

# **ACCUMULATING PROPERTIES OF HYDROGEN IN CONDENSED MATTER. MECHANISMS OF HYDROGEN STORAGE AND HYDROGEN EMBRITTLEMENT**

## **Lecture 2**

# HYDROGEN STORAGE MECHANISMS

Hydrogen can combine with solids either physically or chemically. The two mechanisms of solid state hydrogen storage are therefore called physisorption and chemisorptions respectively. In physisorption hydrogen molecule sticks to the solid surface where as in chemisorptions hydrogen chemically reacts with the solid forming a hydride.

Hydrogen is often present in metals that become loaded during high-temperature processing, when hydrogen from the environment can be absorbed by the metal. At somewhat lower temperatures, H, in atomic or molecular form, can generally diffuse rapidly compared with other elements, but can also become trapped at defects and interfaces. In some situations such trapping leads to gas bubble evolution within the materials, and such bubbles can act as nuclei for cracks.

## PHYSICALLY BOUND HYDROGEN

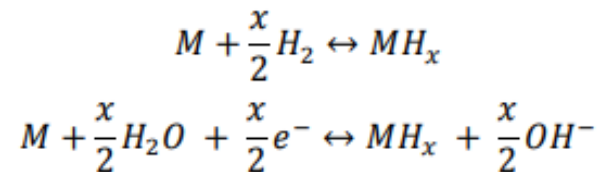
Hydrogen like any other gas, physisorbs onto a surface, the diatomic molecule does not dissociate and is held to the surface through weak van der Waals interactions. The strength of these interactions for hydrogen is very weak with the enthalpy of adsorption  $\Delta H_a$  between 4 and 10 KJ/mol. These weak interactions suggest that low temperatures are needed to obtain significant amount of hydrogen gas adsorbed. Physisorption is a surface phenomenon, thus high surface area materials have been well researched. As per the requisites of mobile applications it possesses no hydrogen loss during adsorption and desorption and very fast kinetics as no activation energy involved. Porous materials which have received considerable attention includes high surface area carbon structures, carbon nanotubes (CNT), metal organic frameworks (MOF), zeolites and more recently polymers of intrinsic porosity (PIMs).

## CHEMICALLY BOUND HYDROGEN

Hydrogen molecule when comes in contact with the solid surface, it dissociates into two hydrogen atoms which diffuse in the solid and form a chemical bond with the solid material. This phenomenon is known as chemisorptions. The classic chemically bound hydrogen storage materials are the metal hydrides. Most of the metals and alloys react reversibly with hydrogen to form hydride. Hydrogen forms metal hydrides with some metals and alloys leading to solid state storage under moderate temperature and pressure that gives them the important safety advantage over the gaseous and liquid storage methods. Metal hydrides have higher hydrogen-storage density ( $6.5 \text{ H atoms/cm}^3$  for  $\text{MgH}_2$ ) than hydrogen gas ( $0.99 \text{ H atoms/cm}^3$ ) or liquid hydrogen ( $4.2 \text{ H atoms/cm}^3$ ). Hence, metal hydride storage is a safe, volume-efficient storage method for on-board vehicle applications.

# CHEMICALLY BOUND HYDROGEN

These are two possible ways of hydriding a metal, direct dissociative chemisorptions and electrochemical splitting of water. These reactions are:



M represents the metal

Metal hydrides compose of metal atoms that constitute a host lattice and hydrogen atoms. Metal and hydrogen usually form two different kinds of hydrides,  $\alpha$ -phase at which only some hydrogen is absorbed and  $\beta$ -phase at which hydride is fully formed. Hydrogen storage in metal hydrides depends on different parameters and consists of several mechanistic steps. Metals differ in the ability to dissociate hydrogen, this ability being dependent on surface structure, morphology and purity.

# **HYDROGEN EMBRITTLEMENT**

The damaging effects of hydrogen in iron and steel were first recognised in the early 1870s, and the first tentative explanation, namely "hydrogen in interspaces impeding the movement of iron molecules", was proposed at this time. This phenomenon has been called hydrogen embrittlement. Constant exposure to hydrogen causes hydrogen embrittlement in many materials. Hydrogen embrittlement can lead to leakage or catastrophic failures in metal and non-metallic components. The mechanisms that cause hydrogen embrittlement effects are not well defined. Factors known to influence the rate and severity of hydrogen embrittlement include hydrogen concentration, hydrogen pressure, temperature, hydrogen purity, type of impurity, stress level, stress rate, metal composition, metal tensile strength, grain size, microstructure and heat treatment history. Moisture content in the hydrogen gas may lead to metal embrittlement through the acceleration of the formation of fatigue cracks.

# **HYDROGEN EMBRITTLEMENT**

There are a number of manifestations of HE, and various terminologies are used to describe different phenomena depending on the source of hydrogen and the type of damage produced. "Internal hydrogen embrittlement" (IHE) involves concentration of pre-existing hydrogen in regions of high hydrostatic stress (applied or residual), resulting in cracking under sustained stresses well below the yield stress. "Hydrogen-environment embrittlement" (HEE), on the other hand, involves sub-critical cracking of materials under sustained loads in hydrogen or hydrogen-sulphide gases. In hydride-forming materials containing high concentrations of hydrogen, embrittlement often involves formation and fracture of brittle hydrides at and ahead of cracks, and is termed "hydride-embrittlement".

