

**IMPACT OF ALLOYING ELEMENTS ON HYDROGEN ADSORPTION,
SOLUBILITY, AND DIFFUSION IN AUSTENITIC STAINLESS STEEL
FOR HYDROGEN ENERGY INFRASTRUCTURE APPLICATIONS:
A DENSITY FUNCTIONAL THEORY APPROACH.**

BY

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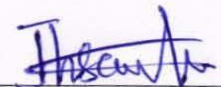
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DEDICATION

To my beloved parents,

Your endless love, sacrifices, and unwavering support have been the foundation of my journey.

To my dear wife,

Your patience, encouragement, and belief in me have carried me through the toughest times.

To my sisters and brothers,

Thank you for your constant inspiration, understanding, and love.

To my friends,

Your companionship and support have made this journey more meaningful.

This work reflects your influence in my life. I dedicate this thesis to all of you with deep gratitude and love.

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Table of Contents

ACKNOWLEDGMENTS	v
Table of Contents	vi
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF ABBREVIATIONS	xiv
ABSTRACT	xvii
ملخص الرسالة	xix
CHAPTER 1: INTRODUCTION	1
1.1 The Problems Fossil Fuels Cause for the Environment and the Search for Sustainable Alternatives.....	5
1.1.1 Effects on the Environment.....	5
1.1.2 The Effect of Fossil Fuels on the Economy.....	6
1.2 Hydrogen: An Essential Energy Source for Sustainable Solutions.....	6
1.3 Hydrogen as an Adaptable Energy Source for Renewable Energy Systems.....	7
CHAPTER 2: BACKGROUND AND LITERATURE REVIEW	9
2.1 Hydrogen Infrastructure: Storage and Transportation.....	9
2.1.1 Hydrogen Storage.....	9
2.1.2 Hydrogen Transportation.....	18
2.2 Metallic Structural Materials for High-Pressure Hydrogen Environment in Hydrogen Energy Systems.....	27
2.2.1 Materials Used in Hydrogen Storage Cylinders.....	29

2.2.2 Pipeline Material for Hydrogen Transportation.....	32
2.2.3 Materials Used in Hydrogen Refueling Stations.....	35
2.3 Hydrogen Embrittlement in Steel.....	40
Mechanisms of Hydrogen Embrittlement.....	41
2.3.1 Hydrogen-Enhanced Decohesion (HEDE).....	41
2.3.2 Hydrogen-Enhanced Localized Plasticity (HELP).....	42
2.3.3 Adsorption-Induced Dislocation Emission (AIDE).....	43
2.3.4 Hydrogen-Induced Phase Transformation (HIPT).....	44
2.3.5 Hydrogen-Enhanced Strain-Induced Vacancy (HESIV) Mechanism	45
2.3.6 Synergistic Models and Mixed Modes.....	46
2.4 Density Functional Theory (DFT).....	46
2.5 Structural Dependence of FCC Iron on Magnetic Model and Magnetization Magnitude.....	49
2.6 Hydrogen Interaction with Alloyed Iron Using DFT.....	59
CHAPTER 3: COMPUTATIONAL METHODS AND MODELING.....	63
3.1 First-Principles Simulations.....	63
3.2 FCC Iron Bulk.....	64
3.3 Hydrogen Adsorption.....	65
3.4 Hydrogen Solubility.....	67
3.5 Hydrogen Diffusion into and Through the Bulk.....	70
CHAPTER 4: RESULTS AND CONCLUSION.....	74

4.1 Adsorption Energy Results.....	74
4.2 Binding Energy Results.....	77
4.3 Diffusion Energy Barrier Results.....	82
4.3.1 Into the Bulk.....	82
4.3.2 Through the Bulk.....	85
4.4 Conclusion.....	90
References.....	92
Vitae.....	113

LIST OF TABLES

Table 2. 1 Materials used in hydrogen compressor diaphragms from different companies	37
Table 2. 2 Hydrogen adsorption results: Height (d_{H-surf}), Adsorption Energy (E_{ads}), Total Barrier for Diffusion ($E_{total_barrier}$), and Bulk Diffusion Energy (E_{bulk}) for 12 γ -Fe surface planes across four magnetic states: NM, FM, AFM1, and AFMD.	58
Table 2. 3 Simulation studies review on hydrogen interaction with BCC and FCC iron using DFT.....	60
Table 4. 1 The binding energy at different octahedral sites for the clean and doped bulks.....	80
Table 4. 2 The binding energy of hydrogen diffusion transition sites, energy barrier, and the total impact of alloying elements on hydrogen diffusion into the doped and clean bulks.	82
Table 4. 3 The activation energy for possible diffusion pathways in both clean and doped bulks.	85
Table 4. 4 The binding energy of hydrogen diffusion transition sites for the clean and doped bulks	87
Table 4. 5 The barrier energy of hydrogen jumps through the doped and clean bulks and the diffusion effective of barrier energy.....	88

LIST OF FIGURES

Fig 1. 1 The hydrogen energy cycle (13).	8
Fig 2. 1 Types of hydrogen storage	16
Fig 2. 2 A conventional on-board liquid hydrogen reservoir setup (21).	14
Fig 2. 3 Options for hydrogen transportation.	19
Fig 2. 4 Comparison of Long-Distance Hydrogen Transportation Methods(49).	25
Fig 2. 5 Different types of high-pressure hydrogen cylinders. (a) Type I, (b) Type II,	30
Fig 2. 6 Yield strength and RRA comparing pipeline steels and austenitic stainless steels (74–76).	33
Fig 2. 7 HRS main facilities.	36
Fig 2. 8 Traps of hydrogen in steels: a) interstitial sites; b) surface traps; c) subsurface traps; d) grain boundary; e) dislocation; f) vacancy (103).	41
Fig 2. 9 Diagrammatic representations of the HEDE process that show how atoms separate by tensile as a result of interatomic bonds being weakened by (i) hydrogen in the lattice, (ii) adsorbed hydrogen, and (iii) hydrogen at particle-matrix interfaces.	42
Fig 2. 10 Diagrammatic representation of the HELP mechanism, which involves a micro void- coalescence process that localizes and facilitates plasticity in areas with high hydrogen contents.	43
Fig 2. 11 Diagrammatic representation of the adsorption-induced dislocation emission (AIDE) process for Hydrogen environment embrittlement (HEE), which involves alternating-slip crack formation from fracture tips (for transgranular routes), allowing cracks to consolidate with voids created in the plastic zone before cracks (110).	44

Fig 2. 12	Diagrammatic representation of subcritical crack propagation that shows the creation and fracture of a brittle hydride at the tip of the crack, followed by hydrogen migration to hydrostatically stressed areas.....	45
Fig 2. 13	Diagrammatic representation of Hydrogen-Enhanced Strain-Induced Vacancy (HESIV) Mechanism.	45
Fig 2. 14	Combined effect of HEDE and HELP mechanism (111).	46
Fig 2. 15	Equation of State and the Corresponding Magnetic Moment Values of FCC (solid lines) and BCC (dashed lines) Iron. Diamonds refer to NM, Squares FM, Open Circles AFM1, and Filled Circles AFMD.....	51
Fig 2. 16	Equation of state of bcc and FCC iron with different magnetic structure.....	52
Fig 2. 17	The local magnetic moment (open circles) and total energy (solid squares) of FM FCC Fe as a function of lattice parameter.....	54
Fig 2. 18	Bulk c/a Ratios of (a) FM, (b) AFM1, and (c) AFMD FCC Iron.	56
Fig 2. 19	Surface Relaxation of (a) NM, (b) FM, (c) AFM1 and (d) AFMD FCC Iron.	56
Fig 3. 1	kinetic energy cutoff for wavefunctions (Ecutwfc) Convergence.	63
Fig 3. 2	Antiferromagnetic double-layer (AFMD) iron FCC Structure.	64
Fig 3. 3	K points convergence.....	65
Fig 3. 4	Schematic diagram of possible adsorption sites on the (001) FCC iron slab: (a) clean slab; the gray atom is iron, and the white atom is hydrogen. (b) doped surfaces with substitutional alloying elements; the yellow atom M stands for each of the seven substitutional alloying elements (Cr, Mn, Mo, Ni, P, S, and Si). (c) doped surfaces with interstitial alloying elements; the brown atom M stands for the two interstitial alloying elements (N and C).....	66

Fig 3. 5 2×2×2 supercell of FCC iron: the yellow atom stands for each of the seven substitutional alloying elements (Cr, Mn, Mo, Ni, P, S, and Si), and the brown atom stands for the two interstitial alloying elements (N and C).....	67
Fig 3. 6 Schematic diagram of possible interstitial sites in FCC iron supercell (a) Clean bulk: the gray atom is iron; the white atom is hydrogen located in octahedral site (Oct) or interstitial site (T). (b) Doped bulks with substitutional alloying elements: the yellow atom stands for each of the seven substitutional alloying elements (Cr, Mn, Mo, Ni, P, S, and Si). (c) doped bulks with interstitial alloying elements; the brown atom stands for the two interstitial alloying elements (N and C).	69
Fig 3. 7 Schematic diagram of hydrogen diffusion into the FCC iron bulk: (a) clean slab; the gray atom is iron, and the white atom is hydrogen; (b) doped surfaces with substitutional alloying elements; the yellow atom stands for each of the seven substitutional alloying elements (Cr, Mn, Mo, Ni, P, S, and Si). (c) doped surfaces with interstitial alloying elements; the brown atom stands for the two interstitial alloying elements (N and C).	71
Fig 3. 8 Schematic diagram of hydrogen diffusion through the FCC iron bulk: (a) clean bulk: the gray atom is iron, the white atom is hydrogen located in octahedral site (Oct) or interstitial site (T); (b) doped bulks with substitutional and interstitial alloying elements: the yellow atom stands for each of the seven substitutional alloying elements (Cr, Mn, Mo, Ni, P, S, and Si), and the brown atom stands for the two interstitial alloying elements (N and C). (We eliminate the second and third layers as well as a few atoms to get a better view of the pathways.). ...	73
Fig 4. 1 Hydrogen adsorption energies for clean and doped surfaces at each possible adsorption site.....	74
Fig 4. 2 Hydrogen adsorption energies for clean and doped surfaces at the hollow site.....	75

Fig 4. 3 (a-j) Differential charge density diagram of H adsorbed on the hollow in the clean and doped surfaces: Yellow regions indicate electron accumulation and blue regions represent electron depletion	56
Fig 4. 4 Hydrogen binding energy for both clean and doped bulks	57
Fig 4. 5 The overall effect of alloying elements on hydrogen binding energy (the red line represents the clean bulk)	59
Fig 4. 6 The overall effect of alloying elements on the barrier energy of hydrogen diffusion into the doped bulks compared to the clean bulk (the red line represents the clean bulk).....	84
Fig 4. 7 Schematic diagram of possible hydrogen jumps through the FCC iron-doped and clean bulks: The gray atom is iron, the white atom is hydrogen located in an octahedral site (Oct) or interstitial site (T), the yellow atom stands for each of the seven substitutional alloying elements (Cr, Mn, Mo, Ni, P, S, and Si), and the brown atom stands for the two interstitial alloying elements (N and C). (We eliminate the second and third layers as well as a few atoms to get a better view of the pathways)	89
Fig 4. 8 The effect of alloying elements on hydrogen diffusion effective barrier energy through the doped bulks compared to the clean bulk (the red line represents the clean bulk)	90

LIST OF ABBREVIATIONS

ABINIT	: Ab-initio software for Density Functional Theory calculations
AIDE	: Adsorption-Induced Dislocation Emission
AFM	: Antiferromagnetic structures
AFM1	: Single-layer antiferromagnetic
ASS	: Austenitic Stainless Steel
BCC	: Body-Centered Cubic
BMW	: Bayerische Motoren Werke AG (automotive company)
CcH ₂	: Cryo-compressed Hydrogen Storage
CGH ₂	: Compressed Gaseous Hydrogen Storage
CI-NEB	: Climbing-Image Nudged Elastic Band
CNTs	: Carbon Nanotubes
DFT	: Density Functional Theory
DOE (US-DOE)	: United States Department of Energy
E _{ads}	: Adsorption Energy
E _{bind}	: Binding Energy
E _{bulk}	: Bulk Diffusion Energy
E _{cutwfc}	: Kinetic Energy Cutoff for Wavefunctions
E _{Diff}	: Activation Energy of Diffusion
E _{total_barrier}	: Total Barrier for Diffusion
FCC	: Face-Centered Cubic

FCG	: Fatigue Crack Growth
FIBA Technologies, Inc.	: U.S.-based manufacturer of high-pressure gas cylinders
FLAPW	: Full Potential Linear Augmented Plane Wave
FM-HS	: Ferromagnetic High-Spin
FM-LS	: Ferromagnetic Low-Spin
GEV	: Global Energy Ventures Ltd
GGA	: Generalized Gradient Approximation
HAZ	: Heat-Affected Zones
HE	: Hydrogen Embrittlement
HEDE	: Hydrogen-Enhanced Decohesion
HEE	: Hydrogen Environment Embrittlement
HELP	: Hydrogen-Enhanced Localized Plasticity
HESIV	: Hydrogen-Enhanced Strain-Induced Vacancy
HFCV	: Hydrogen Fuel Cell Vehicle
HIPT	: Hydrogen-Induced Phase Transformation
HRS	: Hydrogen Refueling Station
JRC	: Joint Research Centre
LDA	: Local Density Approximation
LH ₂	: Liquid Hydrogen Storage
LNG	: Liquefied Natural Gas
LOHC	: Liquid Organic Hydrogen Carriers
MEP	: Minimum Energy Pathway

MOFs	: Metal-Organic Frameworks
NASA	: National Aeronautics and Space Administration
Nieq	: Nickel-Equivalent Content
NVC	: Nanovoid Coalescence
Oct	: Octahedral Site
PAW-GGA	: Projector-Augmented Wave method with Generalized Gradient Approximation
PSA	: Pressure Swing Adsorption
PWneb	: Plane-Wave Nudged Elastic Band
RRA	: Relative Reduction of Area
T	: Tetrahedral Site
T _{dd}	: Tetrahedral site located between two spin-down layers
T _{ud}	: Tetrahedral site between spin-up and spin-down layers
VASP	: Vienna Ab-initio Simulation Package
d _(H-surf)	: Height between Hydrogen Atom and Surface

ABSTRACT

Full Name : Mohammed Hamadouche

Thesis Title : Impact of alloying elements on hydrogen adsorption, solubility, and diffusion in austenitic stainless steel for hydrogen energy infrastructure applications: A density functional theory approach.

Major Field : Material Science and Engineering

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A key step in reducing global carbon emissions is the large-scale adoption of hydrogen as a fossil fuel alternative across various sectors. Achieving this transition requires not only lowering hydrogen production costs but also developing advanced metallic materials and efficient infrastructure suitable for hydrogen storage, transport, and distribution. Hydrogen embrittlement (HE) remains a major challenge for the safe usage of various metallic materials used in such systems, including austenitic stainless steel (ASS). The face-centered cubic (FCC) structure of ASS provides slower uptake of hydrogen making them less prone to HE and more suitable for hydrogen service. Controlling ASS chemical composition represents an effective method for further hydrogen embrittlement mitigation. This study investigates the effect of alloying elements (Ni, Cr, Mn, Mo, P, S, Si, N, and C) and magnetization in ASS (304 and 316) grades, the most widely used in hydrogen

infrastructure, on hydrogen adsorption, solubility, and diffusion into and through FCC iron using first-principles calculations based on density functional theory (DFT). Our DFT modeling results show that N, C, and P have a positive effect on hydrogen adsorption by decreasing the adsorption strength, while the elements P, S, Si, Ni, and Mn reduce the hydrogen solubility within the FCC iron bulk by increasing the binding energy. On the other hand, Cr, S, Mo, Si, Mn, and P increase the hydrogen energy barrier of diffusion into the slab, while Cr and Mo increase it through the bulk. Our findings provide novel atomic-scale insights to guide the design of FCC austenitic stainless steel with improved hydrogen embrittlement resistance for hydrogen infrastructure systems.

ملخص الرسالة

الاسم الكامل : محمد حمادوش

عنوان الرسالة : تأثير عناصر السبائك على امتصاص الهيدروجين وقابليته للذوبان وانتشاره في الفولاذ المقاوم للصدأ الأوستنيتي لتطبيقات البنية التحتية لطاقة الهيدروجين: نهج نظرية الكثافة الوظيفية.

التخصص : هندسة وعلوم المواد

تاريخ الدرجة العلمية : ماي 2025

يُعدّ الاعتماد الواسع النطاق للهيدروجين كبديل للوقود الأحفوري في مختلف القطاعات خطوةً أساسيةً في خفض انبعاثات الكربون العالمية. ويتطلب تحقيق هذا التحول ليس فقط خفض تكاليف إنتاج الهيدروجين، بل أيضًا تطوير مواد معدنية متطورة وبنية تحتية فعّالة مناسبة لتخزين الهيدروجين ونقله وتوزيعه. ولا يزال هشاشة الهيدروجين (HE) يُشكّل تحديًا رئيسيًا للاستخدام الآمن لمختلف المواد المعدنية المستخدمة في مثل هذه الأنظمة، بما في ذلك الفولاذ المقاوم للصدأ الأوستنيتي (ASS). يُتيح الهيكل المكعبي ذو المركز الوجهي (FCC) للفولاذ المقاوم للصدأ الأوستنيتي امتصاصًا أبطأ للهيدروجين، مما يجعله أقل عرضة لـ HE وأكثر ملاءمةً لخدمة الهيدروجين. ويُمثّل التحكم في التركيب الكيميائي للفولاذ المقاوم للصدأ الأوستنيتي طريقةً فعّالةً لتخفيف هشاشة الهيدروجين بشكل أكبر. تبحث هذه الدراسة في تأثير عناصر السبائك (Ni و Cr و Mn و Mo و P و S و Si و N و C) والمغناطيس في درجات ASS (304 و 316) الأكثر استخدامًا في البنية التحتية للهيدروجين، على امتزاز الهيدروجين وذوبانه وانتشاره الى

وداخل كتلة حديد FCC باستخدام حسابات المبادئ الأولى القائمة على نظرية الكثافة الوظيفية (DFT). تُظهر نتائج نمذجة DFT أن N و C و P لها تأثير إيجابي على امتزاز الهيدروجين عن طريق تقليل قوة الامتزاز، بينما تقلل العناصر P و S و Si و Ni و Mn من ذوبان الهيدروجين داخل كتلة حديد FCC عن طريق زيادة طاقة الارتباط. من ناحية أخرى، تزيد Cr و S و Mo و Si و Mn و P من حاجز طاقة الهيدروجين للانتشار إلى الكتلة، بينما تزيد Cr و Mo من الانتشار داخل الكتلة. توفر نتائجنا رؤى جديدة على المستوى الذري لتوجيه تصميم الفولاذ المقاوم للصدأ الأوستنيتي FCC مع مقاومة محسنة لهشاشة الهيدروجين لأنظمة البنية التحتية للهيدروجين.

CHAPTER 1

INTRODUCTION

The majority of the energy consumed in our modern society originates from fossil fuels, which are finite and eventually will run out. It became clear at the beginning of the twenty-first century that our overreliance on fossil fuels was having negative effects. This involved the depletion of fossil fuel reserves and the release of greenhouse gases that are damaging to the environment. To address our ever-increasing energy demands, turning to renewable energy sources is an obvious choice. Among the renewable energy options, hydrogen is the most attractive one as it is non-toxic, will never run out, and so has the potential to be a significant energy source in the future. In addition, it may replace currently employed fossil fuel-based energy systems, assisting in the fight against environmental harm and increasing worldwide temperatures.

For several reasons, hydrogen has become a very attractive substitute for fossil fuels. First and foremost, it is environmentally friendly as water is the byproduct instead of harmful carbon emissions, minimizing any negative effects on the environment. Furthermore, hydrogen is extremely portable and can travel great distances via transmission networks or pipes, much like electricity. Its ecological production process, which uses plentiful natural resources like water, increases its allure. Furthermore, hydrogen is versatile enough to be

used as a chemical fuel in a variety of sectors, which increases its potential and application (1).

Hydrogen, which is produced from water electrolysis using renewable energy, known as 'green' hydrogen, is widely regarded as the most favorable option. However, its higher current cost of approximately 3 to 6 USD per kilogram of hydrogen (kgH_2) (2) compared to 1 to 2.4 USD/ kgH_2 for 'fossil hydrogen' remains the primary hurdle for its widespread adoption across industries and civil applications. Alongside green hydrogen, various other types of hydrogen also exist which are labeled with different colors based on their production methods. These alternative types often come with negative environmental impacts.

Consequently, there is a heated debate surrounding the potential use of low-cost 'non-green' hydrogen as an interim solution during the clean energy transition. This discussion revolves around finding a balance between scaling up production to reduce long-term hydrogen costs and minimizing environmental harm.

Apart from affordable hydrogen production methods, a robust and cost-effective hydrogen infrastructure that includes storage, transportation, and distribution is crucial. This infrastructure plays a dual role: it boosts hydrogen demand, leading to increased production scale and lowered prices. Simultaneously, reduced production costs encourage the expansion and enhancement of the hydrogen infrastructure.

Typically, the current technologies used for storing and transporting hydrogen are derived directly from established technologies in the chemical and gas industries. This is

particularly evident in physical-based storage methods and transportation systems for hydrogen.

However, because hydrogen has unique properties like high diffusivity in metallic materials, extra precautions are necessary. For instance, its extremely low evaporation temperature of 20 K at 0.1 MPa (1 bar) requires a complex liquefaction process and measures to prevent boil-off. Additionally, hydrogen's high diffusivity poses challenges in selecting suitable materials for pipelines and may require reconfiguration of existing natural gas pipeline networks (3).

Hydrogen-resistant alloys are metallic materials capable of resisting HE or maintaining stability in a hydrogen-rich environment over an extended period. Generally, alloys possessing a face-centered cubic (FCC) crystal structure exhibit greater resistance to HE compared to those with a body-centered cubic (BCC) crystal structure due to their superior hydrogen solubility and lower hydrogen diffusion coefficient in hydrogen environments (4). As a result, many hydrogen embrittlement (HE) resistant alloys are austenitic alloys with an FCC crystal structure, such as austenitic stainless steels or iron-nickel-based alloys (4,5).

Austenitic stainless steels such as 316, 316L, 304, and 304L continue to be the dominating structural material in hydrogen energy systems, spanning a wide range of applications such as hydrogen generation, transportation, and storage (6,7). Nevertheless, austenitic stainless steels are susceptible to hydrogen embrittlement (8–12). The synergistic action of hydrogen-enhanced localized plasticity (HELP) and the hydrogen-enhanced decohesion

(HEDE), according to the HELP+HEDE model for HE5 (12–15), is confirmed in both cast and additively manufactured 304 and 304L ASS, depending on the hydrogen concentration (16,17). These indicate that hydrogen - ASS interaction processes like adsorption, solubility, and diffusion dictate both the diffusible hydrogen content in ASS and hydrogen trapping kinetics, which are responsible for hydrogen redistribution and potential activation and predominance of the HEDE mechanism of HE upon local reaching of critical hydrogen concentration (12–15). It is experimentally confirmed that various alloying elements, like Mo, Ni, Si, S, Cr, and Mn, strongly affect the HE susceptibility of ASS (18). Therefore, modifying ASS base chemical composition is an effective method for HE resistance enhancement. Li et al. (19) used first-principles calculations based on density functional theory (DFT) to investigate alloying elements' effect on hydrogen adsorption and diffusion in the system Fe-X (Cr, Mn, Si, Ni). They pointed out that alloying elements' effect on HE and active or simultaneously active HE mechanisms, including HELP and HEDE interactions, is very complex. Furthermore, the combined effects of various alloying elements on HE are not easy to comprehend through atomistic modeling. Nevertheless, they concluded that first-principles quantum chemistry calculations on the influence of alloying elements could provide a sound theoretical background for designing materials with improved HE resistance (19).

