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Topical Review

Properties and processing technologies of high-entropy alloys

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Abstract

High-entropy alloys (HEAs) are emerging materials that are developed based on entropy, and draw significant attention for the potential to design their chemical disorder to bring out different structural and physical characteristics. Over the past two decades, significant salient efforts have been conducted to explore many unique and useful properties of HEAs, such as overcoming the strength–ductility trade-off, outstanding thermal stability, and excellent low temperature plasticity. Here, we review the key research topic of HEAs in the following three aspects: (a) performance advantages and composition design, (b) performance-driven HEAs and (c) fabrication process-driven HEAs. Towards their industrial applications, our article reviews a large range of methods to synthesise, fabricate and process HEAs. We also discuss the current challenges and future opportunities, mainly focusing on performance breakthroughs in HEAs.

Keywords: high-entropy alloys, review, order and disorder, properties, processing

1. Introduction

Entropy is an important physical parameter that reflects the disordered state of a certain system. High-entropy alloys (HEAs) are typical materials developed based on entropy, and draw significant interest. In the past few decades, the development of HEAs has provided a novel philosophy for alloy design [1–3]. The multi-component system, occupying the center regions of phase diagrams, was proposed in 2004 and then known for excellent properties. In contrast with traditional alloys composed of one principal element, HEAs have equimolar or near-equimolar atomic fractions of multiple constituents (generally more than four components), and have drawn extensive attention in their interesting physical, chemical, and structural characteristics [4, 5].

The entropy of a material system usually mainly includes configuration entropy, vibration entropy, magnetic entropy, thermal entropy, etc. For solid-solution, the configuration entropy caused by the mixing of different atoms is the primary consideration [6]. In order to simplify the calculation, the regular solution model is usually used to derive the mixed entropy of the HEAs in the state of random mutual dissolution [7]. The calculation formula is as follows:

$$\Delta S_{\mathrm{mix}} = -R\sum_{i=1}^{n}(c_i \ln c_i) \quad (1)$$

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Future perspectives

As an emerging material, the unique characteristics of high-entropy alloys (HEAs) in dynamics, thermodynamics, and structure have aroused great interest. The ability of HEAs to be designed with unique properties in an unlimited space of alloy compositions is encouraging. To date, many salient efforts have been made with HEAs which demonstrated many attractive properties that break the limits of traditional materials. In the future development of HEAs, we would like to highlight several perspectives as follows:

(a) For the property. Besides the current efforts on breaking the trade-off between strength and ductility and breaking the properties limits of traditional materials, we would like to propose a trade-off between the mechanical properties and the physical properties, such as deformability and soft magnetic properties, thermal stability and mechanical properties stability. Generally, the functional properties are available from traditional materials. However, traditional materials usually fail to function well at extreme conditions, especially with destabilization of mechanical properties. Briefly, developing HEAs with a unique combination of mechanical properties and physical properties is a key point for future development.
(b) For the processing technology. Developing HEAs that are suitable for a wide range of preparation and deformation techniques should be one of the future research projects in HEAs, such as HEAs suitable for casting, HEAs suitable for deformation processing, and HEAs suitable for additive manufacturing. This issue has important significance for promoting industrial applications of HEAs.
(c) Understanding of entropy. Recently, researchers have used Shannon entropy to explain HEAs, in an effort to reveal the information content that is encoded in various local atomic arrangements. In the future, the introduction of Shannon entropy to HEAs may be able to offer a new pathway to describe more atomic details of HEAs, and inspire unknown landscapes.

where, the R is the gas constant ($R = 8.314$ J mol^{-1} K^{-1}); n is the number of alloy components; c_i is the content of the ith component (at. %). When the atomic ratios of the components are equal, the maximum value of mixing entropy is obtained. The novel design concept gives many unique characteristics for HEAs, including high-entropy effects (thermodynamics), sluggish diffusion (kinetics), severe lattice distortion (structures) and cocktail effects (properties) [5, 8].

With the development of HEAs, the definition has been continuously improved and innovated. Currently, the HEAs can be loosely divided into two generations [4, 9]: the first-generation alloys generally show a single solid-solution structure and contain more than five principal elements in equal atomic ratio, and the second-generation alloys show non-equimolar components and multiple phases. Judging by its popularity in the literature, we suspect that the development of HEAs is not aimed at matching the definition, but by regulating entropy to adjust the composition and obtain unique material properties [10]. Therefore, the term 'high entropy' no longer refers to the numerical value of entropy, but also reflects the disordered state of a certain alloy system. In this case, the concept of 'high-entropy' has been successfully applied to traditional alloy systems, such as aluminum alloys [11], superalloys [12–14] and amorphous alloys [15–17]. In recent years, many other new high-entropy materials have attracted more attention, such as high-entropy ceramics [10, 18], high-entropy wires [19–21], high-entropy films [22–25], high-entropy sheets [26], high-entropy composites [27] and high-entropy powder [28].

