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Stress corrosion cracking of high entropy alloys: Mechanism, microstructure and performance

ABSTRACT

Stress corrosion cracking (SCC) presents a significant threat to structural components subjected to the synergistic combination of tensile stress and corrosive environments. While extensively studied in conventional alloys, the SCC behaviour of the emerging class of high-entropy alloys (HEAs) remains a frontier of research. This review synthesizes current knowledge to bridge this gap, systematically examining how the unique attributes of HEAs governed by their core effects of high entropy, severe lattice distortion, sluggish diffusion, and cocktail effect dictate their SCC response. The fundamental mechanisms of anodic dissolution and hydrogen embrittlement were analysed within the context of HEA's complex microstructures and compositional landscapes. Furthermore, the review critically assesses the influential roles of temperature and microstructural evolution on passive film stability and crack initiation. By integrating findings from key HEA systems, it is demonstrated that the core effects can be strategically leveraged to enhance SCC resistance by stabilizing protective films and impeding crack-propagation kinetics. However, this inherent complexity can also introduce vulnerabilities like micro-galvanic corrosion if improperly managed. This work concludes that a fundamental understanding of the interplay between electrochemistry, mechanics, and HEA thermodynamics is paramount for advancing the application of these materials in demanding environments like nuclear power, aerospace, and marine engineering.

Keywords: *stress corrosion cracking, high entropy alloys, core effects, passive film stability, anodic dissolution, hydrogen embrittlement*

1. INTRODUCTION

Stress-corrosion cracking (SCC) is the development of cracks caused by the combined influence of a non-cyclic tensile stress and a reactive environment [1]. SCC often induces rapid fracture of the component when the crack length, developed under the influence of stress and environment, exceeds a critical threshold. Furthermore, SCC poses a serious risk to any component due to the difficulties in detecting the cracks. Additionally, cracks can spread quickly and result in catastrophic failure of any component if they nucleate and reach a critical size [2]. However, to address SCC, several experimental methods have been established.

The slow strain rate tensile (SSRT) test, constant load tensile test, and fracture mechanics-based test (which mostly uses compact tension test specimens) are the commonly recognized techniques [3]. Researchers have documented the first occurrence of SCC in the 19th century, when brass cartridge casings were exposed to ammonia [4]. However, following SCC's emergence, several researchers have observed and investigated its behaviour in a variety of materials. SCC failures include boiler explosions, transmission pipe ruptures, and bridge collapses. Additionally, the "Silver Bridge" connecting Ohio and West Virginia collapsed in 1967 due to SCC, as investigated [5]. Therefore, to avoid the recurrence of such problems, researchers have conducted extensive research to better understand the SCC mechanism in various metals and alloys.

For several decades, conventional alloys (which consist of one principal alloying element with the remaining elements added proportionately to attain the necessary characteristics) were the

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main focus of metallurgical research due to their widespread industrial and economic significance. Consequently, extensive investigations have been conducted on the stress corrosion cracking (SCC) behaviour of these alloys to further understand their failure mechanisms. Based on the extensive SCC research conducted across a wide range of alloy systems, several theories have been proposed to explain the underlying mechanisms of SCC. The three main theories that describe the different but occasionally related mechanisms that regulate stress corrosion failure are anodic dissolution-induced cracking [6], hydrogen-assisted cracking [7], and passive film rupture [8]. In their SCC investigation of Al-Mg and Mg-Al Alloys [9]suggested that there is substantial evidence that hydrogen (H) contributed to the formation of cracks in both alloy systems, with the corrosion that causes H reduction in the Al-Mg alloys coming from the anodic dissolution of the β-phase. Furthermore, in the Al-Mg system, the β-phase typically corrodes entirely before cracks appear, whereas in the Mg-Al system, the cracks undoubtedly advance past the particle due to localized corrosion between the particle and matrix interface or H-induced crack growth through the γ-phase or the particle-matrix interface. [10] investigated the SCC crack growth rate of cold worked 316L stainless steel in par environment. They highlighted that the fracture development rate increased monotonically with temperature when the dissolved oxygen content increased. However, recent studies have taken a significant step forward by extending the understanding of stress corrosion cracking (SCC) beyond conventional alloys. Researchers are now focusing on elucidating the SCC mechanisms in emerging advanced materials such as the high-entropy alloys (HEAs), which contain multiple principal elements and exhibit unique microstructural features. These complex chemical compositions and structural heterogeneities influence corrosion behaviour and crack propagation differently from traditional alloys, thereby prompting renewed interest in identifying how compositional complexity and environmental interactions affect SCC susceptibility in HEAs.

High entropy alloys (HEAs) as synthesized by [11] can be defined as systems with five (but possibly more) primary metallic elements in almost equiatomic ratios that produce one or more solid solution phases. These alloys are known as HEAs because, in contrast to conventional alloys, they have a high entropy of mixing, which theoretically favours the production of solid solution phases. According to an analysis of the literature, several of these HEAs exhibit good mechanical properties [12]. In the early evolution of HEAs, the primary emphasis remained on the single phase equiatomic HEAs. These equiatomic HEAs are referred to as "1st generation HEAs''. The CoCrFeNiMn (at.%) equiatomic HEA is one of the most extensively researched HEAs. After a detailed analysis and understanding of the 1st generation HEAs, non-equiatomic HEAs were synthesized and referred to as "2nd generation HEAs". These HEAs are composed of multiple or complex phases, including transformation-induced plasticity (TRIP) and twinning-induced plasticity (TWIP) HEAs. Furthermore, these alloys, owing to vast compositional space available, provide an ability to tune their properties for various applications [13].

However, while understanding SCC behaviours is paramount, limited research has been published in the literature to examine the passive film behaviour of these recently created HEAs, with an emphasis on how tensile load affects passive film characteristics [14]. This review synthesizes the existing literature to evaluate how the unique microstructural features and compositional complexity of HEAs influence their active stress corrosion cracking mechanisms and resultant performance in aggressive environments.

2. MECHANISM OF STRESS CORROSION CRACKING

If SCC is regulated by the electrochemical environment at the crack tip and includes electrochemical processes [15], then the knowledge of the electrochemical potential, pH, ion concentrations, and reactions taking place at the crack tip is crucial. The electrochemical reactions most likely to occur at the crack tip in low-alloy steels in water are:

Anode

$$M \rightarrow M^{n+} + ne^{-} \quad (1)$$

Cathode

$$O_2 + 2H_2O + 4e \rightarrow 4OH^{-} \quad (2)$$

$$2H^{+} + 2e^{-} \rightarrow H^{+} \quad (3)$$

The two major stages of SCC are initiation and propagation. Cracks can lead to component failure without causing major dimensional changes. Typical cracks often initiate at pits or crevices that can concentrate the stress (fig. 1a). Depending on the circumstances during propagation, these fractures may run along grain boundaries (intergranular) or through the grains (transgranular) into the metal. The ultimate fracture results from mechanical stress, leaving the fracture surface with dimples. The ultimate fracture results from mechanical stress, leaving the fracture surface with dimples. Highly branched cracks (fig. 1b) in the direction perpendicular to the tensile stress axis are developed during SCC.