This research aims to fill the gap in computational studies about the hydrogen interaction with FCC iron alloyed with various elements of the commonly used ASS grades (316, 316L, 304, and 304L) in hydrogen infrastructure. It presents a detailed atomic-scale investigation using first-principles calculations based on density functional theory (DFT)

of the critical steps involved in hydrogen adsorption, solubility, and diffusion. This study offers valuable guidance for the development of future grades of FCC steels with improved HE resistance suitable for hydrogen infrastructure systems. This DFT modeling study does not delve deeply into the complex effects of the change in hydrogen adsorption, solubility, and diffusion due to various elements on active HE mechanisms in ASS.

The thesis is divided into four chapters. The first one introduces the topic and the need to transition from fossil fuels to clean energy by outlining the issues with conventional energy sources and highlighting the potential of hydrogen. The second covers background information on hydrogen infrastructure, including storage and transportation; metallic structural materials for high-pressure hydrogen environments; hydrogen embrittlement in Steel; DFT technique; and a literature review on FCC iron structure magnetization and hydrogen interaction with alloyed iron using DFT. The third provides computational methods and modeling, while the final presents the results and conclusion.

1.1 The Problems Fossil Fuels Cause for the Environment and the Search for Sustainable Alternatives

1.1.1 Effects on the Environment

The power system that exists today, which is primarily based on fossil fuels, raises a number of environmental worries. These consist of greenhouse gas emissions, polluting the atmosphere, climate change caused by the burning of fossil fuels, the reduction of finite energy resources, the

formation of acid rain, and general degradation of the ecosystem. It is projected that between 1990 and 2100, worldwide temperatures will rise by 1.4 to 5.8 °C, which will have detrimental effects on the environment, such as sea level rise, droughts, floods, and heatwaves, all of which will be made worse by the overuse of fossil fuels.

In order to tackle these urgent environmental problems, a zero-carbon infrastructure that is in line with sustainable development objectives is imperative. Investigating substitute fuels that lessen environmental deterioration is required considering this change. The environmental effects of using traditional fuels have drawn attention to the potential benefits of renewable energies, including hydrogen, solar, ocean, wind, and geothermal energy (20).

1.1.2 The Effect of Fossil Fuels on the Economy

The use of fossil fuels has had a major impact on societal progress, quality of life, and economic growth. The availability of fossil fuels and energy use are intimately related to the advancement of the global economy. The unequal and restricted distribution of these resources on Earth, however, is a serious problem and puts financial strain on nations without natural reserves. Furthermore, a multitude of variables contribute to the volatile cost of fossil fuels, hence exacerbating the global energy problem (21). Therefore, there are two serious issues with the current energy infrastructure that need to be resolved right away. Adopting renewable energy sources might provide answers to issues related to traditional fuels that affect the environment and the economy (20).

1.2 Hydrogen: An Essential Energy Source for Sustainable Solutions

There is potential for renewable energy to alleviate the financial and ecological issues related to fossil fuels. However, effective storage in secondary energy carriers is required

due to the erratic nature, timing, and dependency on specific regions of renewable energy sources. Because it combines the three essential elements for sustainable energy solutions: economic cost-effectiveness, energy security, and environmental friendliness. Hydrogen is an ideal energy carrier among the possibilities available.

1.3 Hydrogen as an Adaptable Energy Source for Renewable Energy Systems

Even if renewable energies are environmentally beneficial, there is often a discrepancy between the need and supply of energy because of time, location, and weather. Nonetheless, hydrogen functions as a flexible energy medium capable of filling this void. In systems that use renewable energy, it has been shown to be a promising choice (22,23), providing sustainability and immunity to ecological and health problems. Since hydrogen is the element that is most plentiful and lightest, it can be created and transferred from water with ease. Hydrogen, known to be rich in energy per unit mass and able to be obtained from a variety of sources, including water, biomass, and fossil fuels, differs from traditional sources of energy. Its volumetric energy density is, however, lower than that of conventional fuels, but its higher gravimetric energy content is (24).

In conclusion, hydrogen has several benefits over fossil fuels, making it an interesting energy option for the future (25)

Three key steps are involved in using hydrogen as an energy source: generation, storage and transit, and combustion for use. A closed hydrogen cycle is created by these phases, as depicted in Fig 1. 1.

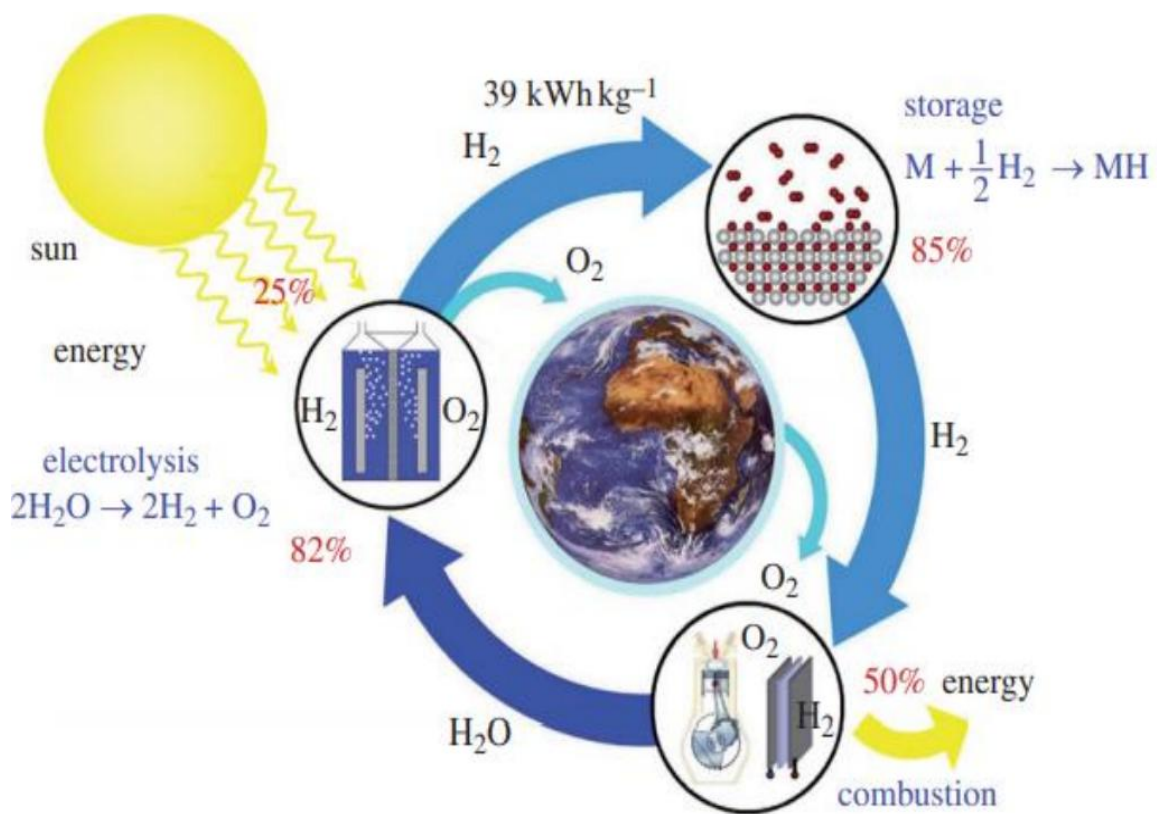


Fig 1. 1 The hydrogen energy cycle (26).

In the upcoming chapter, we will concentrate on the steps involved in storing and transferring hydrogen once it has been produced, going over the various techniques for doing so.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Hydrogen Infrastructure: Storage and Transportation

2.1.1 Hydrogen Storage

The development of hydrogen storage technologies is critical to developing a strong hydrogen infrastructure. The manner of storing hydrogen affects not just how it is delivered, but also its possible applications. Advances in hydrogen storage technologies have the potential to greatly improve and expand the amount of hydrogen consumption. A technical evaluation of a hydrogen storage system typically considers five important aspects (27):

- Gravimetric energy density: 5.5 wt%
- volume density (0.04 kg H₂/L)
- Working temperature: -40°C to 60°C.
- Lifecycle Life (1500 cycles)
- System loading time (1.5 kgH₂/min)

The technical targets mentioned earlier represent the United States Department of Energy's (DOE) objectives for on-board hydrogen storage in light-duty fuel cell vehicles, serving as a benchmark for 2020 (28).

In general, techniques to store hydrogen are divided into two types: physical and chemical storage. Physical-based storage requires modifying hydrogen's physical properties, such as raising the pressure (compressed gaseous hydrogen storage, CGH₂), reducing the temperature under the evaporation point (liquid hydrogen storage, LH₂), or using a combination of both methods (cryo-compressed hydrogen storage, CcH₂). Material-based storage, on the other hand, requires the use of extra materials as 'carriers' that may react with hydrogen molecules or atoms; as a result, storage capacity and security are higher than in physical techniques. However, most chemical storage options are still in labs or are being tested. A general description of the different hydrogen storage techniques is given in Fig 2.1.

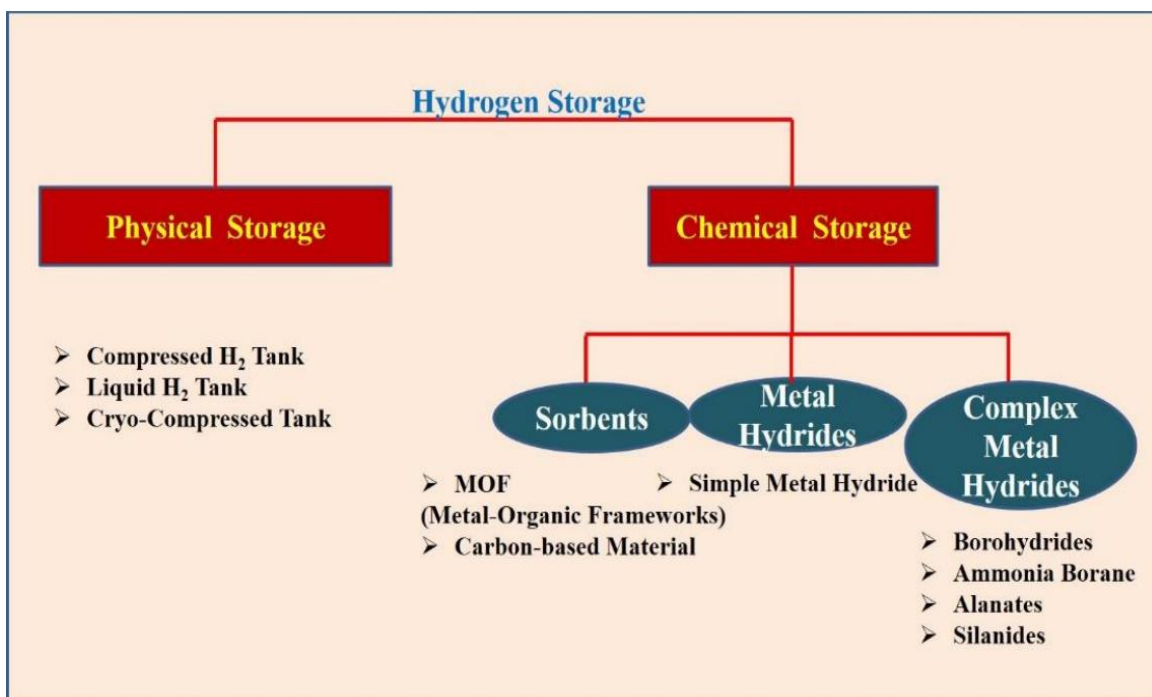


Fig 2. 1 Types of hydrogen storage (20)

a. Physical Storage

Physical storage refers to storing hydrogen in its molecular state. This can be achieved through methods like liquid hydrogen tanks or compressed hydrogen gas tanks.

i. Compressed Gaseous Hydrogen Storage (CGH₂)

When hydrogen is compressed, its storage capacity increases significantly, ranging from 3 to 5 times higher, using tanks with pressures of 5000 and 10,000 psi. High-pressure storage systems can achieve pressures up to 77 MPa using piston-type mechanical compressors,

requiring over 2.21 kWh/kg of work for compression. This process results in a volumetric density of 40 kg/m³ and a gravimetric density of 13 wt%, as indicated in reference (29).

The most basic and proven way for storing hydrogen is to compress and store it in pressure tanks. Currently, four types of established vessels exist. The right vessel type is determined by the individual application, considering technical characteristics as well as financial concerns.

Type 1: Pressure vessels could initially store 25 Nm³ of H₂ at 12 MPa in a half-ton steel container. Nowadays, they typically operate at levels of 15 to 30 MPa. Despite this progress, their small gravimetric energy density limits their usage to stationary applications, notably in-place storage of hydrogen as an industrial gas.

Type 2: Mechanical tests show the uniformly thick walls within the cylindrical form of a metal pressure tank receive more stress than the domes at a given pressure (30). Strengthening the center cylindrical part with resin-impregnated fiber wrapping improves the vessel's capacity to hold hydrogen at greater pressures. By varying the thickness of the bundled fiber, improved resistance to operating pressures can be achieved.

FIBA Technologies, Inc.'s requirements state that Type 2 seamless steel tanks strengthened with carbon fiber wrapping are designed to sustain gas pressures of up to 100 MPa(31).As a result, Type 2 pressure tanks are often adopted to store gas with elevated pressure in place applications, like hydrogen storage chambers at HRS that operate at 87.5 MPa (32).

Types 3 and 4: When the fiber entirely encloses the metallic or polymeric cores, the pressure vessels called Type 3 and Type 4, respectively become significantly lighter, meeting the gravimetric energy density of conserved hydrogen requirements for operations aboard. Pressure vessels of Types 3 and 4 are preferred for usage in tube trucks and integrated into hydrogen transportation containers due to their reduced weight. A growing number of Type 4 containers are being used at hydrogen refueling station (HRS) for fixed reduced-pressure hydrogen storage (32).

ii. Liquid Hydrogen Storage (LH₂)

When hydrogen is in its liquid form, it takes up nearly twice as much space as gasoline. To store liquid hydrogen, it undergoes compression and cooling in cryogenic tanks. This process requires about 15.2 kWh/kg of energy and achieves a volumetric density of 70.8 kg/m³, with the gravimetric density affected by the size of the tank.

Cutting-edge cryogenic tanks designed for storing liquid hydrogen (LH₂) are based on the storage tanks initially created for liquid nitrogen (LN₂) with minimal modifications. They utilize perlite and a vacuum of approximately 10⁻² mbar for insulation, resulting in a thermal conductivity value (k-value) of around 1.0 mW/m²K. The standard loss from boiling off in modern LH₂ tanks ranges from 1% to 5% per day (33).

Reducing the loss from boiling off is a significant technological challenge for LH₂ storage in a cryogenic vessel (as shown in Fig 2. 2). LH₂ evaporates as a result of heat absorption,

which causes material loss. Thermal leaking is primarily caused by radiation, convection, heat conductivity, and ortho-to-para exchange.

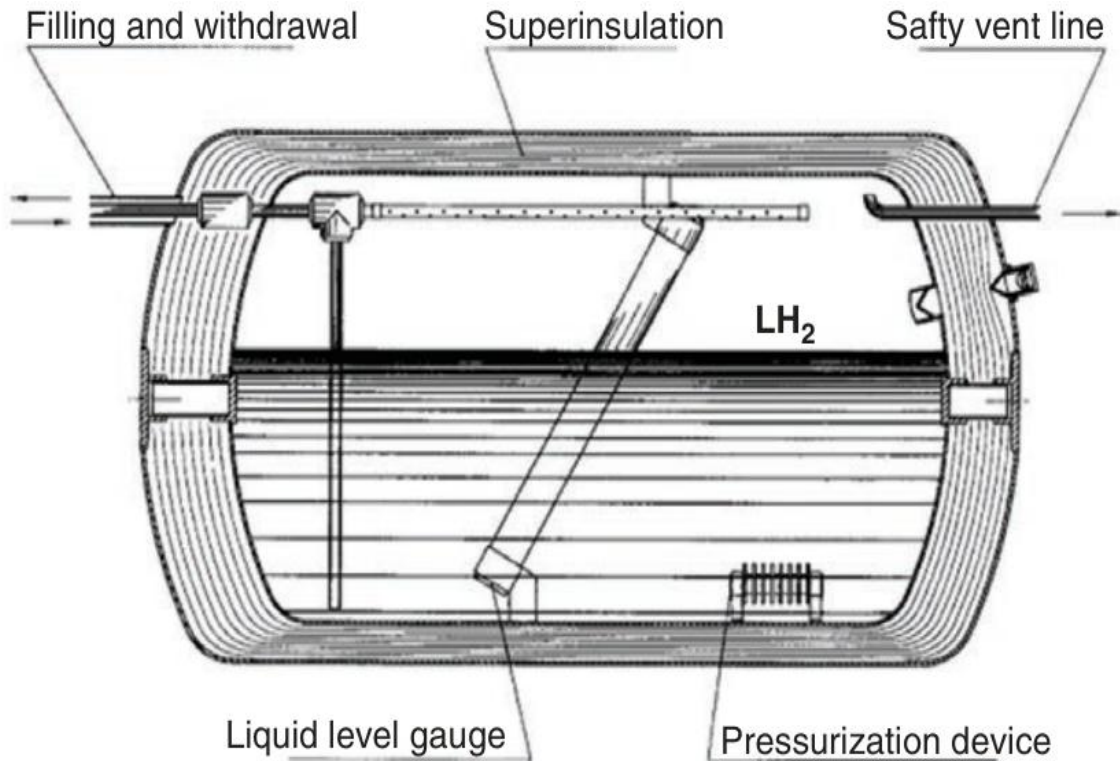


Fig 2. 2 A conventional on-board liquid hydrogen reservoir setup (34).

Recently, various methods have been explored to minimize the boil-off loss in LH₂ tanks. One notable approach is the utilization of multilayer insulation technology combined with a high vacuum level (around 10^{-4} mbar), a method commonly employed for storing liquid helium. With this technology, the estimated boil-off loss for LH₂ storage is reduced to 0.01% and 0.04% per day for large tanks (4×120 m³) and small tanks (5 m³), respectively. Incorporating a refrigeration system into such multilayer insulated tanks can completely

eliminate the loss. This integrated refrigeration and storage (IRAS) system involves using cryogenic gaseous helium as a coolant to absorb heat in the LH_2 through a designed pipe system (35). However, both of these methods are currently not suitable for civilian applications.

iii. Cryo-Compressed Hydrogen Storage (CCH_2)

Liquid hydrogen storage results in greater density compared to its compressed gaseous state. However, the boil-off loss associated with liquid hydrogen limits its practical applications, particularly for on-board storage in vehicles. In response, BMW initiated a study over a decade ago to explore cryo-compressed hydrogen storage (CCH_2). This approach aims to store hydrogen at temperatures above 20 K and pressures below 70 MPa, offering potential advantages in storage efficiency and reduced losses. (36)

The key benefit of CCH_2 storage lies in its ability to attain greater density compared to LH_2 at relatively higher temperatures.

Most of the research on CCH_2 focuses on its application for on-board storage and related areas, distinct from CGH_2 and LH_2 (37,38). A CCH_2 container combines features of CGH_2 pressure vessels and LH_2 tanks. Typically, it includes a Type 3 pressure vessel for CGH_2 , enveloped by multilayer insulation used in LH_2 tanks, and is maintained under vacuum conditions (39). As a result, the cost of a CCH_2 vessel is significantly greater than that of CGH_2 vessels and LH_2 reservoirs, rendering it undesirable for massive amounts hydrogen

storage. However, one advantage of the C_6H_6 container is its ability to store C_6H_6 as well (39)

There are disadvantages to storing hydrogen in its liquid state, and having stored it in the form of gas raises safety problems, necessitates large amounts of physical space, is expensive, and needs high levels of pressure and extremely low temperatures. These difficulties make using these storage techniques for business purposes impracticable.

Due to the various difficulties involved in keeping hydrogen in its liquid and gaseous forms, researchers are now concentrating on the second type of chemical storage. This method improves the volumetric capacity of hydrogen storage while lowering the necessary storage pressure.

b. Chemical Storage

Solid-state materials are used to store hydrogen in the chemical storage method. Researchers have looked at a variety of materials to satisfy the US-DOE requirements, which include a storage capacity greater than 8 weight percent and an operational temperature that varies from 40–85 degrees Celsius (40, 41). Sorbents, light metal hydrides as well, and complex metal hydrides are a few of these materials.

i. Sorbent Systems

Utilizing substances such as metal organic frameworks (MOFs) and C-based materials, sorbent methods for hydrogen storage entail the physical adsorption of hydrogen onto surfaces. These systems have a limited amount of storage, though, and they need very low working temperatures,

which are not easily achieved (42). It has led to the rise in popularity of light metal hydrides and complex metal hydrides. The US-DOE's targets for storage capacity for hydrogen are met and they function at more practical temperatures (43).

ii. Light Metal Hydrides

As hydrogen forms bonds with metals via a variety of processes, light metal hydrides are produced. Interstitial hydrides, for example LaNi_5 and FeTi , are known to have a low capacity to store hydrogen and are not suitable for dynamic or onboard uses (44). On the other hand, covalent or ionic hydrides, like MgH_2 (45), and LiH (46), have a large capacity to store hydrogen but involve extremely elevated temperatures while in use.

iii. Chemical Hydrides

Hydrogen is strongly covalently bonded to chemical hydrides, providing a large amount of storage space. Unfortunately, reversibility is a disadvantage of these hydrides (47,48).

iv. Complex Metal Hydrides

Because of their superior storage capacity, complex metal hydrides are potentially desirable types of hydrides. Nonetheless, they encounter difficulties with thermodynamics and kinetics, requiring a high working temperature of more than $200\text{ }^\circ\text{C}$ and steady hydride production. Catalysts and minimizing particle sizes are two ways to tackle these problems.

Hence, solid-state storage emerges as the leading approach for storing substantial quantities of hydrogen under regular pressure and temperature conditions.

Carbon nanotubes (CNTs) exhibit the ability to store H_2 at low temperatures (196.15 °C) and pressures (6 MPa), providing a gravimetric density of 10.8 wt% and a volumetric density of 41 kg/m³(29). Nanomaterials offer numerous advantages in hydrogen storage, including enhanced sorption kinetics, overcoming barriers present in bulk materials, and achieving optimal release temperatures. Research conducted at the University of South Florida's clean energy research center highlighted that nanomaterials-based catalyst doping can enhance storage capacity and sorption kinetics. This improvement is attributed to the shorter diffusion distance in nanomaterials compared to bulk materials (29) .

2.1.2 Hydrogen Transportation

Hydrogen transportation and distribution methods vary depending on factors such as volume, delivery distance, and local conditions (49). Current options, depicted in Fig. 2. 3, rely on established natural gas transportation systems, including road, pipeline, and shipping methods.

