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Embrittlement behaviour of metal additive-manufactured high-entropy alloy components under gaseous and electrochemical hydrogen charging

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ABSTRACT

Embrittlement is an environmentally induced fracture that primarily affects metallic materials. This phenomenon occurs when hydrogen is absorbed on the metal surface and penetrates to the core, followed by degrading the mechanical properties in a hydrogen-rich environment. This reduction in mechanical properties results in a loss of ductility and toughness in materials, thereby increasing their susceptibility to cracking caused by hydrogen. Embrittlement can be introduced into materials through various means. This work mainly focuses on embrittlement failure that occurs under hydrogen-inducing conditions. Gaseous and electrochemical hydrogen charging exposure are related to this study. Mitigating hydrogen embrittlement involves controlling two aspects: adding alloying elements and treating the metal surface. This work examines the addition of alloying elements to reduce metals' susceptibility to hydrogen uptake, utilising an advanced fabrication method known as metal additive manufacturing in conjunction with high-entropy alloy concepts. Mechanical properties such as tensile strength and fatigue demonstrate the deterioration of hydrogen embrittlement behaviour in structural components, leading to unforeseen catastrophic failures. This work summarizes (i) the hydrogen effects on material performance, (ii) additively manufactured high entropy alloy (HEAs) and the factors influencing embrittlement, (iii) methods of hydrogen charging, (v) hydrogen embrittlement mechanisms, and (vi) various microstructure and mechanical property outcomes of additive and conventional manufacturing processes and their effects on embrittlement.

1. Introduction

The work aims to highlight the properties of additively manufactured high-entropy alloy (HEAs) components and their effect on hydrogen embrittlement (HE) behaviour, subjected to gaseous and electrochemical hydrogen charging [1]. In recent days, materials science and engineering have continuously focused on reducing embrittlement failures and efficiently extending the life of materials, especially in a hydrogen-based environment, with the help of advanced fabrication methods. Ensuring the safety and effectiveness of hydrogen energy storage, nevertheless, poses many difficulties at present. This failure occurred in the form of a catastrophic event. The embrittlement phenomenon has the potential to significantly affect the safety and functionality of materials in various applications. Through embrittlement, a material can lose its ductility and become more brittle. This implies the material loses some of its plastic deformation potential before breaking. Consequently, in a hydrogen environment, materials subjected to stress or impact become embrittled, and the materials are highly susceptible to brittle fracture [2]. The embrittlement caused by a material can be in different forms, such as Environmentally Induced Cracking (EIC) [3], Stress Corrosion Cracking (SCC) [4], Corrosion Fatigue (CF) [5], Liquid Metal Embrittlement (LME) [6], and Hydrogen Embrittlement (HE) [7]. This work particularly considers the embrittlement behaviour in a hydrogen environment. In this form of HE, the materials were first reported by Johnson in 1875, noted by deformation changes with the influence of an acid environment for iron and steel materials [8]. The materials that allow a higher amount of hydrogen atom permeation are an essential consideration for the development of HE failures [6].

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Hydrogen is introduced to the surface of the metal, and its hydrogen atoms penetrate through the metal surface, affecting the atomic bonding levels. Finally, metal failure occurs or a degradation of the properties happens in the materials. Hydrogen may penetrate the surface in different routes (i) during the melting and entrapped during solidification [9], (ii) through hydrogen gas welding and moisture [10], and (iii) through anodic reaction during corrosion [11]. Followed by the indirect form of hydrogen to permit the metals, like heat treatment atmospheres, breakdown of organic lubricants, and electrochemical surface treatment, such as etching, pickling, and phosphate coating. The corrosion removal process also entraps the hydrogen in the metal surface, such as paint stripping and electroplating are susceptible [12]. After penetrating the hydrogen atoms, atomic hydrogen reacts to form brittle components, increasing cracking and causing material failure. The failures occurring in materials are based on hydrogen embrittlement mechanisms. However, the specific mechanism of hydrogen embrittlement remains unknown. The majority of the proposed mechanisms for slip interfaces utilise dissolved hydrogen. The slip interface may result from the deposition of hydrogen around dislocation sites or micro-voids, but the precise hydrogen embrittlement mechanism is still unknown [13]. In this context, HE is considered reversible and irreversible depending on the addition of alloying elements and their binding energy formation and chemical properties. In both cases, hydrogen atoms diffuse and penetrate, which is followed by a secondary process where the penetrated hydrogen escapes from the crystal lattice. A secondary process, such as heat treatment, is termed reversible HE. In this type of reversible HE, the focus is on temporarily reducing strength and controlling ductility balance [14]. When hydrogen diffuses, the influence of alloying elements cannot be returned to the crystal lattice; this is referred to as non-reversible HE, which leads to permanent cracks influenced by hydrogen atoms. The addition of Ti, Ni, and Fe elements is most favourable for developing irreversible HE [15]. These elements contribute to the material's permanent damage, such as microstructural changes, and facilitate crack initiation with the influence of alloying element addition. Meanwhile, incorporating Ti elements into HEAs enhances positive effects, particularly the Thermo-Hydrogen Process (THP). The THP is a type of heat treatment process, specifically Thermal + Hydrogen, that affects the correlation of material properties. Including Ti elements in HEAs promotes higher solubility levels. However, the solubility of hydrogen impacts chemical activity or reactions; here, Ti has low chemical reactivity, resulting in better solubility levels, while alloys with greater reactivity exhibit lower solubility, particularly beta-titanium alloys. In this context, THP influences the improved relationship between microstructure refinement, hydrogen-induced grain refinement, and the enhancement of the materials' superplastic characteristics [16].

Industrial needs should be satisfied through academic research from this perspective, contributing to Industry 4.0 in the modern industrial revolution. Among these, Additive Manufacturing (AM) is one of the technological advancements in Industry 4.0 [17]. Eliminating post-processing, reducing material wastage, achieving high-dimensional accuracy, obtaining high-precision components, and overall cost reduction have been crucial considerations for the selection of AM. Recently, additive manufacturing has become a growing material fabrication method for modern high-performance applications [18]. In AM, the fabrication of materials or the development of net shapes for specimens is based on the layer-by-layer addition of metal powders using computer-aided design parameters. Among them, all AM techniques of powder bed fusion, including Selective Laser Melting (SLM), Selective Laser Sintering (SLS), Multi-Jet Fusion (MJF), and Electron Beam Melting (EBM), play an important role in developing near-net shapes, high density, and better mechanical properties compared to other methods [19]. Compared to all AM techniques, SLM enables the creation of high-precision 3D components, microstructure control, and improved mechanical properties, dimensional accuracy, surface finish, and part integrity, making it particularly suitable for the fabrication of HEAs [20]. EBM offers a broader 3D printing technology, primarily preferred for high precision and zero tolerance component fabrication [21]. This article discusses powder bed fusion and direct energy deposition-based AM methods and the current challenges faced by materials, particularly low-hardness/strength materials that dominate hydrogen storage material development. This challenge also affects HE resistance development. Therefore, the development of new materials is referred to as HEAs. With high hardness/strength and ductility, along with exceptional HE resistance capacity due to their unique properties and ability to accept a wide range of elemental additions, depending on application feasibility, HEAs are vital in modern material development. Element addition and its chemical fluctuations, as well as lattice distortion effects, are essential considerations for selecting HEAs. Elements with lattice effects exhibit significant hydrogen trapping behaviour, helping to prevent the HE. Hydrogen diffusion and trapping determine the performance of materials for hydrogen storage applications. A current issue is the development of HEAs with between 4 and not more than 13 metallic element additions [22]. Key considerations for HEAs include stabilising entropy under all environmental conditions while maintaining a single-phase structure. The addition of alloying elements is a determining factor for phase structure development. Recent research has interesting findings regarding the addition of a range of 5–10 elements to generate BCC or FCC structures; furthermore, adding more than 10 elements can lead to the development of HCP phases in HEAs. The extent of elemental addition influences entropy generation; thus, a higher number of elemental additions leads to greater values of entropy development [23]. This significant improvement directly enhances interest in developing HEAs for better corrosion resistance, improved micro-mechanical properties, enhanced energy storage to control hydrogen embrittlement failures, and various research domains [21,24]. Currently, most sectors are progressing from conventional energy to hydrogen energy, but the substantial challenge remains hydrogen storage due to its fast diffusivity, lower density, and functional safety considerations, such as with compressed hydrogen gas and electrochemical liquefied hydrogen atmospheres. Stainless steel 316L, composite materials like carbon fibre reinforced polymer wrapped with stainless steel or aluminium linear materials are commonly used for hydrogen storage containers; however, these materials have limitations, as they can degrade easily and are susceptible to embrittlement due to their high hydrogen permeability under high-pressure conditions. In contrast, HEAs present a better alternative for hydrogen storage [25]. Based on their mechanical and thermal characteristics, HEAs are noted for their high chemical stability and resistance to chemical vulnerability in energy storage and transportation applications. Development of additively fabricated HEAs will allow for hydrogen induction through gaseous and electrochemical hydrogen charging. During hydrogen gas charging, specimens are enclosed in a high-pressure vessel filled with pure hydrogen gas and typically subjected to elevated temperatures to facilitate diffusion and absorption into the materials [26]. In electrochemical or cathodic hydrogen charging, specimens are immersed in a carefully selected electrolyte solution and subjected to cathodic polarisation, inducing a hydrogen evolution reaction at the specimen's surface, which promotes hydrogen absorption into the material [27]. High-strength materials have a higher likelihood of experiencing hydrogen embrittlement [28], as hydrogen penetration can lead to internal cracking [29], blistering, irreversible damage, high-temperature hydrogen attack, and loss of ductility [30–32]. Such hydrogen attacks can significantly impair the material's lifespan. The important considerations for AM compared to conventional fabrication are (i) microstructure and (ii) grain boundary behaviours. With the help of conventional fabrication (Induction casting), HEAs elements have uniform elemental distribution, followed by developing a coarse-grained microstructure. However, the alloys are prepared with the help of AM, with the influence of temperature gradient effects (fast heating: fast cooling behaviour) developed a fine-grained microstructure and the elements have highly uniform distribution compared to conventionally fabricated specimens. Moreover, due to these effects, the microstructure is in the form of dendritic (high melting point elements) and inter-dendritic (lower melting point elements). In this form, structures are better at balancing the strength-to-ductility ratio. The evaluation of HE resistance performance on the materials is based on (i) rate of surface-hydrogen diffusion and (ii) the depth of the hydrogen interaction zone. Particularly, in the SLM process, to print the additive manufacturing components with a fine grain structure, it develops equiaxed grains due to the faster cooling and rapid solidification process. Also, by the layer-by-layer metal deposition, a thin oxide layer is developed, which impedes the surface-hydrogen absorption and controls the interaction with the hydrogen movement. Based on these aspects, compared to conventional fabrication, metal additive manufacturing demonstrates better resistance to HE failures in a hydrogen environment. Specifically, these effects enhance the elastic deformation limits under hydrogen influence. Interestingly, alloys produced by AM methods during hydrogen exposure in additively manufactured equiatomic FeCoCrNiMn-based HEAs exhibit increased ductility without affecting the alloys' hardness. Followed by, compared to traditional methods, the AM process significantly promotes nanotwin formation. In particular, powder bed fusion-based selective laser melting or selective laser sintering creates high thermal gradients and extremely rapid cooling rates, which favour nanotwin development. This twinning behaviour continuously improves the alloy work-hardening ability. However, with traditional methods, this beneficial effect is limited because the lower thermal gradients result in fewer opportunities for nanotwin formation and, consequently, a reduced ability to resist HE failure [33]. Additionally, the grain structure refinement and microstructure play important roles in controlling HE failures in the material. Grain structure refinement, such as controlling grain boundary segregation and dislocation, has a highly interactive relationship with hydrogen. The movement of hydrogen atoms weakens the grain boundary and causes HE failures; by controlling the optimised printing parameters (laser power, speed, hatch spacing, layer thickness, and volumetric energy density), this is limited in conventional routes. In this way, conventional manufacturing processes like powder metallurgy, mechanical alloying, vacuum induction casting, and spark plasma sintering develop a homogeneous microstructure; meanwhile, additive manufacturing tends to develop a heterogeneous microstructure. This heterogeneous microstructure exhibits better resistance to HE failure [34]. Faster cooling rates and high thermal gradients (averaging 10^6 K/m) are key features of AM parts development. AM-HEA components are highly resistant to hydrogen atom solubility and hydrogen diffusion levels, based on these aspects. Therefore, compared to conventional manufacturing, AM-HEA components improve material durability and reduce hydrogen-induced failures, such as HE degradation [35]. Fabricated materials and their achieved density are important considerations for mechanical and microstructure development; in this regard, the AM-HEA components achieve better density compared to conventional fabrication. The higher the density, the lower the porosity, which helps to control the hydrogen accumulation and reduce the hydrogen movement pathways. To mitigate hydrogen attack, the prevention techniques are summarised as follows: (i) reducing corrosion rates by applying coatings and inhibitors to the surface, (ii) baking, (iii) minimising hydrogen exposure by using alternative materials or substituting alloys, and modifying the electroplating process. Based on these reductions, HE materials are highly preferred for hydrogen storage and transportation applications, including hydrogen vehicles, nuclear components, fuel cells, the petrochemical industry, hydrogen storage on ships, and technological validation. Despite technological advancements, the success or failure of products depends on customer needs and satisfaction. In this regard, the Australian National Survey Testing (ANST) group assesses public willingness to use hydrogen based on various factors, resulting in the following ratings: hydrogen safety 4.5/5, reliability 4.3/5, cost considerations 4.2/5, and overall convenience 3.6/5 [15].

