Xiao *et al. Microstructures* 2023;3:2023006
DOI: 10.20517/microstructures.2022.26

Microstructures

Review

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Environmental embrittlement behavior of high-entropy alloys

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How to cite this article: Xiao B, Liu S, Zhang J, Zhou Y, Li Q, Hou J, Xiao W, Zhang J, Zhao Y, Liu CT, Xu L, Yang T. Environmental embrittlement behavior of high-entropy alloys. *Microstructures* 2023;3:2023006. https://dx.doi.org/10.20517/microstructures.2022.26

Received: 18 Sep 2022 **First Decision:** 11 Oct 2022 **Revised:** 21 Oct 2022 **Accepted:** 14 Nov 2022 **Available online:** 10 Jan 2023

Academic Editors: Huijun Li, Shujun Zhang **Copy Editor:** Fangling Lan **Production Editor:** Fangling Lan

Abstract

High entropy alloys (HEAs), as a new class of structural materials, have attracted extensive interest from numerous metallurgical scientists and engineers. Benefiting from their unique microstructural features and outstanding mechanical performance, HEAs have shown significant potential for applications in many engineering fields, even under extreme conditions. In particular, when exposed to hydrogen and/or intermediate-temperature environments, these HEAs inevitably suffer from severe environmental embrittlement (EE) issues, e.g., hydrogen embrittlement (HE) and intermediate-temperature embrittlement (ITE), resulting in serious premature intergranular failure. In this work, we critically review the state-of-the-art advances of EE in previously reported HEA systems. Particular focus is given to novel strategies to enhance the resistance to EE in different HEAs. Two critical embrittlement phenomena, namely, HE and ITE, are highlighted separately. Finally, we provide perspectives on future research directions and opportunities for EE-resistant HEAs.

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Keywords: High-entropy alloys (HEAs), environmental embrittlement (EE), hydrogen embrittlement, intermediate-temperature embrittlement, EE-resistant HEAs

INTRODUCTION

High-performance structural materials with promising strength and ductility combinations are highly desirable for a wide range of engineering applications[1-4]. Distinct from traditional single-principal-element-guided materials, like steels[5-8], aluminum alloys[9,10], titanium alloys[11,12] and Co/Ni-based superalloys[13-17], the multiple-principal-element paradigm has significantly motivated the rapid development of a new class of metallic structural materials, namely, high-entropy alloys (HEAs), which are also known as multi-principal-component and chemically complex alloys[18-22].

Given their extraordinary physical, thermal and mechanical properties[23-25], emerging HEAs have been expected to benefit many potential engineering applications in the aerospace, automotive, nuclear power, petrochemical and electronic manufacturing fields, as well as many other industries[26-28]. Like most conventional metallic alloys[29,30], HEAs unavoidably face enormous challenges regarding environmental embrittlement (EE) failure, which is critical to the safety and reliability of engineering structures. Intermediate-temperature embrittlement (ITE) and hydrogen embrittlement (HE) are considered to be two crucial EE issues in various advanced metallic structural materials[31-38]. Specifically, due to the synergetic effect of the local stress concentration in the vicinity of grain boundaries (GBs) and environmental GB attacks, most polycrystalline high-temperature structural alloys often undergo serious intergranular embrittlement in intermediate-temperature regimes (i.e., 600-800 °C)[39,40]. Similarly, when exposed to hydrogen environments, the deformation capability of some once ductile metallic alloys dramatically degraded, resulting in poor fracture resistance and intergranular failures[41-46]. This is because the hydrogen generally traps at the GBs and then reduces their cohesive strength. The nucleation and propagation of cracks preferentially occur at GBs during tensile deformation, consequently leading to intergranular fracture[47,48].

Notably, such undesired EE behavior, including HE and ITE, has been frequently observed in different HEA systems[39,49]. To date, many research groups have devoted their efforts to addressing EE problems in new types of HEAs and have made significant achievements. Therefore, in this study, we provide an overview of the recent important discoveries in the EE of representative HEAs. Two major types of typical EE (ITE and HE) behavior and mechanisms (or microstructural factors) are discussed separately, as schematically illustrated in Figure 1. The key strategies for improving the resistance to EE in the HEA systems are highlighted. In this review, different HEA systems are introduced and discussed, as presented in Table 1. Finally, the challenges and future research trends for the development of EE-resistant HEAs are briefly summarized.

HE MECHANISMS AND MITIGATION STRATEGIES IN HEA SYSTEMS

In this section, we summarize the significant progress made in the development of HE-resistant HEAs and the associated governing mechanisms and novel strategies.

In the past few years, numerous studies on HE resistance have been mainly focused on single-phase HEAs, such as the CoCrNi, CoNiV and FeCoCrNiMn systems[49-52]. Generally, hydrogen diffuses into alloys and can be introduced via electrochemical and gas hydrogen charging. Here, we summarize the HE behavior of HEAs in different hydrogen charging approaches. For the former case, when hydrogen is incorporated via electrochemical hydrogen charging, Soundararajan *et al.* demonstrated a relatively high HE resistance of an

Table 1. Summary of different categories of HEAs (at.%)

EE issues	HE	ITE
HEA systems	Equiatomic CoCrNi	39.9Ni-20Co-30Fe-6Al-4Ti-0.1B
	Equiatomic CoNiV	29.9Ni-30Co-13Fe-15Cr-6Al-6Ti-0.1B
	Equiatomic FeCoCrNiMn	46.23Ni-23Co-10Cr-5Fe-8.5Al-4Ti-2W-1Mo-0.15C-0.1B-0.02Zr
	97(CoCrNi)-3Mo	100-x(NbMoTaW)-xB
	Equiatomic FeCoCrNi	
	45Fe-35Mn-10Co-10Cr	
	50Fe-30Mn-10Cr-10Co	

HEAs: High entropy alloys; EE: environmental embrittlement; HE: hydrogen embrittlement; ITE: intermediate-temperature embrittlement.

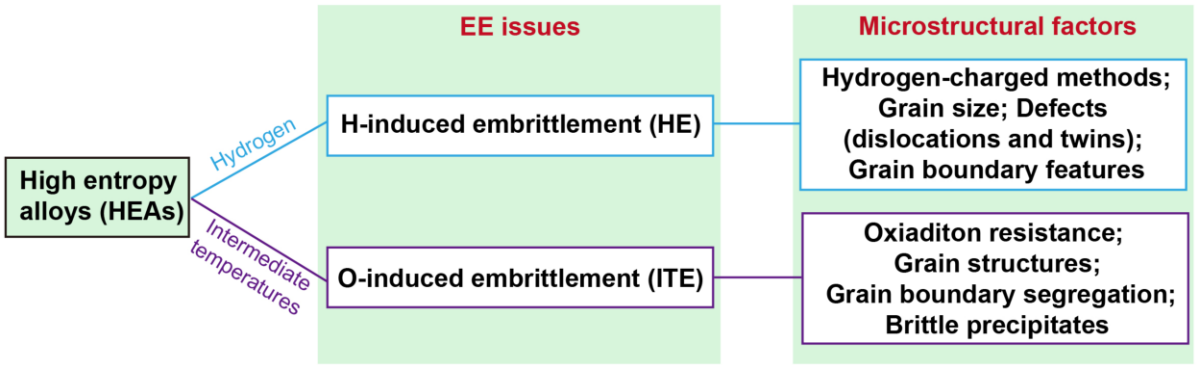

Figure 1. Schematic showing EE phenomena and associated microstructural factors. EE: Environmental embrittlement.

