

International Journal of Minerals, Metallurgy and Materials 矿物冶金与材料学报(英文版)



# Review on the design of high-strength and hydrogen-embrittlement-resistant steels

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Cite this article as:

Zhiyu Du, Rongjian Shi, Xingyu Peng, Kewei Gao, and Xiaolu Pang, Review on the design of high-strength and hydrogenembrittlement-resistant steels, *Int. J. Miner. Metall. Mater.*, 31(2024), No. 7, pp. 1572-1589. https://doi.org/10.1007/s12613-024-2900-1

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# Review on the design of high-strength and hydrogen-embrittlementresistant steels

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(Received: 26 September 2023; revised: 27 March 2024; accepted: 2 April 2024)

**Abstract:** Given the carbon peak and carbon neutrality era, there is an urgent need to develop high-strength steel with remarkable hydrogen embrittlement resistance. This is crucial in enhancing toughness and ensuring the utilization of hydrogen in emerging iron and steel materials. Simultaneously, the pursuit of enhanced metallic materials presents a cross-disciplinary scientific and engineering challenge. Developing high-strength, toughened steel with both enhanced strength and hydrogen embrittlement (HE) resistance holds significant theoretical and practical implications. This ensures secure hydrogen utilization and further carbon neutrality objectives within the iron and steel sector. Based on the design principles of high-strength steel HE resistance, this review provides a comprehensive overview of research on designing surface HE resistance and employing nanosized precipitates as intragranular hydrogen traps. It also proposes feasible recommendations and prospects for designing high-strength steel with enhanced HE resistance.

Keywords: hydrogen embrittlement; surface design; hydrogen traps; nanosized precipitates

# 1. Introduction

In the context of the emerging challenges posed by the scarcity of nonrenewable resources, the energy crisis, and the objectives of carbon peak and carbon neutrality, the steel industry has become a pivotal sector in driving the "dual carbon" strategy [1-4]. The development of high-strength and high-toughness steel, as an inevitable trend toward material lightweight optimization [5-6] and energy efficiency and carbon emission reduction, is particularly significant [7-10]. However, the issue of hydrogen embrittlement (HE) in highstrength steels, whether during manufacturing processes (e.g., smelting, rolling, heat treatment, welding, and electroplating) or during storage, transport, and service, remains a critical bottleneck hindering their application and development [11-14]. Moreover, the higher the strength of the steel, the greater its susceptibility to HE, thus intensifying the problem [15-21].

HE susceptibility significantly affects a material's performance in hydrogen-rich environments, primarily manifesting as an increased tendency for brittle fracture upon hydrogen exposure. Key indicators for assessing this susceptibility include necking or elongation rate, tensile strength, fracture toughness, reduction of area, slow strain rate testing (SS-RT), hydrogen-induced cracking (HIC) phenomena, hydrogen diffusion and trapping characteristics within a material, and hydrogen permeation rate [22–26]. These indicators are evaluated by comparing the performance of materials in environments with and without hydrogen.

Historically, since the first discovery of HE in 1875, numerous scholars have conducted in-depth research on the anti-HE properties and service safety of metal materials, achieving significant progress [27–28]. This includes establishing various HE theories and addressing the issue in lowstrength steels. In recent years, with the advancement of theoretical calculations [29–30] (e.g., first-principle calculations, molecular dynamics simulations, and machine learning) and experimental characterization techniques [31–32] (e.g., threedimensional atom probe technology and *in-situ* transmission electron microscopy), research into hydrogen traps and anti-HE properties in high-strength steels has deepened, providing robust support for designs against HE.

Despite this, the trend toward higher strength and toughness in metal materials has posed even more severe challenges for the anti-HE properties of high-strength steel [33]. In the context of this new era, the safe utilization of hydrogen energy has become a primary focus for the future development of the hydrogen energy industry, with solving the issue of HE being a crucial task. Currently, the primary engineering methods for hydrogen removal include vacuum degassing and stack cooling. These traditional processes are effective in removing some diffusible hydrogen produced during manufacturing. However, their impact is limited to the substantial hydrogen that enters a material during service.



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Therefore, the development of high-strength steels with excellent resistance to HE, combined with high toughness and green, low-carbon characteristics, is of significant practical and strategic importance for safely utilizing hydrogen energy and achieving carbon peak and carbon neutrality goals.

This paper systematically reviews the design concepts of high-strength steel with enhanced HE resistance. It emphasizes two crucial approaches: surface design and intragranular hydrogen traps design. Regarding surface design, approaches involving alloying, surface coatings, and passivation are explored. These techniques aim to establish barrier layers that hinder hydrogen permeation or limit its entry into material interiors, thereby effectively delaying HE. In the design of intragranular hydrogen traps, the effects of factors (e.g., the types of nanosized precipitates, lattice matching, and capture sites) on the efficiency of hydrogen traps are explored. Finally, based on these findings, several prospects are put forward for the design of high-strength hydrogen-resistant steel.

# 2. Design concepts for high-strength hydrogenresistant steel

The current mechanisms of HE in high-strength steels include the hydrogen pressure mechanism, hydrogen-enhanced local plasticity (HELP) model, hydrogen-enhanced decohesion mechanism (HEDE), adsorption-induced dislocation emission (AIDE), hydrogen reduction of surface energy mechanism, and hydrogen-enhanced strain-induced vacancies mechanism (HESIV), among others. The following is a brief introduction to these mechanisms:

(1) Hydrogen pressure mechanism [34].

After being absorbed by a metal surface, hydrogen atoms diffuse inward and accumulate in microstructural defects, such as voids or cracks. This accumulation leads to a significant increase in internal pressure within the defect areas, reducing the local strength of the metal and promoting the expansion of cracks, ultimately resulting in material fracture.

(2) HELP [35–37].

This mechanism proposes that the interaction between hydrogen atoms and dislocations within the metal lattice facilitates the movement of dislocations, particularly in areas of stress concentration (such as crack tips), leading to enhanced plastic deformation. The increase in localized plastic deformation promotes the initiation and propagation of cracks, thereby resulting in the HE of a material.

(3) HEDE [38-40].

The HEDE mechanism, first proposed in 1926, suggests that the accumulation of hydrogen atoms within a metal, particularly around microstructural defects (e.g., grain boundaries and dislocations), significantly weakens the interatomic bonding forces in these areas. This weakening reduces the material's cohesion, increasing the likelihood of crack formation and propagation in these weakened regions. Consequently, the material may undergo brittle fracture even under relatively low external stresses.

(4) AIDE [41–42].

The AIDE mechanism proposes that the adsorption of hy-

drogen atoms reduces the binding energy of atoms on the metal surface, thereby facilitating the formation and emission of dislocations. These newly generated dislocations enhance the local plastic response of the material. However, they may also lead to the formation and expansion of cracks, consequently causing HE in the material.

(5) Hydrogen reduction of surface energy [43].