2. Hydrogen effects on material performance

Meeting the global energy demand, particularly in the transportation sector, depends on fuel with lower CO_2 emissions; for that reason, hydrogen is a better alternative source. However, the important challenge is effective utilisation, especially in terms of hydrogen storage and ensuring the performance of materials under a hydrogen environment. (i) hydrogen embrittlement and (ii) hydrogen attack resistance material development are challenging tasks for improving the material performance. The materials absorb hydrogen and develop a failure in the form of brittle fracture and the formation of cracks. Moreover, the hydrogen attack, especially in high carbon materials and high temperature conditions the hydrogen to diffuse at high pressure, developing an internal crack or hydrogen-induced blistering [36]. The steps involved for the hydrogen interaction with the materials in the form of (i) interfacial diffusion, (ii) vacancy diffusion, (iii) prolonged hydrogen accumulation and (iv) crack propagation. These steps represent Fig. 1. In this type of failure happened in the materials resist with the help of the addition of alloying elements to enhance the material performance. They enhance the material's performance depending on several factors like selection of metallic elements for alloy fabrication, microstructure stability, hydrogen charging methods, hydrogen uptake, diffusion, interaction, trapping and mechanical loading conditions. Based on these conditions, we evaluated with the help of various tests. Fig. 2 illustrates the testing method from a recent hydrogen evaluation study. Among these, the atomic hydrogen analysis approach has emerged as a novel finding method for better understanding the hydrogen-material interaction and effects of material structure changes. These specialised materials must be designed and synthesised with important consideration to ensure proper way of handling and enhance optimal performance. The handling is like transportation and storage with the help of the emerging materials. In this regard, the high-performance metal alloy system has to be introduced with a flourishing technology called additive manufacturing. The advanced fabrication methods are an important consideration in evaluating material performance, durability or sustainability, cost-effectiveness and positive environmental impact. The material with susceptible to HE failure based on hydrogen absorption, permeation and trapping behaviour. Based on the penetration of hydrogen changes in the lattice parameters and crystal structure, they lead to an enhancement of the HE over the materials. Followed by the materials research specifically focuses on the failure models like hydrogen-induced cracks: the reason is that penetrated hydrogen reduces the fracture toughness, leading to material failures such as Hydrogen-Induced Cracking (HIC), Internal Hydrogen-Assisted Cracking (IHAC) and Hydrogen Environment-Assisted Cracking (HEAC) [37]. The degradation behaviour changes from electrochemical and gaseous hydrogenated conditions. Compared to a gaseous environment, the development of cracks is higher than electrochemical hydrogen charging because the aqueous environment has higher hydrogen atom diffusion and accumulation. For gaseous charging, the influence of pressure level variation leads to cracks on the surface. The hydrogen adsorption promotes the internal cracks and blisters called HIC. In the IHAC, the materials inside the hydrogen were dissolved at the time of materials manufacturing and were not experimentally exposed to hydrogen. However, the HEAC refers to the hydrogen atoms absorbing the hydrogen from the gaseous or electrochemical charging, the diffusion of hydrogen in the form of interstitial or vacancy sites to settle, followed by the accumulation of hydrogen. They are developing a degradation phenomenon, like initiating cracks over the surface, and they are leading to the formation of embrittlement or the development of blisters [36,38]. Based on these failures, the AM components are controlled compared to conventionally fabricated components and improve the hydrogen storage material performance.

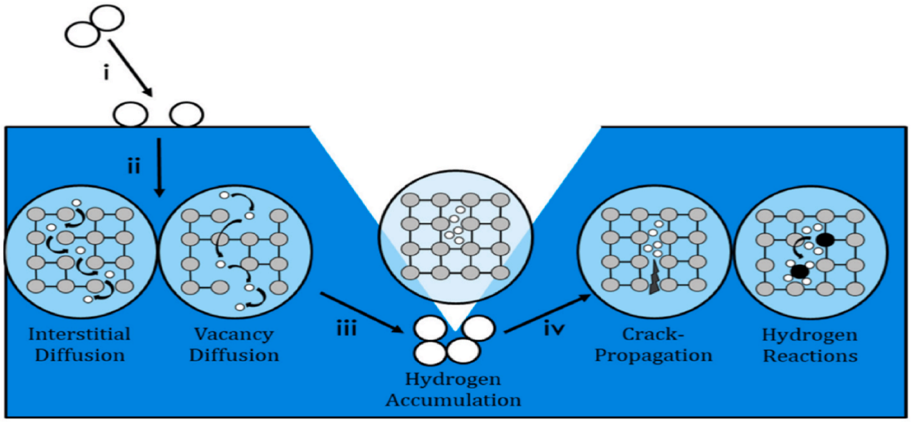

Fig. 1. Hydrogen diffusion with the effects of the crystal lattice [36]. Licensed under CC BY 4.0.

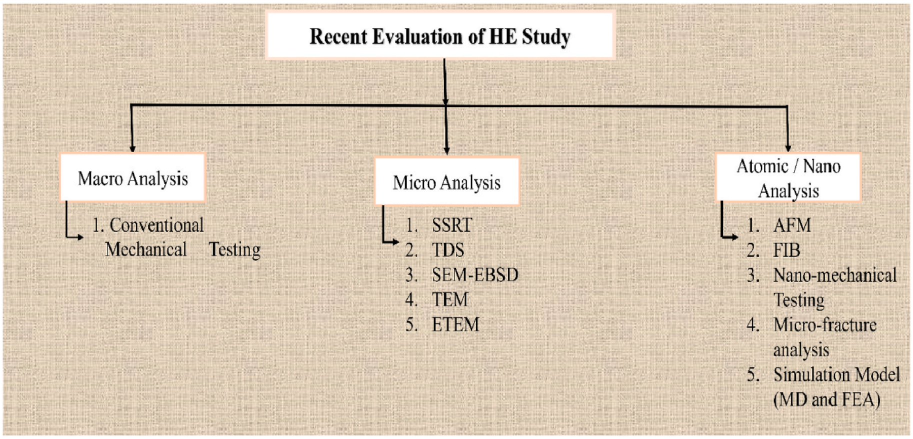

Fig. 2. Various testing methods for HE studies used to evaluate the material's performance.

3. High-entropy alloy

Modern material science development and its growth depend on the innovation of new alloys. That is expressed in the way of development of novel materials, fabrication methods, quality of the object (defect-free), and life span. However, the main objective of new component development is energy-saving perspectives in society. In this way, the modern metal matrix composite introduces a new alloy called HEAs. In 2004, Yeh and Cantor et al. proposed this alloy system [39]. They differentiate the conventional alloy system by eliminating the matrix or adding a base elements concept. These unique properties of HEAs are categorised into (i) the addition of principal metallic elements to develop an alloy and (ii) the generation of entropy. In this advanced alloy, properties are decided based on the phase structure. The phase structure is (i) solid-solution phase; most cases are alloys with BCC, FCC and HCP structure, (ii) intermetallic compound phase and (iii) amorphous phase. This type of structure is developed based on the types of elements added, followed by performance optimisation methods using physical and chemical approaches. Followed by the HEAs development with more than 13 elements addition, they affect the entropy stability, high chances of phase segregation, and unsymmetrical HEAs core effects are developed. Earlier studies represented the Multi-Principal Element Alloy System (MPEAs), also known as HEAs. But the recent results contradict these statements. Because of the addition of alloying elements strategies, core effect, and metallurgical behaviour, their results are the same for MPEAs development, but the HEAs are different in secondary phase formation. If alloys without a secondary phase are developed for HEAs. In most cases, HEAs are a single phase. Either the secondary phase, such as an intermetallic compound, is developed in the alloy system known as MPEAs [40,41].

The alloy's stability depends on the configurational entropy of the system; in this configurational entropy depends on several metallic element additions, the addition of interstitial elements (carbon), alloy fabrication methods, temperature effects, atomic size of the elements, and electronegativity difference. The number of elements added and their equimolar or non-equimolar ratios, which range from a minimum of 5 to a maximum of 35 at%, determine the alloy's properties [42]. From the conventional alloys, the HEAs property variations depend on core effects. With the help of this core effect, they can make alloys superior in terms of strength, resistance to wear in high-temperature conditions, and high corrosion resistance compared to conventional alloys. The core effects, like (i) high entropy effect, explain the phase formation based on the addition of alloying elements, with the help of the formation of entropy generation within the alloy system. The formation of a higher amount of entropy is the backbone of phase stability. Particularly, thermodynamic behaviour and high entropy effects decide the phase formation, i.e., single-phase, intermetallic and complex phases [43]. The higher the alloy's configurational entropy, development better the way to maintain a single-phase structure at high-temperature conditions. (ii) lattice distortion effect, from the one principal elements alloy system, like the nickel element (FCC crystal structure), there are no lattice distortion effects developed because of the similar crystal lattice arrangements between the lattice sites. Followed by the elements, they have similar atomic size, different electronegativity and the same valence electron concentration. For that, similar behaviour is required to reduce the alloys' strength, hardness, and low wear resistance. Followed by this, no lattice distortion effects higher the chances of alloys' dislocation motion because of their uniform bonding throughout the lattice sites. Moreover, the alloys with high dislocation motion, the diffusion or mobility of the hydrogen atoms occurs faster way and which will reduce the grain boundary strength and develop a brittle failure [42]. On the contrary, using a multiple metallic element alloy system, individual elements and their various mechanical and chemical characteristics are used to enhance the mechanical and alloy bonding behaviour. The effective way to increase the number of metallic elements is to add them to enhance the lattice distortion effects. Followed by these different atomic sizes of elements are added to control the alloys' dislocation motion, followed by alloys with high solid solution strengthening to achieve. These effects are related to hydrogen-resistant material development, the alloys developed with a higher atomic size, different from the control hydrogen atom diffusion level. Control the hydrogen atom diffusion, it is not possible to penetrate the hydrogen atom near the lattices, followed by high chances of hydrogen atom trapping, to control the alloy's localized embrittlement behaviour. And the effects of different elements and their atomic size differences enhance the solid-solution strengthening, followed by an increase in the alloys' strengthening behaviour to mitigate the hydrogen-induced crack propagation [44]. (iii) sluggish diffusion effect, leading to the formation of nano-precipitation with various element additions. In the hydrogen environment, the precipitates have some beneficial and detrimental effects on controlling the alloys' ductile-to-brittle phase formation [45]. (iv) cocktail effects, the addition of the various elements to develop alloys and their unexpected outcomes are expressed with the help of the cocktail effects [46]. However, the addition of alloying elements plays a pivotal role in microstructure, mechanical and hydrogen resistance material development. In this regard, the selection of elements decides the crystal structure of the alloy system. The selection of metallic alloying elements plays a pivotal role in the prevention of HE failures, particularly in hydrogen storage and transportation materials. Before the selection of the elements, a clear understanding of the element's hydrogen solubility limit is required. Most commonly, the better way to transport hydrogen transportation using an element such as iron or iron-based alloys. Resistance to hydrogen permeation, corrosion resistance, high-pressure withstanding capacity, easy availability and reasonable cost in the market are important considerations for the selection of Fe or Fe-based alloys. Apport from the Fe-based alloys is a better hydrogen solubility limit at ambient temperature. Fe and Ni have moderate amounts of hydrogen solubility and FCC stabiliser of Ni to control the alloys' BCC formation and reduce the HE failures [47]. From the microstructure and mechanical point of view, the BCC structure has better hardness, strength, and stable thermal properties and alloys to achieve a better density. Followed by the FCC structure materials, which have high toughness and ductility, corrosion resistance, and better phase stability at different temperatures. Meanwhile, the various application points of view on the requirement of the alloy crystal structure are varied. Here, the hydrogen production and transportation application FCC crystal structure is better compared to the BCC structure [48]. Based on these aspects, FCC stabilising elements are recommended for hydrogen storage material development. The FCC stabilising elements are Ni [49], Cu [50], Mn, Co and others [51]. For an interesting note: All FCC crystal structure elements do not have an FCC stabiliser. For example, Al is a soft and FCC structure element. For adding more Al to other elements, the initial FCC structure changed to BCC, and to increase the hardness of the alloy, if the aluminium content increases. The HEAs made of FeCoCrNiCu and FeCrNiCuMo alloys achieved a single-phase FCC structure. Here, the same composition, the addition of FCC structure material like Al, to the influence of this Al addition, the single-phase FCC structure changed to BCC or BCC + FCC structure [50]. The BCC crystal structure has higher brittleness and lower toughness; these characteristics are very difficult for hydrogen applications, followed by higher chances of developing hydrogen embrittlement failure in the materials. Moreover, to increase the Al contents in the FeNiCrCo-Al$_X$ (X = 1.5, 2, 2. 5, and 3) based HEAs to continuously increase the alloys' hardness from 402, 432, 487 and 506 HV, for that reason behind, among them other elements the Al has higher the atomic size compared to Fe, Ni, Cr, and Co elements, for that reason the alloys crystal structure changes and increase the crystal lattices size followed by this effects the alloys with increase the lattice distortion energy then the effects to enhance the alloy solid solution strengthening, thus improve the strength and hardness of the alloys. The high-hardness materials are also not suitable for hydrogen storage applications. For that reason, in the hydrogen storage and hydrogen transportation applications, the influence of the Al element contribution is very less. In recent days, type III pressure vessels have been made of composite materials with wrapped Al-based liner material to increase the high-pressure handling capacity [44]. For structural applications, Fe, Cr, Al, Ti and V are mostly preferable [52]. However, other elements also significantly control hydrogen embrittlement in terms of corrosion resistance. For example, the addition of Co, Cr, Mn, Al, Cu, Zr, and other elements plays an important role in the development of hydrogen storage materials. Here, the selection element depends on two factors: (i) the enthalpy-entropy relation and (ii) the Influence of additional elements and their mechanical property. The enthalpy-entropy relation correlates the phase stability and Gibbs free energy equation, $\Delta G = \Delta H\text{-}T\Delta S$, to guide the mixing enthalpy (ΔH_{mix}) and mixing entropy (ΔS_{mix}) understanding. Based on the binary element, the concentration plays more of a role in the enthalpy and entropy relation.

The influence of negative ΔH_{mix} indicates a strong formation of a stable solid solution. Conversely, positive ΔH_{mix} indicates an unmixed and unstable alloy system, where the elements are highly separated and tend to develop a non-homogeneous solid solution to develop [53]. Binary elements and their enthalpy and entropy mixing directly correlated to the alloys with the solubility, the negative ΔH_{mix} between the binary elements to enhance the solubility, followed by reducing the elemental segregation and enhancing the phase stability, i.e., Fe–Cr: 1 kJ/mol, Fe–Cu: 13 kJ/mol, Fe–Co: 1 kJ/mol, Fe–Mn: 0 kJ/mol, Fe–Ni: 2 kJ/mol, Fe–Al: 11 kJ/mol, Fe–Ti: 17 kJ/mol, and Fe–Mg: 18 kJ/mol. Compared to binary mixing enthalpy, Fe addition to Ti has better mixing enthalpy, which strongly possible to formation of a solid solution and avoids the elemental segregation within the binary alloy system. Similar to Fe with Cu has a positive mixing enthalpy, it reflects high chances of elemental segregation and reduces the mechanical property. It follows that $\Delta H_{mix} \leq 0$ develops a stable single-phase solid solution that exhibits better strength and ductility balance, and $\Delta H_{mix} \geq 0$ forms an unstable single-phase solid solution that exhibits microstructure changes and higher chances of losing phase stability [54]. The addition of metallic elements and their high atomic size difference is one of the important considerations for high negative entropy formation.