As reported, HEAs have shown great possibilities in developing outstanding properties that break the limits of traditional alloys, including overcoming the strength–ductility trade-off [29–31], outstanding thermal stability [32, 33], good irradiation [34–36] and corrosion resistance [37, 38], and attractive low temperature plasticity [39]. Furthermore, another concern here is the preparation process of HEAs. Many preparation methods for HEAs are commonly used in traditional materials. Actually, multiple components in HEAs generally possess various physical and chemical characteristics (melting point, oxidation resistance, reduction potential difference, and magnetic properties, etc), which make a huge challenge for developing novel preparation methods. For example, in the fabrication of HEA powder for additive manufacturing, the high alloying content of Ti or Zr elements in HEAs makes it difficult to prevent the alloy powder from being oxidized, thereby deteriorating performance. Moreover, for the electrodeposited HEAs, it is difficult to deposit multiple elements simultaneously, due to different potential of components and complexity of electrolytes. Currently, many efforts are focused on performance explorations, not process development. The development of mature and feasible preparation processes is also a key issue to make HEAs potential structural materials in a wide variety of technological applications.

In this review, we present some key research topics for HEAs, such as the unique properties, performance advantages, and many novel mechanisms. Furthermore, we discuss HEAs from three aspects: (a) performance-driven HEAs: focusing on various outstanding properties and mechanisms; (b) process-driven HEAs: highlighting the current preparation methods for HEAs; (c) composition design of HEAs: A method for designing HEAs with specific characteristics is proposed, namely 'Trilogy of Alloy Composition Design', which includes machine learning, calculation and simulation, and an experimental combinatorial pathway.

2. Classification and advantages

2.1. Categories from different dimensions

As of now, many works have reported various preparation technologies to fabricate different forms of HEAs, such as general melting, additive manufacturing, film and coating technologies. To clearly summarize the preparation process of HEAs with different forms, we try to classify the HEAs in terms of different dimensions. As shown in figure 1, it mainly classified into three-dimensional (3D) bulk materials, two-dimensional (2D) film and sheet materials, one-dimensional (1D) fiber

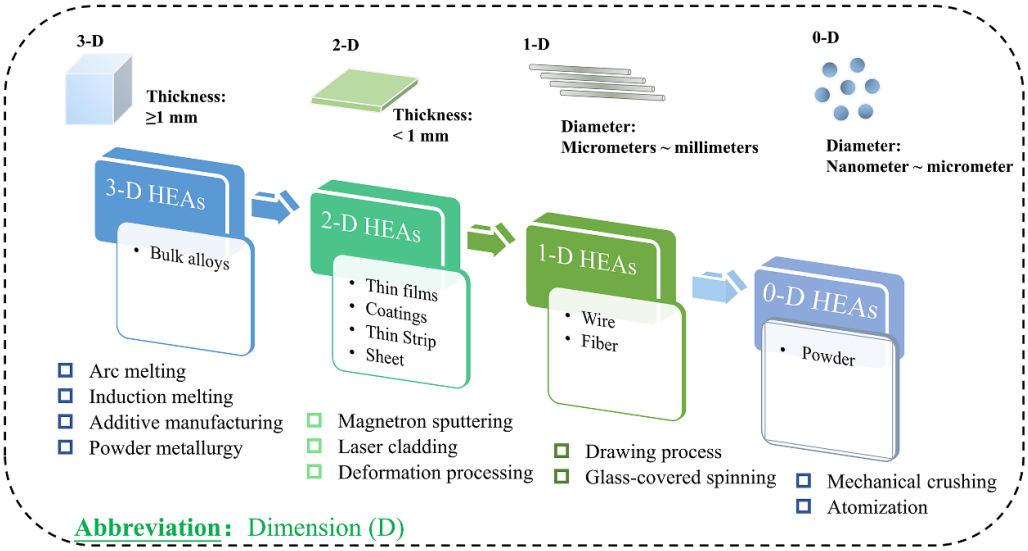


Figure 1. Classification and general preparation methods of HEAs with different dimensions.

materials, and zero-dimensional (0D) powder materials. The 3D HEAs, mainly containing bulk alloys, are generally fabricated by alloy melting, additive manufacturing, and sintering methods, with a weight from several grams to tens of kilograms. According to thickness, the 2D HEAs also can be divided into thin films, coating, sheet, and thin strip. For 1D HEAs, it mainly refers to high-entropy wire and fiber, which is generally obtained by the drawing method and glass covered spinning method. Due to its unique performance combinations, high-entropy wire and fiber are one of the recent research hotspots. Moreover, the high-entropy powders, a kind of 0D HEA, are generally used as raw materials for powder metallurgy and additive manufacturing, as well as a novel catalyst for functional applications [40, 41].

