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A REVIEW STUDY ON HYDROGEN EMBRITTLEMENT OF STEEL
PREGLEDNI RAD O VODONIČNOJ KRTOSTI ČELIKA

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- prevencija

Abstract

A common and intricate phenomenon known as hydrogen embrittlement of steel is the deterioration of the mechanical properties of metal in relation to stress corrosion cracking. This phenomenon has been extensively studied, with numerous works proposed over the last two decades, but there is still a lack of unified solutions and a solid understanding of the phenomenon. The purpose of this paper is to provide a review of the literature and publications on hydrogen embrittlement in steel. It focuses on recent developments and methods that have contributed to a better understanding of the relationship between steel structure, properties, and performance, with a particular emphasis on hydrogen diffusion, characterisation, mechanisms, and prevention of hydrogen embrittlement in structural steel. Furthermore, the paper discusses recent advances in experimental and multi-scale modelling and proposes future studies to address challenges related to hydrogen embrittlement in steels.

Izvod

Uobičajena i zamršena pojava poznata kao vodonična krtost čelika predstavlja pogoršanje mehaničkih svojstava metala povezano sa prslinama od naponske korozije. Ovaj fenomen je do sada proučavan opširno, sa brojnim radovima koji su predstavljeni u poslednje dve decenije, ali još uvek nedostaju jedinstvena rešenja i solidno razumevanje fenomena. Svrha ovog rada je da pruži pregled literature i publikacija o vodoničnoj krtosti čelika. Fokusira se na nedavna dostignuća i metode koje su doprinele boljem razumevanju odnosa između čelične konstrukcije, osobina i performansi, sa posebnim naglaskom na difuziju vodonika, karakterizaciju, mehanizme i sprečavanje krtosti vodonika u konstrukcionom čeliku. Osim toga, u radu se razmatraju nedavna dostignuća u eksperimentalnom i „multi-scale" modeliranju, odnosno, modeliranju na više nivoa (skala) i predlažu se buduća istraživanja u rešavanju izazova vezanih za vodoničnu krtost u čelicima.

INTRODUCTION

Hydrogen plays an important role in clean energy initiatives, finding applications in a wide range of industries such as power plants, fuel cells, and petroleum refineries. However, due to its tendency to interact with structural materials, implementing hydrogen into mechanical systems creates different kinds of challenges. Concerns regarding the safety and reliability of using hydrogen have been brought up by these interactions, especially in the case of transportation and storage systems, where developing safe and affordable solutions is essential. The phenomenon of hydrogen embrittlement in steel is one of the most challenging issues in this field. Steel structures are susceptible to being attacked by hydrogen atoms under certain environmental and stress conditions, which may affect their mechanical integrity with loss in mechanical properties such as tensile strength, fracture toughness, elongation to failure, fatigue life, etc. /1/.

Hydrogen-induced damage can cause catastrophic failures in many areas including vital components. The following examples illustrate the range and potential severity of such failures:

1. X-steel pipelines: high-pressure environments, susceptible materials, and the presence of hydrogen can lead to hydrogen-induced cracking in X-steel pipes, sudden leaks or ruptures in components affecting safety hazards, and potential environmental impact, /2-4/.
2. Bearing steel: temperature, alloy strength, and applied external loads all affect the initiation and development of cracks. Hydrogen absorption is a byproduct of the breakdown of oil, which can be impacted by rolling and compression conditions, /5/.
3. Maraging steel: considerable reduction in the percentage of elongation, time to failure, and notch tensile strength for all experiments carried out in artificial seawater compared to those carried out in air, due to the presence of hydrogen, /6/.
4. Austenitic steel: although this type of steel is less susceptible to hydrogen embrittlement due to low diffusivity and high solubility of hydrogen in the structure, severe environmental conditions (cathodic charging) can lead to brittle fracture at the surface of the sample, /7/.

An in-depth understanding of hydrogen embrittlement in steel is still a difficult task, even after decades of dedicated research. The fact that diffusible hydrogen embrittles the steel has been known since 1875, /8/. Today it is widely accepted that the three major mechanisms for hydrogen embrittlement are: hydrogen-enhanced localised plasticity (HELP), hydrogen-enhanced decohesion (HEDE), and adsorption-induced dislocation emission (AIDE), /9/. However, there isn't a physical model for hydrogen embrittlement that is fully developed and applicable yet. Authors /10/ have proposed a hydrogen embrittlement model for a failed boiler tube that can be used in predictive maintenance in industry, explaining in depth the mechanisms of hydrogen embrittlement.