The importance of elements addition to the HEAs is as follows: the addition of the Cr element is a crucial consideration for developing embrittlement failure, because Cr elements are highly concentrated at the grain boundary accumulation, leading to the formation of brittle intermetallic phases or chromium-rich precipitates at the grain boundary to developed, which weaken the grain boundary strength and result in intergranular fracture and the crystal structure changes to brittle. Beyond that, embrittlement and corrosion are interlinked phenomena. Notably, electrochemical hydrogen charging the corrosion reaction plays a stringent role in this regard; to control of this addition of mutual elements is important. Here, with the Cr element addition, the corrosion resistance and oxidation resistance are improved. But beyond the excess composition limitation, Cr evoked the brittle phase formation [55]. Because the Cr is a better ferrite stabilising element.

The presence of Ni in the HEAs combination within a hydrogen-based environment delays the transition of the crystal structure from ductile to brittle. However, with the addition of Ni, the fracture mode shifts from intergranular to transgranular, ultimately enhancing the HEAs resistance to hydrogen-induced embrittlement. Incorporating nickel addition to the HEAs is an effective method to resist corrosion and embrittlement formation, although it has limitations; the performance impact of nickel in a multi-component alloy system should not exceed 25 wt%, as exceeding this percentage does not enhance the HE's resistance and also destabilises the austenite phase. The addition of Ni to Al promotes FCC formation and enhances the strength-ductility relationship. Both Ni and Al serve as high entropy-enhancing elements in HEAs. In a hydrogen-based environment, adding Mn to the multicomponent alloy system increases the hydrogen solubility limit, particularly in the interstitial regions, and improves hydrogen trapping capacity. Moreover, the equiatomic FeCoCrNiMn alloys supplemented with Al consistently enhance the alloys' structural stability and reduce friction-induced material failures.

While the Cu element addition to the HEAs, particularly in Al-based HEAs, forms a hard BCC structure. While interesting, both Cu and Al have the same FCC structure. The addition of both elements finally formed the hard and brittle BCC structure. For that reason, of differences in atomic sizes between Al and Cu lead to lattice distortion and solute effects that favour BCC structure development. The differences in atomic sizes and varying temperature solute conditions represent significant considerations for alloy crystal structure development. The effects of Nb addition to the FeCoCrNi-based HEAs result develop a negative mixing enthalpy, leading to higher bonding behaviour and high crystal structure stability.

4. Overview of phase structure and physical parameters of HEAs

The phase structure is called phase engineering, which provides detailed information about the HEAs behaviour. The HEAs are typically classified into three types of phases: (i) solid-solution phases (BCC, FCC, and HCP), (ii) intermetallic compounds (μ, χ, σ and Laves phase), and (iii) amorphous phase. Typically, in recent days, significant progress in HEAs has been made based on unconditional elemental selection from the range of 5–35 at%. Based on two approaches, (i) chemical transformation, (ii) physical transformation. The chemical transformation deals with mixing entropy, mixing enthalpy, valence electron concentration, elements' atomic size difference, and electronegativity difference. Physical transformation deals with temperature, stress-strain variation and magnetic field behaviour. This work mainly focuses on element chemical transformation behaviour [56].

The alloys with high entropy to stabilise the mechanical properties, that are a simple understanding of HEAs, and high entropy enhances the alloy's solid-solution formation. Add multiple elements to enhance the individual entropy level of the alloy system (number of elements added α entropy generation). However, entropy-based alloy systems vary with the number of principal elements addition, like the addition of one or two elements to generate the configurational entropy values $\triangle S \leq 1.0R$ for Low Entropy Alloys (LEAs), the addition of three to four elements and their configurational entropy values $1.0R \leq \triangle S \leq 1.5R$ to develop a medium entropy alloy (MEAs), followed by addition of four elements and their configurational entropy $\triangle S \geq 1.5R$ for develop a high entropy alloy (HEAs) [22]. The development of HEAs is based on various factors, it represents the various chemical parameters, such as (i) thermodynamic behaviour: which depends on the development of phase-formation (BCC, FCC and HCP), (ii) Radius mismatch or atomic size difference depends on phase-stability (iii) valence electron concentration depends on crystal structure formation, (iv) electronegativity difference depends on structural stacking properties, (v) chemical combining behaviour, and (vi) melting temperature of alloys.

4.1. Thermodynamic behaviour

The thermodynamic behaviour is related to Gibbs free energy (ΔG_{mix}), mixing enthalpy (ΔH_{mix}), and mixing entropy (ΔS_{mix})

Gibbs free energy is a basic alloy formation rule for developing HEAs.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{i}$$

$$\Delta H_{mix} = \sum_{i=1, i\neq 1}^{n} 4\Delta H_{AB}^{mix} c_i c_j \tag{ii}$$

Here, c_i and c_j atomic percentages of the ith and jth elements. ΔH_{AB}^{mix} = enthalpy of mixing of binary alloys based on Boltzmann's hypothesis. $R = 8.314\ Jk^{-1}mol^{-1}$ gas constant

$$\Delta S_{mix} = -R\sum_{i=1}^{N} c_i \ln c_i \tag{iii}$$

Reduction in mixing enthalpy (ΔHmix) enhances the mixing entropy (ΔSmix) of the alloys and maintains high-temperature phase stability. The addition of alloying elements reduces the Gibbs free energy within the alloy system, improving the mutual solubility level and promoting the formation of single-phase solid-solution phases [57]. However, the ΔHmix = 0 forms an ideal solution with high phase stability, which maintains high ductility in alloys of moderate strength. In contrast, ΔHmix >0 or negative/positive results in a non-ideal solution with multiphase alloys, reducing phase stability and higher strength that are more susceptible to hydrogen-based failure and have increased hardness. [60]. Alloys with more positive ΔHmix reflect the alloys with high elemental separation. While intermetallic compound phase, the high negative ΔHmix is preferable [58].

The hydrogen embrittlement and its mitigating strategies depend on the atomic size difference and electronegativity of the elements, particularly in the context of ideal and non-ideal enthalpy formation due to the strong attraction and repulsion of atoms. The negative ΔHmix results in an exothermic reaction, which reduces hydrogen solubility and controls hydrogen trapping capacity, thereby preventing hydrogen diffusion. Conversely, the positive ΔHmix leads to an endothermic reaction that reduces atomic interaction, promoting alloy phase segregation, which ultimately contributes to embrittlement.

Based on the above ΔS_{mix} equation (iii), further expressed in terms of cation and anion site base.

$$\Delta S_{mix} = -R\left(\sum_{i=1}^{N} c_i \ln c_i\right)_{\text{cation site}} + \left(\sum_{i=1}^{N} c_i \ln c_i\right)_{\text{anion site}} \tag{iv}$$

As mentioned above, the addition of elements to improve the configurational entropy of the alloy system, here we explain the reason for the configurational entropy development, has been considered the alloys with an oxide phase. The oxygen combined with metal or non-metal they are develops the oxide phase in a lattice group. The configurational entropy is different based on the cation and anion present in the alloy system. To increase the metallic elements (Fe, Al and Mg) or non-metallic elements (Fe_3O_4, Al_2O_3, and MgO) additions to the multicomponent alloy system, each element has its configuration disorder to increase the cation to the sublattice. Followed by the anion to occupy the oxygen, its entropy values are zero. As its an anion site, zero is followed by an entropy increase to the total number of cations, so the configurational entropy with the addition of elements [59].

4.2. Atomic size difference (δ)

$$\delta\,\% = 100\% \times \sqrt{\sum_{i=1}^{n} c_i\left(1 - \frac{r_i}{\sum_{j=1}^{n} c_j r_j}\right)^2} \tag{v}$$

Here, r_i and r_j=atomic radius of the ith and jth elements.

Alloys with constant phase stability depend on the radius mismatch of the elements. Decreasing the atomic size difference between the mutual alloying elements, it more favourable to enhance the formation of a solid solution strengthening behaviour. Followed by a similar atomic radius of the elements to control or prevent the phase separation resulting from having a uniform phase structure [60]. Formation of a single-phase solid solution is highly favourable for the atomic size difference. An amorphous or multi-phase alloy developed based on a higher atomic size difference [61]. The HEAs of FeCoCrNiMn alloys, the atomic size difference among the elements is very less, and these elements add to developing a single-phase FCC structure for better strength to ductility behaviour. Along with adding the Al element to these HEAs, the FCC crystal structure disappears and develops a BCC structure. Therefore, the higher atomic size difference creates more excessive strain energy and destabilises the crystal structure. High entropy only enhances the single-phase crystal structure [62]. For that, the atomic size difference between the mutual alloying elements is small (i.e., $\delta \leq 8.5$), and they are favourable to forming the solid solution strengthening. Moreover, the mutual elements and their atomic size difference are higher (i.e., $\delta > 9$), and they form the amorphous phases. Compared to conventional alloys, the HEAs with this type of atomic size difference develop a high stability of the alloys with higher mechanical properties [56].

4.3. *Electronegativity difference ($\Delta\chi$)*

Different metallic elements are combined to develop HEAs. The system has different elements and different chemical properties, along with the addition of individual alloys, which develop different behaviours of atoms and electrons. The different elements and their electronegativity difference are a significant contribution to developing a solid solution, amorphous, and intermetallic phase development. Formation of different phases develops a reason based on HEAs phase segregation [43]. Alloys with $\Delta_\chi < 0.175$ and e/a for-BCC crystal structure $1.6 <$ e/a <1.8. For FCC crystal structure $1.8 <$ e/a <2.3 [63]. Elements with high elemental differences in the combined alloy formation lead to the development of a compound formation to enhance.

$$\Delta\chi = \sqrt{\sum_{i=1}^{n} ci\ (\chi i - \bar{A})^2} \tag{vi}$$

$$\bar{A} = \sum_{i=1}^{n} ci\,\chi i$$

However, the electronegativity difference has a direct correlation with hydrogen-related studies, especially hydrogen embrittlement (HE). The materials that experience HE failures depend on factors such as the diffusion of hydrogen atoms at lattice positions, hydrogen solubility levels, and trapping sites. In this context, materials with the highest electronegativity difference are most effective for controlling the mobility of hydrogen atoms, resulting in better trapping sites. Conversely, materials or alloys with lower electronegativity differences exhibit weak atomic bonding, leading to increased hydrogen mobility and a higher likelihood of brittleness as well as the development of embrittlement under the influence of hydrogen [64].

4.4. *Valence electron concentration (VEC)*

$$VEC_{avg} = \sum\nolimits_{i=1}^{n} c_i\ (VEC)_i \tag{vii}$$

Here, $(\mathrm{VEC})_i =$ Valence electron concentration of *i*th component and $c_i =$ concentration of the component.

The alloy formation, which depends on the Hume-Rothery criteria based on these criteria helps to develop a solid solution formation. But in the modern day, with the revolution of material development and modern fabrication methods, the rules are not satisfied in the same way as HEAs development. The rules say to develop alloys with the addition of the same VEC to develop alloys. In a multi-component alloy system, the rules are not satisfied instantaneously; the new criteria are considered to develop HEAs, named as electronic and thermodynamic (e/a) factors, particularly in metallic materials. The VEC is one of the chemical constant parameters to evaluate the crystal structure (BCC or FCC structure) and atomic arrangement. The VEC between the range of VEC ≥ 8 is favourable for forming the FCC phase, and VEC <6.87 for developing the BCC phase [65]. The increase or decrease of the VEC values does not enhance the phase stability; it depends only on the crystal structure. Most research in HEAs is based on FCC and BCC structure-based. Limited work focuses on HCP structure because HCP structures have limited phase stability and entropy generation. In recent days, the dual-phase FCC + HCP structure alloys are interesting for higher ductility and strength balance. Addition of lanthanide metals to enhance the HCP phases [66]. Some metallic elements are mostly considered to have the FCC and BCC structure stability maintenance, i.e., the addition of Al, Cr, Mo and Si with BCC stabiliser and lower VEC. Followed by the addition of Ni and Co results in high stability in the FCC phase with high VEC.

4.5. *Combining effects (Ω)*

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \tag{viii}$$

$$\mathrm{T_m} = \sum_{i=1}^{n} ci\ Tmi$$

Here, $\mathrm{T_m}$ = melting temperature of alloys, $\Delta \mathrm{S_{mix}}$ and $\Delta \mathrm{H_{mix}}$ are mixing entropy and enthalpy of alloys. Alloys with the phase formation predicted with the help of this combined effect. In the previous cases, the entropy-enthalpy relations are used to decide the alloys' solid-solution formation, but compared to this relation, the chemical combining behaviour is a more accurate prediction to find the solid-solution formation behaviour [56]. Chemical combining behaviour (Ω) is related to the alloys with an entropy contribution to the Gibbs free energy. In most cases, the combining behaviour helps to find the solid-solution formation within the alloy system. The alloy system with $\Omega \geq 1.1$ and $\delta \leq 6.67$ forms the single-phase solid solution phases. Followed by $\Omega \leq 1$, which denotes the intermetallic compound formation [67].

4.6. *Geometrical parameter (Λ)*

As the name suggests, geometrical parameters mention the geometrical information about the lattice configuration and the radius of the atoms. The higher the geometrical parameter, the higher the possibility of developing a Disordered Solid Solution (DSS). The HEAs with stable or increasing entropy is an important way to consider mechanical property development. In this regard, the alloys with higher DSS enhance the mechanical properties. For DSS, the alloys with entropy generation have ΔSmix >1.61R [50]. The element with the smaller atomic size difference is most favourable for the formation of DSS; meanwhile, the higher the atomic size difference, the more favourable it is for compound formation [68]. They are strongly recommended by the suggested $\delta \leq 66$ % and $\Omega \geq 1.1$ support for the formation of DSS [69].