The adsorption or diffusion of hydrogen atoms on a metal surface leads to a reduction in surface energy, which in turn causes a continuous decrease in the critical stress required for crack instability and expansion, ultimately leading to cracking.

#### (6) HESIV [44-45].

During the plastic deformation of metals, vacancies or nanoscale voids accumulate. The ingress of hydrogen into the material promotes the nucleation and growth of these vacancies or microvoids. The aggregation of these vacancies or voids, under the influence of hydrogen, rapidly leads to the formation and expansion of cracks, ultimately resulting in HE.

Although each of the six mechanisms reveals different pathways and impacts of hydrogen within materials, the occurrence of HE in actual material applications often results from the combined action of multiple mechanisms [46-47]. Specifically, HELP and HEDE are regarded as key factors in promoting HE behavior in many high-strength steels. These mechanisms do not always act independently but instead, through interaction and their synergistic effect, jointly affect a material's sensitivity to HE. That is, the HELP mechanism increases local plasticity by facilitating dislocation movement, which may lead to more areas of plastic deformation under low-stress conditions. Meanwhile, the HEDE mechanism, by weakening metallic bonds, makes the material more susceptible to fracturing in these areas of plastic deformation [48–50]. This collaborative effect results in high-strength metals potentially displaying unanticipated brittleness when exposed to hydrogen under specific conditions.

Furthermore, beyond the direct synergistic effect of HELP and HEDE, recent research has introduced the HELP-mediated HEDE model, further deepening our understanding of the interaction mechanisms of HE. In this model, hydrogen initially boosts local plasticity via HELP, which, at the microscale, alters the internal stress distribution within the material, thereby providing more favorable conditions for the HEDE mechanism. In essence, the localized plasticity enhanced by the HELP mechanism can "mediate" the HEDE mechanism, making the otherwise unlikely or weaker decohesion effects significantly more pronounced and thereby promoting crack formation and expansion [50-51]. The introduction of this model not only revealed the complex interactions among HE mechanisms but also offered new perspectives and challenges for designing high-strength steels resistant to HE.

Having delved into the major mechanisms of HE, let us now pivot to discussing the countermeasures against these mechanisms, specifically critical design concepts for highstrength, hydrogen-resistant steels. These mainly include the

following aspects: reduction of environmental hydrogen exposure, minimization of internal hydrogen concentration. mitigation of internal stress (especially in stress concentration regions), development of hydrogen-blocking coatings (e.g., face-centered cubic metals and oxide protective coatings), incorporation of hydrogen-resistant grain boundaries design, and implementation of dispersed hydrogen traps. The design of hydrogen resistance surfaces primarily involves the controlled accumulation of alloving elements on a material's surface. This design aims to achieve the following objectives: (1) reduce the adsorption energy to inhibit the dissociation of hydrogen molecules (or water molecules); (2) facilitate the recombination of hydrogen atoms into hydrogen molecules, promoting their subsequent release; (3) enhance the energy barrier for hydrogen diffusion from the surface to the interior, effectively preventing hydrogen ingress into the material's core and thus augmenting its resistance to HE.

In addition to designing hydrogen-resistant surfaces, hydrogen inevitably permeates into the interior of materials, often accumulating at defects such as grain boundaries and impurities, thereby leading to HE. Random grain boundaries serve as deeper hydrogen traps, and the accumulation of hydrogen at these boundaries can compromise their strength. To mitigate hydrogen enrichment at grain boundaries, apart from indirectly reducing hydrogen concentration (e.g., through intragranular hydrogen traps design), the hydrogen-resistant grain boundaries design strategy can be employed. This approach aims to decelerate or prevent intergranular cracking induced by HE. In this regard, researchers such as Zhong et al. [52] investigated HE in martensitic stainless steel subjected to constant stress and hydrogen exposure. Their findings revealed that hydrogen-induced intergranular cracking exhibited selectivity and predisposition, with high-energy, low-coincidence, and large-angle grain boundaries being more susceptible to cracking. Conversely, low-energy, highcoincidence, and low- $\Sigma$  boundaries can suppress HE cracks. Furthermore, refining the grain size can enhance hydrogen resistance because smaller grains reduce the hydrogen concentration per unit area of the grain boundaries and minimize strain localization.

The following sections focus on reviewing the applications of hydrogen-resistant surface design and deep intragranular hydrogen traps design within the development of high-strength hydrogen-resistant steel.

# 3. HE-resistant surface design

Enhancing material surfaces for HE resistance involves the implementation of surface passivation films or coatings. By creating hydrogen-blocking layers on or beneath a material's surface, hydrogen ingress is prevented or minimized, thus effectively preventing or delaying the occurrence of HE.

## 3.1. Introduction of alloying elements

Generally, the introduction of alloying elements to metal materials can induce changes in surface structures, resulting

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in alterations in the kinetics of hydrogen adsorption and other surface processes. When alloying elements preferentially accumulate at the material surface and form a dense passivation film, they can effectively hinder the penetration of hydrogen into the material, thus reducing the internal hydrogen content and consequently improving HE resistance. For instance, aluminum (Al) can form a dense oxide film on the material surface. Park et al. [53] investigated the effect of different Al contents (0-2wt%) on the HE resistance of twinning-induced plasticity (TWIP) steel. The results showed that TWIP steel with trace amounts of Al displayed superior HE resistance. This was mainly attributed to the significant reduction in the diffusible hydrogen content entering the material interior after the addition of Al, with higher Al content leading to lower diffusible hydrogen content. This outcome stemmed from the existence of a dense (Fe<sub>0.8</sub>Mn<sub>0.2</sub>)O layer covered with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, which acted as an effective barrier against hydrogen penetration into the material interior. Although Al has a significant impact on the material surface structure, its influence on internal precipitation and twinning microstructures must be accounted for, as these factors contribute to variations in HE performance [54–56].

Likewise, the incorporation of silicon (Si) into Fe–18Mn– 0.6C–xSi TWIP steel (0–3wt%) was studied by Lee *et al.* [57]. Si addition was found to partially inhibit the hydrogen content entering the material interior. This effect was attributed to the formation of a dual-layer oxide, (Fe,Mn)O and (Fe,Mn)<sub>2</sub>SiO<sub>4</sub>, on the material surface. However, the HE susceptibility of the Si-added samples increased. This phenomenon was primarily attributed to the resultant suppression of twinning in the steel due to the addition of Si, leading to the formation of  $\varepsilon$ -martensite phase transformation. Thus, although the addition of microalloy elements can create an oxide film on the material surface to hinder hydrogen ingress into the interior, its influence on the material's inherent structure cannot be underestimated.

## 3.2. External surface coatings

Besides incorporating microalloying elements into the material matrix to form surface barrier layers, extensive research has shown the application of external surface coatings for designing and developing hydrogen-resistant layers. These coatings, such as oxides, nitrides, carbon materials, metals, and alloy coatings [35,58–60], can slow down or even prevent hydrogen permeation, thereby enhancing a material's resistance to HE.

