UDC 669.017:539.16

THE MOST PROBABLE MECHANISMS OF MATERIAL CHARACTERISTICS DEGRADATION DUE TO ACCUMULATION OF HYDROGEN AND PREDICTING THE POSSIBLE SCENARIOS OF MAINTAIN ITS RESOURCE

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The review considers the results of theoretical and experimental studies of hydrogen solubility, diffusion and permeation; the nature of hydrogen bonding with defects; critical levels of hydrogen accumulation, its distribution in the material bulk and mechanisms of interaction with the crystal. Changes of material structure in the presence of hydrogen are discussed, as well as the influence of external thermo-irradiation fields and the duration of annealing on these processes. Hydrogen localization and possible mechanisms of hydrogen-induced material destruction are analyzed. Recommendations for minimizing the negative effect of hydrogen and for preventing the reduction of operating characteristics of structural materials are considered.

INTRODUCTION

Structural materials of modern technical devices operate under extreme conditions (high temperatures, high mechanical stresses and high radiation doses). In nuclear reactors, thermonuclear devices, space vehicles, the crystalline structure of materials is constantly undergoing to changes at the atomic level due to nucleation of various kinds of defects. Their appearance dramatically changes the physical properties of materials, they begin to swell, embrittle, harden, “creep”, etc. [1].

Two processes are involved in the radiation damage of materials: a reversible process of displacements and the formation of defect clusters and an irreversible process of transmutation of elements of the initial material in nuclear reactions. As a result of nuclear reactions, gaseous impurities are formed in the materials, in particular, helium and hydrogen [2].

Prediction of the material properties under the circumstances of interaction with hydrogen is an important aspect of modern physics and solid-state mechanics [3–6]. Of greatest interest is the study of the features of hydrogen interaction with metals and its effect on the mechanical characteristics of the material, since hydrogen, accumulating in the metal parts of the structures, facilitates the appearance of defects, and as a consequence the destruction – the manifestation of the phenomenon of hydrogen embrittlement [7–19].

The investigation of hydrogen behavior in materials is also largely related to the problems of creating a nuclear fusion reactor. According to calculations [20, 21], the hydrogen permeability of the first wall can lead to significant diffusion leakage when used the fuel element – tritium.

The purpose of the review is to analyze the published data of hydrogen effect on the change of microstructure and mechanical properties of structural materials. The most probable mechanisms of processes caused by the accumulation of hydrogen and leading to the degradation of material characteristics are considered. The issues of predicting possible scenarios for preserving material resource are discussed based on data on the nature of the bond, diffusivity, and localization of hydrogen in the material.

1. HYDROGEN-ASSISTED DEGRADATION OF MATERIALS

There are a lot of sources of hydrogen in steel: gaseous hydrogen, liberation of atomic hydrogen by the iron-water or iron-H_2S reactions, decomposition of water molecules, electrolytic and corrosion processes including a cathodic reaction, absorption of hydrogen from seawater etc.

In nuclear power plants hydrogen is formed in the material both in nuclear reactions and as a result of corrosion upon contact with the environment [1].

1.1. FEATURES OF HYDROGEN GENERATION IN TRANSMUTATION REACTIONS

In the general case, the generation rate of transmutant nuclei is determined by the product of the cross section of the transmutation reaction and the neutron flux. Therefore, the generation level of transmutant elements will be comparable (or exceed) with the concentration of individual elements that make up the material, and may influence the parameters and evolution of the radiation microstructure.

The feature of hydrogen generation in steels of various compositions under irradiation with fast neutrons ($E_H > 0.1$ MeV) is its continuous formation in (n, p) reactions which do not lead to a change in the elemental composition, because the atoms – products of this reaction are short-lived radioactive isotopes, and their β-decay leads to the original maternal isotope [22].

In fusion reactors, the plasma facing (first wall, divertor) and breeding-blanket components will be exposed to plasma particles and electromagnetic radiation and will suffer from irradiation by an intense flux of 14 MeV neutrons.

In the neutron spectrum of a fusion reactor, the cross section for the reactions of hydrogen and helium formation is by ~ 2 order of magnitude higher than in fission reactors and reaches the values of more than $100 \cdot 10^{-27}$ cm^2 for hydrogen and more than $40 \cdot 10^{-27}$ cm^2 for helium. This leads to the participation of these reactions in the evolution of the elemental composition of the irradiated material and to an increase by ~ 2 order of magnitude of their generation level, reaching ~ 1000 appm H/year for hydrogen. This level increases significantly if the steel contains nickel ($\sigma = 374 \cdot 10^{-27}$ cm^2).

In next-generation nuclear energy technologies (Generation IV), electronuclear systems for neutron generation use the charged particles accelerators (electrons or protons) with energy from 100 to 1000 MeV. The energy spectrum of neutrons extends to energies of 100 or more MeV and the cross sections of the nuclear transmutation reactions (n, 2n), (n, p) and (n, α) increase. Thereby, the rate of transmutational change in the elemental composition of steels and the level of transmutational formation of gaseous transmutants increase [1].

The operating conditions of materials for a number of operated and future nuclear reactors are given in Tabl. 1 [23].

Table 1

Irradiation parameters in nuclear facilities

Reactor type	Parameters			
	Rate of helium generation	Rate of hydrogen generation	Rate dose	Used materials
Thermal reactors	~ 280 appm/year	~ 60* appm/year	3 dpa/year	WWER-1000: PVI steel 18Cr10NiTi Pressure vessel 15Cr2NiWA
Fast reactors	20…30 appm/year	–	30…40 dpa/year	Austenitic stainless steels, ferritic/martensitic steels
Fusion reactors	300 appm/year	800 appm/year	20 dpa/year	Ferritic/martensitic steels, vanadium alloys
Reactors of IV generation, electro nuclear systems	950…3500 appm/year	3000…4000 appm/year	5…40 dpa/year	Austenitic stainless steels, ferritic/martensitic steels
*F. Garner had revealed 3380 appm of hydrogen instead of expected 700 appm at 33 dpa.				

1.2. HYDROGEN DEGRADATION OF METALLIC MATERIALS

Synergic action of stress and environment may result in various types of degradation of metallic materials.

