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Review

The synergistic action and interplay of hydrogen embrittlement mechanisms in steels and iron: Localized plasticity and decohesion

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A B S T R A C T

Component failures due to the hydrogen embrittlement (HE) were observed in different industrial systems, including high-pressure hydrogen storage tanks, aircraft components, high-strength alloy components, and high-strength steel fasteners. The contemporary approach in studying the effects of hydrogen on the mechanical properties of steels and iron at different scales is based on the implementation of various multiscale (macro, micro-meso, and nano-atomic) modeling approaches and the applications of advanced experimental methods. A large number of contemporary studies confirmed the multiple effects and activity of different HE mechanisms in steels and iron. The coexistence and synergistic activity – concurrent action and effects in a cooperative manner of different HE mechanisms, including the hydrogen-enhanced localized plasticity (HELP) and the hydrogen-enhanced decohesion (HEDE), were recently detected and confirmed through computations-simulations, as well as experimentally in different grades of steel. However, the critical evaluation and quantification of synergy between the HELP and HEDE mechanisms, enhanced plasticity and decohesion, hydrogen-deformation/dislocation interactions and their simultaneous effect on the mechanical properties (hardening and softening), still do not exist. In this review paper, the multifaceted nature of the synergistic interplay of HE mechanisms is covered through extensive literature overview regarding the chronological development of ideas related to the HELP + HEDE concept and HELP mediated HEDE model. The particular emphasis is given to the proposal of the novel and unified HELP + HEDE model based on the specific microstructural mapping of the dominant HE mechanisms with implications on the fracture process and resulting hydrogen-assisted fracture modes. Most of up-to-date experimental and modeling approaches, current trends and future challenges in the investigation of the synergistic interplay of HE mechanisms in different grades of steel, including the most advanced, and iron, are also included and critically discussed.

1. Introduction, hydrogen-deformation interactions

The multifaceted nature of hydrogen embrittlement (HE) and both electrochemical and non-electrochemical control of different hydrogen damage in metals and alloys are broadly covered in the reference world literature [1–10] and within the recent review papers [11–21]. These references discussed the HE phenomenon from different points of view, depending on numerous influencing factors which can be generally grouped as environmental, mechanical, and materials influences [22–27]. Still, there is a strong

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Nomenclature

A	austenite
AFM	atomic force microscopy
AIDE	adsorption-induced dislocation emission mechanism (model)
B	bainite
bcc	body-centered cubic structure
C	cleavage fracture
Ce	cementite
C_H	hydrogen concentration value
$C_{H(0)}$ and $C_{H(Critical)}$	characteristic values of hydrogen concentrations
CTOD-R	crack tip opening displacement
CZM	cohesive zone modeling
DBT	ductile to brittle fracture transition
DFT	density functional theory
D	ductile
DP	dual-phase steel
E	experimental research (approach)
EC	electrochemical charging
EI	electrochemical in-situ (during operation) charging
ESEM	environmental scanning electron microscope
ETEM	environmental transmission electron microscopy
F	ferrite
FG	fatigue crack growth test
F/P	ferrite/pearlite
FE	finite element simulation
FIB	focused-ion beam microscope and machining
FPB	four-point bending test
FPZ	fracture process zone
FT	fracture toughness test
G	gaseous charging
GB	grain boundary
GBs	grain boundaries
H	hydrogen
HAC	hydrogen-assisted cracking
HE	hydrogen embrittlement
HEAC	hydrogen environment assisted cracking
HEDE	hydrogen-enhanced decohesion mechanism (model)
HELP	hydrogen-enhanced local plasticity mechanism (model)
HESIV	hydrogen-enhanced strain-induced vacancy mechanism (model)
HID	hydrogen-induced decohesion
I	immersion charging
IG	intergranular fracture
IHAC	internal hydrogen assisted cracking
IPB	in-situ bending tests
IT	charpy impact test
KCV_I	crack initiation component of impact strength
$KCV_{TOT.}$	impact strength
KCV_P	crack propagation component of impact strength
M	modeling research (approach)
Ma	martensite
MC	Monte Carlo simulation
MD	molecular dynamics simulation
MVC	microvoid coalescence fracture
N.UTS	ultimate tensile strength measured for notched specimens
P	pearlite
PAGB	prior austenite grain boundary
PdM	predictive maintenance model
PRHIC	plasticity related hydrogen induced cracking
QC	quasi-cleavage fracture
S	simulation approach
SEM	scanning electron microscopy
SiM	structural integrity model
SSRT	slow strain rate testing
T	tensile test
TDS	thermal desorption spectroscopy
TEM	transmission electron microscopy
TeS	tearing and shearing fracture
TG	transgranular fracture
TPP	thermal power plant
TRIP	transformation induced plasticity steel
TS	tensile strength
UTS	ultimate tensile strength
wppm	weight parts per million
YS	yield strength
α	bcc (body-centered cubic structure)

disagreement and polarization of opinions among researchers on the inherent nature of the viable and active HE mechanisms and general HE models [8,9,17,23,24,26,28]. Particularly, their coexistence or a synergistic interplay in steels and iron is still not completely resolved [13,16,29–36]. Activation of the particular HE mechanism and its effects on the degradation of mechanical properties in different grades of steel, iron and structural materials depends on [2,10,13,22,23,27,29,36,37]:

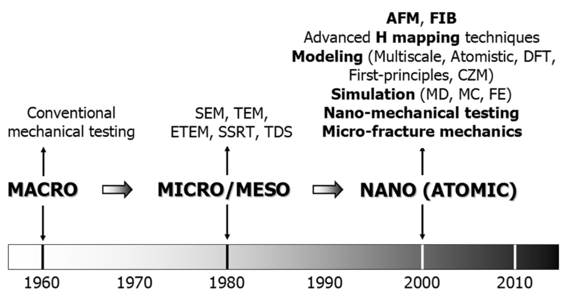

Fig. 1. Historical overview of approaches to HE study.

(1) material microstructure - defect and impurity density…);
(2) source of hydrogen, hydrogen charging, uptake, diffusion, the interaction between hydrogen and different traps and trapping conditions;
(3) hydrogen content and its global and local distribution and concentration in the material; and
(4) global and local factors of environmental and mechanical loading conditions at different scales (macro, micro-meso, and nano-atomistic).

The historical overview of approaches to the HE study is presented in Fig. 1 [10,13]. A shift in the scale of study can be observed from a macro approach, through a micro-meso approach, up to the nano and atomistic approach used in most contemporary research. The most contemporary research (nano and atomistic approach) discusses the hydrogen-materials interaction, effects of hydrogen on the mechanical properties, and the multiple HE mechanisms in metallic materials. It is mainly based on the usage of advanced methods of microscopy, computational modeling/simulation, hydrogen mapping and other experiments, Fig. 1. A particularly important aspect is the synergistic interplay of HE mechanisms, including prerequisites and conditions for activations and dominance of a specific HE mechanism. Various multidisciplinary and multiscale (macro, micro-meso, and nano-atomistic) approaches [25,38–41] were successfully used for quantification, kinetic analysis, and multi-scale characterization of hydrogen effects and hydrogen-deformation interactions in materials.

Different advanced experimental techniques and computational modeling and simulations were successfully used in numerous HE studies, including:

i. scanning electron microscopy (SEM) [9,10,13,17];
ii. transmission electron microscopy (TEM) [9,17];
iii. environmental transmission electron microscopy (ETEM) [15,23,26,33,40,42,43];
iv. atomic force microscopy (AFM) [42–45];
v. focused-ion beam (FIB) microscope and machining [42,43,46,47];
vi. thermal desorption spectroscopy (TDS) analysis [48–54];
vii. atomistic/quantum/meso/macro mechanical models: density functional theory (DFT) modeling and first-principles modeling [11,12,32,55–60], cohesive zone modeling (CZM) [19,32,61–66], molecular dynamics (MD) simulation and Monte Carlo (MC) simulation, [58,67–71], finite element (FE) simulation of polycrystalline materials [41,51,55,70,72,73]; and
viii. advanced macro-, micro- and nano-mechanical testing, like slow strain rate testing (SSRT) [74–77], nano indentation testing [20,22,29,40,78], including micro-fracture mechanics models [32,55,63,79–89].

A large amount of research confirmed material degradation under load caused by hydrogen, which is manifested in a change of materials macromechanical properties. Typically affected mechanical properties are: (i) tensile strength (TS); (ii) yield strength (YS); (iii) hardness; (iv) fracture toughness; (v) impact strength; (vi) elongation to failure; (vii) fatigue life; and (viii) crack propagation rate [1–10,13,17,21–23]. Also, numerous comprehensive reviews about the hydrogen effects on the mechanical properties in different types of steel have been published. These reviews include: (i) low carbon steels [13,36,90]; (ii) stainless steels [91–94]; (iii) advanced high-strength steels [14,52]; (iv) medium-strength steels [53,95–97]; (v) low carbon pipeline steels [98,99]; (vi) ferritic/martensitic steel [100]; (vii) high manganese nitrogen strengthened, austenitic stainless steel [101]; (viii) high-strength dual-phase (DP) steels [18,102]; (ix) transformation induced plasticity (TRIP) steels [52,103]; and (xi) low carbon martensitic steels [104].

In numerous published studies conclusions are often very controversial and show that previously mentioned tensile properties (TS, YS) but also ductility [14,52,99,100,105–111] and hardness [13,36,53,92,93,112–114], could be significantly influenced by hydrogen, depending on numerous factors [94]. The typical factors are: (i) source of hydrogen (gaseous/electrochemical charging); (ii) hydrogen global and local content in the material; and (iii) hydrogen concentration gradient in the specimen. Often, depending on the hydrogen content, hydrogen-dislocation interactions and local trapping/distribution processes in different types of steels, the effects of hydrogen are opposite. The tensile properties/ductility: strengthening/softening [94,115] and hardness: hardening/softening [116] were observed. Sometimes, hydrogen effects on the change of the macromechanical properties in some steels are negligible [10]. Murakami et al. [94] pointed out that hydrogen can have two opposite effects on the dislocation mobility in steels: pinning (or dragging) and enhancement of mobility. The hydrogen-induced hardening is the result of possible hydrogen-dislocation interactions. As a result of supersaturation with hydrogen around dislocations, the decrease of its movements appears and hardness increases (a dislocation pinning effect), [93,94,117,118], or due to increased slip planarity [58,119].

Perhaps, the greatest challenge in the analysis of HE mechanisms is the occurrence of enhanced plasticity of material and enhanced dislocation activity and mobility due to hydrogen-dislocation interactions. The localized plasticity effects were detected at the micro- and nano-level, even in the case of a macroscopically brittle fracture. Beachem [128] originally proposed the definition of so-called hydrogen-enhanced localized plasticity (HELP) mechanism of HE responsible for the hydrogen-related fracture. It is based on the hydrogen-enhanced dislocation mobility and dislocation slip behavior around a crack tip [7,23,30], which leads to material softening [115,116,121] and YS decrease [90,95,98]. However, the opposite and often contradictory conclusions about the effects of hydrogen on the enhancement of dislocation mobility were detected and published in the literature. The previously mentioned enhancement of dislocations mobility and the opposite findings of dislocations pinning due to the hydrogen were detected within a large number of both atomistic simulations [58,69,121–125] and experimental [40,91,126] studies.

Katzarov et al. [122] and Taketomi et al. [127] confirmed by modeling approach that different hydrogen-dislocation interactions could exist simultaneously. Both hydrogen enhancement of dislocations mobility and pinning (reduction of dislocations mobility) were detected, depending on the boundary of environmental/mechanical conditions. Other important factors influencing hydrogen-dislocation interactions are hydrogen concentration, applied stress/strain-rate and temperature. The precise knowledge about hydrogen interactions with dislocations in a wide range of hydrogen concentration and other loading/environmental variables is crucially important for defining the governing HE mechanisms and their synergistic interplay. A prerequisite for the second HE mechanism activation, so-called hydrogen-enhanced decohesion (HEDE) mechanism, is the local reaching of a sufficiently high "critical hydrogen concentration" in a metal [10,13,35,36,112]. The HEDE mechanism is based on the hypothesis that interstitial hydrogen lowers the cohesive strength by dilatation of the atomic lattice [128–131]. This hydrogen concentration-dependent HE mechanism is also known as a hydrogen-induced decohesion (HID).

The activation of a particular HE mechanism and extent of its influence on the fracture process are primarily caused by the successive processes at the micro- and nano- levels in the fracture process zone (FPZ) ahead of the crack tip. These successive processes also include the transport of hydrogen by dislocations and the local reaching of the critical hydrogen concentration [13,29]. Depending on the local concentration of hydrogen, the kinetics of these processes will vary. The transient hydrogen diffusion and accumulation near the crack tip depends on many factors, including all active HE mechanisms, and appears to be a critical factor in understanding of HE mechanisms for different grades of steels [10,13,36].

In their recent modeling studies of active HE mechanisms in body-centered cubic (bcc) iron Matsumoto et al. [67] and Solanki at al. [70] indicated that the multiple HE mechanisms can occur and be active in the same material. The included multiple HE models are different hydrogen-enhanced plasticity models, like HELP, hydrogen-enhanced strain-induced vacancy (HESIV) [8,28], adsorption-induced dislocation emission (AIDE) [9,17], and Defactant concept [22,78,132], together with HEDE. The degree of activity and dominance of a particular HE mechanism and a mechanism map for the prediction of HE according to different applied approaches to simulations depend on numerous parameters. The major parameters are: (i) boundary conditions; (ii) concentration of hydrogen in its proximity to the crack tip; (iii) lattice defects; (iv) initial conditions of the materials; (v) loading rate; (vi) hydrogen chemical potential; (vii) initial crack size; (vii) effective hydrogen diffusion activation enthalpy; (vii) temperature; and (ix) cleavage stress intensity [58,67,69,70]. However, an overview, critical evaluation, and quantification of the synergy between different proposed HE mechanisms in steels and iron still do not exist. Particularly, the combined effects of "the plasticity-driven" HE mechanisms like HELP, HESIV, AIDE and a decohesion-based HEDE mechanism on the macro and micromechanical properties are missing.

The typical approach used in studies about the effects of hydrogen on the mechanical properties and ductility of different grades of steels is mainly based on the laboratory saturation of samples with some hydrogen content. In that case, hydrogen is commonly uniformly distributed throughout the whole volume of the sample. The usual next step is a comparison of the obtained test results for hydrogen charged specimens with the results for uncharged specimens [13]. However, the steel components of industrial plants are very unevenly saturated with hydrogen during their actual operation. Their operation is characterized by a high heterogeneity of hydrogen distribution and the presence of local microstructural areas with a locally very high hydrogen concentration. This is due to the effects of numerous factors that influence the nonuniform distribution of hydrogen content in different industrial plant components. The major influencing factors are: (i) the source of environmental hydrogen, local kinetic of hydrogen-induced corrosion and corrosive potential of fluid in contact with the metal; (ii) nonhomogeneous distribution of thermal load and stresses in a particular component; (iii) protective oxide layers state and deposits on metal surfaces; and (iv) upsets in the plant operation [13,22,36,133–136]. Therefore, degradation of the mechanical properties of industrial components from the presence of dissolved hydrogen usually result in a decrease of fracture resistance and subcritical cracking [36]. Long-term in-situ material degradation can be significantly different from the type and degree of degradation of the mechanical properties due to HE obtained by a laboratory test. Such tests are typically done on the samples uniformly saturated with hydrogen made of the same material.

In our previous papers [10,13,36,112], we pointed out that a critical experiment or computational model that would allow realistic simulation of the kinetics of development of a certain type of hydrogen damage, including multiple active HE mechanisms, is difficult to conduct. Such experiment should be in strict compliance with the actual degradation kinetics and HE mechanisms in the components of industrial plants exposed to hydrogen during service. For example, recent nanoindentation and TDS study by Zhao et al. [116] confirmed the pronounced effect of the hydrogen charging methods (electrochemical versus gaseous) on different mechanical properties of low carbon steel. They highlighted that the electrochemical hydrogen charging conditions produced hardening. In such case, the typically higher hydrogen content exists and non-uniform distribution - concentration gradient through the specimen thickness only due to the weakly trapped hydrogen. Contrary, softening was observed after gaseous hydrogen charging (lower hydrogen content and uniform distribution). The same authors also concluded that the hardening/softening behavior is content-dependent, i.e. relatively higher hydrogen content causes hardening, while lower content induces softening [116]. This indicates possible changes in the HE mechanism and the coexistence of different mechanisms in a certain range of hydrogen concentration in the material [13,36]. The preconditions for the coexistence also strongly depend on the experimental conditions. Therefore, experimental conditions should precisely simulate the in-situ hydrogenation conditions of industrial components. Accordingly, Barnoush [137] pointed out the need to perform critical experiments for the mechanistic study of HE. Such critical experiments need to be done on the fully characterized samples (composition, microstructure, impurity concentration, defect density, etc.). Also, the precise definition of experimental conditions is very important (hydrogen charging method/condition, mechanical loading, global/local hydrogen content - distribution in a material, temperature, pressure, etc.). Therefore, investigations of hydrogen effects on the mechanical properties of materials at the micro- and nano-scale, integrated with in-situ hydrogen charging, are important for better understaning of the HE phenomena. Such approach should provide better understanding of the influence of hydrogen-dislocation interactions, stacking faults and hydrogen diffusion/trapping processes on the kinetics of multiple and synergistically active HE micro-mechanisms [138].

As indicated by Djukic et al. [10,13], for decades scientists have debated different HE models and still have not advanced the state of true understanding of the HE phenomena in a manner that will provide practical models for industrial application. Implementation of the methods for evaluation, control and prevention of hydrogen-assisted mechanical degradation processes and HE in metals requires that the variables relevant to the application be incorporated into the basic concept that defines all necessary successive steps [13]. This represents a necessary prerequisite for the development of the future practically-applicable industrial and predictive model, Fig. 2. Such model should provide the critical evaluation and quantification of the synergy between the HE mechanisms and their simultaneous effect on the macromechanical properties [10,13,36,112]. The proposal for the global 5-step approach in preventing the hydrogen-assisted mechanical degradation processes and HE in steels and iron for the practical industrial application consists of the following steps, Fig. 2:

(1) phenomenology analysis of hydrogen-related degradation (multiscale modeling and simulation of HE phenomena);
(2) investigations of hydrogen sources and entry into metal/component;
(3) establishment of a structural integrity (SiM) model;
(4) predictive maintenance (PdM) model which should provide the basis for the future;
(5) reliable and accurate HE damage prediction of different industrial components.