2.2. Performance advantages

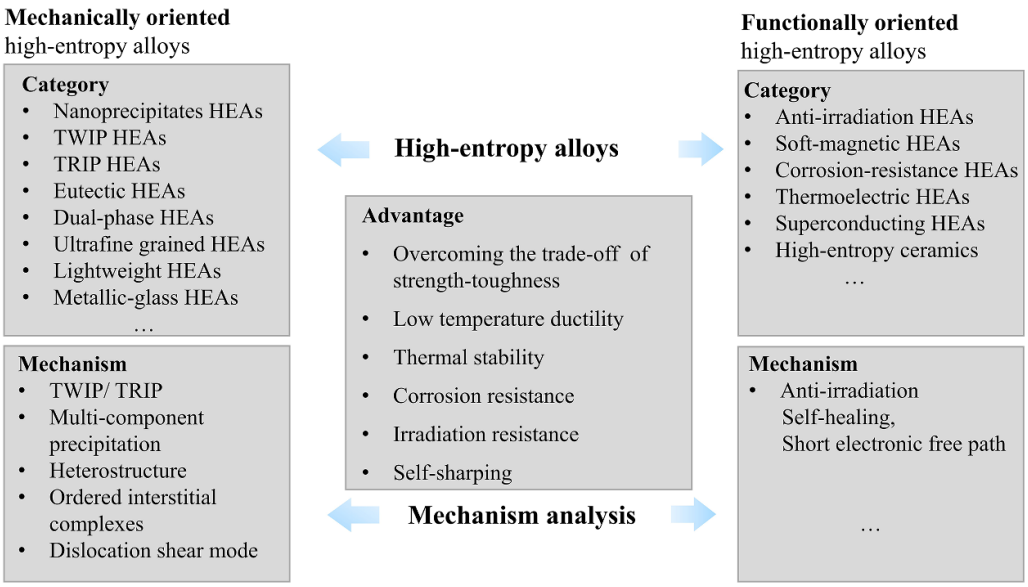
The unique characteristics of HEAs in thermodynamics, kinetics, structure and performance have inspired many excellent properties that can break through the limits of traditional materials. As shown in figure 2, Yan and Zhang summarized the five advantages of HEAs which have been proven by many published works [36]. Here, we want to briefly discuss the related mechanisms for these attractive performances.

2.2.1. Overcoming the strength–ductility trade-off. The solid-solution structure in HEAs is more concentrated than that of traditional alloys, which causes significant solid solution strengthening effect. Moreover, the severe lattice distortion, a core effect in the design of HEAs, has been proven to effectively improve both yield stress and sensitivity to grain size. In this case, fine grain strengthening effect plays a more positive role in HEAs, which improving strength as well as optimizing the deformation stability. On the other hand, taking advantage of wide compositional space, tailoring the stability of the constituent phases in HEAs is also a key approach for breaking the strength–ductility trade-off, which mainly includes designing phase transformation, twinning, and regulating the chemical short-order and nanoprecipitates. Especially for designing transformation/twinning-induced plasticity, it has been proven that it not only improves the strength by enhancing trans-grain and inter-grain slip resistance, but also increases the strain hardening capacity, and hence, increases ductility.

2.2.2. Low temperature ductility. HEAs with fcc structure show excellent mechanical properties under low temperature, such as CoCrFeMnNi alloy [42] (Cantor alloy), CoCrFeNi alloy [39], and $Al_{0.3}$CoCrFeNi fiber [19]. Such unconventional performance, 'the lower the temperature, the stronger and tougher the alloy', is mainly attributed to the low stacking fault energy (SFE) of fcc HEAs. Liu *et al* prosed that the lower SFE of CoCrFeNi at the liquid-helium temperature directly facilitates the formation of abundant twins [39]. The deformation twinning derives from the FCC to HCP phase transformation, which enables the highly-effective-defects (twin boundaries, phase interfaces, and dislocations) storage, microstructure refinement (intersecting twins and subdivision of grains).

2.2.3. Thermal stability. Severe lattice distortion caused by multiple components and complex interaction between the different atoms will seriously affect the co-operative diffusion, thereby limiting the diffusion rate in HEAs. The slow co-diffusion effect slows down the phase transition rate, hinders grain growth, and further improves creep resistance.