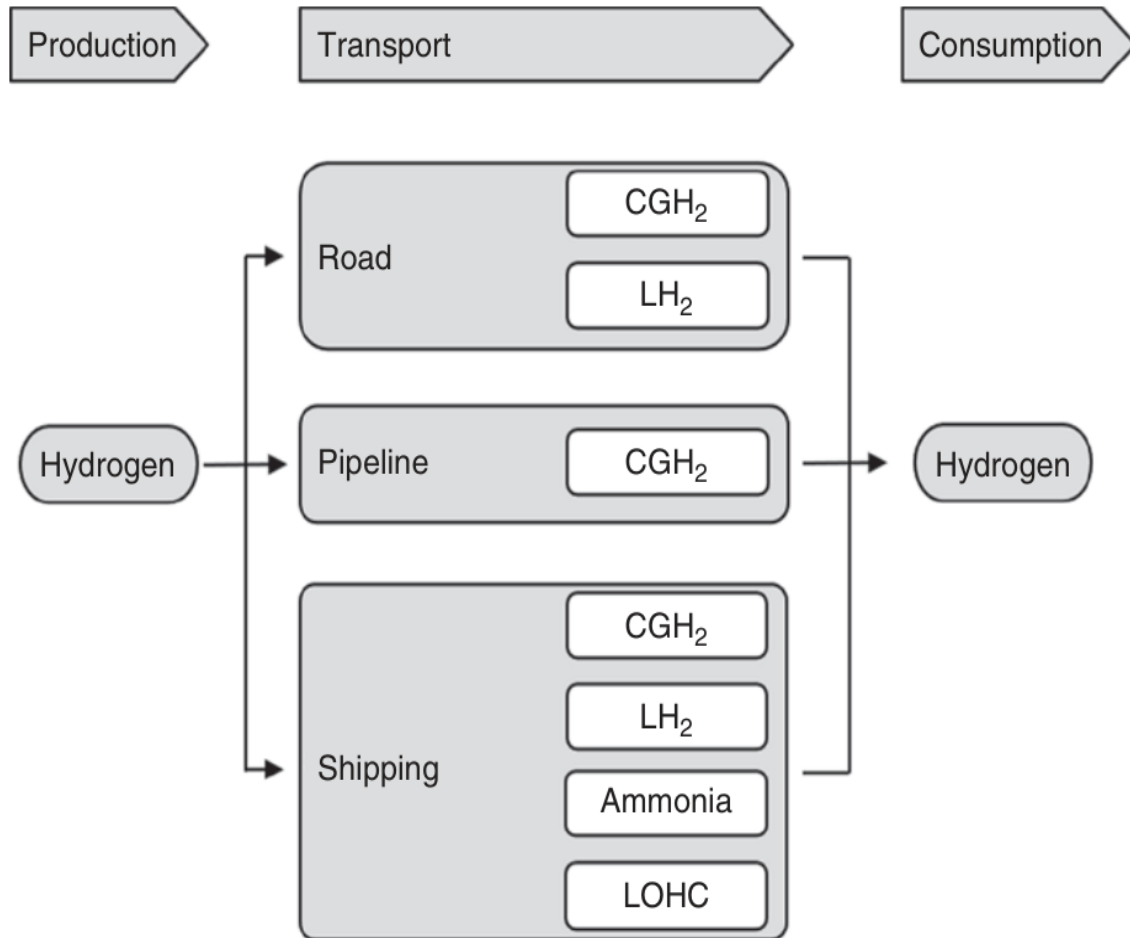


Fig 2. 3 Options for hydrogen transportation.

For road transport, hydrogen is moved using trucks or trailers, either as compressed gas or in liquid form. This relies on established storage methods like pressure vessels and cryogenic tanks, as mentioned earlier.

Much like natural gas, hydrogen in pressurized gaseous form can also be conveyed through pipelines. Despite the initial cost being high, this method proves economically viable for

transporting substantial hydrogen volumes, making it suitable for delivering hydrogen to significant industrial consumers.

Shipping serves as an alternative means for transporting significant quantities of hydrogen, particularly for intercontinental journeys. This method is especially advantageous for transporting hydrogen not only in its elemental states like (CGH_2) or (LH_2) but also in compound forms such as liquid organic hydrogen carriers (LOHC) or ammonia.

Besides the primary methods of hydrogen transportation mentioned earlier, there are also inventive concepts like using Zeppelin airships for air transport of hydrogen.

a. Road Transportation of Hydrogen

i. Compressed Gaseous Hydrogen Trailer

For low hydrogen demands, transporting compressed hydrogen in pressure vessels is straightforward. When demand is higher, multiple Type 3 or 4 pressure vessels can be grouped in standard containers or frames and transported by truck.

Typically, hydrogen pressure is kept between 20 and 50 MPa for cost-effectiveness and safety, allowing a single truck to carry 200–1000 kg of hydrogen.

Gas tube trailers, commonly used for natural gas, are also adaptable for hydrogen transport, often using horizontally grouped Type 3 vessels with a maximum pressure of 25 MPa in the USA (50), equating to about 380 kg per trailer. By using Type 4 vessels instead, a trailer

could carry 560–900 kg of hydrogen. However, CGH₂ trailers are best suited for short-distance transport (100–200 km) to small-scale refueling stations due to their limited capacity (51).

ii. Liquid Hydrogen Trailer

Alternatively, hydrogen can be transported in its liquid form, a method well-suited for medium distances (>130 km based on a German case study (52)). Liquid hydrogen (LH₂) is produced at a central liquefaction plant and then delivered to customers. LH₂ trailers offer a higher volumetric storage density compared to compressed gaseous hydrogen (CGH₂), allowing them to transport larger quantities of hydrogen. However, the transportation of LH₂ faces a significant technical challenge known as boil-off, discussed earlier. Despite this, specially designed cryogenic tanks in transport can withstand pressures up to 12 bar, significantly higher than stationary bulk hydrogen storage tanks (53).

In practice, it's not possible to deliver the entire amount of hydrogen initially transported in both CGH₂ and LH₂ trailers to the customer. The remaining hydrogen in a CGH₂ trailer is dependent on the pressure level in the supply chain. For LH₂ delivery, around 10% of the liquid should be left in the tank to maintain cryogenic temperatures(53). This residual hydrogen is typically recycled back to the liquefaction plant instead of being released into the atmosphere during a normal delivery operation.

b. Pipeline Transportation of Hydrogen

Gaseous hydrogen can be transported via pipelines, akin to natural gas, making it a cost-effective method, especially suitable for meeting large hydrogen demands in densely populated and industrial areas. However, setting up a new pipeline system solely for hydrogen transport entails significant costs. Therefore, repurposing existing natural gas pipelines for hydrogen transport is a preferable, cost-effective solution whenever feasible.

One advantage of hydrogen is its higher compressibility factor (slightly above 1), resulting in lower pressure drop over long pipeline distances compared to natural gas. This allows for reducing the inlet pressure for transporting pure hydrogen in pipelines to around 2–3 MPa (54). However, due to its lower heating value, hydrogen transportation is less energy-efficient than that of natural gas. Another concern is the potential for material failures in metallic pipelines due to hydrogen migration. The degradation of heat-affected zones (HAZ) and fatigue crack growth (FCP) in the pipeline's base material are the primary mechanisms contributing to such material degradation (55).

Results from Research Centre Jülich in Germany revealed that steel X70(56), commonly used for pipelines in Europe, exhibits no heat-affected zone (HAZ) issues and reduced fatigue crack propagation (FCP) compared to other pipeline steels like X60. They conducted a comprehensive cost analysis, comparing different options for repurposing existing pipelines to transport pure hydrogen with the cost of constructing new hydrogen pipelines, focusing on the German market.

Their analysis included evaluating the cost of subsequent purification processes. They concluded that introducing 0.015% oxygen into the transported hydrogen, a method proven effective in limiting hydrogen embrittlement in metallic materials(55,57,58), which is the most cost-effective approach for repurposing existing pipelines with small diameters (< 250 mm) for hydrogen transport.

For transporting hydrogen through pipelines with larger diameters, using existing pipelines without modifications might be more cost-effective than constructing new ones. However, applying protective coatings to the inner walls of existing natural gas pipelines through excavation, due to the lack of on-site coating technology, increases the cost significantly. Another costly approach is integrating specialized hydrogen delivery pipelines within existing natural gas pipelines, known as the pipe-in-pipe approach.

When it comes to transporting hydrogen through pipelines, the purity of hydrogen becomes crucial. Even repurposed or new hydrogen pipelines might not deliver hydrogen pure enough for fuel cell applications. To meet these stringent requirements, additional purification steps are often necessary. For instance, employing pressure swing adsorption (PSA) purification technology can achieve a maximum purity of 99.9999% (59).

In 2020, the operator of the natural gas transmission system introduced the 'Vision Hydrogen Network' concept. This plan outlines approximately 5900 km of pipelines connecting key hydrogen production and consumption hubs across Germany, including industrial, mobile, and heating sectors, along with several underground storage facilities. Notably, over 90% of this visionary pipeline system utilizes the existing natural gas

network, leading to significant cost savings(60).The initiative is set to commence in north-western Germany, with the 'H₂ Start Grid 2030' expected to span 1200 km in North Rhine-Westphalia and Lower Saxony by 2030.

The 'European Hydrogen Backbone' is a collaborative effort involving 31 European energy infrastructure operators. Their objective is to foster the development of the European hydrogen market by outlining the hydrogen infrastructure using both existing and newly constructed pipelines. As outlined in their vision (61), this initiative envisions a pan-European hydrogen pipeline network connecting 25 European countries with a total length of nearly 53,000 km by 2040. The estimated investment required to realize this ambitious vision ranges from 80 to 143 billion euros. Upon completion of the pipeline system, the projected cost to transport 1 kg of hydrogen over a distance of 1000 km would range from 0.11 to 0.32 euros, contingent on the pipeline's location.

c. Hydrogen Shipping

In a global green hydrogen economy, the transportation of hydrogen across seas becomes essential and economically advantageous, especially for international hydrogen trade. This scenario is particularly relevant when countries with abundant renewable energy resources suitable for producing green hydrogen for export are geographically distant from those needing to import hydrogen(62). Fig. 2. 4 illustrates that shipping hydrogen would be more cost-effective than constructing new pipelines for distances exceeding 7000 km. While pipelines are viable for long-distance transport, they are fixed geographically and subject to potential political changes in crossing countries, which could impact long-term

commitments to pipeline projects. In contrast, shipping hydrogen offers greater flexibility and independence.

Currently, there are limited pilot projects focused on shipping hydrogen across countries and continents. However, studies suggest that in the future, hydrogen supply chains leveraging shipping methods, whether in elemental form like LH_2 or CGH_2 , or compound form like ammonia or LOHC, could be established based on considerations such as distance, energy consumption, and required supporting infrastructure (63,64).

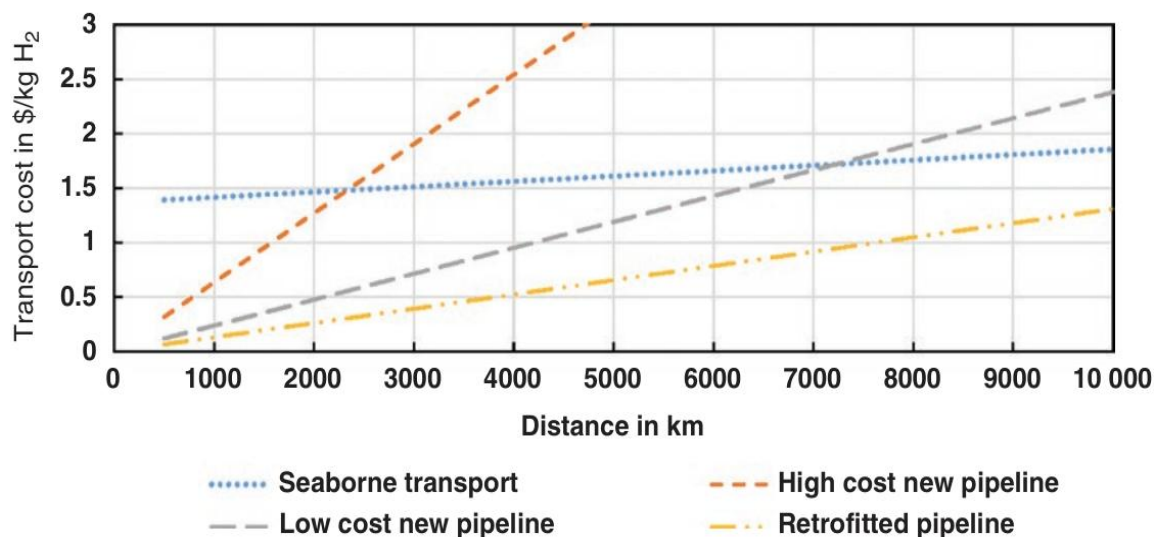


Fig 2. 4 Comparison of Long-Distance Hydrogen Transportation Methods(62).

i. CGH_2 Shipping

Shipping hydrogen in its gaseous state is the most straightforward method due to its low energy consumption during gas compression, estimated at around 1.1 kWh/kg H_2 , to compress hydrogen from 2 to 25 MPa, as calculated by Global Energy Ventures Ltd (GEV),

a marine transportation company in Australia (63). Additionally, the compressed hydrogen can be directly injected into the ship, requiring minimal supporting infrastructure compared to other shipping methods. The primary challenge with this approach is the low volumetric storage density, similar to CGH₂ storage.

GEV is developing the world's first compressed hydrogen cargo ship, C-H₂, featuring two cylindrical tanks with a 12-meter diameter. Operating at 25 MPa, this ship can transport 430 tonnes of hydrogen. The initial technology demonstration project is scheduled for construction in 2023, aiming for commercial use by 2025. The project's design and engineering aim to use C-H₂ as a model for a larger cargo ship with two 20-meter-diameter cylindrical tanks capable of transporting 2000 tonnes of hydrogen. GEV has noted that the hydrogen supply chain using CGH₂ shipping is highly competitive within a 2000 nautical mile distance (3700 km, equivalent to the route between Australia and Singapore) and remains competitive for transporting hydrogen from Australia to Japan, South Korea, and China (63)

ii. LH₂ Shipping

The use of liquid hydrogen (LH₂) for shipping has gained popularity due to its high volumetric density and the integration of proven cryogenic technologies from LNG shipping. LH₂ shipping technology is influenced by LNG shipping, which already transports natural gas at extremely low temperatures internationally (65) Europe's existing LNG terminals can be upgraded for LH₂ import/export, leveraging shared infrastructure and the adaptability of current systems (66) LH₂ shipping benefits from energy-efficient

liquefaction plants situated in regions with readily available and inexpensive energy sources, such as renewable energy for green hydrogen production.

However, LH₂ shipping faces challenges like boil-off loss due to its low boiling point, similar to stationary storage. Re-liquefying boil-off hydrogen on ships is currently impractical, leading to venting excess vapor when tank pressure exceeds limits. Future solutions may involve higher-pressure tanks, active LH₂ cooling systems, and advancements in compact, energy-efficient liquefaction equipment to mitigate boil-off loss.

One strategy to address boil-off loss is using evaporated hydrogen as fuel, converting it into electricity through fuel cells or direct combustion in engines derived from LNG ships. Despite these advancements, boil-off limits the maximum sailing time and distance for LH₂ shipping. The optimal shipping range for LH₂ spans between 2500 and 16,000 km (64) covering routes like Saudi Arabia to Rotterdam according to the Joint Research Centre (JRC) (67).

2.2 Metallic Structural Materials for High-Pressure Hydrogen Environment in Hydrogen Energy Systems

As the need for hydrogen fuel increases, high-pressure hydrogen systems require important components such as hydrogen pipes, storage cylinders, and hydrogen refueling stations (HRSs). Hydrogen embrittlement (HE) is a prevalent problem in structures made of metal in such situations, resulting in reduced ductility and probable failures that are affected by materials, operating conditions, and stress levels. To reduce hydrogen embrittlement (HE)

in metals in hydrogen power plants operating at elevated pressures and guarantee the security of hydrogen energy systems, NASA recommends assessing the HE sensitivity of materials using the relative reduction of area (RRA) determined through a tensile test with a slow strain pace, determined by the formula below (68)

$$RRA = \varphi_H / \varphi_0$$

φ_0 : The area lost in the atmosphere (or He gas)

φ_H : The loss of area in hydrogen (or following hydrogen charge).

Elongation changes can serve as indicators of hydrogen embrittlement (HE) sensitivity in specific cases, where materials with a high relative reduction of area (RRA) exhibit lower sensitivity to HE.

There are a range of structural materials crucial for hydrogen energy facilities, including austenitic stainless steels, pipeline steels, iron-based alloys, nickel-based alloys, Cr-Mo steels, aluminum alloys, and copper alloys. Testing methods for hydrogen embrittlement (HE) can be categorized into two main types: pre-charging hydrogen experiments (internal hydrogen) and environmental hydrogen experiments (external hydrogen). Pre-charging hydrogen experiments involve saturating the material with hydrogen prior to conducting mechanical property tests, while environmental hydrogen experiments entail testing the material directly in a hydrogen-rich environment. It's important to note that the relative reduction of area (RRA) obtained from internal hydrogen testing may differ from that obtained from external hydrogen testing.

Austenitic stainless steel remains the predominant structural material in hydrogen energy systems, covering various aspects like hydrogen production, transportation, and storage. However, the susceptibility to hydrogen embrittlement (HE) increases due to strain-induced martensitic transformation, which affects the hydrogen resistance of austenitic stainless steel (69,70). Researchers often use the nickel-equivalent content (Nieq) as a measure to estimate the stability of the austenite phase and assess HE sensitivity (71). Nieq, proposed by Hirayama et al. (72) is calculated using the equation:

$$\mathbf{Nieq = Ni + 12.93C + 1.11Mn + 0.72Cr + 0.88Mo - 0.27Si + 7.55N} \quad \mathbf{Eq. 2. 1}$$

Regardless of the testing method used, the HE sensitivity of austenitic stainless steel tends to decrease with higher Nieq values.

2.2.1 Materials Used in Hydrogen Storage Cylinders

There are several physical and chemical ways for storing hydrogen, all having unique features and capacities. These technologies might aid in the development of a hydrogen-based infrastructure.

Compressing hydrogen into a high-pressure container is the more extensively used method for hydrogen storage due to its commercial application and advanced technology (73,74).

Four high-pressure hydrogen cylinders were established to meet the specifications for storage as seen in Fig 2. 5 (75,76)

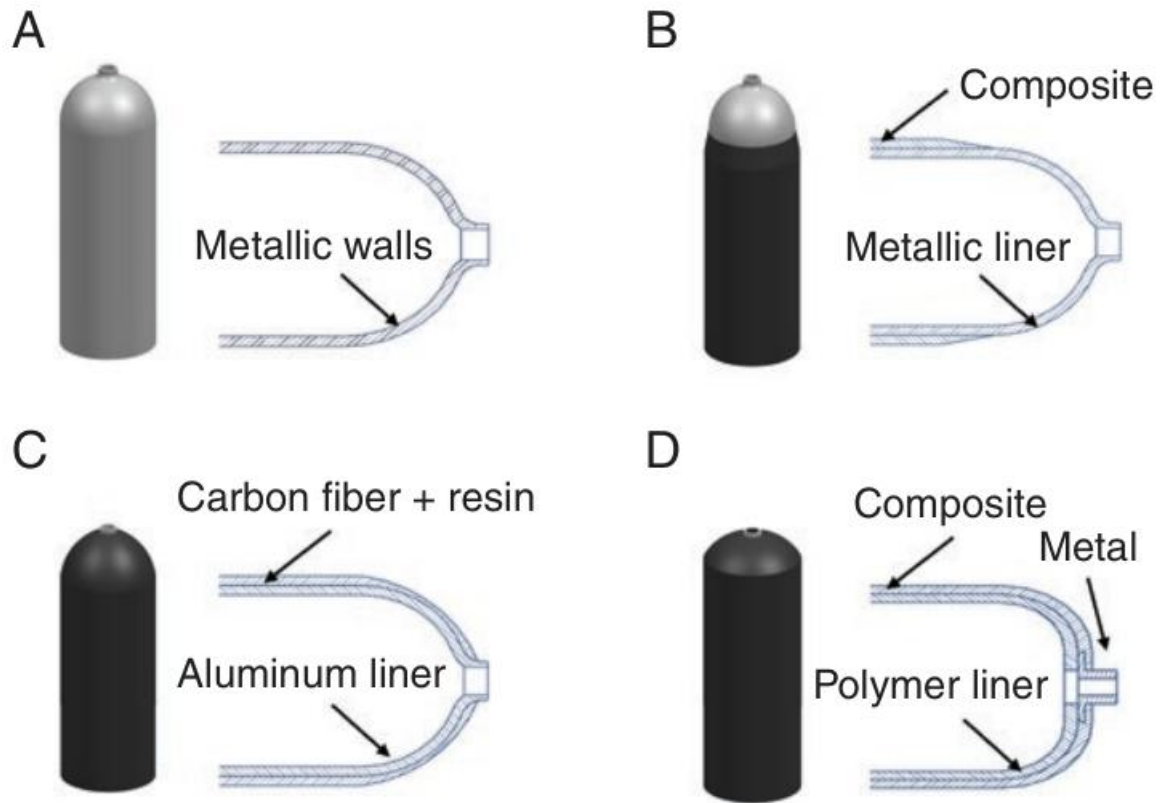


Fig 2. 5 Different types of high-pressure hydrogen cylinders. (a) Type I, (b) Type II, (c) Type III, (d) Type IV.

Type I is a pressure vessel made entirely of metal. Increasing hydrogen pressure requires thicker metal materials, resulting in heavier cylinders that are not suitable for lightweight storage.

Type II design comprises enclosing the metallic liner in composite on the cylindrical portion. Type II can be between 30 to 40 percent lighter than Type I, thereby saving 50% on shipping expenses(77).

Type III wraps the aluminum liner with carbon fiber and resin on all cylindrical components to overcome Type I's advantage.

Type IV has seen significant changes in comparison to Types I, II, and III. Type IV cylinders include a polymer liner, a composite body (fiber and resin), and a metal valve, making them lightweight and ideal for transportable storage.

High-pressure hydrogen cylinders require metal structural materials that are both strong and ductile to sustain the operating conditions. Type II and III metal-based liners are commonly constructed of austenitic stainless steel or aluminum alloys. Type I is mostly composed of austenitic stainless steels like 316, 316L, 304, and 304L (78) Carbon steels, such as Cr-Mo, have high yield strength, which can help reduce wall thickness. This material is commonly used to make hydrogen cylinders with an operating pressure of less than 80 MPa (79–83).

While all of the three kinds of hydrogen cylinders provide advantages over Type I, they are more costly and harder to deploy on a big scale. Thus, Type I is still the more broadly utilized hydrogen cylinder (77) But just austenitic stainless steel and Cr-Mo steel are accepted as potential materials. Hydrogen significantly affects the fatigue characteristics of these materials. The development of a cost-effective, high-strength hydrogen storage cylinder material that withstands fatigue and fracture is extremely important.

2.2.2 Pipeline Material for Hydrogen Transportation

The material utilized in hydrogen pipes is an important structural part of the hydrogen energy system as high-pressure hydrogen gas must travel via tubes in an effective and secure way.

Hydrogen in gas form is now transported using two different techniques. Short-distance hydrogen transportation is handled by tube trucks, whereas long-distance hydrogen transportation is handled by natural gas pipes already in place (84). Austenitic stainless steel for distribution facilities or transportation over short distances (85), and low alloy pipeline steels for lengthy distances are the two types of materials utilized in hydrogen pipes (86).