The aim of this critical review is to present all the most up-to-date experimental and computational modeling approaches and published results related to the synergistic interplay of HE mechanisms in steels and iron. This paper provides a critical overview of

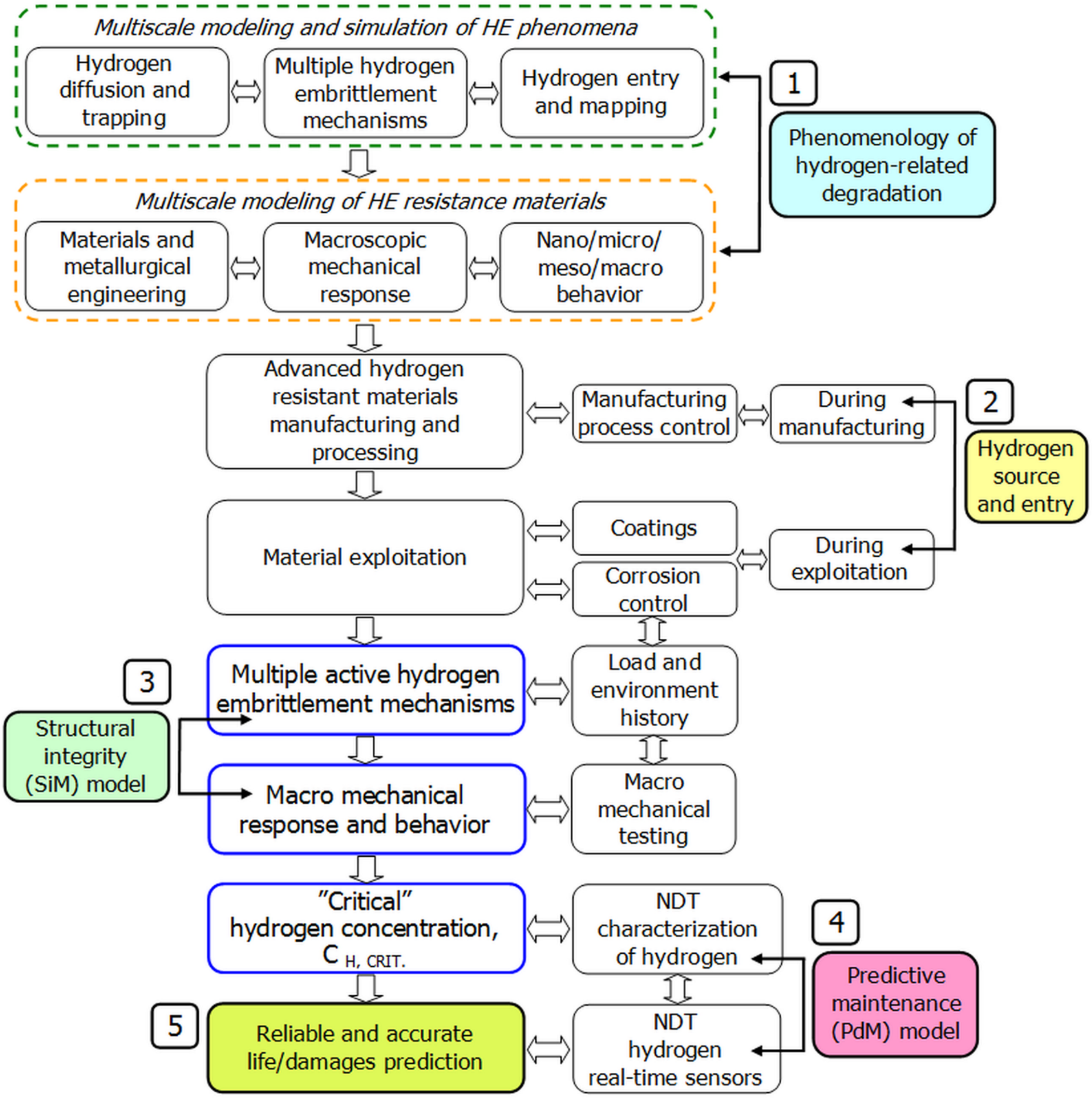

Fig. 2. A contemporary approach in evaluation, control and prediction of hydrogen-assisted mechanical degradation processes in steels and iron.

Table 1
HE models, the coexistence of models and hydrogen-deformation interactions in steels.

HE model	Operating HE mechanisms	Hydrogen-deformation interactions and processes	Source
1. Hydrogen-enhance plasticity	(a) HELP[a] (b) AIDE[b] (c) HESIV[c] (d) Defactant concept[d]	– Enhanced dislocation mobility and velocity, material softening, promotion of planar slip and localization of a plastic flow (HELP) – Nucleation and dislocation emission from the crack tip due to H adsorption (AIDE) – Enhanced of the density and clustering of vacancies (HESIV) – Lower energy barrier for the generation of dislocation loops (Defactant concept) – Enhanced local plasticity (HELP, AIDE, and HESIV)	[a][15,23,24] [b][9,17] [c][8,28] [d][22,78,132]
2. Hydrogen-enhanced decohesion	(e) HEDE[e]	– A weakening of the interatomic bonds – Local reduce of the cohesive strength – Ductile to brittle fracture transition at the – critical H concentration – Enhanced brittleness and hardening	[e][81,129–131]
3. Hydrogen- enhance plasticity mediated decohesion	(f) HELP mediated HEDE[f]	– Dislocation motion and locally increased dislocation density and H concentration – Plasticity (HELP) mediated "brittle" (intergranular and quasi-cleavage) fracture – Plasticity (HELP) mediated decohesion	[f][7,15,23,24]
4. The synergistic action of hydrogen- enhance plasticity and decohesion	(g) HELP + HEDE[g] (h) AIDE + (HELP/HEDE)[h]	– Simultaneous action of hydrogen-enhanced plasticity and decohesion (HELP + HEDE) – Ductile to brittle fracture transition at the critical H concentration (HELP → HEDE) – The dominance of one of the mechanisms (HELP or HEDE) depending on the H concentration and the material-stress state-environmental factors – AIDE initiated HELP or HEDE	[g][10,13,34,36] [h][9,17]
5. Hydrogen-induced phase transfor-mation	(i) HIPT[i]	– Hydrogen-induced martensitic transformation[i] – Hydride formation (not applicable in steels)	[i][139,140]

HELP - hydrogen-enhanced local plasticity; AIDE - adsorption-induced dislocation emission; HEDE - hydrogen-enhanced decohesion; HESIV - hydrogen-enhanced strain-induced vacancy; HIPT - hydrogen-induced phase transformation.

different hydrogen-enhanced plasticity HE models together with the decohesion model, and also their synergistic effects in steels and iron. The actual material degradation kinetics due to material hydrogenation during service and active HE mechanisms depend primarily on the local stress state and hydrogen concentration at the degradation site, i.e. at the crack tip. Therefore, the knowledge and detailed study about: (i) hydrogen evolution reactions; (ii) hydrogen entry kinetics; (iii) permeation rate through metal (iv); transport kinetics; (v) lattice diffusion/dislocation transport; and (vi) redistribution and trapping processes at key microstructural features play a fundamental role in the HE phenomenon understanding [8–10,25,27,37]. This paper is mainly focused on the hydrogen redistribution and trapping processes at different microstructural features, as a result of the simultaneous action of HE mechanisms (Section 3). However, the detailed analysis of the mechanisms and transport stages of hydrogen to the microstructural sites, where degradation and HE in steels and iron occurs, certainly deserves another review paper. Special emphasis in this paper is placed on the hydrogen-assisted mechanical degradation processes due to the synergistic action of just one of the proposed plasticity mediated HE models, i.e. the HELP model, together with the HEDE model. This also includes the crucial transition from ductile to brittle dominated fracture mode resulting from the concurrent - synergistic and/or due to the competing action of hydrogen-enhanced plasticity and hydrogen-enhanced decohesion. Also, a general critical review is given of the significance and possible synergistic action of the HELP model, as well as other proposed plasticity-mediated HE models (AIDE [9,17], Defactant concept [22,78,132], HESIV [8,28] and other [2,3,8,10]) are also briefly highlighted. However, the complete analysis of all other proposed plasticity-mediated HE models and universal validity/applicability of the HELP model only in steels and iron is generally beyond the scope of this critical review. These ongoing and justified controversies about different proposed plasticity-mediated HE models (questioning of the HELP model validity and universality) are already discussed elsewhere. For example, in comprehensive reviews about other proposed plasticity-mediated HE models more details were already pointed out by Lynch (AIDE model [9,17]) and by other authors (Defactant concept [22,78,132] and HESIV model [8,28]). These often opposed approaches will provide even a broader picture of other proposed plasticity-mediated HE models and further experimental evidence pieces of synergy between various HE models (plasticity-mediated HE models + HEDE).

This paper provides recent results in the next Section (2) in an overview-form of critical discussion about the synergistic action and interplay of HE mechanisms in steels and iron, models and experiments. This includes (i) HELP + HEDE concept (Section 2.1); (ii) HELP mediated HEDE model (Section 2.2); and (iii) synergy of hydrogen-enhanced plasticity and decohesion - HELP + HEDE model (Section 2.3) [13,36]. The HELP + HEDE model section consists of two subsections: modeling approach (Section 2.3.1) and experimental confirmations (Section 2.3.2) in different types of steels. The Section 2.3.2 presents a background for the analysis of the synergistic interplay of the HE mechanisms in ferritic-pearlitic low carbon steel, grade 20 (St.20, equivalent to AISI 1020) according to the HELP + HEDE model proposed by Djukic et al. [13,36].

The last Section (3) provides a summary of published results and findings of the synergy of hydrogen-enhanced plasticity and decohesion in steels and iron. It also proposes a unified model for the synergistic interplay of HE mechanisms (HELP + HEDE and HELP mediated HEDE) in steels (HELP + HEDE model). The unified HELP + HEDE model represents the proposal for the specific microstructural features/hydrogen trapping sites together with the corresponding fracture modes induced due to an activity of a particular HE mechanism (plasticity-mediated HE models and/or HEDE). The synergistic action and interplay of HE mechanisms in total four different grades of steels were also analyzed and summarized with respect to the applied hydrogen charging methods and mechanical testing methods. Lastly, it outlines the major conclusions and recommendations for the future necessary research related to the synergistic action and interplay of HE mechanisms in steels and iron.

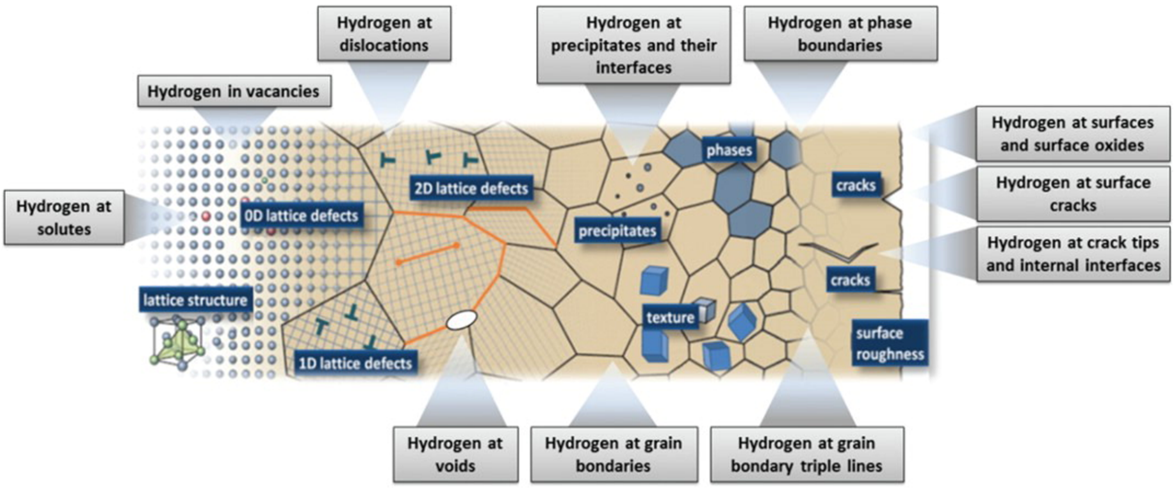

Fig. 3. Different hydrogen trapping sites in steels [25]. “Reprinted from Mater Sci Technol, 33/13, Koyama M, Rohwerder M, Tasan CC, Bashir A, Akiyama E, Takai K, et al., Recent progress in microstructural hydrogen mapping in steels: quantification, kinetic analysis, and multi-scale characterisation, 1481–1496, Copyright, The Authors (2017), Under a creative commons license CC BY-NC-ND 4.0”.

2. The synergistic action and interplay of HE mechanisms in steels and iron: Models and experiments - critical discussion

The results obtained in comprehensive HE studies were usually attributed to the independent activity of one of the proposed plasticity-mediated HE models (HELP, HESIV, AIDE, and Defactant concept), or a decohesion based (HEDE) model [1–17,22–24,26]. Different HE studies mostly highlighted the dominance of a particular HE mechanism only. By modeling approaches and experiments, the cooperative action of multiple HE mechanisms has been also recently confirmed. A summary of results for five major HE models and their coexistence in steels is presented in Table 1. Also, a brief description of various hydrogen-deformation interactions for a particular HE mechanism, or due to their simultaneous action is given.

Hydrogen transport by dislocations or driven by the stress, hydrogen trapping processes, and processes at the crack tip FPZ are crucial for the activation of a particular HE mechanism, or multiple active mechanisms, Table 1. Turnbull [141] indicated that validation and future consensus about different proposed HE models at a crack-tip FPZ is essential to better understanding of hydrogen-deformation interactions. This is a necessary step in providing future preventive and predictive HE models for steels and iron [10,13,36,112]. Furthermore, Dadfarnia et al. [15,26] noted that hydrogen mapping/identification at key microstructural features and measurements of the hydrogen concentration are needed to provide breakthroughs in the HE phenomena understanding. They

Table 2
Selected studies on the synergistic interplay of HE mechanisms in steels and iron.

HE mechanisms - model	Material	Approach[a]	Authors	Year/source
HELP + HEDE	Iron	M	Gerberich et al.	1991/[81]
	Different metallic materials	Concept	Katz et al.	2001/[29]
			Delafosse et al.	2001/[142]
			Birnbaum	2003/[16]
	Low alloy steel	M	Ahn et al.	2007/[89]
	Different metallic materials	Concept	Gerberich et al.	2009/[30]
			Robertson et al.	2009/[31]
	Low carbon pipeline steel	E	Wang	2009/[143]
HELP + HEDE model	Martensitic steel	E + M	Novak et al.	2010/[32]
HELP + HEDE	Steels	M	Falkenberg et al.	2010/[144]
HELP mediated HEDE model	Low carbon pipeline steels	E	Martin et al.	2011/[42,43]
	Martensitic steel	E	Nagao et al.	2012/[33] 2018/[145]
HELP + HEDE	Austenitic Fe-Ni-Co alloy and high-strength steels	M	Dadfarnia et al.	2012/[83] 2017/[84]
	High-strength low alloy steel	M	Brocks et al.	2012/[146]
AIDE + (HELP/HEDE)	Different metallic materials	E	Lynch	2012/[9,17]
H-triggered ductile to brittle transition	Iron and other metalls	M	Song and Curtin	2013/[58] 2013/[69]
HELP + HEDE	Fe-Ni dissimilar weld	M	Barrera et al.	2013/[147] 2014/[148] 2016/[149]
HELP/AIDE + HEDE	Iron	M	Taketomi et al.	2013/[150] 2017/[127]
HELP + HEDE model	Low carbon heat resistant steel	E	Djukic et al.	2014/[35] 2015/[36] 2016/[13]
HEDE + HELP model	Dual-phase steel	E	Koyama et al.	2014/[34]
HELP mediated HEDE	Ultra-high strength steels	E	Rehrl et al.	2014/[151]
Multiple HE mechanisms	Iron	M	Matsumoto et al.	2014/[67]
HELP + HEDE	Austenitic stainless steel	E	Wang et al.	2014/[152]
HELP mediated HEDE	Martensitic steel	E	Sasaki et al.	2015/[153]
	Iron	M	Wang et al.	2016/[154]
HELP + HEDE	High-strength steel	M	Yu et al.	2016/[62]
	Martensitic stainless steel	E	Kumar et al.	2017/[74]
		E	Fan et al.	2017/[75]
	Ultra-high strength steel	E	Hu et al.	2017/[76]
	Low carbon heat resistant steel	E	Dmytrakh et al.	2017/[155] 2018/[156]
	High-strength steel	E	Li et al.	2018/[157]
HELP + HEDE model	Austenitic stainless steel	E	Li et al.	2018/[158]
HELP + HEDE	CrMoV steel	E	Song et al.	2018/[159]
	High-strength steel	E + M	Wang et al.	2018/[160]
	Martensitic stainless steel	E + M	Hüter et al.	2018/[161]
	Steels	M	Weikamp et al.	2018/[162]
HELP + HESIV + HEDE	Iron	E	Ogawa et al.	2018/[163]
HELP mediated HEDE	Low carbon pipeline steel	E	Wang et al.	2018/[164]
HELP + HEDE	CrMo and CrMoV steels	E	Peral et al.	2019/[165]
	Iron	M	Wan et al.	2019/[166]

[a] E - experimental research; M - modeling research.

also stressed the importance of a critical evaluation and quantification of the synergistic interplay between the hydrogen-enhanced plasticity and the decohesion effects of the HE. Koyama et al. [25] concluded that (i) microstructure-specific hydrogen mapping; (ii) diffusion/redistribution within a wide range of trapping sites; and (iii) analysis of its non-uniform distribution, are the most important aspects for providing a critical evaluation of all proposed HE models in steels, Fig. 3. Such analysis can provide the necessary background for determining the conditions under which various HE models are viable, predominant, individually active or simultaneously active in steels [13,36], Fig. 3 (see also Fig. 2 and Table 1).