These various parameters are considered for entropy stabilisation, like $\Delta \mathrm{H_{mix}}$, $\Delta \mathrm{S_{mix}}$, $\mathrm{T_m}$, δ and Ω. Including this new geometrical parameter (Λ) is important for predicting phase identifications of single, two, and multiphase HEAs. It is formulated by,

$$\Lambda = \frac{\Delta S_{mix}}{\delta^2} \tag{ix}$$

The HEAs with the single phase have the geometrical parameters $\Lambda > 0.96$, for two-phase $0.24 < \Lambda < 0.96$, followed by multi-phase $\Lambda < 0.24$ [40]. As mentioned by the above criteria, FeCoCrNiMn-based HEAs to obtain the $\Lambda = 1.251$ and δ have 3.27 favourable for the formation of a single-phase FCC structure [70], and HEAs of FeCoCuNiV-based HEAs to achieve a $\Lambda = 2.755$ and δ have 2.20 favourable for the formation of a single-phase FCC structure [61]. However, HEAs of FeCoCrNiTiAl-based alloys to achieve a $\Lambda = 0.352$ and δ have 6.35 favourable for the formation of a two-phase FCC + B2 structure [71]. Followed by alloys with multiphase to develop a FeCrNiCuZr, the $\Lambda = 0.128$ and δ have 10.24 to develop a B2+compound phase are developed [50]. The elements with the addition of Ni and Al are most favourable to form the B2 phase, which is developed in HEAs. Based on the elemental addition, some noticeable features are identified based on the Λ parameters. Importantly, with the help of elemental addition to high geometrical parameters to enhance the DSS, followed by higher to lower values of Λ phases are developed by the sequence of DSS → FCC (L12) → BCC (B2) →Compounds (Laves phase, σ-phase) this way also mentioned in DSS → DSS + L12 → DSS + B2 → DSS + complex phase [68].

In conventional alloy systems, different phases are formed, like terminal solutions, intermediate solutions, and intermetallic compounds. In the terminal solutions, the addition of elements is entirely dispersed in the base metals without developing separate phases. Intermediate solutions must define the composition range between adding individual elements and different microstructures to be obtained after the fabrication of base metals, based on different pressure-temperature conditions in the different phases. In intermetallic compounds, the addition of different metals or metalloids is used to obtain an ordered structure with high strength and hardness [63]. Based on this conventional alloy compared to the HEAs system, the various phases formed are like simple or random solid solutions, e.g., FCC and BCC structures. Super lattices/ordered solid solution, e.g., B2 and $L1_2$, C12–W, cF4-Cu, hP2-Mg. And intermetallic phases, e.g., laves phases, σ, and μ structure, are formed [63,72]. Moreover, the HEAs are further converted into (i) Simple Disordered Phase (SDP), (ii) Simple Ordered Phase (SOP), and (iii) Complex Ordered Phase (COP).

These types of phases are formed in HEAs depending on the enthalpy of mixing (ΔHmix), the entropy of mixing (ΔSmix), and atomic size differences (δ). Table 1 shows the different parameters for the development of the SDP phase. Table 2 shows the different parameters for developing the SOP and COP phases.

Valence electron concentration (VEC), Pauling electronegativity difference (Δ_X), and mobile electron concentration (e/a) are empirical criteria for the prediction of phase structure in HEAs. $\Delta_X < 0.175$ and e/a for-BCC crystal structure $1.6 < e/a < 1.8$. For FCC crystal structure $1.8 < e/a < 2.3$ [63].

5. Metal additive manufacturing

3D printing technology, also known as additive manufacturing (AM), involves developing various types of components by adding materials layer by layer, particularly through metal deposition based on the required design and applications. Furthermore, this process enables the use of common materials in AM, such as metals, ceramics, and polymer-based components. This work focuses on metal-based 3D printing and its significance concerning hydrogen-based applications and limitations. Additionally, it examines the hydrogen embrittlement behaviour of 3D printed parts versus conventionally developed materials [76]. These comparative results depend on factors such as the selected alloy system, microstructural effects, hydrogen charging methods, and hydrogen-induced crack initiation. Recently, the development of AM parts has exhibited significant advantages over conventionally manufactured parts, including dimensional accuracy, high precision, performance, reliability, and durability in structural component development. The primary advantage of 3D printing lies in its capability to create parts with high geometric complexity while minimising material waste during pre- and post-processing fabrications [77]. In a hydrogen-based environment, a comparative study of both wrought (conventional fabrication) and AM parts in gaseous and electrochemical settings shows that AM parts exhibit better mechanical property enhancement than conventionally fabricated wrought alloys due to superior surface features. Conventionally fabricated alloys tend to have more surface cracks and reduced resistance to hydrogen environments, whereas AM parts are better at resisting hydrogen-induced surface cracks due to their higher cooling rate for fabrication time, which contributes to intrinsic property development based on microstructural characteristics [78]. Metal additive manufacturing utilises established methods for preparing HEAs and other alloy types while adhering to ASTM F2792-12a standards. Powder-Bed Fusion (PBF) and Direct Energy Deposition (DED) are the most common techniques for producing powder-based raw materials for AM. In PBF, high-energy lasers or electron beams melt or sinter the pre-spread powder in layers on the machine bed, creating the required profile. Sintering or melting the powder utilises a high-energy laser or electron beam source, and this process continues until the entire part is constructed. In DED, pre-spreading of the powder is not necessary; instead, it develops a build-up layer model to focus a high-energy source (laser/electron) and deposit the feedstock metal objects, which can be in wire or powder form. The effectiveness of printed parts depends on various features such as fast sample heating, rapid cooling based on cooling methods, chamber efficiency, and high thermal gradients within a small melt pool. These thermal gradients influence the development of mechanical and thermal properties. Table 3 shows the important parameters in AM. Followed by, Table 4 represents the comparative study of both PBF and DED methods.

Table 1
Criteria for the development of an SDP phase structure.

S. No	Parameters	Values
1	enthalpy of mixing (ΔHmix)	$-15 \le \Delta H\ mix \le 5$ kJ/mol
2	entropy of mixing (ΔSmix)	$12 \le \Delta S\ mix \le 17.5$ J/(K mol)
3	atomic size differences (δ)	$\delta \le 4.3$

Table 2
Criteria for the development of both SOP and COP structures.

S. No	Parameters	Values
1	enthalpy of mixing (ΔHmix)	$-22 \le \Delta Hmix \le 7$ kJ/mol,
2	entropy of mixing (ΔSmix)	$11 \le \Delta Smix \le 19.5$ J/(K mol)
3	atomic size differences (δ)	$\delta \le 8.5$

As mentioned in Table 4, the various parameters directly and indirectly influence material property development. Followed by the (i) energy density in AM parts, the total amount of energy to be released per unit volume of the materials per unit time. The energy density values are functions of microstructure, such as phase transformation, uneven-grain size of build parts, and internal defects such as porosity [73]. (ii) Build Direction Time (BDT); depends on materials properties or the addition of alloying elements, machine capabilities, and part geometry. Increase the BDT, and the effect of deposition duration is slower. The slower deposition time increases the adhesion bonding strength of the printed

Table 3
Important parameters to consider in metal additive manufacturing of both PBF and DED methods.

Parameters	PBF		DED	
Feedstock		Powder	Wire	Powder
Nomenclature	EPBF	LPBF	EDED	LDED
Heat source	Electron beam	Laser power	Electron Beam	Laser power
Power	–	50–1000 W (Approximate)	500–2000 W (Approximate)	100–3000 W (Approximate)
Scanning speed	–	10–1000 mm/s	1–10 mm/s	5–20 mm/s
Beam spot size	–	≤100 μm	N/A	Up to mm ranges
Powder particle size	60–105 μm	10–60 μm	N/A	50–150 μm
Layer thickness	50–100 μm	≤100 μm	NA	≤500 μm
Hatch distance	200 mm	≤400 mm	N/A	≤1 mm
Atmosphere	High vacuum	Nitrogen, argon	High vacuum	Air, nitrogen, and argon

Table 4

Comparative study of PBF and DED-based AM and their results.

Process	DED	Results/ Remark	PBF	Results/Remark
Energy density	High	Wire/coarse powder is used, resulting in larger melt pools (1 mm)	Low	Smaller spot size results in the development of smaller melt pools (100 μm)
Build rate	Fast	Improve the layer quality	Moderate	Good bonding strength
Cooling rate	Slow	The slow cooling rate in the AM prevents the distortion and warping of printed parts.	Fast	Influence of microstructure modification on grain size.
Surface finish	Low	–	Better	–
Geometrical accuracy	Low	–	Very high	–
Sub-systems	LDMF, LENS, DLF, DMD.	–	SLM, SLS, EBM.	–
Applications	–	–	High-dimensional accuracy is obtained in PBF, so it is mostly used in the medical and aerospace sectors.	–

material [74]. (iii) Cooling rate: The effect of 3D-printed parts and their hardness depend on the cooling rate. The effects of a higher cooling rate to achieve the fine microstructure, which is one of the influencing factors for improving the strength and hardness of the 3D printed materials [75]. (iv) Surface finish; compared to DED, the PBF achieves a better surface finish and greater resolution, and parts to print [76]. The lower surface finish in DED further needs machining [77]. DED follows this to obtain a higher energy density compared to PBF. Because the wire or coarse powder serves as a feedstock in DED. This type of deposition results in a higher volume of melt pools and a faster deposition rate. In this way, the AM-HEAs are a recently growing field in modern materials development. The research will move forward with the material fabrication from conventional techniques to AM in the future due to its better property development. AM of HEAs and the development of their components in hydrogen storage and transportation applications are important for industrial utilisation based on their mechanical properties, and the mitigating nature of HE behaviour is an important consideration for HEAs development. The effects of degradation of mechanical properties are called HE in terms of material failures. Materials with high hardness are a positive effect for structural applications, but the high hardness allows high hydrogen susceptibility, in terms of developing hydrogen embrittlement failure. The PBF-based SLM technology enhances the property development in terms of materials to develop a high hardness and resistance to HE failures. Particularly in SLM, to develop an ultrafine microstructure to resist the HE with better hardness. The AlCoCrFeNi-based HEAs elucidate this strength-ductility-hydrogen embrittlement contradiction, to develop nano-cellular structured B2 phase eutectic HEAs. This kind of structure is to maintain the UTS and yield strength for 48 and 72 h of electrochemical hydrogen exposure [77].

Ni-based alloys are mostly preferable for hydrogen storage devices for the replacement of Fe-based alloys. The Fe-based alloys have fast hydrogen diffusion and fewer chances for hydrogen trapping, followed by a microstructure that is difficult to form. Moreover, using Ni-based alloys with less hydrogen diffusion and higher hydrogen trapping behaviour. The addition of Ni-elements has a very good austenitic stabiliser to withstand the FCC crystal structure's greater resistance to HE. In recent days, to overcome these positive effects develop SLM SLM-processed FeCoCrNiMn-based HEAs have been developed. In terms of achieving a high strength and high HE resistance [38]. The development of 3D-printed HEAs is based on the various applications for the addition of alloying elements to be selected. Table 5 shows the application related to the help of element selection [78].

The distinct features of the PBF and DED depend on microstructure changes that happen during metal printing and on the laser beams with the material interaction. The PBF, the metal powders prefilled in the chamber, and the laser source fused the metal powder based on the required specification. Elemental solubility is an important consideration for effective 3D printing techniques it depends on the laser power source. Lattice parameters also affect the laser power. For the DED to consider the direct injection of metal powder based on the complex configuration. Here, the differences are in PBF at the time of metal printing; only the beam travels. Moreover, the DED, the beam along with powder/wire travelled for that difference, reflects the thermomechanical properties and thermogenetic property variation [55]. Based on the geometrical features, the PBF prints intricate, difficult modelling with better dimensional accuracy, with an excellent surface finish. Moreover, the DED prints the large-scale component with moderate accuracy, and a rough surface finish is obtained based on the feedstock materials [79].

6. Hydrogen embrittlement behaviour of laboratory hydrogen charging exposure

Hydrogen-to-metal interaction behaviour is an important consideration for the development of HE failures. In this, hydrogen interacts with the metallic materials are two ways: (i) high-pressure gaseous charging and (ii) electrochemical hydrogen charging. These types of hydrogen charging are discussed in the chapters. Accumulation of hydrogen is an important consideration in developing HE and crack initiation over the material's surfaces, particularly AM components. The microstructural variation depends on the laser source, power, scanning speed, layer thickness, scan pattern, and powder characteristics, such as structure and misfit energy [80]. It depends on the time of layer-by-layer metal addition; they create an interface between the different phases, enhancing the material's structural discontinuity, which causes the difference in the misfit energy. The misfit energy difference is mostly considered in multi-component alloy systems. The energy is associated with discrepancies in the lattice structure of the HEAs system. These misfit energy differences impact the performance of the alloys and significantly impact the mechanical properties and structural integrity of the 3D-printed components. Materials with HE failures are reduced by (i) reducing the corrosion rate, (ii) baking the materials after plating, (iii) welding parts to proper welding practices, steels, using less

Table 5

Element selection based on required HEAs development.

Alloys	Applications
Aluminium-based HEAs	Lightweight aerospace applications.
Titanium-based HEAs	Good corrosion resistance; biomedical implant development; high-temperature applications; energy, oil, and gas storage; marine.
Cobalt-based HEAs	Good corrosion resistance, Aerospace, and Medical.
Chromium-based HEAs	Hydrogen storage vessels, Corrosion resistance.
Nickel-based HEAs	High-temperature equipment, Aerospace, corrosion resistance, and machinability.
Iron and chromium alloys (SS316L, 304L)	Hydrogen energy storage and transportation applications; Eliminating hydrogen embrittlement parts; Corrosion resistance; tools and moulds.
Precious metals	Consumer products and medical.

susceptible materials, and (iv) grain boundary modification. The addition of carbide and boron to the HEAs, for example, the addition of alloying elements CoCrNi along with boron, enhanced the HE because boron has grain boundary decoration and better doping agent. The addition of boron to the CoCrNi-based MEAs with gaseous hydrogen charging changes the fracture behaviour from intergranular to trans granular; meanwhile, the development of the fracture area is reduced from 71 % to 46 % with 1.5 % boron addition [81]. In this type of fracture or failure, the materials depend on crystal structure changes from FCC to BCC. For the BCC crystal structure, the highest brittleness and a high chance of developing a catastrophic failure are observed. So, the FCC structure materials are highly ductile and have less chance of developing a catastrophic failure. In this FCC structure, characters particularly improve hydrogen storage devices and mitigate hydrogen embrittlement failure. Based on these aspects, the 3D-printed components are developed. These 3D-printed components are better structural applications, especially for tensile behaviour. Magnetic behaviour depends on higher magnetic saturation, and a lower temperature represents a better superconductor, followed by the FCC crystal structure, which will represent the better hydrogen storage capability behaviour [21,82]. Important considerations include the high resistance to HE failure in 3D-printed and conventional fabrication methods, the grain boundary cohesive strength, and the reduction of hydrogen-induced cracking in grain boundaries. For gaseous hydrogen, charging requires high pressure, with and without temperature conditions for hydrogen uptakes. Followed by electrochemical or cathodic hydrogen charging, it requires a simple setup like an electrochemical cell, charged over acidic, neutral, and alkaline solutions. Compared to gaseous charging, electrochemical charging of the materials significantly affects the mechanical properties. Because the cathodic hydrogen charging method grater the hydrogen uptakes, followed by higher hydrogen fugacity [83].