# HYDROGEN EMBRITTLEMENT

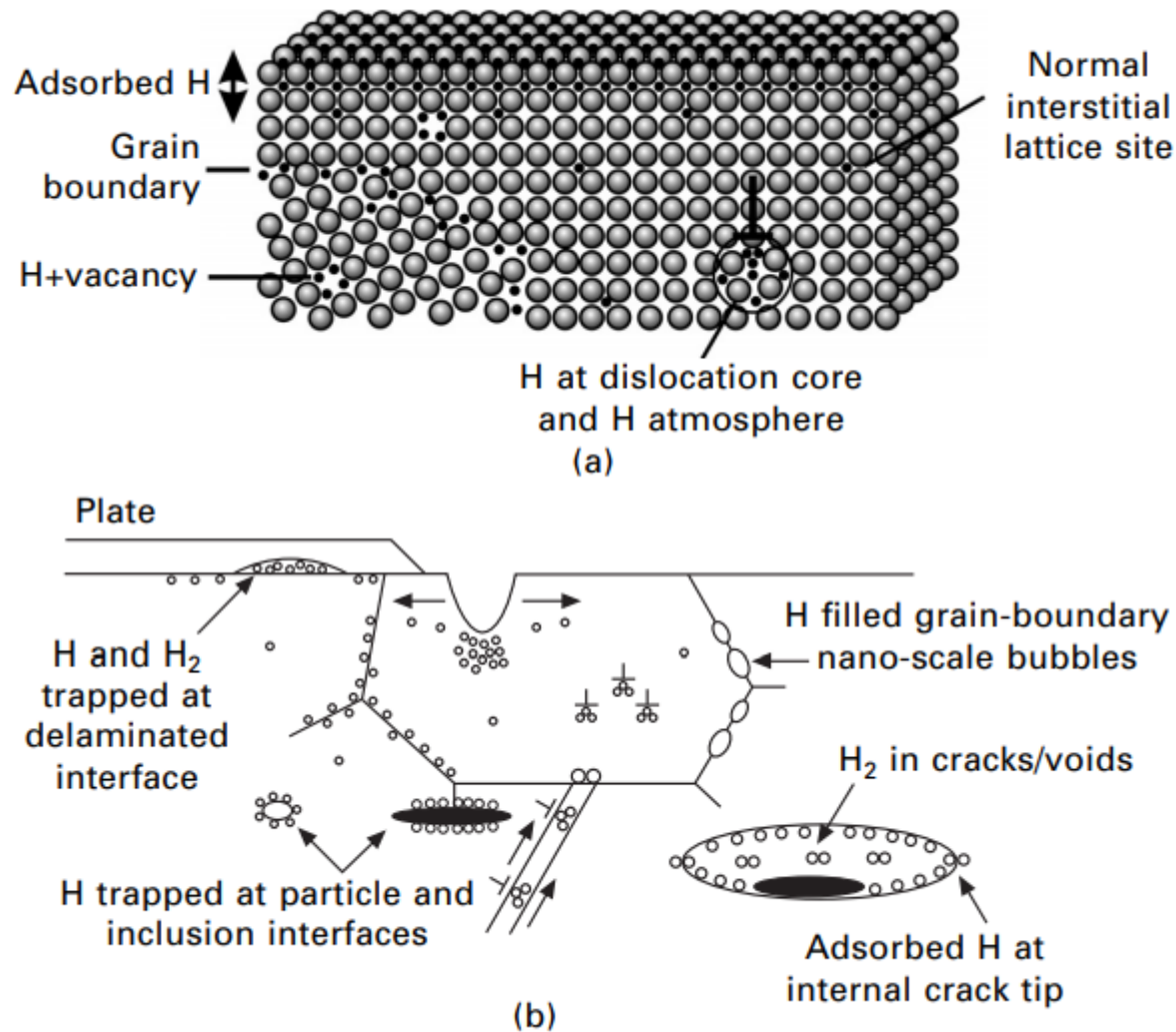
Other forms of hydrogen damage are "blistering" and "hydrogen-attack". Blistering occurs when solute hydrogen re-combines to form high-pressure hydrogen gas at cracked inclusion/matrix interfaces near surfaces. The high pressure causes voids to expand by plastic deformation and cracking, causing surface swelling. Hydrogen-attack, also called "hydrogen-reaction embrittlement", occurs when some materials such as steels and copper are exposed to hot hydrogen-bearing gases, leading to hydrogen diffusion to, and reaction with, carbides and oxides: High-pressure methane and steam, respectively, can then be produced, leading to internal voids and cracks.



# HYDROGEN EMBRITTLEMENT

Solute hydrogen occupies and diffuses between interstitial lattice sites in metals, and can be trapped to various degrees at other sites (i.e. occupy lower potential-energy sites relative to normal interstitial sites). These other sites, listed roughly in order of trapping strength, include: (1) some solute atoms, (2) free surfaces and sites between the first few atomic layers beneath surfaces, (3) mono-vacancies and vacancy clusters (which are present in concentrations well in excess of thermal equilibrium values because hydrogen reduces the vacancy formation energy), (4) dislocation cores and strain fields, (5) grain boundaries (including prior-austenite grain boundaries in martensitic steels), (6) precipitate/matrix interfaces and strain fields around precipitates, (7) inclusion/matrix interfaces, and (8) voids and internal cracks.

# HYDROGEN EMBRITTLEMENT



Schematic illustrations of sites and traps for hydrogen in materials (a) on the atomic scale, and (b) on a microscopic scale.

# **HYDROGEN EMBRITTLEMENT**

The high concentrations of hydrogen on or just beneath surfaces will also be present at crack-tip surfaces. For HEE, hydrogen gas will dissociate and adsorb at crack-tips, while for IHE, solute hydrogen will diffuse to, and adsorb at, internal crack-tip surfaces. Solute hydrogen can also precipitate as hydrogen gas (sometimes resulting in high pressures) in voids and at delaminated non-porous plating/substrate interfaces, and can then be re-absorbed and diffuse under applied stresses. Hydrogen in normal interstitial lattice sites will concentrate ahead of notches and cracks where high hydrostatic stresses result in a slightly expanded lattice.