Huge complexities of the hydrogen-steel interactions and hydrogen-deformation interactions have been extensively investigated with broad implications on the fracture process and resulting hydrogen-assisted fracture features and modes [1–10,12–18,23,36]. The activity of each of the proposed HE mechanisms-models (HELP, AIDE, HESIV, Defactant concept, and HEDE - see Table 1) individually could lead to the ductile, mixed-mode or brittle fracture features resulting from hydrogen. Typical observed hydrogen-assisted fracture modes are different, ranging from the completely ductile microvoid coalescence (MVC), quasi-cleavage (QC), i.e. cleavage-like, cleavage (C), to macroscopic brittle transgranular (TG) and intergranular (IG).

Table 2 chronologically summarizes selected studies published in the last 30 years about the coexistence and synergistic activity - concurrent action and effect in a cooperative manner of different plasticity mediated HE models (HELP and others) and the HEDE model in steels and iron. Table 2 includes studies, starting from the general HELP + HEDE concept proposed at the end of the 20th century [16,29–31,145] up to the most recent results for synergy between the hydrogen-enhanced plasticity and decohesion.

There are many different HELP + HEDE models that were proposed based on the simulations - modeling (M), experiments (E), or through the application of both approaches (E + M). Generally, all published results (Table 2) which indicate the cooperative action of multiple HE mechanisms in steels and iron could be broadly classified into two categories:

(1) HELP mediated HEDE model, which is based on the assumption that the governing mechanism of HE in steels and other materials is always the HELP mechanism. In this case, an initial activity of HELP is always a prerequisite for the eventual activation of the decohesion-based (HEDE) mechanism at specific microstructural locations [7,15,23,24,26,33,42,43,145,153,156];
(2) HELP + HEDE model, which indicates the synergistic effect of both mechanisms (HELP + HEDE) [13,32,34–36,62,74–76,81,83,84,143,144,146–148,150–162,164,165]. According to this model, some or multiple of the plasticity-mediated HE mechanisms (HELP, AIDE or HESIV) together with the decohesion-based (HEDE) mechanism are responsible for HE [9,17,67,127,149,162]. In this case, one of them dominates under specific conditions [13,31,32,35,36,67,127,149,154,155,162].

The distinctions outlined in this paper between the HELP mediated HEDE model and the different proposed HELP + HEDE models are very important. The HELP mediated HEDE model is based on the experimental results which indicate that the assumed activity and dominance of the HELP [7,15,23,26,31,89,119,128] is a necessary precondition for the activation of decohesion (HEDE) in steels and iron. The results are mostly interpreted within the framework of the proposed mechanism of dislocation (HELP)-mediated decohesion [33,42,43,145,154,164]. In this case, authors presume that there is a universal quality to the HELP mechanism in materials such as nickel, iron and ferritic, martensitic and austenitic steels [23,24]. Moreover, the same group of authors suggest that the HELP mechanism is actually the governing plasticity-mediated HE mechanism. They further suggested that its activity is a necessary prerequisite for eventual HEDE activation in most of the metallic materials. However, some authors, Lynch [9,17], Song and Curtin [58,69], and others [8,22,28,78,132] questioned the necessity of the HELP mechanism activity and its assumed dominance. Apart from the proposed HELP model of HE, other plasticity-mediated HE models (AIDE, HESIV, Defactant concept, and others) were proposed and listed in Table 1 and discussed elsewhere [8,9,17,22,28,78,132]. An important open question is whether it is necessary to always invoke additional dislocation nucleation or enhanced plasticity - dislocation mobility due to HELP during the interpretation of different hydrogen-deformation interactions. As mentioned in introduction, such analysis is beyond the scope of this paper.

On the other hand, most HELP + HEDE models based on the experimental results [13,32,36,74–76,142,155,158] and different modeling approaches [62,81,127,142,147–150,160–162] have revealed that, actually, the synergistic effects of different HE mechanisms are responsible for HE in steels and iron (see Table 2). In such cases, the simultaneous and often concurrent or opposite effects of both different plasticity-mediated models and the decohesion model (HELP + HEDE or other plasticity-mediated mechanisms [9,17] + HEDE) are independently or mutually responsible for HE. The models indicate that the degree of activity and the dominance of a particular HE mechanism (hydrogen-enhanced plasticity-based or hydrogen-enhanced decohesion-based, see Tables 1 and 2) depend on numerous factors. They are: (i) steel microstructure [13,27,34–37,39,163]; (ii) source of hydrogen (gasous/electrohemical) and charging condition [116,143,167]; (iii) hydrogen local distribution/trapping processes [13,34–37,39,67,163]; (iv) local hydrogen concentration - critical hydrogen concentration [13,35,36,67,112,127,143,150,155,156]; (v) hydrogen-dislocation interactions (dislocation nucleation and dislocation mobility) [30,40,47,58,69,93,94,117,118,138]; and (vi) applied stress rate conditions [36,67,127,150,163,166].

Moreover, despite the fact that there is experimental HELP evidence (in-situ ETEM observations) about the hydrogen-enhanced dislocations motion [7,15,23,33,42,43,89,128,145,154,164], there are also opposite findings. Recent advanced in-situ hydrogen charging experiments, modeling studies and the results of atomistic calculations clearly indicate contrary findings. The hydrogen-enhanced dislocation activity at a crack-tip can also lead to the other, quite different and opposite phenomena. This includes: (i) high stresses and accumulation of hydrogen [3,5,36,81]; (ii) interactions between vacancies and hydrogen [8,28,124,126,168,169]; (iii) enhanced dislocation nucleation [40,47,138]; (iv) suppression of dislocation emission from the crack tip [40,58,69]; and (v) hindered dislocation mobility - pinning effects [40,47,58,69,115,124,127,132,138,150,170–174]. Consequently, due to the plasticity reduction at crack tip, the activation of HEDE mechanism [13,36,80,81,175–177] can appear independently. This process can provoke a change in the dominant HE mechanism, from HELP to HEDE [36]. Also, activation of other HE mechanisms in steels and iron is possible, which is not in accordance with the HELP [9,17].

More details are presented in the following three Sections (2.1–2.3) with a critical discussion about the synergistic action and interplay of HE mechanisms in steels and iron. The following subsections include a critical overview of the general HELP + HEDE concept (2.1), HELP mediated HEDE model (2.2) and models based on the synergistic action of hydrogen-enhanced plasticity and decohesion, HELP + HEDE models (2.3).

2.1. HELP + HEDE concept

In line with the decohesion model of HE (HEDE) [128–131], the so-called “brittleness - based” model, proposed in the mid-20th century, contemporary research attributes great importance to hydrogen-enhanced localization of plasticity, see Tables 1 and 2 [7,128]. Gerberich et al. [80,81] and Gangloff [2,3,5,178] published different overviews of recent advances in the study of HEDE based models. These models provide a background for calculations of the crack growth based on the semi-quantitative predictions of the macroscopic value of the threshold stress. They further indicated the necessity for both plasticity and brittleness during the internal hydrogen assisted cracking (IHAC) or hydrogen environment assisted cracking (HEAC) of structural alloys [2,3]. Recently, Robertson et al. [23] and Martin et al. [24] have summarized the current state of the art in HE understanding, mainly based on the dominance of only a “plasticity - based” (HELP) model. This model was originally proposed in 1971 by Beachem [120] and further formulated and explained as the HELP mechanism of HE by Birnbaum and Sofronis in 1994 [128], or recently in 2001 as the HELP mediated HEDE model [33].

Even without hydrogen in steels and iron, the role of plasticity and dislocations activity during brittle and semi-brittle fracture processes is critical [179]. Gerberich et al. [30,81] demonstrated that dislocations emanating from the crack tip significantly enhance local stresses in the FPZ. This process can also provoke significant hydrogen accumulation in the vicinity of the tip of a crack that leads to the activation of HEDE - decohesion mechanism. Due to the hydrogen-reduced cohesive strength of atoms (HEDE), fracture initiation is the result of the crack tip-opening stresses which become locally higher than the cohesive strength [180,181]. On the other hand, the presence of hydrogen at the crack tip could also provoke local plastic deformations at a micro- and nano-level. The facilitated local plastic deformation is due to dislocations nucleation and enhanced mobility in accordance with the HELP mechanism [128].

Having in mind the exponential dependence on hydrogen concentration with hydrostatic stresses at the crack tip, the hydrogen localization in the FPZ [182] plays a central role in the HELP + HEDE concept for the hydrogen-assisted cracking. Also, the possible effects of hydrogen-enhanced transport by dislocations (HELP) and hydrogen diffusion to the crack tip should not be excluded from the analysis. These stepwise processes lead to further local hydrogen accumulation, which could simultaneously induce the interface decohesion (HEDE), depending on the crack tip stresses and the rate of hydrogen diffusion to the crack tip. The HELP + HEDE concept was proposed by different authors at the end of the 20th and beginning of the 21st century [16,29–31,142]. The concept includes simultaneous effects of both plasticity and brittleness during the HE. In 2009 Robertson et al. [31] reported that it is more feasible that several HE mechanisms operate simultaneously in metals, one dominating under specific conditions. In addition, it is also possible that only one HE mechanism (HELP or others) initially dominates, but then the other HE mechanism (HEDE) can become dominant due to the conditions changes [36]. Katz et al. [29] noted that different internal and external factors involved during hydrogen transport and hydrogen-deformation interactions in materials could influence stepwise processes responsible for the activation of a particular HE mechanism. Responsible stepwise processes are (i) hydrogen entry; (ii) hydrogen diffusion and trapping; and (iii) possible local stress/strain relaxation or intensification. Depending on the local stepwise processes involved during hydrogen-deformation interactions, different hydrogen-dislocation and hydrogen-fracture plane interactions were detected. These commonly opposing interactions could be successfully interpreted within the framework of the HELP + HEDE concept [13,36,112]. The hydrogen transport/local accumulation kinetics could be very different, depending on the internal (material, microstructure, etc.) and external (hydrogen source, type of loading, etc.) factors. Important considerations in further development of the HELP + HEDE concept were pointed out in 2009 by Gerberich et al. [30]. They further interpreted various stages of hydrogen-dislocation interactions, including effects on the nucleation of dislocations, the local density of dislocations and the enhancement of dislocations velocity. Moreover, they highlighted the possible two-stage hydrogen-deformation process, which consists of Stage I: Incipient hydrogen-enhanced plasticity (HELP) and Stage II: Possible combined action of both HELP and HEDE mechanisms. Stage 2 is affected by the later stage of hydrogen-enhanced plasticity (HELP) interactions with: (i) the crack process and multiple fracture modes and features (MVC, C, QC or IG); (ii) hydrogen transport by dislocations; and (iii) possible reaching of a locally very high hydrogen concentration (HEDE). Gerberich et al. [30] further stressed that both micro and meso/macro aspects of HE, in general, are always dependent on plasticity. The micro aspect includes the hydrogen-enhanced dislocation nucleation and the slip localization process (shear instabilities) due to high local stresses and high strain rates at singularities like the crack tip. Finally, they emphasized that the meso/macro aspect is primarily related to the hydrogen-enhanced dislocation velocity at smaller stresses in a large volume of material [30].

Wang [183] reported that the crack tip emitting dislocations, in the case of low mobility of dislocations, may behave in a fully brittle manner. If the motion of dislocations is impeded by hydrogen, then the shielding effects are reduced. Based on the proposed thermodynamic-kinetic model for the change in cohesion induced by hydrogen segregation, Wang further indicates that the decohesion process (HEDE) may cause the ductile to brittle fracture transition. The decohesion process can occur even in the presence of a large amount of plastic deformation, which appeared in the crack tip FPZ. In that case, the degree of the hydrogen-induced reduction in cohesion depends strongly on hydrogen mobility [183]. These observations further pointed to the great importance and interconnectedness between different hydrogen-deformation interactions and hydrogen-enhanced decohesion (HEDE) process. The

HELP + HEDE concept introduces the importance of hydrogen-enhanced mobility/localized plasticity (HELP) as the possible previous process involved in reaching the conditions for HEDE activation. The kinetics of a transient elastoplastic hydrogen diffusion can be enhanced by movements of dislocations carrying hydrogen. This could further induce hydrogen accumulation near the crack tip according to different proposed plasticity-mediated HE models, including HELP too. The opposite hydrogen-dislocation interaction, i.e. hydrogen-impeded localized plasticity due to the hydrogen-impeded mobility of dislocations, could also lead to the HEDE initiation. In that case, the HEDE can be treated as an independent HE process [36] and dominant upon reaching the local critical hydrogen concentration at the crack tip FPZ. Both of these cases are incorporated and analyzed within the proposed HELP + HEDE model that follows in Section 2.3. However, the hydrogen-assisted degradation of a crack propagation resistance by assisting the microscopic processes that constitute crack tip advance, including different possible fracture modes, remains still not fully resolved [13]. It also became evident, based on numerous published and often controversial results (see Tables 1 and 2), that any viable HE model should necessarily include all of the detected preconditions and processes at the micro- and nano-levels at the crack tip FPZ, including:

(1) stress-strain field and localization processes at the crack tip (FPZ);
(2) dislocation-hydrogen interactions: dislocation nucleation - generation and emission [9,17]/shielding [32,80,167,178,184];
(3) enhanced/impeded dislocation mobility, i.e. both detected effects: hydrogen enhanced localized plasticity (HELP) [7,15,23,26,31,89,119,128] and/or hydrogen-impeded localized plasticity [40,47,58,69,115,124,127,138,150,170–174];
(4) hydrogen-enhanced defects, their formation and emission (vacancies, dislocations, micro- and nano-cavities) [8,9,17,22,28,78,132,176,177]; and
(5) locally high hydrogen accumulation and decohesion (HEDE) processes [2,3,13,36,68,80,129–131].

2.2. HELP mediated HEDE model

The micro-meso approaches in the studies of fracture surfaces of the hydrogen-saturated samples introduced the use of an environmental TEM (ETEM). The ETEM usage provides a condition for in-situ deformation experiments in real time. These approaches have provided a better revealing of the effect of hydrogen on dislocation dynamics (hydrogen-dislocation interactions) [128,137]. The results indicated that the introduction of hydrogen gas during in-situ ETEM deformation experiments induced dislocations motion and enhanced their mobility [185] and slip localization [186] in 310 s stainless steel and iron [187]. The observation represents the basis for the proposition of the HELP mechanism of HE. Robertson [167] reported in 2001, based on the results by Tabata et al. [187], that the activity of dislocation is involved in both nucleation and propagation stages of a macroscopically brittle IG crack in iron. He revealed that the crack only follows the contour of the grain boundary, but actually does not cause the failure of the grain boundary, Fig. 4.

The HE phenomena at a grain boundary in steels and effects on the crack nucleation, crack growth and plastic deformation mechanisms are strictly related to different but interrelated processes. The processes include: (i) interaction between the dislocation and the grain boundary including the slip transfer of dislocations across the grain boundary [188]; (ii) grain boundary sliding, migration and twinning [189,190]; and (iii) ability for crack-tip dislocation emission, which leads to the localized plasticity, crack blunting and prevention of a completely cleavage-like separation [191]. Different mechanisms highlight the importance of plastic deformation associated with hydrogen during the ductile to brittle fracture transition from the HELP-mediated ductile fracture to the macroscopically and seemingly completely brittle TG and IG fractures. They are based on the hydrogen-enhanced dislocation activity and different hydrogen-dislocations interactions, as proposed by Robertson [167], Gavrilyuk et al. [192], Astafurova et al. [193] and others. One of the early research studies that provided a sound basis for some later formulation of the hydrogen-enhanced-plasticity-mediated decohesion model (HELP mediated HEDE model) is the paper by Novak et al. [32], Fig. 5. This paper on a statistical micromechanical model of hydrogen-induced IG fracture in steels was published in 2010 and also listed in Table 2, together with other

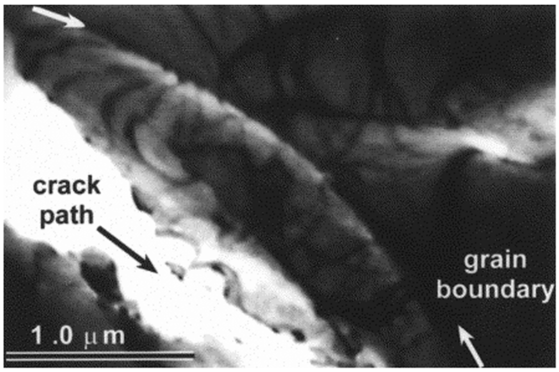

Fig. 4. IG failure in iron due to hydrogen. The IG crack propagates in the vicinity and only follows the contour of the grain boundary [167]. "Reprinted from Eng. Fract. Mech., 68/6, Robertson IM, The effect of hydrogen on dislocation dynamics, 671–692, Copyright (2001), with permission from Elsevier".