Austenitic stainless steel with an elevated Ni content is less susceptible to HE, as seen in Fig 2. 6. Unfortunately, because of its low strength and expensive cost in massive usage, austenitic stainless steel is not a good choice for lengthy hydrogen delivery. Pipeline steels are seen to be the safest and most ecologically friendly option for big-scale, lengthy hydrogen transmission because the majority of pipelines are beneath the surface (84).

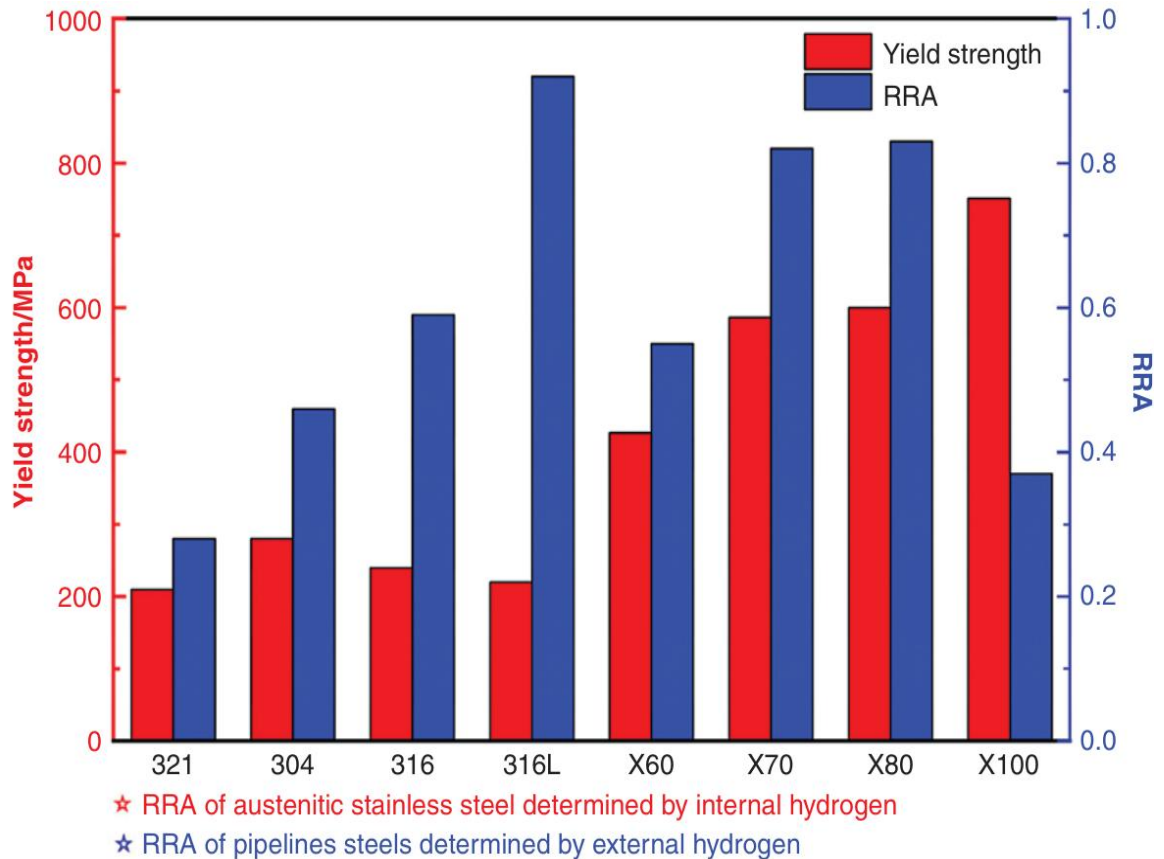


Fig 2. 6 Yield strength and RRA comparing pipeline steels and austenitic stainless steels (87–89).

a. Austenitic Stainless Steel

To establish if a material is appropriate for use in a hydrogen environment, a clear association between Nieq and RRA may be found (71,90). ASS, like 316L, finds it challenging to go through martensitic transition when Nieq is less than 28.5 mass % (91). It can be used in an atmosphere with hydrogen and has a stable austenitic structure. Except

for 316L, 304 (N), and 316, ASS steel expresses HE, as demonstrated by Yamabe et al. (92).

Consequently, 316L and 304 are the most often used ASS steels in hydrogen transmission lines.

b. Pipeline Steels

Regarding publications (93), which state that low-grade materials no greater than X52 are typically utilized to make pipeline steel designed to carry hydrogen. But low-grade pipeline steels aren't strong enough to be utilized for transporting hydrogen under high pressure. Thus, adopting highly resistant pipeline steel for hydrogen delivery has to be taken into account from an efficiency standpoint. Several investigations have demonstrated that the HE sensitivity of pipeline steels rises with strength (94). It is the primary disadvantage of high-strength pipeline steels in hydrogen transport networks.

Li et al. (95) discovered that the microstructure of high-grade pipeline steels affects their susceptibility to HE, with bainite and acicular ferrite being more resistant than martensite. X100 pipeline steels include a significant amount of martensite, while X70 and X80 steels feature microstructures of acicular ferrite, bainite, or a combination of both. This provides one of the explanations for the greater RRA compared to X100 in (Fig 2. 6), X70 and X80 are ideal for transporting high-pressure hydrogen across long distances via pipelines.

Heat treatment (96) and impurities (97,98) alter the HE of pipeline steels. Optimizing heat treatment and smelting processes for pipeline steels is crucial for strengthening their resilience to HE.

Blending with natural gas is also proposed to minimize pipeline steel embrittlement and the cost of hydrogen delivery (99).

At present, austenitic stainless steels (304 and 316L) are utilized for short-distance hydrogen transportation, whereas low-grade pipeline steels are employed for long-distance hydrogen transport. X70 and X80 are potential possibilities for long-distance distribution of high-pressure hydrogen.

However, there are still critical difficulties to be addressed. There are few material alternatives for hydrogen pipelines. The absence of high-strength, hydrogen-resistant, and cost-effective pipeline materials prevents the expansion of hydrogen energy.

2.2.3 Materials Used in Hydrogen Refueling Stations

Hydrogen refueling stations (HRSs) are essential to the hydrogen energy sector and fuel cell car advancement. In Fig 2. 7, hydrogen is brought to the facility by tube trailers or pipes, compressed by a hydrogen compressor, and then preserved in a high-pressure cylinder. Hydrogen is supplied to the fuel cell car via a dispenser.

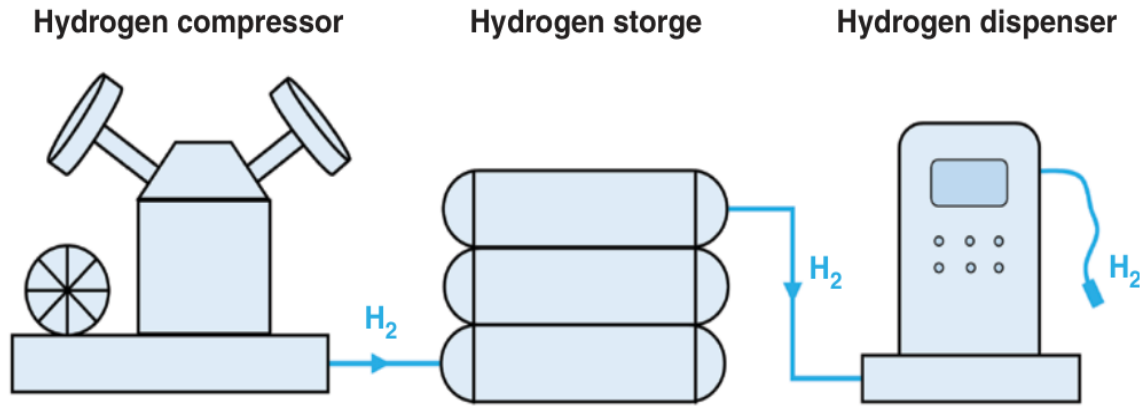


Fig 2. 7 HRS main facilities.

Currently, most hydrogen stations follow the 35-MPa requirement, with just a small percentage in China meeting the 70-MPa level.

Every hydrogen station has a daily capacity of 160 kilograms, sufficient to supply 300 hydrogen fuel cell vehicles (HFCVs). In the early phases of commercialization, production rates might reach 450 kg/day, necessitating an increase in the HRS's hydrogen pressure norm to 90 MPa. For the HRS to function securely and steadily, it requires reliable structural materials in its main components.

a. Materials Used for Hydrogen Compressors

Diaphragm hydrogen compressors are commonly made to compress hydrogen to very high pressures for use in hydrogen plants. In the compression zone, the diaphragm and cylinder head are subjected to strong cyclical stresses and changes in temperatures (ranging from ambient temperature to 200°C). The service life of the diaphragm and cylinder head determines the efficiency as well as safety of hydrogen compressors and HRSs. Efficient

diaphragms and cylinder heads may save expenses and increase efficiency. A high-pressure hydrogen compressor uses a three-layer diaphragm construction, with a gas-side, middle, and oil-side diaphragm. This structure ensures safety. The gas-side diaphragm is more sensitive to HE due to its operation in a hydrogen environment(100).

Table 2.1 displays the materials utilized in diaphragm hydrogen compressors from three distinct businesses. It can be observed that austenitic stainless steel remains the preferable structural material in hydrogen settings.

Table 2. 1 Materials used in hydrogen compressor diaphragms from different companies

Manufacturers	Gas diaphragm	Middle diaphragm	Oil diaphragm
Sundyne (101)	ASS	ASS	ASS
PDC (102)	ASS / Inconel alloy	Brass	ASS
Hofer (103)	ASS	Be–Cu	Dual phase steel

ASS is currently the most often utilized structural material for hydrogen compressors. Alloy 625, a nickel-based alloy, is suitable for high-pressure diaphragms, however dependability and stability are important factors to consider. Developing cost-effective, high-strength diaphragm materials for hydrogen compressors continues to be important.

b. Materials for Hydrogen Storage Systems in HRSs

In HRSs, hydrogen may be stored in two ways: gaseous or liquid form.

In China, high-pressure gaseous-hydrogen storage is primarily employed, with type I and Type II cylinders being the most common kind. The Type I metallic is constructed of stable austenitic stainless steel or Cr-Mo steel, whereas the Type II liner is built of an aluminum alloy.

Liquid hydrogen storage is widely employed in HRSs in Europe, Japan, and the United States. Liquid hydrogen storage involves a decrease in temperature gaseous hydrogen to less than -253°C via a liquefaction technique (84). Metallic materials frequently undergo brittle transitions from ambient temperature to cryogenic temperatures. It depends on the chemical composition of the components (104). Austenitic stainless steels (316 and 316L) are commonly employed in liquid-hydrogen storage due to their great resistance to cryogenic temperatures (105). However, Ni and N have a considerable impact on ASS embrittlement at cryogenic temperatures (106). Ni can decrease the brittleness of ASS and prevent martensite transition. N improves strength but decreases ASS stacking faults and raises brittleness.

316LN and 304LN ASSs might be utilized with caution in cryogenic vessels with increased nitrogen concentration compared to grades 316L, 316, 304L, 304, and 301 (107).

Metal materials often experience HE at ambient temperature, but a latest study found it can happen at cryogenic temperatures (108). However the majority of the data for HE is collected in gaseous hydrogen circumstances, and there is no clear proof that liquid

hydrogen may cause embrittlement of materials (109). Storage facilities experience heat cycles throughout activities, exposing valves and joints to high-pressure gaseous hydrogen from evaporation at extreme temperatures (110). As a result, materials remain susceptible to HE. Austenitic stainless steels that contain elevated nickel and nitrogen amounts have been shown to be more resistant in hydrogen-containing environments (111,112) .

ASS was previously used for liquid hydrogen storing. Further study is needed on the mechanical characteristics, and HE processes of austenitic stainless steel at cryogenic temperatures. Materials for cryogenic hydrogen storing vessels must be carefully chosen and designed.

c. Materials Used for Hydrogen Dispensers

The hydrogen distributor refuels and measures hydrogen for HFCVs. Hydrogen comes into the distribution system via the inlet valve, high-pressure filtering mechanism, pneumatic shift valve, and then flows into the car's hydrogen storage chamber via the nozzle. Nozzles, filters and valves are essential connecting elements in the process.

When selecting materials for hydrogen-containing elements, it's important to take into account not just pressure resistance, security, and reliability, but also the HE resistance of metals.

Some findings (113) suggest that because of ASSs' low hydrogen diffusion coefficient and extended service, items with a thickness of more than 1 mm require just a surface layer of

hydrogen. The aforementioned parts are constructed of austenitic stainless steel, such as 316L, and some include aluminum alloy liner.

2.3 Hydrogen Embrittlement in Steel

Hydrogen embrittlement (HE) in steels is a complex degradation phenomenon involving hydrogen adsorption, dissociation, absorption, diffusion, trapping, and subsequent fractures due to several interaction mechanisms. These mechanisms through which HE manifests are still under active investigation and are strongly dependent on material microstructure, hydrogen source, environmental conditions, and mechanical loading.

Hydrogen enters the steel through electrochemical reactions, corrosion, or high-pressure gas exposure. Once inside, hydrogen diffuses through interstitial sites typically tetrahedral in BCC and octahedral in FCC bulks and accumulates at microstructural traps such as dislocations, grain boundaries, vacancies, and inclusions. These traps are classified based on their binding energy Fig 2. 8: reversible (e.g., dislocations) or irreversible (e.g., carbides and voids) (114–116). The mechanisms of hydrogen movement are governed by concentration gradients, hydrostatic stress, and dislocation movement

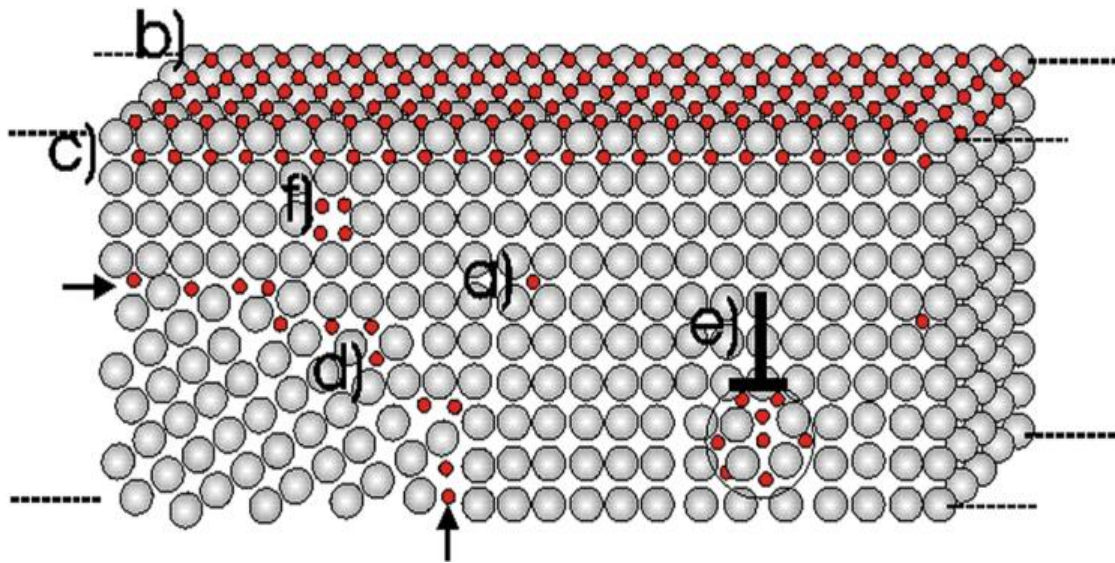


Fig 2. 8 Traps of hydrogen in steels: a) interstitial sites; b) surface traps; c) subsurface traps; d) grain boundary; e) dislocation; f) vacancy (117).

Mechanisms of Hydrogen Embrittlement

Several mechanisms have been proposed to explain HE, and their activation largely depends on material microstructure, loading conditions, and hydrogen concentration.

2.3.1 Hydrogen-Enhanced Decohesion (HEDE)

The HEDE model suggests that hydrogen reduces the cohesive strength of metallic bonds, particularly at crack tips, grain boundaries, and phase interfaces Fig 2. 9. This weakening facilitates atomic separation under relatively low stress levels. The stress-dependent local hydrogen concentration can be described using a modified cohesive stress model (118) and is further influenced by hydrostatic stress and plastic strain (119,120). The effect of hydrogen on grain boundary strength has been shown to linearly reduce cohesive energies

in theoretical studies (121), and this is supported by intergranular fracture observations (122).

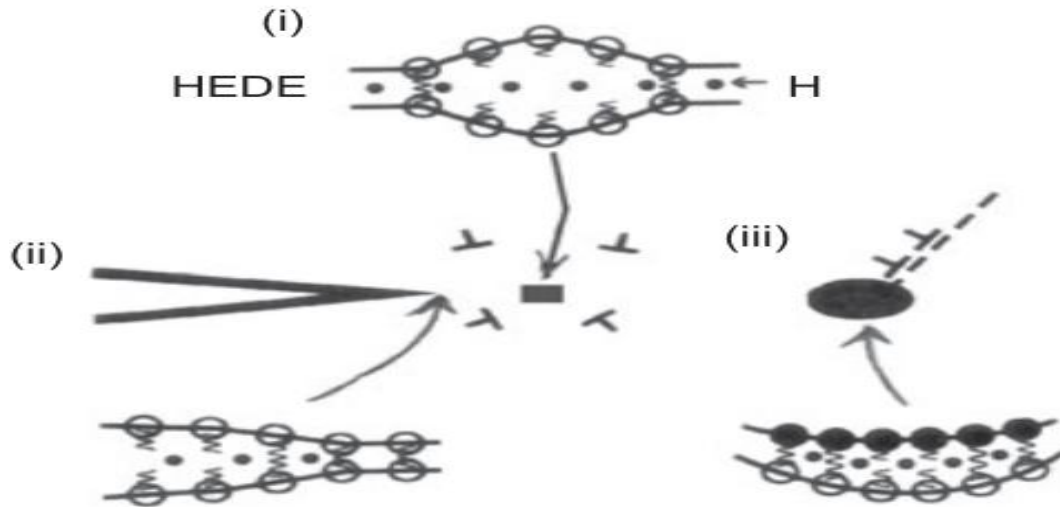


Fig 2. 9 Diagrammatic representations of the HEDE process that show how atoms separate by tensile as a result of interatomic bonds being weakened by (i) hydrogen in the lattice, (ii) adsorbed hydrogen, and (iii) hydrogen at particle-matrix interfaces.

2.3.2 Hydrogen-Enhanced Localized Plasticity (HELP)

In the HELP mechanism, hydrogen enhances dislocation mobility by reducing the interaction between dislocations, leading to localized plastic deformation ahead of the crack tip. This results in strain localization and premature failure Fig 2. 10. In-situ TEM observations confirm hydrogen's role in accelerating dislocation nucleation and motion (123). However, some studies also report hydrogen as a drag force on dislocations, indicating the mechanism may be condition dependent.

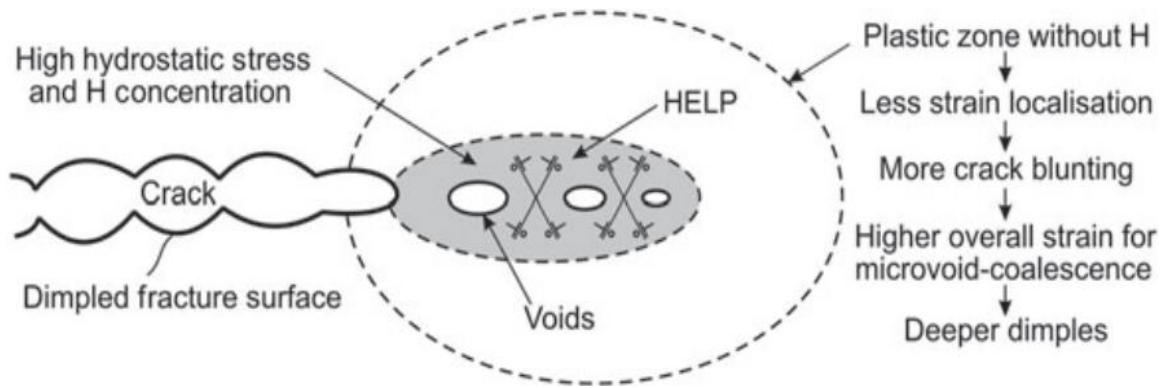


Fig 2. 10 Diagrammatic representation of the HELP mechanism, which involves a micro void-coalescence process that localizes and facilitates plasticity in areas with high hydrogen contents.

2.3.3 Adsorption-Induced Dislocation Emission (AIDE)

AIDE extends the HELP concept by focusing on the role of adsorbed hydrogen at crack tips in initiating dislocation activity. It emphasizes that dislocation emission is not limited to the crack tip but occurs in zones where hydrogen adsorption lowers bond strength, enabling easier plastic deformation and nano-void formation. This mechanism accounts for observed mixed-mode fractures and is often coupled with HELP in models (Fig 2. 11).

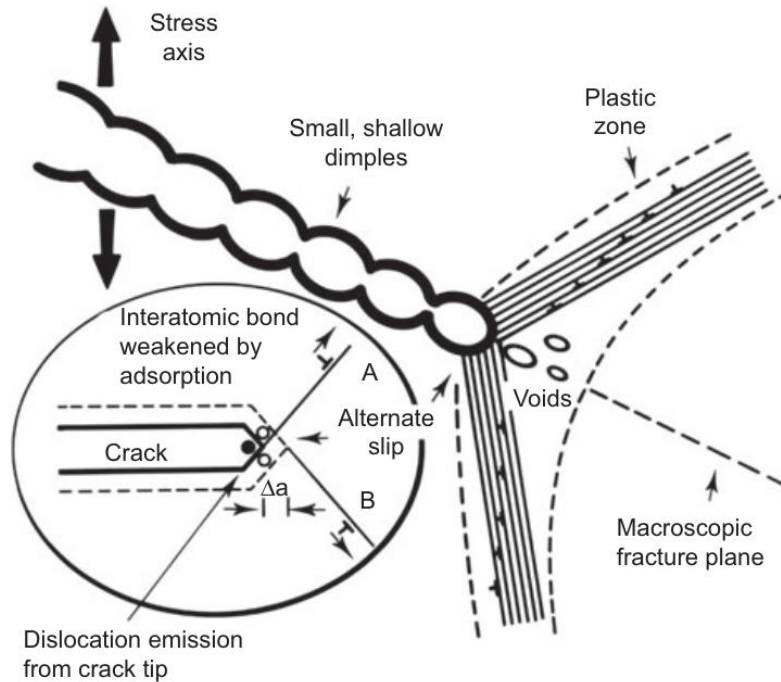


Fig 2. 11 Diagrammatic representation of the adsorption-induced dislocation emission (AIDE) process for Hydrogen environment embrittlement (HEE), which involves alternating-slip crack formation from fracture tips (for transgranular routes), allowing cracks to consolidate with voids created in the plastic zone before cracks (124).

2.3.4 Hydrogen-Induced Phase Transformation (HIPT)

This mechanism is particularly relevant for hydride-forming metals but can also apply to certain steels. Hydrogen accumulation at high-stress areas results in hydride nucleation, which embrittles the microstructure. Fracture then proceeds along the cleavage planes of these brittle hydrides before being arrested at the hydride-matrix interface, repeating cyclically (Fig 2. 12).