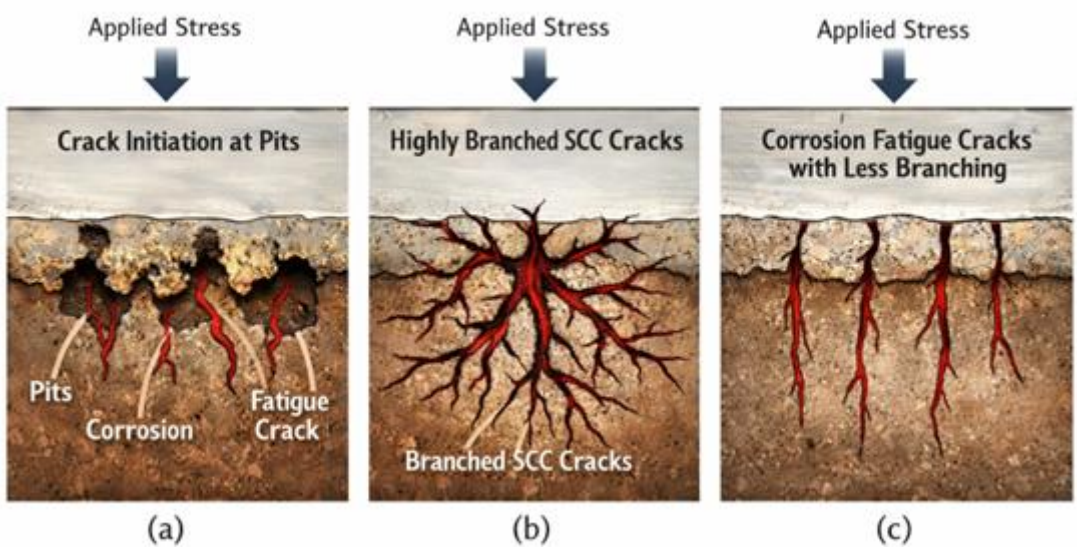

Figure 1. (a) Initiation of SCC and corrosion fatigue cracks at pits, (b) highly branched SCC cracks, and (c) corrosion fatigue cracks with less branching [16]

Furthermore, at the crack tip, local electrochemical conditions, such as electrode potential, solution pH, and oxygen availability, determine which cathodic reaction is dominant. These factors are critical in identifying the dominant mechanism of stress corrosion cracking (SCC) under the current conditions, which is either anodic dissolution (AD) or hydrogen embrittlement (HE).

2.1. Anodic Dissolution

Anodic dissolution (AD) is a fundamental concept that explains how stress corrosion cracking (SCC) evolves in metals and alloys subjected to harsh conditions. It is also known as the slip-dissolution or film-rupture process [17]. According to this mechanism, the main cause of crack propagation is localized electrochemical dissolution activities that occur at the fracture tip when mechanical stress and a corrosive liquid are coupled [18]. In addition to the AD model, the crack tip serves as an active anodic site where metal atoms are selectively oxidized and dissolved into the electrolyte. At the same time, a passive coating frequently covers the fracture sides to shield them from further damage, preserving the high aspect ratio that characterizes a stress corrosion crack [19]. The electrochemical potential gradient along the crack length results in selective dissolution at the crack tip, where mechanical deformation continuously ruptures the passive film, exposing fresh metal to the environment [20]. The crack front advances gradually due to the recurring process of film rupture, anodic dissolution, and repassivation. The subsequent loading cycle causes plastic deformation and film breakdown due to stress concentration at the tip. This is followed by localized anodic dissolution and the creation of a new passive film. The balance between rupture rate and repassivation kinetics determines the crack propagation rate [21].

Environmental factors such as solution composition, pH, temperature, and potential significantly influence the anodic dissolution process [22]. Stable passive film-forming metals, such high-entropy alloys, nickel-based alloys, and stainless steels, frequently display SCC in conditions that encourage recurrent film breakdown, such as solutions containing thiosulfate and chloride [17]. The presence of oxidizing agents or limited oxygen diffusion at the crack tip can alter the local potential and consequently affect the dissolution rate. Furthermore, from the mechanistically perspective, the AD model works effectively in systems with minimal hydrogen production and fracture surfaces that exhibit anodic attack rather than brittle cleavage, and the microstructural features, such as grain boundaries, inclusions, and residual stresses, can localise anodic activity, promoting intergranular or transgranular crack propagation depending on the alloy and environment [23].

2.2. Hydrogen embrittlement

In metallic systems, hydrogen embrittlement (HE) is one of the most prevalent and intricate processes that leads to stress corrosion cracking (SCC), especially in high-strength steels, nickel-based alloys, and titanium alloys. It results from the ingress, diffusion, and trapping of atomic hydrogen into the metallic lattice under the combined influence of mechanical stress and a corrosive environment [24]. In aqueous environments,

hydrogen is produced from the cathodic reactions during corrosion or electrochemical polarization, and a fraction of these atomic hydrogen species penetrate the metal surface, diffusing rapidly through lattice defects such as dislocations and grain boundaries [25]. The resulting alteration of microstructural cohesion promotes localized plastic instability and decohesion at microstructural stress concentrators. However, a number of mechanistic hypotheses have been put up to explain the involvement of hydrogen in SCC including adsorption-induced dislocation emission (AIDE), hydrogen-enhanced decohesion (HEDE), hydrogen-enhanced localized plasticity (HELP), and hydride production in certain alloys, have been put up to explain the involvement of hydrogen in SCC[26]. In the HEDE framework, atomic hydrogen facilitates fracture initiation and propagation at relatively modest applied stresses by weakening the cohesive strength of atomic bonds at grain boundaries or interfaces [27]. The HELP mechanism, on the other hand, proposes that hydrogen promotes dislocation mobility by lowering the stress necessary for dislocation motion, resulting in microvoid coalescence and localized plastic deformation before the crack tip [26]. Both mechanisms may operate simultaneously, depending on alloy composition, microstructure, and environmental conditions.

Additionally, the susceptibility of steels to hydrogen-assisted cracking is profoundly influenced by microstructural traps, strength level, and strain rate [28]. Quenched and tempered steels, for example, are particularly susceptible because intergranular fracture propagation and hydrogen entrapment are facilitated by tempering-induced heterogeneities and impurity segregation at grain boundaries [29]. Hydrogen buildup at the fracture tip weakens fracture toughness under prolonged strain, encouraging brittle transgranular or intergranular fracture modes. Furthermore, electrochemical potential is greatly influenced by hydrogen ingress, and extremely low cathodic protection potentials can speed up hydrogen creation and make SCC more susceptible, even while they are successful in reducing anodic dissolution [30]. Nevertheless, at the atomic scale, ab initio and molecular dynamics simulations demonstrate that hydrogen weakens metallic interactions and stabilizes vacancies, supporting experimental findings of nanovoid generation and fracture propagation through void coalescence [31]. Further studies using synchrotron technique have shown dynamic hydrogen redistribution close to fracture tips, highlighting the connection between stress fields and gradients in hydrogen concentration[32].