There are the following several specific types of hydrogen-induced damage of metals and alloys [6]:

- hydrogen embrittlement;
- cracking from precipitation of internal hydrogen;
- cracking from hydride formation;
- hydrogen attack;
- hydrogen-induced blistering.

Hydrogen Embrittlement

The issue of hydrogen and metals, and in particular the phenomenon known as “hydrogen embrittlement” (HE) [24–30], is very old. In the year 1875, Johnson [31] revealed extraordinary changes in the toughness and breaking-strain of iron that was immersed temporarily in acid for just a few minutes. A number of acids were studied and only those that produce hydrogen by their action on iron were found to lead to a deterioration of properties. In following decades, the problem became interesting to many researchers, and although several HE mechanisms have been proposed, there was no consensus.

Hydrogen has impact on following forms of environmentally assisted cracking: hydrogen embrittlement, stress corrosion cracking, and corrosion fatigue [32]. Deleterious hydrogen effect at temperatures below 200 °C is termed as low-temperature hydrogen attack. Hydrogen degrades properties of steels mainly by delayed cracking at stress below the yield strength – hydrogen stress cracking, and by the loss of ductility in a tensile test as reflected by a decreased reduction in area which is generally called hydrogen embrittlement (HE) (Fig. 1). When local hydrogen concentration is high enough (reaches critical concentration) it may cause hydrogen induced cracking (HIC) or may manifest as advancement of crack propagation (crack has been initiated by mechanical damage or corrosion) [33].

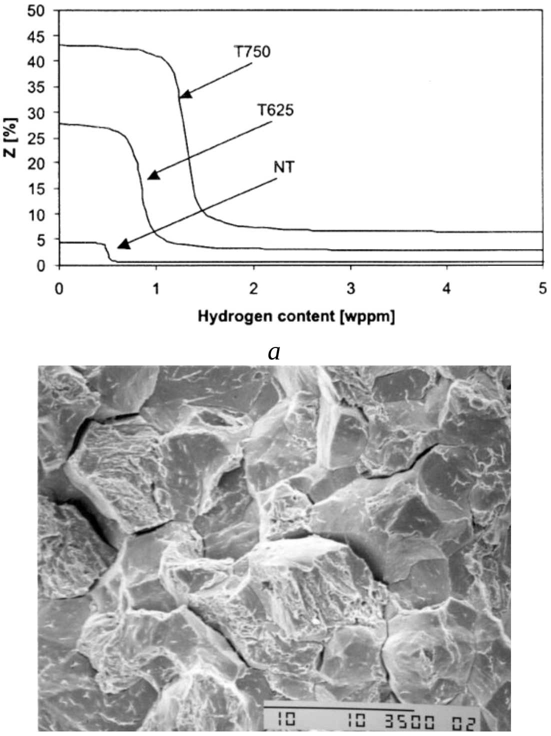
For a given system, the mechanism of hydrogen embrittlement can change, depending on the source of hydrogen and the nature of the applied stress [34–40]. The following mechanisms of hydrogen embrittlement are highlighted in [6].

Internal Pressure Model. Precipitation of molecular hydrogen at internal defects (nonmetallic inclusions, voids) develops high internal pressure. This pressure is added to applied stress and thus lowers the apparent fracture stress.

Hydrogen Induced Decohesion Model. Dissolved hydrogen reduces the cohesive strength of the lattice, i. e. interatomic bonds and thereby promotes decohesion. There is absence of direct experimental measurements supporting this mechanism.

Surface Energy Model (Adsorption Model). The hydrogen adsorption reduces the surface energy needed to crack nucleation and thus lowering of fracture stress. There are no direct experimental observations and reliable calculations that hydrogen can reduce surface energy.

Adsorption Induced Localised Slip Model. Adsorption of environmental hydrogen atoms at crack tip results in weakening of interatomic bonds facilitating dislocation injection from a crack tip and then crack growth by slip and formation of microvoids.



a

b

Fig. 1. Effect of hydrogen on the ductility reduction of F82H martensitic steel after different heat treatments (a) and SEM image of the fracture surface for NT material (0.61 wppm H content), showing typical intergranular H-fracture with several secondary cracks (b). The bar corresponds to 10 μm [18]

Hydrogen Enhanced Localized Plasticity (HELP) Model. Absorption of hydrogen and its solid solution increases the ease of dislocation motion or generation, or both.

Corrosion Enhanced Plasticity (CEP) Model. This model takes into account the generation of vacancies due to localized anodic dissolution and hydrogen evolution by cathodic reaction at the newly depasivated crack tip. Thus, corrosion produces an enhanced localized plasticity. The activated dislocations along slip bands form pile-ups interacting with obstacles. The resulting high local stress can initiate cracking.

Hydrogen Rich Phases Model. Formation of hydrogen rich phases – hydrides, whose mechanical properties differ from those of matrix. Cracking could proceed by the formation and cracking of brittle hydride near the crack tip.

Ultimately hydrogen embrittlement is described as a three-step process. *Firstly,* hydrogen is introduced into the metal, via electrochemical charging or via gaseous absorption. In some cases, hydrogen may be introduced in the lattice prior to stressing (e. g. during fabrication). This situation is commonly referred to as internal hydrogen embrittlement. *Secondly*, atomic hydrogen is transported through the metal lattice or forcibly introduced by irradiation, increasing its concentration in the tensile-stressed surroundings of the crack tip due to gradients in the chemical-potential. In the absence of a crack, atomic hydrogen may be transported to an initiation location. *Thirdly*, the combined action of stress and hydrogen concentration leads to failure of the metal in an embrittled zone [41].

Prevention of hydrogen embrittlement in the operation of structures and products is complicated by at least three circumstances.

Firstly, the forms of manifestation of hydrogen fragility are so varied that it is not so easy to envisage all possible variants of its action.

Secondly, hydrogen in metals is very mobile and easily redistributed under the influence of stress, temperature, electrical potential. This can lead to dangerous local enrichment of parts and structural elements with hydrogen, although its average content in the metal is certainly less than those at which hydrogen fragility can develop.