There have been several numerical models created to study the hydrogen embrittlement effect on low-alloy steels /11-12/ aiming to develop a fully functional numerical model that can predict fracture behaviour of steel in the presence of hydrogen.

The objective of this paper is to provide a better understanding of the mechanisms of hydrogen embrittlement as well as factors influencing susceptibility for different steel types. It also highlights the gaps and difficulties in multiscale modelling. Identifying these issues is crucial since it can help to focus future research that can result in the safe and reliable integration of hydrogen technologies in a wide range of industrial applications.

MECHANISMS OF HYDROGEN EMBRITTLEMENT

Hydrogen can enter the metal in two ways: /1/

- during the manufacturing processes (welding, chemical cleaning, heat treatment, electroplating), or
- during operational processes (gaseous hydrogen exposure, cathodic electrochemical reactions).

In the literature /1/ hydrogen damage mechanisms for iron, carbon and low alloy steels are divided into:

- hydrogen-induced cracking (HIC)
- hydrogen stress cracking (HSC)
- hydrogen embrittlement (HE), and
- high-temperature hydrogen attack (HTHA).

The exact mechanism of hydrogen embrittlement is complex and can involve multiple processes. Historically, there have been three types of approaches to HE studies, shown in Fig. 1:

1. macro approach (mid 20th century),
2. micro-meso approach (late 20th century),
3. nano and atomic approach (early 21st century).

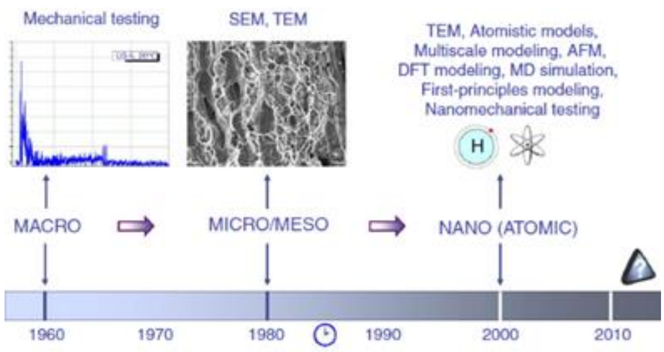

Figure 1. Historical approaches to hydrogen embrittlement, /1/.

Depending on the source of hydrogen, there are three types of hydrogen embrittlement (HE), /1/:

1. internal HE, where the hydrogen source already exists inside the metal from the manufacturing process,
2. external HE, where hydrogen enters the metal in the operational phase,
3. environmental HE, where hydrogen comes from environmental conditions.

HE has three main mechanisms /13/ that are generally accepted (shown in Fig. 2):

- adsorption - induced dislocation emission (AIDE),
- hydrogen-enhanced decohesion (HEDE), and
- hydrogen-enhanced localised plasticity (HELP).

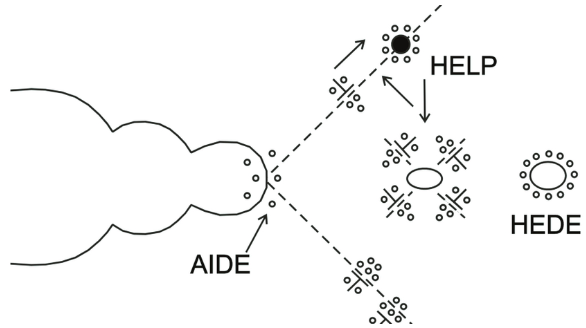

Figure 2. Schematic illustration of three hydrogen embrittlement mechanisms, /13/.

Adsorption-induced dislocation emission (AIDE) is a combination of the other two mechanisms, HEDE and HELP. Hydrogen atoms are adsorbed at the metal surface in the regions of stress concentration, weakening the atomic bonds (HEDE) followed by dislocation and crack growth with formation of microvoids (HELP), /14/.

They can act alone or combined, although proving simultaneous action between HELP and HEDE mechanisms is difficult to spot in the material sample. Activation of a mechanism depends on the type of material, hydrogen charging, content and distribution in the sample, as well as environmental and mechanical loading conditions.

Hydrogen-enhanced decohesion (HEDE) is an atomic-level process. In stressful condition, hydrogen atoms are diffused inside the metal, and they reduce the binding forces between matrix atoms resulting in intergranular fracture, /14/. Hydrogen-induced cracks mostly appear at grain boundaries, phase boundaries, or in areas of high dislocation density.