2.2.4. Corrosion resistance. It can be attributed to the synergistic effect of slow diffusion, easy design of amorphous and nanocrystalline structure, and strong passivation layers formed by doping with high content of elements.



Abbreviations: Twinning-induced plasticity (TWIP), Transformation-induced plasticity (TRIP).

Figure 2. The advantages and mechanisms of HEAs. Reproduced and adapted with permission from [36]. Copyright 2020 Acta Materialia Inc. Published by Elsevier Ltd.

2.2.5. Irradiation resistance. Effective self-healing mechanisms in HEAs are key factors, which can be discussed from three aspects [36, 43–45]. Firstly, motion path of the interstitial atoms is totally different with conventional alloys. The short-range 3D motion of interstitial clusters in HEAs significantly increases the probability of vacancy-interstitial recombination, thereby reducing the defect density and void swelling. Secondly, high atomic-level stresses in HEAs destabilize the solid solution facilitating amorphization. Thermal spikes caused by particle irradiation bring local melting and recrystallization, which improve the orderliness of alloys, and reduce the densities of defects. Furthermore, the electron mean free path decreases significantly with the increase of component elements, which means a lower energy consumption efficiency in HEAs. This action can prolong thermal spike and promotes the recovery from the injured state.

3. Composition design of high-entropy alloys

3.1. Research frequency of different alloy systems

Compared with the conventional alloys, the composition design of HEAs is more complex and diverse. Based on the reported works, we summarize the alloy systems of HEAs that have been developed so far. Taking the 'component number' and 'frequency of research' as *Y* axis, respectively, 47 different alloy systems have been counted and classified by Python, as shown in figure 3. For HEAs, the five-component alloy systems account for the largest proportion, followed by quaternary alloys. Among them, CoCrFeMnNi (i.e. the Cantor alloy) has been studied and published the most times, more than 7000 times. The AlCoCrFeNi and CoCrFeNi alloy systems are also two of the most researched alloy systems. It should be noted that, each alloy system usually contains many different compositions, as well as various structures and performances. How to choose ideal alloys in such a large compositional space is a huge challenge for researchers.

3.2. Trilogy of composition design for high-entropy alloys

Compared with conventional alloys, the composition design of HEAs is more complex and diverse due to their entropic characteristic. In fact, in addition to relying on experimental verification, machine learning, calculation, and simulation are also effective methods for designing HEAs. Here, we propose a systematic design pathway of HEAs, namely 'trilogy of composition design', including (a) machine learning, (b) empirical models and calculations, and (c) combinatorial experimental approaches, as shown in figure 4. It is expected that 'trilogy of composition design' can help us obtain interested HEAs in a short time span and pave the way for designing and synthesizing entropic alloys with intriguing properties.

The machine learning is generally conducted based on the reported results. Data analytics and machine learning can help effectively achieve rapid screening in vast compositional space. Steingrimsson *et al* have successfully predicted temperature-dependent ultimate strengths of bcc HEAs via machine learning [46]. They proposed a bilinear log model for predicting the ultimate strengths of HEAs under different temperatures, evaluating effectiveness by 21 compositions. Briefly, machine learning can help us effectively organize the data in a meaningful fashion and extract complex, hidden relationships.

For calculation and simulation, it mainly contains empirical models, first-principles calculations, and calculation of phase diagrams (CALPHAD), which can help for predicting the phase formation and properties in various conditions [47, 48].

