**Hydrogen in steel**

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 Hydrogen (H) (atomic number 1， atomic weight 1.008) is a colorless gas. It has a density of 0.0899 g/l. The melting point of hydrogen is -259.2 degrees C and the boiling point is -252.8 degrees C. The phase diagram of fee-hydrogen is shown in Figure 1.

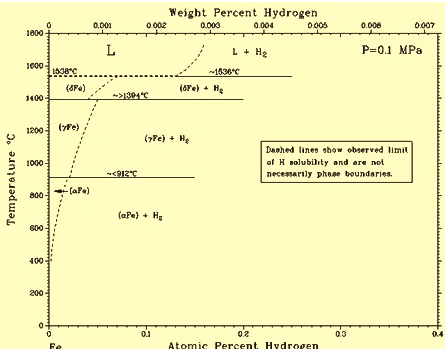


Figure 1 Fe-H phase diagram

H in steel is considered to be an undesirable impurity and quite harmful in some applications. It has always been a source of various problems in steel production due to its general detrimental effect on the processing characteristics and serviceability of steel products. Just a few parts per million of H dissolved in steel is enough to cause harm. Therefore， it should be avoided or removed as required when necessary.

Sources of hydrogen

Hydrogen has several sources and can enter the steel in several ways. In primary steelmaking furnaces， the source of hydrogen is water， which enters the furnace through wet scrap， molten material， ferroalloys and refractory materials that are not completely dry. The water dissociates on contact with the steel， producing H， which is absorbed by the steel. This H is usually removed by the purging action of carbon (C) boiling， but some remains in the steel.

Contact of the steel with moisture and/or moist air in the ladle refractory can result in the absorption of H by the steel.

Hydrophilic calcium oxide (CaO) in the slag and decomposition of the refractory (which requires sufficient resistance to thermal shock) can also cause H to enter the steel.

The dissociation of the water vapor contained in the furnace gas produced during steelmaking using hydrocarbon fuel combustion (equation below) produces H that can be absorbed by the steel.

H2O (g) = 2[H](g) + [O](g)

However， at any point in steelmaking， the H content of the steel is determined by the balance between the entry of H from the gas into the steel and the competing reactions of H removal by carbon boiling and degassing.

At low levels of carbon， the rate of H uptake is higher than its rate of removal. The dissolved H content in the steel melt drops to a minimum level at the end of carbon boiling， but it increases again with the addition of ferroalloys and synthetic slag.

The H content of liquid steel is lower when steel is made in a high frequency induction furnace compared to the practice of electric arc furnace steelmaking. Also， the hydrogen content of steel produced under oxidizing acid slag is lower than that produced under reducing slag.

Steel in the solid state can also absorb hydrogen by the action of electrochemical reactions that occur on the steel surface. The most common examples of this phenomenon are pickling， electroplating， cathodic protection and corrosion. The H released during the electrochemical reaction is partially absorbed by the surface of the steel before recombining into harmless hydrogen bubbles. The presence of sulfides， arsenides， phosphides and selenides in the electrolyte contributes to the absorption of H in steel because these compounds inhibit the recombination reaction of H.

H can also enter steel when it is exposed to gases at high temperatures and pressures. This is a fairly common phenomenon for H absorption in chemical and petrochemical processing equipment. Water vapor and hydrocarbons are also harmful in this respect.

Usually， H dissolves in the interstitial spaces of steel in the form of single atoms， but it is not known whether it dissolves as atoms or protons.

Solubility of hydrogen in steel

The units used to express the H content in steel are parts per million (ppm) and milliliters or cubic centimeters of H per 100 grams of steel corrected for standard temperature and pressure. the relationship between these two units is: 1 ppm = 1.11 ml/100 gm.

The solubility of H in steel depends to a large extent on the crystal structure， temperature and composition. h is much more soluble in austenite (iron) than in ferrite (Fe and Fe).

Diatomic H gas reacts with steel and dissolves into it in atomic form according to Sievert's law.The data on the solubility of H are summarized by the following equation and shown in Figure 2

H2 (g) =2 [H] (dissolved in steel)

The following equation represents the equilibrium constant in the above reaction.