3. OVERVIEW OF STRESS CORROSION CRACKING IN HIGH-ENTROPY ALLOYS

In extreme situations, HEAs have been suggested for applications in components including heat exchangers, downhole equipment, and wellbore casings. The strategic modification of elemental compositions to satisfy various environmental and structural application requirements is made possible by the adaptable design space of high-entropy alloys [33]. In comparison to conventional materials, HEAs exhibit superior performance [34]. Higher configurational entropy, matching metallic element characteristics, and mixing enthalpy combinations that promote the formation of solid solutions, such as BCC or FCC over intermetallic compounds, result in solid solution phase stability at elevated temperatures. These distinguishing properties of high-entropy alloys (HEAs) come from the collective interactions among their major constituents, manifested through the four core effects, namely the high-entropy effect, severe lattice distortion effect, sluggish diffusion effect and cocktail effect (fig. 2)[35]. Each of these effects is critical in determining the electrochemical stability, mechanical responsiveness, and microstructural development of HEAs in corrosive and tensile environments. Their combined effect establishes the alloy's resistance or susceptibility to stress corrosion cracking (SCC). These impacts specifically alter elements such as elemental segregation at the fracture tip, diffusion-controlled crack propagation, localized deformation behaviour, and passive film development [36,37]. Therefore, understanding the individual and cumulative contributions of these effects is therefore necessary for building HEAs with higher SCC resistance for structural and engineering applications [38].

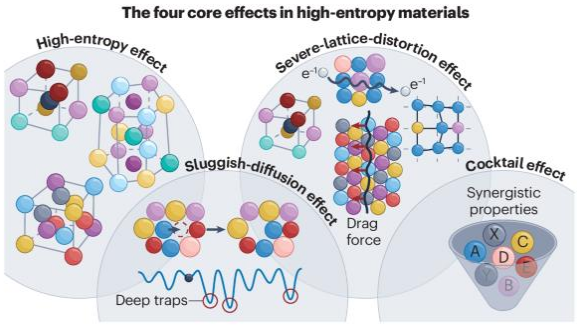

Figure 2. Schematic representation of the four fundamental effects governing high-entropy alloys (HEAs) [39].

3.1. Sluggish diffusion effect

The sluggish diffusion effect is one of the distinguishing characteristics of high-entropy alloys (HEAs), which significantly influence the alloys'

oxidation stability, corrosion resistance, and stress corrosion cracking (SCC) behaviour. In contrast to conventional alloys, which have fast oxidation and heterogeneous passive film production due to high atomic mobility, HEAs frequently show significantly lower diffusion rates, which results in homogeneous passive films, delayed oxidation kinetics, and improved long-term stability[40]. Thus, the sluggish diffusion effect reduces the breakdown of oxide films and the instability of passive layers, which are important elements that often lead to localized corrosion and the formation of cracks under tensile stress [41].

In conventional materials relatively fast-moving atoms can speed up the formation of oxides, resulting in compositional inhomogeneities and interfacial defects that serve as preferred locations for anodic dissolution and hydrogen ingress, two crucial processes in SCC. Conversely, HEAs with sluggish diffusion characteristics show limited atomic movement, which enables more chemically stable passive layers and regulated oxidation[42]. This stability delays the formation of corrosion-assisted microcracks at the metal–film contact in addition to suppressing localized corrosion. By limiting possible variations across microstructural areas, the passive film's homogeneity additionally minimizes the galvanic interactions that cause SCC to occur[43].

Furthermore, the slow diffusion effect performs an important function in preventing elements leaching and selective dissolution. In conventional alloys such as stainless steels or Ni-based superalloys, constituents like Fe and Ni may preferentially dissolve in harsh conditions, decreasing passivation and encouraging localized attack[44]. HEAs, on the other hand, exhibit noticeably reduced leaching rates, particularly in environments that are rich in chlorides and marine life, and they continue to retain their structural integrity and chemical homogeneity even when subjected to combined electrochemical and mechanical stresses. The local chemistry surrounding the crack tip is stabilized by this resistance to selective dissolution, which effectively lowers crack tip propagation rates[43]. Collectively, the sluggish diffusion effect improves SCC resistance in HEAs by lowering hydrogen transport and segregation close to fracture tips, stabilizing passive films, and decreasing diffusion-controlled crack propagation. For high-temperature structural, marine, and aerospace applications where materials are subjected to mechanical loads and corrosive conditions, these combined advantages make HEAs attractive options [45].

3.2. Severe lattice distortion effect

High-entropy alloy (HEA) coatings' remarkable resistance to corrosion and stress corrosion cracking (SCC) is also largely due to the severe lattice distortion effect, which results from the large atomic size mismatch between multiple key elements. In contrast to conventional alloys with comparatively orderly crystal structures, HEAs have very strained and deformed lattice configurations, which lead to significant atomic-level abnormalities and local stress fields[34]. These distortions decrease anodic dissolution and delay the formation of cracks by obstructing the migration of hydrogen atoms and corrosive species[46].

Lattice distortion improves corrosion resistance by disrupting the transport of aggressive ions like chloride (Cl^-), which cause pitting, film disintegration, and localized corrosion in marine and acidic environments[47]. In conventional materials, grain boundaries and passive coatings frequently provide preferred penetration paths for these ions, intensifying localized attack and acting as SCC initiation sites. On the other hand, HEAs' high lattice strain and uneven atomic spacing provide a powerful diffusion barrier that hinders the migration of hydrogen atoms or corrosive ions through the microstructure [48]. This suppression of ionic transport not only preserves the integrity of the passive film but also reduces the likelihood of hydrogen-assisted cracking under applied stress.

Furthermore, the disordered atomic **structure** inherent to HEAs suppresses anodic dissolution and enhances passive film stability, even under high mechanical loading. Due to their dual resistance to mechanically induced crack propagation and electrochemical degradation, lattice-distorted HEA surfaces are especially suitable for harsh operating environments like nuclear reactors, offshore structures, and aerospace, where materials must simultaneously withstand high mechanical stress and corrosive media [43]. Nevertheless, the mitigation of SCC susceptibility and the maintenance of long-term structural dependability under high service conditions are significantly aided by severe lattice distortion in HEAs, which minimizes localized electrochemical reactivity and establishes a strong atomic-level diffusion barrier[49].

3.3. Cocktail effect

High-entropy alloys' (HEAs') remarkable resistance to stress corrosion cracking (SCC) is increasingly attributed to not just the sum of their individual element characteristics but to the intricate and synergistic interactions known as the cocktail effect[35][50]. This phenomenon explains the emergent features that result from the special

chemical environment of HEAs, where electron dispersion, atomic diffusion, and phase stability are influenced by high configurational entropy and severe lattice distortion. The primary indicator of the cocktail effect in the context of SCC is its impact on the stability, composition, and generation of passive films. The coexistence of many alloying elements encourages the development of dense, self-healing oxide layers that are very resistant to localized breakdown, which is an essential phase before the initiation of SCC[51]. This synergistic enhancement of passivity, often unattainable in conventional alloys, represents one of the most significant outcomes of the cocktail effect in HEAs.