Hydrogen-enhanced localised plasticity (HELP) shows the embrittling effect on ductility. Hydrogen atoms accumulated near the crack tip reduce the stress field of the dislocation. In the presence of hydrogen, lower external stress can trigger a dislocation movement, compared to a hydrogen-free environment, causing local dislocation pileups and premature failure of the material, /14/.

A group of authors /10/ investigated the simultaneous action of HELP and HEDE mechanisms (HELP + HEDE) in St.20 steel. They spotted a mixed fracture mode - brittle transgranular fractures by HEDE mechanism and ductile fracture due to HELP mechanism.

At lower hydrogen concentrations, the dominant mechanism was HELP with a slight increase in hardness and no significant decrease in ductility. Higher hydrogen concentrations activated the HEDE mechanism characterised by a sharp drop in the impact strength (KCV_{TOT}), and the crack propagation component (KCV_P), with a negligible change in the crack initiation component KCV_I value, resulting in sharp ductile-brittle fracture transition, /10/, Fig. 3.

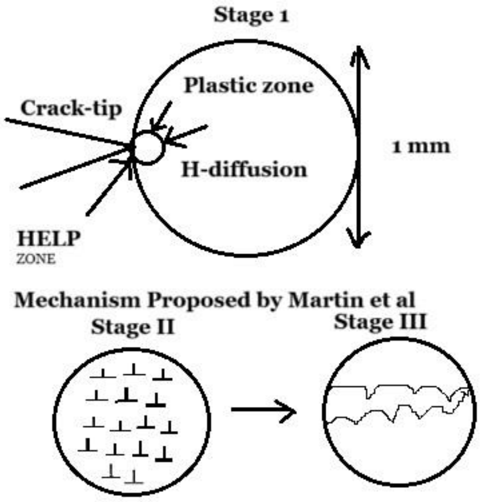

Figure 3. HEDE + HELP mechanisms, /15/.

In 2012, a new type of combined mechanism was proposed, nanovoid coalescence (NVC) mechanism (Fig. 4). It presents a simultaneous effect of HEDE, HELP, and HESIV mechanisms. In stage I hydrogen diffuses into the metal and accumulates in stage II. Hydrogen-vacancies complexes form in stage III which leads to vacancy clusters combining into nanovoids (stage IV), similar to microvoids in the traditional macroscale ductile fracture, /15/.

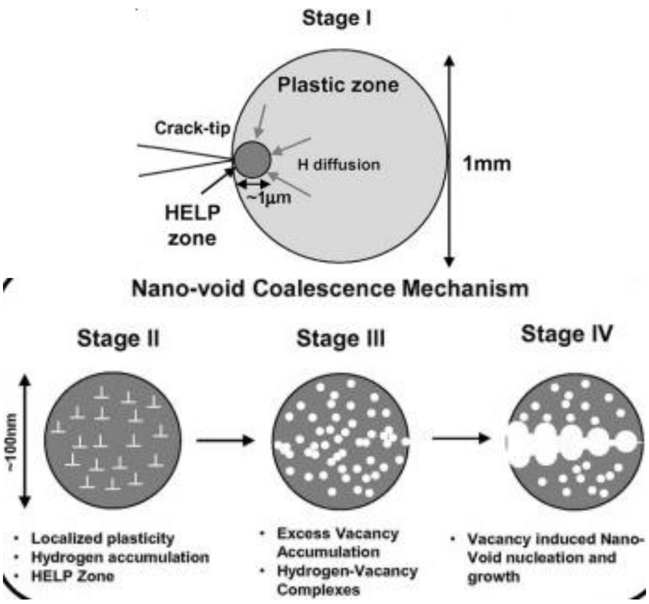

Figure 4. Nanovoid coalescence (NVC) mechanism, /15/.

FACTORS INFLUENCING SUSCEPTIBILITY

Hydrogen as the lightest element, can dissolve in most metals and alloys. It enters the material in the form of atoms and affects the mechanical characteristics through interactions with material defects. Internal and external sources can bring hydrogen into metals, mostly from electrochemical charging, high pressure hydrogen gas environment, and corrosion reactions, /15/.

The diffusion process begins with adsorption of hydrogen atoms on the metal surface due to van der Waals interactions between hydrogen gas and the surface, this process is reversible. The next stage is chemical absorption within a single atom layer which is irreversible and a slow process leading to hydrogen dissolution. On the surface there is a high number of hydrogen traps, such as vacancies, dislocations, grain boundaries and surface hydrogen traps, shown in Fig. 5.