K = [ppm H]/ (pH2)?

For α， δ (bcc) iron， γ (fcc) iron and liquid iron (liquid)， the temperature dependence of K at equilibrium at pH2 = 1 atm is given by the following equation

Log K(α， δ) = -1418/T+ 1.628

Log K (gamma) = -1182/T+ 1.628

Log K (liquid) = -1900/T+ 2.423

where the temperature T is in degrees Kelvin.

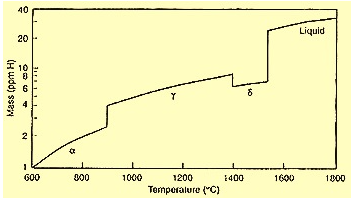


Figure 2 Solubility of H in pure iron or low-alloy steel at 1 atm H

The solubility of H in steel increases with temperature from less than 1 ppm at room temperature to about 8 ppm at 704 degrees Celsius.

Celsius usually increases the solubility of H， but the situation is quite complicated at high temperatures due to the formation of methane (CH4). Manganese (Mn) also has a complex effect， probably based on the crystal structure. Silicon (Si) and aluminum (Al) reduce the solubility of H Chromium (Cr) in amounts up to 10% increases the solubility of H， but higher concentrations decrease it. This effect can be explained by the crystal structure， since about 10% Cr closes the g-loop， and higher concentrations lead to complete ferrite of the steel before the melting point. Nickel (Ni) increases the solubility of H， which in this case is proportional to the amount of Ni. Molybdenum (Mo) has no effect on the solubility of H. Tungsten (W) decreases the solubility of H. Vanadium (V)， titanium (Ti)， niobium (Nb)， zirconium (Zr) and tantalum (Ta) all increase the solubility of H， especially at low and moderate temperatures.

Cold working of the steel has no effect on the solubility of H in pure iron， but the presence of carbides leads to a significant increase in solubility. This is due to the migration of H into and its aggregation in the internal voids formed next to carbides and inclusion particles. Thus， when cold worked steel is annealed， some， but not all， of the H is removed by diffusion.

Hydrogen permeability

Although the diffusivity of H is an important physical property， it is more common to consider permeability， which is defined as the product of diffusivity and solubility. In contrast to solubility， the permeability of H is lower in austenite than in ferrite. this property of H facilitates its removal from the steel by heating the steel.

In addition， different alloying elements show different effects on the permeability of H. C decreases the permeability， but H decarburizes Fe3C at high temperatures. mn has only a small effect on the permeability. mo has no effect at all on the permeability of H. Si decreases the permeability. cr decreases the permeability of H in ferrite， but has no great effect in austenite. The permeability of hydrogen in steel increases with increasing nickel content until about 6% Ni， then it decreases.

Effect of hydrogen on steel

Hydrogen is usually harmful to steel， but in many cases most steels can be tolerated. High strength steels and those used under severe service conditions are more sensitive to H

Hydrogen has an effect on three forms of environmentally assisted cracking (EAC)， namely (i) hydrogen embrittlement， (ii) stress corrosion cracking， and (iii) corrosion fatigue. At temperatures below 200 degrees Celsius， the deleterious effect of H is known as low temperature hydrogen attack (LTHA). Hydrogen degrades steel properties primarily through delayed cracking at stresses below the yield strength (YS)， called hydrogen stress cracking (HSC)， and loss of ductility in tensile testing， reflected in the reduction of area， generally referred to as hydrogen embrittlement (HE). When the local H concentration is sufficiently high (reaching a critical concentration)， it may lead to hydrogen-induced cracking (HIC) or manifest as advancement of crack extension (cracking has been initiated by mechanical damage or corrosion). The hydrogen effect is greater near room temperature and decreases with increasing strain rate. Hydrogen degradation becomes more pronounced with increasing hydrogen content or with increasing charge rate.