equiatomic CoCrNi medium entropy alloy (MEA) with ultimate tensile strength as high as ~1 GPa, as shown in Figure 2A[51]. The authors argued that the superior HE resistance is primarily attributed to the enhanced dynamic strain hardening caused by hydrogen-promoted mechanical nanotwinning [Figure 2B]. However, an inconsistent observation of this equiatomic CoCrNi MEA can be found under gas hydrogen charging, where the CoCrNi MEA displayed a pronounced ductility reduction (~70.9%) compared to the uncharged sample. Interestingly, it was further shown that boron doping (400 at. ppm) can obviously decrease the hydrogen-induced ductility loss (~45.8%) in this MEA, which is basically ascribed to the GB decoration of boron [Figure 2C-E]. The boron segregation not only significantly increases the cohesive strength of GBs but also reduces the hydrogen diffusivity along GBs, resulting in improved HE resistance[49]. Therefore, it should be noted that different hydrogen charging approaches can create distinctive mechanical responses in the same HEA. This is because hydrogen atoms are largely concentrated on the surface region of the samples via electrochemical charging, whereas hydrogen is more homogeneously distributed in the gas hydrogen-charged samples[53]. In addition to the effect of boron on the resistance to HE, it was also reported that a small addition of boron (0.2-1.6 at.%) can improve the malleability of brittle eutectic HEAs, which is primarily attributed to the transition in eutectic morphology from lamellar eutectic to dendrite eutectic. Such a transition is believed to result from the increased constitutional undercooling caused by boron additions[54].

Additionally, the HE resistance of the equiatomic CoCrNi MEA can be further enhanced via Mo doping (~3 at.%). As shown in Figure 3, Mo can promote the formation of nanotwins (NTs) in the hydrogen-charged specimen during the deformation process[55]. It was claimed that the existence of NTs can impede the local accumulation of hydrogen and disturb the continuous motion of dislocation interacting GBs, thereby inhibiting the intergranular decohesion and improving the HE resistance. Nevertheless, it is

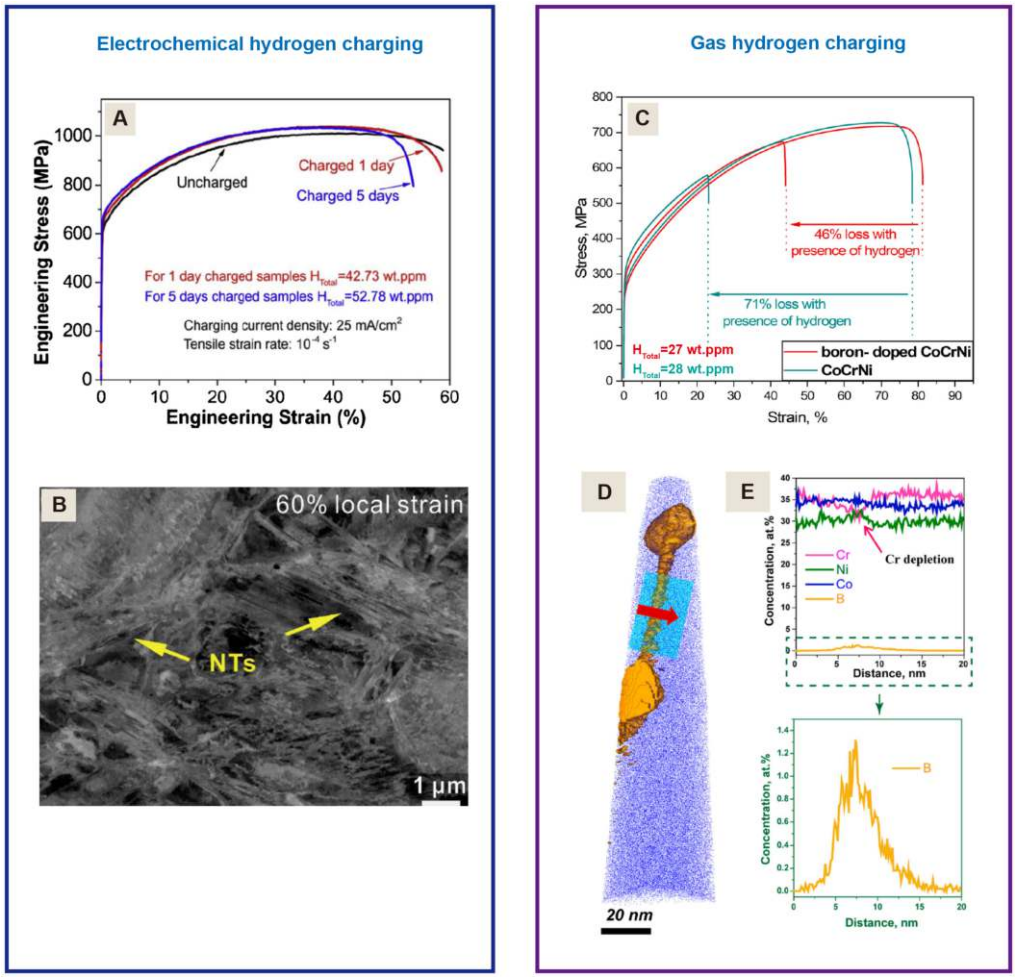

Figure 2. Tensile properties and associated mechanisms of equiatomic CoCrNi MEA under different hydrogen-charged conditions. (A) Engineering stress-strain curves under electrochemical charging. (B) Electron channeling contrast images of samples at 60% local strain levels with 5 d (52.78 wt. ppm) of hydrogen charging showing high-density NTs (Reproduced with permission[51]. Copyright 2020, Elsevier). (C) Engineering stress-strain curves of undoped and boron-doped CoCrNi MEAs under gas hydrogen charging. (D and E) Detailed reconstruction and one-dimensional composition profiles of boron-doped (400 at. ppm) CrCoNi alloy using 0.4 at.% B isosurface[49]. MEA: Medium entropy alloy; NTs: nanotwins.

noteworthy that the local chemistry of GBs has not been identified here and its effect on the improved hydrogen resistance remains elusive. More strikingly, through a combination of molecular dynamics simulations and high-resolution TEM observations, our very recent study demonstrated that an increased concentration of Fe from 2.5 to 25 at.% can effectively suppress the hydrogen-induced GB embrittlement in the Fe-Co-Cr-Ni HEA system due to the unique nanoscale segregation of Cr at the GBs. It was reported that the interfacial Cr segregation is mainly motivated by the strong repulsive force between Fe and Cr and the strong self-bonding tendency of Cr[56].