6.1. *Embrittlement behaviour in gaseous hydrogen charging*

Hydrogen in the form of gas has recently become a versatile and effective alternative compared to traditional fuel, particularly in the field of transportation. In that regard, the material-based research focuses on optimised material development, especially for hydrogen storage applications. However, based on this concept, the developing material is HEAs with the fabrication of grooming technology, like additive manufacturing. The development of materials may not fully avoid HE failures; instead, they have to control the HE problems. In the gaseous hydrogen charging, the molecular hydrogen (H_2) is a source. Followed by lower surface effects compared to electrochemical charging and low fugacity [84]. Accumulation of hydrogen atoms inside the grain boundaries and crystal lattices is an important consideration for gaseous hydrogen storage materials development. Grain size, grain boundary features, hydrogen diffusion, hydrogen trapping and crystallographic orientation are related factors for grain boundary and interstitial lattice site consideration. Alloys with hydrogen diffusion and trapping to represent the GB weakening. Followed by the interstitial lattice region, which represents the hydrogen diffusion pathway, storage of hydrogen, and its internal pressure and temperature conditions. Materials with a higher hydrogen absorption and delayed diffusion develop lower hydrogen trapping sites, leading to factors for hydrogen embrittlement.

In recent days, embrittlement behaviour based on materials' crystal structures, particularly an alloy of CrCoNi-based alloys, has received significant attention for single and polycrystalline materials. The gaseous hydrogen exposure with the high pressure and temperature maintained for three days in controlled chamber conditions, in single-crystalline materials, eliminates the dislocation motion in polycrystalline materials and extends the dislocation to GB and interstitial lattice sites [85]. Susceptibility of hydrogen embrittlement in a material due to hydrogen diffusion and trapping behaviour. Nano-indentation is an effective evaluation method for hydrogen-diffused samples for polycrystalline materials. A single-crystal electrochemical permeation test is better for single-crystal materials [86,87].

6.2. *Embrittlement behaviour in electrochemical hydrogen charging*

Embrittlement was first identified by an acid-based environment (i.e., H_2SO_4, HCl), followed by the development of an electrochemical hydrogen testing method that has been investigated recently. Environmental impacts like (i) acidic, and (ii) alkaline environments directly impact the hydrogen attack on the surface. The electrochemical hydrogen charging, the amount of hydrogen penetration, absorption and diffusion are measured with the help of the electrochemical cell method proposed by Devanathan and Stachurski in 1962 [88]. In this electrochemical cell method, the hydrogen atoms are generated with the help of an electrochemical charging station. Within the electrolytic solution via cathodic charging, atomic hydrogen is generated electrochemically with a faster rate of hydrogen uptake than gaseous hydrogen charging. Here, compared to gaseous hydrogen charging, a complicated setup preparation is needed for electrochemical hydrogen charging. The setup needed for the experiment includes an electrolytic solution, electrolytic cell, power supply, working electrode, counter electrode, and reference electrode. Electrochemical hydrogen charging has a higher vulnerability to hydrogen attack on the surface compared to gaseous hydrogen charging. Especially near the metal surface [27]. Due to the reason of the higher amount of hydrogen flux, it immediately absorbed the hydrogen into the atmosphere or region. The influence of these acids over the surface of the material continuously reduces the toughness and ductility of the material, followed by the crystal structure, making it brittle. Over the research improvement, the pure acidic environment changes over electrical and chemical-based studies are developed [8]. For the electrochemical hydrogen charging over the material behaviour changes depend on pressure, temperature ranges, time period of exposure. The influence of temperature is an important reason for the hydrogen penetration level. For higher temperatures, the hydrogen penetration has a rigorous effect within a short period; however, in this penetration, it forms without an oxide layer to develop, followed by the crack formation [89]. Electrochemical hydrogen charging, the charging current density, is an important consideration for HE and mechanical properties evaluation. To increase the charging current density, the need to directly reflect alloys' ductility and strength is reduced [90]. In those days, the influence of Fe-based alloys better the retention for electrochemical industries due to low cost and availability, but higher chances of developing an embrittlement behaviour influenced by a hydrogen environment. Here, with Fe-based alloys exposed to electrochemical hydrogen charging, evaluation is based on the potential of hydrogen (pH). The influence of pH plays a crucial role in hydrogen. Based on this concept, the Fe-based alloy system to different from the pH range, like acidic: 1 M H_2SO_4 diluted with 0.25 g/l As_2O_3 and alkaline: 3.5 % of NaCl solutions with aqueous medium. The results reveal that compared to an alkaline medium, the acidic medium is more vulnerable to hydrogen attack [27].

6.3. *Comprehensive summarization of gaseous and electrochemical hydrogen charging*

In recent days, gaseous and electrochemical methods of hydrogen charging have widely evoked the hydrogen interaction behaviour in the materials. The source and purity of hydrogen play a considerable role in the development of effective hydrogen storage material. The source and purity will determine the method of hydrogen usage. In this regard, the gaseous hydrogen has high purity and a high uniform distribution of hydrogen through the samples. For the gaseous charging, hydrogen diffusivity depends on the pressure level inside the chamber. Followed by the metal surface to absorb the hydrogen. The electrochemical hydrogen charging involves the development of hydrogen ions from the electrolyte medium. Uniform hydrogen distribution is a challenging task. Hydrogen absorption based on electrochemical reactions [91].

Both gaseous and electrochemical hydrogen uptake depend on charging time, temperature and pressure medium in gaseous charging. Electrochemical hydrogen charging controls the hydrogen uptakes with the help of charging current density. Based on the application point of view, the industries and customers' needs are compactness, efficiency and safety. In this view, the gaseous hydrogen has high gravimetric energy density and high efficiency, an energy density of approximately 120–142 MJ kg^{-1} [48]. This high gravimetric energy density is particularly effective in reducing weight-carrying, making it highly efficient, and improving the passengers' handling capacity for the aviation industry. Based on this method of gaseous and electrochemical hydrogen, the effects on materials easily penetrate and dissolve into the grain and grain boundaries to alter the crystal structure, which develops an embrittlement failure. Hydrogen with high contact with the surface can easily penetrate directly and react with the material interface. Here, the hydrogen interaction with the material surface leads to a decisive embrittlement reaction. In this scenario, compared to gaseous hydrogen, the electrochemical hydrogen charging methods play a pivotal role because of the very fast hydrogen evolution reaction compared to the gaseous hydrogen environment [87,90]. The hydride formation is another important consideration for developing embrittlement failure in the materials at the time of hydrogenation. The hydrogen does not dissolve in the elemental interfacial bonding. An accumulation of hydrogen with the host metal elements with hydrides is formed, followed by hydrogen easily dissolving the elemental interface to prevent the hydride formation and enhance the resistance to HE. Higher hydride accumulation higher the chances of the material's crystal structure changing from ductile to brittle and leading to the embrittlement behaviour of the alloys. In some cases, the hydrides develop a surface oxide layer closer to the hydrogen atoms inside the materials [92]. The direct correlation between hydrogen desorption and mechanical property evaluation based on hydrogen content and hardness, evaluated by (i) TDS and (ii) Nanoindentation study, regarding this characterisation subjected to electrochemical and gaseous hydrogen charging, the method of electrochemical charging has subjected to high hydrogen content, but in electrochemical limitations, there are non-uniform hydrogen distribution levels to obtain higher material hardness, followed by gaseous charging, which has subjected to lower hydrogen content, followed by higher hydrogen uniformity, to better distribution to obtain less hardening values or materials that are subjected to softening. Finally, the authors conclude that the electrochemical and gaseous methods of materials' hardness and softness behaviour particularly depend on hydrogen contents and distribution levels [93].

7. Hydrogen-induced degradation mechanism based on mechanical properties

The hydrogen-induced effects expressed the (i) Hydrogen-Enhanced Decohesion (HEDE) and (ii) Hydrogen-Enhanced Localised Plasticity (HELP) mechanisms. The important parameters are the hydrogen concentration (electrochemical and gaseous), material fabrication methods, lattice defects, loading conditions, effects of hydrogen diffusion, cleavage stress intensity, initial crack size, and temperature [127]. The HEDE model is also called a brittleness-based model [128]. The HEDE mechanism model is followed by the materials, with the influence of hydrogen penetration into the alloy system, which affects the alloy's atomic bonding, followed by, to reflect a reduction in the alloy's interatomic bonding strength due to the material's loss of ductility. Due to the reduction of materials reducing the cohesive strength is reduced. However, the HEDE mechanism expresses the ductile-to-brittle transition followed by fracture-induced initiations. Followed by the material failure in the form of intergranular or phase boundary form, which is expressed as an HEDP mechanism [38].

The presence of hydrogen atom accumulation inside the grain boundary on the alloy system enhances the dislocation mobility, which enhances the leading to plastic deformation due to the reduction of the repulsive force, as expressed by the HELP mechanism. The HELP mechanism, also called the plasticity-based model, enhances plastic deformation and ignores brittle fracture. Encouraging the ductile fracture with a higher number of dimples to present on the fractured surface [47]. For the plasticity behaviour to promote the materials' softening and planar slip localisation of plastic flow [129]. For the alloys with better resistance to HE, the controllable dislocation is critical; it helps to reduce the crack initiation and propagation, which enhances the alloy's plasticity behaviour based on the HELP mechanism [130]. In recent days, HELP has enhanced the mechanical property development compared to the HEDE mechanism because of the alloys with controlled plasticity to prevent the hydrogen atom accumulation between the grain and grain boundaries and localised to cover the interfacial hydrogen accumulation [131].

Comparative study of HEDE and HELP mechanisms, the HELP mechanism mediated the HEDE model. Because of the mechanism with lower chances of HELP failures, to mitigate the HE for the alloy system. Alloying elements addition with Ni, Fe, Co, Mo, and V to improve the material toughness, and control the failure-induced cracking behaviour. The higher the hydrogen concentration, the more materials enhance brittleness and hardness.

8. Microstructure, mechanical, and hydrogen-related studies of additively manufactured HEAs

8.1. Microstructure properties of AM-HEAs

Inherently, to control the HE failures of the materials are two methods, particularly focused on extrinsic and intrinsic ways. Extrinsic methods focus on surface coating to control the hydrogen penetration level. Intrinsic focus on microstructure changes to control the HE failures. This part focuses on mitigating hydrogen embrittlement with the help of intrinsic-based microstructure development. The alloys with the microstructure change depend on the addition of alloying elements and their grain size, dislocation density of the printed materials, and phase structures, are decide the hydrogen embrittlement resistance properties. The influence of hydrogen and its property variations clearly illustrate the microstructural features. The various considerable features like atomic level hydrogen reaction, hydrogen-infused, permeation, transportation kinetics, and hydrogen trapping behaviour [94]. Compared to conventional manufacturing methods, the fabrication of the AM method involves the highest directional solidification with narrow melt pools and a high cooling rate. These characteristics are high resistance to HE failures. In AM, the heating and cooling rates are the most influential factors for microstructure stability [73]. In most cases, the development of AM components and their microstructure include different features (i) coarse and fine microstructure based on various slow and fast cooling behaviour, (ii) effects of bonding natures, which improves process setting, (iii) as-build components and its directional solidifications and its anisotropic microstructure because of its grains are elongated in build directions, (iv) solute trapping, metastable phases and other are influence factor for non-equilibrium microstructure development, (v) addition of various elements are combined to produce a new alloy system followed by the different compositions and melting behaviour the fast cooling in as-build components [95]. For AM, the heat treatment is an effective process for withstanding the high microstructural stability, particularly AM-HEAs components. Furthermore, this heat treatment effect obtains a high density and increases the printed parts' strength/hardness and toughness. Also, the effective heat treatment to directly increase the ultra-high strength, particularly yield and ultimate tensile strength, increases the ductility up to 20 % [77].

The prevalent defects identified in additive manufacturing components include (i) incomplete melting or un-melted powders resulting from inadequate laser or electron beam power, (ii) excessive fusion rates of alloying elements, (iii) unstable operating mode that can create keyhole defects, which contribute to increased porosity in the printed parts, (iv) development of internal or outside cracks is developed because of the time of metal printing and the laser source to provide insufficient energy as an input or higher energy to be utilised for printing, the energy difference develops stress that leads to developing cracks (v) delamination factors, (vi) different layer thickness, (vii) ejecting molten droplets [96].