Mechanistically, the significance of the cocktail effect in mitigating SCC can be understood through its dual effects on anodic dissolution and hydrogen embrittlement the two principal forms of SCC failure. Certain elements, such as Cr, Mo, and Al, have demonstrated to function collectively to create multicomponent passive films that are rich in CrO_3, AlO_3, and Mo-oxides [52]. In chloride conditions, chromium increases overall corrosion resistance, molybdenum inhibits pit nucleation and aluminium increases film stability and repassivation kinetics[53]. They work together to provide a passive barrier that is resistant to defects in HEAs, which effectively delays anodic disintegration at the crack tip. In parallel, severe lattice distortion and sluggish diffusion effects inherent to HEAs serve as hydrogen traps, reducing hydrogen diffusivity and accumulation at critical microstructural sites [54]. This improves the structural dependability of HEAs in demanding service conditions by reducing hydrogen-assisted cracking and raising the threshold stress intensity for SCC initiation and propagation.

Therefore, the strategic application of the cocktail effect is essential to the logical design of SCC-resistant HEAs. Research on CoCrFeNi-based HEAs has demonstrated that even small alloying additions can result in disproportionately significant gains in corrosion and mechanical performance[55]. For example, the addition of Al or Ti enhances matrix strengthening and passive film compactness, while Mo or Nb additions improve grain boundary stability and reduce intergranular corrosion susceptibility [56]. However, the cocktail effect can also be detrimental if chemical heterogeneity or brittle intermetallic phases brought on by compositional imbalance encourage stress localization and micro-galvanic corrosion [57]. Therefore, to customize the microstructure and surface chemistry of HEAs, a thorough grasp of the thermodynamic and kinetic interactions among component materials is necessary. Superior SCC resistance in high-performance structural applications may be attained by taking use of the advantageous characteristics of the cocktail effect through the optimization of these intricate interactions.

3.4. High entropy effect

The high-entropy effect, a defining characteristic of high-entropy alloys (HEAs), plays a pivotal role in dictating their stress corrosion cracking (SCC) behavior. Due to the existence of several primary elements in almost equal amounts, single-phase solid solutions are stabilized by a high configurational entropy[35]. According to the Gibbs phase rule, the number of phases (P) in a given alloy at constant pressure in equilibrium condition is:

$$P = C + 1 - F \qquad (4)$$

where C is the number of components and F is the maximum number of thermodynamic degrees of freedom in the system. In the case of a 6-component system at given pressure, one might expect a maximum of 7 equilibrium phases at an invariant reaction. However, to our surprise, HEAs form solid-solution phases rather than intermetallic phases [58]. This is not to claim that solid solution phases will develop at the center of the phase diagram when all multi-components have an equal molar ratio. In fact, solid solutions rather than intermetallic compounds will only form from carefully selected compositions that meet the HEA-formation conditions. Furthermore, the high entropy effect in HEAs reduces phase segregation and inhibits the creation of secondary brittle intermetallics, in contrast to conventional alloys where microstructural inhomogeneity frequently provides sites for localized corrosion or crack initiation[59]. The resultant structural homogeneity and thermodynamic stability yield a more consistent electrochemical reaction over the alloy surface, which is crucial for mitigating localized anodic dissolution that commonly initiates stress corrosion cracking (SCC). The resultant structural homogeneity and thermodynamic stability yield a more consistent electrochemical reaction over the alloy surface, which is crucial for mitigating localized anodic dissolution that commonly initiates stress corrosion cracking (SCC)[60].

Mechanistically, the high-entropy impact modifies the pathways that control SCC, including anodic dissolution and hydrogen embrittlement. First, the creation of chemically uniform and compositionally stable passive films is encouraged by the thermodynamic stability of a single-phase solid solution. These films tend to be enriched with

mixed oxides (e.g., Cr_2O_3–Al_2O_3–MoO_x), which exhibit enhanced compactness and self-healing capability [61]. The uniform passive film distribution decreases potential gradients and inhibits localized breakdown under tensile stress, therefore preventing fracture formation. Secondly, the high-entropy effect is directly connected to slow diffusion, which reduces the mobility of metallic atoms and hydrogen. This decrease in atomic mobility delays hydrogen entry and mitigates the accumulation of hydrogen at the crack tip, thus minimizing hydrogen-assisted cracking [62]. The combined effects of enhanced passivity and reduced hydrogen mobility translate into an elevated threshold stress intensity factor and prolonged crack incubation times.

4. PREVIOUS STUDIES ON THE STRESS CORROSION CRACKING IN HIGH ENTROPY ALLOYS

Although limited studies have focused on stress corrosion cracking (SCC) in high-entropy alloys (HEAs) as illustrated in fig. 3. There is a growing and urgent need for comprehensive investigation in this field. This is driven by the increasing industrial demand for structural materials that can withstand harsh corrosive environments while retaining high mechanical integrity. HEAs have shown remarkable potential in this regard, exhibiting superior strength, thermal stability, and corrosion resistance compared to many conventional alloys. Table 1 summarizes previous investigations on SCC behaviour in various HEAs and highlights their key findings.

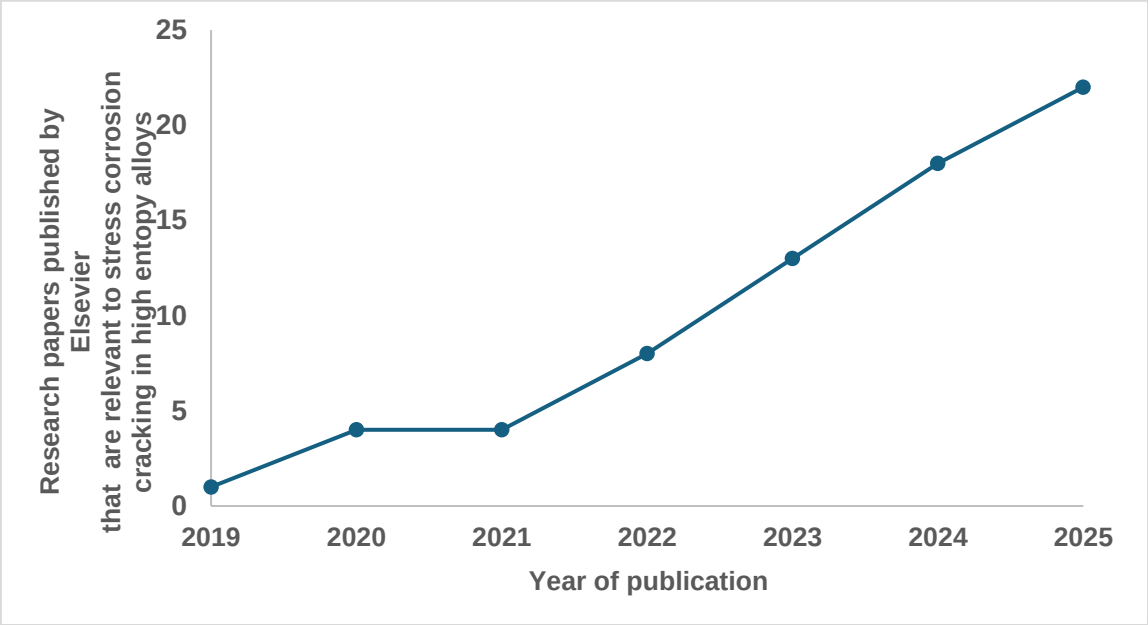

Figure 3. Total number of research papers published by Elsevier that are relevant to the keywords of the review title versus the year of publication