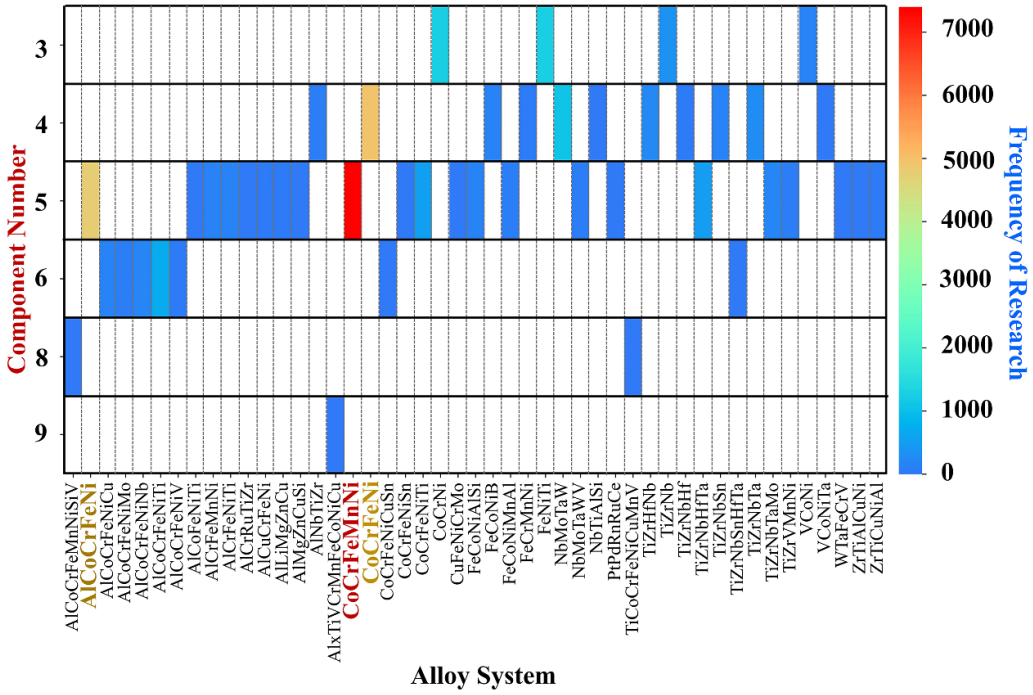


Figure 3. Statistics of research frequency and component number of different HEA systems based on Python language.

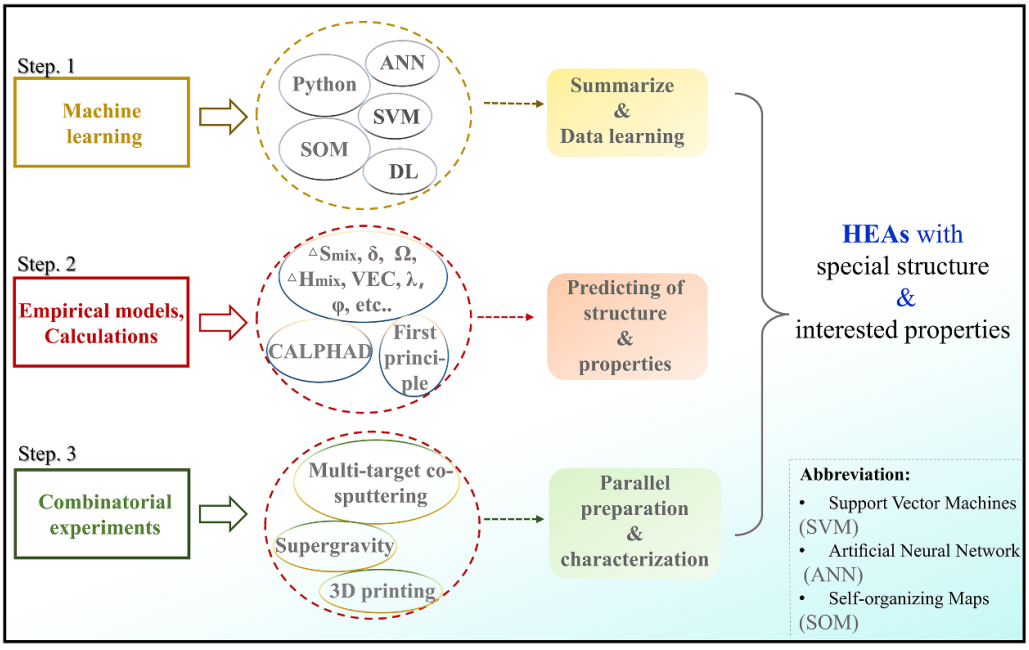


Figure 4. Schematic diagram of 'trilogy of composition design for HEAs'.

The CALPHAD method is based on Gibbs–Helmholtz free-energy formulations to derive equilibrium-phase of each phase. The CALPHAD method allows the identification of co-existing phases as well as their compositions and volume fractions. Gorsse and Senkov have examined the limitations of CALPHAD databases applied to HEAs, and concluded that it is still sufficient to correctly predict thermodynamic properties of quaternary alloy systems [47]. Ye *et al* have successfully predicted the formation possibility of a $(Zr_{0.25}Nb_{0.25}Ti_{0.25}V_{0.25})C$ high-entropy ceramics by the first-principles calculations and thermodynamical analysis [49]. The calculation results showed that the high-entropy ceramics are thermodynamically stable above 959 K, which is consist with the experimental results fabricated by hot pressing sintering technique.