3.2.1. Oxide coatings

Oxide coatings represent one of the earliest studied categories of hydrogen-resistant coating materials. These include various oxides, such as Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Er<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>. Some coatings have been extensively researched and applied in the design of high-strength hydrogen-resistant steels.

The formation of an oxide protective layer on the material surface can effectively enhance its HE resistance. For instance, Ladicicco *et al.* [61] developed a multifunctional

Al<sub>2</sub>O<sub>3</sub> coating that could address tritium permeation and lead–lithium corrosion simultaneously. By optimizing the pulsed laser deposition process, they successfully obtained a fully dense Al<sub>2</sub>O<sub>3</sub> film with a permeation reduction factor (PRF) exceeding  $10^4$ . Combined with the mechanical effects obtained in another study [62], the growth of Al<sub>2</sub>O<sub>3</sub> thin film demonstrated their potential as protective coatings against HE. Meanwhile, Hatano *et al.* [63] prepared a 180-nm-thick ZrO<sub>2</sub> coating on a ferritic steel surface using dip-coating and electrolytic deposition techniques. The coating exhibited excellent HE resistance, and a thinner 100-nm coating showed an order of magnitude of improvement in PRF during hydrogen permeation testing at 300–500°C.

Lu *et al.* [64] developed a  $\text{TiO}_2/\text{TiC}_x$  composite coating using a two-step process of carbon ion implantation and oxidation under ultralow oxygen partial pressure. As shown in Fig. 1, the  $\text{TiC}_x$  layer contained numerous nanocrystals. These high-density grain boundaries could act as hydrogen traps. The composite coating oxidized at 550°C exhibited the lowest carrier concentration, indicating a lower defect density, which could effectively reduce hydrogen permeation. The oxide layer maintained high stability in the hydrogen environment, serving as an excellent hydrogen barrier. Additionally, free carbon atoms in the substrate provided addi-



Fig. 1. TEM images of samples oxidized at 550°C before (a) and after (e) carbon ion implantation. (b) and (f) are local enlarged views of the coating; (c), (d), (g), and (h) are HR-TEM images of the area bounded by the box [64]. Reprinted from *Int. J. Hydrogen Energy*, 45, Z.X. Lu, Q.Y. Zhou, Y.H. Ling, *et al.*, Preparation and hydrogen penetration performance of  $TiO_2/TiC_x$  composite coatings, 14048-14061, Copyright 2020, with permission from Elsevier.

tional hydrogen capture sites, and the abundance of nanocrystals in the TiC layer further inhibited hydrogen diffusion. 3.2.2. Nitride coatings

Nitride coatings belong to a class of HE-resistant materials with significant research and application potential. Examples of such coatings include TiN, SiN, CrN, and AlN. These coatings form a nitride protective layer on the material surface, significantly enhancing its resistance to HE. In this regard, Tamura and Eguchi [65] investigated the hydrogen permeation characteristics of TiN-coated stainless steel and measured the grain size of the thin films. In comparison with the uncoated substrate, the thin film exhibited a reduction in hydrogen permeation rate by a factor of 100-5000. Moreover, larger grain sizes within the film corresponded to higher hydrogen permeation rates. Furthermore, as grain boundaries can serve as hydrogen traps, a polycrystalline microstructure with multiple grain boundaries can improve the hydrogen-blocking effect. Vincenč et al. [66] studied the hydrogen resistance performance of SiN coatings. They prepared SiN coatings on the surface of ferritic stainless steel using radiofrequency magnetron sputtering and evaluated the hydrogen resistance performance of the coatings using a gasphase hydrogen permeation method. The 500- and 700-nm thick films, prepared at 400°C, exhibited a PRF of up to 2000, highlighting their remarkable hydrogen barrier properties. Nevertheless, inadequate matching was observed to lead to a decline in PRF to 25 for the SiN coating. This decrease was attributed to the presence of cracks or voids on the coating surface, subsequently diminishing its hydrogen-blocking effectiveness.

#### 3.2.3. Carbon material coatings

MXene, with its two-dimensional nanosheet structure, can serve as a physical barrier to resist hydrogen permeation. Previously, Shi *et al.* [67] prepared an MXene coating on an X70 pipeline using a simple spin-coating method. The anti-hydrogen performance of the coating was evaluated through electrochemical hydrogen permeation testing and slow strain rate tensile experiments. The results showed that MXene improved the resistance to HE, with the permeation rate of the coating being one-third of the substrate, and the diffusion coefficient also decreased.

After that, another study [68] prepared multilayer graphene on an X70 pipeline steel using the ion implantation method, as shown in Fig. 2(a). This structure can increase the diffusion path and time for hydrogen (Fig. 2(b)). Compared with the base material, the hydrogen diffusion coefficient of the multilayer graphene is reduced by 123 times, and the hydrogen permeability is reduced by 48 times, demonstrating excellent hydrogen resistance.

In another study, Yang *et al.* [69] designed a novel graphene oxide (GO)–Al<sub>2</sub>O<sub>3</sub> composite coating as a deuterium (D) permeation barrier using the sol–gel method. At 500°C, the PRF of 0.5wt% GO–Al<sub>2</sub>O<sub>3</sub> composite coating was nine times higher than that of the pure Al<sub>2</sub>O<sub>3</sub> coating. The improvement can be attributed to the ability of GO nanosheets to hinder D diffusion.



Fig. 2. (a) Microstructure of the graphene coating. (b) Hydrogen blocking mechanism of graphene [68]. Reprinted from *Appl. Surf. Sci.*, 573, K.J. Shi, S. Xiao, Q.D. Ruan, *et al.*, Hydrogen permeation behavior and mechanism of multi-layered graphene coatings and mitigation of hydrogen embrittlement of pipe steel, 151529, Copyright 2022, with permission from Elsevier.

#### 3.2.4. Metal and alloy coatings

Jeon *et al.* [70] investigated the influence of Zn coating on the surface of hot-dip galvanized TWIP (HDG\_TWIP) steel on HE. The Zn-coated steel reduced susceptibility to HE, as shown in Fig. 3(a). This outcome could be attributed to the role of the  $\eta$ -Zn layer and Fe–Zn intermetallic compound layer as effective hydrogen traps, possessing activation energy of approximately 70 kJ/mol and thus effectively impeding hydrogen ingress (Fig. 3(b)). Nevertheless, the presence of a brittle Fe–Zn intermetallic compound layer led to a slight reduction in elongation compared with the base material.

Yoo *et al.* [71] controlled the Al–Si coating and heat treatment conditions on the surface of 22MnB5 high-strength steel to tailor the microstructure and coating thickness. By suppressing the formation of the Fe<sub>2</sub>Al<sub>5</sub> phase and promoting the body-centered cubic FeAl layer, the hydrogen introduced during the coating process was rapidly diffused out through the coating, thereby enhancing the high-strength HE resistance steel.