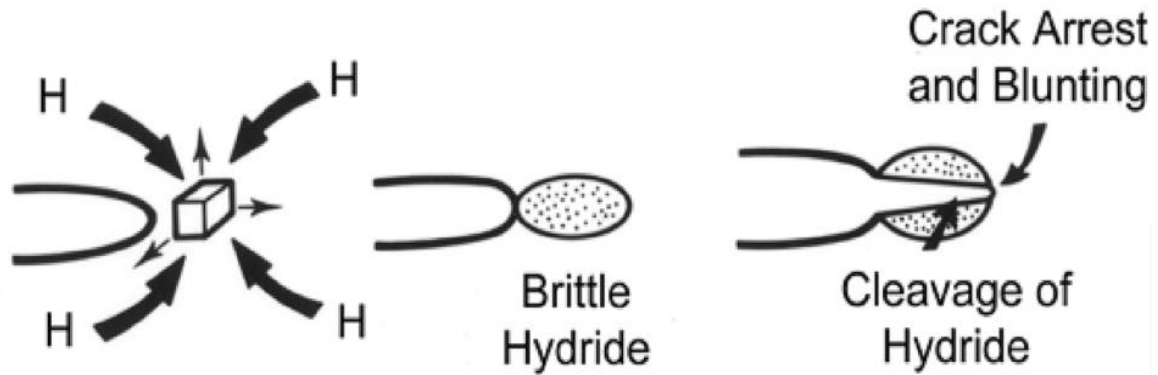


Fig 2. 12 Diagrammatic representation of subcritical crack propagation that shows the creation and fracture of a brittle hydride at the tip of the crack, followed by hydrogen migration to hydrostatically stressed areas.

2.3.5 Hydrogen-Enhanced Strain-Induced Vacancy (HESIV) Mechanism

In the HESIV mechanism, hydrogen stabilizes vacancies created by plastic deformation, which then evolve into nano-voids. These voids coalesce and contribute to crack propagation. It also facilitates the Nanovoid Coalescence (NVC) mechanism (Fig 2. 13).

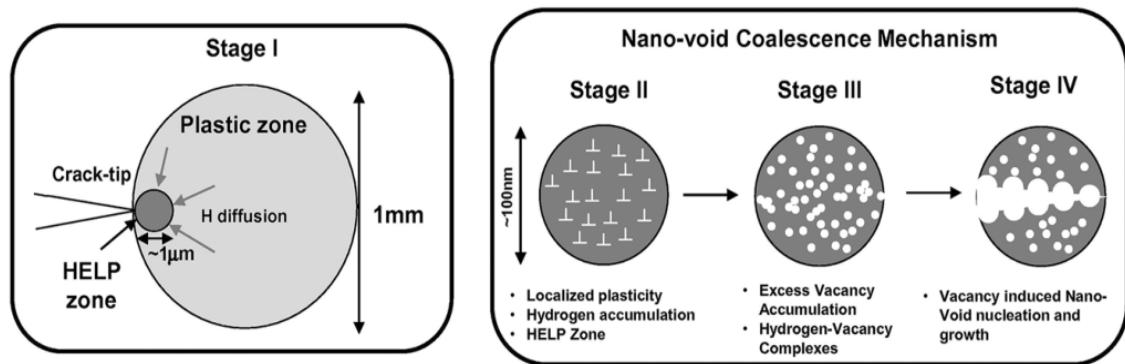


Fig 2. 13 Diagrammatic representation of Hydrogen-Enhanced Strain-Induced Vacancy (HESIV) Mechanism.

2.3.6 Synergistic Models and Mixed Modes

Recent models acknowledge that HE mechanisms often coexist. For instance, a hybrid HEDE–HELP mechanism has been proposed to explain fracture surfaces and microstructural changes that exhibit both brittle cleavage and localized ductile features (Fig 2. 14). These models are supported by experimental data showing alternating roles of decohesion and plasticity based on hydrogen concentration and stress state.

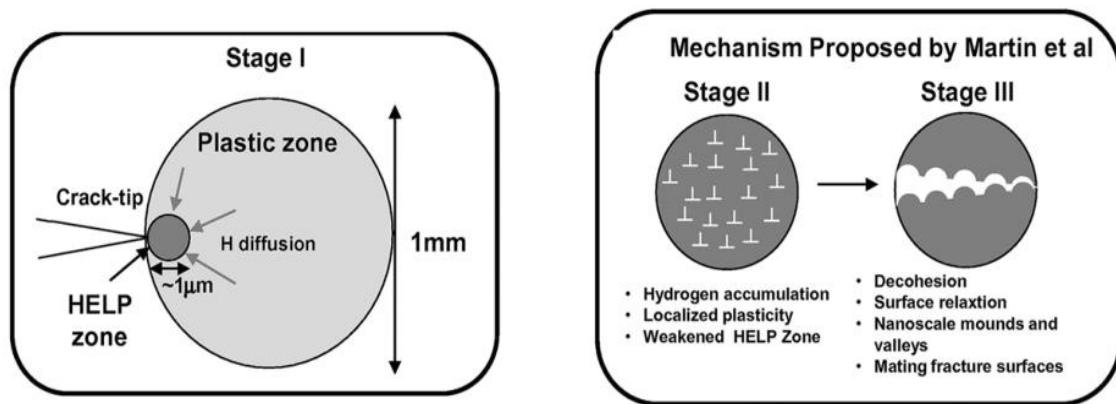


Fig 2. 14 combined effect of HEDE and HELP mechanism (125).

2.4 Density Functional Theory (DFT)

Density Functional Theory (DFT) is a quantum mechanical modeling method used to investigate the electronic structure (principally the ground state) of many body systems, particularly atoms, molecules, and solids. It is a powerful computational quantum mechanical modeling method widely used in physics, chemistry, and materials science for calculating the electronic properties of systems with a large number of particles.

DFT originated from the Thomas-Fermi model in the early 20th century, but its practical application was limited due to its simplicity. The real breakthrough came in the 1960s with the work of Hohenberg and Kohn, who proved that the ground state properties of a many-electron system are uniquely determined by its electron density, rather than its many-body wavefunction (Hohenberg-Kohn Theorems) (126). This was followed by the Kohn-Sham equations, which reformulated DFT to include kinetic energy in a more manageable form by introducing a system of non-interacting particles that have the same density as the interacting system (127).

At the core of DFT is the concept of electron density $\rho(\mathbf{r})$, which is a function of spatial coordinates and determines the ground-state properties of the system. The key advantage of using electron density over the many-electron wavefunction is the reduction in complexity; while the wavefunction of an N -electron system depends on $3N$ spatial coordinates, the electron density depends only on three. DFT relies on approximations to the exchange-correlation functional, $E_{xc}(\rho)$, which encompasses all the quantum mechanical interactions between electrons. Various approximations exist, such as the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA), each providing different balances of accuracy and computational cost (128).

DFT is employed in various fields due to its versatility and relative computational efficiency. In materials science, it is used to predict the structural, electronic, magnetic, and optical properties of materials. For example, it helps in understanding and designing new materials with desired properties by providing insights into their electronic structure and potential reactivity (129).

The implementation of DFT involves solving the Kohn-Sham equations self-consistently. This typically requires iterative numerical methods and high-performance computing resources. Popular software packages for performing DFT calculations include VASP (Vienna Ab-initio Simulation Package), Quantum ESPRESSO, and ABINIT, among others (130).

Despite its widespread use, DFT is not without limitations. The accuracy of DFT calculations heavily depends on the choice of exchange-correlation functional. While LDA and GGA are widely used, they may not always provide accurate results for systems with strong correlation effects, such as transition metal oxides. More advanced functionals, such as hybrid functionals and those incorporating van der Waals interactions, have been developed to address some of these issues, but they come at a higher computational cost (131).

Ongoing research in DFT aims to improve the accuracy of exchange-correlation functionals and develop more efficient computational algorithms. Machine learning techniques are also being integrated with DFT to predict electronic properties more efficiently and accurately. These advancements will expand the applicability of DFT to more complex and larger systems, further solidifying its role as a crucial tool in theoretical and computational chemistry and materials science (132).

2.5 Structural Dependence of FCC Iron on Magnetic Model and Magnetization

Magnitude

Considering the magnetization effects when modeling magnetic metals is of great importance since it may change the crystal cell dimension and even type, which in turn, has an impact on other characteristics of the metal.

At room temperature, unlike most metals that show FCC structure, BCC is the most stable form of iron, referred to as α -iron. Nevertheless, iron can still be arranged in FCC form (denoted by γ -iron) but at elevated temperatures above 1000 K. The reason behind the iron's exception as a BCC structure is its magnetization, that is, due to its four unpaired electrons in each atom, iron exhibits significant magnetic behavior (133). However, the magnetic effect that turns the iron into FCC can be disabled only by adding specific alloying elements that stabilize FCC steel at room temperature e.g., manganese austenitic steels and austenitic stainless steel. The most famous alloying elements used for that purpose are nickel and manganese, also known as austenite stabilizers, that is, they lead to austenitic steel, which in turn is practically non-magnetic.

Since iron atoms are the same in both γ and α -iron, that is, each atom has four unpaired valence electrons, the difference in the observed magnetic behavior attracted intensive investigation. Many studies were performed to investigate the secret behind the non-ferromagnetic nature of gamma-iron, which led to the general concept of antiferromagnetism, or in other words, the pattern of alignment of opposite magnetic moments that result in zero magnetization (134–136).

H. C. Herper et al performed an ab initio study to investigate the magnetic characteristics and structural properties of two suggested antiferromagnetic structures (AFM) (137). The first structure is the single-layer antiferromagnetic, denoted by AFM1. In this structure, layers along the [001] direction (001 planes) are given equal magnetic moment values, but in opposite directions for each layer after layer, that is, alternative spin-up spin-down single layers will be found along [001]. The second magnetic structure is the double-layer antiferromagnetic (AFMD). Here, rather than the opposite magnetic moment that comes after each single layer in AFM1, two subsequent layers are given the same magnetic moment in the same direction after which two other layers are given the same magnetic moment value but in the opposite direction.

Using the full potential linear augmented plane- wave function (FLAPW) within the general gradient approximation (GGA) the equation of state and the equilibrium magnetic moment values were obtained for the mentioned magnetic structure along with the ordinary ferromagnetic and nonferromagnetic states for both BCC and FCC iron Fig 2. 15.

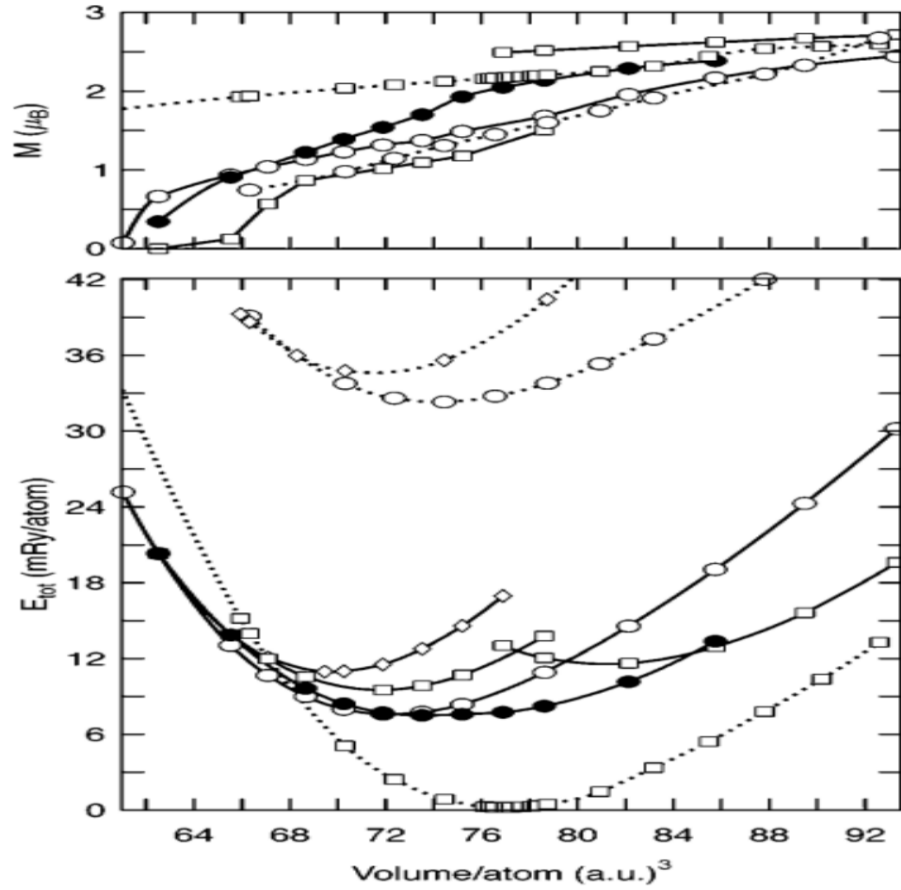


Fig 2. 15 Equation of State and the Corresponding Magnetic Moment Values of FCC (solid lines) and BCC (dashed lines) Iron. Diamonds refer to NM, Squares FM, Open Circles AFM1, and Filled Circles AFMD.

One can notice that the most stable pure iron structure at 0 K is the FM one, which has the lowest energy at its optimum lattice parameter. The AFMD and AFM-I FCC irons come in second and third place respectively with no considerable energy difference at their optimum lattice parameter. D. E. Jiang and Emily A. Carter reproduced the equation of the state for

the same magnetic and crystal structures but by using the projector-augmented wave method (PAW-GGA) to study the carbon dissolution and diffusion of the best magnetic model Fig 2. 16 (133).

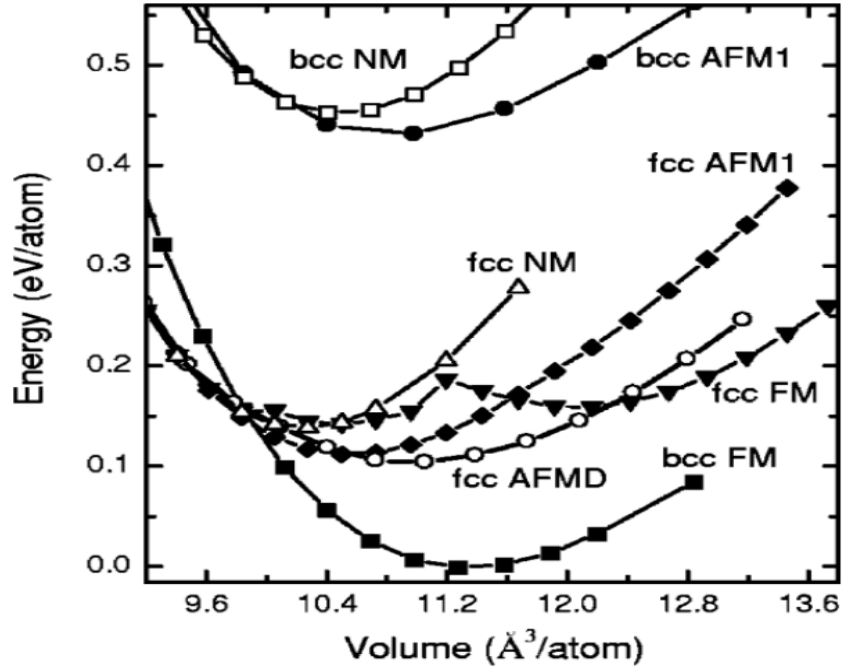


Fig 2. 16 Equation of state of bcc and FCC iron with different magnetic structure.

Even though there are some differences in the optimum resulting lattice parameters for AFM structures, the overall trend showed perfect agreement for both PAW and FLAPW methods.

Generally, PAW results agreed with the FLAPW results except for some magnetic structures which show lattice parameter difference up to 0.2 Å. However, since both studies

affirmed that the AFMD magnetic model is the most stable form of FCC structure, comparing its

characteristics with experimental data are essential to figure out how realistic it could be.

Acct M

et al (138) derived the lattice parameter value of gamma iron at 4 k by extrapolating from the results of iron alloys. The resulting value was 3.56 Å for FCC AFM (133), which is quite close to the predicted values by AFMD theoretical calculations, that is 3.52 to 3.53.

Furthermore, experiments suggest that the magnetic structure of iron is not a collinear spin like the AFMD structure, but rather, a noncollinear spin known as a spin spiral state (139).

This suggestion is also supported by other theoretical investigations (140,141).

Nevertheless, and based on another study (142), the AFMD magnetic structure is still regarded as a good approximation of the magnetic state of gamma iron.

It is important to notice that not only the magnetic structures (how spin moments are arranged) influence the lattice parameter and the material's properties but also the magnetization value itself. For the ferromagnetic FCC iron, where magnetic moments are aligned in one direction, two states are possible depending on the magnetic moment magnitude, namely the low-spin and high-spin ferromagnetic FCC (FM-LS and FM-HS respectively). Fig 2. 17 shows the dependence of the equilibrium lattice parameter on the magnetic moments' magnitude in which two minimums can be observed, one with a higher volume, higher energy for FM-HS, and the other with a lower volume, lower energy for the FM-LS. Unlike FM-LS and NF, AFM (spin spiral state) and FM-HS have been

experimentally observed (143), hence, these phases are the best choice for modeling the FCC iron for any type of computational investigation. D. E. Jiang and Emily A. Carter adopted the FM-LS model to calculate the diffusion barrier for carbon in gamma-iron, their result was lower than the experimentally obtained value by about 0.60 eV (133), which means it cannot be regarded as a good approximation of the paramagnetic state of gamma iron, and difference of the lattice parameter of that is due to the magnetic phase is affecting the diffusion barrier.

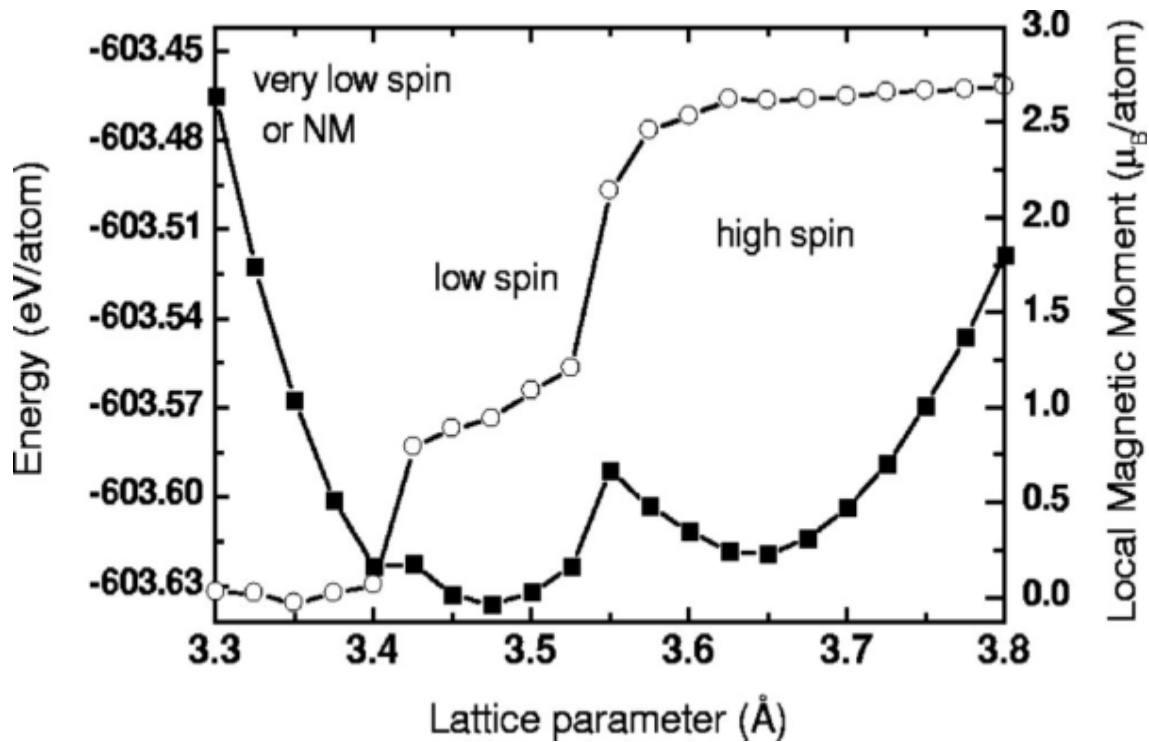


Fig 2. 17 The local magnetic moment (open circles) and total energy (solid squares) of FM FCC Fe as a function of lattice parameter.

Chohan et al (144) studied hydrogen adsorption and diffusion in gamma iron (100), (110), and (111) surfaces, even though they didn't report the magnetic model they used, one still

can infer this information from the lattice parameter value they obtained which is 3.43 Å. This value most closely refers to the NM FCC iron. Their diffusion of activation energy proved in great agreement with experimental results, while on the other hand, the diffusion barrier results were twice the experimentally measured ones. This outcome is reasonably justified since the real gamma iron has a larger free volume than the modeled one (0.13 Å longer lattice constant) which makes it easier for carbon atoms to diffuse within the bulk.

In ref (145) Chohan considered the magnetization effect on the structural and surface characteristics and the diffusion and adsorption energetics. This time, the investigation was done only on the (001) surface but for the previously mentioned four magnetic structures: NM, FM, AFM1, and AFMD. The magnetic structure type is attributed to the spin direction of the 3d free electrons which might interact with interstitial atoms, therefore it is justified to study the isolated effect of the magnetic state independently. Figs 2. 18 and 19 show the structural optimization and surface relaxation results, respectively, of the different magnetic models. One can notice that when magnetization is considered, the gamma iron structure is no longer a perfect cube, but rather, a tetragonal with different c/a ratios governed by the specific spin arrangement. Due to magnetic repulsion, the FM model has a larger c/a ratio. Due to the same reason, it showed a net expansion after being in the surface form not unlike typical surfaces, that is, 1.18% contraction between the first two layers and 0.98% + 1.08% expansion between the last three layers. Furthermore, the AFM1 surface structure proved structural stability in which the layers barely moved from their bulk positions contributed to the effect of opposite spin exchange interaction (146). At the same time, NM and AFMD

behaved as typical surfaces with contraction between the first two layers, expansion between the second and the third layer, and contraction again between the last two layers.

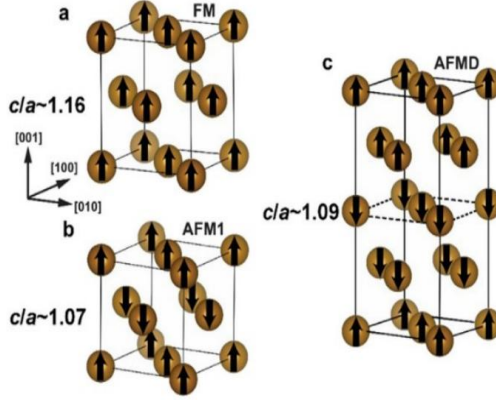


Fig 2. 18 Bulk c/a Ratios of (a) FM, (b) AFM1, and (c) AFMD FCC Iron.

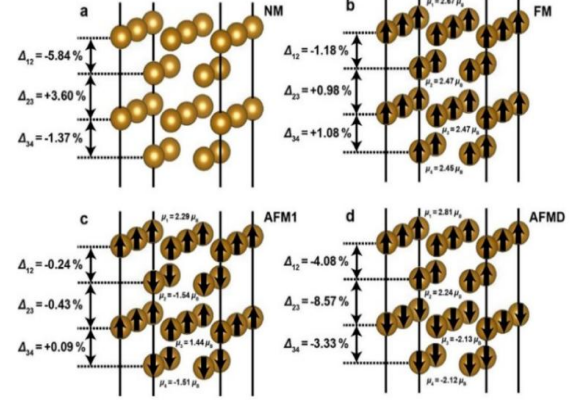


Fig 2. 19 Surface Relaxation of (a) NM, (b) FM, (c) AFM1 and (d) AFMD FCC Iron.

