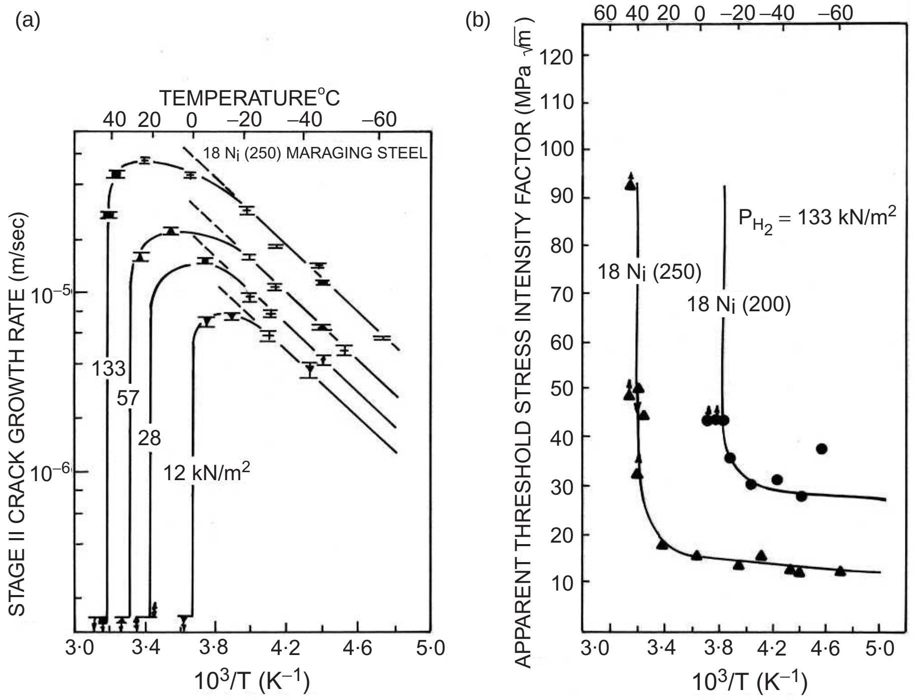

Figure 15. Effect of temperature on **(a)** stage II crack growth rate for 18Ni (250) maraging steels, **(b)** K_{IHE} for two grades of maraging steel (Gangloff 1977).

5.3 *Yield strength*

For a wide variety of environments, K_{IHE} exhibits a two-stage dependence on yield strength (figure 16) (Akhurst & Baker 1981). Below a yield strength of 690 MPa, crack growth susceptibility is not affected by yield strength. But at higher strength levels, K_{IHE} decreases and reaches a lower limiting value at 1300 MPa (Akhurst & Baker 1981). Our investigations (Parvathavarthini 1995) on 9Cr–1Mo ferritic steel also showed similar trends (figure 17). In this investigation, constant load experiments on single-edge notch specimens of different yield strengths with *in situ* hydrogen charging were conducted with varying K_I values. High strength material (water-quenched from annealing temperature) exhibited lower K_{IHE} compared to low strength material (air-cooled from annealing temperature). The crack growth

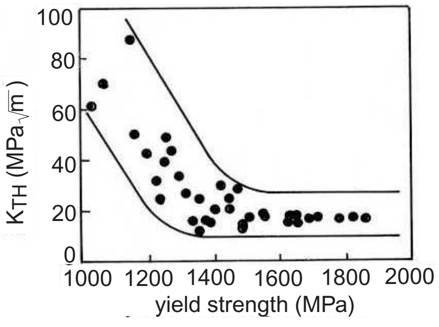

Figure 16. K_{IHE} as a function of yield strength for 4340 steel (Akhurst & Baker 1981).

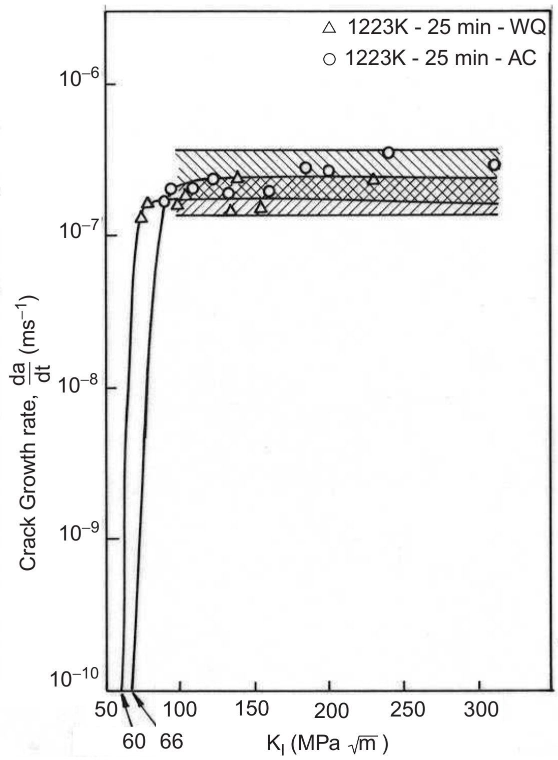

Figure 17. Influence of yield strength on K_{IHE} of 9Cr–1Mo steel in NaCl solution (Parvathavarthini *et al* 1995).