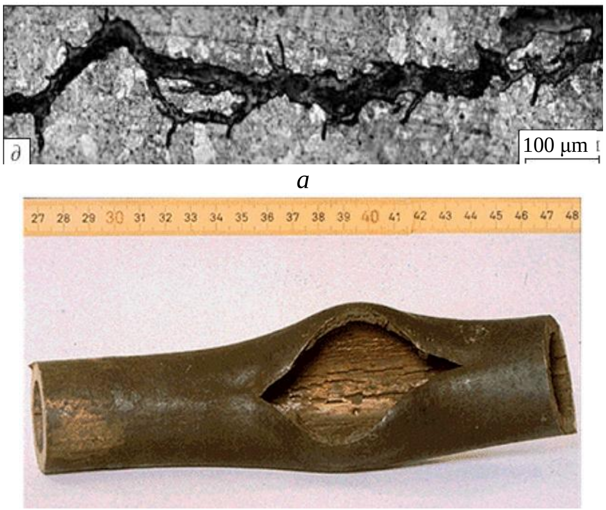
Thirdly, there are no sufficiently accurate criteria for estimating the maximum reasonable hydrogen concentrations for a certain construction and operating conditions. Critical hydrogen concentrations, determined in laboratory tests with samples of small cross sections, tend to be overestimated and do not guarantee the absence of hydrogen embrittlement in large structures with a rigid stressed state [42].

Cracking from Precipitation of Internal Hydrogen

Cracks that result from the precipitation of internal hydrogen have been termed fisheyes shatter cracks, and flakes. These forms of hydrogen damage occur in forgings, welds and castings and are attributed to hydrogen absorption in the molten metal (Fig. 2,a).

Hydrogen Attack

Hydrogen attack occurs when absorbed hydrogen interacts with alloying or impurity elements in the microstructure to form an insoluble, generally gaseous, phase (see Fig. 2,b).



a

b

Fig. 2. Fragment of a crack in the metal pipe [43] (a), high temperature hydrogen attack of carbon steel cooler pipe of a heat exchanger [32] (b)

Cracking from Hydride Formation

Zirconium, titanium, tantalum and other transition, rare earth metals form hydrides when the hydrogen concentration exceeds a certain level. When the hydrogen content of zirconium, titanium, uranium and other hydride forming metals exceeds the solubility limit, metal hydrides precipitate. The hydrides are typically low density, brittle compounds whose presence degrades the ductility of the alloy. Both α (ferrite) and γ (austenite) phases of iron form only solid solutions with hydrogen and no evidence of hydride has been observed.

Hydrogen Induced Blistering

Hydrogen induced blistering occurs during or after hydrogen has been absorbed by the metal. The mobile hydrogen atoms collect at traps in the alloy. Hydrogen traps include the interface between inclusions and the metallic matrix as well as laminations in a wrought structure. Such interfaces are mechanical bonds and provide surfaces inside the metal. As hydrogen collects at this surface the nascent atoms recombine to molecular form and pressure at the lamination or the inclusion-matrix interface occurs (Fig. 3).

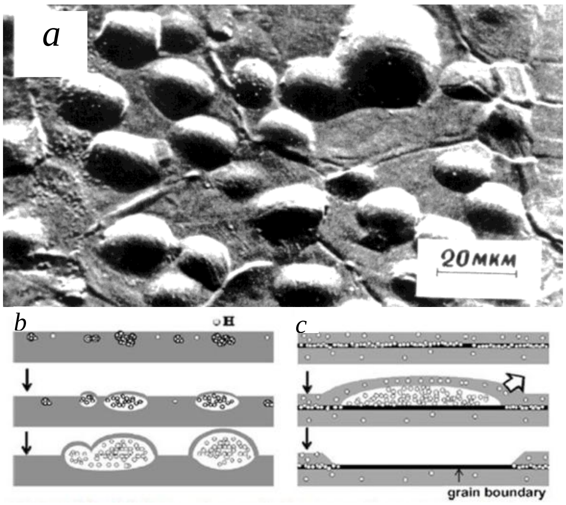


Fig. 3. Surface microstructure of EP-450 ferritic-martensitic steel irradiated with low-energy hydrogen plasma to a dose of 10^{24} H_2^+/m^2 at 283 K [44–46] (a), a model picture for H retention and resulting in surface deformation such as blistering with two different mechanisms appears: accumulation of gas bubbles with smaller radius and high pressure inside (b) and exfoliation of grain boundaries at the deeper region of the saturated layers (c) [47, 48]

In order to produce preventative measures, both the source of the hydrogen and the degradation mechanisms must be known at least approximately.

2. PREDICTION OF POSSIBLE SCENARIOS FOR CONSERVATION OF MATERIAL RESOURCES ON THE BASIS OF DATA ON THE CHARACTER OF BOND, DIFFUSIVITY AND LOCALIZATION OF HYDROGEN

2.1. HYDROGEN SOLUBILITY AND DIFFUSIVITY IN IRON AND IRON-BASE ALLOYS

A large amount of data was obtained in studies of thermodynamic and kinetic features of the iron-hydrogen system [49–59]. At the same time, the data of various researchers often show discrepancies in solubility, and especially in the diffusion ability of hydrogen. Much work has been focused on the analysis of anomalies related to the interaction of hydrogen with defects that occur during pre-treatment or existing on the surface of the metal, as well as associated with the properties of iron lattice. Several possible factors that lead to observed disagreements are considered. The most important are the following effects that lead to "distortion" in the measurements of solubility: 1) the interaction of hydrogen atoms with point defects (interstitial and vacancies) in a lattice of iron; 2) the influence of metallurgical factors, such as grain boundaries and impurities; 3) deformation-related defects, such as dislocations; 4) traps or contaminations on the material surface.

About 100 years ago, it was shown that the solubility of hydrogen in iron is proportional to the square root of the external pressure of hydrogen. In the following decades, many experimental studies were devoted to the study of hydrogen solubility in this metal.

The diffusion of hydrogen in non-irradiated stainless steels practically does not depend on the composition of austenite. As shown in [37], the diffusion coefficients determined using various experimental techniques in studies with several types of 300 series austenitic stainless steels coincide within the experimental error.