In ref. (147) and after studying the hydrogen adsorption and diffusion for the three main crystal planes, (100), (110), and (111), of NM FCC iron in ref. (144) and performing a similar investigation on the (100) surface but for four different magnetic states for the same material and structure in ref. (145), Chohan completed the picture by finding all the energetics of the 12 combinations resulting from the three surfaces and four magnetic phases, in addition to studying the hydrogen adsorption and diffusion for all 12 cases. Table 2. 2 summarizes the results of the related calculations. It can be seen that the magnetic

structure in itself does not significantly affect the adsorption height ($\approx 0.1 \text{ \AA}$) which has similar values of about $1 \text{ \AA}$ for (100) and (111) surfaces and about $0.6 \text{ \AA}$ for the (100) surface. However, it is not the same case regarding the magnetic state effect on the adsorption and diffusion energetics that show considerable change in values between each model for the same surface. In other words, the magnetic state does not influence the extent of interaction between the surface and the hydrogen atom. Still, once the interaction has been made, its nature will be governed by the values and directions of magnetic spin moments. For the (100) and (111) surfaces, the bulk energetics are largely affected by the magnetic model change than the adsorption energetics, on the other hand, the opposite is true for the (110) surface which proves the point of the spin direction impact on the exchange magnetic interaction between the hydrogen atom and the iron atoms. As can be seen in the table, the total energy barrier for diffusion is greater in the case of (111) surface, therefore, a polycrystalline Gamma iron with higher (111) surfaces (also energetically favorable) will be less exposed to hydrogen embrittlement (HE) (148), which is a phenomenon of the metals' failure due to hydrogen atoms' penetration through the metal bulk. T. Hickel et al accepted the AFMD model as an efficient approximation of the paramagnetic gamma iron and applied it to calculate the hydrogen solubility (149). They found that the solution enthalpy is not greatly affected by the increase in lattice parameter value in FCC iron while it was sensitive to this structural change in BCC iron. This was interpreted by the difference in free volume between the tetrahedral site in BCC iron and the octahedral site in FCC iron, that is, since the free volume is larger in the FCC site, the stresses and pressure over the lattice are already at a minimum compared to that of BCC

interstitial site. The solution enthalpy in tetrahedral BCC was twice that of the octahedral FCC, which means Gamma iron has a higher hydrogen solubility.

Table 2. 2 Hydrogen adsorption results: Height (d_{H-surf}), Adsorption Energy (E_{ads}), Total Barrier for Diffusion ($E_{total_barrier}$), and Bulk Diffusion Energy (E_{bulk}) for 12 γ -Fe surface planes across four magnetic states: NM, FM, AFM1, and AFMD.

FCC-Fe (Adsorption Site)	Magnetic State	d_{H-surf} (Å)	E_{ads} (eV)	$E_{total_barrier}$ (eV)	E_{bulk} (eV)
100 (4f)	NM	0.9	4.07	1.3	0.6
	FM	1.0	4.12	0.9	0.2
	AFM1	0.9	4.03	1.4	0.4
	AFMD	1.0	4.05	1.2	0.5
110 (4f)	NM	0.6	3.92	1.2	0.5
	FM	0.7	4.36	1.1	0.6
	AFM1	0.6	4.28	1.1	0.7
	AFMD	0.7	3.76	1.0	0.6
111 (3f)	NM	1.0	4.05	1.7	1.2
	FM	1.0	4.27	1.4	0.5
	AFM1	1.0	4.18	1.3	0.6
	AFMD	1.1	4.35	1.4	0.9

2.6 Hydrogen Interaction with Alloyed Iron Using DFT

A wide range of density functional theory (DFT) studies have explored hydrogen interaction with both clean and alloyed iron surfaces, particularly on BCC and FCC structures. Table 2. 3 presents a classification of these studies by surface index, alloying elements, and interaction types including adsorption, dissociation, absorption, diffusion, and desorption. On clean iron surfaces, adsorption has been the most widely investigated process, particularly on the (100), (110), and (111) planes, with BCC iron receiving broader attention. Diffusion studies are also well represented, particularly for (100) and (110) BCC surfaces, indicating a focus on subsurface hydrogen penetration.

While extensive DFT studies have been conducted on hydrogen interaction with clean BCC and FCC iron surfaces, a clear research gap exists in the investigation of hydrogen behavior in alloyed FCC iron systems. The literature shows that most adsorption, diffusion, and dissociation studies involving alloying elements such as Cr, Ni, C, Mo, Si, Mn, Al, and Cu are concentrated in the BCC phase, particularly on the (100) and (110) surfaces. In contrast, for FCC iron, alloying effects remain significantly underexplored, with only a limited number of references addressing hydrogen adsorption and diffusion on alloyed (100) FCC surfaces, and little to no data available for other FCC planes such as (110) and (111). This limited focus hinders the comprehensive understanding of how common alloying elements influence hydrogen trapping, diffusion, and embrittlement resistance in austenitic (FCC) steel materials widely used in hydrogen-rich environments. Addressing this gap is crucial, as alloying can alter the electronic structure, magnetic state, and local stress environment, all of which impact hydrogen energetics. Therefore, more systematic DFT investigations are needed on hydrogen interaction with multi-element alloyed FCC iron phase across

various crystallographic orientations to support the design of advanced, hydrogen-resistant austenitic steels.

Table 2. 3 Simulation studies review on hydrogen interaction with BCC and FCC iron using DFT. (150–195)

Surface	Alloying element	Interaction type	BCC	FCC
(100)	Clean	Adsorption	151,152,156,157,163,165,168, 170,171,172,173,174,177,178, 183,184,187,189,191,194,195	154,159,160,164,167,17 6,194
		Absorption	151,152,163,177	
		Diffusion	151,152,174,177,186,194	154,160,164,176,194
		Dissociation	152,156,165,168,171,177,184, 195	
		Desorption	157	
	Cr	Adsorption	164,168,169,170	
		Diffusion	169	
		Dissociation	168	
	Ni	Adsorption	164,168,169	
		Diffusion	169	
		Dissociation	168	
	C	Adsorption	166,167	
		Diffusion	166	

	Mo	Adsorption	168	
		Dissociation	168	
	Si	Adsorption	169	
		Absorption	153	
		Diffusion	153,169	
	Mn	Adsorption	169	
		Diffusion	169	
	Al	Adsorption	167	
		Absorption	153	
		Diffusion	153	
	Cu	Adsorption	187	
		Diffusion	187	
	(210) (211) (310) (321)		Adsorption	157,172
			desorption	157
(110)	Clean	Adsorption	150, 154, 155, 162, 172, 173, 174, 180, 181, 185, 186, 188, 193, 194	160, 164, 179, 194
		Absorption	151,155	
		Diffusion	150, 151, 154, 174, 188, 194	160, 164, 179, 194
		Dissociation	186,188	
	C	Adsorption	190	
		Absorption	190	
	Co	Adsorption	182	

		Diffusion	182	
		Dissociation	182	
	Al	Absorption	153	
		Diffusion	153	
	Si	Absorption	153	
		Diffusion	153	
(111)	Clean	Adsorption	157, 172, 173, 194	160, 161, 164, 175, 181, 192, 194
		Diffusion	194	160,164,194
	C	Adsorption		175

CHAPTER 3

COMPUTATIONAL METHODS AND MODELING

3.1 First-Principles Simulations

Our first-principles calculations are based on the density functional theory (DFT) (196,197) and performed using the Quantum Espresso Simulation Package (198), which applies the density functional theory to perform studies on materials at the atomic level scale. The projector augmented wave pseudopotential is used to describe core electrons' interaction with the outer shell (199); moreover, the Perdew-Burke-Ernzerhof GGA-based exchange-correlation functional is employed to ensure better accuracy (200). The kinetic energy cutoff for wavefunctions is set to 85 Ry (Fig 3. 1).

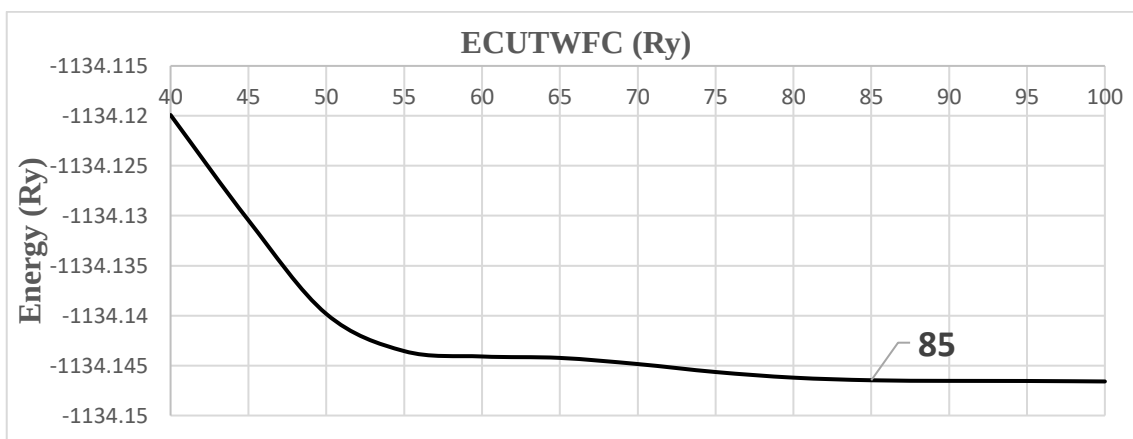


Fig 3. 1 kinetic energy cutoff for wavefunctions (Ecutwfc) Convergence.

3.2 FCC Iron Bulk

Based on the literature, we modeled the magnetic behavior of FCC iron using the double anti-ferromagnetic (AFMD) approximation, represented by the magnetic configuration $\uparrow\uparrow\downarrow\downarrow\ldots$ with alternative magnetic moments of the same value in the [001] direction with a total of 4 layers (Fig 3. 2), in other words, the bottom two layers spin down while the top two layers spin up. This structure dictates a $4 \times 4 \times 2$ k points mesh to ensure balanced calculations (Fig 3. 3). The starting magnetization is 2.4 Bohr.

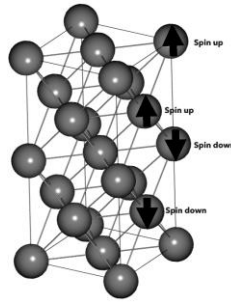


Fig 3. 2 Antiferromagnetic double-layer (AFMD) iron FCC Structure.

The consideration of magnetization in FCC iron turns its cell from a cubic crystal to a tetragonal one, resulting

in a lattice parameter value of 3.48 Å and $c = 3.65$ Å, which is near to ($a = 3.46$ Å, $c = 3.74$ Å) previous simulation study (201,202) additionally our c/a ratio of 1.05 is very close to the reference (203) ratio's value of 1.09 and others studies (204,205). Furthermore, our lattice parameter closely matches experimental observation of FCC AFM (3.56 Å). The experimental value was determined by extrapolating the lattice parameter of FCC Fe alloys at 4 K to a pure Fe concentration (206).

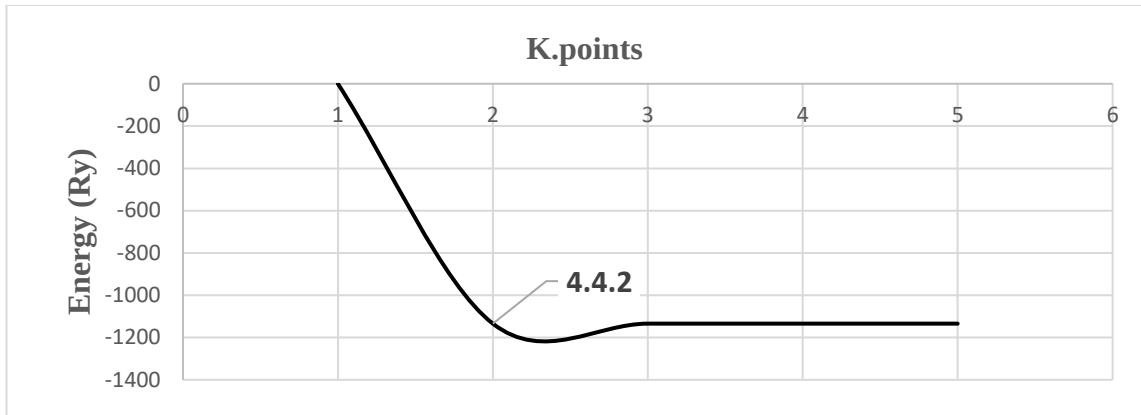


Fig 3. 3 K points convergence.

3.3 Hydrogen Adsorption

To simulate the surface and bulk of FCC-Fe, a six-layer slab configuration with dimensions of 2×2 in the x-y plane was created along the direction $[0\ 0\ 1]$. Since our software simulation set the magnetic moment along the z-axis by default, we selected the $(0\ 0\ 1)$ plane to model the hydrogen adsorption. The two bottom layers were fixed to simulate the bulk region below the surface, while the top four layers were allowed to relax, enabling surface reconstruction. A vacuum spacing of 20 Å.

For the calculation of hydrogen adsorption energies, three high-symmetry adsorption sites: top, bridge, and hollow—were examined on the clean slab Fig 3. 4 (a). For doped surfaces with substitutional alloying elements, an extended set of five high-symmetry adsorption sites was considered: top on Fe atom (Top-Fe), top on alloying element atom (Top-M), hollow, bridge between two Fe atoms (Fe-Fe Bridge), and bridge between a Fe atom and an alloying element atom (M-Fe Bridge) Fig Fig 3. 4 (b). For doped surfaces with interstitial

alloying elements, four possible adsorption sites were considered, the same as in Fig 3. 4 (b), except for the last site Fig 3. 4 (c).

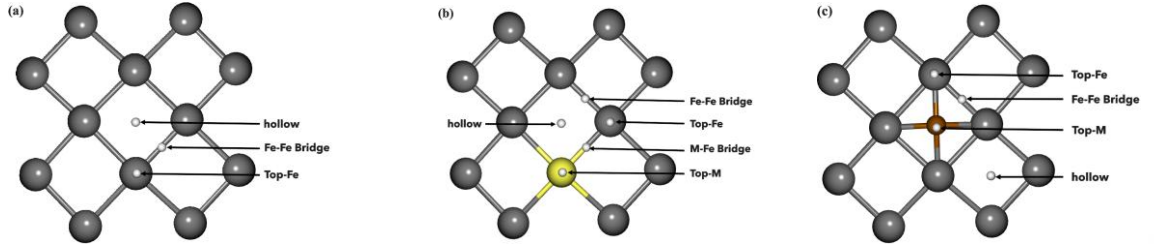


Fig 3. 4 Schematic diagram of possible adsorption sites on the (001) FCC iron slab: (a) clean slab; the gray atom is iron, and the white atom is hydrogen. (b) doped surfaces with substitutional alloying elements; the yellow atom M stands for each of the seven substitutional alloying elements (Cr, Mn, Mo, Ni, P, S, and Si). (c) doped surfaces with interstitial alloying elements; the brown atom M stands for the two interstitial alloying elements (N and C).

The adsorption energy (E_{ads}) at each site on the (001) surface was computed using the relation:

$$E_{ads} = E_{slab+H} - (E_{slab} + E_{H2}/2) \quad \text{Eq 3. 1}$$

Where E_{slab+H} total energy of the slab with hydrogen absorbed, E_{slab} energy of the pristine surface, and E_{H2} ground state energy of an isolated hydrogen molecule confined within a $10 \times 10 \times 10 \text{ \AA}^3$ box.

This approach enables the determination of the energetically preferred adsorption sites and provides insights into the effects of doping elements on hydrogen adsorption behavior.

3.4 Hydrogen Solubility

The solubility of hydrogen in FCC iron bulk was investigated by calculating the binding energy of a hydrogen atom at interstitial sites within the bulk lattice. Octahedral and tetrahedral sites were considered as potential interstitial locations. The calculations were performed using a $2 \times 2 \times 2$ supercell of FCC iron to model the bulk structure (Fig 3. 5).

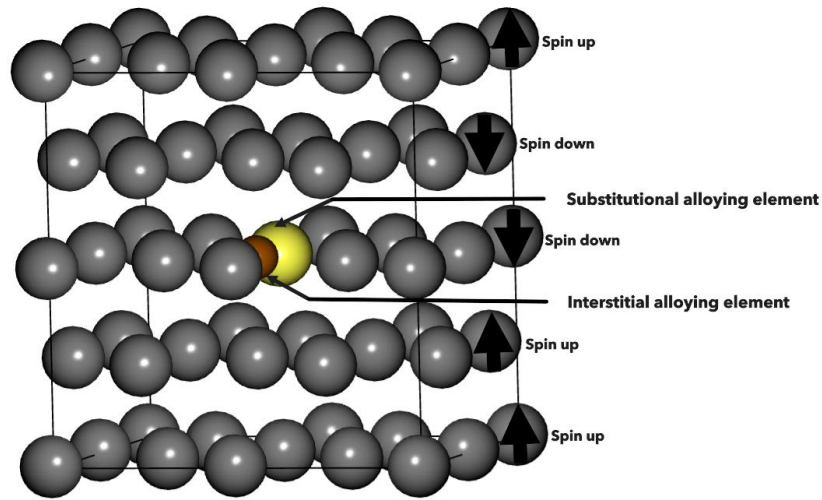


Fig 3. 5 $2 \times 2 \times 2$ supercell of FCC iron: the yellow atom stands for each of the seven substitutional alloying elements (Cr, Mn, Mo, Ni, P, S, and Si), and the brown atom stands for the two interstitial alloying elements (N and C).

For the investigation of hydrogen solubility in FCC iron bulk, a representative set of interstitial sites was selected. In the case of the clean bulk system, only one octahedral site (Oct1) was chosen since all other octahedral sites are symmetrically equivalent. Additionally, two tetrahedral sites were considered: the first (T1) is situated between two spin-down layers, while the second (T2) is located between spin-up and spin-down layers. Fig 3. 6 (a).

For the doped bulk systems, a more extensive selection of interstitial sites was required to account for the localized effects of alloying elements. Four octahedral sites were selected for systems doped with substitute alloying elements: Oct1, located above the alloying element atom; Oct2, positioned beside the alloying element; Oct3, found below the alloying element atom; and Oct4, considered far from the alloying element Fig 3. 6 (b). While bulks doped with interstitial alloying elements, three octahedral sites were selected: Oct1 and Oct3 are similar to the previous ones, while Oct2 is positioned behind the alloying element Fig 3. 6 (c).

Furthermore, eight tetrahedral sites were analyzed in both doped systems. These sites were chosen to evaluate the effects of their proximity to the alloying element and their specific position relative to spin orientation layers, such as between spin-up and spin-down or within same-spin configurations Fig 3. 6. (For a clearer view of the sites, we remove the second and third layers along with a few atoms).

This comprehensive selection of interstitial sites was designed to provide insight into the local alloying element and magnetic effects on hydrogen binding in both clean and doped FCC iron systems.

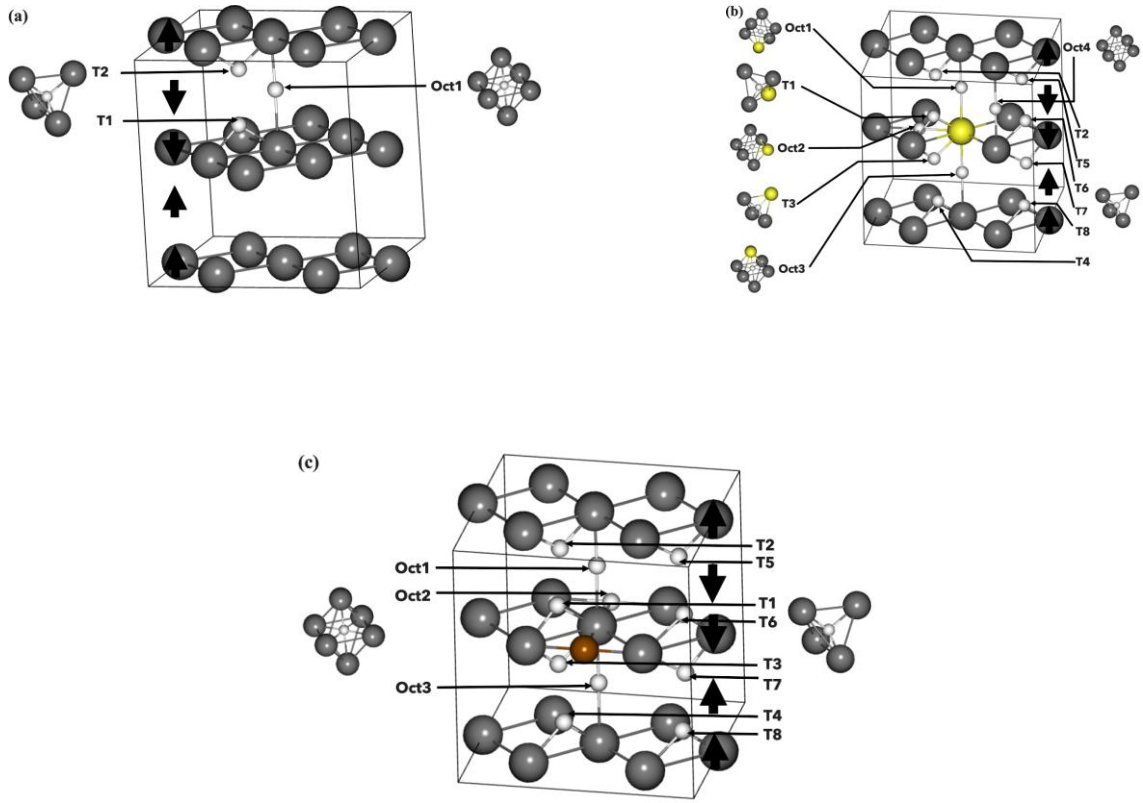


Fig 3. 6 Schematic diagram of possible interstitial sites in FCC iron supercell (a) Clean bulk: the gray atom is iron; the white atom is hydrogen located in octahedral site (Oct) or interstitial site (T). (b) Doped bulks with substitutional alloying elements: the yellow atom stands for each of the seven substitutional alloying elements (Cr, Mn, Mo, Ni, P, S, and Si). (c) doped bulks with interstitial alloying elements; the brown atom stands for the two interstitial alloying elements (N and C).

The binding energy (E_{bind}) was determined using the following relation:

$$E_{bind} = E_{bulk+H} - (E_{bulk} + E_{H2}/2) \quad \text{Eq 3. 2}$$

Where $E_{\text{bulk+H}}$ total energy of the bulk system with a hydrogen atom presents in the interstitial site, E_{bulk} total energy of the pristine bulk structure, and E_{H_2} is the total energy of a single free H_2 molecule in a $10 \times 10 \times 10 \text{ \AA}$ box.

