An Overview of Hydrogen Degradation of Structural Materials in Nuclear Energy System

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*Keywords : Hydrogen Embrittlement, High Temperature Hydrogen Attack, Hydrogen Permeation

1. Introduction

Transitioning the energy supply from fossil fuels to alternative, clean, sustainable, and renewable sources is crucial for ensuring future energy sustainability and global security. Renewable Energy (RE) resources, particularly hydrogen, are poised to play a pivotal role in advancing towards clean and sustainable energy systems. Therefore, developing technologies for the effective utilization of hydrogen as an energy source, including its production, purification, storage, and transportation, is essential [1].

The High-Temperature Gas-Cooled Reactor (HTGR) or Very-High-Temperature Reactor (VHTR), both considered as Generation IV Reactors, have the potential to facilitate hydrogen production through the thermochemical sulfur-iodine cycle, due to the high operating temperature range of 750 to 950 °C) [2]. However, the structural materials such as carbon steels, low-alloy steels, stainless steels, and nickel-based alloys exposed to high temperature hydrogen environment in the production, storage and transportation, may suffer hydrogen induced degradation. Therefore, understanding the fundamental mechanisms of the hydrogen induced degradation of the materials, especially in high temperature environments, is important.

In this review, the basic physical and chemical properties of hydrogen related to the embrittlement of steel materials is examined and examines the hydrogen behavior theory of how hydrogen permeates into the structural materials then diffuses and trap inside the materials and releases.

2. Hydrogen Embrittlement Theory and Hydrogen Behavior of Steel Materials

Among the physical properties of hydrogen in relation to the hydrogen embrittlement of steel materials, the most basic consideration is the size of hydrogen. The atomic radius of hydrogen is known to be about 0.373 Å, so if a hydrogen atom has flowed into the steel in any way, a position that can be interstitial solution in the crystal lattice site of iron is of interest.

Table. 1 Interstitial site and size of BCC and FCC structure

		Interstitial Site	Radius Size (Å)
FCC	Octahedral Site	$\left(0 \ \frac{1}{2} \ 0\right), \left(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}\right)$	0.52
	Tetrahedral Site	$(\frac{1}{4}\frac{1}{4}\frac{1}{4})$	0.28

BCC	Octahedral Site	$\left(0\frac{1}{2}0\right), \left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$	0.19
	Tetrahedral Site	$\left(0 \frac{1}{2} \frac{1}{4}\right)$	0.35



Fig. 1 Octahedral (O) and Tetrahedral (T) sites in FCC lattice and BCC lattice [3]

As shown in Figure 1 and Table 1, octahedral site and tetrahedral site may exist in FCC and BCC, which are representative iron crystal structures, respectively, and in FCC structure such as austenite, the radius of octahedral site with a larger interstitial site space is 0.52 Å, which is larger than the radius of the hydrogen atom, so a large amount of hydrogen atoms can be dissolved in to the material as solute. On the other hand, in BCC such as ferrite, the larger interstitial sites are tetrahedral site and the size of the tetrahedral site is 0.35 Å, which could be quite low in hydrogen solute compared to the radius of the hydrogen in FCC steels is generally larger than that of BCC steels.

Another important property of the hydrogen is chemical reaction. Since the chemical reaction $H(g) + H(g) \rightarrow H_2(g) + Q$ (436kJ/mol) is exothermic reaction, hydrogen atoms trapped within specific lattice defects can readily form hydrogen gas bubbles which expanded in size. So once these atoms transform into hydrogen molecules within the matrix, they are unable to escape from the defects and become trapped, influencing the mechanical properties.

When hydrogen atoms exist inside a steel material, the higher the temperature, the greater the thermal

vibration of the crystal lattice, making it easier for hydrogen atoms to dissolve and diffuse. The hydrogen atoms can exist in an interstitial form within the crystal lattice as the temperature decreases. The solubility gradually decreases so that hydrogen can diffuse out and be trapped by an energetically more stable place. The locations where hydrogen can be trapped inside steels include non-metallic inclusions, the space between precipitates and the matrix, solidification shrinkage cavities (voids), dislocations, and grain boundary, around alloying elements or solute elements, etc. For example, when as the temperature decreases, the hydrogen atoms dissolved inside the steel coalesce and form large spaces, such as around the surrounding Eshelby's inclusions or in voids, rather than existing in the lattice space, and the collected hydrogen atoms become energetically stable. Because they are immediately combined with hydrogen molecules, the concentration of hydrogen atoms themselves in the defect space does not easily increase, and therefore the hydrogen atoms dissolved in the matrix can continue to diffuse into the defect space until it is saturated. These trapped hydrogen gas can work as a large internal pressure and eventually result in fracture of the steel.

The size of the binding energy between these various types of trap sites and hydrogen varies greatly depending on the trap site type. Depending on the strength of this binding energy, the diffusion and diffusion speed of hydrogen vary, and the hydrogen embrittlement characteristics of the steel is also a function of the strength of this binding energy. Hydrogen that remains without diffusing over a relatively long period of time due to its very low binding energy is classified as nondiffusible hydrogen, and hydrogen that is released within 2 to 3 days is classified as diffusible hydrogen.

Considering the solid solution and diffusion behavior of hydrogen in terms of temperature, it can be considered that there are two main agents that cause hydrogen embrittlement in steel materials: hydrogen atoms and hydrogen molecules. When stress is added to a material during hydrogen embrittlement, the deteriorations of mechanical properties such as cross-sectional shrinkage, tensile strength, and rupture strength are due to hydrogen atoms existing in an interstitial form in the crystal lattice, which reduces the bonding strength of metal crystals, or hydrogen atoms around dislocations. It is presumed that embrittlement is caused by atomic factors affecting dislocation movement when stress is applied. On the other hand, even if the external stress of the material is not given, the embrittlement phenomenon caused by the increase in internal pressure is embrittlement due to the molecular factor of hydrogen, and representative examples include Hydrogen Induced Crack (HIC) and Blister.

3. Hydrogen Induced Degradation and Fracture [4]

There are various mechanisms for the initiation and propagation of cracks in a metal matrix due to residual stress or externally applied load. The damage of a metal matrix is not caused by a single mechanism, but by a combination of factors, and each degradation mechanism is also caused by one or more metallographic factors acting in a complex manner. In an atmosphere containing hydrogen, steel fracture takes the form of brittle fracture and is largely divided into intergranular fracture and intragranular fracture. This type of fracture exhibits more complex behavior than the typical metal fracture phenomenon.

Hydrogen in steel can directly or indirectly contribute to the fracture of the steel. The direct case is when the bonding force itself between atoms is weakened, and the indirect case is when hydrogen precipitates on defects such as grain boundaries, precipitates, inclusions, and vacancies within the structure, causing embrittlement. Steels in general use are prone to brittle fracture due to hydrogen even in the absence of an external load due to inclusions of various alloy elements. Elements that can segregate at grain boundaries include antimony, arsenic, boron, carbon, manganese, nitrogen, oxygen, phosphorus, silicon, sulfur, and tin. Additionally, secondary phases like carbides, nitrides, and intermetallic compounds may precipitate near these boundaries.

4. Conclusion

In this paper, the hydrogen induced degradation mechanism of structural materials in nuclear energy systems is reviewed. In general, the degradation phenomenon caused by hydrogen appears to occur when steel is directly exposed to a hydrogen environment or is absorbed by impurities introduced during the steel manufacturing process, causing hydrogen to dissociate and flow into the steel. It seems necessary to develop technology to prevent hydrogen from permeate into the structural material by coating the surface of commercial structural material with a different material with excellent hydrogen penetration resistance.

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