rates were also higher in higher strength material. It was concluded that as strength decreases, K_{IHE} increases and the tempered material with lower strength was found to be immune to hydrogen embrittlement. Increase in crack growth rate with increase in yield strength was also reported by Magdowski (1987). His results are shown in figure 18. The criteria for crack to grow is that the local tensile stress must be equal to maximum cohesive force which is critically affected by local hydrogen concentration and yield strength. Under elastic conditions, hydrostatic stress in front of a crack is directly proportional to the yield strength and so is the hydrogen concentration. Therefore critical concentration is achieved more easily and quickly and hence K_{IHE} decreases and crack growth rate increases.

5.4 *Chemical composition and microstructure*

As seen above, susceptibility to hydrogen embrittlement is a strong function of yield strength. It is difficult to separate the influence of minor variations in chemical composition and heat treatment effect from that of the yield strength. Therefore, the influence of variation in chemical composition can be realised through its influence on yield strength. However, certain elements such as P, S and Sb which are segregated at the grain boundaries increases crack growth susceptibility leading to intergranular fracture. Sb has the strongest effect on toughness followed by Sn and P. Phosphorous has been found to greatly affect the hydrogen induced cracking in various low and high alloy steels (Dayal & Grabke 1987, 1987). In most steels, grain boundary segregation of P and S are primarily responsible for temper and hydrogen embrittlement. It can be seen from figure 19 that as (P + S) concentration increases, K_{IHE} decreases (Moody & Robinson 1990). At high impurity concentration, severity of impurity

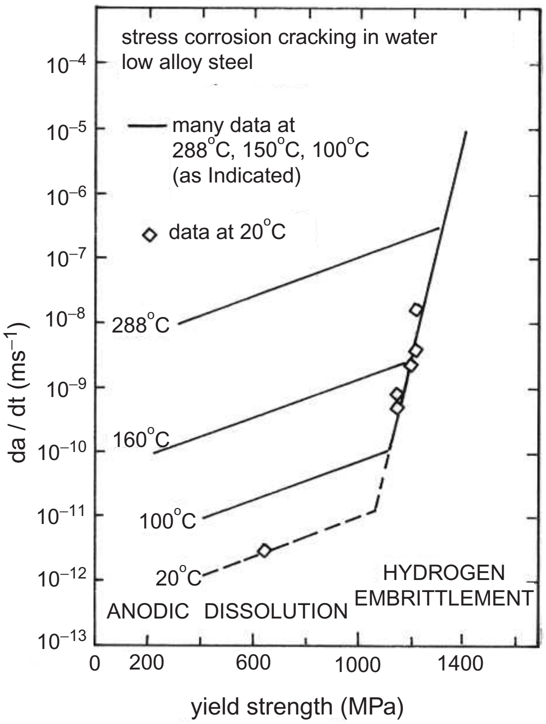

Figure 18. Influence of yield strength on crack growth rate of low alloy steel in water (Magdowski 1987).

effects approaches a lower limit. More than the bulk composition, impurity concentration at grain boundary is important. Grain boundary segregation is dependent on alloy composition. Ni, Cr, Mn and Si promote grain boundary segregation.

6. Hydrogen embrittlement mechanisms

From the foregoing information, one can see that hydrogen embrittlement is dependent on many variables such as temperature, pressure, level and type of stresses, environment, phys-

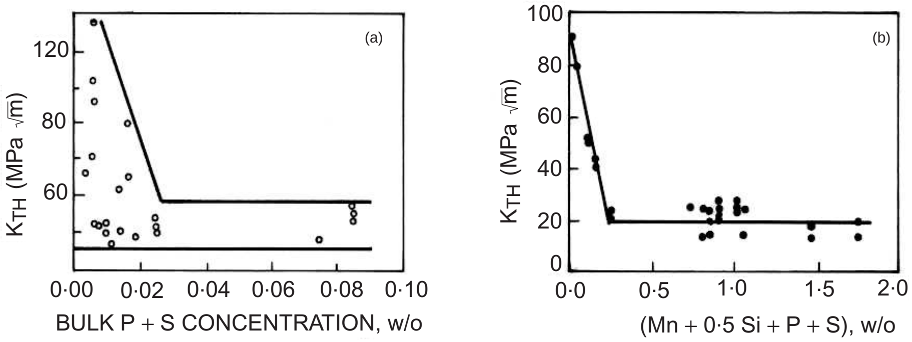

Figure 19. Reduction of K_{IHE} as a function of **(a)** P + S concentration, **(b)** composition parameter (Moody & Robinson 1990).