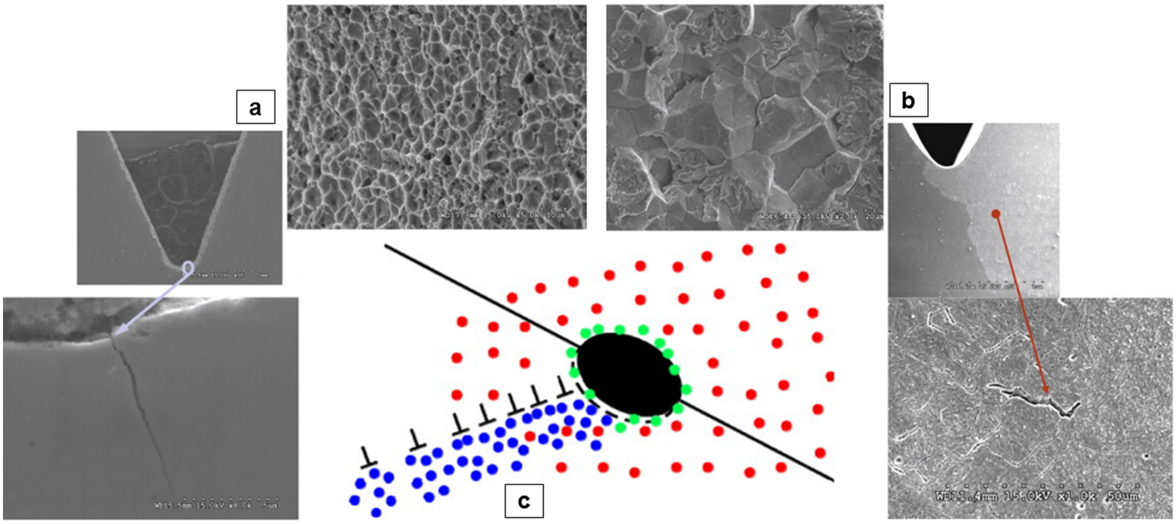

Fig. 5. "Dislocation pile-up induced decohesion" in steels: (a) SEM micrograph - strain-controlled ductile fracture associated with MCV initiating at the notch in a non-charged sample; (b) SEM micrograph - stress-controlled brittle fracture associated with IG cracking initiating ahead of the notch in a 138 MPa hydrogen-charged sample; (c) Mechanistic steps in the generation of IG fracture in the presence of hydrogen and "dislocation pile-up induced decohesion" activity at a carbide/matrix interface (hydrogen atoms are denoted by colored circles: blue for hydrogen carried by the dislocations, green for hydrogen trapped at the carbide, red for hydrogen at normal interstitial lattice sites) [32]. "Reprinted and adapted from J. Mech. Phys. Solids, 58/2, Novak P, Yuan R, Somerday BP, Sofronis P, Ritchie RO, A statistical, physical-based, micro-mechanical model of hydrogen-induced intergranular fracture in steel, 206–226, Copyright (2010), with permission from Elsevier" (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

HELP mediated HEDE model papers. They proposed a new HE model in martensitic steel previously exposed to gaseous hydrogen charging. The model is based on the change from the strain-controlled purely ductile fracture by MVC, initiated at the notch tip in a non-charged sample (Fig. 5a) to the completely brittle stress-controlled IG fracture ahead of the notch tip in a charged sample, Fig. 5b [32].

These findings were interpreted as the synergistic interplay of the HELP and HEDE mechanisms. According to the proposed "dislocation pile-up induced decohesion" model, activation of the HEDE at the carbide-matrix interface and a brittle IG fracture has occurred after the impingement on the carbide-matrix interface of high-density dislocations in pile-ups [32]. The model is based on

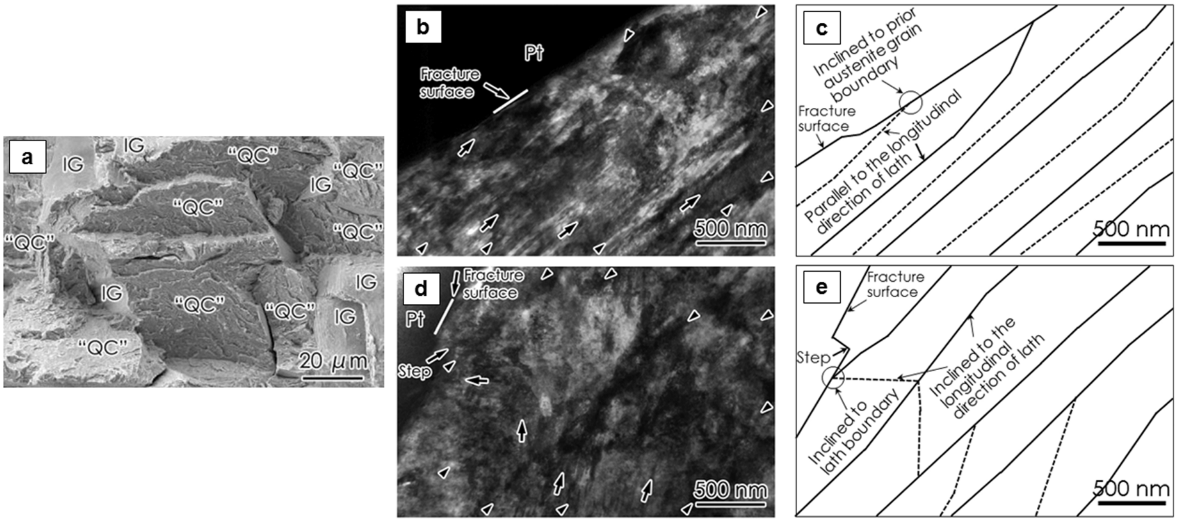

Fig. 6. HELP mediated HEDE model in steels: (a) SEM micrograph of the fracture surface of the specimen: "flat" IG and "QC" features; (b, c) TEM micrographs of the microstructure immediately beneath the hydrogen-induced IG fracture surface; (d, e) TEM micrographs of the microstructure immediately beneath the hydrogen-induced "QC" fracture surface (Arrows and arrowheads in (b, d) indicate slip bands and lath boundaries, respectively; tracings in (c, e) include slip bands (- - -) and lath boundaries (–)) [196]. "Reprinted from Procedia Mater. Sci., 3, Nagao A, Smith CD, Dadfarnia M, Sofronis P, Robertson IM, Interpretation of hydrogen-induced fracture surface morphologies for lath martensitic steel, 1700–1705, Copyright, The Authors (2014), Open access funded by European Structural Integrity Society under a creative commons license CC BY-NC-ND 4.0".

the previous HELP mechanism activity. Accordingly, hydrogen facilitates dislocation movements and provoked high-densities dislocation pile-up, Fig. 5c [185]. As a consequence, hydrogen transported by dislocations increases hydrogen concentration at the carbide and other dislocation barriers, and hence provoked HEDE activation.

Numerous modern experiments also used the FIB microscope and machining [194]. They revealed the microstructure that has evolved beneath different types of the macroscopically ductile and brittle fracture modes (MVC, QC, C, and IG) [23,24]. These experiments have provided more insights about different fracture pathways found on the hydrogen-induced fracture surfaces in different metallic materials, including iron [154,195], low carbon pipeline steels [42,43,164] and lath martensitic steels [33,145]. The most recent fatigue crack propagation study in α-iron after gaseous hydrogen charging [173] and molecular dynamics calculations of hydrogen effects on the dislocation-grain boundary (GB) interactions [188] provides additional insights. These authors observed that the brittle hydrogen-assisted fracture processes and transition in fracture modes from MVC to TG, QC, and IG are always followed by micro-plasticity behavior (plastic strain localization). Such observations seem to be in agreement with the hydrogen-enhanced-plasticity-mediated decohesion model (HELP mediated HEDE model) [154,195]. Beneath the “QC” and IG fracture surfaces of lath martensitic steel specimens, Fig. 6a, an increased dislocation density was detected, Fig. 6b–e [196]. Specimens were fractured using a four-point bend test after hydrogen charging in a high-pressure gaseous hydrogen environment (138 MPa) at elevated temperature (250 °C) for 21 days [196]. The interpretation of this finding was linked to increased activity of plasticity-mediated processes (HELP mechanism activity) [33,42,43,196]. Nagao et al. [33] assumed that TEM micrographs revealed the previous activities of the HELP mechanism detected in the microstructure immediately beneath the IG and “QC” fractures. The results of the HELP mechanism activity is the refinement in the dislocation cell structure and extensive plasticity in the form of intense slip bands [33,42,43,196]. The slip bands are in the “IG” fracture case approximately parallel to the longitudinal direction of laths, Fig. 6b and c, while the intersection between the slip bands and the interface is inclined to the prior austenite grain boundary. In the case of “QC” fracture, slip bands are inclined to the longitudinal direction of laths and the intersection is inclined with respect to the lath boundaries, Fig. 6d and e [196]. However, Lynch [197] has questioned such experimental TEM observations of dislocation structures beneath transgranular cleavage-like fracture surfaces [43] and the overall conclusion about the activity of only HELP mechanism. He further pointed out that the relative importance of AIDE, HEDE and HELP is likely to depend on the fracture mode [9,17] and that the TEM observations make it impossible to distinguish between the AIDE and HELP mechanisms and their relative contributions [197].

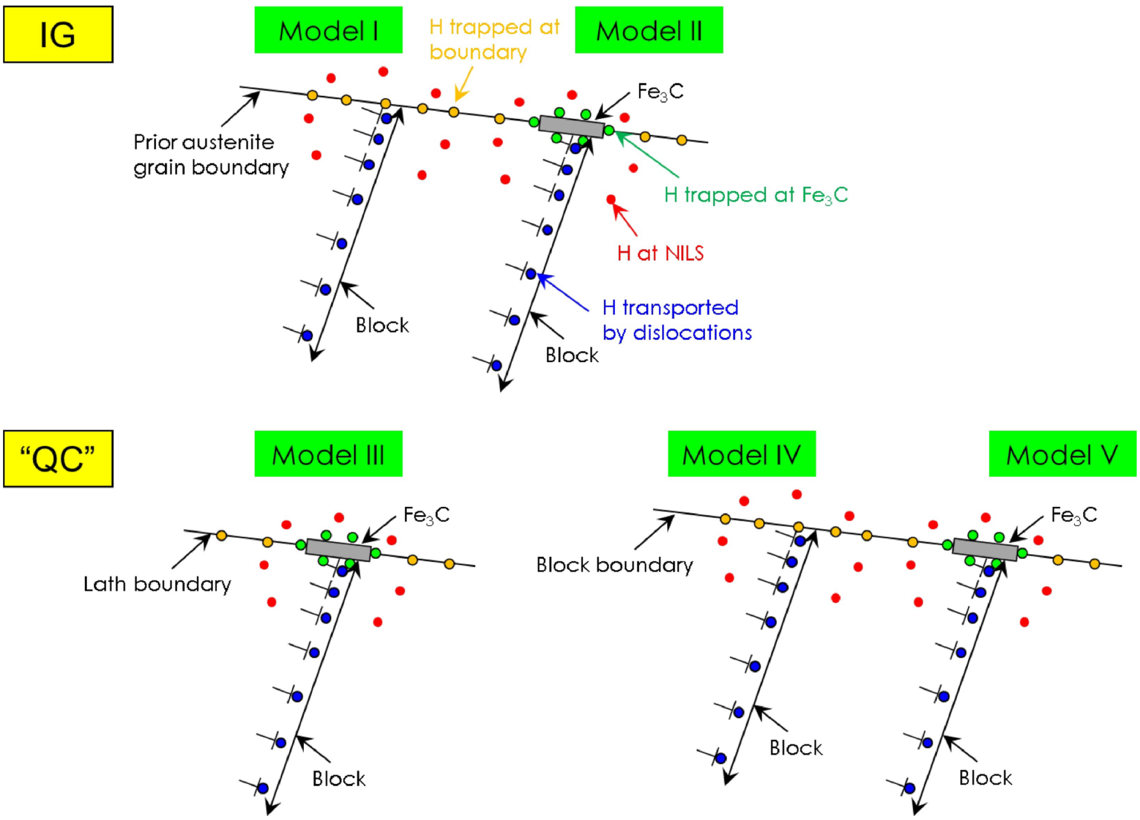

Fig. 7. HELP mediated HEDE model in steels. The previous activity of hydrogen-enhanced localized plasticity (HELP) is responsible for the activation of a decohesion (HEDE) mechanism and the generation of hydrogen-induced IG and “QC” fracture features in a lath martensitic steel [145]. “Reprinted from J. Mech. Phys. Solids, 112, Nagao A, Dadfarnia M, Somerday BP, Sofronis P, Ritchie RO, Hydrogen-enhanced-plasticity mediated decohesion for hydrogen-induced intergranular and ”quasi-cleavage“ fracture of lath martensitic steels, 403–430, Copyright (2018), with permission from Elsevier”.

The HELP mediated HEDE model highlights the significance of localized plasticity, while the previous activity of the HELP mechanism is critical for reaching the condition for activation of the decohesion - HEDE mechanism. Then the HEDE mechanism activates at grain boundaries, different phase boundaries and carbide-matrix interfaces. As a consequence, QC and IG fracture modes are observed in steels [145] and iron [154,195]. Sasaki et al. [153] have indicated that also Mn segregation and MnS inclusions promote hydrogen-assisted cracking (HAC) in tempered martensitic steel due to the HELP mediated HEDE. Rehrl et al. [151] provided a similar interpretation of the causes, based on the HELP mediated HEDE model, for observed hydrogen-induced "QC" fracture surfaces. The fracture surfaces were obtained after the low strain rate tensile testing of electrochemically hydrogen-charged specimens made of four different ultra-high strength grade sheets of steel. According to the HELP mediated HEDE model, Fig. 7 (see also Tables 1 and 2), the previous activity of the HELP mechanism brings the required stress through slip banding against the high-angle boundaries, which is a prerequisite for the HEDE mechanism activation [145].

Nagao et al. [145] assumed that the HEDE mechanism activation is assisted by the HELP mechanism due to additional hydrogen deposited and trapped at different microstructural locations. Such typical hydrogen traps in a lath martensitic steel are: (i) block boundaries in lath martensite; (ii) martensitic lath boundaries carbides; (iii) carbide - lath martensite interfaces ("QC" fracture case) or prior austenite grain boundaries (PAGB); and (iv) carbide - PAGB interfaces (IG fracture case), Fig. 7 [145].

Alvaro et al. [198] indicated that the hydrogen transport stages to the sites, where degradation occurs, are of the utmost importance for understanding the multiple HE phenomenon in steels and iron. The hydrogen transport kinetics and diffusion mechanisms, apart from all HE mechanisms such as HELP or HEDE, also determine the incubation period and the local critical hydrogen concentration build-up before fracture [198]. This is a prerequisite for the HEDE activation locally within the crack tip FPZ [13,36,81,96,129–131], regardless of the previous HELP mechanism activity and its possible synergistic effects (HELP + HEDE) [34–36]. The hydrogen softening effect and the HELP mechanism have been recently investigated by Barrera et al. [149] using notched tensile plates and the coupled mechanical-diffusion analysis. Their findings based on the simulations indicate that hydrogen-induced softening does not lead to localization of strain and a macroscopic brittle response. They concluded that in order to explain macroscopic embrittlement, softening processes due to the HELP mechanism activity must be combined with the HEDE mechanism [149].

Recently, Li et al. [199] have investigated hydrogen effects on the fracture toughness of a low carbon high-strength pipeline steel. They found that an increased dislocation density, dislocation pile-ups and plasticity-mediated processes due to the HELP mechanism near the crack tip beneath the "QC" fracture surface are missing. Therefore, they concluded that the movement of the dislocations near the crack tip was actually highly restricted in hydrogen charged specimens. These observations are inconsistent with the proposed HELP mediated HEDE model and underline that the HEDE effects, without the necessary previous activity of the HELP mechanisms, are more pronounced in this case [36]. Likewise, Barnoush et al. [40] investigated hydrogen-assisted cracking in the Fe-Al intermetallic alloy. They used the in-situ hydrogen charging method, notched micro-cantilever specimens and bending (small scale) tests together with the environmental scanning electron microscope (ESEM). They similarly concluded that when a high amount of hydrogen is present ahead of the notch tip, the synergistic action of the detected processes results in the accelerated crack growth and drop in the fracture toughness values. The processes detected were as follows: (i) hydrogen-enhanced dislocation nucleation; (ii) hydrogen-provoked suppression of dislocations emission from the crack tip (hydrogen-reduced plastic zone size at the crack tip); and (iii) hydrogen-reduced dislocation mobility [40]. The hydrogen-provoked suppression of dislocations emission from the crack tip was also experimentally detected. This phenomenon is experimentally detected in the case of a twinning-induced plasticity steel (TWIP) [138] and Fe-Al-Cr alloy [47], and in α-iron by modeling approach [58,69]. Also, the hydrogen-reduced dislocation mobility was observed in α-iron through the atomistic and MD simulations [125,127,150,200], and also experimentally by the tensile test [115,170,171]. The degree of reduction in mobility mostly depends on the hydrogen concentration and stress level.

More recently, Harris et al. [201] have done the critical experiment in polycrystalline nickel. The main idea was to investigate (i) the contribution of mobile hydrogen-deformation interactions; (ii) interactions between the HELP and HEDE mechanisms; and (iii) the governing HE mechanism responsible for the hydrogen-induced IG cracking. One of the ideas in this research was also to check the universal validity of the HELP mediated HEDE model, already proposed in the case of nickel [202]. Further, they tried to estimate quantitatively if the mobile hydrogen-deformation interactions, i.e. HELP activity, are always the necessary precondition for reaching the condition required for the IG fracture due to the HEDE. Such hypothesis was similarly proposed within the HELP mediated HEDE model [24,33,42,43,145,164,195] in iron and steels [24,33,42,43,145,164,195,196] and previously explained in this subsection. For that purpose, they used tensile testing of specimens thermally charged with gaseous hydrogen in a furnace at room temperature (25 °C) and low temperature (−196 °C). The idea was to establish fully opposed conditions, where mobile hydrogen-deformation interactions are enabled (at 25 °C) and effectively suppressed (at −196 °C). Such conditions were achieved, because of the significant decrease in the diffusivity of hydrogen in nickel from ~10–11 cm^2/s at 25 °C to ~10–31 cm^2/s at −196 °C [203]. High hydrogen concentrations of 78–81 wt parts per million (wppm) were measured [201]. They found that the IG fracture due to the decohesion - HEDE mechanism was predominantly initiated due to high initial grain boundary hydrogen concentration prior to deformation. In this case, mobile hydrogen-deformation interactions and the HELP mechanism activity, i.e. hydrogen-enhanced dislocation mobility and increased dislocation pile-ups, have a secondary contribution to the IG microcrack initiation [201]. They also found that the grain boundary-dislocation interactions and dislocation cell distributions beneath similar IG fracture surfaces of specimens tested at room and low temperatures are quite alike. The observed dislocation cell structure is not significantly altered at −196 °C compared to 25 °C. The mobile hydrogen-deformation interactions and the HELP mechanism at a low temperature are effectively suppressed. Contrary, at room temperature all preconditions for the previous HELP mechanism activity are completely satisfied. At room temperature, suppression effects are not operative, which enables the HELP mediated decohesion effects to be active, according to the HELP mediated HEDE model [201,202]. Despite this, the HELP mechanism activity at room temperature according to this research was minor. However, the same authors have also emphasized that the relative contributions of the initial grain boundary hydrogen concentration and mobile hydrogen-deformation interactions (HELP) to IG cracking also depend on the lattice hydrogen concentration [201].