Homogeneous distribution of metal powders in the AM process is an important consideration for various property improvements. In this way, inoculation treatment is one of the important methods for improving the homogeneity and refining the microstructure [97]. Recent studies based on columnar microstructure show the effect of high thermal shocks carried in columnar structures that lead to the development of intergranular hot cracking and cause mechanical failure. After the inoculation treatment, the columnar microstructure is converted into equiaxed grains. In most AM parts, the grain morphology is in the form of epitaxial columnar grains developed with a high thermal gradient (10^6 K/m approximately) [78]. During the solidification, the prevention of surface crack formation is an important consideration for AM. Because of the addition of different elements, they have different physical and chemical natures and different melting points; for that reason, the higher the influence of laser melting, the higher the chances for elemental segregation, making it easy to develop surface crack formation. From the microstructure point of view, the elimination of the surface crack control is an important consideration. During the laser beam melting, the controlled element solidification rate or partial solidification is better for avoiding surface crack development. The solidification rate of powders due to the influenced by laser heat, which increases the chances of developing surface crack formation [98]. The elemental segregation happens in particular materials, which are changed to cause the microstructural changes and initiate the different regions in the microstructure. Especially the formation of cellular or dendritic regions and interdendritic regions. This kind of region is formed due to the reason of various elements and their temperature differences, particularly solid-liquid interface differences, during the melting process. In general, the hydrogen atom accumulates in the crystal lattice, followed by weakening the ductility and strength of the material, based on conventional fabrication. However, the additive manufacturing of the microstructure in the form of a cellular structure enhances the ductility and strength of the materials. These are better ways to enhance the resistance to HE [99]. Based on this, different solidification structures depend on the G/R ratio, where G denotes the thermal gradient and R denotes the solidification growth rate. In alloys that reach the melting point, the higher-temperature elements cover the dendritic region, and the lower-temperature elements settle over the interdendritic region. Notably, this region has higher thermal stress and more chances to develop a surface crack [100]. Meanwhile, alloys with temperature-different thermal contraction and volumetric shrinkage are developed for the 3D-printed parts [98]. Alloys with higher thermal gradients with low growth rates express a high G/R ratio and develop a columnar grain. In contrast, alloys with low thermal gradients and high growth rates express a high G/R ratio and develop cellular-type grains. In the AM, special features are developed in terms of mechanical property development based on heat treatment of as-printed parts. The prevention of HE is directly influenced by microstructural modification, and for that, microstructural modification is done with the help of heat treatment. In this regard, the 3D-printed HEAs are recently emerging materials for resistance to HE, the HEAs of CoCrFrNiMn in SLM-printed parts. Due to the influence of heat treatment as an effective way to change the surface cell wall modification, the effects of heat treatment continuously increase the deformation twins and reduce the HE in 3D-printed parts [101,102]. The twin formation in the alloy system lowers susceptibility to HE and enhances the hydrogen-enhanced local plasticity [103]. The considerable role in the twin formation is to improve the surface strengthening and control of the materials' stacking fault behaviour and suppress the hydrogen embrittlement failures. The development of twinning layers to continuously increase the alloy strain hardening behaviour and enhance the ductility. Meanwhile, to control the hydrogen-induced fracture forever to mitigate the embrittlement-based failure [104]. The twin developed over the surface of CoCrFeMnNi-based HEAs in electrochemical charging. The effects of twin formation and their results evaluation based on nano-indentation test, reveal that without a hydrogen charged condition, there are no hardness differences from the surface to the core parts of the samples. Moreover, the hydrogen-charged samples with the influence of nano-twin structure have high surface hardness. From surface to core. For that reason, the effects of nano-twins have a higher energy density compared to the core region. Also, the twins develop a higher surface separation energy and lower hydrogen solubility to control the penetration of the hydrogen atoms into the surface. Fig. 3 shows the effects of twin formation on the surface morphology of tensile morphology in the core in hydrogen-charged conditions. (a) Without hydrogen charging, the samples represent the transition from the surface to the core, to represent them without twin effects higher number of dimples shows particular dimples in the form of the ductile form. (b) With a hydrogen supply, the dimples are changed from ductile into brittle form based on a different region. Compared to (c) and (f) without twin formation the fracture surface of the entire ductile dimples but the twin developed the influence of hydrogen, the effect of twins to restrict the hydrogen penetration of the brittle dimples in surface and ductile dimples in the core region represents the (g) and (h) images. The formation of twins impedes the dislocation and resistance to crack propagation. (d) and (e) the surface to the core of both regions developed a dimpled fracture without hydrogenated condition [103].

For the alloy's material behaviour and hydrogen-induced performance, decide on (i) hydrogen diffusion concentration and (ii) depth of hydrogen penetration into the materials, which represent the Slow Strain Rate Tensile (SSRT) test results [105]. The 3D-printed parts and their hydrogen susceptibility evaluation based on SSRT is a better way to reveal the impact of hydrogen embrittlement and its degradation under hydrogen exposure conditions. For a hydrogen environment mostly preferred the SSRT test. The effective test rate of SSRT is $1\text{x}10^{-4}$ to 10^{-2} S^{-1}. For that slow strain rate to allow high hydrogen to dissolve into the samples, particularly to evaluate the microstructure features like grain boundaries and hydrogen-induced traps [88]. The materials with maintain the same elongation behaviour after the hydrogen charging have lower susceptibility to hydrogen embrittlement. This reduction in the elongation loss was measured (δ_{loss}) with the help of equation (1).

$$\delta_{\text{loss}} = \frac{\varepsilon 0 - \varepsilon H}{\varepsilon 0}\, x100\ \% \tag{x}$$

Here, δ_{loss} = elongation loss, ε_0 = strain to failure in a material without hydrogen, and ε_{H} = strain to failure in a material with hydrogen-induced.

Equation (x) represents that the higher the percentage of elongation loss (δ_{loss}), the lower the strain to failure within the material without hydrogenated condition (ε_0), and the higher the percentage of elongation loss, the higher the strain to failure within the material with hydrogenated condition (ε_{H}).

As reported earlier, the influence of heat treatment on metal 3D printing significantly enhances resistance to HE failures and reduces susceptibility to hydrogen-induced cracks. In this regard, pure Ni-based HEAs were developed for SLM-3D printing and evaluated for hydrogen-induced susceptibility under both as-printed and heat-treated conditions. Fig. 4 illustrates the stress-strain behaviour under different conditions: (i) as-printed with hydrogenation, (ii) as-printed without hydrogenation, (iii) as-printed and heat-treated with hydrogenation, and (iv) as-printed and heat-treated without hydrogenation. The non-hydrogenated samples exhibited a ductility loss of 82.8 %, while the hydrogenated heat-treated samples showed a ductility loss of 45.9 %. The influence of heat treatment on controlling ductility loss is crucial for enhancing the alloys' structural safety, which helps prevent HE, improve

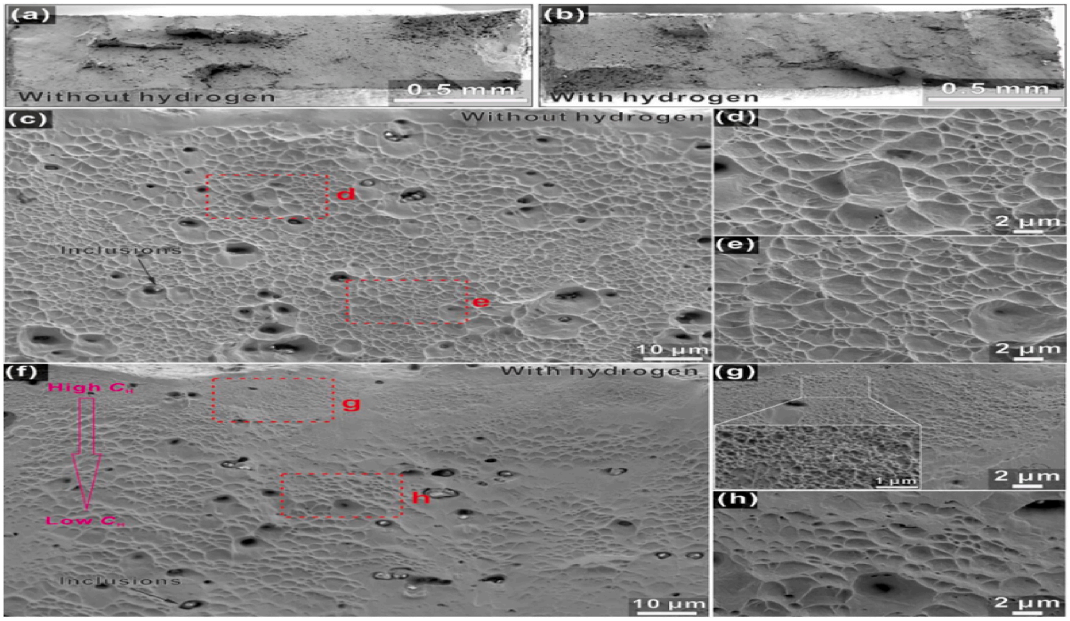

Fig. 3. Influence of (a) with and (b) without hydrogen supply to the CoCrFeNiMn-based HEAs. (c) Without hydrogen from the ductile-dimple fracture, (d–e) High magnified dimple images, (f) brittle and ductile dimple fracture up to particular limits, (g) high magnified brittle and (h) high magnified core ductile fracture representation [103]. Reusing content in a journal or magazine requires permission from the Copyright Clearance Center (CCC).

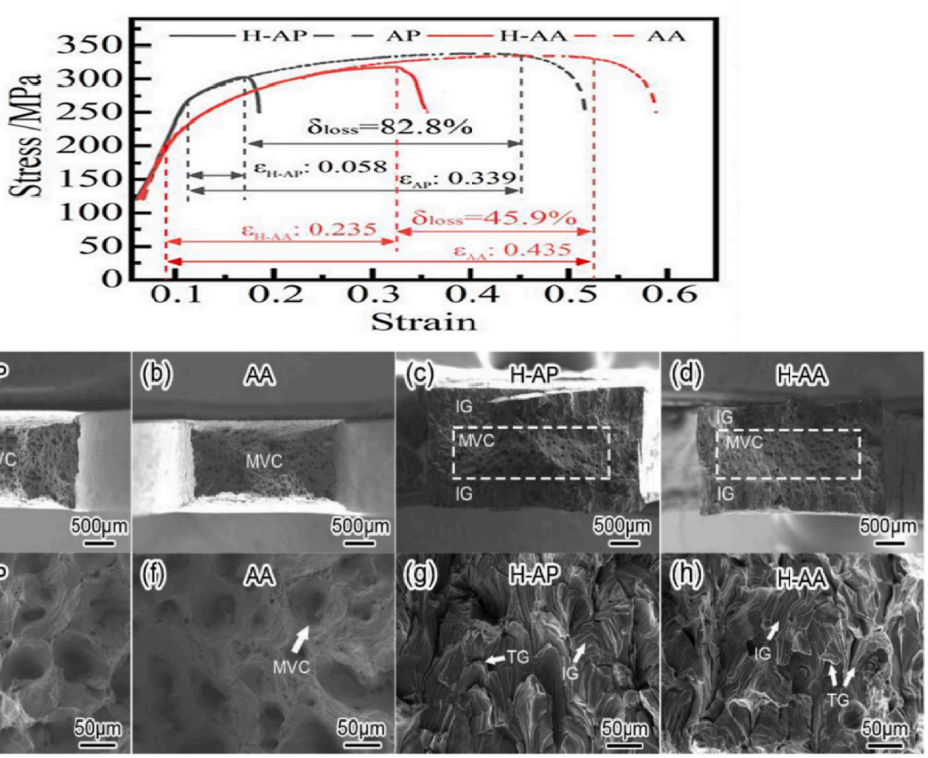

Fig. 4. Stress-strain behaviour under different conditions of hydrogen and without hydrogen charging conditions. 4a, 4b represent the without hydrogen supply of as-printed (AP) and as-annealed (AA) samples for low magnification SEM analysis. 4c and 4d represent the with hydrogen supply of as-printed (H-AP) and as-annealed (H-AA) for low magnification. 4e and 4f to identify the Micro Void Coalescence (MVC) fracture without hydrogen supply conditions of the high magnification SEM analysis. 4g and 4h to identify the MVC fracture of the hydrogenated samples with high magnification [101]. Reusing content in a journal or magazine requires permission from the Copyright Clearance Center (CCC).

fatigue resistance, and control fracture initiation. The SSRT samples and their fractography reveal that the (a,e and b,f) as-printed without heat treatment, and the as-printed with heat treatment show that the heat-treated samples reduce micro-void coalescence fractures. In the same conditions as hydrogenated samples (c,g and d,h), the influence of induced hydrogen changes the fracture mode from ductile to brittle, with a higher amount of trans granular fracture observed in heat-treated samples. The increased presence of *trans*-granular and intergranular fractures, intergranular material tends to fail suddenly or catastrophically, whereas *trans*-granular material failure occurs progressively [101].

Fig. 5 also illustrate the same conditions mentioned above: the influence of HT does not change the grain size (a and e) or grain distribution (b and f); instead of reducing the misorientation, it represents (c and g) the Kernel Average Misorientation map and Geometrically Necessary Dislocations (GNDs) (d and h). The GNDs of as-printed and as-annealed samples are 1.33×10^{14} m^{-2} and 1.30×10^{14} m^{-2} [56]. However, the SLM-based CoCrFeNiTi HEAs, when compared to Inconel 718, based on alloy heat-treatment and after testing for embrittlement, the heat-treated HEAs are more resistant to HE then Inconel 718. [24]. The elemental variation and heat-treatment effects of CoCrFeNiTiX-based MPEAs fabricated using AM technology involve alloys with reduced Ti element additions, which control and reduce HE susceptibility.

Adding Ti elements increases the likelihood of precipitate formation during alloy development, influenced by temperature. The Ti precipitate settles over the grain boundary, leading to an increase in the alloy's strength and hardness, which directly increases HE susceptibility. Furthermore, heat treatment of the same alloys under different conditions, such as (i) Solution-heat Treatment (SHT) and (ii) Ageing-heat Treatment (AHT), also prevents precipitation formation at the grain boundaries. This type of precipitation at the grain boundaries causes a high localised hydrogen atom concentration, which develops or enhances HE. Fig. 6 illustrates the effects of precipitation formation on hydrogen de-trapping sites. Compared to hydrogen accumulation, dislocation regions and grain boundary region precipitation exhibit a higher de-trapping behaviour because the precipitation acts as a barrier to hydrogen movement, settling over a prolonged period and leading to significant HE failures, especially in materials with a BCC structure. Specifically, the first three regions (dislocation, grain boundary, and precipitation with a coherent interface) are under reversible hydrogen trapping; in these regions, the trapping energy is below 50 kJ/mol, indicating that these materials have lower HE susceptibility. The fourth region involves precipitation with a semi-coherent interface, which is associated with irreversible hydrogen trapping behaviour, resulting in higher susceptibility to HE. Dislocation and grain boundary trapping behaviours are common lattice defects. In comparison to lattice defects, precipitation with a semi-coherent interface leads to increased HE failures [106].