In addition to the CoCrNi MEA system, Luo *et al.* investigated the hydrogen effect on a strong and ductile CoNiV MEA under electrochemical hydrogen charging[52]. The results show that only a marginal reduction can be found in the hydrogen-charged sample, indicating the excellent HE resistance of the CoNiV MEA. Such a good combination of properties could be ascribed to four effects: (I) the single face-centered cubic (FCC) phase minimizes the local micromechanical contrast for hydrogen accumulation; (II) the solid solution elements give rise to a sluggish diffusion of hydrogen and no hydride is formed; (III) the hydrogen-

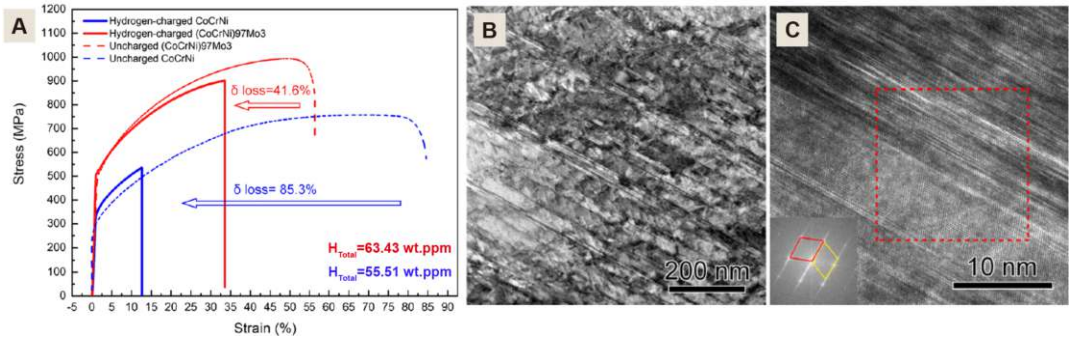

Figure 3. Superior tensile properties and deformation microstructures of hydrogen charged 97(CoCrNi)-3Mo samples. (A) Engineering stress-strain curves of Mo-doped and undoped CoCrNi alloys with and without hydrogen. (B and C) Microstructures of hydrogen-charged 97(CoCrNi)-3Mo alloy near the fracture surface showing high-density NTs. Note that hydrogen charging was performed in a 100 MPa hydrogen gas environment at 200 °C for a duration of 160 h (Reproduced with permission[55]. Copyright 2021, Elsevier). NTs: Nanotwins.

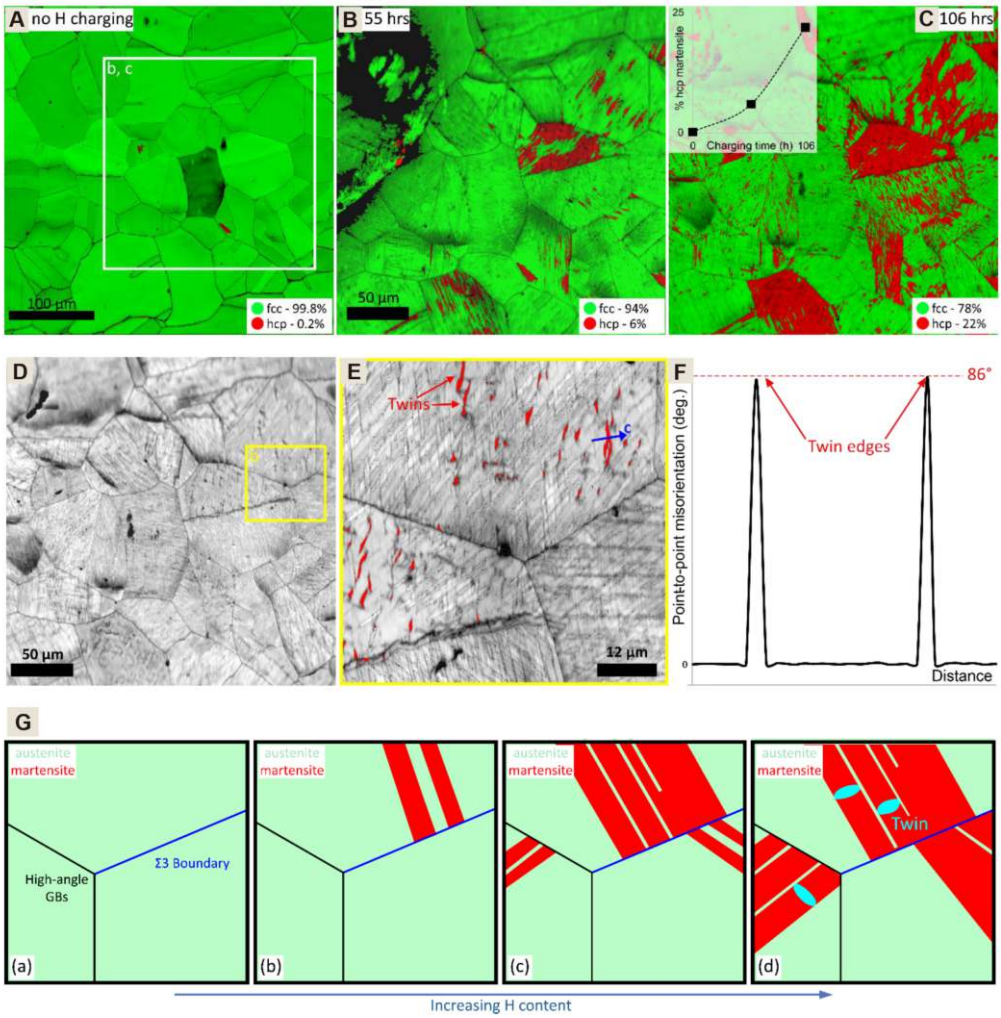

Figure 4. Hydrogen-induced phase transformations and schematic overview of metastable 45Fe-35Mn-10Co-10Cr HEA. (A-C) Electron backscatter diffraction (EBSD) phase maps of no-hydrogen charging after 55 h of hydrogen charging and 106 h of hydrogen charging. (D) Image quality map of a hydrogen-charged sample for 106 h. (E) Enlarged region with hydrogen-induced twins is highlighted in red. (F) Point-to-point misorientation across a hydrogen-induced twin[28].

induced decrease in stacking fault energy promotes the formation of NTs for increased work hardening; and (IV) the dense surface oxide film can keep the hydrogen from being absorbed and thus improves the HE resistance[52].

It is noteworthy that similar mechanisms and/or strategies (i.e., tailoring of diffusion kinetics, regulation of GB features, and so on) have been reported in other alloy systems like Al alloys and steels[57-59]. For instance, Li *et al.* simultaneously achieved the improved mechanical strength and corrosion resistance of Mg-Li-Al alloy by solid solution treatment because of the low diffusion kinetics of the solid solution phase[57]. Furthermore, the stress corrosion cracking resistance and the strength of the 7056 Al alloy with a high content of Zn were also concurrently enhanced by tailoring GB architectures (i.e., the formation of GB precipitates)[58].

In contrast to the above single-phase HEAs, Ronchi *et al.* demonstrated that hydrogen can produce a phase transformation in the metastable 45Fe-35Mn-10Co-10Cr (at.%) HEA[28]. Based on microstructural characterization [Figure 4], it was found that hydrogen induces the γ- to ε-martensite phase transformation in the metastable HEA, which preferentially occurs in the <101> and <111> oriented grains along Σ3 coincident site lattice boundaries. Additionally, high concentrations of hydrogen can promote the formation of the extension twinning within the martensite[28], which may further contribute to enhancing the HE resistance. Unfortunately, the mechanical response of the metastable HEA with hydrogen charging was not demonstrated in the study.

Additionally, the effects of hydrogen on the mechanical response and embrittlement behavior of stable and metastable HEAs (i.e., 20Fe-20Mn-20Ni-20Cr-20Co and 50Fe-30Mn-10Cr-10Co, at.%, respectively) pre-charged with 100 MPa hydrogen gases have been experimentally investigated. Figure 5A and B show the engineering stress-strain curves of the stable and metastable HEA with and without hydrogen charging, respectively. Both HEAs with hydrogen charging exhibited severe degradation in tensile plasticity. It was found that hydrogen-assisted cracking of the metastable HEA occurred via localized plasticity for both the austenite and ε-martensite phases [Figure 5C-F][60].