For the combinational experiments, many different combinatorial methods have been applied on the parallel preparation of HEAs, such as supergravity, 3D printing, and

combinatorial thin-film materials libraries. Zhang *et al* have made many efforts on the parallel preparation and screening of HEAs, mainly including Al–CrFeNi–Ti [50], WTa–FeCrV [51], and Zr–Ti–Nb [52] alloy systems. For example, the parallel preparation of a ternary Ti–Nb–Zr system alloy was achieved by co-sputtering deposition method combined with physical masking, and successfully screened a bcc HEAs with excellent mechanical properties [52, 53]. Based on combinatorial thin-film materials libraries, Xing *et al* have also investigated the solar absorptivity of HEAs with the change of phase structural and microstructures [51]. In addition to obtaining different alloy compositions at one time, different microstructures can also be designed by combinational experiments. Li *et al* have applied the supergravity method to prepare the graded Al–Zn–Li–Mg–Cu alloys [54]. They found that the morphology of the alloy significantly changes from the bulk intermetallic to eutectic structures along the supergravity force direction.

4. Performance-driven high-entropy alloys

4.1. Alloys focused on mechanical properties

Excellent compressive mechanical properties under a wide temperature range is one of the most representative advantages of HEAs. There are many salient works that have developed HEAs with high strength and good ductility, which show great application potential in a new generation of structural materials. Li *et al* have reported that $Fe_{80-x}Mn_xCo_{10}Cr_{10}$ (at. %) alloy systems successfully overcome the strength–ductility trade-off by regulating metastable phase [30]. Transformation induced plasticity and dual-phase strengthening are two key contributions for such breakthrough. Lei *et al* proposed a novel strengthen mechanism by inducing ordered oxygen complexes in HEAs [29]. They found that the tensile strength is enhanced and ductility is substantially improved when doping a model TiZrHfNb HEA with 2.0 at. % oxygen, which can be attributed to the ordered interstitial complexes changing the dislocation shear mode from planar slip to wavy slip, and promoting double cross-slip. Yang *et al* reported a strategy to break this trade-off by controllably introducing high-density ductile multicomponent intermetallic nanoparticles in complex alloy systems [55]. Results show that the AlCoCrFeNiTi alloy possess ultrahigh strengths of 1.5 GPa and ductility of 50% in tensile test.

Yan *et al* [31] have summarized an Ashby diagram to declare the general relationship between the yield strengths and tensile strains of reported HEAs with different structure, as shown in figure 5. In this work, HEAs were classified into six types, including fcc, bcc, hcp, and dual-phase structures between each other. Among them, bcc alloys show the highest strengthen, and dual-phase structure is slightly inferior, while fcc alloys show relatively low yield strengths. Amorphous alloys generally have high strengths but fail to undergo tensile deformation. Here, we would like to discuss the correlation between strength and atomic radius difference (δ) of HEAs, intermetallic and amorphous, as shown in figure 6. Overall, there is a positive correlation between strength and δ, which

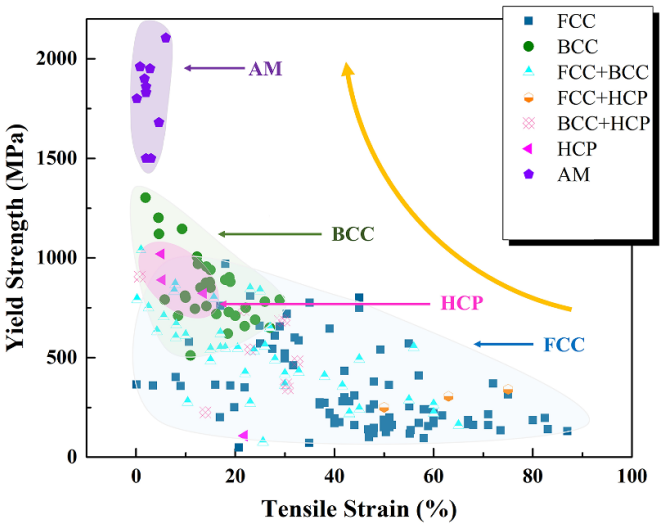


Figure 5. Map of yield strength versus tensile strain of reported HEAs with different structure at room temperature (AM: amorphous materials). Reproduced and adapted with permission from [31]. Copyright 2021 Published by Elsevier Ltd on behalf of Chinese Society for Metals.

can be attributed to significant solid-solution strengthening caused by large lattice distortion. In general, the bcc structural alloys have a larger atomic size mismatch accompanied with higher strength, fcc structural alloys show a low size mismatch level with relatively low strength, while alloy with bcc and fcc dual phase occupy the middle region. The amorphous materials (AM) and intermetallic that exhibit high hardness and high strength generally have higher atomic mismatches. Therefore, the parameter δ can give a direct guidance to the phase structure and strength of the HEAs.