The results represent lower Ti addition to the CoCrFeNi alloys high resistance to prevent the HE failures, for the lower Ti addition samples HT via SHT. The same alloy was further HT to AHT conditions for 1, 2, 4 and 8 h, to increase the AHT-HT, the alloys undergo an increase the hardness with less precipitate and better resistance to HT [41]. The comparative work of AlCoCrFeNi-based HEAs is fabricated for different technologies like SLM and LENS, among them, the development of SLM-based HEAs is characterised by high resistance to HE due to the reason of size and shape of the AlCoCrFeNi HEAs morphology and B2 phase stability. Fig. 7 illustrates the SLM-based AlCoCrFeNi HEAs (a) to (b) cross-section view of hydrogen-induced tensile test samples from different magnifications. (c) visibility of slip-bands formation with high magnification, to show the visible crack formation. For that interesting note, in the slip-band formation area, no cracks are formed, because in that particular region, the FCC phase is present. EBSD analysis results of (d) to (e) grain boundary variation with the influence of the hydrogen-induced crack. The SLM-based HEAs performance is evaluated after the hydrogen charging of the tensile test, a large number of intergranular and *trans*-granular cracks are developed from the phase boundary of b2 and FCC phase. (f) KAM mapping with grain boundary features, along with representing the GNDs. Followed by (g) to (i) electron channelling contrast (ECC) images to show two regions of crack development: (i) FCC and (ii) B2 regions. The cracks are propagated in a discontinuous manner in both the FCC and B2 regions, but in most cases, near the B2 regions, they initiate the crack failure [77].

8.2. *Mechanical properties of AM-HEAs*

Fabrication methods are one of the influencing factors in achieving better mechanical properties. In this way, the AM-HEAs are the best possible outcome compared to conventionally fabricated HEAs for the same alloy compositions, and also, the AM-HEAs can achieve a better strength-to-ductility trade-off. Achieving better strength/hardness without compromising ductility is a special consideration of AM-HEAs [107]. But in AM, drawbacks are the anisotropic properties. Alloy development in PBF methods involves the powder in the form of finer particles, and stimulates the fast-cooling rate of as-printed components and developing a high tensile strength but lower ductility [108]. The microstructure is one of the factors for better mechanical property achievement in any alloy system, but different microstructure is developed in different AM methods in the same alloy system, which results in different properties for the same composition or alloy system. Before that, various properties and various environments led to the mechanical property deviations. Most of the properties are considered hydrogen-influenced, like strength, hardness, tensile testing, yield strength, fracture toughness, elongation to material failure, fatigue life span of the materials, crack initiation, and propagation. Followed by

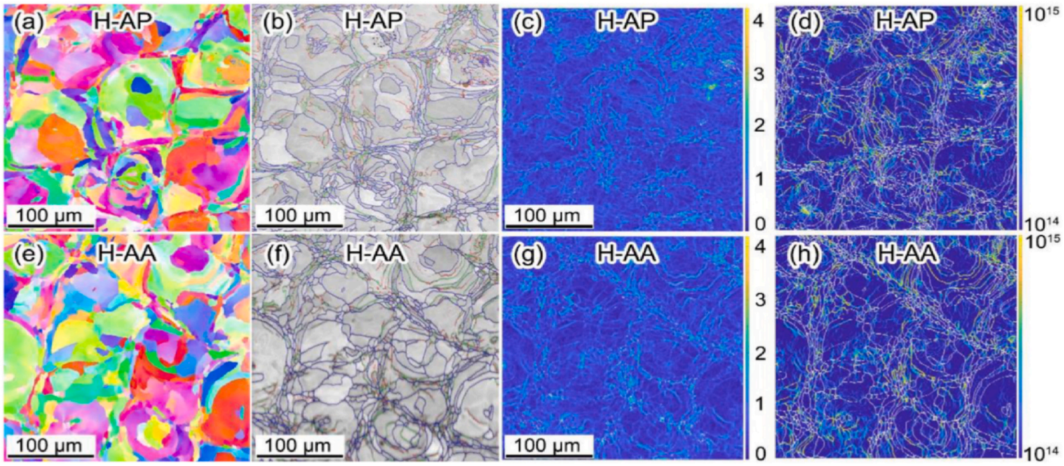

Fig. 5. EBSD results of 5a and 5e for hydrogen-induced AP and AA samples and their grain orientation distribution maps. 5b and 5f for H-AP and H-AA for grain boundary distribution maps. 5c and 5g for H-AP and H-AA for kernel average misorientation map (KAM) distribution maps. 5d and 5h for geometrically necessary dislocations (GNDs) maps [101]. Reusing content in a journal or magazine requires permission from the CCC.

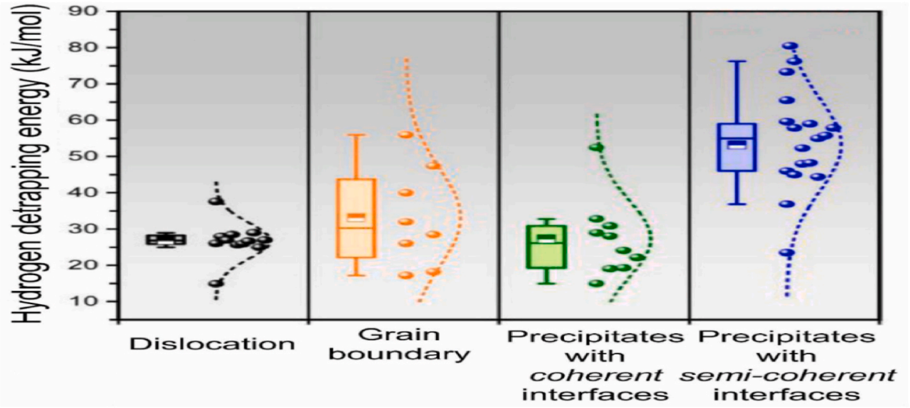

Fig. 6. Hydrogen de-trapping behaviour in various features of BCC structured materials [106]. Open access licensed under CC BY 4.0.

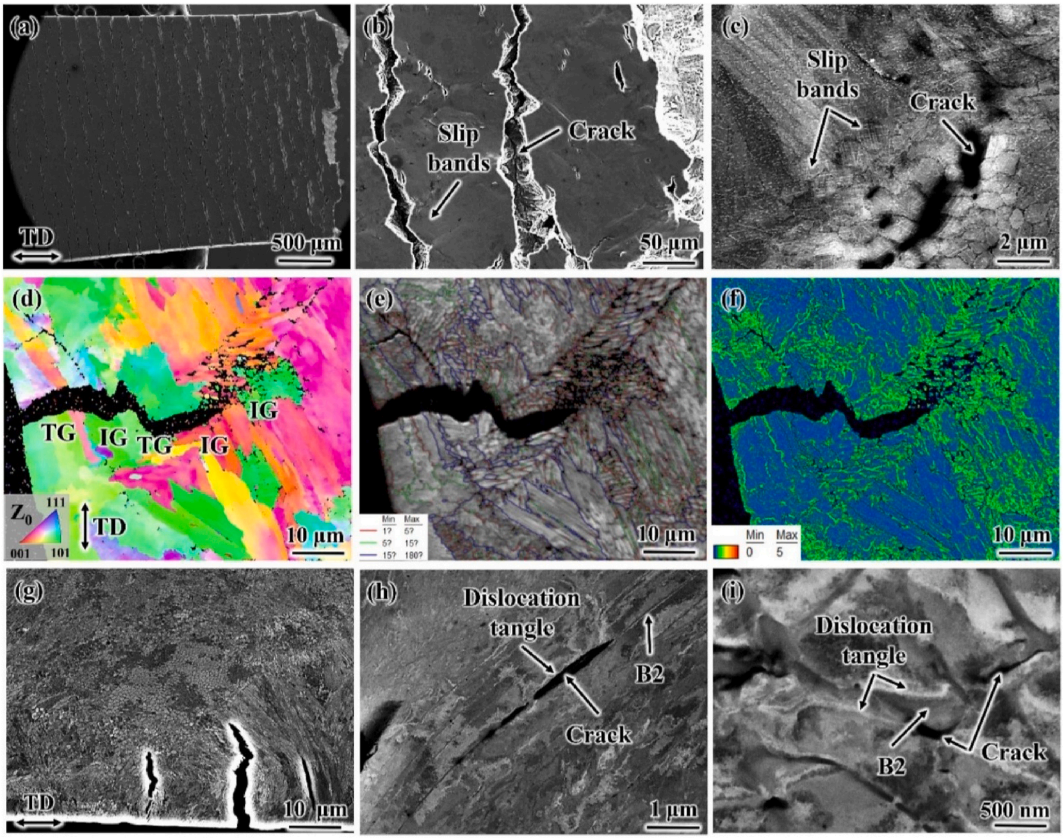

Fig. 7. Tensile test results of hydrogen-induced AlCoCrFeNi-based HEAs, (a) to (c) represent low to high magnified ECC images, (d) represents the EBSD mapping of Grain boundary cracks with IPF mapping; (g) to (i) cross-section view of ECC images [77]. Reusing content in a journal or magazine requires permission from the CCC.

various testing environments (i) In-situ and (ii) Ex-situ. The performance evaluation of the materials is based on the hydrogen environment; the in-situ hydrogen charge testing results are highly accurate compared to ex-situ type testing because of the in-situ methods to evaluate the material performance in real-time working conditions, followed by the loss of hydrogen being less for in-situ hydrogen charging and the in-situ type the hydrogen in a closed environment and the hydrogen distribution to the sample is uniform or saturated the hydrogen through the materials.

In conventionally fabricated HEAs, properties like ultimate tensile strength, yield strength, and percentage of elongation are calculated in the X-axis for characterisation purposes. Still, in AM, the Y-axis represses the above characterisation purposes because AM is anisotropic are more scattered in final properties [109,110]. The HEAs of CoCrFeMnNi SLM-based comparative study of as-printed with and without hydrogen charging for non-heat-treated conditions, and as-printed with and without hydrogen charging for heat-treated conditions. For non-heat-treated conditions, the alloy with the yield (σ_y) and Ultimate Tensile Strength (UTS) and elongation (%) of 546, 644, and 17.4 % with hydrogen charging, followed by heat-treated 536,628 and 20.7 %. The influence of HT in 3D-printed parts has to reduce the σ_y and UTS, moreover, to increase the total elongation limits. Followed by heat treatment, the HEAs with the σ_y, UTS, and elongation have 427, 655, and 31 %, without hydrogen conditions 413, 642, and 26.5 %. The influence of HT in the same alloys increases the σ_y, UTS, and elongation limit. For that results reveal that heat treatment is an effective way to improve the mechanical properties, particularly the elongation limit Because the HE occurs due to the reason alloys reduce the ductility, to continuously increase the brittleness, here the total elongation improves with HT, and with hydrogen charging the better the way to highly resist the HE in 3D printed parts [102]. Based on this report also revealed that a better elongation property is achieved in 3D-printed HEAs compared to SS304 for hydrogen-based environments [111].

8.3. Hydrogen diffusion

The diffusion mechanism describes the movement of hydrogen atoms within materials, which can occur through gaseous or liquid hydrogen charging methods. The effects of diffusion depend on various factors, including the microstructure of alloys, the selection and segregation of alloying elements, surface texture, temperature variations, grain size, dislocation density, precipitation, reversible and irreversible hydrogen traps, and unexpected inclusions in alloy development and manufacturing conditions. The factors, like microstructure variations, depend on the physical and chemical absorption of hydrogen. Addition of alloying elements like Ti, Ni, Cr and Mo to reduce the hydrogen diffusivity. Surface texture modification based on additive manufacturing differentiates the as-print direction (X and Y direction) and the as-built direction (Z direction). The as-print directions have higher hydrogen diffusion [112]. The effects of higher dislocation density depend on hydrogen diffusivity. Alloys with higher dislocation density, lower diffusivity occur, followed by lower dislocation density alloys with higher diffusivity. Those behaviours depend on the deformation behaviour of the alloys [113]. Because of the alloys with high or lower deformation behaviour, similar to an increase or decrease the diffusivity behaviour. The hydrogen permeation test is an effective method for evaluating hydrogen diffusion behaviour in alloys. Devanathan and Stachurski initially proposed hydrogen permeation methods based on electrochemical hydrogen charging techniques. Typically, hydrogen diffusion behaviour is used to assess hydrogen transportation systems, such as pipelines for transporting hydrogen. Hydrogen atoms ingress into the alloy and occupy the crystal structure and interstitial sites, such as the O-site (Octahedral) and T-site (Tetrahedral). The sites that hydrogen atoms occupy depend on the sizes of the O and T site radii, i.e., (ri/rh), where ri = interstitial site radius and rh = host lattice radius. Generally, the crystal structure of FCC and HCP occupies the O-sites, while BCC occupies the BCC structure. Compared to T and O sites, which demonstrate higher hydrogen diffusivity, this is observed due to a lower atomic packing density and a lower hydrogen barrier for migration [114].

8.4. Hydrogen trapping

Compared to various microstructural features, hydrogen-induced trapping is a better way to prevent HE failures in the materials, depending on their reversible and irreversible nature. The higher hydrogen trapping behaviour reflects to control of the hydrogen diffusion, accumulation and embrittlement reaction over the materials [115]. Compared to hydrogen diffusion, hydrogen trapping takes a longer period to release the hydrogen from the lattices, so the trapping behaviour is used to control the hydrogen diffusion movements [116]. The high trapping behaviour is used to control the hydrogen atom movements, followed by slower dislocation motion. This hydrogen trapping is one of the thermal activation processes. This behaviour is used to mitigate the HE because the slower the hydrogen atom movement lower the embrittlement activities and the lower the hydrogen trapping, followed by avoiding brittle failure [117]. To better the way to reduce the susceptibility of HE failure, hydrogen trapping is better, because the accumulation of hydrogen in the lattice space controls the trapping that prevents its diffusion sites. In this trapping, consider the reversible and irreversible based on the development of binding energy. The alloy binding energy $\Delta G < 35$ kJ/mol for the reversible hydrogen trap and $\Delta G > 35$ kJ/mol for irreversible hydrogen trapping [114]. The reversible trapping of the already accumulated hydrogen to release in a very fast manner is mostly considered in dislocations and grain boundaries. Followed by irreversible hydrogen trapping, hydrogen accumulation is permanent, or it takes a longer period for diffusion. This permanent hydrogen accumulation develops permanent hydrogen-induced failures like embrittlement, and deeper voids and controls the ductility. Effects of grain size variation are also an important consideration for hydrogen trapping behaviour. Compared to coarse-grain, the fine grains exhibit higher hydrogen trapping behaviour due to an increase in the grain boundary areas. However, the reversible hydrogen trapping is largely associated with the grain boundary; alloys with fine grains provide high trapping sites, followed by enhanced hydrogen trapping [118]. The recent results reveal that fine grains with lower hydrogen atom mobility and reversible hydrogen trapping occur. Particularly, the reversible hydrogen trapping is considered at the lattice sites, such as grain boundaries, dislocations, and vacancies. The alloys with the size of the grains and area of the grain boundaries play an important role in hydrogen trapping and diffusion behaviour.