Cadmium, tin, and nickel can also serve as protective coatings on steel surfaces [72]. The diffusion coefficient of hydrogen in these coatings is significantly lower than that in ferrite. Nickel coatings have a similar effect because of the presence of hydrogen traps. Research has also shown that, compared with other elements, Cr more readily forms Cr–H bonds [73]. Additionally, Cr can provide more valence electrons, leading to the formation of stable Cr–H bonds [74], which can enhance the hydrogen resistance of the coating. However, the brittleness of pure Cr coatings makes them more prone to cracking. Therefore, Cr alloy coatings are typically used [75].

#### 3.2.5. Multilayer structured coatings

Yamabe *et al.* [76] examined the impact of layered structures on hydrogen-blocking performance. They prepared two types of Al-based multilayer films using a hot-dip-coating method: a two-layer (Al<sub>2</sub>O<sub>3</sub>/Fe–Al) and a three-layer (Al<sub>2</sub>O<sub>3</sub>/Al/ Fe–Al) Al-based coating. After exposure to hydrogen gas at 100 MPa and 270°C for 200 h, the three-layer coating demonstrated superior resistance to hydrogen permeation. This enhanced performance was speculated to be due to the combined effects of Al<sub>2</sub>O<sub>3</sub>, Al, and Fe–Al in inhibiting hydrogen ingress. In another study, Zheng *et al.* [77] successfully developed a layered Cr/Cr<sub>x</sub>N coating on a substrate using an innovative electroplating-based nitridation technique. This coating achieved a deuterium PRF of 3599 at 500°C, which is one of the highest values reported so far.



Fig. 3. Effects of different Zn contents on the HE of TWIP steel: (a) engineering stress–strain curves of TWIP, TWIP<sub>H</sub> (the H-charge TWIP specimen), HDG\_TWIP, and HDG\_TWIP<sub>H</sub> (the H-charge HDG\_TWIP specimen); (b) H desorption rate curves of TWIP, HDG\_TWIP and HDG\_TWIP<sub>H</sub> [70]. Reprinted from *Corros. Sci.*, 111, H.H. Jeon, S.M. Lee, J. Han, I.J. Park, and Y.K. Lee, The effect of Zn coating layers on the hydrogen embrittlement of hot-dip galvanized twinning-induced plasticity steel, 267-274, Copyright 2016, with permission from Elsevier.

In addition, Jo et al. [78] designed multilayer structures to achieve excellent HE resistance in high-strength steel. Through a combination of heating, rolling, and heat treatment, they developed two sandwich-structured 1.2-GPagrade multilayer steels: "martensitic steel-TWIP-martensitic steel" (MTM) and "TWIP-martensitic steel-TWIP" (TMT). TMT steel exhibited significantly superior resistance to HE compared with the MTM structure, as shown in Fig. 4(a) and (b). Hydrogen trap capacities analysis unveiled that TMT steel contained lower hydrogen content and higher hydrogen traps binding energy. Moreover, fracture observation revealed that MTM steel exhibited interfacial delamination and intergranular fracture between martensitic steel and TWIP steel, whereas TMT steel showed partial quasi-cleavage brittle fracture, with the rest being ductile fracture, as shown in Fig. 4(c)–(e). Although this design approach differed from the creation of surface passivation films or coatings, the fundamental concept remained the same, which was to use hydrogen barrier layers to inhibit hydrogen ingress into the material. This approach aimed to reduce internal hydrogen content and immobilize hydrogen through the design of "hydrogen traps", curbing its rapid diffusion and accumulation,

thereby mitigating HIC.

The design of an anti-HE surface is a complex system that must consider both blocking hydrogen from entering the material from the environment and ensuring rapid hydrogen effusion during the preparation process. This presents a delicate balance that must be carefully coordinated. From an anti-HE perspective, the fundamental goal is to avoid hydrogen enrichment at grain boundaries, impurities, and other defects, which can lead to HE.

# 4. Design of hydrogen traps in high-strength steels

In high-strength martensitic steels, various defects, including point defects (e.g., vacancy and solute atom), line defects (e.g., dislocation), planar defects (e.g., phase and grain boundaries), and volumetric defects (e.g., precipitated phase and impurities), are abundant and can act as hydrogen traps, thus influencing HE performance [79]. Therefore, systematically analyzing and understanding the hydrogen trap capacities of different microstructures in martensitic steels is of crucial importance for studying their HE behavior. In such



Fig. 4. Effects of multilayer structures on the HE resistance of steel: the SSRT tests on (a) the MTM sheet and (b) the TMT sheet; (c) H desorption-rate curve obtained via thermal desorption spectroscopy (TDS); (d) SEM fractography images for the MTM sheet at a current density of 3 mA/cm<sup>2</sup>; (e) high magnification image of the Mart layer near the interface [78]. Reprinted from *Mater. Sci. Eng. A*, 800, M.C.Jo, M.C.Jo, J. Yoo, *et al.*, Strong resistance to hydrogen embrittlement via surface shielding in multi-layered austenite/martensite steel sheets, 140319, Copyright 2021, with permission from Elsevier.

complex microstructural environments, the dissolution and diffusion behaviors of atomic hydrogen in lattice interstices are particularly crucial. Atomic hydrogen dissolved in lattice interstices can diffuse into hydrogen traps, whereas hydrogen captured in these traps can also escape back into the lattice interstices. Upon reaching equilibrium, the following significant relationship is established:

$$K = C_{\rm T}/C_{\rm L} = \mathrm{e}^{E_{\rm b}/RT} \tag{1}$$

where *K* is the reaction equilibrium constant;  $C_T$  is the equilibrium concentration of hydrogen in traps, ppm;  $C_L$  is the equilibrium concentration of hydrogen in lattice interstices, ppm;  $E_b$  is the binding energy of hydrogen traps, kJ/mol; *R* is the gas constant, 8.314 J·mol<sup>-1</sup>·K<sup>-1</sup>; *T* is the absolute temperature, K.

From Eq. (1), it can be concluded that the binding energy of hydrogen traps,  $E_{\rm b}$ , is an important parameter of hydrogen traps, indicating the strength of the trap's ability to capture hydrogen. Building on this discussion, it must be noted that experimental measurements generally provide activation energies, whereas simulation calculations yield binding energy. The difference between the activation energy and binding energy is typically in the range of 6.9-8.7 kJ/mol (known as the saddle-point energy associated with lattice diffusion activation energy) [80–81]. For the sake of simplicity and analysis in the following research and summary, we ignored this difference and uniformly used the term "hydrogen traps binding energy" to represent both while acknowledging their existence. By selecting and analyzing 208 data sets from nearly a hundred papers, which essentially cover all hydrogen traps currently studied in the research, we obtained Fig. 5. Detailed sources of the statistical data on hydrogen traps can be found in previous studies [15,18,80,82-100]. The collected hydrogen traps data were categorized into eight types: vacancy, solute atom, dislocation, phase boundary, grain boundaries, precipitated phase, impurities, and other (such as tetrahedral and octahedral interstitial sites). By statistically analyzing the hydrogen trap capacities of different microstructures and defects in martensitic steels, a deeper understanding of their hydrogen-trapping nature can be achieved, guiding the design and control of hydrogen traps to obtain high-strength and HE-resistant steels [20].