They also underlined that the HELP mechanism activity may be predominant at lower lattice and GB hydrogen concentrations. In that case, the effects of the HELP mechanism on an additional hydrogen content deposition at the GB, and consequently the mobile hydrogen-deformation (HELP) mediated and provoked decohesion (HEDE) at grain boundaries (GBs) may be much more pronounced. Such HELP effects may be in agreement with the proposed HELP mediated HEDE model, as analogously assumed in the case of IG fractures in different steels [33,42,43,145,153,164], nickel [202] and iron [154,173,195]. Also, possible synergistic effects of other plasticity-mediated HE mechanisms on the hydrogen-induced IG cracking in steels and iron, such as AIDE [9,17,197], HESIV [8,28], Defactant concept [22,78,132], and others [58,69], can not be excluded either. The summary of these opposing findings is listed in Tables 1 and 2 and briefly mentioned in Section 2. Further analysis of the complex interplay between the HELP (and/or other proposed plasticity-mediated HE mechanisms) and the HEDE mechanism is highlighted in Section 2.3.

These controversial results and conclusions indicate that hydrogen-induced IG cracking in metallic materials, mostly or completely due to the HEDE activity only, is also possible under some conditions. In such cases, the previous activity of the HELP mechanism was not a significant source of additional hydrogen deposited and trapped at different microstructural locations. Consequently, the initially local high hydrogen concentration already achieved at grain boundaries and other locations in the microstructure (hydrogen traps) provides sufficient conditions for the HEDE activation and dominance [2,13,34,36,204–208]. Then the brittle hydrogen-induced IG cracking could occur without the necessity for the significant previous activity of the hydrogen-provoked localized plasticity and HELP. Also, the synergistic and in some cases rather competitive and non-mediated action of both mechanisms independently: HELP + HEDE was also detected and confirmed in steels [10,13,34,36,143,158–162] (see Table 2 for more references). In such cases, the HELP mechanism contribution in the HE and mixed-modes (MVC + QC + TG + IG) or completely brittle stress-controlled TG and IG fracture modes, gradually, and in some cases significantly decrease [36], and hence becomes negligible [36,204] or completely non-existent [13,36,205–208]. This is particularly pronounced upon local reaching of a high hydrogen concentration close to or above the critical hydrogen concentration (HEDE dominance) at key microstructural locations and hydrogen trapping sites [2,10,13,15,25,26,36,141]. The following Section 2.3: The synergy of hydrogen-enhanced plasticity and decohesion (HELP + HEDE model) gives more details about this topic.

The universality of the HELP mediated HEDE model still needs to be further checked and confirmed. Particularly for different grades of steel and for different experimental, hydrogen charging and mechanical loading conditions [209] within a broad range of lattice and grain boundary hydrogen concentrations. It seems that there are five basic and still unresolved dilemmas. The dilemmas refer to the true connection between the HELP and HEDE mechanisms, particularly regarding previous HELP activity, as a governing HE mechanism and a necessary precondition for the activation of the HEDE mechanism:

(1) Is the HELP mechanism always a governing mechanism for HE in steels?
(2) Is previous activity of the HELP mechanism always critical for reaching the condition of decohesion activation - HEDE mechanism?
(3) What are the effects of (i) the chosen hydrogen charging conditions; (ii) static/dynamic loading conditions: high/low strain rates during mechanical testing; and (iii) obtained uniform/non-uniform hydrogen concentration profiles, including the initially very high hydrogen concentration in steels, on the viability and real significance of the previous HELP activity (diffusible hydrogen and hydrogen transport by dislocations) prior to the HEDE activation?
(4) Are (i) the hydrogen-enhanced dislocations mobility; (ii) an increase in dislocations density; (ii) dislocations movement near the crack tip; (iii) dislocation pile-ups; and (iii) hydrogen transport by dislocations and accumulation in the FPZ ahead of the crack tip always simultaneously active and present necessary prerequisites for the HEDE activation?
(5) What are simultaneous and multifaceted effects of the coexistence and synergistic activity - concurrent action in a cooperative manner of multiple HE mechanisms (HELP + HEDE), or of an individual activity of different plasticity-mediated HE mechanisms (HELP, AIDE, HESIV and other), including their accompanying mobile H-deformation interactions, and the decohesion - HEDE mechanism (see Sections 2.3 and 3)?

2.3. The synergy of hydrogen-enhanced plasticity and decohesion (HELP + HEDE model)

The synergistic interplay of HE mechanisms in steels and iron required interdisciplinary observation of (i) the hydrogen uptake/diffusion/trapping processes [10,27,37,141,211–213]; (ii) hydrogen-materials interactions [210]; and (iii) interactions between all viable HE mechanisms [10,13,23,24,36,209,211,214–218]. Djukic et al. [13] pointed out that depending on the experimental and simulation approach, particularly adopted and applied length scale: macro-, micro-, nano/atomistic-scale, there is a large scattering in conditions established in the hydrogen-steel system. As a consequence, this favors the conditions for the occurrence of only specific HE mechanism in accordance with the plasticity-enhanced models (HELP, AIDE, HESIV and other), or the decohesion model (HEDE). For the specific applied experimental conditions or the combination of simulation parameters, different HE mechanisms, one or more simultaneous, can predominate [13]. Therefore, the coexistence of different HE mechanisms and their simultaneous effects in steels and iron (see Table 2), are still not well documented, while the recognition of a dominant mechanism, one or more, is an extremely challenging but crucial problem [36].

2.3.1. HELP + HEDE model - modeling approach

Despite a large number of published atomistic/quantum/meso/macromechanical models about the HE mechanisms and their interactions in steels and iron, summarized in [11–13,19,65], reliable techniques for resolving atomistic crack tip processes are still missing. The same applies to the quantification of hydrogen concentrations at the crack tip FPZ on the nanoscale, including sufficiently realistic atomistic modeling of crack growth [5,80] (see Table 2 for more references). Jemblie et al. [65] have noted that a cohesive zone modeling (CZM) approach for simulating hydrogen-induced cracking proved to be able to reproduce particular experimental results by the appropriate fitting of the cohesive parameters. They also highlighted obvious limitations existing in the attempt to transfer these results to different hydrogen-metal systems [65]. A particular problem in HE modeling under conditions of simultaneous activity of both HELP and HEDE mechanisms is how to provide the coupled interactions of hydrogen diffusion and induced softening, with the reduction of a cohesive strength due to the HEDE. Falkenberg et al. [144] and Brocks et al. [146] developed a predictive model for hydrogen-induced cracking, which includes coupling aspects of HELP + HEDE in high-strength low alloy steel. They provided good agreements between simulated crack tip opening displacement (CTOD-R) curves for various deformation rates and experimental results. Recently, Traidia et al. [11] and Barrera et al. [12] have summarized published results and provided comprehensive reviews about hydrogen-assisted cracking micromechanical models for the application to service lifetime prediction of steels. A review paper by Traidia et al. [11] gives an overview of the coupled early HELP + HEDE model proposed by Ahn et al. [89] for prediction of hydrogen-assisted subcritical ductile crack propagation and failure in a low carbon pressure vessel steel. Also, advanced multidimensional models for HAC in steels are discussed, which involves both hydrogen-assisted elastoplastic deformation and the thermodynamic theory of decohesion. The models were initially proposed [83] and then broadly discussed by Dadfarnia et al. [15,26,84].

The computational continuum mechanics model based on the synergetic effect of HELP and HEDE mechanisms has been recently proposed by Barrera et al. [147–149] for Fe-Ni dissimilar welds. The model emphasizes and also advocates the competitive relationship between HELP and HEDE mechanisms. They revealed the initiation of microcracks due to the decohesion (HEDE) process at the matrix/carbide interface, followed by plastic flow localization due to the HELP activity [147–149]. An atomistic investigation of HE mechanisms in α-iron and dislocation dynamics analysis results given by Taketomi et al. [127,150] gives additional insights. The results indicate the possible change of HE mechanism from hydrogen-induced softening (HELP, HESIV, etc.) to the brittle type HEDE fracture and hydrogen-induced hardening. The transition between HE mechanisms depends on the boundary conditions: hydrogen concentration and applied stress conditions [127,150], which is in agreement with the HELP + HEDE model [13,36], Fig. 8. Moreover, based on the complex modeling approach which included: MD simulation of crack propagation, nano-indentation simulation, and tensile loading simulation, Matsumoto et al. [67] have reached similar conclusion. According to their simulation, various HE mechanisms like HELP, HEDE, HESIV, and Defactant concept can occur and have synergistic effects in α-iron. The degree of their activity depends on the boundary and initial material conditions and lattice defects.

More recently, Wan et al. [166] have proposed a "hybrid" HE model based on the dislocation-grain boundary reaction by dislocation impingement/emission on the grain boundary. According to this model, a locally activated state of the GB is the trigger mechanism for the transition from the plasticity-mediated "QC" and IG fracture modes at lower hydrogen concentrations to the macroscopically pure brittle IG mode at higher hydrogen concentrations. The transition is followed by a negligible sign of previous dislocation-driven plasticity in α-iron. They further report that at lower hydrogen concentrations the dislocation activities nearby the grain boundary are required to trigger decohesion and "QC" and IG fractures. This conclusion at lower hydrogen concentrations complies with the HELP mediated HEDE model. Contrary, at a very high hydrogen concentration fewer dislocation activities nearby

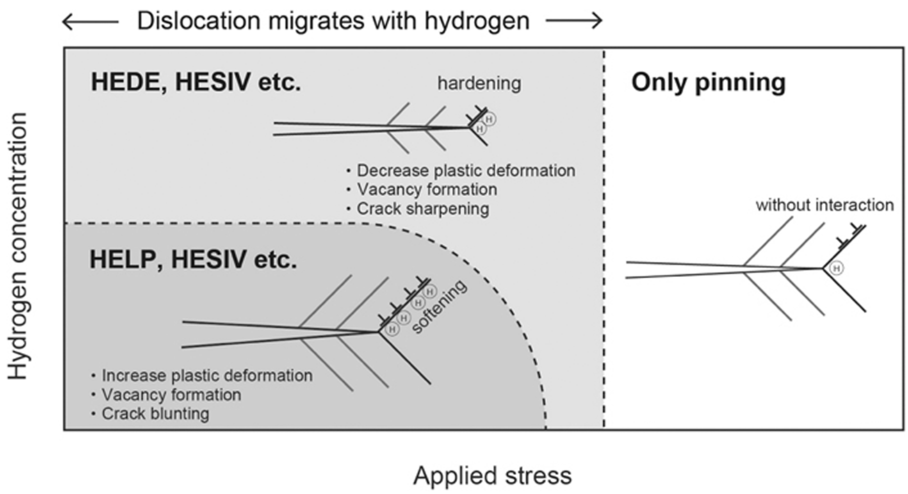

Fig. 8. HELP + HEDE model: Schematic of the transition of the HE mechanism, HELP (HESIV) → HEDE (HESIV), for different hydrogen concentrations and applied stress conditions [127]. "Reprinted from ISIJ Int., 57/11, Taketomi S, Matsumoto R, Hagihara S, Molecular statics simulation of the effect of hydrogen concentration on {1 1 2} ⟨1 1 1⟩ edge dislocation mobility in alpha iron, 2058–2064, Copyright (2017), with permission from the Iron and Steel Institute of Japan".

the GB are required, and hence the IG fracture is mostly initiated and controlled by the HEDE mechanism activity. These observations related to the governing HE mechanism responsible for ductile to brittle dominated fracture transition at a high hydrogen concentration and "QC" and IG fractures are in agreement with the experimental findings in nickel [201] and different grades of steel [13,36,74–76,112,143,155–160]. This topic is discussed in more detail in Section 2.3.2. HELP + HEDE model and experimental confirmations. It is also important to mention that the current state-of-the-art computational and modeling techniques for grain boundary calculations [161] still have some limitations. Modeling techniques still do not give a precise description of the sharp ductile to brittle transition process in steels [35,36,112], from the predominantly plasticity-mediated fracture mode at lower hydrogen concentrations, to the fully decohesion-controlled mode upon reaching the critical hydrogen concentration [13,36]. Computational modeling results still exhibit significant discrepancies compared to the experimental results [161].

Numerous proposed computational models at different scales provide simulations and a relatively reliable prediction of hydrogen-induced cracking. They also exhibit a reasonable agreement with experimental results in the case when applied modeling approaches take into account only one mechanism of the HE (plasticity-mediated one or HEDE). However, modeling of the experimentally confirmed simultaneous action of the plasticity-mediated (HELP and/or others) and HEDE mechanisms in different grades of steel (see Table 2 and the next subsection), still represents a challenging task. Models for HE at atomistic and electronic scales still cannot be used easily for the assessment of active HE mechanisms, their interactions and the corresponding degradation of mechanical properties at different scales (macro-micro-nano/atomistic) [66]. The overview of the HE phenomenon investigation and the application of a multiscale modeling approach have been recently summarized by Djukic et al. [13]. They also listed the main reasons for a large scatter of obtained results and conclusions reported in different computational HE modeling studies [13]. The key limitations are further extended, modified and highlighted here as follows (1–7):

(1) Computational models often do not take into account all details of the microstructure of a polycrystalline material at micro and nano-level.
(2) Some recent multiscale modeling techniques [41,72,73] attempt to enable the inclusion of the effects of microstructural heterogeneity through the complex coupled micro-meso-macro models for the HE investigation in polycrystalline materials.
(3) There is a time and spatial scale gap that presents a problem in interpreting the results obtained from the atomistic-, nano-, and micro-simulations, and their correlation with the degradation of macromechanical properties, particularly when multiple HE mechanisms are active [13].
(4) Atomistic MD and MC simulations of HE are certainly very powerful tools for investigating and accessing different hydrogen-materials interactions and accompanying processes at longer time scales.
(5) There are restrictions in the MD and MC method application [67–70]. Special care is necessary during modeling of the hydrogen-dislocation dynamic interactions so as to correctly predict the behavior at the atomic scale [23].
(6) First-principles and ab initio modeling of HE is mainly based on rather small system sizes ranging up to a few nanometers, and hence it is very difficult to capture all complexities of hydrogen-materials interactions (HE mechanisms) [13].
(7) In the case of multiphase complex microstructures, the possibility for incorporation of the results obtained at lower scale into higher scale models and accuracy at larger length-time scales should be carefully checked [219,220].

2.3.2. HELP + HEDE model - experimental confirmations

Despite the mentioned obstacles during computational modeling of GBs with hydrogen segregations, computational results [161] have confirmed numerous results experimentally obtained supporting the HELP + HEDE model (Table 2). These together also indicate the competitive relationship between hydrogen segregation at dislocations and GBs, and between multiple and complex hydrogen-deformation interactions. It is also stressed the importance of interaction between diffusive hydrogen and GBs. According to the well established decohesion theory of the HE (HEDE mechanism) [81,129–131], failure occurs when a sufficiently high, so-called "critical hydrogen concentration" is attained locally at locations of high triaxial stresses. This is also a prerequisite for the HEDE mechanism activation within the crack tip FPZ. The HEDE mechanism activation is typically followed by a sudden and sharp transition from ductile to brittle dominated fracture mode in steels [10,13,36,81,112,129–131]. The term "critical hydrogen concentration" with still insufficiently defined and understood physical meaning [10,13] is typically connected with the IG fracture, cleavage decohesion or some other types of brittle fracture [221,222]. It is also often used in HE studies of different metallic materials, including steels and iron, while in different studies the term "critical hydrogen concentration" has rather different physical meanings [223]. The amount of hydrogen that can be dissolved in a bulk steel specimen is much lower than the very high "critical hydrogen concentration" necessary for the HEDE mechanism activation [81,129–131]. Having this in mind, the major challenge in understanding the HELP + HEDE model is the ETEM based experimental finding of the localized plasticity-enhancement caused by hydrogen [6,7,9,17,23]. Such localized plasticity enhancement effects and hydrogen-deformation interactions due to the HELP or other plasticity-enhanced mechanisms activity could have synergistic effects with the HEDE (see Table 2) [13,36].

The transition from ductile to brittle dominated fracture mode in steels resulting from the synergistic activity of HELP + HEDE mechanisms is mainly controlled by the competition between dislocation nucleation/emission from the crack tip and decohesion of the interface [81,129–131,221,222]. This transition from typically "ductile" to "brittle" macro-behavior, irrespective of the degree of activity of a particular HE mechanism or their synergistic effects, is essential for a better understanding of the HE phenomena. Hence, understanding of the phenomenon which occurs in steels upon reaching the critical hydrogen concentration and accompanying decohesion processes is mandatory for the analysis of the transition from the ductile to brittle dominated HE fracture in steels [10,13,36,112,223].

All accompanying HE phenomena in steels, according to the HELP + HEDE model by Djukic et al. [36], which could occur before a local reaching of the critical hydrogen concentration, are proposed [224]. They can be classified as (i) the HELP mechanism dominance and effects (HELP + HEDE) [36]; (ii) possible HELP mediated HEDE influence; and (iii) an incipient HEDE mechanism activity. Accordingly, the phenomena upon reaching the critical hydrogen concentration can be classified as (i) the HEDE mechanism dominance and effects (HEDE + HELP) [36]; and (ii) the remaining influence and effects of the HELP mechanism (HEDE + HELP) [224]. Also, this classification does not exclude the possibility for activities of other plasticity-enhanced mechanisms (AIDE, HESIV, Defactant concept, etc.), independently (different plasticity-enhanced models + HEDE), or synergistically with the HELP. Djukic et al. [10,13] have presented an overview of published phenomena, proposed by different authors in steels and iron upon reaching the critical hydrogen concentration, which is further expanded and modified here:

(1) the end of the incubation time for crack growth in high-strength low alloy steels at a certain hydrogen concentration required for the crack propagation [225];
(2) change in hydrogen influence from the enhanced plasticity to the HE in a low carbon heat resistant steel [226];
(3) change in the damage mechanism from decohesion to the formation of microcrevices at the grain and phase boundaries followed by a decrease in the plasticity of low carbon heat resistant steels [227];
(4) the local crack initiation in low-strength steels, high-strength steels, and niobium, and the establishment of the local fracture criteria [228];
(5) the critical loss of a local strength at the notch in low carbon pipeline steels [229], advanced high-strength steels and TRIP steels [230];
(6) change of the fracture mode from ductile to brittle IG in transformation induced plasticity (TWIP) steels and high-strength steels [204–208];
(7) hydrogen-induced delayed fracture at a crack tip or a notch root in high-strength steels [231];
(8) the drop of ductility and a sharp ductile to brittle fracture transition in a low carbon heat resistant steel (the increased activity and dominance of the HEDE mechanism, HELP + HEDE model (HEDE > HELP) [13,36,112,224].