ical and mechanical properties of bulk materials, type and concentration of impurities in the metal, thermomechanical history, hydrogen diffusion rate and surface conditions. The picture is further complicated because the above listed variables have complex interrelationships. Various mechanisms are proposed for steel except hydride mechanism which is not applicable in the case of iron and steel. Each theory explains some experimental observations and industrial experience.

6.1 *Pressure theory*

This theory attributes hydrogen embrittlement to the diffusion of atomic hydrogen into the metal and its accumulation at internal defects (Zappfe & Sims 1941). The pressure developed by this precipitation is added to the applied stress and thus lowers the apparent fracture stress. The very high internal pressure enhances void growth and crack propagation. This is true in blister formation but not relevant to cases of reduced ductility or increased rate of crack propagation induced by exposure to low pressure hydrogen (Kerns & Stahle 1972; Smialowski 1977). It has also been suggested that dislocation transport could create large internal pressures in voids even when the source of hydrogen was at low fugacities (Louthan 1974; Tien *et al* 1976).

6.2 *Surface adsorption theory*

According to this theory hydrogen is adsorbed on the free surface created adjacent to the crack tip decreasing the surface free energy for crack growth (Petch & Stables 1952; McMahon & Vitek 1979). However, it cannot explain why surface free energy reduction due to the adsorption of oxygen or any other gases does not have the same deleterious effect as hydrogen.

6.3 *Decohesion theory*

Hydrogen in solution in any of the transition metals decreases the cohesive strength of the cubic cleavage planes, due to the filling of the *d* bands of the metals by the electrons of hydrogen atoms. This aspect was quantitatively studied by Oriani & Josephic (1974). They proposed that the crack growth will occur when local elastic tensile stress normal to the plane of the crack equals the local maximum cohesive force per unit area. The maximum cohesive force is determined by the concentration of hydrogen drawn to the crack tip by the effect of elastic stresses on chemical potential of hydrogen and hydrogen diffusion is a necessary step.

6.4 *Hydrogen enhanced localised plasticity mechanism*

Hydrogen/plasticity interactions are the most controversial of all corrosion/deformation phenomena. Robertson (1999) has recently reviewed the effect of hydrogen on dislocation dynamics. Beachem (1972) has observed tear ridges and dimples on the fracture surfaces of hydrogen embrittled steel and suggested that the effect of hydrogen was to unlock rather than lock dislocations. Hydrogen allows dislocation to multiply or move at reduced stresses. Sirois & Birnbaum (1992) proposed a mechanism in which hydrogen formed an atmosphere around dislocations and other elastic stress centers. The redistribution of the hydrogen atmospheres as the stress fields merge effectively shields the dislocation from the elastic center reducing the interaction energy between the dislocation and the obstacle. Consequently dislocations can move at lower levels of applied stress. As a result of the linear superposition of the stress fields of the dislocations the distribution of hydrogen around the dislocations changes as they move closer. With increasing hydrogen concentration, the shear stress experienced by one dislocation due to the other decreases. Consequently the effect of hydrogen is to reduce the applied stress necessary to move an edge dislocation with a hydrogen atmosphere through a field of elastic obstacles. Hydrogen/plasticity interactions has been reviewed (Gerberich *et al* 1997) and it has been concluded that in high strength steels in the presence of high hydrogen contents, plastic constraint (thick sections) decohesion mechanism predominates whereas low strength steels, low hydrogen levels, low constraint (thin sections) tend to favour hydrogen enhanced localised plasticity.

7. Preventive measures

As brought out in the previous section, the interaction of hydrogen with steel is quite complex and therefore the problems are multifold. Some of the measures have already been mentioned in the previous sections. Timmins (1997) has summarized the solutions to hydrogen embrittlement which can be used for any type of attack irrespective of the operating mechanism. According to this, by increasing the critical concentration of hydrogen required for hydrogen embrittlement (C_K) and decreasing the hydrogen content (C_H) the steel becomes inherently better and most of the problems can be solved. The parameters influencing C_K and C_H are collectively presented in figure 20 (Timmins 1997). To minimize hydrogen content in steel, good steel making practice should be followed eg. vacuum melting and degassing techniques. Moist raw materials should not be used and enough time should be given for solidification of the molten metal so as to liberate hydrogen trapped due to decreasing solubility.