The hydrogen diffusivity in ferrite-martensitic steels are also slightly different from each other [50]. Tabl. 2 shows the hydrogen diffusion coefficients in steels with bcc and fcc structure.

Table 2

Hydrogen solubility and diffusion coefficients (D) in iron and steels

Material	T, K	Solubility, N_H/N_{Fe}	$D = D_0 \exp(-E_m/kT)$, m^2/s	D (573 K), m^2/s
X18H10T	423…723	$10^{-4}…10^{-3}$	$D=8.4\cdot10^{-7}\exp(-0.58/kT)$	$6.5\cdot10^{-12}$
SS316	373…723	$10^{-4}…10^{-3}$	$D=6.2\cdot10^{-7}\exp(-0.535/kT)$	$1.19\cdot10^{-11}$
Fe	373…743	$10^{-8}…10^{-6}$	$D=6.7\cdot10^{-8}\exp(-0.087/kT)$	$1.15\cdot10^{-8}$
EUROFER	523…873	$10^{-6}…10^{-4}$	$D=1\cdot10^{-7}\exp(-0.14/kT)$	$5.84\cdot10^{-9}$

Low solubility (1...10^2 appm) and high diffusion mobility (10^{-11}...10^{-8} m^2/s) contribute to minimizing of hydrogen accumulation in iron and steels in the absence of microstructural defects. But the concentration of hydrogen that can cause the embrittlement of metals is also quite small (~ 1 wppm). At the same time, it is extremely important to estimate the effect of impurities on the dissolution energy of hydrogen in a metal that affects the content of hydrogen. Such an estimate will allow the identification of impurities capable of hydrogen trapping and thereby preventing the formation of bubbles, that opens the way to controlling the solubility of hydrogen and to prevent negative impacts on the mechanical strength of materials.

2.2. INTERACTION OF HYDROGEN WITH CRYSTAL DEFECTS

To date, a large amount of information has been accumulated on the theoretical and experimental study of the interaction of hydrogen atoms and defects in the crystal structure. The most reliably established general regularities are as follows [60, 61]:

- In perfect crystal the energetically favorable positions for hydrogen atoms are octapores in fcc and tetrapores in bcc crystals. In a defective crystal, hydrogen shifts from the center of the O-pore to a distance of $\sim 0.4 \cdot 10^{-10}$m. The location of hydrogen can vary depending on its concentration, interaction with radiation defects, an increase of irradiation temperature, and so on.
- The self-interstitial atoms can be considered as possible traps for hydrogen.
- The binding energy of hydrogen with a mono vacancy in iron and nickel is about 0.4…0.5 eV. Vacancy clusters are stronger hydrogen traps having binding energy of 0.7…0.8 eV. The role of vacancies in increasing of hydrogen mobility and, conversely, the effect of hydrogen on mobility of vacancies is determined with insufficient accuracy.
- Hydrogen stabilizes primary defects and small clusters preventing their merging in TEM-visible defects at an early stage, and also impedes the diffusion of defects and, consequently, the enlargement of pores and loops in the late stage of irradiation.
- Hydrogen bubbles are usually observed in metals with low solubility and diffusivity of hydrogen.
- Hydrogen in micro bubbles can chemically interact with impurity atoms, for example, carbon, forming CH_4, that stimulates the formation of pores and stabilizes them.
- The interaction of hydrogen atoms with interstitial impurities is weak. Theoretical calculations have shown that the binding energy of a hydrogen atom with impurity interstitial atoms is small both for inert gases (0.01 and 0.17 eV for He and Ne) and for active elements (0.05…0.08 eV for C, N, O), i. e. the bond of the atom H to any impurity interstitial atom is realized not as a result of chemical interaction, but as a result of the appearance of stress fields created around the defect.
- Substitution impurities have a significant effect on the behavior of hydrogen in iron. This give the possibility of controlling hydrogen degradation by directional alloying of steels.
- Dislocations are attributed a dual role in the interaction with hydrogen – the role of traps and ways of accelerated hydrogen transport.

2.3. SCENARIOS FOR PREVENTING HYDROGEN DEGRADATION AND CONSERVATION OF MATERIAL RESOURCE

2.3.1. Hydrogen trapping

Capturing of hydrogen in areas of material where there are no critical microstructure defects can be used as one of the possible methods to resist the phenomenon of hydrogen degradation.

Reversible and Irreversible Traps. The term “*irreversible”* in the present context means that trapped hydrogen is not able to re-enter the lattice and contribute to diffusible hydrogen during the service conditions of the steel. This definition differs from specifying a particular trap energy that distinguishes reversible from irreversible traps [62] because such approach does not take into account a number of circumstances. For example, low temperature hydrogen release during thermal desorption represents weakly trapped hydrogen fraction while the strong (“irreversibly”) trapped hydrogen is evolved only at higher temperatures. However, in real thermal desorption experiments, the actual temperature at which significant quantities of hydrogen are de-trapped, depends also on the heating rate. The equilibrium between the trapped and dissolved hydrogen means that as the latter escapes, the trapped one will tend to de-trap for restoring equilibrium, a phenomenon confirmed directly using autoradiography [63].

As pointed out in [64] a trap with a binding energy of $100\ \mathrm{kJ \cdot mol^{-1}}$ is considered irreversible at ambient temperature but becomes reversible at a sufficiently high temperature.

Point defects of the crystal lattice. L. Darken and R. Smith [65] were the first to suggest that point defects of the crystal lattice can serve as traps for hydrogen atoms. The most convenient and practical method for controlling hydrogen trapping is the use of substitutional impurities. Transitional elements are promising candidates for this purpose.

The interaction of hydrogen with impurities in metals can arise for several reasons. The most significant of them are of an elastic and electronic nature. These include: a) the elastic distortion of the lattice, caused by dissolved impurity; b) the difference between the interactions of hydrogen with the atoms of the matrix and the impurity. The question of the nature of the electronic state of the hydrogen atom in iron remains controversial. There are two opposite points of view: the proton model (the electron of the H atom pass over to the free electronic levels of the matrix near the Fermi level, that leads to a positive charge of the H ion) and the anion model (the electrons of the matrix are captured by low-lying hydrogen levels, that leads to the emergence of a negatively charged H ion) [66].