Typically， H problems in steel are associated with flake formation， the occurrence of fractures during continuous casting and H embrittlement. The harmful effect of hydrogen is due to its dissolution behavior. h is much more soluble in liquid steel than in solid steel. As a result， diatomic H is formed during cooling and solidification of the steel. H gas forms pressure points in the steel matrix， which may cause failures or surface defects.

The remaining H after steelmaking migrates to internal defects， where it recombines to form gaseous H2. The pressure generated by this precipitated H can be significant. For example， if the H content in liquid steel is about 10 ppm， a pressure in excess of YS can be generated before the steel cools to room temperature. This will result in the formation of flakes. Nickel-containing steels are particularly prone to flaking， but in general， H levels below 2.5 ml/100 gm are considered safe.

H that enters solid steel can also collect in internal voids. When the pressure in these voids increases， the familiar hydrogen blistering can occur. CrMo steels are resistant to this form of attack at high temperatures and are therefore widely used where potential H hazards are known to exist.

Dissolved interstitial hydrogen is also very harmful， leading to an increase in YS and a corresponding decrease in ductility and impact properties. This is a form of H embrittlement. More important， however， is the effect known as delayed failure or static fatigue. This occurs in high-strength steels that have been cathodically or otherwise injected with H and loaded under tension to a stress below their YS. After a period of a few minutes to a few weeks， depending on the H content， temperature and stress level， the steel fails in a completely brittle manner.

Hydrogen is also known to cause weld cracking， especially in high strength steels with tensile strengths above 1690 MPa. The mechanism is related to delayed failure and can be prevented by the use of low-hydrogen electrodes or post-weld heat treatment.

Controlling hydrogen-related problems

The H content in the molten steel can be minimized by ensuring that all furnace charge， furnace and ladle additions and refractory materials are sufficiently dry. Although it is difficult to avoid contact between the molten steel and furnace gas or atmospheric moisture， steelmaking methods employed to prevent reoxidation can help prevent H from entering the steel.

A number of techniques have been developed for the removal of H from the steel. these techniques include argon (Ar) bubbling， argon-oxygen decarburization (AOD) and some processes using vacuum treatment. the AOD and vacuum treatment processes are the most effective and are therefore more widely used. Steel can be degassed in the ladle， in AOD to remove H， or passed from the ladle to another vacuum chamber as a stream of fine droplets. The liquid steel can also be cast into an expendable electrode and subsequently remelted by arc under vacuum. In all cases， the aim is to reduce the dissolved H content to below a harmful threshold (about 2.5 ml/100 g).

H can be removed from the solid steel by annealing or baking. the removal rate of H depends on the temperature and the square of the diameter of the part to be treated. The H removal rate at 205 degrees C is about 250 to 400 times higher compared to the removal rate at room temperature. However， the annealing temperature should not be too high because the solubility of H increases with increasing temperature. Small parts such as plated screws can be baked in the temperature range of 190 degrees Celsius to 205 degrees Celsius.

Large forgings that are prone to spalling require more most treatment. Forging ingots should be cooled slowly to allow as much H as possible to diffuse out of the steel. Then， depending on the residual H content and section size， the forgings can be further degassed by soaking at 650 degrees Celsius.

H degradation is a serious problem in many industries as it leads to dangerous failures and causes serious losses. These industries facing H degradation problems include chemical (ammonia， cyanide)， refineries (catalytic crackers， storage tanks)， power plants (boilers， turbines)， marine structures， long distance sour gas transport pipelines， automotive and aircraft components. Hydrogen embrittlement is one of several causes of failure of high-strength structural steels used in offshore industrial production. The problem here is due to the absorption of H from seawater， which is promoted when steel is cathodically protected to control corrosion. Hydrogen-induced cracking remains a common problem in construction manufacturing in the form of cold cracking of welds.

There have been several reports of failures of automotive and marine engine components due to H The probable cause of these failures is that engine oil can absorb moisture and become acidic， which creates H at the crack tip and promotes crack growth.

H spalling is also destructive in heavy section forgings， which has led to catastrophic failures in many large crankshafts and turbine rotors， among other items.