Fig. 5 presents a summary of hydrogen traps binding energy in different microstructures of martensitic steels, where "Atom" refers to the solute atom. The comparison is presented in box plot format with upper whisker, upper quartile, median, mean, lower quartile, and lower whisker values. Fig. 5 illustrates significant variations in hydrogen trap capacities among different microstructures in martensitic steels, and each microstructure's hydrogen traps binding energy data exhibit considerable dispersion. This indicates that factors such as different microstructural parameters and research methods can influence the hydrogen traps binding energy. Particularly, for the precipitated phase, its hydrogen traps binding energy exhibits significant fluctuations and randomness, ranging from approximately 10 to 150 kJ/mol, and the calculated values align well with experimental values. Because of the diverse types, compositions, and microstructural parameters (e.g., size and coherency) of the precipitated phase in martensitic steels, the differences among various precipitated phases may have contributed to the fluctuation and randomness observed in the statistical hydrogen traps binding energy.

#### 4.1. Influence of different types of nanosized precipitates

Because precipitated phases can act as deep hydrogen traps and are less prone to HIC, the previously mentioned nanosized precipitates may serve as excellent hydrogen traps, thereby achieving the purpose of resisting HE. Therefore, in this section, we discuss the influence of various types of nanosized precipitates on the HE susceptibility of martensitic high-strength steels [101–110].

Martensitic steels contain a wide variety of nanosized precipitates. In the field of HE research, carbides have been the most extensively studied and widely recognized nanosized



Fig. 5. Summary of hydrogen traps binding energy in different microstructures of martensitic steels as compiled in this study.

precipitates used in designing resistance to HE. Therefore, using the same method, we obtained Fig. 6, which represents the hydrogen traps binding energy data for different types of nanoprecipitates. We selectively collected, statistically analyzed, and summarized the hydrogen traps binding energy of dislocation, grain boundaries, VC, TiC, NbC, and other precipitates, as shown in Fig. 6. The category "other precipitates" mainly includes cementite, copper nanosized precipitates, and others. The statistical results indicate that VC, TiC, NbC, and other carbides have been widely studied and that their hydrogen traps binding energies varied, generally exceeding those of grain boundaries. Meanwhile, other nanosized precipitates exhibited relatively lower binding energies, with some even approaching the binding energy of dislocation. Next, we summarized and discussed the effects of VC, TiC, NbC, and other nanosized precipitates on HE on the basis of the current research status.

## 4.1.1. VC nanosized precipitates

VC has been widely studied as an effective hydrogen trap. In recent years, with the development of advanced characterization techniques, such as the three-dimensional atom probe (3DAP), the characterization of VC's resistance to HE has become more intuitive and has made significant progress in both theoretical calculations and experimental characterizations.

To investigate the interaction between VC and hydrogen, Echeverri Restrepo *et al.* [80] used density functional theory (DFT) calculations. They compared the solubility of hydrogen at different sites and found that, although the perfect interface had weak hydrogen adsorption capability, carbon vacancies (both at the interface and within VC) significantly enhanced hydrogen adsorption, indicating a tendency for hydrogen to preferentially accumulate at the vanadium carbide interface. Meanwhile, Shi *et al.* [111] achieved an excellent HE resistance and satisfactory work hardening capability in high-strength spring steel through multi-microalloying with

1.04wt% Cr and 0.14wt% V. This process resulted in the precipitation of cementite/VC, which acted as effective hydrogen traps, thereby reducing the HE susceptibility by 23%. Dong et al. [112] studied the effect of V and Re microalloying on the HE of Fe-18Mn-0.6C TWIP steel using a lowspeed linearly increasing stress test. They found that the VC precipitate dispersed mechanical twins, transforming brittle cleavage fracture surfaces from flat and smooth to tortuous and rough. This microalloying technique increased the HE resistance of TWIP steel by 0.20wt%. Lee et al. [99] conducted a detailed study on the resistance to HE of VC nanosized precipitates. They replaced Mo with V in NIMS17 steel and added 0, 0.20wt%, 0.50wt%, and 1.01wt% V to the Fe-0.60C-2.00Si-0.20Mn-1.00Cr (wt%) base alloy. The research results showed that with the increasing V content, the size and quantity of VC precipitated phase increased; however, when the V content reached 1.01wt%, large unsolved VC appeared, leading to susceptibility to HE. As the V content increased, a higher hydrogen trap capacities was achieved, but 0.20wt% V steel exhibited the best HE resistance among the studied samples.

Takahashi *et al.* [113] and Chen *et al.* [114] used 3DAP technology to directly observe the distribution of D on VC interfaces in experimental steels after D charging. Most D atoms were distributed on large VC particles (plate-like particles ranging from tens to a few hundred nanometers) rather than small VC particles (a few nanometers). Additionally, semicoherent disc VC exhibited stronger hydrogen trap capabilities. This has allowed the study of VC's resistance to HE to enter the stage of atomic-scale direct observation. Regarding the mechanism of VC's HE resistance, specifically how VC interacts with hydrogen, hydrogen is believed to enrich the carbon vacancy at the (001) interfaces of V<sub>4</sub>C<sub>3</sub> and the iron matrix [115]. However, some researchers propose that hydrogen may be associated with defects at the interface of VC and the matrix [100] or that hydrogen could accumu-



Fig. 6. Summarized chart of hydrogen traps binding energy for dislocation, grain boundaries, VC, TiC, NbC, and other precipitated phases in this study.

# late inside VC [116].

# 4.1.2. TiC nanosized precipitates

Research on the HE resistance of TiC has been conducted in-depth and thoroughly, including macroscopic, microscopic characterizations, and theoretical calculations. Current studies mainly focus on investigating the hydrogen trap sites at different interfaces of TiC nanosized precipitates.