An experimental evaluation of the interaction of 3*d*- and 4*d*-metals with hydrogen in iron on the basis of thermal desorption measurement [67], internal friction [68], Mossbauer spectroscopy, inelastic neutron scattering, and ion beams [69–71] has shown that many of them, in particular Ti [72, 73], and Y [74], bind H atoms. In the review [70] a large number of experimental values of hydrogen interaction energy with impurities in metals is given. In all cases, the values obtained in the experiment do not exceed 0.3 eV. However, it should be noted that all the mentioned experimental methods do not allow to reliably estimate the trapping energy of the hydrogen atom, since in all cases this value is determined not directly, but on the basis of models whose accuracy can be challenged [66].

The selection for impurities that provide a strong hydrogen trapping should be carried out in two directions: a strong variation of the density of states at the Fermi level, and a local change in the elastic properties or free volume within the matrix.

In [75] it is shown that the atoms of Y, Sc, Zr, Cd, Ti, Mg have the highest binding energy of hydrogen atoms.

Carbon atoms dissolved in the steel have an association with hydrogen [76], but they represent weak traps [77]; if the diffusible hydrogen in the lattice reaches a concentration below that expected in equilibrium with such a trap, then the hydrogen would be expected to re-enter solution.

It should be noted, that even weak traps reduce the ability of hydrogen to diffuse through the steel. Thus, water-quenched, martensitic 2.25Cr1Mo steel has an apparent hydrogen diffusivity at ambient temperature, as measured by permeation, to be $D_H = (0.21…0.31)\cdot10^{-10}$ m$^2\cdot$s^{-1}. After tempering at 640 °C to generate a variety of carbides, the diffusivity increases to $D_H = (0.29…0.47)\cdot10^{-10}$ m$^2\cdot$ s^{-1}, but the quantity of irreversibly trapped hydrogen increases by about an order of magnitude relative to the un-tempered state [77].

In [78] it was suggested two novel methods for the prevention of hydrogen embrittlement in iron: one involves the low-energy implantation of helium, which is usually an element harmful to metals, into iron, the other is inducing damage to the iron surface by ion irradiation. In general, irradiation with high-energy particles leads to metal brittleness. In the former method, the driving force for hydrogen embrittlement in iron is weakened, in the latter method; hydrogen diffusion in iron is prevented because of trapping of hydrogen atoms in the vacancies produced by the irradiation. As a result, hydrogen embrittlement in iron was suppressed by both methods.

The defects of dislocation type are often regarded by researchers as possible trapping sites of hydrogen isotopes in metals. In particular, Ono [80] for Fe 9Cr 2W ferritic alloy clearly demonstrated deep correlation between the TDS of deuterium gas and dislocation loop annihilation. According to [80], deuterium ions irradiated on the specimen were trapped at dislocation loops and affects their thermal stability.

In the case of austenitic steel (AISI 316) [81], the microstructure remains virtually unchanged throughout the temperature range where the gas desorption process is observed. The size growth of the dislocation defects begins at annealing temperatures of about 1000 K. At these temperatures, well-resolved dislocation loops were found. Their disappearing has been registered at ~ 1200 K. It was established that the correlation between the evolution of dislocation loops during annealing, which begins at 1000 K, and the temperature intervals of thermal desorption ending at 600 K, is completely absent.

It should be noted that according to [82, 83], the binding energy of hydrogen with dislocation-type defects in fcc metals is 0.05...0.15 eV, and therefore dislocations cannot have a significant effect on deuterium capture in stainless steels at room temperature of irradiation.

Using the technique of mechanical spectroscopy of hydrogenated samples of Ni-based alloy Inconel 718, the enthalpies of hydrogen migration, the bond of hydrogen atoms to dislocations, and the condensation temperature of hydrogen atmospheres on dislocations have been obtained. This allows to determine the temperature range of hydrogen embrittlement of a given alloy. It is shown that hydrogen reduces the activation stress of dislocation sources and increases the dislocation velocity. This means that despite the macroscopic brittleness of the hydrogenated samples, there is a localized softening induced by hydrogen in the vicinity of hydrogen atmospheres at dislocations, which completely agrees with the electronic concept of hydrogen-enhanced localized plasticity.

In austenitic steels at certain hydrogen concentrations an increase of the density of electron states at the Fermi level is observed, and, accordingly, an increase of the density of conduction electrons is expected. Hydrogen stimulated increase of the density of states at the Fermi level enhances the metallic nature of the interatomic interaction that should lead to a decreasing of the shear modulus. Additionally, hydrogen atoms are surrounded by atmospheres of conduction electrons and, if they accompany dislocations during their movement, this should manifest themselves in facilitating dislocation slip, reducing the starting stress of dislocation sources and increasing the number of dislocations in planar clusters. This should result in the early microcracks nucleation.

It was shown in [6] that doping with nickel leads to increasing of hydrogen migration, to weakening of the hydrogen-dislocation bond, and to decreasing of the condensation temperature. Silicon, manganese and chromium, in turn, slow the migration of hydrogen, enhance the bond of hydrogen atoms to dislocations, and promote hydrogen condensation on dislocations.

Voids into which hydrogen locates and combines to form the molecular variety would in general fall into the irreversible category because the molecular hydrogen would need to dissociate before it can re-enter the iron lattice.

Hydrogen traps are also grain boundaries, pores and many other structural defects [84].

The efficiency of traps

It has been suggested that there is a critical diffusible-hydrogen concentration H_C below which delayed fracture does not occur for a steel with the microstructure defined. If the amount of hydrogen that enters the steel from the environment is less than H_C, then delayed fracture is said not to occur in service [5].

Hydrogen traps in materials perform a dual function: first, they reduce the mobility of hydrogen, and in cases of a large amount of incoming hydrogen, they actually increase the uptake of hydrogen. If the trapped hydrogen is in local equilibrium with the lattice, and if the binding energy of hydrogen atom with trap is small, then such a trap can act as a source of diffusible hydrogen if the concentration in the matrix becomes depleted below the equilibrium value. In this case the traps will not inhibit the embrittlement of steel.