One approach to minimize HIC is to impede hydrogen entry into steel. This can be achieved by direct deposition of a solid on the surface so that hydrogen entry is lowered . In some cases corrosion products formed on the surface also act as barrier to hydrogen entry. Coating steel with Cd, Au, Ag, Pt, Cu, Al, austenitic steel or ceramic oxide will lower hydrogen diffusion inside steel. In the case of ferritic substrate, elements with low hydrogen diffusivity and solubility can be coated. Providing hydrogen with surface traps is another alternative. Ion implantation of Ti has reduced hydrogen entry by providing atomic traps at the surface (Timmins 1997). Similarly amorphous layers obtained by implanting phosphorus ion on steel has reduced the hydrogen permeation rate through composite material (Ensinger & Wolf 1989). Nitrogen ions implanted on extra low carbon steel (Brass *et al* 1989) and cobalt ions deposited on palladium coated extra low carbon steel have been reported to impede hydrogen entry (Miranda *et al* 1991). However, galvanic cells should not be formed due to such coatings because these aggravate the problem by enhancing the corrosion reactions.

Another approach is to reduce the corrosion dependent hydrogen formation rate by adding noble elements, which may enrich on the surface layers and improve passivity and thus decrease hydrogen diffusivity. Surface compressive stresses can be introduced by shot peening which reduces both hydrogen permeability and diffusivity but care has to be taken to avoid notch effects.

As shown in figure 20, the critical hydrogen concentration for HIC, depends upon size, shape, segregation, coherence, distribution, density and reversibility of various traps. For instance, the shape of an inclusion greatly influences the susceptibility. Elongated inclusions are dangerous and spherical shape is desirable. Such shapes can be achieved by rare earth addition. Size of the inclusions can be decreased by thermomechanical treatment. Heterogeneous distribution of inclusions or particles that act as strong traps should be avoided.

Several inhibitors or elements that reduce the activity of hydrogen in the environment can be used. Nitrile compounds, nitrogen-containing organic compounds such as substituted imi-