It is important to make distinctions between the critical hydrogen concentration defined in different HE studies as (i) a global (total) or average hydrogen concentration in the specimen; (ii) local hydrogen concentration at the trap site that causes cracking; or (ii) local hydrogen concentration at a crack tip or a notch root. The measurements of the local critical hydrogen at a crack tip are very difficult to conduct [26]. In most of the mentioned HE studies the term "critical hydrogen concentration" is related to the lattice (global) hydrogen concentration or the calculated (local) hydrogen content at the trap site. In both cases, the critical hydrogen concentration depends strongly on the material system, experimental conditions, as well as the stress/strain level [204–208,224–231]. It seems that the critical hydrogen concentration is mostly related to a hydrogen content at the crack initiation site [231]. However, there is still disagreement about the true meaning of the critical hydrogen concentration value at the global and local levels [13,36,112,224–231]. It is still very difficult to theoretically-numerically calculate or experimentally measure the local critical hydrogen concentration, particularly at the crack tip [231]. Also, the same applies to the modeling of hydrogen diffusion, hydrogen distribution at a crack tip [141] and validation of crack-tip mechanics under the simultaneous action of HE mechanisms (plasticity-enhanced models + HEDE). Wang et al. [231] pointed out that it is necessary to understand the stress-driven hydrogen

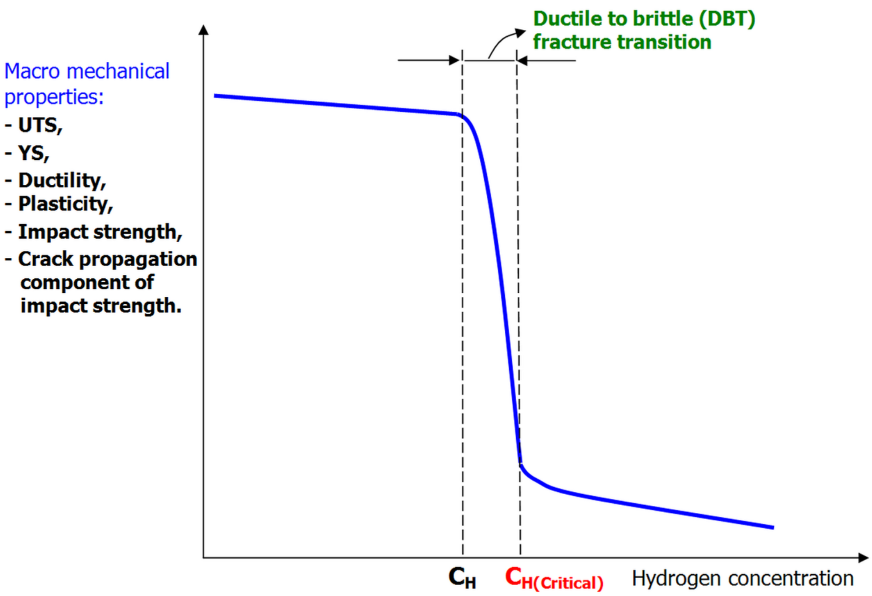

Fig. 9. The sharp drop in various mechanical characteristics and ductility in steels upon local reaching a critical hydrogen concentration and activation of the HEDE mechanism of HE.

diffusion and accumulation at the crack initiation site in order to determine the local critical hydrogen concentration. Therefore, it is still very challenging and rather difficult to define the critical hydrogen concentration unequivocally in different steels under different hydrogen charging and experimental conditions. Dadfarnia et al. [26] indicated that identification and measurement of the hydrogen concentration at key microstructural features and trapping sites in steels is necessary for better quantification of the synergy between all proposed HE mechanisms. Upon reaching the critical hydrogen concentration in steels and iron ($C_{H(Critical)}$) locally, a sudden and sharp drop in various mechanical characteristics and ductility occurs [10,13,36,112,205–208,223,224,226,229,230]. This is due particularly to the critical loss of a local strength, which leads to the typical change of the fracture mode from ductile to brittle dominated because of the decohesion (HEDE mechanism of HE) [36], Fig. 9. The phenomenon is marked as “Ductile to brittle (DBT) fracture transition” in Fig. 9 and should not be confused with the term ductile to brittle transition in steels and iron at low temperatures.

Lovicu et al. [230] have investigated the HE susceptibility of different advanced high-strength steels. They found that upon reaching the critical hydrogen concentration a sharp drop in ultimate tensile strength (UTS) takes place. This drop was measured for notched specimens (N.UTS) and occurred after the tensile (SRRT) test of previously electrochemically charged specimens with different hydrogen amounts (C_H), Fig. 10a. The post-tensile fractographic analysis of uncharged and hydrogen charged specimens shows the ductile MVC fracture for the as-received uncharged specimen, Fig. 10b. With increased hydrogen content approaching the critical one, hydrogen-induced QC mode with the presence of some fine secondary cracks occurs, Fig. 10c. Finally, at a hydrogen concentration higher than the critical, IG fracture mode also occurs, and the secondary cracks also enlarge, Fig. 10d.

Similar observations were highlighted by Hüter et al. [161] within the experimental findings for martensitic stainless steel. They conducted research based on the previous electrochemical charging of specimens with different hydrogen contents (Fig. 11a) with further analysis of corresponding fracture surfaces after the SSRT test, Fig. 11b.

The initial hydrogen content of 1.5 ppm exhibits a fully ductile (D) - MVC fracture mode with very fine dimple sizes. It changes after charging with 5 ppm hydrogen to the mixed TG and IG mode with a few ductile MVC islands, the cracks propagating through the prior austenite grain boundaries (PAGB), as well as the martensite lath. However, with a further increase of the hydrogen content above the critical concentration, the TG and IG fractures are more prominent and the decohesion (HEDE) occurs mostly along the PAGBs, Fig. 11b [161]. In the previously explained examples (see Figs. 10a and 11a), the phenomenon of decohesion and activation of the HEDE mechanism of HE occurs when the critical value of hydrogen content is reached. However, the possible previous effects of the HELP mechanism at a lower hydrogen content, or the synergy between HELP and HEDE mechanism (HELP mediated HEDE and HELP + HEDE models) have not been considered and further analyzed. The correlations between mixed fracture modes and active

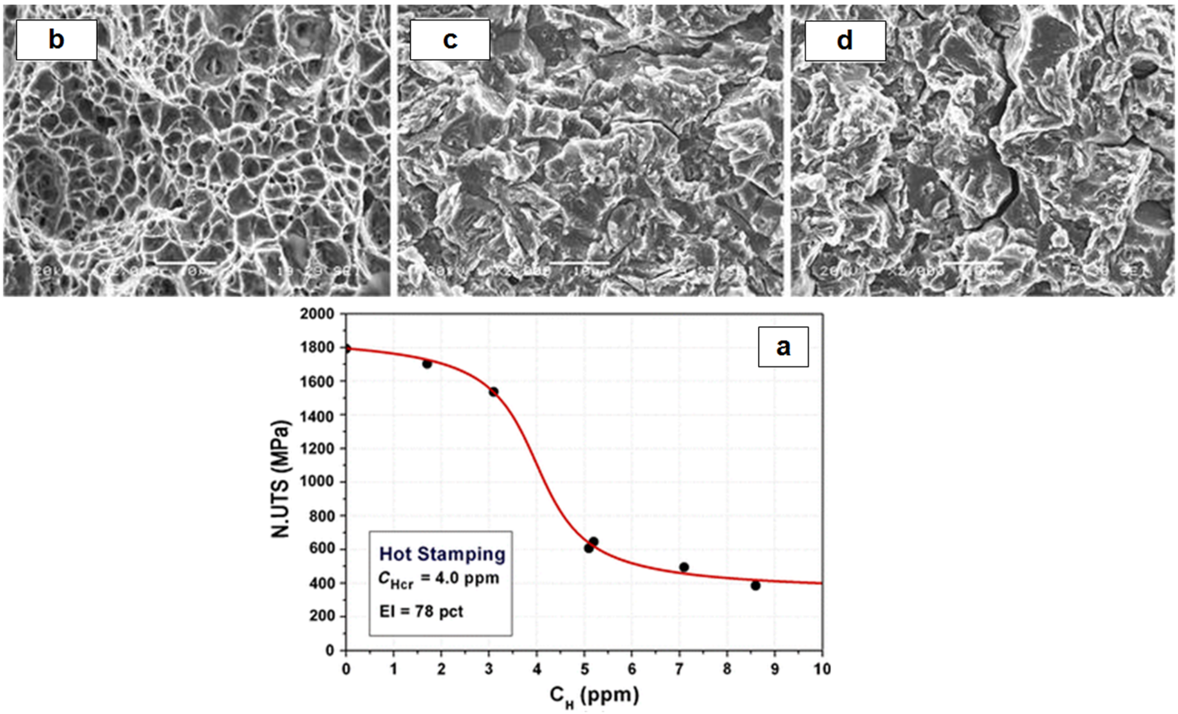

Fig. 10. HE susceptibility of advanced high-strength steels and the effect of critical hydrogen concentration: (a) so-called embrittlement curve, i.e. the strength vs hydrogen concentration for the advanced high-strength steel (the critical hydrogen concentration is about 4 wppm); Micrographs of fracture surface of: (b) uncharged specimen; (c) sample charged at 2.6 wppm (lower than the critical hydrogen concentration); (d) sample charged at 7.1 wppm (higher than the critical hydrogen concentration) [230]. “Reprinted from Metall. Mater. Trans. A, 43/11, Lovicu G, Bottazzi M, D’Aiuto F, De Sanctis M, Dimatteo A, Santus C, et al., Hydrogen embrittlement of automotive advanced high-strength steels, 4075–4087, Copyright (2012), with permission from Springer”.

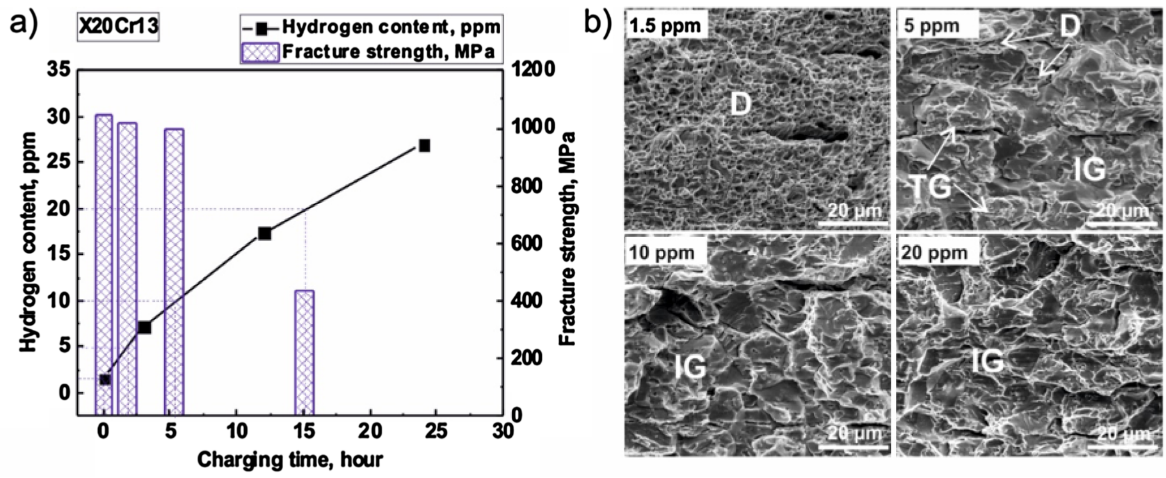

Fig. 11. Hydrogen-induced cracking in a martensitic stainless steel: (a) evolution of hydrogen contents and the fracture strength according to the hydrogen charging time determined by the SSRT test; (b) fracture surfaces of specimens with different amounts of pre-charged hydrogen [161]. "Reprinted from Metals, 3, Hüter C, Shanthraj P, McEniry E, Spatschek R, Hickel T, Tehranchi A, et al., Multiscale modelling of hydrogen transport and segregation in polycrystalline steels, 430., Copyright, The Authors (2018), Open access under a creative commons license CC BY 4.0".

HE mechanisms and the transition from ductile to brittle dominated fracture mode followed by a sudden drop in the fracture strength also have not been further analyzed. The same applies to the case of previously published experimental HE studies along with mentioned lack of consensus about which of the critical hydrogen contents is responsible (global or local).

Together with the concept of HE, which includes both plasticity and brittleness, i.e. the HELP + HEDE concept (Section 2.1), and the HELP mediated HEDE model (Section 2.2), different experimental studies were published within the framework of the HELP + HEDE model [36]. The corresponding HELP + HEDE studies, starting from the beginning of the 21st century up to the present day, are chronologically listed in Table 2. The results of selected important HELP + HEDE studies will be further analyzed and critically discussed within this subsection (see also Section 3: Tables 3 and 4).

One of the earlier studies (2009), which indicated the HELP + HEDE model credibility was the experimental research of hydrogen effects on the fracture toughness and active HE mechanisms in a low carbon pipeline steel. This study by Wang [143] has included both electrochemical hydrogen pre-charging of specimens and dynamic hydrogen charging conditions. The fracture morphology analysis revealed that both mechanisms (HELP + HEDE) are responsible for both the observed increase (hydrogen concentrations below a critical hydrogen concentration) and the reduction (hydrogen concentrations above a critical hydrogen concentration) of the fracture toughness. Both mechanisms are also responsible for a ductile MVC fracture followed by a reduction of the size of dimples (HELP) under the hydrogen pre-charging conditions, and the fracture ahead of the crack followed by a brittle C fracture morphology (HEDE) under the dynamic hydrogen charging condition [143]. Finally, he concluded that compared to the hydrogen pre-charging condition, the dynamic hydrogen charging condition lowers the fracture toughness considerably and the hydrogen-assisted hardening exists even when the hydrogen concentration is lower than the critical.

In 2014 two groups of researchers further highlighted the significance and validity of the HELP + HEDE model: Koyama et al. [34] in a dual-phase (DP) steel and Djukic et al. [35,36] in a low carbon heat resistance steel. Koyama et al. [34] investigated hydrogen-assisted decohesion and localized plasticity phenomena in electrochemically charged ferritic-martensitic dual-phase steel. The research is based on special experimental approaches applied during the analysis of the concurrent and synergistic or competing action of HELP and HEDE mechanisms. They used in-situ microstructural observations during tensile and three-point bending tests and the advanced quantitative analysis of the hydrogen-assisted damage evolution during the tensile tests. The main research idea was to reveal underlying HE micro-mechanisms and their interactions. They concluded that the simultaneous action of the HEDE and HELP mechanisms is responsible for reducing the damage nucleation regime and increasing of the crack growth rate. The observed IG cracking on the ferrite-martensite interfaces was primarily due to the HEDE mechanism activity and dominance (HELP also contributes with local ductile MVC fractured areas in the predominant brittle QC fracture mode). On the other hand, the ferrite-martensite boundary sliding and ferrite cracking mechanisms were a consequence of the enhanced dislocation mobility, i.e. HELP mechanism activity [34].

Djukic et al. [36] investigated the effect of hydrogen on various, but interrelated mechanical properties (UTS, YS, hardness, impact strength, and its crack initiation and propagation components) of the low carbon ferritic-pearlitic heat resistant steel, grade 20 (St.20, equivalent to AISI 1020). They placed special emphasis on the transition from ductile to brittle dominated fracture mode upon reaching the critical hydrogen concentration resulting from the concurrent and synergistic or a competing action of HELP and HEDE mechanisms of HE. They used a special multiscale approach applied during subsequent post-mortem experimental investigations of HE mechanism in samples unevenly enriched with hydrogen and damaged during the service of an industrial component [13,35,36], Fig. 12. Furthermore, they confirmed the coexistence of HELP and HEDE mechanisms depending on the local hydrogen concentration (C_H) in investigated steel [36]. The HELP + HEDE model for HE in steels proposed by Djukic et al. [13,36] is based on the correlation

Table 3
HELP + HEDE and HELP mediated HEDE models, microstructural features, hydrogen trapping sites and corresponding fracture modes.