In order for traps to be effective, they must have a large enough binding energy so that the equilibrium concentration of diffusible hydrogen in the matrix is much smaller than required to cause embrittlement. The required trapping efficiency is provided, for example, by carbides and matrix-precipitate interfaces that have sufficiently high binding energies with hydrogen atoms and which can be formed by appropriate selection of the steel components and heat treatment.

So, at the moment, two strategies for reducing and preventing hydrogen embrittlement in steels have been developed. The first strategy is to reduce the mobility of hydrogen atoms in the steel, typically by hydrogen trapping, in order to make hydrogen harmless. The second strategy is to diminish the intake of hydrogen by applying coating that act as diffusion barriers to prevent the ingress of hydrogen.

2.3.2. Effect of initial state of material

The effect of the initial state of EP-450 ferritic-martensitic steel on blisters development during irradiation with a glow discharge hydrogen plasma (particle energy ≤ 1 keV) has been studied in [85]. A comparative study of the samples of four series was carried out.

Samples of the series 1 after cold rolling (c.r.) and stabilizing annealing consist of ferrite grains and grains with the products of decomposition of the high-temperature austenite – sorbit. The grain size is about 20…30 μm. Fine-dispersed carbides are distributed almost uniformly over the grain.

Samples of series 2 after the rolling at room temperature and subsequent annealing at 1323 K for 0.5 h have a structure consisting of ferritic grains with dimensions of 90…200 μm. In addition, multiple carbide precipitates are observed, both along the grain boundaries and inside the grains (sub-grain from the primary structure).

In the structure of samples of series 3, which were not subject to annealing after deformation, ferritic grains and grains with austenite decomposition products were observed. The grains of the metal are elongated in the rolling direction, their dimensions decrease in a direction perpendicular to rolling (compressed). The metal has a fibrous structure.

The microstructure of the series 4 samples after conventional heat treatment (CHT) [86] represents a duplex structure of tempered martensite (sorbit) and ferrite in a ratio of approximately 1:1. Relatively small (hundreds of nanometers) spherical $M_{23}C_6$ carbides are located both at grain boundaries and inside martensitic plates and rails, most often with a row distribution inside the crystalline of martensite. The martensitic structure contains nano-sized particles of the MX type carbonitrides of V, Nb, and Mo with dimensions ≤ 10 nm.

The investigation of the blister size distribution depending on the different initial states of the EP-450 steel, showed the formation of different degrees of blistering for the samples of the first three series. Blisters were not observed on the surface of the series 4 samples after CHT. Irradiation has shown that the samples are subjected only to the sputtering (Fig. 4) [85].

This is due to the formation of a ferrite structure with a low dislocation density and carbides along the grain boundaries through $\gamma\rightarrow\alpha$-transformation at low cooling rates in the upper temperature range during CHT. Ferritic grains have a significantly higher hardness compared to the conventional α-phase in low-carbon steel due to V, Mo, Nb, and Cr alloy doping (150…180 kg/mm^2).

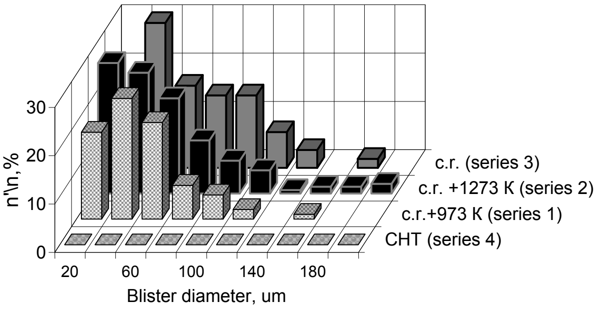


Fig. 4. Histograms of the distribution of blisters in terms of diameter: n' – number of blisters of a given diameter; n is the total number of blisters on the samples of the 1–4 series (normalized to 1 cm^2). The dose is $1\cdot10^{24}$ H_2^+/m^2, the temperature is 283 K

It was shown in [87] that in the Charpy impact sample martensite and ferrite specimen aged for 100 h, which was fractured at 213 K, the cracks were generated on large and continuous $M_{23}C_6$ carbides along the grain boundaries and propagated into ferrite even after aging. Based on the results of mechanical tests and analysis of phase microstructure, it was concluded that the improvement of the Charpy test results after aging for samples with martensite and ferrite is due to spheroidization and improvement of $M_{23}C_6$ carbides structure at the boundaries of ferrite grains, which makes it difficult to start the development of a crack.

The absence of crack nucleation and development of blisters after CHT is attributed to the modification of the microstructure of ferritic-martensitic steels under traditional heat treatment. Effect is provided by the joint action of sub-structural (grain and subgrain boundaries, high dislocation density), solid-solution and dispersion hardening ($M_{23}C_6$ carbides and MX carbonitrides), spheroidization and reduction the sizes of $M_{23}C_6$ carbides on grain boundaries [86].

Thus, the greatest blistering is observed in materials with a high degree of deformation without further annealing. Blister parameters depend on the phase component of ferritic-martensitic steels, their morphology and grain size. The presence of ferrite, coarse grains, cracks nuclei after deformation and the presence of inert gases are the main factors that enhance the accumulation of hydrogen, stimulating blistering.

2.3.3. The role of coatings as barriers for hydrogen permeation

The practical usefulness of the coating depends on the service conditions. If the coated regions are subjected to localized stresses or thermal fields then the coating may wear out or detach. Such coatings as alumina, TiC, TiN, TiO_2, BN, H_3PO_4 glass, Cr_2O_3, and WC, all are in principle formidable barriers to the permeation of hydrogen, although the actual performance depends on the structural integrity and defect structure of the coating [88].

It has been shown [89] in experiments on high-vacuum stainless steel systems, that 1 μm TiN-films reduce the hydrogen outgassing rate from the steel by five orders of magnitude. Films of Cr_2O_3 just 3 nm thick have been shown to present barriers to the diffusion of hydrogen; an iron-rich oxide of the Fe_2O_3 type on stainless steel that is deliberately oxidized can be even more effective as a barrier to passage of hydrogen than the pure chromium film. TiC of near stoichiometric composition has a hydrogen diffusivity many orders of magnitude smaller than that in austenite.