3.5 Hydrogen Diffusion into and Through the Bulk

The interaction between hydrogen and materials also involves the diffusion of hydrogen into and in metallic materials. Interstitial sites inside the crystal lattice are usually occupied by hydrogen atoms when they penetrate an alloy. Diffusion of hydrogen is a process that involves moving between interstitial positions. The Arrhenius equation is a widely recognized experimental relationship that links temperature and diffusion rate (207) as follows:

$$D(T) = D_0 \exp \left(- \frac{E_{\text{Diff}}}{kT} \right) \quad \text{Eq 3. 3}$$

Where E_{Diff} is the activation energy of diffusion, k is Boltzmann's constant, T is the absolute temperature value, and D_0 is the pre-exponential coefficient of diffusion.

To investigate how alloying elements affect the penetration of hydrogen into and through the bulk, we used the climbing-image nudged elastic band (CI-NEB) method (208,209) to calculate the activation energy of hydrogen diffusion E_{Diff} into and through FCC Fe bulk. (CI-NEB) calculations were computed using the same slab of hydrogen adsorption for hydrogen diffusion into the bulk and the same supercell $2 \times 2 \times 2$ of hydrogen solubility for hydrogen diffusion through the bulk. The computational parameters, including plane-wave cutoffs and k-point sampling, were consistent with those used for the previous calculations.

To ensure accurate convergence, 10 images were used, and a force tolerance of 0.05 eV/Å was applied during the optimization process.

This approach, implemented within the PWneb module of the Quantum ESPRESSO package (198), allows for the determination of the minimum energy pathway (MEP) for atomic migration.

The pathway used for hydrogen diffusion into the slab begins at the hollow (H) (the favorable site of all hydrogen adsorption cases) and ends at the tetrahedral site (T) located between the top two layers of the six-layer slab, as illustrated in (Fig 3. 7).

Because of magnetization, we considered two different pathways: the first ends at (T_{ud}), which is located between spin-up and spin-down layers ($H \rightarrow T_{ud}$), and the second ends at (T_{dd}), which is located between two spin-down layers (T_{dd}) ($H \rightarrow T_{dd}$).

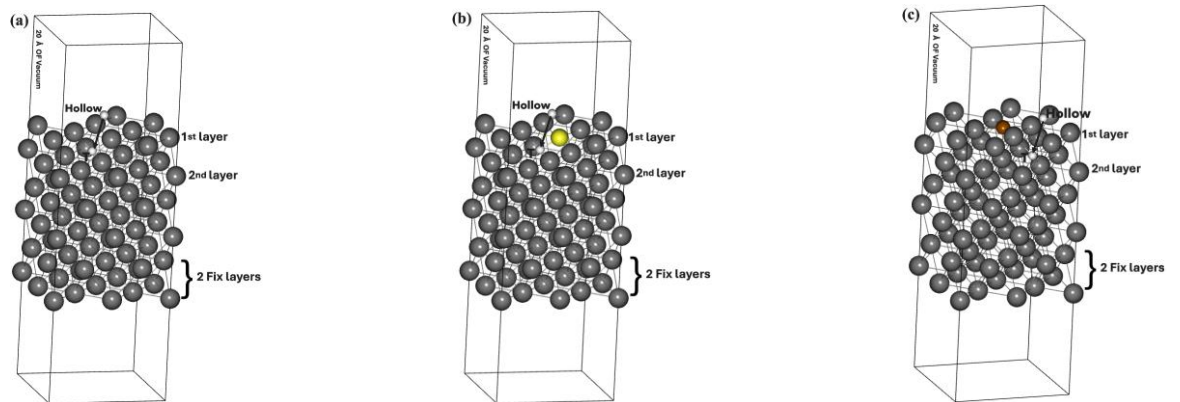


Fig 3. 7 Schematic diagram of hydrogen diffusion into the FCC iron slab (001): (a) clean slab; the gray atom is iron, and the white atom is hydrogen; (b) doped surfaces with

substitutional alloying elements; the yellow atom stands for each of the seven substitutional alloying elements (Cr, Mn, Mo, Ni, P, S, and Si). (c) doped surfaces with interstitial alloying elements; the brown atom stands for the two interstitial alloying elements (N and C).

The diffusion of hydrogen through the FCC iron bulk occurs between octahedral sites, which are energetically favorable interstitial sites. The diffusion pathway involves two primary steps: migration from an octahedral site to a neighboring tetrahedral site (Oct $\rightarrow$ T) and from this tetrahedral site to another octahedral site (T $\rightarrow$ Oct). In this study we only determined the activation energy for the initial jump from Oct to T since this transition typically corresponds to a greater energy barrier, making it the rate-limiting stage in the diffusion process.

For the clean bulk, we selected two hydrogen diffusion pathways; the first one passes through tetrahedral site T1 (Oct1 $\rightarrow$ T1) located between two spin-down layers, while the second passes through tetrahedral site T2 (Oct1 $\rightarrow$ T2) situated between spin-up and spin-down layers. Fig 3. 8 (a).

In doped systems, where alloying elements are introduced into the FCC iron lattice, the presence of alloying elements alters the local electronic structure and magnetic environment, significantly impacting the energy barriers. To assess these effects, we selected four hydrogen diffusion pathways, focusing on two paths near the alloying element and two paths farther away. Among the pathways near the alloying element, one passes through T1 (Oct1 $\rightarrow$ T1) located between two spin-down layers, while the other passes through tetrahedral site T3 (Oct3 $\rightarrow$ T3) situated between spin-up and spin-down layers. For

the pathways farther from the alloying element, one passes through tetrahedral site T2 (Oct1→T2) positioned similarly to T3 between spin-up and spin-down layers, and the other passes through tetrahedral site T4 (Oct3→T4), which is analogous to T1, being located between two spin-up layers. Fig 3. 8 (b). These pathways were chosen to evaluate how alloying elements, and magnetic properties influence hydrogen diffusion.

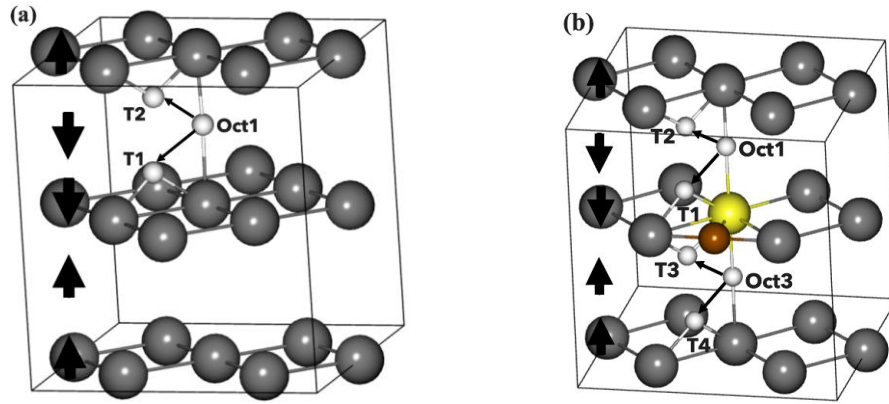


Fig 3. 8 Schematic diagram of hydrogen diffusion through the FCC iron bulk: (a) clean bulk: the gray atom is iron, the white atom is hydrogen located in octahedral site (Oct) or interstitial site (T); (b) doped bulks with substitutional and interstitial alloying elements: the yellow atom stands for each of the seven substitutional alloying elements (Cr, Mn, Mo, Ni, P, S, and Si), and the brown atom stands for the two interstitial alloying elements (N and C). (We eliminate the second and third layers as well as a few atoms to get a better view of the pathways.).

CHAPTER 4

RESULTS AND CONCLUSION

4.1 Adsorption Energy Results

In hydrogen-containing environments, dissociative adsorption of H_2 occurs spontaneously on steel surfaces during manufacturing, processing, and servicing operations, resulting in chemisorbed H atoms that eventually penetrate the bulk.

The results of hydrogen adsorption energies for clean and doped surfaces at each possible adsorption site are shown in Fig 4. 1.

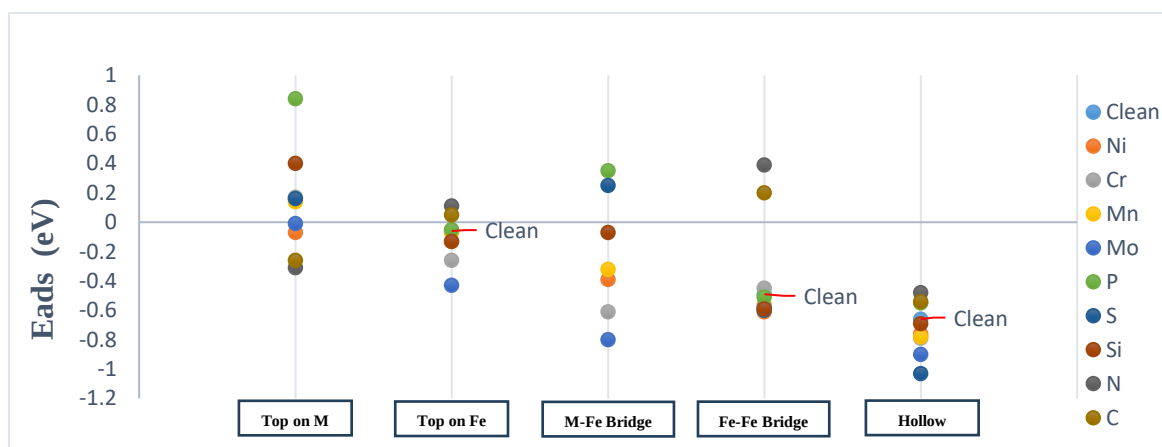


Fig 4. 1 Hydrogen adsorption energies for clean and doped surfaces at each possible adsorption site.

We found that the hollow site in the pure FCC Fe (001) surface exhibited the lowest adsorption energy (-0.66 eV) and the shortest H-to-surface distance (0.77 Å). The bridge

site displayed an adsorption energy of -0.49 eV and an H-to-surface distance of 1.17 Å. The on-top site had the highest adsorption energy (-0.06 eV) and the largest H-to-surface distance (1.55 Å).

We conclude that the hydrogen atom prefers to adsorb on the hollow site of the pure FCC Fe (001) surface. These results are consistent with previously reported computational studies (210–213). This behavior was also observed for all doped surfaces where the hollow was the preferred adsorption site. For this reason, we will discuss the effect of alloying elements on hydrogen adsorption at the hollow site, as illustrated in Fig 4. 2.

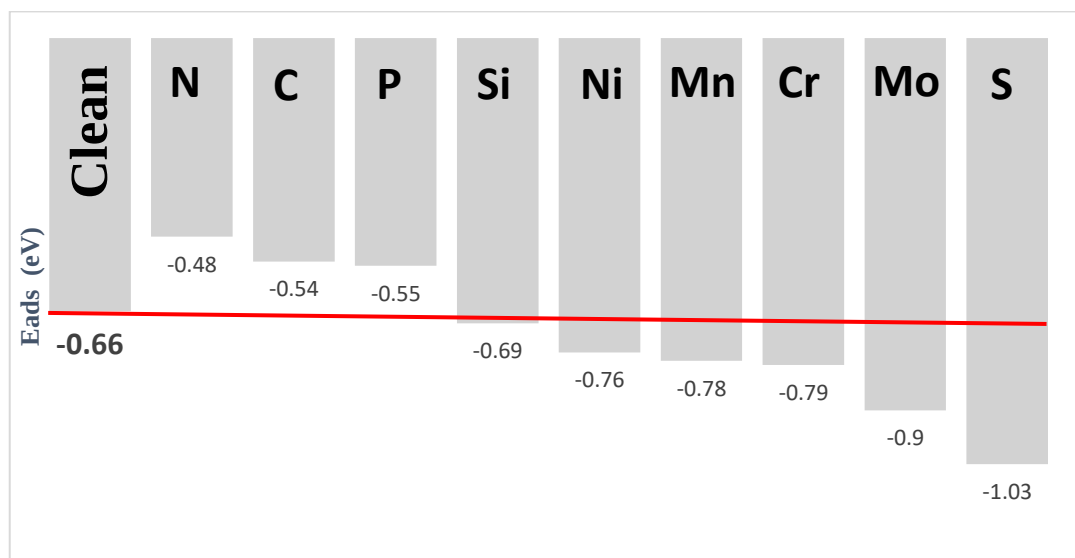


Fig 4. 2 Hydrogen adsorption energies for clean and doped surfaces at the hollow site.

Doping with Si, Ni, Mn, Cr, Mo, and S results in a reduction of adsorption energy at the hollow site compared to pure iron, with decreases of 0.03, 0.1, 0.12, 0.13, 0.24, and 0.37 eV, respectively. In contrast, doping with N, C, and P increases the adsorption of energy by 0.18, 0.12, and 0.11 eV, respectively. This means that N, C, and P have a positive effect on hydrogen adsorption by decreasing the adsorption strength of hydrogen on this site and

therefore making the absorption process less favorable, while the remaining alloying elements have a negative effect by increasing the adsorption strength of hydrogen on this site and making the adsorption process more favorable.

To clarify the differences caused by the doping of different alloying elements and how they affect adsorption behavior, charge differential density diagrams were created for hydrogen adsorbed at the hollow site for clean and doped surfaces. These images provide a visual representation of differences in crystal electron density, as shown in Fig 4. 3.

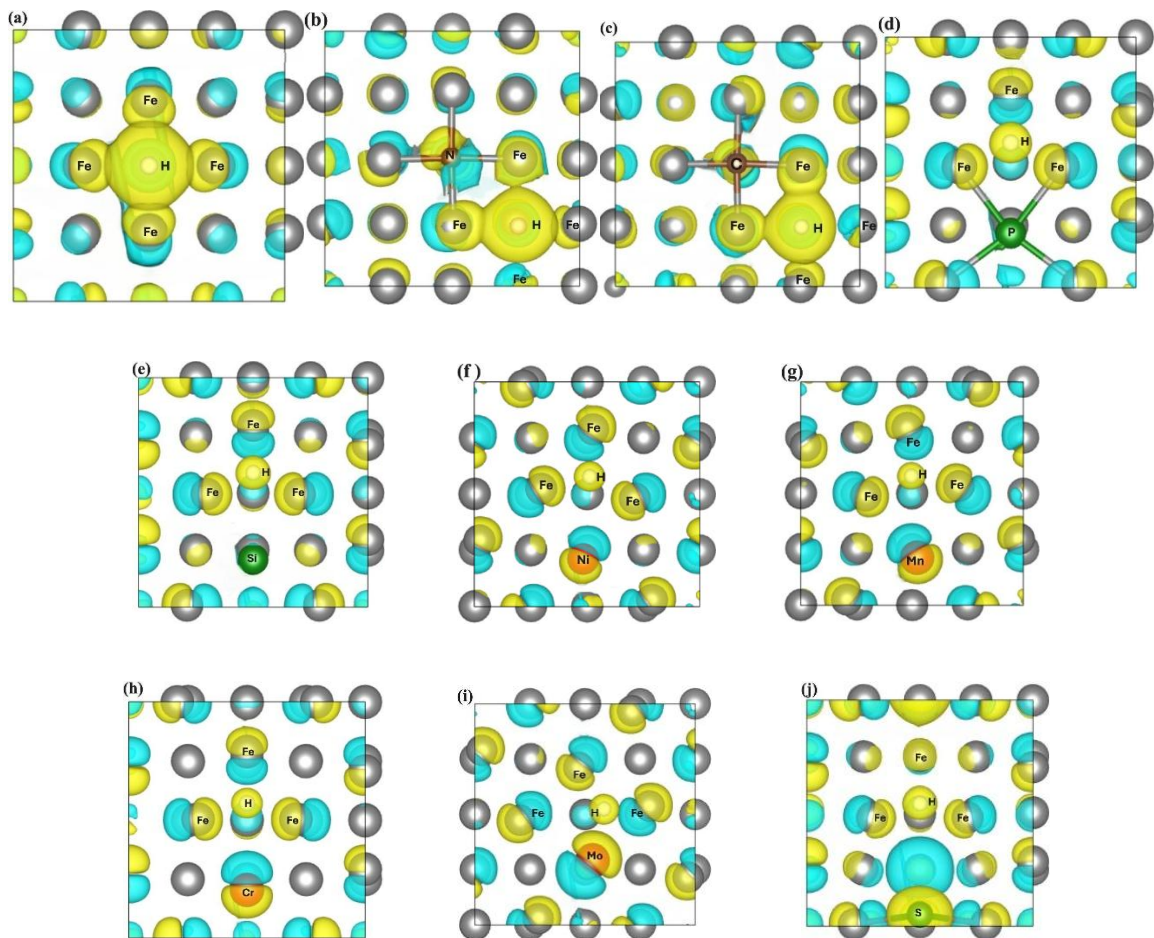


Fig 4. 3 (a-j) Differential charge density diagram of H adsorbed on the hollow in the clean and doped surfaces: Yellow regions indicate electron accumulation and blue regions represent electron depletion.

In the clean iron surface, the electron density is equally distributed, allowing for balanced Fe–H interaction. Elements like N, C, and P reduce hydrogen adsorption by concentrating charge around them, lowering Fe–H bonding. Charge density images confirm intense Fe–N, Fe–C, and Fe–P interactions that limit the ability of hydrogen to adsorb well. Contrary to this, elements such as Si, Ni, Mn, and Cr enhance hydrogen adsorption by redistributing charge near hydrogen, enhancing the strength of Fe–H bonds. This is found to be most intense for Mn and Cr, which display higher charge accumulation near hydrogen. The strongest adsorption energies are between Mo and S, for which charge density images reveal very localized charge accumulation around Fe and hydrogen atoms, describing strong Fe–H interactions. Sulfur in particular shows the strongest charge localization and is therefore the most effective element for hydrogen stabilization on the surface.

4.2 Binding Energy Results

When the binding energy is negative, the absorption is thermodynamically favorable. In contrast, a positive binding energy means that the absorption of hydrogen is thermodynamically unfavorable. By this definition, the stronger the interaction, the lower the binding energy due to the strong affinity; consequently, more hydrogen will be absorbed by the metal, increasing its solubility.

The results of hydrogen binding energy for each site and each different bulk are summarized in Fig 4. 4.

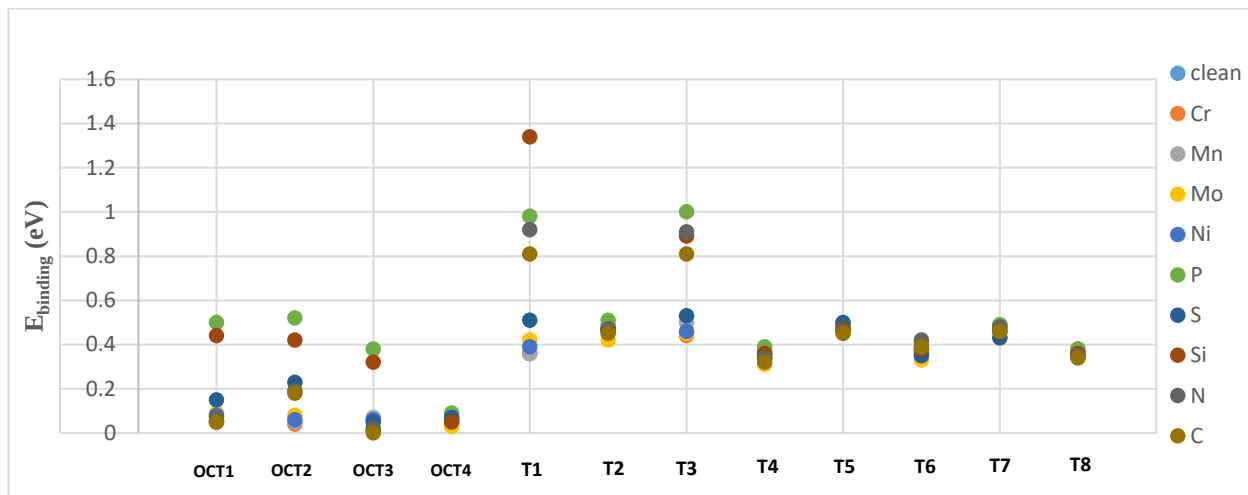


Fig 4. 4 Hydrogen binding energy for both clean and doped bulks.

First, we can see from the figure that the preferred binding site is the octahedral for both clean and doped bulks. For the clean bulk, the binding energy of Oct1 is 0.05 eV, aligning with previous computational studies (214) and identifying it as the most energetically favorable site. This observation is consistent with earlier theoretical research (215) as well as empirical research using neutron spectroscopy (216) and the neutron diffraction work by Machida et al., who found that the octahedral sites in non-magnetic FCC iron crystals are the sites that deuterium atoms prefer (217).

In comparison, the tetrahedral sites T1 and T2 are less favorable, with binding energies higher by 0.31 eV and 0.43 eV, respectively. This behavior can be described in terms of geometry. The obtained H-Fe bond length for the octahedral site is closer to the optimal value in the unrelaxed case because of the larger size of this site, which leads to a lower value for the binding energy.

Second, the effect of magnetic behavior is observed only in tetrahedral sites because they are located between different spin layers, unlike octahedral sites, which are located within the layers. The sites (T2, T5, and T7) that are located between layers of different spin orientations have higher binding energy than the sites (T4, T6, and T8) that are located between layers with the same spin orientation (Fig. 4). This behavior can also be described geometrically: the layers with the same spin orientation ($\uparrow\uparrow\downarrow\downarrow\dots$) repulse (~ 0.265 Å interlayer spacing), resulting in a larger tetrahedral size and lower binding energy; in contrast, layers with different spin orientations ($\uparrow\downarrow\uparrow\downarrow\dots$) exhibit attraction (~ 0.254 Å interlayer spacing), leading to a smaller site.

Lastly, the effect of the alloying element is pronounced in the sites (Oct1, Oct2, Oct3, T1, and T3) that are directly bonded to the substitutional alloying element or very near to the interstitial alloying element (Fig 3. 6 b and c).

The discussion of the effect of alloying elements on binding energy will only focus on the octahedral site because it is the preferred binding site of hydrogen in FCC iron bulk. The results of binding energy at different octahedral sites are summarized in Table 4. 1.

To estimate the overall binding energy for different octahedral sites in doped bulks, we used the standard configurational free energy of mixing form (Eq 4.1) which is used in trap-diffusion thermodynamics (218,219),

$$E_{eff}(T) = -k_B T \ln \left[\frac{\sum_{i=1}^n g_i e^{-E_i/k_B T}}{\sum_{i=1}^n g_i} \right] \quad \text{Eq 4.1}$$

For n symmetry-inequivalent octahedral sites i surrounding one alloying element M , each with degeneracy g_i and DFT binding energy E_i , the temperature-dependent effective binding free energy $E_{\text{eff}}(T)$ is the Boltzmann average. In our calculation we considered $k_B T = 0.026$ eV and an equal degeneracy $g_i = 1$. The last column in Table 4. 1 displays the effective binding energy of doped bulks, arranged from largest to smallest.

Table 4. 1 The binding energy at different octahedral sites for the clean and doped bulks, and the effective binding energy of doped bulks.

E_{bind} (eV)	Oct 1	Oct 2	Oct3	Oct4	$E_{\text{eff}}(T)$ (eV)
Clean	0.05	-	-	-	
P	0.5	0.52	0.38	0.09	0.13
Si	0.44	0.42	0.32	0.05	0.09
S	0.15	0.23	0.05	0.07	0.08
Ni	0.08	0.06	0.06	0.06	0.06
Mn	0.05	0.05	0.07	0.06	0.06
N	0.07	0.19	0.02	-	0.04
Mo	0.09	0.08	0.02	0.03	0.04
Cr	0.05	0.04	0.01	0.05	0.03
C	0.05	0.18	0	-	0.02

Fig 4. 5 represents the differences between the effective binding energy of doped bulks and clean bulk, arranged from largest to smallest. We can see that the overall positive effect of alloying elements on binding energy is observed in the elements (P, S, Si, Ni, and Mn). By increasing the binding energy, these elements can contribute to reducing the hydrogen solubility within the FCC iron bulk. Conversely (N, Mo, Cr, and C) reduce the binding energy in comparison to the clean bulk, which can increase hydrogen solubility.