Material	Hydrogen charging method	Testing method	Microstructural features and H trapping sites: – HELP/(+)HEDE^{1} – HELP mediated HEDE^{2}	Fracture modes due to: – HELP/(+)HEDE^{1} – HELP mediated HEDE^{2}	Authors	Source
Low carbon steels						
Heat resistant steels	EI	T + IT	(pearlite/ferrite, MnS, pearlite-ferrite interfaces)^{1}	(MVC, QC/MVC, QC, TG, IG, cracks)^{1}	Djukic et al.	[13,35,36]
	EC	FG	(ferrite-pearlite)^{1}	(ductile TeS, QC/QC)^{1}	Dmytrakh et al.	[155,156]
Pipeline steels	EC	FT	(ferrite-pearlite)^{1}	(MVC/MVC, C, cracks)^{1}	Wang	[143]
	G	T + FG	(ferrite-pearlite/ferrite, grain boundaries)^{2}	(QC/QC, TG, IG, cracks)^{2}	Wang et al.	[164]
		FT	(ferrite-pearlite)^{2}	(QC/QC, IG)^{2}	Martin et al.	[42,43]
Low alloy heat resistant steels						
CrMo and CrMoV steels	G	FT	(tempered Ma, carbides/PAGB, Ma boundaries)^{1}	(MVC, PRHIC/PRHIC, IG, cracks)^{1}	Peral et al.	[165]
CrMoV steel	I		(bainite/grain boundaries)^{1}	(MVC/MVC, QC, C, cracks)^{1}	Song et al.	[159]
High strength steels						
Ultra-high strength M stainless steel	EC	SSRT	(lath Ma/Ma-Ma lath interfaces, Ma packet boundaries, PAGB, and incoherent carbides)^{1}	(MVC, QC/QC, IG, cracks)^{1}	Hu et al.	[76]
Ultra-high strength steels		T + SSRT	a) complex phase^{1}, b) dual-phase^{1}, c) Ma^{1}	(MVC, QC/QC, cracks)$^{1+2}$	Rehrl et al.	[151]
High-strength M steels	G	SSRT + FPB	(lath Ma/carbide-matrix interfaces)$^{1+2}$	(MVC/IG)$^{1+2}$	Novak et al.	[32]
			(lath Ma/PAGB, cementite particles on PAGB (block and lath boundaries), block boundaries)^{2}	(MVC/QC, IG)^{2}	Nagao et al.	[33,145]
		T	(lath Ma/PAGB, Ma lath boundaries, Mn segregations, MnS inclusions)$^{1+2}$	(TG, cracks)$^{1+2}$	Sasaki et al.	[153]
High strength low alloy steels	EC	SSRT	(Ma, bainite/Ma-matrix interfaces, matrix-inclusion interfaces)^{1}	(MVC, QC/QC, TG, IG, cracks)^{1}	Li et al.	[157,160]
Dual-phase steel		T + IPB	(ferrite/ferrite-Ma interfaces)^{1}	(QC/IG, cracks)^{1}	Koyama et al.	[34]
Stainless steels						
M stainless steels	EC	SSRT	(Ma, carbides, and ferrite/PAGB interfaces)^{1}	(MVC, QC/QC, IG, cracks)^{1}	Kumar et al.	[74]
			(lath Ma/PAGB, Ma lath boundaries, tempered Ma-newly formed Ma boundaries)^{1}	(MVC, QC/QC, IG)^{1}	Fan et al.	[75]
			(lath Ma/PAGB, Ma lath boundaries)^{1}	(MVC, QC/QC, TG, IG)^{1}	Hüter et al.	[161]
Austenitic stainless steel		T	(austenite, α′ Ma/twins, grain boundaries)^{1}	(MVC, QC/QC, IG, cracks)^{1}	Wang et al.	[152]
			(austenite, α′ Ma/twins, phase boundaries)^{1}	(MVC, QC/QC, C, IG, cracks)^{1}	Li et al.	[158]

Legend: HELP/(+)HEDE^{1}, HELP mediated HEDE^{2} - see text for explanation; EI - electrochemical in-situ (during operation) charging; EC - electrochemical charging; G - gasous charging; I - immersion charging method; MnS - manganese sulfide inclusions; Ma - martensite/martensitic; PAGB - prior austenite grain boundaries; T - tensile test; IT - Charpy impact test; FG - fatigue crack growth test; FT- fracture toughness test; SSRT - slow strain rate tensile test; FPB - four-point bending test; IPB - in-situ bending tests; TeS - tearing and shearing fracture; MVC, QC, C, TG, IG - see text for explanations; PRHIC - plasticity related hydrogen induced cracking.

Table 4
The background for a unified model of synergistic interplay of HE mechanisms in steels: localized plasticity and decohesion (HELP + HEDE and HELP mediated HEDE models).

Used methods in HE studies		Major conclusions related to the synergistic interplay of HE mechanisms in steels [13,32–36,42,43,74–76,112,143,145,151–153,155–161,164,165,224]					
		Affected microstructural locations/H trapping sites due to **the dominance of**:			Characteristic fracture modes/features due to **the dominance of**:		
H charging methods	Mechanical testing methods	H concentration increase →			H concentration increase →		
		HELP	**Transition HELP → HEDE**	**HEDE**	**HELP**	**Transition HELP → HEDE**	**HEDE**
Low carbon steels							
EI, EC, G	T, IT, FC, FT	– P – F/P	– F/P	– MnS – F – F/P interfaces – GBs	– MVC – ductile TeS – QC	– MVC, QC	– MVC – QC – TG – IG – cracks
Low alloy heat resistance steels							
G, I	FT	– tempered Ma – carbides – B	–	– PAGB – Ma boudaries – GBs	– MVC	– MVC – QC – PRHIC	– QC – C – IG – cracks
High-strength steels							
EC, G	T, SSRT, FPB, IPB	– lath Ma – Ma – F – B	– PAGB – Ce particles – block boundaries	– Ma/Ma interface – Ma packet boundaries – PAGB – incoherent carbides – Ma lath boundaries – MnS – Mn segrations – Ma/matrix interfaces – F/Ma interfaces – matrix/inclusion interfaces	– MVC	– MVC – QC – PRHIC	– QC – C – IG – cracks
Stainless steels							
EC	SSRT, T	– Ma – lath Ma – carbides – F – A – α′ - M	–	– PAGB – Ma lath boudaries – newly formed Ma – boudaries – twins – GBs – phase boudaries	– MVC	– QC	– C – TG – IG – cracks

Legend: H - hydrogen; EI **-** electrochemical in-situ (during operation) charging; EC - electrochemical charging;
G **-** gaseous charging; I **-** immersion charging; MnS - manganese sulfide inclusions; F - ferrite; P - pearlite;
F/P - ferrite/pearlite; B **-** bainite; A - austenite; Ma - martensite; Ce - cementite; PAGB - prior austenite grain boundaries; GBs - grain boundaries; T - tensile test; IT - Charpy impact test; FG - fatigue crack growth test; FT- fracture toughness test; SSRT - slow strain rate tensile test; FPB - four-point bending test; IPB - in-situ bending tests; TeS - tearing and shearing fracture; MVC, QC, C, TG, IG - see text for explanations; PRHIC - plasticity related hydrogen induced.

of mechanical properties to SEM fractography analysis of Charpy specimens fracture surfaces, Figs. 12–14. The hydrogen concentration in steel was in this case very uneven and locally very high, especially for specimens located in the vicinity of hydrogen damage caused during the operating of boiler tubes, Fig. 12. Such high local hydrogen concentration in steels is also typical of other industrial components exposed to the in-situ electrochemical corrosion with hydrogen as a byproduct [13,35,36,134–136,224], Fig. 12. An uneven saturation of industrial components with hydrogen [133,226,227,232–234], made of different grades of steel, is a typical phenomenon for the in-situ hydrogenation during their operation. In such cases, hydrogen entered into metal typically during the local acidic corrosion of steels - the source of hydrogen, mainly provoked by chlorine with the simultaneous action of other electrochemical corrosion processes [35,36,133].

In 2016, Djukic et al. [36] proposed a special model-concept for the structural integrity analysis, prevention and prediction of HE in steel [13,112], Fig. 13. The model complied with the previously developed HELP + HEDE model in steels [10,13,35,36,112,224]. In accordance with the proposed HELP + HEDE model (Fig. 14), Djukic et al. [36] concluded that at the lower hydrogen

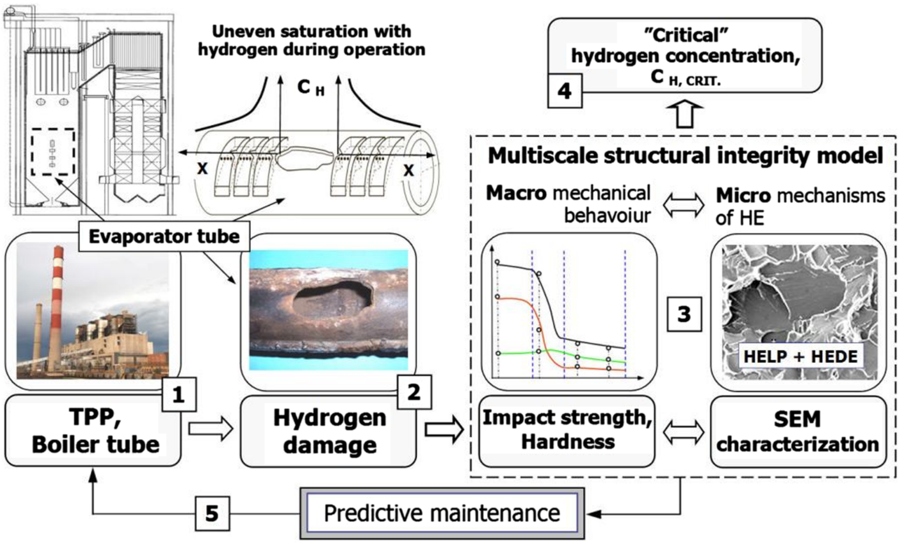

Fig. 12. The special multiscale approach for investigation of the coexistence of the HELP and HEDE mechanisms (HELP + HEDE model [34]): (1) Industrial component, thermal power plant -TPP boiler tube; (2) Hydrogen damage of boiler evaporator tube unevenly saturated with hydrogen during exploitation; (3) Application of a structural integrity model-correlation between material macromechanical behavior and simultaneously active HE micro-mechanisms; (4) Assessment of hydrogen critical concentrations; (5) Predictive maintenance activities [36,112]. "Reprinted from Proc. Struct. Integr., 2, Djukic MB, Bakic GM, Sijacki Zeravcic V, Rajicic B, Sedmak A, Mitrovic R, et al., Towards a unified and practical industrial model for prediction of hydrogen embrittlement and damage in steels, 604–611, Copyright, The Authors (2016), Open access funded by European Structural Integrity Society under a creative commons license CC BY-NC-ND 4.0".

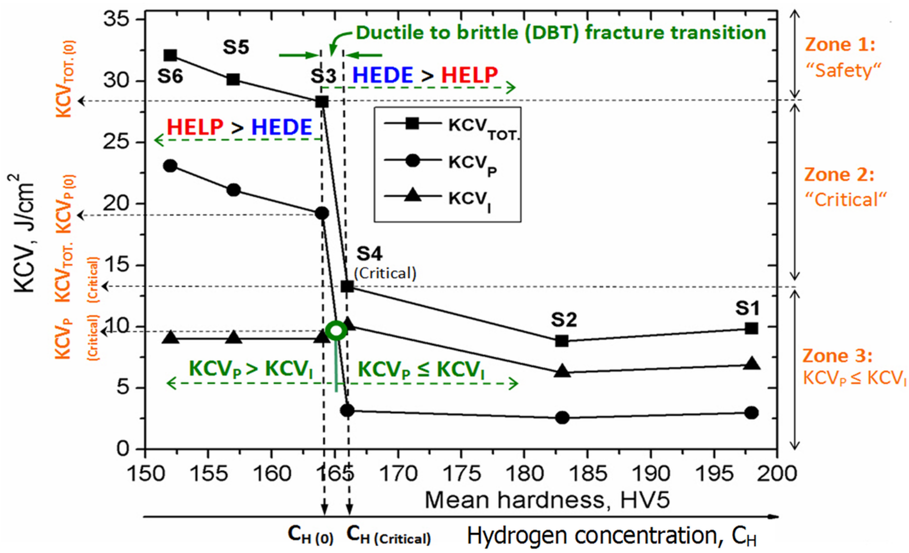

Fig. 13. The special model for a structural integrity analysis and prediction of HE in industrial components based on the HELP + HEDE model, HELP (HELP > HEDE) and HEDE (HEDE > HELP) dominance [13,36]: Variation of impact strength ($KCV_{TOT.}$), and its crack propagation energy component (KCV_P), and crack intiation energy component (KCV_I) as a function of the specimen hardness (hydrogen concentration). Zone 1 - "Safety" ($KCV_{TOT.(Measured)} > KCV_{TOT.(0)}$), Zone 2 - "Critical" ($KCV_{TOT.(0)} > KCV_{TOT.(Measured)} > KCV_{TOT.(Critical)}$), and Zone 3 - $KCV_{TOT.(Measured)} < KCV_{TOT.(Critical)}$ and/or $KCV_P \leq KCV_I$. Ductile to brittle fracture (DBT) transition; two characteristic values of hydrogen concentrations in a steel are $C_{H(0)}$ and $C_{H(Critical)}$. Adapted from [36]. "Reprinted and adapted from Eng. Fail. Anal., 58, Djukic MB, Sijacki Zeravcic V, Bakic GM, Sedmak A, Rajicic B., Hydrogen damage of steels: A case study and hydrogen embrittlement model, 485–498, Copyright (2015), with permission from Elsevier".

concentration (specimens S5 and S3, Fig. 14) the HELP mechanism is dominant (HELP > HEDE).

The HELP dominance (HELP > HEDE) has provoked an increase in a ductile MVC fracture mode of pearlite microconstituent (MVC > > TG) within the mixed "QC" - like fracture mode of an initial ferrite-pearlite microstructure [36], Fig. 14b. Consequently, the two distinctive fracture features (MVC + TG) within the mixed "QC" - like fracture mode, as a result of synergistic HELP + HEDE

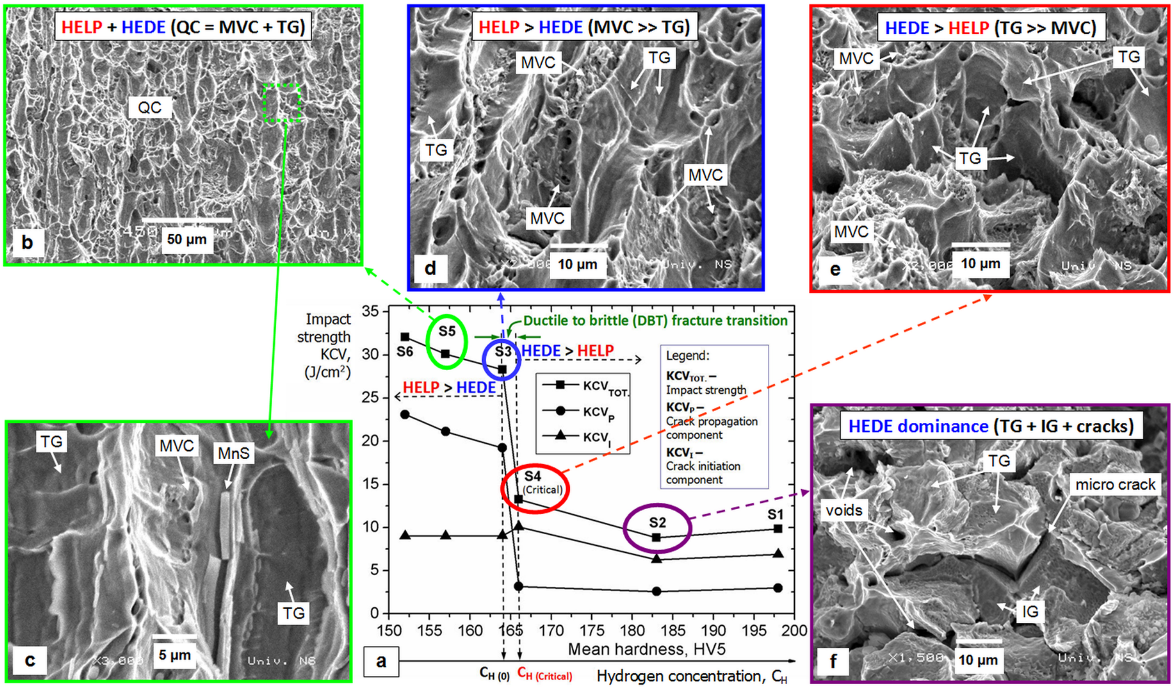

Fig. 14. HELP + HEDE model in steels: Variation of impact strength ($KCV_{TOT.}$) and its crack propagation component (KCV_P) and crack initiation component (KCV_I) of Charpy specimens (S1-S6), as a function of the specimens hardness (hydrogen concentration); (b-f) SEM fractographs of the fracture surfaces of Charpy specimens (S2-S5) [36]. "Reprinted and adapted from Eng. Fail. Anal., 58, Djukic MB, Sijacki Zeravcic V, Bakic GM, Sedmak A, Rajicic B., Hydrogen damage of steels: A case study and hydrogen embrittlement model, 485–498, Copyright (2015), with permission from Elsevier".

activity, could be observed, Fig. 14b–d. The observed mixed "QC"- like fracture mode is similar to plasticity related hydrogen induced cracking (PRHIC) [235]. The HE mechanisms, one or more, which lead to this imprecisely defined "QC"- like fracture mode, still are not uniquely defined. [9,13,23,24,36,235,236]. The observed dimples (specimen S3) in the MVC fracture mode are mostly elongated and parabolic with a somewhat corrugated appearance, Fig. 14d [13]. This indicates localized plasticity and ductile tearing and also implying that the local shear fracture was enhanced by the HELP mechanism activity [114,186,237,238].

However, there still is not a sharp drop in mechanical - impact properties at the characteristic value of hydrogen concentration ($C_{H(0)}$) lower than the critical ($C_{H(Critical)}$), Fig. 14a - specimens S3 and S5. The first characteristic hydrogen concentration is $C_{H(0)}$, beginning from which hydrogen significantly affects impact strength of material $KCV_{TOT.}$, particularly its component KCV_P. The second one is the critical concentration $C_{H(Critical)}$ [13], Figs. 13 and 14a. The prevailing TG of ferrite (TG > > MVC) with significantly reduced plasticity (MVC-mode) in the mixed "QC" - like fracture mode (TG + MVC) for specimen S4 compared to S3 is a consequence of the increased activity of HEDE mechanism (HEDE > HELP), Fig. 14e.

This is the result of more intensive local in-situ (during operation) hydrogenation of specimen S4, which leads to the local reaching of the critical hydrogen concentration ($C_{H(Critical)}$). The prevalence of the HEDE mechanism (HEDE > HELP) is followed by a sharp drop in impact strength ($KCV_{TOT.}$) due to the decline of a crack propagation component (KCV_P) for S4 compared to S3, Fig. 14a - specimen S4. Further drop in impact strength ($KCV_{TOT.}$) is observed on the instrumented Charpy machine in the case of specimen S2 (HEDE dominance) [36]. An additional drop in impact strength for specimen S2 compared to S4 was due to a drop in a crack initiation component (KCV_I) at the hydrogen concentration higher than the critical ($C_H > C_{H(Critical)}$), Fig. 14a - specimen S2.