Wei and Tsuzaki [81] studied the evolution of TiC nanosized precipitates with different degrees of coherency (orientation relationship) with the iron matrix and their interaction with hydrogen, as shown in Fig. 7. With the increase in tempering temperature, the orientation relationship between the TiC nanosized precipitates and the matrix changed from the Baker–Nutting semicoherent relationship (550°C tempering) to a noncoherent interface relationship (1000°C tempering), as shown in Fig. 7(a)-(f). The size of TiC gradually increased to a steady-state value, and the morphology transformed from plate-like to spherical, as shown in Fig. 7(g). TDS curves for different tempered samples are shown in Fig. 7(h). The authors suggested that the TDS peaks for samples tempered at low temperatures (<500°C) mainly occurred at low temperatures (~120°C) and were mainly generated by dislocation. With the increase in tempering temperature, the TDS peak shifted to higher temperatures (~230°C) for samples tempered at 500-550°C. For samples tempered at temperatures higher than 550°C, the low-temperature peak split into two, and the TDS peak at 520–60°C was attributed to noncoherent TiC. In the case of semicoherent TiC, hydrogen could only be trapped at the interfaces and could be electrochemically absorbed at room temperature with adsorption of 1.3 H/nm<sup>2</sup>, and the amount of hydrogen adsorption was related to the interface area. However, noncoherent TiC could only trap hydrogen during high-temperature tempering, with hydrogen traps located inside the particles (tetrahedral carbon vacancy); it could not trap hydrogen electrochemically charged at room temperature. Additionally, the activation energies for hydrogen traps in semicoherent and noncoherent TiC particles were different, measured as 55.8 and 68–137 kJ·mol<sup>-1</sup>, respectively.

Fang *et al.* [117] investigated the impact of TiC precipitates on hydrogen absorption capability, noting that a significant potential difference existed between the TiC precipitates and the matrix after hydrogen charging, especially at the phase interface. Consequently, TiC precipitates were proven to be effective hydrogen capture sites. Depover and Verbeken [98] conducted a series of TDS, SSRT, and analyses in their study on HE in Ti-containing steel. Under the same conditions of electrochemical hydrogen charging, the TiC-containing tempered samples showed higher HE compared with quenched samples. This was attributed to the higher hydro-



Fig. 7. Morphologies of TiC nanosized precipitates and their orientation relationship with the matrix at different tempering temperatures: (a) 550°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C, and (f) 1000°C; (g) variation of TiC size and shape with tempering temperature; (h) TDS spectra of samples after electrochemical hydrogen charging at different tempering temperatures [81]. Reprinted by permission from Springer Nature: *Metall. Mater. Trans. A*, 37, Quantitative analysis on hydrogen trapping of TiC particles in steel, F.G. Wei and K. Tsuzaki, Copyright 2006.

gen content in the tempered samples under the same hydrogen charging conditions. However, after being charged with the same amount of hydrogen, the tempered samples exhibited superior resistance to HE. These experiments demonstrated that TiC nanosized precipitates possess superior resistance to HE. In another study, Jun *et al.* [118] used the 3DAP technique to directly observe hydrogen traps in TiC nanosized precipitates at the atomic level. They showed that hydrogen accumulated at the interfaces of nanoscale TiC precipitates. This observation not only provided a new experimental approach for the three-dimensional observation of TiC nanosized precipitates and their hydrogen traps distribution but also offered a feasible means for inhibiting HE by utilizing TiC.

In the first-principle calculations regarding the HE resistance of TiC nanosized precipitates, Di Stefano et al. [101] investigated the interaction between hydrogen and different interfaces of TiC particles and the iron matrix. These interfaces included coherent interface, semicoherent interface, mismatched dislocation, and carbon vacancy. The computational results demonstrated that the most effective hydrogen adsorption site was the carbon vacancy inside the TiC particles, with a binding energy exceeding 1 eV (equivalent to 96.5 kJ/mol). However, because of its high energy barrier, hydrogen traps at carbon vacancies were not feasible at room temperature. The semicoherent interfaces between TiC particles and the iron matrix were more favorable for hydrogen adsorption, with a binding energy of -0.32 eV. The core of the mismatched dislocation also exhibited a binding energy of -0.50 eV. The presence of a large number of nanosized precipitates reduced the hydrogen content at dislocation in the matrix, thereby suppressing HE.

#### 4.1.3. NbC nanosized precipitates

Compared with VC and TiC, there has been relatively less research on the HE resistance of NbC nanosized precipitates. However, the application of Nb microalloying has become a recent research focus, leading to an increased interest in the study of NbC resistance to HE, which has shifted from macroscopic performance experiments to more microscopic investigations.

In this respect, Zhang et al. [119] explored the effect of NbC precipitates on the HE of martensitic steel using methods such as slow strain rate tensile testing, hydrogen permeation experiments, 3DAP, and microstructural examination. They found that the higher the content of NbC, the lower the susceptibility to HE. Meanwhile, Wallaert et al. [110] conducted transmission electron microscopy (TEM) observations and TDS experiments to study the hydrogen trap capabilities of NbC nanosized precipitates under different heat treatment conditions. The TDS experiments were performed using both electrochemical hydrogen charging and high-temperature gas-phase hydrogen charging. Under electrochemical hydrogen charging conditions, TDS curves exhibited peaks in the range of 300-500 K (27-227°C). Meanwhile, with high-temperature gas-phase hydrogen charging, because of the presence of large-sized NbC, peaks appeared in the range of 700-900 K (427-627°C). Based on the TDS fitting results, the activation energy for small-sized NbC was determined to be in the range of 39–48 kJ/mol, whereas it was in the range of 63–68 kJ/mol for large-sized NbC.

Ohnuma *et al.* [120] employed the small-angle neutron scattering (SANS) technique to investigate the SANS curves of samples containing NbC nanosized precipitates before and after hydrogen charging and after high-temperature hydrogen annealing. The SANS curve intensity was higher after hydrogen charging, which was different from the states without hydrogen or after hydrogen removal, thereby indirectly inferring the trapping effect of NbC on hydrogen.

Chen *et al.* [121] utilized the cryo-transfer 3DAP technique to directly observe the hydrogen traps by NbC for the first time. In their study, they charged D into the experimental steel containing NbC (Fe–0.23C–0.92Mn–0.24Si– 0.049Nbwt%) and observed the hydrogen enrichment at the interfaces of ellipsoidal NbC nanoscale particles. Meanwhile, Shi *et al.* [122] conducted high-resolution transmission electron microscopy (HRTEM) observations, DFT calculations, and TDS experiments to reveal that the mismatched dislocation cores at the semicoherent interfaces between NbC and the matrix were the origins of deep hydrogen traps in NbC. This finding provided a theoretical basis for further controlling NbC to achieve high-strength and HE-resistant steels, as illustrated in Fig. 8.

Furthermore, Wei *et al.* [123] conducted a comparative study on the hydrogen trap capabilities and structure differences of NbC, TiC, and VC nanosized precipitates. In experimental steels containing the same molar fractions of NbC, TiC, and VC subjected to the same heat treatment process, the hydrogen trap capabilities followed the order NbC > TiC > VC. Furthermore, through the characterization of the structures of NbC, TiC, and VC nanosized precipitates under the same heat treatment conditions, it was found that they had differences in size and structure. These results suggest that the mismatch degree varied among the three nanosized precipitates. Therefore, NbC nanosized precipitates exhibited stronger hydrogen trap capabilities. However, at present, there is no direct and conclusive evidence to accurately determine the hydrogen trap sites of NbC.