Moreover, regardless of electrochemical and gas hydrogen charging, the equiatomic FeCoCrNiMn HEA system shows superior resistance to HE when compared with typical steels, i.e., 304, 316L and X80[50,61,62], which is expected to be an important candidate for HE-resistant HEAs. Thereafter, extensive efforts have been devoted to further enhancing the HE resistance of the FeCoCrNiMn HEA by tailoring its architectures[50,63-65]. For example, as shown in Figure 6A, through hydrogen-induced gradient NT structures, the equiatomic FeCoCrNiMn HEA demonstrated an excellent property combination at 77 K[63]. Furthermore, the gradient-structured FeCoCrNiMn HEA shows both high yield stress (500-700 MPa) and good ductility (15%-33%) under hydrogen environments [Figure 6B], where the gradient structures containing surface NTs are introduced via the surface mechanical attrition treatment technique[66]. Additionally, it was reported that grain refinement can also contribute to improving the HE resistance of equiatomic FeCoCrNiMn and FeCoCrNi HEAs[64,65]. Specifically, the hydrogen-charged FeCoCrNiMn HEA with an average grain size of 1.9 μm exhibited a high tensile strength that was 1.5 times greater than that of the hydrogen-charged HEA with a grain size of 22 μm and there was no significant decrease in tensile elongation [Figure 6C and D][64]. Moreover, as shown in Figure 6E, incorporating the modified cellular structures by selective laser melting and annealing treatment can also effectively improve the HE resistance of the FeCoCrNiMn alloy[67]. Such excellent resistance to HE is ascribed to the delayed crack initiation and propagation by hydrogen-enhanced local plasticity with the formation of NTs and dislocation cells [Figure 6F]. These above strategies should be further explored in many other HEA systems, like CoCrNi, CoNiV, and so on.

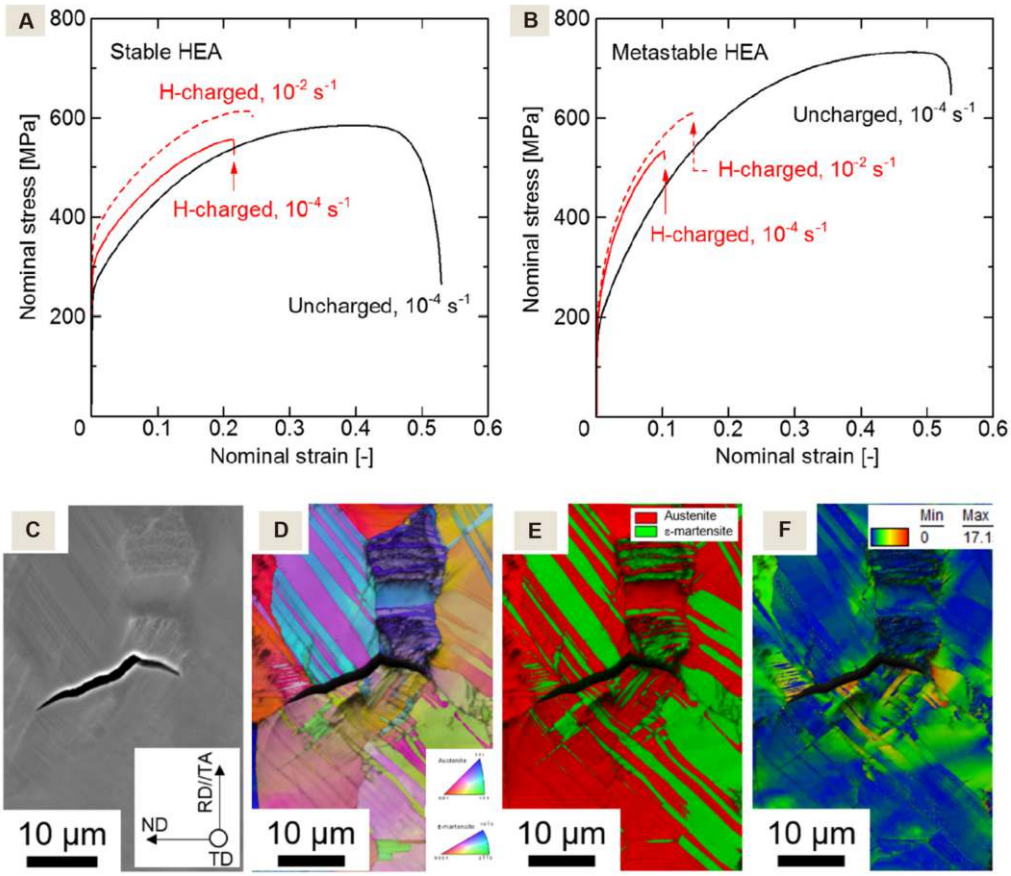

Figure 5. Tensile mechanical responses and corresponding micro-mechanisms of stable and metastable HEAs under gas hydrogen charging conditions. (A and B) Engineering stress-strain curves of stable and metastable HEAs with and without hydrogen. (C-F) Surface cracks and associated EBSD images of metastable HEA (Reproduced with permission[60].Copyright 2018, Elsevier). HEAs: High entropy alloys.

Despite the experimental evidence that HEAs exhibit excellent HE resistance, the atomic mechanisms of HE in HEA systems have further been investigated through multiscale simulations and calculations[68,69]. Zhou *et al.* presented a new theory of embrittlement in FCC metals by considering the role of hydrogen in driving an intrinsic ductile-to-brittle transition at a crack tip [Figure 7A-C][68]. This theory can be used to quantitatively predict the hydrogen concentration at which a transition to embrittlement occurs for SS304, SS316L, CoCrNi, CoNiV, CoCrFeNi and CoCrFeMnNi. For example, the predicted results show that the SS316L steel has a higher HE resistance than the CoCrFeMnNi and CoCrFeNi HEAs. The CoNiV MEA exhibits the strongest HE resistance among all the alloys [Figure 7D]. In addition, hydrogen diffusion and its interaction with dislocations also play a crucial role in the HE of HEAs. With the assistance of first-principles calculations, Xie *et al.* showed that the unique lattice distortion in HEAs causes a wide distribution of local hydrogen solution energy and the trapping of hydrogen in low-energy sites increases the diffusion barriers[69]. Furthermore, the transfer of electrons between hydrogen and metal atoms results in the reduction of unstable and stable SFEs, which contributes to the formation of deformation twins and thus increases the corresponding plasticity.