Table1. SCC behaviour in various HEAs

Alloy system	phase	Processing technique	Test environment	What to deduce	Ref.
Fe40Ni40Cr20	FCC	Reactive atomistic simulations	Vacuum and High temperature/ pressure water	The presence of a high temperature/pressure water environment alters the deformation mechanism of the Fe40Ni40Cr20 alloy, leading to a phase change from FCC to HCP in vacuum to FCC to BCC in water.	[63]
Fe39Mn20Co20 Cr15Si5Al1	Dual phase (HCP + FCC)	Vacuum arc casting	3.5 wt.% NaCl	Applying a tensile load significantly alters the properties of the passive layer that forms on the HEA surface. In comparison to the no-load (unstressed) condition, the passive film becomes less stable under load, exhibits more flaws, and ruptures more frequently.	[64]

AlCoCrFeNi2.1	Dual phase (BCC+ FCC)	Vacuum arc melting & Electron beam remelting	Simulated seawater environment and acidic environment	The remelted layer's improved microstructure slows down the initiation and propagation of cracks in corrosive and stressed conditions by having less segregation, fewer flaws, and a more uniform phase distribution.	[65]
Fe27.5Ni28. 1Mn26.5Cr17.9	FCC	Vacuum induction melting	Elevated temperature hydrogenated water	The FeNiMnCr HEA is extremely vulnerable to the beginning of SCC even though it creates a Cr-enriched oxide layer above the grain boundary and is resistant to intergranular oxidation.	[66]

Studied [63] the mechanisms of chemical-reaction-induced tensile deformation of an Fe/Ni/Cr alloy revealed by reactive atomistic simulations. They discovered that in vacuum, Shockley partial dislocations from the surface and grain boundary generate layered HCP phases from the FCC matrix during tensile simulation. Additionally, while the alloy surface is oxidized by reactions with water in a corrosive water environment, this oxidized surface layer can suppress the generation of Shockley partial dislocation and the resulting FCC-to-HCP phase transition. Instead, the BCC phase is preferred to release the stored elastic energy and tensile stress, which results in a reduced ductility and an enhanced elastic modulus. Exploring the influence of tensile load on the nature of passive film during stress corrosion cracking in a TRIP $Fe_{39}Mn_{20}Co_{20}Cr_{15}Si_5Al_1$ (at.%) high entropy alloy as investigated by [64]. They unravelled that the microstructural characteristics, such the TRIP alloy's inherent phase boundaries (γ→ε transition phases), in conjunction with the tensile stress, act as preferred locations for pit initiation and passive film rupture and that the passive film in these regions shows a compromised integrity under load. Furthermore, despite the base alloy's advantageous mechanical characteristics (caused by the TRIP effect), they do not ensure that it will not succumb to SCC when subjected to tensile stress in corrosive conditions.[65] examined the excellent resistance to stress corrosion cracking of electron beam remelted layer of high-entropy alloy $AlCoCrFeNi_{2.1}$. during the studied they discovered that the $AlCoCrFeNi_{2.1}$ high-entropy alloy's electron-beam remelted (EBR) layer exhibited a significantly enhanced resistance to stress-corrosion cracking (SCC) when compared to the base (unremelted) material. Furthermore, the performance is enhanced by the refined, homogenized microstructure created by the remelting process. According to corrosion studies conducted in conditions that encourage SCC, the remelted layer limits the transition from passive corrosion to crack initiation by maintaining a more stable passive film with lesser breakdown phenomena. And this was attributed to the microstructural refinement and possibly changes in elemental distribution (such as a greater prevalence of Cr or Al-rich phases) in the remelted layer.[66] investigated the environmental degradation behaviour of FeNiMnCr high entropy alloy in high temperature hydrogenated water. They discovered that both Cr and Mn diffuse outward along the grain boundary during the oxidation of this HEA, causing boundary migration. Additionally, when the sample is unstressed, the Cr flux aids in the formation of a protective oxide layer over the grain boundary that inhibits penetrative intergranular oxidation; nevertheless, the oxide that is created is extremely porous because of the dissolution of Mn and is readily breached under stress.

5. INFLUENCE OF MICROSTRUCTURE ON CORROSION PERFORMANCE OF HEAS

Understanding the HEAs' microstructure provides a blueprint for forecasting their corrosion behaviour. Due to structural flaws and elemental segregation, grain boundaries in HEAs may be preferred locations for the onset of corrosion. Moreover, the development and durability of protective oxide layers are impacted by the local chemical compositions that are changed by the presence of precipitates and the second phase. The kinetics of oxide production and corrosion processes are also influenced by the microstructure, which also influences the diffusion paths for corrosive agents like oxygen and steam. Furthermore, surface morphology, which refers to the implication of roughness and grain size, plays a role in the adhesion and stability of oxide scales, ultimately affecting the overall corrosion behaviour of HEAs[67][68].

The addition of chromium to HEAs can significantly enhance their resistance to corrosion by stabilizing simple solid solution phases, promoting the formation of protective oxide layers, and synergizing with other alloying elements, such as Al. $Mo_{0.5}VNbTiCr_{x(x = 0, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0)}$ shows that the addition of Cr significantly correlates with

corrosion[69]. With the least amount of mass gain, the Laves phase forms when the Cr content in the HEAs rises over 1.0. The predicted Laves phase is clearly detected in Cr1.5 and Cr2.0 alloys (Fig. 4), which improves corrosion resistance under extreme conditions (superheated steam at 400 °C and 10.3 MPa for 1680 h). Furthermore, [70] investigated on $Al_{0.3}Cr_xFeCoNi$ high-entropy alloys with high corrosion resistance and good mechanical properties. During the microstructural characterization, the $Al_{0.3}Cr_xFeCoNi$alloys with x = 0–1.0 exhibited the single FCC structure. The alloys with x = 1.5–2.0 consisted of the FCC + BCC/B2 structure, and the amount of the BCC/B2 phases increased with increasing the Cr content in the alloys. Additionally, the stability of FCC and BCC solid solutions in HEAs has been suggested to be determined by the valence electron concentration (VEC) of the HEA. For a specific HEA system, the FCC phase is stable at a higher VEC, while the BCC phase is stable at a lower VEC[71]. The VEC values of Al, Cr, Fe, Co, and Ni are 3, 6, 8, 9, and 10, respectively[72]. Consequently, the increase of Cr content in the $Al_{0.3}Cr_xFeCoNi$ alloys led to a reduction in the VEC values of the alloys. The decrease in VEC values of the current alloys indicates enhanced stability of the BCC phase, aligning with the influence of Cr in promoting BCC phase development in the alloys[73][74]. Furthermore, the Cr content in the BCC/B2 and FCC phases of the alloys with x = 1.5–2.0 increased with the increase chromium concentration of the alloys. The elevated Cr concentrations in the $Al_{0.3}Cr_xFeCoNi$ (x = 1.5–2.0) alloys led to the development of chromium-rich BCC/B2 and FCC phases, hence improving the corrosion resistance of these alloys, as evidenced by immersion, potentiodynamic polarisation (PDP), and EIS measurements. The PDP curves is shown in fig. 5.