Simultaneous action of both HE mechanisms (HELP + HEDE) is responsible for the decline in ductility and drop in the impact properties of a low carbon heat resistant steel [13,36]. However, the impact of the HELP dominance (HELP > HEDE), or the HEDE dominance (HEDE > HELP) during their synergistic action (HELP + HEDE) on the crack initiation and crack propagation components of the impact strength, are rather different. The effects of increasing the hydrogen content in the specimens (S5-lowest, S3, S4, S2-highest) on the impact properties ($KCV_{TOT.}$ and its components: KCV_I and KCV_P) under the synergistic, and competitive action of HE mechanisms (HELP + HEDE) were further analyzed, Fig. 14. The effects of the HELP dominance (HELP > HEDE) on impact properties are characterized by a moderate drop in KCV_P (specimen S5: $C_H < C_{H(0)}$ and S3: $C_H = C_{H(0)}$) with a steady value of KCV_I. Local reaching of the critical hydrogen concentration produces a sharp drop in KCV_P and $KCV_{TOT.}$, consequently (specimen S4: $C_H = C_{H(Critical)}$), with a negligible rise of KCV_I value. Further, the effects of the HEDE dominance (HEDE > HELP) on impact properties are characterized by a moderate drop in KCV_I with a very slight additional drop in KCV_P (specimen S2: ($C_H > C_{H(Critical)}$). There are two trends in the impact properties decline for specimens S4: $C_H = C_{H(Critical)}$ and S2: $C_H > C_{H(Critical)}$ which both characterize the predominance of the HEDE. The first trend is related to the observed sharp drop in KCV_P value after local reaching of the critical hydrogen concentration (S4). The second is related to the observed additional drop in $KCV_{TOT.}$ value due to KCV_I decline at the hydrogen concentration higher than the critical (S2), Fig. 14a - specimens S4 and S2 [36]. Both of these trends in impact properties decline were not only the result of the HEDE mechanism activity (S4: HEDE > HELP, S2: HEDE dominance) and the cohesion strength decline, Fig. 14a. The other important synergistic factor is a noticeable decrease in the level of the localized plasticity with increasing hydrogen concentration and accompanying reduction of the HELP mechanism activity (HEDE > HELP) after severe hydrogenation [36]. Similar interpretation was proposed in the model based on the calculation of the microscopic critical stress intensity factor as a function of cohesive energy by Jok et al. [239]. The synergistic activity of HE mechanisms (HELP + HEDE model) was further considered by Dadfarnia et al. [15] and Teter et al. [240] in the case of the transition from ductile to brittle (IG) dominated fracture mode in β-titanium alloy after severe hydrogenation.

The local TG fracture with the larger flat and elongated facets, which are unlike typical cleavage (C) facets in steels [13], was also observed in the vicinity of elongated manganese sulfide - MnS inclusions (specimen S5) present in the initial microstructure [35,36], Fig. 14c. Such local TG fracture mode within the mixed "QC" - like mode (MVC + TG) indicates local reaching of a high hydrogen concentration above the critical at a typical trapping site (MnS inclusion) in steels [35,36,153]. During such local decohesion incidents, a global critical hydrogen concentration in the specimen S5 still was not reached (S5: $C_H < C_{H(Critical)}$). Consequently, there still is no significant drop in impact properties for specimen S5, Fig. 14a - specimen S5. On the other hand, the critical hydrogen concentration provokes HEDE dominance and a sharp drop of the impact properties, as in the case of S4: $C_H = C_{H(Critical)}$ and S2: $C_H > C_{H(Critical)}$ specimens. As an alternative criterion for reaching of $C_{H(Critical)}$ in steels, Djukic et al. [13] proposed the phenomenon that a KCV_P has become less than KCV_I ($KCV_P \le KCV_I$), Fig. 13 and 14a. This phenomenon is a consequence of increased activity and the global dominance of the HEDE mechanism (HEDE > HELP) with an increase in hydrogen concentration, Fig. 14a - specimens S4 and S2 [13,36]. The global HEDE dominance is further characterized by the prevalence of a brittle IG fracture mode in the mixed fracture mode (TG + IG + cracks) at a high hydrogen concentration much above the critical, Fig. 14f: specimen S2 [36].

Djukic et al. [36] also concluded based on the hardness measurement results that the hydrogen-assisted hardening exists, Fig. 14a. It is the result of the synergistic or a competing action of HELP and HEDE mechanisms (HELP + HEDE model). The degree of hardening depends on the hydrogen concentration in specimens (the rising trend: from S5 - lowest hardness up to S2 - highest hardness), Fig. 14a. The hardening is observed even when the hydrogen concentration is lower than the critical ($C_H < C_{H(Critical)}$) and when the HELP mechanism is dominant (HELP > HEDE) [36]. These findings are in accordance with results of HE studies indicating hydrogen-provoked hardening after severe electrochemical hydrogen charging in low carbon steels [35,112,116,143] and austenitic stainless steels [116]. The enhancement in the mobility of dislocations due to hydrogen, as a continuous function of hydrogen concentration, was detected over a wide range of hydrogen concentrations [10,15,239,240]. The degree of activity of the HELP mechanism in steels also strongly dependent on the hydrogen concentration [35,36,112], material-environment-mechanical loading influences, and metallurgical factors [241]. The activity of the HELP mechanism or other possible and active plasticity-mediated HE mechanisms can become minor, but not completely negligible with the increase of hydrogen content in steels. Especially, when the hydrogen content approaches the critical hydrogen concentration or when it is much higher [13,35,112,224]. Accordingly, the influence of the HELP mechanism on the abrupt loss in ductility at a high-critical hydrogen concentration, and particularly at even higher hydrogen concentration than the critical one, is rather questionable. In such cases, based on the experimental research of HE in a low carbon ferritic-pearlitic heat resistant steel [35,112,155,156], TWIP steels [204,208], and high-strength steels [205–207], it seems that effects of HELP were practically insignificant or completely excluded. Consequently, the corresponding regime of a "dominant decohesion" (dominance of the HEDE mechanism of HE) corresponds with specific hydrogen-deformation interactions in steels at high hydrogen concentrations above the critical [13,36,223].

Recently (2014–2019), numerous researchers have adopted the previously analyzed HELP + HEDE model [36] for explanation of the hydrogen-induced MVC, QC, C, TG, and IG fracture modes in steels and switching from one mode to another (ductile-mixed-brittle mode) [34–36,62,74–76,155–162,165,166], see Tables 2 and 3. The experimental studies of active HE mechanisms and the coupled modeling-experimental studies provided similar interpretations and conclusions (HELP + HEDE model). Research studies include experimental HE studies in: (i) low carbon heat resistant steels [13,36,112,155,156,223]; (ii) low alloy heat resistant steels [159,165]; (iii) high-strength steels [62,76,157]; (iv) stainless steels [74,75,152,158]; and (v) iron [163]. Also, there are other HE studies based on the coupled modeling-experimental approach in stainless steel [161] and high-strength steel [160], as well as based on the modeling approach only in iron [67,127,150,166]. More details about these experimental findings for the specific microstructural features and H trapping sites affected by the activity of a particular mechanism (HELP, HEDE), or HELP + HEDE, in accordance with both HELP + HEDE and HELP mediated HEDE models, are presented in the final Section 3. Also, the corresponding fracture modes due to both HE mechanisms activities in steels, together with the hydrogen charging and mechanical testing methods, are summarized in Tables 3 and 4.

Still, it seems that there are four open questions about the true connection between the HELP (or other plasticity-mediated HE mechanisms) and the HEDE mechanisms within the proposed HELP + HEDE model [13,36]:

(1) What is the importance and effects of hydrogen-dislocation/GB interactions at high hydrogen concentrations above the critical one?
(2) What are the governing factors for interconnectedness and the possible domination of the HELP, AIDE, HESIV, HELP mediated HEDE, HELP + HEDE or HEDE mechanism exclusively?
(3) Is the HELP mechanism the only governing and always predominant HE mechanism at low hydrogen concentrations much below the critical one and/or at low-stress conditions?

(4) What is the true meaning of the term “critical hydrogen concentration” at different scales (macro, micro-meso, and nano-atomic) as a probable prerequisite for activation and dominance of the HEDE mechanism?

3. Summary about the synergy of hydrogen-enhanced plasticity and decohesion

A lot of research has been devoted to revealing the correlations between the microstructure of different grades of steels and the active HE mechanisms. The results commonly indicate the activity and dominance of a particular HE mechanism or the synergistic actions of different mechanisms, depending on the adopted experimental conditions. The diffusible hydrogen is generally recognized as one of the dominant factors responsible for HE in steels [21,141]. The diffusion of hydrogen in steels and iron is strongly influenced by different trapping sites in the steel microstructure, like GBs, phase interfaces, precipitates, vacancies, microvoids, etc. [21,27,37,141,241–243].

Therefore, the focus in this final section is on the summary of experimental results that have revealed the coexistence of both HE mechanisms, HELP and HEDE, in total four different grades of steels. It is necessary to carefully analyze the microstructural characteristics of a particular steel grade and hydrogen trapping sites affected by the activity of a particular mechanism (HELP or HEDE), or due to their simultaneous action [36]. The next step is to correlate the corresponding fracture modes affected by both HE mechanisms activities as a function of the local-critical hydrogen concentration in steels and applied experimental conditions. In order to clearly explain the multifaceted aspects, differences and similarities between the synergistic action of HELP and HEDE mechanisms in steels, a comprehensive overview of experimental findings are given in Table 3. The hydrogen charging method and mechanical testing method used in particular listed research are also given. The microstructural features/hydrogen (H) trapping sites predominantly affected by the activity of a particular HE mechanism, in accordance with both HELP + HEDE and HELP mediated HEDE models, are also displayed in Table 3. Also, the corresponding fracture modes due to both HE mechanisms activities are presented. In order to highlight the influence of individual mechanism during their synergistic action in steels, the specific microstructural features/H trapping sites and fracture modes affected by a particular HE mechanism are specially designated in Table 3. Both, the HELP mechanism activity and dominance prior to the HEDE mechanism activation and the HEDE mechanism activity and dominance in the case of the HELP + HEDE or HELP mediated HEDE models, are marked. They are separated with the “/” sign in both cases and correspondingly designated as HELP/(+)HEDE and HELP/(mediated) HEDE.

The dominance of HELP or HEDE or both mechanisms in accordance with the proposed HELP + HEDE model [36] (Section 2.3) and previously considered HELP mediated HEDE model are also indicated. The HELP + HEDE is designated with the “[1]” sign, while the HELP mediated HEDE model is designated with “[2]” sign in Table 3.

The indicative example of a specific microstructure and trapping sites and fracture modes affected by the dominance of HELP or HEDE or both mechanisms, presented in Table 3, looks like: “The microstructural features and H trapping sites”: (pearlite/ferrite, MnS, pearlite-ferrite interfaces)[1 or 2] “Fracture modes due to”: (MVC/MVC, QC, C, cracks)[1 or 2]. The explanation for this indicative example is that findings are in accordance with the [1] - HELP + HEDE model and the [2] - HELP mediated HEDE model. Further, the microstructure affected by HELP is pearlite; microstructures affected by HEDE are ferrite, MnS, and pearlite-ferrite interfaces; the fracture mode due to the HELP activity is MVC; and the fracture modes due to the HEDE activity are MVC, QC, C, and cracks.

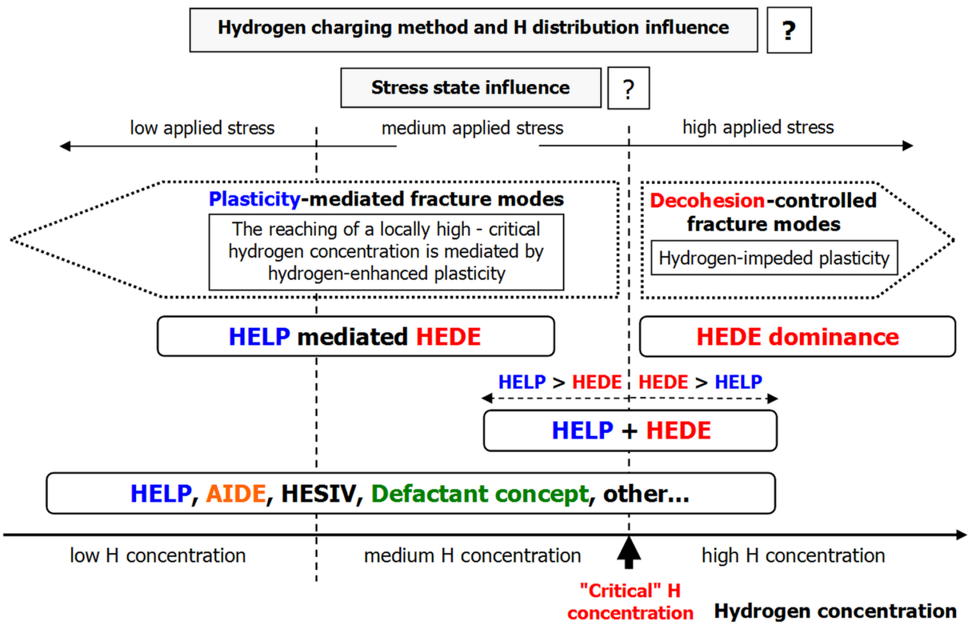

Fig. 15. Summary of the unified model for synergistic interplay of HE mechanisms in steels: localized plasticity and decohesion (HELP + HEDE model).

The following backgrounds for a unified model for the synergistic interplay of HE mechanisms (HELP + HEDE and HELP mediated HEDE) in steels are proposed and given in Table 4. The model background is based on findings summarized in Table 3, presented conclusions (HELP + HEDE model [13,36]) in previous sections, and a critical overview of the extensive published literature related to the synergistic action of HE mechanisms in steel and iron. It places emphasis on the specific microstructural locations/hydrogen trapping sites affected by the activity and dominance of a particular mechanism (HELP and HEDE) in the total of four different grades of steels. The following grades of steel were considered: (i) low carbon steels; (ii) low alloy heat resistant steels; (iii) high-strength steels; and (iv) stainless steels. Also, the corresponding fracture modes and features obtained due to the dominance of the HELP and HEDE mechanisms, including the transition mode from the localized plasticity dominance to the decohesion dominance (transition HELP → HEDE), were listed. These fracture modes were conditioned by different applied hydrogen charging and mechanical testing methods used in different HE studies. The dominance of a particular HE mechanism depends on the realized hydrogen concentration in steel during the experimental hydrogen charging. Total hydrogen concentration, diffusion, distribution, and a local concentration at the microstructural locations/trapping sites also strongly depends on the material-environment-mechanical loading conditions [10,13,36,137,143,225–227] and metallurgical factors [241–243]. Various methods for hydrogen charging and mechanical testing were used in studies that tackled the synergistic effect of the HE mechanisms, Table 4.

These include the electrochemical in-situ (during operation) method and experimental (laboratory) electrochemical or gaseous charging methods. The effects of using different hydrogen charging and mechanical testing methods on the synergistic effect of the mechanisms and their dominance in various applied experimental approaches are extremely difficult to estimate. This primarily referes to the influence of used hydrogen charging [94,115,116] and the mechanical testing [205,206,244] methods on the hydrogen content, distribution and concentration gradient, as well as the global/local stress state in the material.

Nevertheless, the proposal for the unified model for synergistic interplay of HE mechanisms in steels: localized plasticity and decohesion (HELP + HEDE model) is shown in Fig. 15.

This schematic diagram is an attempt to systematize a large number of recent research studies (see Tables 3 and 4 for references) that clearly pointed out the synergistic influence of HE mechanisms in steels and iron, critically analyzed in this review paper. The proposed dependence between the hydrogen-provoked localized plasticity and the decohesion processes, typical controlled fracture modes and the hydrogen concentration also emphasized the necessary further HE research trends. Therefore, the underlying multifaceted effects of hydrogen charging conditions, applied mechanical testing methods and stress state influence on the hydrogen-deformation interactions (operative HE mechanisms) in steels were still marked with question marks.

Finally, it is important that the emergence of the intrinsic embrittlement and the dominant brittle TG and IG fracture modes or a predominance of ductile MVC/mixed “QC” fracture modes due to the increase of plasticity depends on the choice of experimental conditions, Fig. 15. The most influential parameters used during experimentation are hydrogen charging methods (electrochemical versus gaseous; in-situ versus ex-situ) and mechanical testing methods (SSRT versus high strain rate testing), or computational modeling parameters. The lower hydrogen concentrations and stress conditions, including lower stress rates during mechanical testing, favor the activity of plasticity-mediated HE mechanisms, as well as HELP, Fig. 15. Contrary, the dominance of decohesion and the HEDE mechanism is more probable at higher hydrogen concentrations and stress conditions, plus higher stress rates during mechanical testing. The interlinked processes primarily controlling the transition from ductile to brittle dominated fracture mode are (i) local accumulation of stresses due to enhanced localized plasticity; (ii), hydrogen-deformation interactions; and (iii) hydrogen diffusion conditions and its local accumulation. Very often, the choice of experimental conditions precludes the possibilities for proper detection of the coexistence and synergistic activity, or competing effects of both HELP and HEDE mechanisms of HE [13,36,224], Fig. 15.

Therefore, the implementation of new and contemporary future critical experiments which will involve the possibility of proper and simultaneous validation of the contribution of:

(1) mobile hydrogen-deformation interactions (HELP and other plasticity-mediated HE models);
(2) decohesion processes (HEDE) at different microstructural locations and hydrogen trapping sites at critical hydrogen concentration;
(3) interactions between the HELP and HEDE mechanisms (HELP + HEDE);
(4) hydrogen-assisted hardening and softening phenomena;
(5) governing HE mechanisms responsible for the hydrogen-induced fracture, corresponding ductile-, mixed- and brittle-fracture modes and transition modes;

is of utmost importance to achieve a unified model for HE based on the synergy between localized plasticity and decohesion (HELP + HEDE model) in steels, iron and other metallic materials.

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