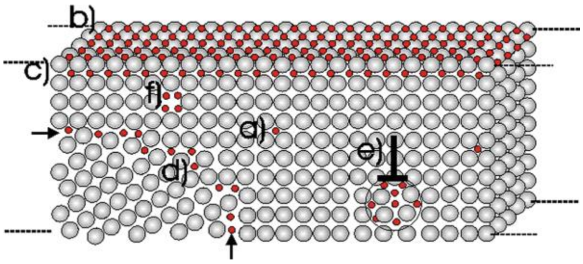

Figure 5. Hydrogen traps in steels, /15/: a) interstitial sites; b) surface traps; c) subsurface traps; d) grain boundary traps; e) dislocation traps; f) vacancy traps.

These traps can be divided into two groups:

- Reversible hydrogen traps (E_b < 60 kJ/mol): include interstitial sites, dislocations, and grain boundaries. Hydrogen can be released during service due to a reduced potential energy barrier.
- Irreversible hydrogen traps (E_b > 60 kJ/mol): carbides, inclusions, precipitates, with low probability of hydrogen escaping due to the large potential energy barrier, where E_b is hydrogen trap activation energy. Hydrogen atoms move and group inside the metal by stress-induced hydrogen diffusion and dislocation-induced hydrogen migration, /15/.

Factors that make the material susceptible to hydrogen embrittlement are shown in Fig. 6.

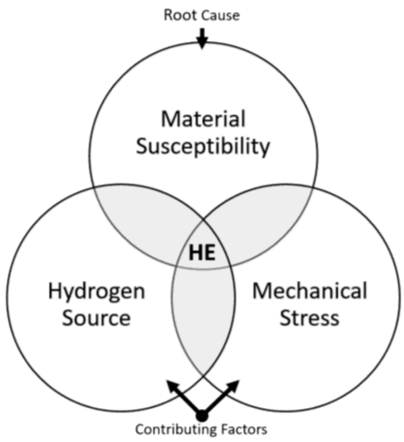

Figure 6. Contributing factors and root cause for HE.

Since hydrogen source and mechanical stress cannot be fully eliminated in industrial applications, the root cause of hydrogen embrittlement is the material itself. Material susceptibility to hydrogen embrittlement can be divided into two groups: steel microstructure and alloy composition.

Steels with strength above 1000 MPa are prone to hydrogen embrittlement, as well as aluminium, titanium, and magnesium alloys, /15/. There is limited research on hydrogen embrittlement in stainless steel, /16-18/. These steels are less susceptible to hydrogen embrittlement due to the low diffusivity and high solubility of hydrogen in FCC structures. Hydrogen content decreases from the surface of the samples to the centre due to the low diffusivity which is activated by plastic deformation and is time dependent. It transports by moving dislocations and can accumulate on grain boundaries and their intersections. The results /17/ show that hydrogen-induced martensite forms in grain boundaries and leads to embrittlement and intergranular fracture. Finer grain size improves the resistance to hydrogen-induced cracking. For fine-grained steel, the main fracture mode was ductile tearing for a Ni content between 12-30 % /9/, while for coarse-grained steel the main fracture mode was transgranular. Decreasing the grain size increases the mechanical properties and resistance to hydrogen embrittlement for S316, S321, and S347, /16/. Cathodic polarization resulted in severe reduction of ductility (55 to 15 %) and hardness (by 10.8 %), /17/.

The mechanism of transportation of hydrogen in low carbon steel is not fully known. Steels with yield strength below 900 MPa are immune to hydrogen embrittlement, /18/. By increasing the hydrogen charging time from 1 to 5 hours, the yield strength of the steel sample decreases. For cold worked samples to 80 % and hydrogen charging time of 3, 4, and 5 hours, there was a constant increase in the tensile strength. However, new dislocations that have been created by the cold deformation process interact with the dislocations that already existed in the sample, their movement becomes limited resulting in strain hardening of the material. SEM studies show different types of fractures, such as intergranular tears and high-pressure fracture locations, /18/.

In the case of maraging steel, the susceptibility of hydrogen depends on air humidity and temperature. For aged samples (at 510 °C for 3.5 hours) charged in air and artificial seawater, the results show significant loss in % of elongation and tensile strength for tests conducted in artificial seawater, compared to those tested in air, /6/.