In this trapping of hydrogen followed by principles (i) activation energy to control the HE in a lattice site (E_d), (ii) activation energy to control the HE in a trapping site (E_s), (iii) binding energy of hydrogen in a trapping site (E_b) and (iv) de-trapping energy of hydrogen needs to trap the hydrogen in the lattice site (E_a) [106]. Fig. 8 shows the schematic view of the energy profile in the lattice and trapping site. Here, the E_a and E_b denote the energies of the various hydrogen-trapping sites. The E_d and E_s have atomic structure energy misfits concerning the lattice site. The energy sites of E_a denote the reversibility of the hydrogen trap; it evaluates $-E_a$ more than 50 kJ/mol. The influence of hydrogen trapping is related to dislocation motion; the trapping energy is lower than the dislocation and the dislocation motion carry the hydrogen diffusion. For that reason, the mobile trap (dislocation) is increased.

At the time of hydrogen trapping, either the hydrogen in the form of a hydrogen source or hydrogen sinks [119]. Hydrogen diffusivity is an important consideration for hydrogen trapping behaviour. The FCC materials have higher trapping sites and lower E_d than BCC. The lattice site (E_d) energy of FCC is higher (44 kJ/mol) compared to BCC (4.5–5.5 kJ/mol), based on iron [106]. This hydrogen trapping involves not only crystal lattices, but they are also forms in various regions of the materials, like grain boundaries, dislocations near the cell walls, twins, vacancies, stacking faults, and various strain field regions, which is illustrated in Fig. 9. Also, this figure represents the trapping behaviour, particularly in various regions like nano, meso and micro regions, depending on alloying element addition. Compared to nano and meso regions, highly effective trapping is involved in the micro regions.

8.4.1. Features of hydrogen trapping

The performance of hydrogen trapping is based on several features, including grain boundaries, dislocations, vacancies, and second-phase interfaces [120]. The very small hydrogen atoms move quickly and diffuse rapidly, particularly in the BCC structure. The faster movement of hydrogen atoms continuously reduces the development of mechanical properties, specifically in stress-strain behaviour. This is represented by

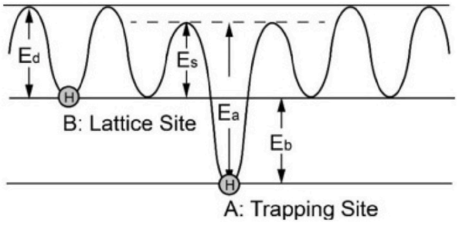

Fig. 8. Energy distribution schematic view in the lattice and trapping site [106]. Creative Commons CC-BY 4.0. This permits unrestricted use.

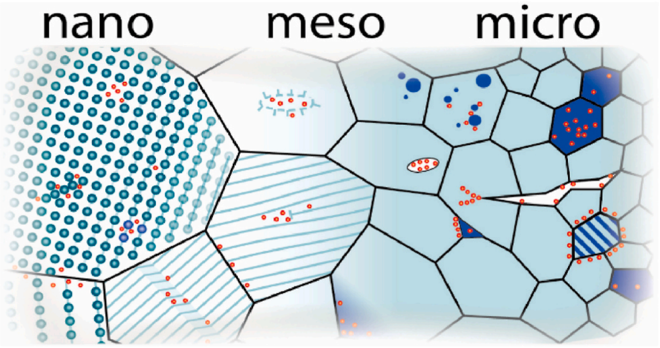

Fig. 9. Comparative illustration for hydrogen trapping behaviour for nano, meso and micro regions features [106]. Open access licensed under CC BY 4.0.

slower stress-strain measurements, which visualise the fracture mode. This phenomenon significantly affects hydrogen's tendency to cause brittle fractures, while also enhancing resistance to hydrogen, which exhibits ductile characteristics. For HEAs with lower binding energy, they develop dislocations. The dislocations-rich regions typically develop a weak hydrogen trapping behaviour, making the material more susceptible to HE failures. The influence of hydrogen-induced defects is based on diffusion kinetics; the faster the diffusion, the more unfavourable for resistance to HE. For the FCC structure, austenitic stainless steel is less effective in diffusion kinetics [121]. For that, hydrogen diffusivity in metallic alloys depends on crystal structure, various temperatures, hydrogen concentration, development of microstructure, working environment, dislocation, and trapping behaviour. In recent days influence of a small percentage of nitrogen induced in hydrogen environments has been used to control the failures. In the nitrogen over the hydrogen environment to control the alleviated mechanical property degradation, the electrochemical hydrogen charging method of hydrogen exposure to the sample with 0.1 wt% to 0.3 wt%, to increase the nitrogen content to control the HE failure for the hydrogen environment. For that reason, the influence of nitrogen is to control or decrease the hydrogen diffusivity and better the austenitic stabiliser at the time of Ni element addition and improve the corrosion resistance [122]. Following the nitrogen environment, the hydrogen behaves to increase the hydrogen solubility, for the high solubility of hydrogen postpones the accumulation level inside the materials, for that reason, to control the embrittlement behaviour [123]. However, the equiatomic and non-equiatomic-based HEAs, $Fe_{20}Co_{20}Cr_{20}Ni_{20}Mn_{20}$ and $Fe_{22}Co_6Cr_2Ni_{30}Mn_{40}$, for variation of the Cr element and the influence of hydrogen diffusion and trapping behaviour. For that reason, the Cr element exhibits strong solid-solution-forming behaviour and interacts more effectively with hydrogen, as increasing the Cr content from 2 % to 20 % (from non-equiatomic to equiatomic) slows the hydrogen diffusivity and enhances resistance to hydrogen embrittlement failures. Lowering the hydrogen diffusivity is a better way to prevent the HE in HEAs [124]. As mentioned earlier, due to the less diffusivity behaviour of austenitic stainless steels are used nowadays for most hydrogen storage applications, but compared to SS, the HEAs have very low diffusivity, achieved with a very small percentage of ductility loss before and after hydrogen exposure [103]. The diffusivity limit of BCC ferritic steels is 10^{-9} m^2/s, and FCC austenitic steels are 10^{-16} m^2/s for room temperature conditions [125]. Especially the precipitation evoked by the hydrogen-trapping site [126], meanwhile, the nano-precipitation settled over the grain boundaries, followed by controlling the dislocation motion because of the precipitate-like hard-BCC crystal structure.

Both hydrogen diffusion and trapping are highly correlated based on the alloy's microstructural features, such as temperature variations, grain size, dislocation density, precipitation, reversible and irreversible hydrogen traps. The hydrogen diffusion depends on movements of hydrogen atoms, which depend on microstructural features. The hydrogen trapping influences the influence of diffusion, and the hydrogen atoms accumulate with a reversible or irreversible nature the alloys' performance to change.

9. Summary and outlook

This work discusses the current state of research on developing materials for hydrogen transportation and storage using additive-manufactured high-entropy alloys concepts, focusing on gaseous and electrochemical hydrogen charging conditions. In particular, the additive-manufactured powder bed fusion (selective laser melting) and direct energy deposition-based material development studies are examined concerning hydrogen embrittlement concepts. Recent research worldwide emphasises the development of environmentally sustainable renewable energy sources as alternatives to conventional fossil fuels. In this context, hydrogen is the most suitable option for a renewable energy resource. Accordingly, materials science research aims to develop efficient energy storage devices for hydrogen storage applications. The challenge of developing an effective hydrogen storage device arises from hydrogen's potential to cause embrittlement failure. This failure, occurring in a hydrogen environment so is referred to as hydrogen embrittlement. Recent investigations into controlling HE failure based on high-entropy alloy concepts suggest that HEAs demonstrate superior performance in hydrogen-related research. Because nowadays using ferrous-based SS316L and SS304 materials are preferred for hydrogen transportation and storage. However, recent results indicate that HEAs exhibit higher resistance to HE failures and are more desirable for lower chemical attack under both gaseous and electrochemical hydrogen charging conditions. Compared to SS 316L and 304 alloys. For these reasons, the key insights are as follows:

Hume-Rothery Rules are the foundation for HEAs development. The flexibility in the selection of alloying elements presents significant advantages for discovering novel materials today. According to this rule, the core effects of HEAs enhance material performance. Specifically, high entropy effects increase the alloys' entropy level and thermodynamic stability, thereby improving the solid-solution behaviour of the alloys. Sluggish diffusion effects enhance the kinetic action of alloying elements and contribute to better homogenization of the alloy composition. Regarding lattice distortion effects, atomic size differences are crucial for the formation of simple solid solutions and enhance the balance of strength and ductility in the alloys. However, limitations arise from atomic size differences that can lead to elemental segregation during the alloy fabrication process; thus, leveraging these effects is essential to control elemental segregation and enhance the structural stability of the alloys. The cocktail effects generate unexpected phase or microstructural synergies. Recently, advanced technologies like additive manufacturing have been implemented based on these advantages. Recent research strongly suggests that parts produced via additive manufacturing exhibit significantly higher resistance to hydrogen embrittlement (HE) compared to those made through conventional methods. The findings indicate that resistance to HE in materials is influenced by hydrogen diffusion and trapping behaviour. The greater the hydrogen trapping, the better the resistance to HE, resulting in less chemical attack due to hydrogen influence. Trapping is dependent on both thermodynamic, element selection and environmental factors. Thermodynamic behaviour influences alloy phase stability, distinguishing between reversible and irreversible hydrogen trapping. Alloys with high phase stability allow for reversible trapping, whereas those with low phase stability experience irreversible hydrogen trapping. The significance of irreversible hydrogen trapping in materials greatly impacts embrittlement behaviour. Environmental factors, including pressure, temperature, and hydrogen content/concentration, further influence hydrogen trapping behaviour. HEAs are regulated based on physical parameters, particularly valence electron concentration (VEC) and atomic size differences, in light of these hydrogen-induced failures. Considering these physical parameters can help elucidate the strengthening mechanisms of HEAs, with VEC <6.87 for BCC and VEC ≥8 for FCC crystal structures. The FCC structure is preferable for hydrogen storage applications due to its moderate strength and high ductility. Additionally, the difference in atomic size contributes to the strengthening effects through two models: (i) Fleischer's model, which suggests dilution of the concentration of HEAs results in increased yield strength of the alloy; and (ii) Labusch's model, which indicates that atomic size differences provide significant solid solution strengthening. For additive manufacturing, the **alloys with microstructural stability depend on fabrication methods. Specifically, the influence of thermal gradient and continuous cooling effects acts to develop an alloy with a non-equilibrium microstructure to promote. In this consideration, the AM has high directional solidification and a high cooling rate to achieve fine microstructure development and resistance to HE failures and improve the mechanical property development. For AM components with as-built conditions, the materials with heat treatment have the most effective way to control the HE failures. Compared to other microstructures, the cellular structure has an effective HE resistance behaviour. Further,** compared to conventional manufacturing, AM components have greater deformation twins. The favourable effects of twins in hydrogen environments are used to control the alloys' deformation behaviour, which reduces and mitigates HE. Moreover, the twins act as barriers to dislocation motion while simultaneously reducing dislocation motion to balance the strength-ductility relationship. The Mn, Cr, Co, and Fe have been reported to enhance twin formation in the development of HEAs. The above-mentioned results may vary based on various environmental factors, testing conditions, and methods of characterisation. Particularly, the hydrogen testing results differ from in-situ and ex-situ testing conditions. Among them, in-situ hydrogen charging and testing results are more efficient with the influence of hydrogen-induced effects. The losses of hydrogen atoms present are less for in situ. For highly effective homogeneous distribution of hydrogen in the in-situ hydrogen charging. For ex-situ hydrogen charging, the small atoms of hydrogen are distributed in a nonhomogeneous manner, and losses of hydrogen atoms present are very high for ex-situ hydrogen charging.

Nomenclature section:

AHT	Aging-Heat Treatment
AM	Additive Manufacturing
ANST	Australian National Survey Testing
BCC	Body-Centered Cubic
BDT	Build Direction Time
CCC	Copyright Clearance Center
CF	Corrosion Fatigue
COP	Complex Ordered Phase
DED	Direct Energy Deposition
DLF	Directed Light Fabrication
DMF	Direct Metal Deposition
DSS	Disordered Solid Solution
EBM	Electron Beam Melting
ECC	Electron Channelling Contrast
EIC	Environmentally Induced Cracking
EPBF	Electron Beam Powder Bed Fusion
FCC	Face-Centered Cubic
GNDs	Geometrically Necessary Dislocations
HCP	Hexagonal-Close packed
HE	Hydrogen Embrittlement
HEAs	High Entropy Alloys
HEAC	Hydrogen Environment-Assisted Cracking
HEDE	Hydrogen-Enhanced Decohesion
HELP	Hydrogen-Enhanced Localised Plasticity
HIC	Hydrogen-Induced Cracking
IHAC	Internal Hydrogen-Assisted Cracking
KAM	Kernel Average Misorientation Map
LEAs	Low-Entropy Alloys
LDMF	Laser Direct Metal Forming
LENS	Laser Engineered Net Shaping
LME	Liquid Metal Embrittlement
LPBE	Laser Powder Bed Fusion
MEAs	Medium Entropy Alloy
MPEAs	Multi-Principal Element Alloy System
MJF	Multi-Jet Fusion
MVC	Micro Void Coalescence
PBF	Powder-Bed Fusion
SCC	Stress Corrosion Cracking
SDP	Simple Disordered Phase
SLM	Selective Laser Melting
SLS	Selective Laser Sintering
SOP	Simple Ordered Phase
SS	Stainless-Steel
SHT	Solution Heat Treatment
SSRT	Slow Strain Rate Tensile
TDS	Thermal Desorption Spectroscopy
THP	Thermo-Hydrogen Process
UTS	Ultimate Tensile Strength
VEC	Valence Electron Concentration

Symbols and their meanings:

Symbols	Meaning
$\Delta Smix$	Entropy of mixing
$\Delta Hmix$	Enthalpy of mixing
ΔG	Gibbs free energy
$\Delta\chi$	Electronegativity difference
$\Delta\delta$	Atomic size difference
Ω	Combining effects
Λ	Geometrical parameter
δ_{loss}	Elongation loss
E_d	Activation energy on the lattice site
E_s	Activation energy on the trapping site
E_b	Binding energy on the trapping site
E_a	Binding energy on the de-trapping site

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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