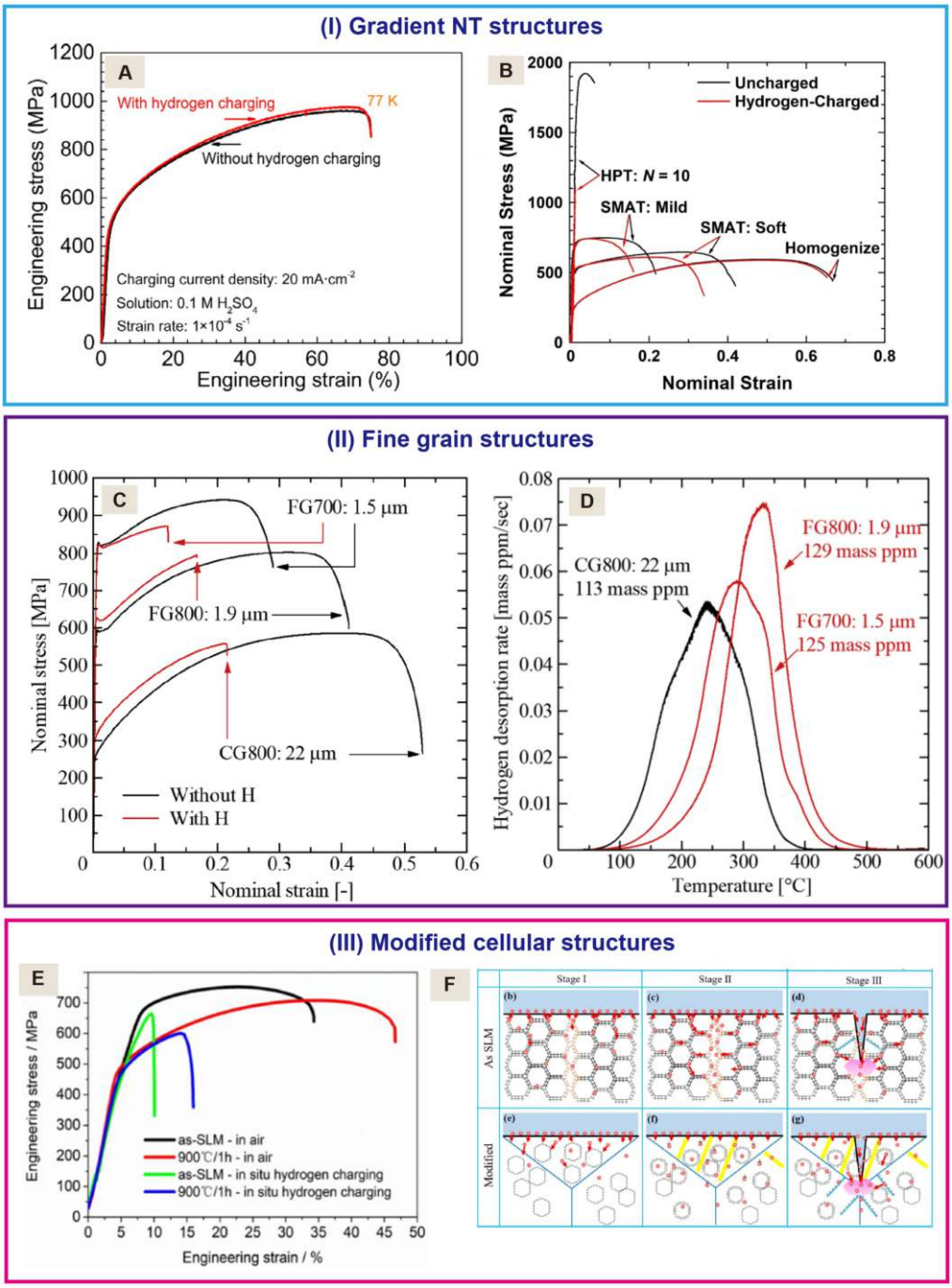

Figure 6. Enhanced HE resistance of FeCoCrNiMn HEA system via regulation of microstructural features. (A and B) Hydrogen-induced gradient NT structures (electrochemical hydrogen charging and tension) (Reproduced with permission[63]. Copyright 2018, Elsevier) (Reproduced with permission[66]. Copyright 2022, Elsevier). (C and D) Fine grain structures (gas hydrogen charging and tension) (Reproduced with permission[64]. Copyright 2019, Elsevier). (E and F) Modified cellular structures (electrochemical hydrogen charging and tension) (Reproduced with permission[67]. Copyright 2021, Elsevier). HE: Hydrogen embrittlement; HEA: high entropy alloy.

ITE MECHANISMS AND STRATEGIES FOR HEA SYSTEMS

In this section, the significant progress in the design of ITE-resistant HEAs and the associated underlying dominant mechanisms are summarized. Among recently developed HEA systems, it has been extensively

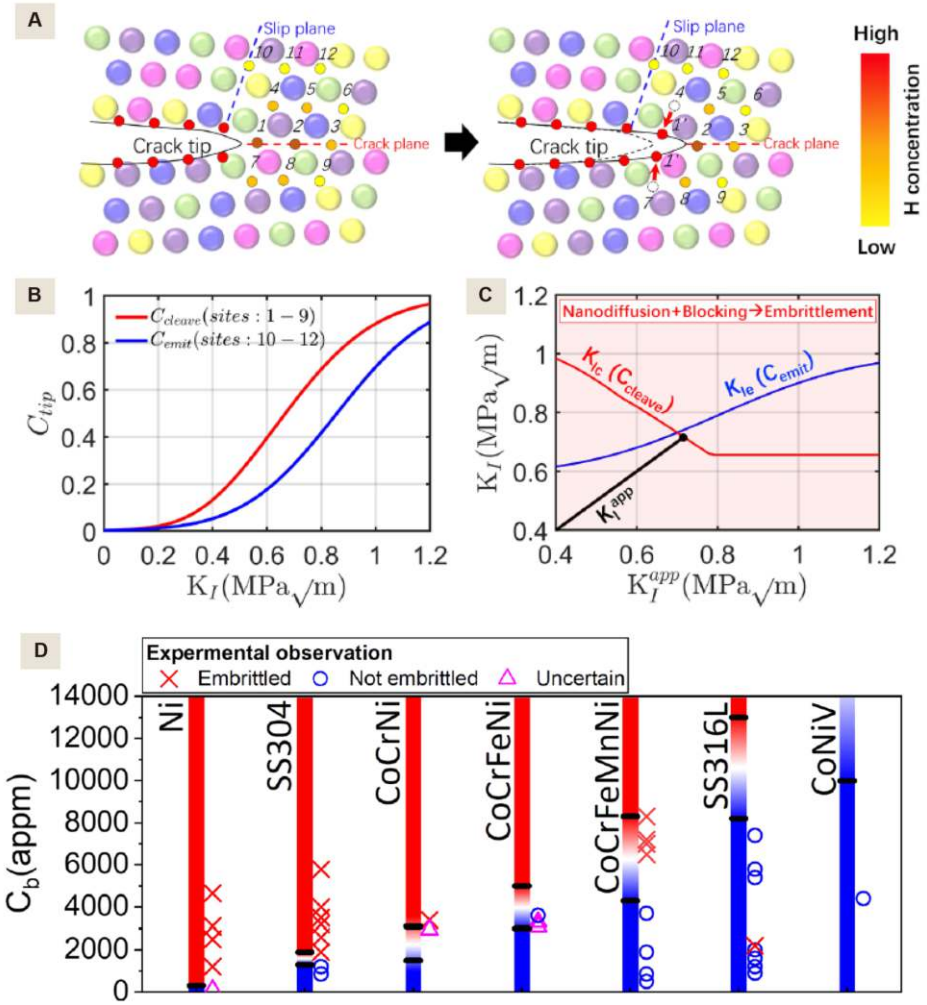

Figure 7. Mechanism and prediction of HE in various alloy systems. (A) Schematic of embrittlement process at crack tip. (B) Schematic of crack tip hydrogen concentrations C_{cleave} and C_{emit} that control embrittlement as a function of KI^{app}. (C) Predicted embrittlement due to nanodiffusion and blocking of dislocation emission: KI^{app} reaches *KIC* prior to reaching K_{Ie}. (D) Predicted embrittled and unembrittled domains of hydrogen concentration for six alloys and Ni. The transition region corresponding to the upper and lower limits of K_{Ie} is indicated by thick black lines (Reproduced with permission[68]. Copyright 2021, American Physical Society). HE: Hydrogen embrittlement.