For bearing steels, oil compression and rolling conditions affect the decomposition of oil resulting in hydrogen absorption. Lubricants containing water can induce hydrogen embrittlement with water splitting by electrolysis. Only a few ppm of dissolved hydrogen can cause hydrogen flakes, blistering, loss of ductility, and high porosity. Therefore, development of hydrogen embrittlement resistant lubricants is as important as the development of steels, /5/. At temperatures above 200 °C, a process known as internal decarburization occurs, molecular hydrogen reacts with carbides forming methane and gas voids within the matrix which leads to formation of blisters and cracks due to the internal stress /5/.

Hydrogen sources can be internal and external; thus, hydrogen embrittlement is divided into internal (IHE) and external (HEE). Hydrogen embrittlement is enhanced by slow strain rate and surface hardness above 37 HRC, /14/.

Martensite transformation increases local hydrogen diffusion in fatigue cracks which leads to crack growth. Pre-existing α’ can act as diffusion highways increasing the transport and uptake during hydrogen exposure, but α’ induced by prior deformation is the main cause for hydrogen embrittlement of 300 steel series, /19/.

The combination of poorly executed weld, thermal loads and local metal enrichment due to corrosion were a cause of failure of an evaporator tube in the form of a ‘window’ type fracture caused by the high temperature hydrogen attack (HTHA) damage mechanism, /10/. In this case, the simultaneous presence of HELP and HEDE mechanisms was detected, depending on the hydrogen concentration. At lower hydrogen concentrations, the dominant damage mechanism is HELP without significant decrease in the ductility of the material and a tiny increase in hardness. After reaching the critical hydrogen concentration, the dominant damage mechanism is HEDE followed by a sharp ductile-brittle fracture, /10/.

PREVENTION AND MITIGATION STRATEGIES

To prevent hydrogen embrittlement, the exact cause and damage mechanism must be known. Since material susceptibility is the root cause for hydrogen embrittlement, a material should be used according to the environmental condition and mechanical stress.

The diffusion process of hydrogen depends on microstructure: phases, grain boundaries, grain size, vacancies, dislocations, inclusions, etc., which can reduce the mobility of hydrogen by acting as hydrogen traps, /20/. There are two approaches for preventing and mitigating hydrogen embrittlement:

1. Preventing external hydrogen embrittlement by surface coating and surface modifications, and
2. Optimisation of the microstructure with alloy elements and heat treatments.

Surface coating for hydrogen resistance by electroplating or hot-dip galvanizing processes can induce hydrogen in the material. To reduce this, heat treatment is done at different temperatures, depending on steel type. During the ‘baking’ process diffusible hydrogen comes out from the material, under the assumption that the treatment itself does not harm the mechanical properties of the steel, /14/.

Using thin Zn, Ni, Sn, Cd, TiC, TiO_2, Cr_2O_3 coatings reduces the amount of hydrogen permeation, /21/. It is very important to optimise the coating properties (plasticity, hardness) to be compatible with the steel properties and prevent further damage mechanisms from appearing.

Hydrogen embrittlement can also be avoided by reducing the amounts of C, Si, P, and S, /15/. In pipeline steels, reducing Mn levels helps to avoid different grain size and dislocation densities, /20/.

In the manufacturing process, vacuum degassing can be used to reduce the hydrogen content in the melt. After casting, steel should be annealed at low temperatures to avoid side transformations. This is a time-consuming process that depends on the part’s geometry, /21/. Shot peening is used to improve durability and corrosion resistance by inducing compressive residual stresses and forming substructure in the surface layer, /20/.

Another option is to provide trapping layers for hydrogen with sufficient trapping capabilities in order to absorb any hydrogen that may enter during working life. Ion implantation of Ti has reduced hydrogen entry by providing atomic traps at the surface, /20/.

Mitigation strategies include vacuum treatments to remove absorbed hydrogen, annealing and mechanical deformation processes that can reduce the hydrogen content at susceptible areas, alloy additives such as niobium, titanium, and environmental control during the operating process (temperature and humidity).

CONCLUSIONS

The paper reviews the serious challenges associated with hydrogen embrittlement in different steel types. Significant progress has been made in understanding the hydrogen damage mechanisms HELP, HEDE, and AIDE, while a fully developed physical and universally applicable model remains a challenge.

The role of reversible and irreversible hydrogen traps shows the importance of microstructure optimisation for the prevention and mitigation of hydrogen embrittlement. There still remain gaps and challenges that need to be addressed, especially in the area of multi-scale modelling.

It is crucial to recognize these obstacles in order to focus future research efforts on enhancing hydrogen technology and ensuring its safety and reliability in various industrial settings.

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