4.1.4. Other nanosized precipitates

In addition to the studies on VC, TiC, NbC, and other nanosized precipitates mentioned above, there have been research investigations on the HE resistance of other nanosized precipitates, such as (Ti,Mo)C [15,124], NbN [110], and cementite [124–126]. Furthermore, studies have been conducted on the HE resistance of retained austenite or reverse transformation austenite in martensitic steels [127]. These research efforts collectively contribute to the study of hydrogen traps and play a crucial role in the design of high-strength and HE-resistant steels by controlling internal microstructures to prevent hydrogen accumulation within a material.

# 4.2. Influence of hydrogen trap sites in nanosized precipitates

The coherency of nanosized precipitates has a significant impact on hydrogen traps, mainly because of the variations in



Fig. 8. (a, b) HRTEM observation of misfit dislocations at NbC/ $\alpha$ -Fe semicoherent interfaces, where the " $\perp$ " symbols and the Burgers circuits (dashed-line circuit) indicate high-density misfit dislocations,  $b^{(1)}$  and  $b^{(2)}$  are the two sets of misfit dislocations. (b) Enlarged image corresponding to the green dotted zone in (a). (c, d) Comparison of hydrogen traps capabilities and HE resistance, where  $E_a$ ,  $\phi$ , and  $T_p$  are the hydrogen desorption activation energy, heating rate, and desorption peak temperature, respectively. (e) First-principle calculation study: the (001) NbC/ $\alpha$ -Fe coherent interface with the Baker–Nutting (B–N) orientation relationship (OR) before (e<sub>1</sub>) and after (e<sub>2</sub>) hydrogen segregation; the (001) NbC/ $\alpha$ -Fe coherent interface with the Kurdjumov–Sachs (K–S) OR before (e<sub>5</sub>) and after (e<sub>4</sub>) hydrogen segregation [122]. Reprinted from *Acta Mater.*, 200, R.J. Shi, Y. Ma, Z.D. Wang, *et al.*, Atomic-scale investigation of deep hydrogen trapping in NbC/ $\alpha$ -Fe semi-coherent interfaces, 686-698, Copyright 2020, with permission from Elsevier.

hydrogen trap sites. To better understand and comprehend the hydrogen trap sites of nanosized precipitates at different coherency levels and consequently utilize this knowledge for designing nanosized precipitates to enhance the HE resistance of martensitic high-strength steels, this section explores the physical nature of hydrogen trap sites in nanosized precipitates using statistical results from relevant literature.

First, we conducted a statistical analysis of the most extensively studied nanosized precipitates, including coherent interfaces, interface carbon vacancy/mismatched dislocation, and internal carbon vacancy, as referenced previously [50,115,128–133]. The results of this analysis, which demonstrated the influence of these nanosized precipitates phase trapping sites on hydrogen trap energy, are presented in Fig. 9. This figure was created by comprehensively processing and analyzing the collected data, illustrating the specific effects of different nanoprecipitates phase trapping sites on hydrogen traps binding energy. The statistical results revealed that the hydrogen trap energy at coherent interfaces was very low (averaging 27 kJ/mol), even lower than that of dislocation (averaging 29 kJ/mol). The leading hydrogen trap sites at coherent interfaces were in tetrahedral interstitial positions [134], originating from the elastic strain fields caused by phase mismatch. For interface carbon vacancy and mismatched dislocation, their hydrogen trap energies was higher (averaging 53 kJ/mol), surpassing that at grain boundaries (averaging 45 kJ/mol). However, for internal carbon vacancy, the hydrogen trap energies were significantly higher (averaging 97 kJ/mol).

Moreover, Di Stefano *et al.* [101] conducted first-principle calculations to systematically investigate hydrogen trap sites and their binding energies at different interfaces of TiC nanosized precipitates. Although coherent nanosized precipitates contribute to precipitation strengthening while maintaining plasticity, they are not suitable for designing deep internal hydrogen traps within nanosized precipitates to develop high-strength, HE-resistant steels as their hydrogen trap energies are too low to effectively capture hydrogen. Therefore, coherent interfaces are not suitable as deep hydrogen traps within nanosized precipitates when designing highstrength, HE-resistant steels.

In the following discussion, we focus on the interaction between hydrogen and interface carbon vacancy/mismatched dislocation, as well as internal carbon vacancy, which act as potential deep internal hydrogen traps. Distinguishing different hydrogen trap sites from an energetic perspective requires considering both the hydrogen traps binding energy and the energy barrier. On the one hand, in terms

of binding energy, the internal carbon vacancy has higher binding energy than the interface carbon vacancy/mismatched dislocation. On the other hand, from the viewpoint of energy barriers (saddle point energy), hydrogen must overcome a certain energy barrier to be trapped by the trap sites. However, different hydrogen traps may have different energy barriers; thus, the role of energy barriers in hydrogen traps must be considered. As shown in Fig. 10, the energy barrier for hydrogen diffusion to interface carbon vacancy/mismatched dislocation is equivalent to the diffusion energy barrier within the iron lattice [81] and is only 0.09 eV (8.7 kJ/mol) [101]. Therefore, hydrogen can be easily captured by interface carbon vacancy/mismatched dislocation through lattice diffusion at room temperature or under conditions like electrochemical hydrogen charging. Meanwhile, the energy barrier for hydrogen to enter internal carbon vacancy is much higher, reaching 1.61 eV (155 kJ/mol). Consequently, internal carbon vacancy cannot efficiently trap hydrogen at room temperature (e.g., under electrochemical hydrogen charging conditions) but can only capture hydrogen during high-temperature heat treatment [81]. Although a continuous network of carbon vacancy connecting from the precipitated phase interface to the interior phase can possess both high binding energy and relatively low energy barriers, the probability of forming such a carbon vacancy network is low, resulting in a very low hydrogen trap densities  $(10^{-10}-10^{-9} \text{ mol/mm}^3)$ , whereas the hydrogen trap densities of interface carbon vacancy is generally in the range of  $10^{-9}$ -10<sup>-7</sup> mol/mm<sup>3</sup> [131,135].

In summary, although internal carbon vacancies in nanosized precipitates have high binding energy, their trapping energy barrier for hydrogen is also very high, making it difficult for hydrogen to enter the internal carbon vacancies at room temperature. As high-strength steels are typically used and operated at room temperature, the use of internal carbon vacancy presents challenges in engineering practices to en-

![](_page_12_Figure_6.jpeg)

Fig. 9. Influence of hydrogen trap sites of nanosized precipitate phase on hydrogen traps binding energy as observed in this study.

![](_page_13_Figure_1.jpeg)

Fig. 10. Hydrogen binding energy obtained from first-principle calculations for different trapping sites [101]. Reprinted figure with permission from D. Di Stefano, R. Nazarov, T. Hickel, *et al.*, *Phys. Rev. B*, 93, 184108 (2016). Copyright 2016 by the American Physical Society.

hance HE resistance. Meanwhile, carbon vacancy/mismatched dislocation at the interfaces between nanosized precipitates and the matrix can balance both the binding energy and energy barrier requirements. Therefore, controlling the carbon vacancy/mismatched dislocation in nanosized precipitates can be effective as deep hydrogen traps to improve HE resistance.