recognized that coherent $L1_2$-type precipitate-strengthened HEAs are some of the most promising candidates for high-temperature structural applications due to their exceptional thermal and mechanical properties at a wide range of temperatures[20,70-72]. Unfortunately, like many high-strength metallic structural materials, such $L1_2$-strengthened HEAs also usually exhibit temperature-dependent premature tensile failure. As shown in Figure 8, it has been claimed that environmentally (i.e., oxygen)-assisted GB damage plays a vital role in premature intergranular failure at intermediate-temperature regimes[39,73]. Additionally, the potentially formed second phases at GBs also act as sites for crack initiation and propagation, leading to brittle intergranular fracture during tensile deformation[39].

Therefore, extensive efforts have been made to overcome this ITE issue in these $L1_2$-strengthened HEAs. Several advances have demonstrated that the ITE resistance can be effectively improved in some typical HEA systems through careful compositional optimization and structural regulation. For the former, it was found that Cr doping can introduce compact protective oxide layers in a 39.9Ni-20Co-(30-x)Fe-xCr-6Al-

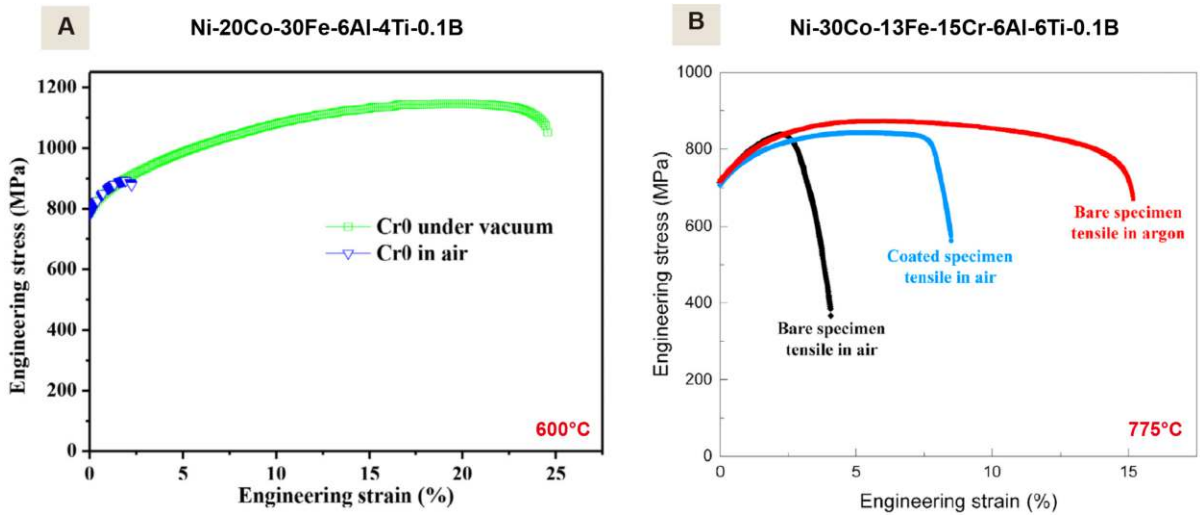

Figure 8. Oxygen-assisted failure mechanism in various HEA systems at intermediate-temperature regimes. Tensile curves of (A) Ni-20Co-30Fe-6Al-4Ti-0.1B (at.%) HEA at 600 °C in air and vacuum conditions (Reproduced with permission[73]. Copyright 2022, Elsevier) and (B) Ni-30Co-13Fe-15Cr-6Al-6Ti-0.1B (at.%) HEA at 775 °C with different surface treatments and testing environments (Reproduced with permission[39]. Copyright 2022, Elsevier). HEA: High entropy alloy.

4Ti-0.1B (at.%) HEA, which not only improves the oxidation resistance of the HEA but also hinders the inward oxygen diffusion and thus results in a substantial increase in tensile plasticity at 600 °C [Figure 9A and B][73]. This suggests that enhancing oxidation resistance via tailoring the chemical composition is a useful pathway for the innovation of ITE-resistant HEAs. Moreover, for the latter, our previous work[26] innovatively proposed a duplex-aging strategy in an $L1_2$-strengthened 39.9Ni-30Co-13Fe-15Cr-6Al-6Ti-0.1B (at.%) HEA. Such a duplex-aging strategy can controllably eliminate the intergranular brittle phases, the so-called Heusler phase, therefore achieving a distinct brittle-to-ductile transition at 700 °C, as shown in Figure 9C. More strikingly, Cao *et al.* designed a heterogeneous columnar-grained (HCG) structure in the 39.9Ni-30Co-13Fe-15Cr-6Al-6Ti-0.1B (at. %) HEA via regulating thermomechanical treatments[74]. This new type of HCG HEA exhibits superior resistance to intergranular fracture at 800 °C compared with the equiaxed counterpart with severe brittleness along GBs, which could be originated from the unique GB characteristics and distributions in the HCG HEA. Specifically, the HCG HEA shows an unusually large tensile ductility of ~18.4% combined with a high yield strength of ~652 MPa at 800 °C, as demonstrated in Figure 9D.

In addition, it is noteworthy that the serrated grain boundary (SEG) architectures can effectively solve this intergranular premature cracking issue in an $L1_2$-strengthened HEA (46.23Ni-23Co-10Cr-5Fe-8.5Al-4Ti-2W-1Mo-0.15C-0.1B-0.02Zr, at.%) at 1000 °C. This kind of HEA with SEG structures shows a brittle-to-ductile transition and achieves a superior strength as high as ~260 MPa while maintaining a uniform elongation of ~6.5% [Figure 10][75]. This finding further demonstrates that SEGs can produce enhanced resistance to intergranular crack nucleation and propagation at higher temperatures.

In addition to intergranular embrittlement in the intermediate-temperature regimes, some refractory HEAs also suffer from obvious brittleness at room temperature[76], which is essentially attributed to the GB segregation of the oxygen contaminant during fabrication, thereby weakening GB cohesion. Wang *et al.* reported that GB engineering with the addition of either metalloid B or C in a NbMoTaW refractory HEA can effectively alleviate the GB brittleness and changes the fracture morphology from intergranular to transgranular fracture[76]. The doped small-sized metalloids preferentially replace oxygen at GBs and