4.2. Alloys focused on thermal stability

The excellent thermal stability of HEAs can be attributed to a multi-component alloy system which inspires complex interaction between the different atoms, and significantly limits the diffusion rate in HEAs. In general, the refractory bcc-HEAs with larger lattice distortion are more stable than fcc-HEAs with small lattice distortion during long-time thermal annealing. As we all good known, larger lattice distortion causes higher level atomic interaction force which meaning higher atomic migration barrier. In this case, the bcc-HEAs generally show great potential in refractory materials. Zou *et al* have investigated high temperature performances of NbMoTaW thin films and small-sized pillars, which is annealed at 1100 °C for 3 d [33]. In contrast with the conventional superalloy W, the NbMoTaW HEAs shows a good microstructure stability as well as the mechanical stability, as shown in figure 7. The pure W alloy showed obvious structural instability with the morphology changing from needle-like shapes to equiaxed-crystal structures, while the post-annealed NbMoTaW alloy retained uniform needle-like morphology without obvious grain growth.

Senkov *et al* have also investigated the phase structure of NbMoTaW and NbMoTaWV [70]. After annealing at 1400 °C

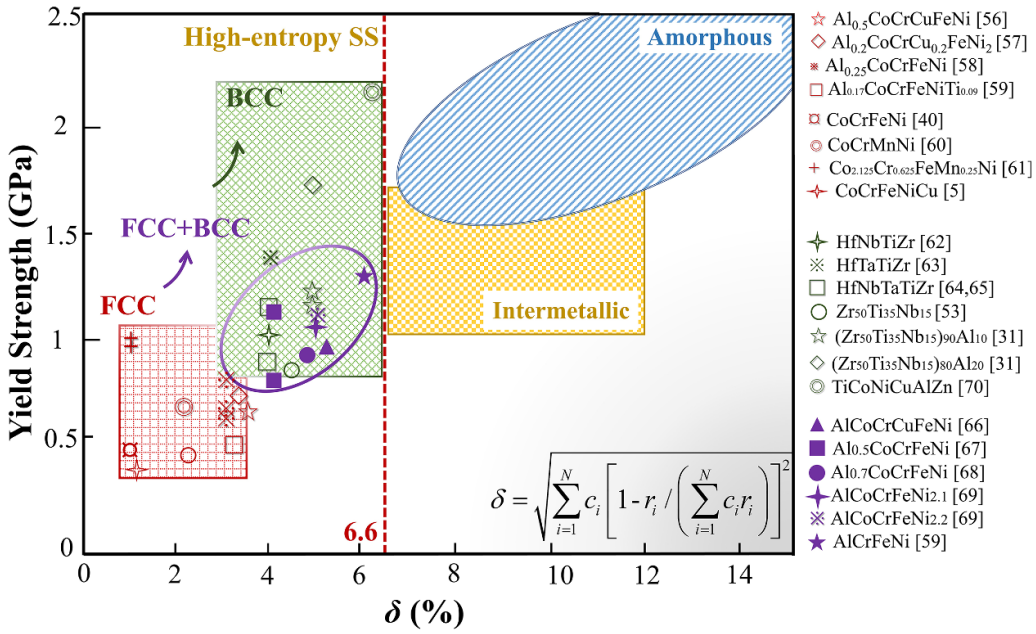


Figure 6. General relationship between strength and atomic radius difference (δ) for HEAs, intermetallic and amorphous [5, 13, 31, 40, 53, 56–69].