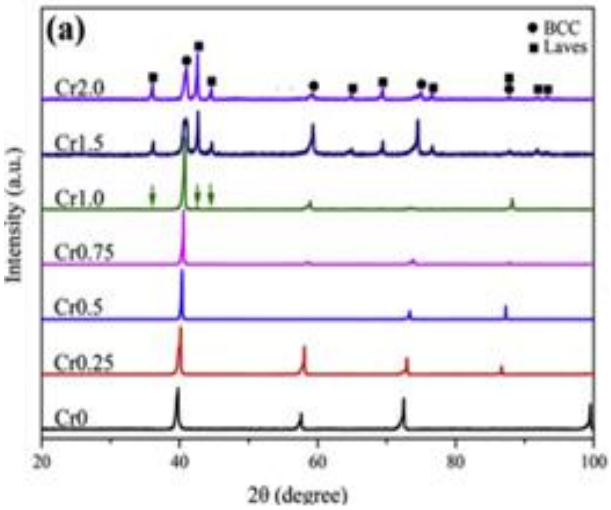

Figure 4. X-ray diffraction patterns of the Mo0.5VNbTiCrx (x ¼ 0, 0.25, 0.5, 0.75, 1.0, 1.5, and 2.0) alloys after HIP at 1200 C and 150 MPa for 2 h and annealing at 1200 C for 72 h [69]

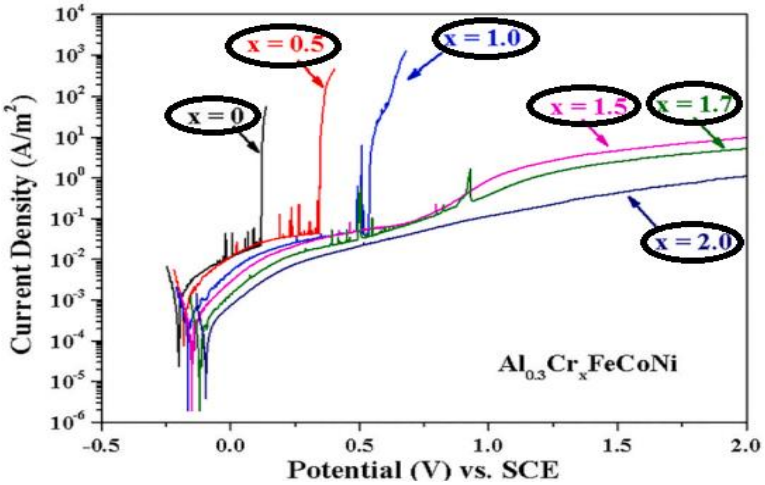

Figure 5. Potentiodynamic-polarization curves of the $Al_{0.3}Cr_xFeCoNi$ (x = 0–2.0) alloys in the 3.5 mass% NaCl solution[75]

Similarly, $Al_xCrCuFeNi_{2(x\ =\ 0.2,\ 0.4,\ 0.6)}$[76] HEAs exhibit a similar pattern when the concentration of Al rises. The FCC solid solution of the CoCrFeNiMo alloy is formed by a high concentration of Mo in the (Mo, Cr) rich phase. This results in decreased corrosion resistance by lowering the concentration of Cr in the other phases (Mo-rich and Ni-Fe-rich phases) [77].

The as-cast FeNiCrCuAl [78]HEAs have a NiAl-rich BCC (B2) phase surrounding the FeCr-rich area, forming a petal-like microstructure, which results in smaller mass gains. This is significantly lower than that of austenitic stainless steels and Ni-based alloys under equal corrosion circumstances (1000 hours at 550°C and 25 MPa). A comparable family of alloys. Additionally, the as-cast

$CrFe_{1.5}MnNi_{0.5}$ alloy, which is a four-component and Al-free composition, exhibits a face-centered cubic (fcc) solid solution with an α-FeCr structure, as shown by the XRD patterns in fig. 6.

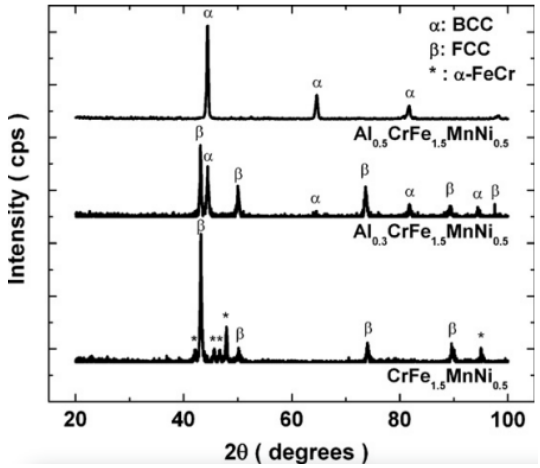

Figure 6. XRD patterns of the as-cast $Al_xCrFe_{1.5}MnNi_{0.5}$ alloy[80].

However, as the aluminium content increased, the peak intensities of the body-centered cubic (bcc) phase increased. The as-cast $Al_{0.3}CrFe_{1.5}MnNi_{0.5}$ (five-component) alloy consists of mixed fcc/bcc phases, whereas the alloy with 0.5 mol aluminium has a single bcc structure. Comparatively, ferritic stainless steels, such as type 430 stainless steel, are fundamentally iron-chromium alloys with structures mostly of the bcc α-iron type. However, the structures of austenitic stainless steels (such type 304 stainless steel) are of the fcc γ-iron type and are ternary iron–chromium–nickel alloys. Indeed, the austenitic stainless steels normally have greater corrosion resistance than the ferritic stainless steels [79]. These facts may explain why the fcc structure of the CrFe1.5MnNi0.5 alloy is more corrosion-resistant than the bcc structure of the AlxCrFe1.5MnNi0.5 (x = 0.3 and 0.5) alloys