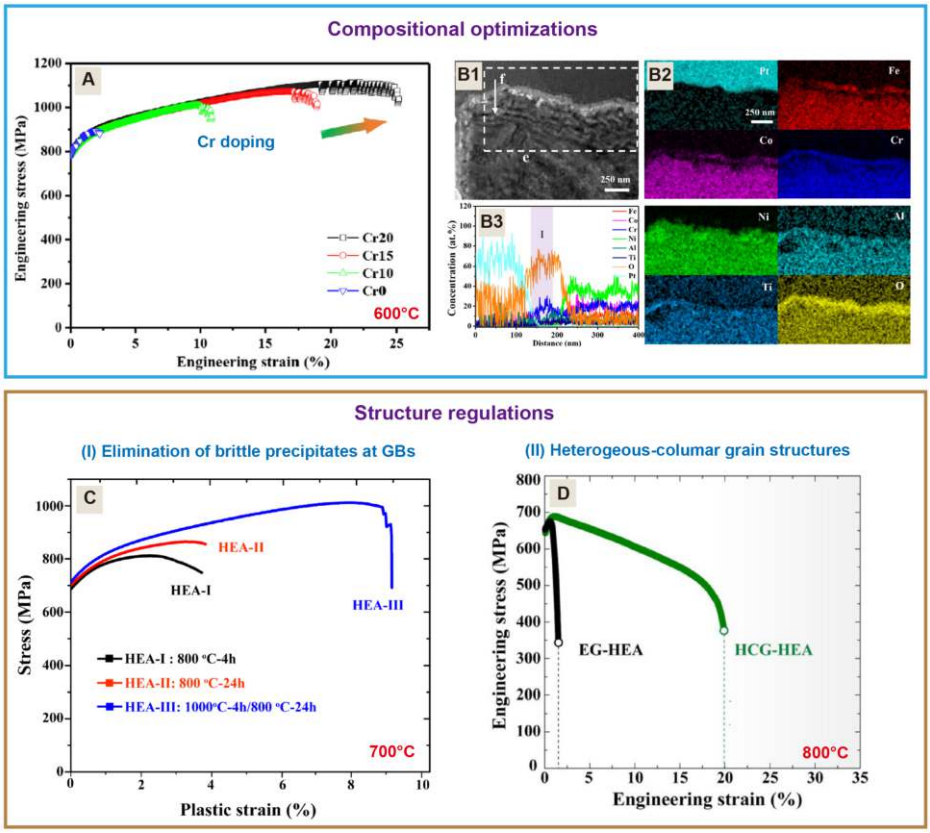

Figure 9. Overcoming ITE phenomena in $L1_2$-strengthened HEAs under tensile deformation via compositional optimization and structural regulation. (A) Cr doping enhanced tensile ductility at 600 °C. (B) Compact protective oxide layers introduced by the addition of Cr (Reproduced with permission[73]. Copyright 2022, Elsevier). (C) Elimination of brittle precipitates (Heusler phases) at GBs via a duplex-aging treatment (Reproduced with permission[26]. Copyright 2020, Elsevier). (D) Incorporation of heterogenous-columnar grain structures by controlling recrystallization durations (Reproduced with permission[74]. Copyright 2021, Elsevier). HEAs: High entropy alloys; ITE: intermediate-temperature embrittlement.

promote stronger electronic interaction with the host metals [Figure 11][76]. As earlier, a similar strategy has been reported to improve the HE resistance because of boron segregation at GBs[49].

OUTLOOK AND FUTURE WORK

As a new class of structural materials, HEAs have demonstrated distinctive microstructural architectures and promising mechanical properties, which hold significant potential for a wide of engineering applications. As summarized above, when exposed to hydrogen and/or immediate-temperature environments, these HEAs often display a serious premature embrittlement issue, like HE and/or ITE, raising enormous challenges for their practical structural applications. In this situation, more fundamental and comprehensive studies should be systematically carried out to further promote the innovation of novel high-performance HEAs together with superior EE resistance. Here, we briefly summarize several crucial issues and give some research directions on advanced structural HEAs with extraordinary EE resistance for future work.

(1) Previous efforts have been primarily focused on the development of HE-resistant steels and Al alloys[30,42,77]. The discovery of the HEAs opens a new pathway for the design of HE-resistant alloys, especially for single-phase NiCoCr and FeCoCrNiMn. However, unlike conventional alloys, such HEA

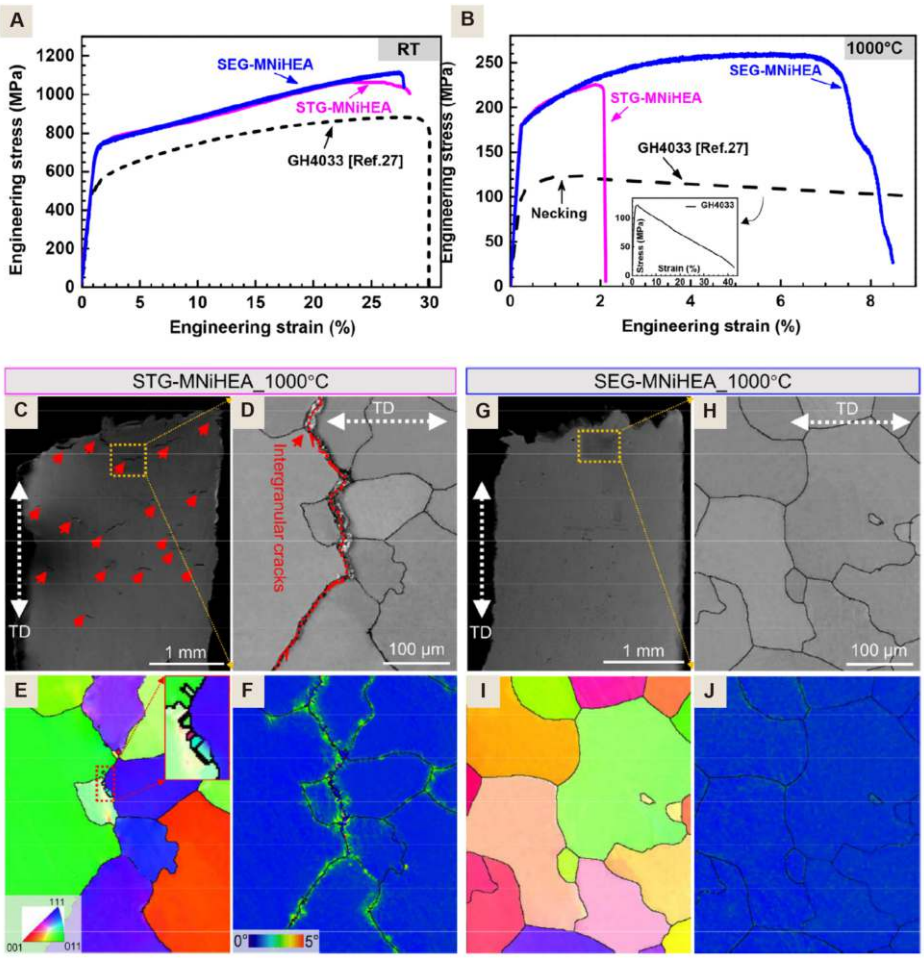

Figure 10. Tensile properties of straight grain boundary (STG)-MNiHEA and SEG-MNiHEA samples at (A) room temperature and (B) 1000 °C. Microstructures of fracture surfaces in STG-MNiHEA and SEG-MNiHEA tensioned at 1000 °C: (C and G) scanning electron microscopy images; (D and H) EBSD band contrast maps; (E and I) inverse pole figure map; (F and J) Kernal-angle misorientation maps (Reproduced with permission[75]. Copyright 2021, Elsevier).