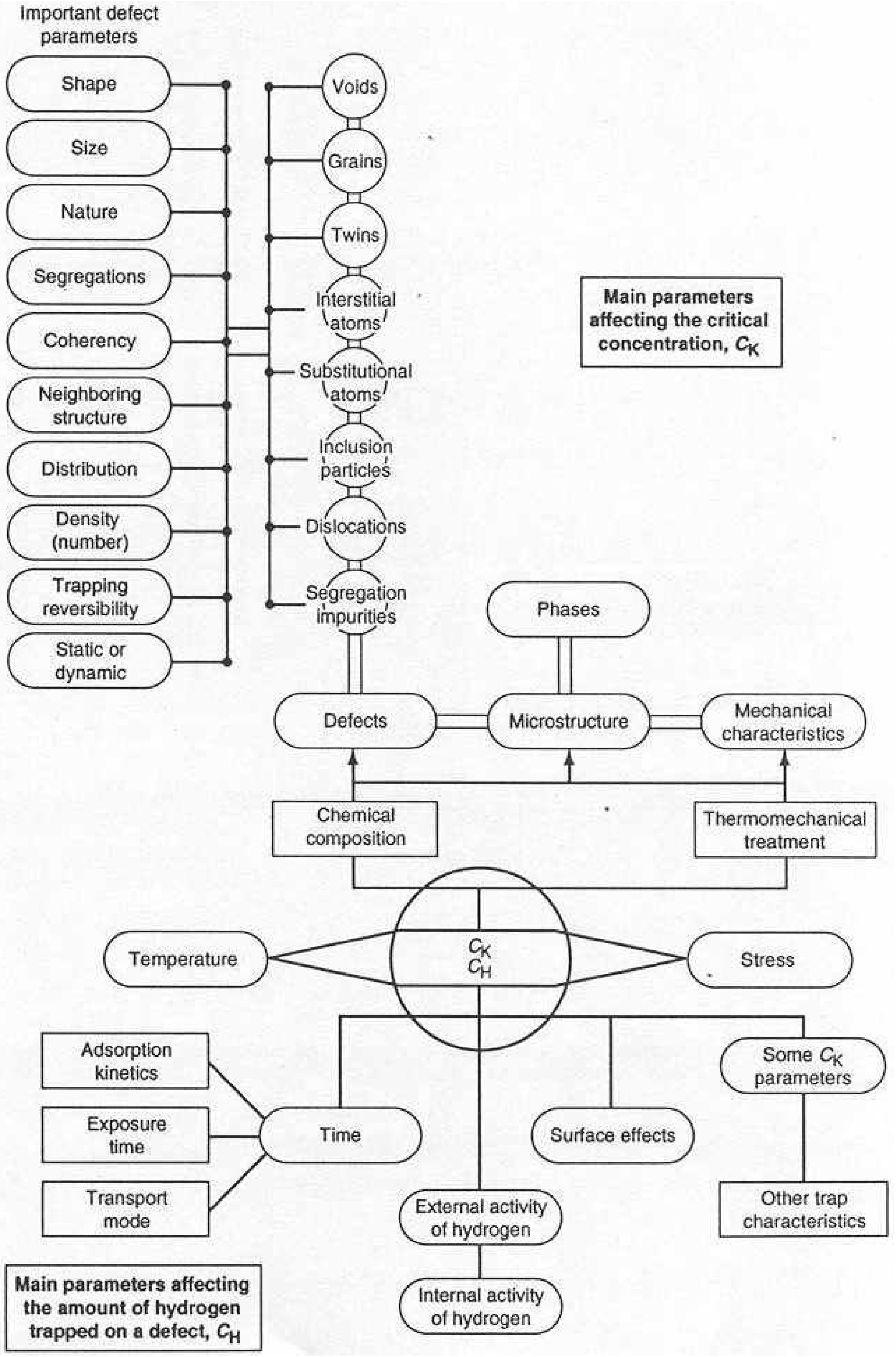

Figure 20. Factors affecting C_K and C_H (Timmins 1997).

dazolines, aliphatic amines, quaternary ammonium salts, nitrites and phosphate can be used. In gas-phase hydrogen atmosphere, even a small amount of oxygen present may eliminate subcritical crack growth rate.

Elements such as As, Se, Te, S, P, Sn, Hg, Pb and Bi that promote hydrogen entry by inhibiting hydrogen recombination reaction should be strictly avoided in hydrogen ion-containing environments. These elements when present inside steel segregate to grain boundaries and should be avoided as much as possible. Avoiding cathodic cleaning, pickling or activation treatments, and by using alkaline soak cleaning, anodic etching or electropolishing, hydrogen embrittlement can be eliminated. If pickling is necessary, inhibited acid can be used to decrease metal dissolution. Electroplating can be replaced by using vacuum coating or organic coating. Baking of pickled or electroplated parts enhances resistance to hydrogen embrittlement.

To avoid HIC during welding, the amount of hydrogen entering the weld metal can be limited by the use of clean, low hydrogen consumables. Electrodes should be stored at an appropriate temperature in ovens or used from freshly opened airtight containers. Cleanliness of weld preparation, welding wire and welding apparatus is also important. Paint, rust, grease, degassing agents can all be hydrogen sources. Lubricants from wire-drawing operation are another potential source. An additional approach to hydrogen control is to allow hydrogen removal by diffusion so that the levels are reduced to acceptable values by the time the weld has cooled. This is done by pre-heating which decreases the cooling rate and allows more time for the hydrogen to diffuse. Moisture and contamination are also burned off by this. Using higher welding heat inputs also increases the weld thermal cycle time.

Residual stresses developed in the welded assembly are often difficult to control, although a certain degree of control can be exercised by altering the design. The residual stress may also be reduced to a degree by heating the weld preparation and the surrounding base metal prior to welding. This preheating reduces the non-uniformity of cooling and allow more time for relaxation of residual stress by reducing the weld metal cooling rate.

Diffusivity of hydrogen at ambient temperature can be vastly different for consumables and base plate materials. Hence it is better to use steels of matching composition for depositing the consumable rather than those recommended in different standards. The higher the strength of the steel, the lower the acceptable weld hydrogen content which can be as low as 1 or 2 ml $H_2/100$ g deposit metal. With proper selection and use of welding consumable, a minimal hydrogen content can be introduced to the weld pools.

8. Conclusions

Hydrogen embrittlement has caused failures of various steel components in power plants. Some of such failures have been described in this article. The effect of hydrogen in steels, classification of damage types, influence of different factors and related mechanism have been explained. Several preventive methods to minimize the hydrogen embrittelment problems have been provided. Based on the discussion it can be concluded that there is no general remedy for hydrogen embrittlement problems and specific problems require specific solutions. The best way is to understand the phenomenon thoroughly before providing any solution to HIC.

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