Furthermore, the SEM microstructure of the $Al_xCrFe_{1.5}MnNi_{0.5}$ alloys in 0.5 M H_2SO_4 following anodic polarisation beyond the breakdown potential (>1.25 V) is shown in fig. 7. Except for minor overall material dissolving on the $CrFe_{1.5}MnNi_{0.5}$ alloy's surface, fig. 7a shows nearly no pitting. However, the surface of the $Al_{0.3}CrFe_{1.5}MnNi_{0.5}$ alloy experienced a small amount of shallow attack (~25 μm in diameter and 5–10 μm in depth) (fig. 7b). Furthermore, compared to the $Al_{0.3}CrFe_{1.5}MnNi_{0.5}$ alloy, the localised corrosion of the $Al_{0.5}CrFe_{1.5}MnNi_{0.5}$ alloy is greater and deeper (~45 μm in diameter and ~50 μm in depth) in fig. 7c.At a greater magnification, fig. 7d illustrates this localised corrosion of the $Al_{0.5}CrFe_{1.5}MnNi_{0.5}$ alloy and reveals many surface holes. Aluminium forms a porous oxide coating in H_2SO_4 and contributes to galvanic assault on the weaker and more porous oxide area; the passivation behaviour of Fe–Al alloys dramatically deteriorates when the Al concentration is less than 20 at%[81][82].

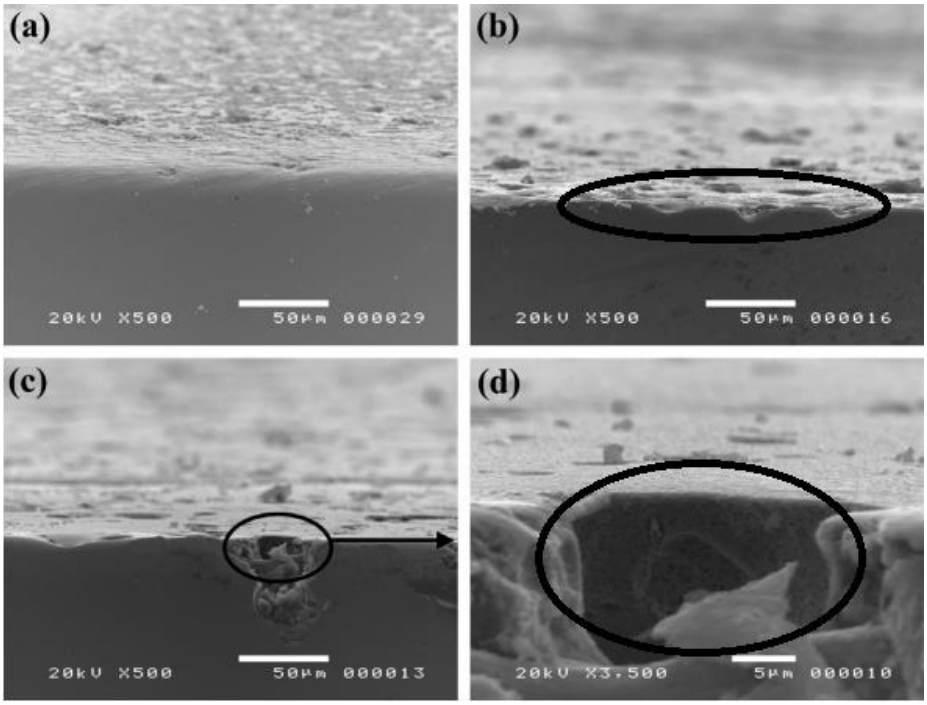

Figure 7. SEM micrographs for the $Al_xCrFe_{1.5}MnNi_{0.5}$ alloys with aluminium content (a) x = 0, (b) x = 0.3 mol, (c) x = 0.5 mol, (d) Higher magnification of micrograph 7(c) after anodic polarization exceeded the breakdown potential (>1.25 V_{SHE}) in 0.5 M H_2SO_4[82]

Therefore, the corrosion behaviour of HEAs is largely determined by their microstructure. Segregation, precipitate distribution, grain size, and phase composition all work together to determine how stable and protective passive films are. The ideal balance of alloying elements like Cr, Al, and Mo is essential for preserving corrosion resistance; they also affect the rates of oxide formation and interfacial stability. HEAs' vulnerability to localized corrosion is reduced by heat treatment and solidification conditions, which further improve microstructural homogeneity. Therefore, modifying the microstructure through compositional design and processing control is still an important strategy for improving HEAs' corrosion performance.

6. INFLUENCE OF TEMPERATURE ON STRESS CORROSION CRACKING (SCC) IN HIGH-ENTROPY ALLOYS (HEAS)

Temperature has a significant impact on the stress corrosion cracking (SCC) behaviour of high-entropy alloys (HEAs), affecting electrochemical activity, phase stability, hydrogen transport, and passive film integrity[83]. At high temperatures, the kinetics of anodic and cathodic processes increase, resulting in quicker oxide formation and greater corrosion rates. Studies on FeNiMnCr and FeNiCr-based HEAs have revealed that while thicker oxide coatings grow under high-temperature settings, these films typically contain structural flaws and compositional gradients that impair their protectiveness and enable localized corrosion or fracture initiation [84]. Furthermore, temperature alters the passive film's composition. At moderate temperatures, chromium-rich oxides often predominate and offer better protection, whereas high-temperature oxidation can produce spinel-type oxides with worse mechanical adhesion [85].

In addition to its electrochemical effects, temperature greatly increases the production and transport of hydrogen, especially in hydrogenated aqueous environments like supercritical water conditions or pressurized water reactors. Investigations on FeNiMnCr and other Fe-based HEAs show that high-temperature hydrogen intrusion enhances intergranular cracking through hydrogen-assisted decohesion and oxidation-assisted weakening of grain boundaries [84]. As a result, when hydrogen is easily created or absorbed, SCC susceptibility tends to rise with temperature. Moderate heating (up to around 100–200 °C) in chloride solutions increases pit development and passive-film rupture, which results in pit-to-crack transitions. On the other hand, the predominant mechanism changes from pit-induced SCC to oxidation- and hydrogen-assisted intergranular cracking in supercritical or hydrogenated water, highlighting the environment-specific character of temperature effects. Similarly, high-temperature oxidation of MnCoCrFeNiHEAs reveals that the protective α-Mn_2O_3/Cr_2O_3 oxide formed at 600 °C transforms into Mn_3O_4 at 800–900 °C, accompanied by Cr and Mn depletion in the substrate and pore formation near the oxide layer, which collectively reduce film integrity and corrosion resistance (fig. 8) [86]