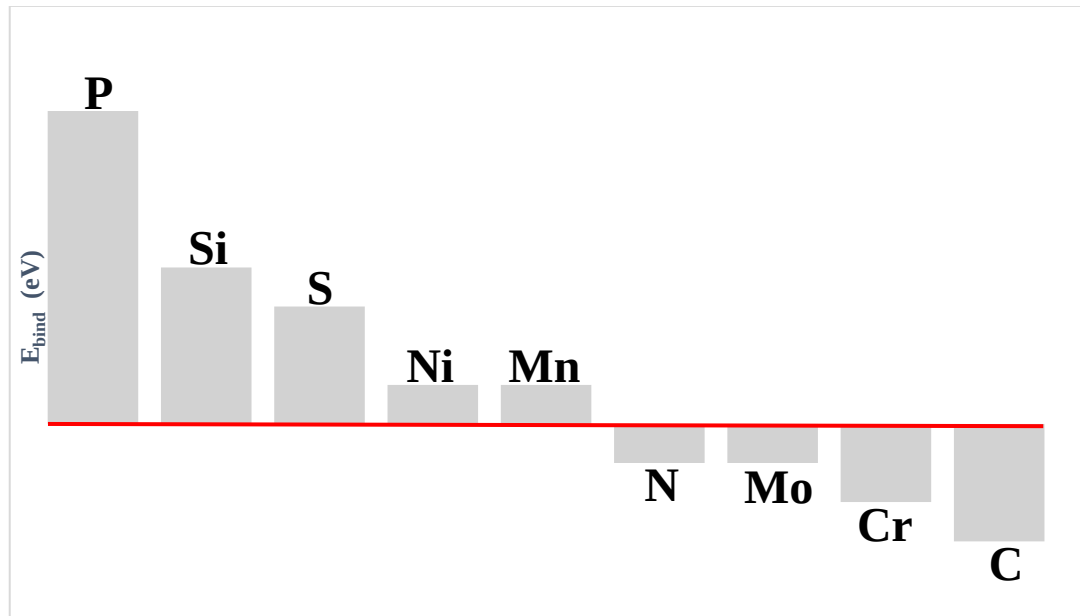


Fig 4. 5 The overall effect of alloying elements on hydrogen binding energy (the red line represents the clean bulk).

4.3 Diffusion Energy Barrier Results

4.3.1 Into the Bulk

Table 4. 2 shows the results of the hydrogen diffusion energy barrier into the doped and clean slabs for both cases described in the methodology, the binding energy of hydrogen diffusion transition sites (T_{ud} , T_{dd}), and the surface energy of both doped and clean slabs.

Table 4. 2 The barrier energy of hydrogen diffusion, the binding energy of transition sites, and the surface energy of both doped and clean slabs.

Path 1($H \rightarrow T_{ud}$)	clean	S	Mo	Mn	C	P	Cr	N	Ni	Si
E_{Diff} (eV)	1.15	1.22	1.21	1.19	1.09	1.09	1.06	1.05	1.04	1.02
E_{bind} (eV)	0.44	-0.02	0.46	0.72	0.47	0.45	0.33	0.46	0.43	0.44
γ (eV/m²)	0.58	36.99	-106.74	-69.36	-8.35	42.17	-50.84	-13.11	-20.66	46.44
Path 2($H \rightarrow T_{dd}$)	clean	Cr	S	Mo	Si	Mn	P	Ni	N	C
E_{Diff} (eV)	1.02	1.14	1.13	1.11	1.07	1.05	1.04	0.77	0.74	0.74
E_{bind} (eV)	0.29	0.35	0.1	0.24	0.18	0.44	0.25	0.18	0.24	0.17
γ (eV/m²)	0.55	-50.88	36.96	-106.77	46.41	-69.39	42.13	-20.69	-13.14	-8.38

The first pathway ($H \rightarrow T_{ud}$) in the clean (001) slab has a surface diffusion barrier energy of 1.15 eV, which is quite similar to Ursulaan K et al.'s finding of 1.25 eV for the (001) surface (203).

The barrier energy of hydrogen diffusion into the slab through the first $H \rightarrow T_{ud}$ pathway is higher than the second $H \rightarrow T_{dd}$ pathway for almost all the doped and clean slabs because the first pathway ends at T_{ud} , which is located between spin-up and spin-down layers. This makes the size of this site smaller due to the attraction of these layers, which increases the binding energy (Table 4.2) compared to T_{dd} , leading to an increase in the energy barrier through this pathway. Except for S, where the binding energy of T_{ud} is lower than T_{dd} but the barrier energy through the first path remains higher than the second, this could be due to the effect of this element on hydrogen diffusion. For the Cr and Si, the barrier energy of hydrogen diffusion through the second $H \rightarrow T_{dd}$ pathway is higher than the first $H \rightarrow T_{ud}$ pathway. This might be because of the stronger effects of these elements or due to a surface reconstruction, where the Cr increases both barrier and binding energy and Si raises only the barrier energy through the second $H \rightarrow T_{dd}$ pathway.

The S, Mo, and Mn have a positive effect on the barrier energy of hydrogen diffusion into the doped slabs compared to the clean one through the first $H \rightarrow T_{ud}$ pathway, while C, P, Cr, N, Ni, and Si have a negative effect. For the second $H \rightarrow T_{dd}$ pathway, Cr, S, Mo, Si, Mn, and P have a positive effect, while Ni, N, and C have a negative effect. We can notice that the positive effect of alloying elements is more pronounced through the second $H \rightarrow T_{dd}$ pathway than through the first $H \rightarrow T_{ud}$ pathway.

To determine which configuration of spin layers will be on the top surface of the slab, we evaluated the surface energy of doped and clean slabs using the equation below (Eq 4.2):

$$\gamma = \frac{E_{slab} - N_1(E_{Bulk}/N_2)}{2A} \quad \text{Eq 4.2}$$

Where γ is the surface energy (eV/m²), E_{slab} is the total energy of the slab, N_1 is the number of atoms in the slab, E_{bulk} is the energy of the bulk, N_2 is the number of atoms in the bulk, A is the surface area of one side of the slab, and the factor 2 accounts for two surfaces (top and bottom) of the slab.

According to the results of surface energy (Table 4. 3), the slab ending with the same spin layers showed lower surface energy; based on that, we selected the second $H \rightarrow T_{\text{dd}}$ pathway to present the effect of alloying elements on surface diffusion of hydrogen. Fig. 4.6 represents the differences between the barrier energy of hydrogen diffusion into the doped slabs and the clean slab through the second $H \rightarrow T_{\text{dd}}$ pathway. The elements (Cr, S, Mo, Si, Mn, and P) have a positive effect on the barrier energy of hydrogen diffusion into the doped slabs compared to the clean slab, while Ni, N, and C have a negative effect.

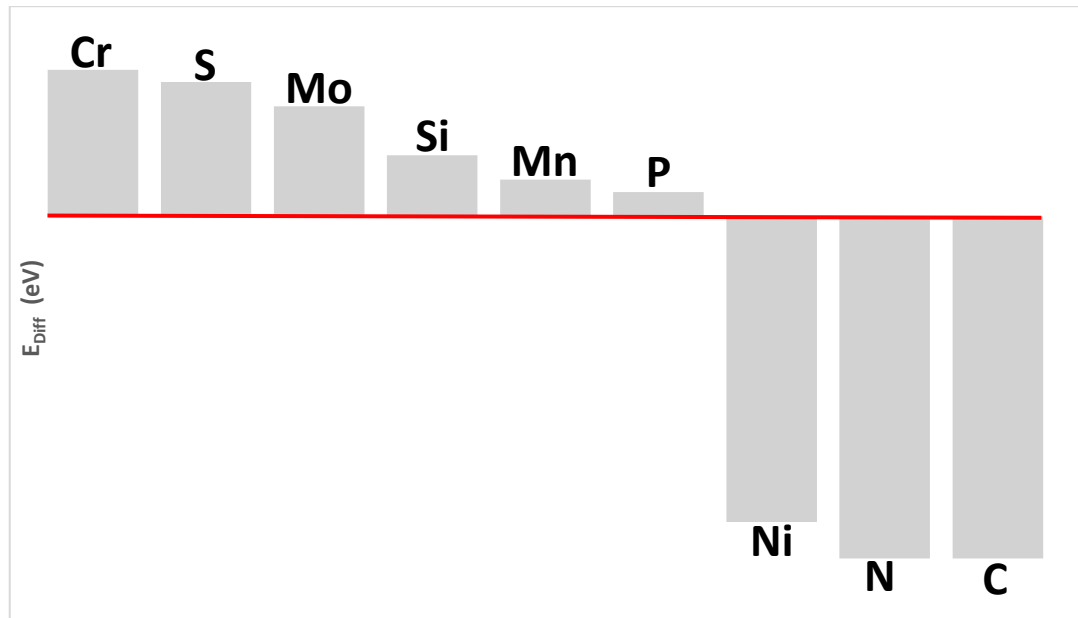


Fig 4. 6 The effect of alloying elements on the barrier energy of hydrogen diffusion into the doped slabs compared to the clean slab (the red line represents the clean bulk).

4.3.2 Through the Bulk

Oriani et al. (220) compared several experimental studies of the diffusivity of hydrogen through austenitic stainless steels and pure γ -Fe. They discovered that pure γ -Fe has an activation energy of ~ 0.5 eV, which is close to the activation energy of austenitic stainless steels (approximately 0.5–0.7 eV). This value was obtained using a variety of methods, including thermal desorption and hydrogen permeation testing (221–229). Our results of hydrogen diffusion barrier energy for the clean bulk through the pathway (Oct1 $\rightarrow$ T1) is equal to pure γ -Fe of these experiments results and very close to the bulk-like activation energy through the (100) surface (0.6 eV) in reference (230). For the doped bulks the barrier energies, through different pathways, are within or near the activation energy range of austenitic stainless steels.

The results of the hydrogen diffusion energy barrier through the doped and clean bulks are summarized in table 4 .3.

Table 4. 3 The Activation energy for possible diffusion pathways in both clean and doped bulks.

E_{Diff} (eV)	Oct3$\rightarrow$T3	Oct1$\rightarrow$T1	Oct1$\rightarrow$T2	Oct3$\rightarrow$T4
Clean	-	0.5	0.59	-
N	0.9	0.87	0.55	0.49
C	0.84	0.8	0.56	0.49
Cr	0.61	0.54	0.59	0.55

Mo	0.69	0.64	0.48	0.45
Si	0.78	0.9	0.29	0.29
Mn	0.61	0.52	0.61	0.5
Ni	0.54	0.5	0.54	0.49
P	0.72	0.68	0.27	0.28
S	0.53	0.45	0.52	0.45

Table 4. 3 shows that the barrier energies are increased through the Oct3→T3 pathway for almost all doped bulks compared to its equivalent pathway in the clean bulk (Oct1→T2 0.59 eV), except for Ni and S, with a small decrease of 0.05 and 0.06 eV, respectively. This is because the oct3→T3 pathway combines the dual effects of alloying elements and magnetization, passing next to the alloying element and ending at the T3, which is located between the spin-down and spin-up layers (Fig 3. 8(b)). This makes the size of this site smaller due to the attraction of these layers, which increases the binding energy (Table 4. 4), resulting in a rise in the energy barrier through this pathway.

The Oct1→T1 pathway is passes next to the alloying element and ends at T1, which is located between two spin-down layers. Fig 3. 8(b). This makes its binding energy lower than T3. Table 4: Except for Si and N, this might be explained due to the stronger effect of these elements on binding energy. The barrier energy is still higher for almost all doped bulks compared to the Oct1→T1 pathway in the clean bulk (0.5 eV), except for S, which decreases by 0.05 eV and remains unchanged for Ni.

The Oct1→T2 pathway is far away from the alloying element and ends at T2, which is located between spin-up and spin-down layers (Fig 3. 8(b)) and has higher binding energy than T4 (Table 4. 4). The barrier energy decreases for almost all doped bulks compared to the Oct1→T2 pathway in the clean bulk (0.59 eV), except for Mn, which increased by 0.02, and stayed the same for Cr.

Comparing the last two pathways, we can notice that the effect of alloying elements is stronger than that of magnetization.

The last pathway, Oct3→T4, is far away from the alloying element and ends at T4, which is located between two spin-up layers (Fig 3. 8 (b)) and has lower binding energy than T2 (Table 4. 4). The barrier energy decreases for almost all doped bulks compared to its equivalent pathway in the clean bulk (Oct1→T1 0.5 eV) except for Cr, which increases by 0.05 eV, and Mn, which doesn't change.

Table 4. 4 The binding energy of hydrogen diffusion transition sites for the clean and doped bulks

E_{bind} (eV)	T3	T1	T2	T4
Clean	-	0.36	0.48	-
Cr	0.44	0.36	0.47	0.36
Mn	0.5	0.36	0.49	0.38
N	0.91	0.92	0.47	0.34

C	0.81	0.81	0.45	0.32
Ni	0.46	0.39	0.46	0.36
Mo	0.45	0.42	0.42	0.31
Si	0.89	1.34	0.47	0.36
P	1	0.98	0.51	0.39
S	0.53	0.51	0.47	0.34

To estimate the diffusion effective barrier energy of hydrogen, we considered a possible pathway of hydrogen diffusion through the bulk jumping between the nearest octahedral to the alloying elements, this pathway starts from T2 and ends at T4 as depicted in Fig 4. 7. The last column in Table 4.5 represents the diffusion effective barrier energy of doped and clean bulks, arranged from largest to smallest which was calculated using the previous equation (Eq 4.1), where $E_{\text{eff}}(T)$ is the diffusion effective barrier energy, E_i is the barrier energy of each path i , and we used the same previous parameters ($k_B T = 0.026$ eV, $g_i = 1$).

Table 4.5 The barrier energy of hydrogen jumps through the doped and clean bulks and the diffusion effective of barrier energy.

E_{Diff} (eV)	T2-Oct1	Oct1-T1	T1-Oct2	Oct2-T3	T3-Oct3	Oct3-T4	$E_{\text{eff}}(T)$ (eV)
Clean	0.17	0.5	-	-	-	-	0.19
Cr	0.17	0.54	0.22	0.61	0.18	0.55	0.2
Mo	0.15	0.64	0.27	0.63	0.25	0.45	0.2
Mn	0.17	0.52	0.21	0.62	0.14	0.5	0.18
Ni	0.16	0.5	0.17	0.56	0.14	0.49	0.17
P	0.26	0.68	0.21	0.69	0.09	0.28	0.14
S	0.2	0.45	0.22	0.53	0.05	0.45	0.1
C	0.17	0.8	0.02	0.78	0.03	0.49	0.05
Si	0.25	0.9	0	0.72	0.21	0.29	0.05

N	0.16	0.87	0.004	0.84	0.01	0.49	0.04
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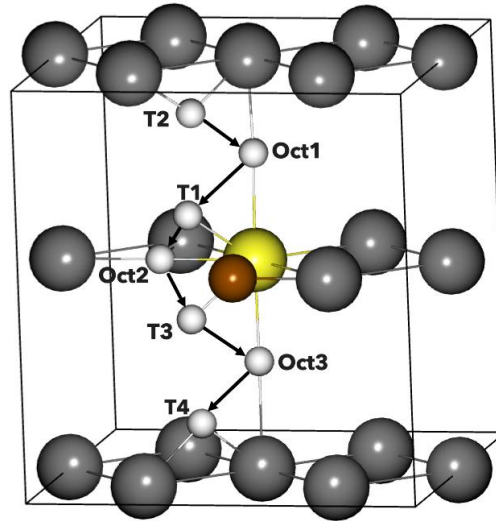


Fig 4.7 Schematic diagram of possible hydrogen jumps through the FCC iron-doped and clean bulks : The gray atom is iron, the white atom is hydrogen located in an octahedral site (Oct) or interstitial site (T), the yellow atom stands for each of the seven substitutional alloying elements (Cr, Mn, Mo, Ni, P, S, and Si), and the brown atom stands for the two interstitial alloying elements (N and C). (We eliminate the second and third layers as well as a few atoms to get a better view of the pathways.).

Fig 4. 8 represents the differences of hydrogen diffusion effective barrier energy ($E_{\text{eff}}(T)$) between the doped bulks and the clean bulk, the figure shows that the alloying elements Cr and Mo have a positive effect on the effective barrier energy of hydrogen diffusion compared to the clean bulk, while Mn, Ni, P, S, C, Si, and N have a negative effect.

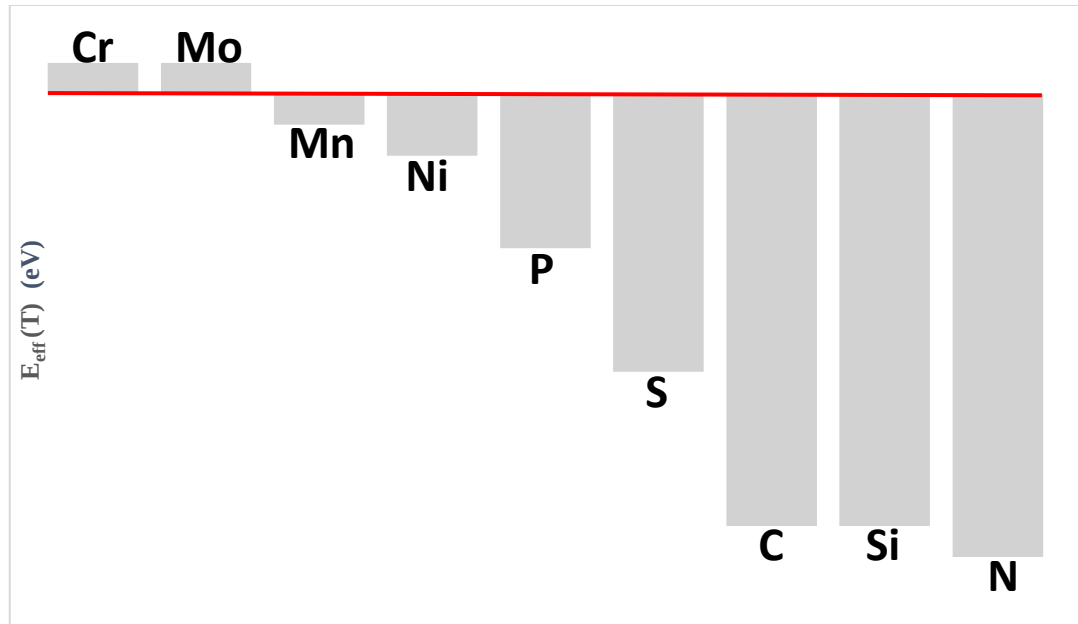


Fig 4. 8 The effect of alloying elements on hydrogen diffusion effective barrier energy through the doped bulks compared to the clean bulk (the red line represents the clean bulk).

4.4 Conclusion

The development of a robust and reliable hydrogen infrastructure is essential for enabling the transition toward a low-carbon energy future. This infrastructure which includes production, storage, transportation, and distribution systems relies heavily on metallic materials that must withstand the challenges posed by hydrogen environments, particularly hydrogen embrittlement (HE). Austenitic stainless steels such as 304 and 316 are widely used in hydrogen infrastructure due to their favorable microstructure properties and corrosion resistance. However, their long-term performance under hydrogen exposure still requires further optimization.

This study provides a comprehensive first-principles investigation into the impact of various alloying elements in austenitic stainless steels (304 and 316) on the steps of hydrogen embrittlement (HE) in FCC iron. Using density functional theory (DFT), we evaluated the effects of nine alloying elements (Ni, Cr, Mn, Mo, P, S, Si, N, and C) on hydrogen adsorption, solubility, and diffusion into and through the bulk.

Our findings reveal that elements such as N, C, and P have a positive effect on hydrogen adsorption by decreasing the adsorption strength and making the process less favorable. Second, the elements P, S, Si, Ni, and Mn reduce the hydrogen solubility within the FCC iron bulk by increasing the binding energy and making the process of bonding less favorable. Lastly, the elements Cr, S, Mo, Si, Mn, and P increase the hydrogen diffusion energy barrier into the slab, while Cr and Mo increase it through the bulk.

It is important to consider the combined impact of these alloying elements on the overall material performance. Modifying such elements can influence some significant properties such as corrosion resistance, mechanical strength, ductility, weldability, phase stability, and production expenses. For instance, decreasing the amount of Ni that harms hydrogen adsorption, and diffusion can alter the stability of FCC iron phase, which is more resistant than BCC iron against HE. Therefore, the alloy composition optimization involves a trade-off between hydrogen embrittlement resistance and these other factors to keep the alloy viable for economy-scale production and use in hydrogen energy facilities.

These results can serve as a guide for improving the existing grades of FCC stainless steels used in hydrogen infrastructure and for designing new FCC stainless steels that can resist hydrogen embrittlement in hydrogen energy systems.

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Vitae

I am Mohammed Hamadouche, a motivated Materials student with a solid academic background and practical experience in the field of materials science. I hold a master's degree in Materials Science and Engineering (2022–2025) from King Fahd University of Petroleum and Minerals (KFUPM), Saudi Arabia. I also earned a Master's in Expertise and Control of Materials (2018–2020) and a Bachelor's in Materials Engineering (2013–2018) from the University of Science and Technology Houari Boumediene (USTHB), Algeria. My research interests include hydrogen embrittlement in metallic materials, DFT simulations, materials design for hydrogen energy infrastructure, corrosion and degradation of metals, welding process and metallurgy, non-destructive testing (NDT), and cathodic protection.

Publications

My thesis research is being recognized through an upcoming publication: Mohammed Hamadouche, Hussein Al-Adwan, Ihsan Ul Haq Toor, Milos B. Djukic, Abduljabar Alsayoud. (Forthcoming, 2025). Impact of alloying elements on hydrogen adsorption, solubility, and diffusion in austenitic stainless steel for hydrogen energy infrastructure applications: A density functional theory approach.

Experience and Training

My practical training includes several specialized short programs that enriched my technical capabilities. I completed non-destructive testing training at the Naval Repair Company in Algiers from March 27 to April 1, 2018. In December 2018, I undertook a training on cathodic protection at the National Pipeline Company in Algiers. Most recently,

I attended a workshop on Finite Element Analysis (FEA) for nonmetallic composite casing and tubing held from October 29 to November 2, 2023, at KFUPM.

In addition to academic training, I gained hands-on technical experience through a part-time job at King Fahd University of Petroleum and Minerals (KFUPM), where I was responsible for installing and updating software programs in the laboratories of the College of Computing and Mathematics (CCM). This role lasted four months, from January to May 2025, and enhanced my practical IT skills and collaborative work experience in an academic environment.

Skills

I possess a versatile skill set that spans simulation, testing, and collaborative work environments. I am proficient in Density Functional Theory (DFT) simulation and have practical experience in non-destructive testing and cathodic protection. I am known for my sense of responsibility, adaptability, and ability to work effectively in teams. My excellent physical fitness enables me to sustain full-day work schedules with focus and efficiency.

Languages

I am a native Arabic speaker, have intermediate proficiency in French, and a working knowledge of English, demonstrated by my TOEFL iBT test.

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