Regarding carbon vacancy in nanosized precipitates, Takahashi et al. [115] directly observed hydrogen traps at the (001) coherent interface of the V<sub>4</sub>C<sub>3</sub> nanosized precipitate using 3DAP. They determined the V<sub>4</sub>C<sub>3</sub> nanosized precipitate to have a V/C atomic ratio of 4:3 from the 3DAP data, indicating the presence of sufficient carbon vacancy in the  $V_4C_3$ precipitate. Additionally, they observed D atoms localized at the (001) coherent interface of the nanosized precipitates, confirming the carbon vacancy at the interface as hydrogen trap sites. Furthermore, HRTEM was employed to investigate V<sub>4</sub>C<sub>3</sub> precipitates, and very few mismatched dislocations in V<sub>4</sub>C<sub>3</sub> were found. The limited presence of mismatched dislocation, especially in long  $V_4C_3$  precipitates with only two mismatched dislocations, ruled out the contribution of mismatched dislocation at the interface as hydrogen trap sites, ultimately confirming that carbon vacancy at the interface of  $V_4C_3$  nanosized precipitate acted as hydrogen trap sites.

Although interface carbon vacancies have been confirmed as the leading hydrogen trap sites in  $V_4C_3$  nanosized precipitates, as observed using 3DAP, the situation may be different for TiC and NbC. Unlike  $V_4C_3$ , TiC and NbC nanosized precipitates do not contain a significant number of carbon vacancies based on the ratio of metal atoms to carbon atoms. Therefore, interface carbon vacancies may not be the essence of their hydrogen traps. Although Wei *et al.* [136] observed interface mismatched dislocation in TiC nanosized precipitates, a systematic study on the nature of hydrogen traps at the interface mismatched dislocation in TiC and NbC nanosized precipitate is still lacking and remains a subject for further investigation.

## 4.3. Others

In the previous summary and discussion, we primarily fo-

cused on hydrogen traps in nanosized precipitates with coherent, semicoherent, and incoherent orientations to the matrix. However, when the steel contains a high content of microalloying elements, undergoes longer tempering times, or is tempered at higher temperatures, the formation of large undissolved particles or the coarsening of nanosized precipitates may occur [99]. These particles can reach sizes of several hundred nanometers or even micrometers and may have adverse effects on HE resistance.

In recent years, research on the nature of hydrogen traps in nanosized precipitates within grains and the mechanisms of HE resistance have been continuously deepening and broadening. Particularly, studies on hydrogen trap sites, contents, and HE resistance of single carbides in steel have made significant progress. The nature of hydrogen traps in single carbides is now well understood as mainly originating from defects in nanosized precipitates, such as interface mismatched dislocation and interface carbon vacancy. However, our current understanding and characterization of the nature of hydrogen traps and HE resistance mechanisms in complex nanosized precipitates in steel is still not comprehensive enough and remains at the basic level, focusing on single nanosized precipitates.

Recent research efforts have started to address this limitation. For example, Lin *et al.* [137] achieved a significant improvement in hydrogen traps by co-precipitating Cu and TiC through alloying treatments. Meanwhile, Zhao *et al.* [138] showed that multiphase nanosized precipitates in 7xxx aluminum alloys can effectively mitigate HE, but different nanosized precipitates had different hydrogen trap capabilities. Therefore, by leveraging the coupling effects of microalloying elements (e.g., Nb, Ti, V, and Mo), which are more conducive to forming hydrogen traps more readily, composite nanosized precipitates can be designed and regulated as excellent hydrogen traps, thus leading to effective strategies for HE resistance design [20].

#### 5. Conclusion and outlook

Amidst the rapid technological advancements and the

pressing imperative for carbon neutrality within our global society, the deployment of metallic materials, especially steel, has gained paramount importance across various sectors, including aerospace, marine engineering, offshore resource exploration, and the pursuit of lightweight automotive designs. These application fields have put forward an urgent need for high-strength and high-toughness materials, which has promoted the development of high-strength, HE-resistant steel in the scientific and engineering fields. However, HE in high-strength steels has emerged as a global challenge in the development of high-strength steels. To develop steels that are both high-strength and resistant to HE, a scientific understanding and in-depth comprehension of the nature of HE is imperative. This understanding should enable the targeted proposal of design concepts and implementation strategies to combat HE.

This article systematically reviewed various mechanisms of HE that have been proposed, including the hydrogen pressure mechanism, HELP, HEDE, AIDE, hydrogen reduction of surface energy, and HESIV. Although these mechanisms may seem contradictory, they emphasize different aspects, each with its own conditions and limitations. Frequently, in varying external environments and material systems, one mechanism may dominate, or several mechanisms may operate in conjunction. Fundamentally, the essence of HE is the reduction of atomic bonding strength by hydrogen. During service, the stress is within the elastic range, typically leading to intergranular cracking due to the continuous distribution of hydrogen at grain boundaries. Therefore, the design against HE can focus on preventing hydrogen ingress into materials, namely, through the design of hydrogen-resistant surfaces or by inhibiting the accumulation of hydrogen at grain boundaries, thereby reducing hydrogen concentrations at these critical locations to mitigate embrittlement. This discourse also delved into the two main directions in anti-HE designs: surface design for HE resistance and the current state of research on nanoprecipitates as internal hydrogen traps. In terms of surface design for HE resistance, it covers various types of coatings, including oxide coatings, nitride coatings, carbon material coatings, metal and alloy coatings, and multilayered coatings. Oxide coatings have been widely studied for their high barrier properties, whereas multilayered coatings are notable for effectively extending the hydrogen permeation path, among others. In the study of nanoprecipitates as internal hydrogen traps, attention was paid to the role of different types of nanoprecipitates and their capture sites in HE resistance, revealing the interaction between nanoscale structures and hydrogen, which is significant for the development of new high-performance materials.

In summary, the design against HE constitutes a comprehensive engineering endeavor that demands an understanding and formulation from various perspectives. It necessitates not only a thorough consideration of all contradictions but also adherence to scientific principles underlying HE resistance. Ultimately, this approach aims to achieve an optimization of overall performance enhancements.

# Acknowledgements

The work was financially supported by the National Key Research and Development Program of China (No. 2022YFB3709000), the National Natural Science Foundation of China (Nos. 52201060 and 51922002), the China Postdoctoral Science Foundation (Nos. BX20220035 and 2022M710347), Science Center for Gas Turbine Project (No. P2022-B-IV-008-001), and the Open Fund of State Key Laboratory of New Metal Materials, University of Science and Technology Beijing (No. 2022Z-18).

# **Conflict of Interest**

Xiaolu Pang is an editorial board member for this journal and was not involved in the editorial review or the decision to publish this article. The authors have no competing interests to declare that are relevant to the content of this article.

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