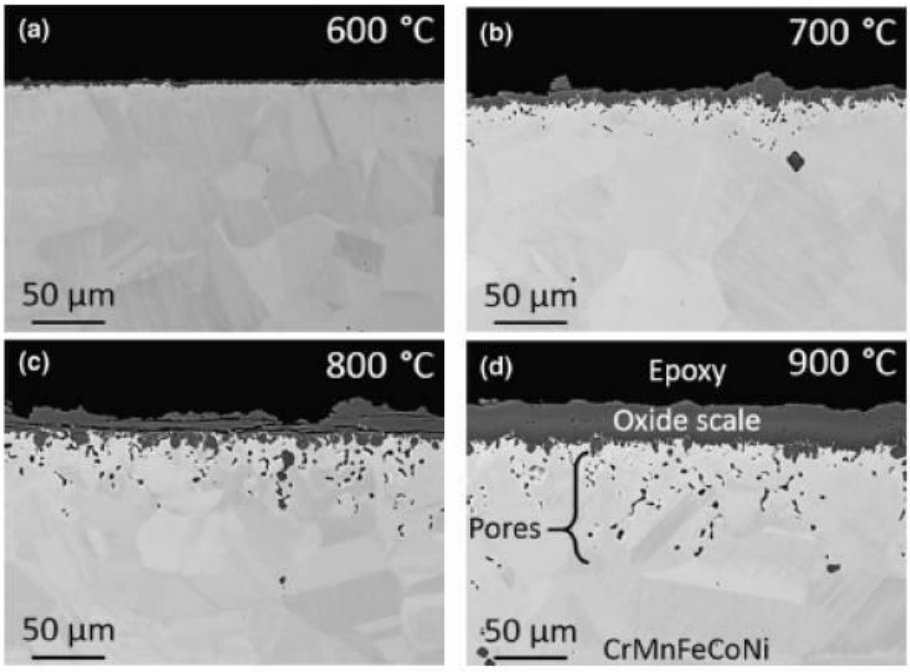

*Figure 8. SEM images of oxide layers on HEAMnCoCrFeNi in cross section after 100 h at: (**a**) 600 °C; (**b**) 700 °C; (**c**) 800 °C; (**d**) 900 °C [86]*

Additionally, temperature controls microstructural development and phase stability, both of which have an impact on SCC processes. Temperature-dependent transitions like ordering, precipitation, or σ-phase formation occur in many HEAs, which are metastable. For example, at high temperatures, eutectic and Al-containing HEAs may form ordered B2 or σ phases, resulting in microgalvanic interaction between phases and decreasing fracture resistance[87]. Meanwhile, transformation-induced plasticity (TRIP) HEAs, such as $Fe_{39}Mn_{20}Co_{20}Cr_{15}Si_5Al_1$, have a temperature-sensitive FCC↔HCP transition that can either absorb local strain and postpone cracking at low temperatures or accelerate boundary-localized corrosion at increased temperatures [64]. Thus, temperature-induced microstructural changes directly influence both electrochemical reactivity and mechanical deformation behaviour during SCC.

Future perspectives

Future research should move toward multi-scale and data-driven frameworks that bridge atomistic, microstructural, and macroscopic perspectives of SCC in HEAs. Despite considerable experimental advances, the intricate coupling between mechanical stress, chemical environment, and compositional disorder remains difficult to quantify using conventional approaches.

Integrating molecular dynamics (MD) simulations with machine learning (ML) offers a promising path forward. MD can analyse atomic-scale processes such as hydrogen diffusion, oxide breakdown, and crack-tip plasticity under varying stress and temperature conditions, while ML can detect hidden correlations in large datasets, enabling rapid prediction of SCC susceptibility from alloy composition and processing history. Such hybrid computational–experimental workflows can guide the design of HEAs with tailored passive films, optimized microstructures, and controlled elemental segregation. Additionally, in-situ electrochemical and microscopic techniques should be expanded to validate predictive models and capture dynamic SCC processes under realistic service environments. The future of SCC research in HEAs thus lies in combining mechanistic insight, high-throughput computation, and intelligent data analytics to enable safer, longer-lasting materials for extreme conditions.

7. CONCLUSION

This review has systematically elucidated the current state of knowledge on stress corrosion cracking in high-entropy alloys. The distinct behaviour of HEAs under SCC conditions is not merely a sum of their constituent elements but is profoundly dictated by their foundational core effects. The sluggish diffusion effect enhances passive film stability and retards crack tip kinetics, while the severe lattice distortion effect acts as a potent barrier to the diffusion of corrosive species and hydrogen. The cocktail effect enables the formation of highly protective, multi-component passive films and can be strategically leveraged through alloying to mitigate both anodic dissolution and hydrogen embrittlement. Finally, the high-entropy effect itself promotes microstructural homogeneity and suppresses the formation of deleterious intermetallic phases that often serve as crack initiation sites.

However, this inherent complexity is a double-edged sword; improper compositional design can lead to elemental segregation, detrimental phase precipitation, and micro-galvanic effects that exacerbate SCC susceptibility. The microstructural evolution, particularly in metastable systems like TRIP-HEAs, and the operational temperature are critical external variables that can override intrinsic resistance. The compiled evidence confirms that HEAs hold immense promise for applications demanding high SCC resistance. Realizing this potential requires a concerted, interdisciplinary effort that couples advanced experimental characterization with predictive computational tools to navigate the immense compositional space and tailor HEA microstructures for resilience in the face of combined mechanical and environmental degradation.

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IZVOD

PUCANJE USLED NAPONSKE KOROZIJE LEGURA VISOKOG ENTROPIJSKOG SASTAVA: MEHANIZAM, MIKROSTRUKTURA I PERFORMANSE

Pucanje usled korozije pod naponom (SCC) predstavlja značajnu pretnju strukturnim komponentama izloženim sinergijskoj kombinaciji zateznog naprezanja i korozivnih sredina. Iako je opsežno proučavano kod konvencionalnih legura, ponašanje SCC-a kod nove klase legura visoke entropije (HEA) ostaje granica istraživanja. Ovaj pregled sintetiše trenutna znanja kako bi se premostio ovaj jaz, sistematski ispitujući kako jedinstvene osobine HEA, određene njihovim osnovnim efektima visoke entropije, jakog izobličenja rešetke, spore difuzije i koktel efekta, diktiraju njihov SCC odgovor. Osnovni mehanizmi anodnog rastvaranja i vodonične krtosti analizirani su u kontekstu složenih mikrostruktura i kompozicionih pejzaža HEA. Štaviše, pregled kritički procenjuje uticajne uloge temperature i mikrostrukturne evolucije na stabilnost pasivnog filma i nastanak pukotina. Integracijom nalaza iz ključnih HEA sistema, pokazano je da se osnovni efekti mogu strateški iskoristiti za poboljšanje otpornosti na SCC stabilizacijom zaštitnih filmova i sprečavanjem kinetike širenja pukotina. Međutim, ova inherentna složenost može takođe uvesti ranjivosti poput mikrogalvanske korozije ako se nepravilno upravlja. Ovaj rad zaključuje da je fundamentalno razumevanje interakcije između elektrohemije, mehanike i termodinamike visokotemperaturnih elemenata (HEA) od najveće važnosti za unapređenje primene ovih materijala u zahtevnim okruženjima kao što su nuklearna energija, vazduhoplovstvo i pomorsko inženjerstvo.

***Ključne reči**: Pucanje usled korozije pod naponom, legure visoke entropije, efekti jezgra, stabilnost pasivnog filma, anodno rastvaranje, vodonična krtost.*

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