Reduction of hydrogen saturation of zirconium alloys using a modification of the surface due to complex ion-plasma treatment was observed in [90].

The method of nuclear reactions measured depths-concentration distribution of deuterium in the initial zirconium alloy and alloy coated with CrN, CrAl, and Al_2O_3 after saturation of the gas phase at a temperature of 600...900 K ($P_D = (2…9)\cdot 10^{-5}$ mm Hg, period = = 120 min) or by ion implantation. It was established that in the investigated range of temperatures and pressures coatings CrN, CrAl, and Al_2O_3 are the barrier and protect the zirconium from the interaction with the isotope of hydrogen – deuterium (Fig. 5) [90].

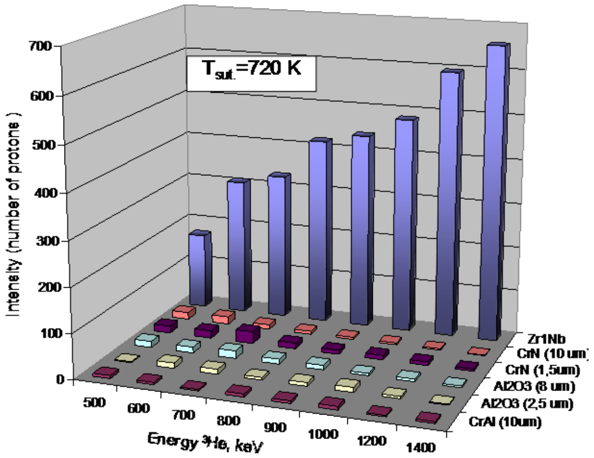


Fig. 5. Energy dependences of integral proton yields for Zr1%Nb samples with and without coatings after saturation with deuterium at a temperature of 720 K

It is established that when samples are saturated with deuterium from the gas phase, deuterium does not penetrate into the volume of coatings, but adsorb in their near-surface regions. At deuterium implantation in the CrN coating on the Zr1%Nb alloy, its fixation is observed within the ion range, unlike of it redistribution throughout the entire volume of uncoated alloy.

Most structural elements of tokamaks that contacting with plasma are multilayer structures, and the calculation of hydrogen accumulation and transport must take this into account. In addition, using of protective coatings is one of the possible ways to reduce the accumulation of hydrogen in materials contacting with plasma. For example, the tungsten coatings, α-aluminum deposition on Eurofer steel for reduction of hydrogen permeability through it, the coating of steel with erbium oxide, etc. are considered.

The interaction of plasma with the wall is a complex problem in the physics of fusion reactors. Interaction processes are important for the choice of wall material for a thermonuclear reactor, as well as for its correct operation, taking into account the constraints imposed by interaction with the wall. Active research in this area has cleared up a large number of issues related to the interaction of plasma with solids, however leave enough misunderstood problems. The state of research in this area is reflected in a large number of books and reviews. It is especially difficult to understand the phenomena associated with the mutual influence of processes occurring in the near-wall plasma and the processes of hydrogen isotopes recycling in the first wall.

There are the following three issues that play a key role in the interaction of the plasma with the first wall material:

1 – the lifetime of materials facing the plasma;

2 – dust formation;

3 – tritium accumulation of in the materials of the vacuum chamber.

The last two items determine the safe operation limits of the installation because there is always a danger of accidental contact of toxic (beryllium) and radioactive (due to the accumulation of tritium) materials with the environment. In addition, in case of accidental water leakage, active hydrogen release is possible, that in the case of air breakthrough is explosive per se. The presence of dust serving as a catalyst will exacerbate the consequences of such explosion. It is also clear that the amount of tritium accumulated in the chamber should be as minimal as possible in order to avoid environmental contamination and the evacuation of the local population due to its accidental release. Accordingly, for the international thermonuclear experimental reactor (ITER) the following “administrative” limits are established: 670 kg of dust and 700 g of tritium accumulated in the chamber, which ensure that safety-critical values will not be achieved even with allowance for measurement error [90, 92].

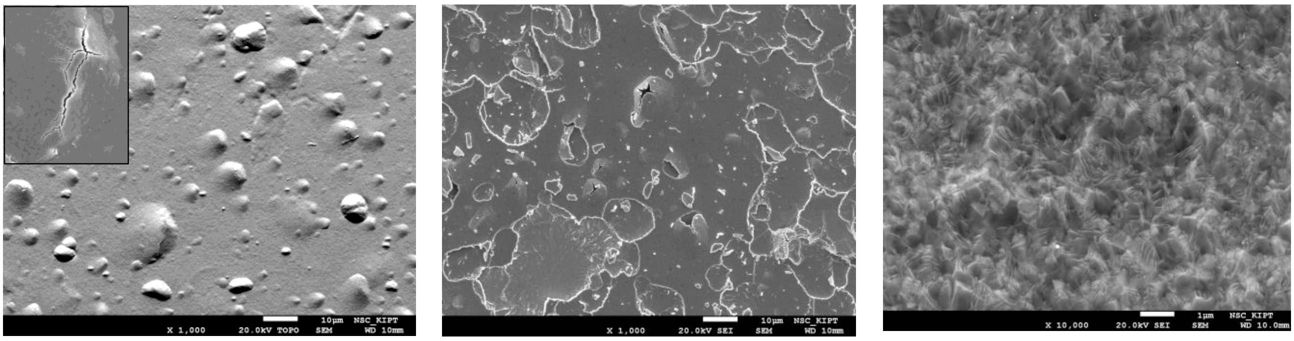
The surface topography of W and W+Ta coatings that are deposited by the cathodic arc evaporation and the argon ion sputtering and a comparison of changes of the surface microstructure under the influence of particles of low-energy hydrogen (deuterium) plasma (0.5 keV/H^+) and dose equal to $1\cdot 10^{24}$ ion/m^2 at 300 K were studied [93, 94].