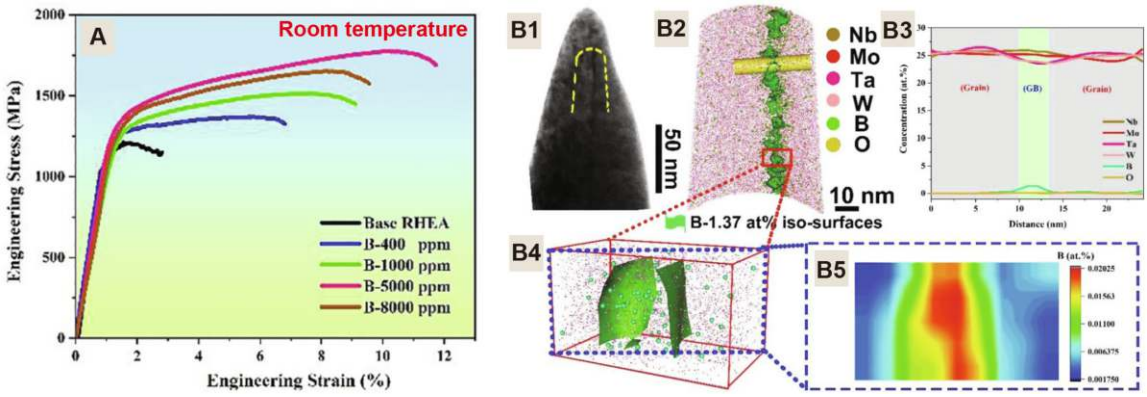

Figure 11. (A) Stress-strain curves of as-cast base refractory HEA (black) and doped HEAs with different contents of boron at room temperature under compression. (B) One-dimensional concentration profiles across a GB for the 5000 ppm (0.5 at.%) doped refractory HEA (Reproduced with permission[76]. Copyright 2022, Elsevier). HEAs: High entropy alloys.

systems exhibit complex structures and substantial compositional constitutions, which could significantly influence hydrogen diffusion and the associated mechanical responses. Therefore, the effects of structures (i.e., phase structures, vacancies and dislocations) and constitutions (substitutional and interstitial atoms) in HEAs on hydrogen-induced mechanical behavior and the underlying mechanisms should be carefully studied. Notably, a quantitative model has been proposed by Nag *et al.* and Kamachali *et al.*, which demonstrated that the solute-solute interactions and internal stresses can significantly affect the thermodynamic properties and strengthening mechanisms of HEA systems[78,79]. If the H atoms are incorporated into the HEAs with highly-diverse chemistries, the effects of complex chemistry on the mechanical responses and deformation mechanisms in the HEAs with H atoms should be experimentally and theoretically carried out. The role of complex chemistry in the formation of "surfaces" in crack formation and propagation also needs to be explored.

(2) As earlier demonstrated, hydrogen atoms are preferentially partitioned into GBs and then reduce the cohesive strength of GBs. Therefore, the structural features of GBs play a key role in determining the HE resistance of alloys. Based on this, it could be an effective routine to achieve enhanced HE resistance in HEAs via elaborately designing the GB architectures (e.g., introducing precipitates at GBs and creating GB segregation). Therefore, further research should be focused on the innovative design of novel GB structures in the HEAs.

(3) For HE-resistant materials, hydrogen local concentration is a critical parameter in governing the resistance to HE. When exposed to hydrogen environments for sufficient durations, a low hydrogen concentration stems basically from low hydrogen solubility and sluggish hydrogen diffusion in most metallic alloy systems. Therefore, the effect of a specific element on hydrogen solubility and hydrogen diffusion in different HEA systems should be systematically investigated. We believe that studies along this direction could help to significantly accelerate the design of HEAs that are intrinsically resistant to HE.

(4) It is well known that atomic-scale microstructural traps can substantially limit hydrogen diffusion. For instance, Chen *et al.* showed that hydrogen can be trapped in the core of finely dispersed V-Mo-Nb carbides in ferritic steels[30]. Furthermore, it was also reported that hydrogen concentration is observed at carbon-rich dislocations and incoherent interfaces between niobium carbides and the surrounding steel[80]. Therefore, it could be an effective strategy to enhance the resistance to HE in HEAs via engineering hydrogen traps, i.e., nanoscale carbides and low-energy dislocation nanostructures[81]. In addition, state-of-the-art microstructural characterization techniques like cryogenic atom probe tomography should be employed to directly observe the hydrogen distribution of HEA systems.

(5) Similar to Ni-based superalloys, $L1_2$-strengthened HEAs have shown significant promise in high-temperature applications. However, it has been recognized that oxygen-assisted GB damage plays an important role in the ITE issue. Therefore, improving oxidation resistance may be an efficient avenue that can hinder the oxygen-accelerated GB damage. Furthermore, as earlier reported, serrated GBs and columnar-like grains can effectively address the ITE issues. It should be noted that such unique GB structures can greatly reduce the diffusion kinetics of the oxygen and then delay intergranular cracking. As a result, careful tailoring of GB features should be carried out to further improve the resistance to ITE in HEAs. In contrast, it has been recognized that creating hydrogen traps and reducing diffusion kinetics can effectively improve the resistance to HE. We expect that $L1_2$-strengthened HEAs with unique GB features are also highly HE resistant, owing to the suppressed diffusion kinetics (serrated GBs and columnar-like grains) and high-density hydrogen traps ($L1_2$/matrix interfaces).

(6) At the present time, studies are mainly focused on the static tensile properties of the HEAs with hydrogen charging and intermediate temperatures. More importantly, the dynamic mechanical properties (fatigue, creep and fatigue/creep crack propagation) should be evaluated under *in-situ* hydrogen gas charging environments and intermediate temperatures. Subsequently, associated physical-based lifetime prediction models of HEAs should be developed. These studies are expected to ensure the reliability and safety of EE-resistant HEAs in engineering applications.

CONCLUSIONS

HEAs have received growing interest from metallurgical scientists and engineers due to their special microstructures and superb mechanical properties, which can potentially be used in many important engineering fields, including aerospace, nuclear power and chemical processing applications. In the present work, we have critically reviewed the recent major achievements in EE behavior and the associated underlying mechanisms of HEAs. In particular, two critical EE phenomena (HE and ITE) have been separately summarized. The representative HE- and ITE-resistant HEAs and the corresponding micro-mechanisms have been discussed in detail. Although some advances have been achieved, research on this topic is only just starting to develop at present and there are numerous unaddressed critical issues. In future work, to further accelerate the design of novel HEAs with superior resistance to HE and/or ITE, significant efforts should be made to fundamentally elucidate the hydrogen (oxygen) diffusion behavior and associated static/dynamic mechanical responses of HEAs. In the meantime, compositional optimization and structural regulation should be systematically studied to improve the resistance to HE and ITE of HEAs. Finally, atomic-scale microstructural characterizations are required to directly observe the hydrogen distribution and better understand the HE mechanism in HEA systems.

DECLARATIONS

Authors' contributions

Organized the literature review and drafted the original version: Xiao B, Yang T
Revised the manuscript: Liu S, Zhang J, Zhou Y, Li Q, Hou J, Xiao W, Zhang J, Zhao Y, Liu CT, Xu L
Conceived and supervised the project: Yang T, Zhao Y

Availability of data and materials

Not applicable.

Financial support and sponsorship

This project was financially supported by the Hong Kong Research Grant Council (RGC) (Grant No. CityU 21205621, 11214820, 11209021, and C1017-21G), the National Natural Science Foundation of China (Grant No. 52101151 and 52101135), and the Shenzhen Science and Technology Program (Grant No. SGDX20210823104002016 and RCBS20210609103202012).

Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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