It was found plasma-induced blistering on surface of W and W-Ta coatings deposited by argon ion sputtering and having a columnar structure. It was observed formation of blisters as dome and burst or delaminated structures. The W-Ta coating shows improved characteristics: smaller sizes and densities of blisters and a significantly lower thickness of the delaminated layer.

The average size of blisters is comparable for the tungsten foil and coating, but the density of blisters is more than four times less in the coating.

Within the W coating deposited by the cathodic arc evaporation the grains with dimensions in the μm range and the absence of a pronounced columnar structure have been observed. Irradiation of tungsten coatings produced by the cathodic arc evaporation did not lead to the formation of blisters. Only the process of physical sputtering is observed. Sputtering coefficients are $1.14 \cdot 10^{-2}$ at./ion for hydrogen exposure (рис. 6).

Thus, the evolution of surface structure and depth distribution profiles of hydrogen depend on the physical and chemical properties of the material and its initial structure.



a *b* *c*

Fig. 6. SEM images of W coating (a, c) and W+Ta (b) bombarded at 300 K with 1 keV D_2^+ *to* $1 \cdot 10^{24}$ D_2^+/m^2. *W (a) and W+Ta coatings (b) had a original columnar structure [95]*

Fig. 7 illustrates the key mechanisms that exist to improve the hydrogen resistance in steel. An abundance of coatings exist that have been demonstrated to reduce either the outgassing of hydrogen in vacuum systems, or serve as diffusion barriers to the ingress of hydrogen.

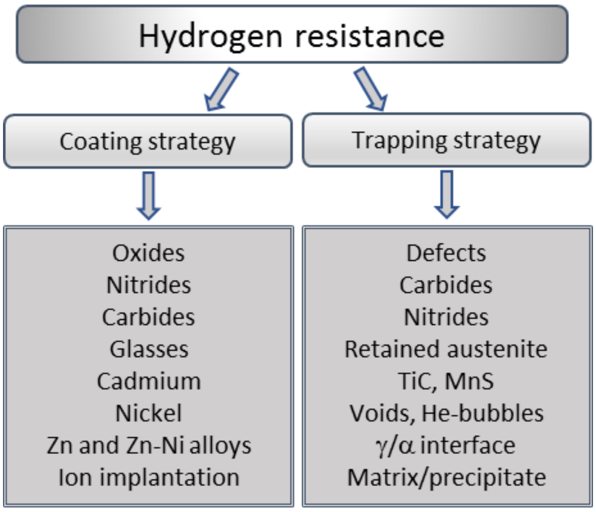


Fig. 7. Mechanisms available for the modification of steel for higher hydrogen resistance

However, the choice of coatings available decreases when the coating has to perform multiple functions, for example to resist abrasion and impact. The thickness and integrity of the coating will vary with the manufacturing process and has to be compatible with the service conditions of the protected component. The quality of the coating can depend on the chemical composition and structure of the substrate. Ion implantation can be used to favorably alter the surface of the steel.

Unfortunately, the most advanced coatings cannot prevent the accumulation of hydrogen in materials subjected to intense neutron irradiation, since in this case hydrogen is generated directly in the bulk of the material through transmutation reactions. In such a situation, in order to neutralize the harmful effect of hydrogen and increase the resistance of materials to hydrogen embrittlement, the concept of using hydrogen traps, which capable to reliably retain it the entire service lifetime in the whole operating temperature range of the nuclear facility, purchases the key importance.

CONCLUSION

Hydrogen embrittlement is manifested in different modes of material destruction depending on alloy composition and microstructure. There is no general mechanism for this type of degradation. Embrittlement is probably a conjunction of several elementary actions of hydrogen: surface adsorption, transport through the structure, trapping, etc. The effect of hydrogen in steels, classification of damage types, influence of different factors have been considered.

To produce materials that are resistant to hydrogen it is necessary to control diffusible hydrogen. This can be achieved by introducing strong benign traps in the material bulk or preventing the ingress of hydrogen by using special barrier coatings.

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Article received 31.08.2018

НАИБОЛЕЕ ВЕРОЯТНЫЕ МЕХАНИЗМЫ ДЕГРАДАЦИИ ХАРАКТЕРИСТИК МАТЕРИАЛОВ, ВЫЗВАННЫЕ НАКОПЛЕНИЕМ ВОДОРОДА, И ПРОГНОЗИРОВАНИЕ ВОЗМОЖНЫХ СЦЕНАРИЕВ СОХРАНЕНИЯ ИХ РЕСУРСА

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Рассматриваются результаты теоретических и экспериментальных исследований растворимости, диффузии и проницаемости водорода; характер связи водорода с дефектами; критические уровни накопления водорода, его распределение по объему и механизмы взаимодействия с материалом. Обсуждаются изменения структуры материала в присутствии водорода, а также влияние внешних термических и радиационных полей и продолжительности отжига на эти процессы. Проанализированы местоположение водорода в материале и возможные механизмы разрушения, вызванного водородом. Рассмотрены рекомендации по минимизации отрицательного влияния водорода и предотвращению снижения эксплуатационных характеристик конструкционных материалов.

НАЙБІЛЬШ ЙМОВІРНІ МЕХАНІЗМИ ДЕГРАДАЦІЇ ХАРАКТЕРИСТИК МАТЕРІАЛІВ, ВИКЛИКАНІ НАКОПИЧЕННЯМ ВОДНЮ, І ПРОГНОЗУВАННЯ МОЖЛИВИХ СЦЕНАРІЇВ ЗБЕРЕЖЕННЯ ЇХ РЕСУРСУ

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Розглядаються результати теоретичних і експериментальних досліджень розчинності, дифузії і проникності водню; характер зв'язку водню з дефектами; критичні рівні накопичення водню, його розподіл в об`ємі та механізми взаємодії з матеріалом. Обговорюються зміни структури матеріалу в присутності водню, а також вплив зовнішніх термічних і радіаційних полів і тривалості відпалу на ці процеси. Проаналізовано локалізацію водню в матеріалі та можливі механізми руйнування, викликаного воднем. Розглянуто рекомендації щодо мінімізації негативного впливу водню і запобігання зниженню експлуатаційних характеристик конструкційних матеріалів.