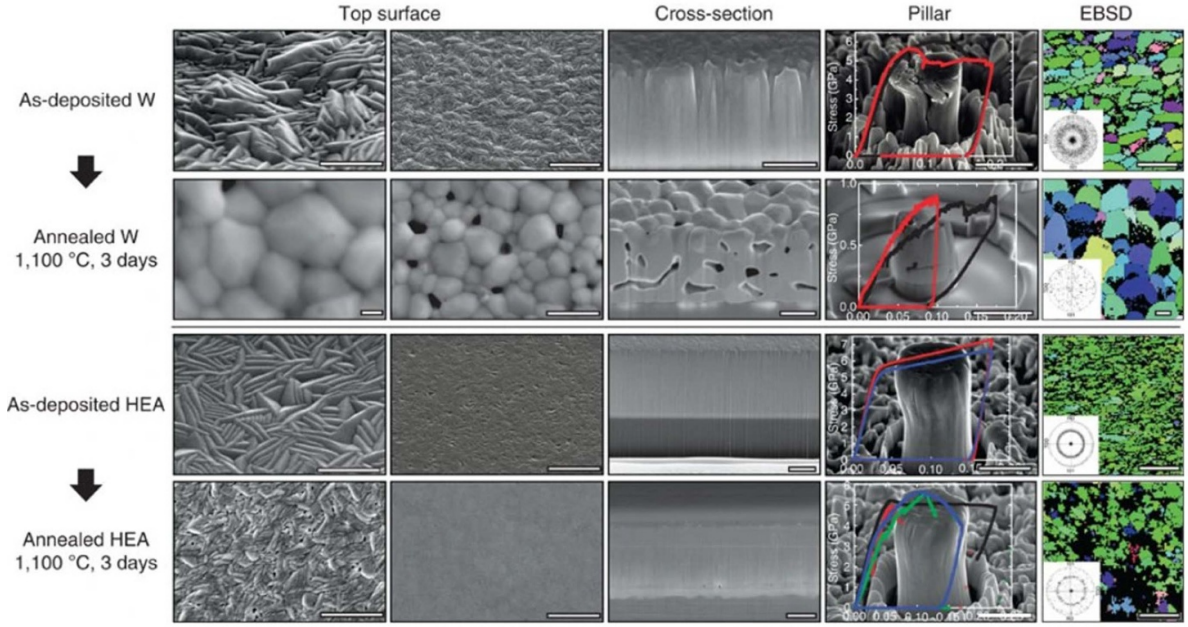


Figure 7. Pre- and post-annealing microstructures of the W and HEA films. Reproduced and adapted with permission from [33].

for 19 h, results proved that alloys are stable upon heating at least up to 1400 °C. There is no evidence for an order–disorder transition in these alloys under high temperature. Zhang *et al* have also studied the heat-softening resistance of WTaFeCrV alloys, as shown in figure 8 [14]. It is found that the yield strength of the $FeCrV(WTa)_{0.1}$ and $FeCrV(WTa)_{0.2}$ alloys are higher than those of superalloys with temperature up to 800 °C.

4.3. Alloys focused on functional properties

The unique characteristics of HEAs in dynamics, thermodynamics, and structure make it possible to develop special functional properties. Recently, much research on HEAs has focused on their potential applications on functional materials, such as radiation resistant materials [34], superconducting materials [71], soft magnetic materials [26], catalysts [28] and

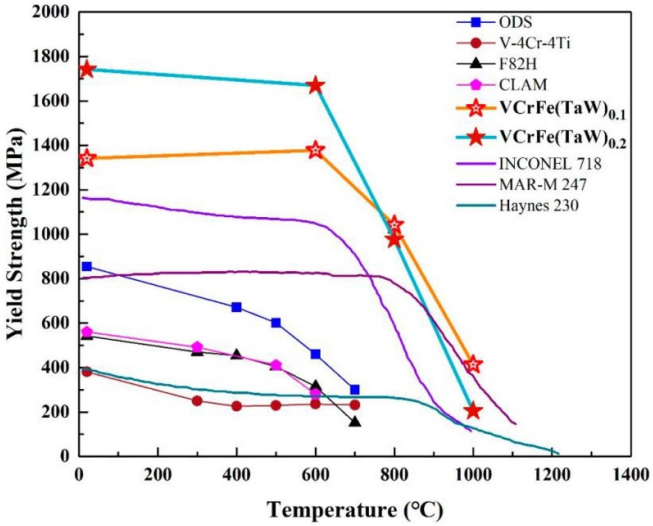


Figure 8. Temperature dependence of the compressive yield strength of superalloys, reported HEAs, and low activation alloys. Reproduced and adapted with permission from [14].

photothermal conversion materials [15]. It is worth noting that the outstanding mechanical performances of HEAs in extreme environments are also a huge driving force for making potential functional materials. Developing HEAs with a unique combination of mechanical properties and physical properties is a key point for future development.

5. Process-driven high-entropy alloys

5.1. Deformed high-entropy alloys

Excellent processing and deformation ability is one of the most important factors for HEAs to achieve their industrial applications. Rolling is a direct way to obtain high-entropy sheets. In much reported research, it can be found that the performance improvements of most HEAs are based on the deformation processing and subsequent heat treatment, such as ZrNbTiAl [31], CoCrFeNi [39], and AlCoCrFeNi [19] alloy systems.

Moreover, based on the deformation processing, Zhang *et al* have developed a novel high-entropy material: HEA wires. Hiromoto *et al* [38] have successfully prepared $Al_{0.3}$CoCrFeNi wires with a diameter of 1 mm, which displayed remarkable tensile strength and ductility (1207 MPa and 7.8%) at 298 K, increasing to 1600 MPa and 17.5% at 77 K, as shown in figure 9. Furthermore, micron-level HEA wires with a diameter of 60 μm through a drawing process have also been prepared. The room temperature tensile strength of these wires reached as high as 2.8 GPa, and together with an elongation of 2.4%. Liu *et al* also reported a novel CoCrNi medium-entropy alloy wire with a diameter of 2 mm, and tested its low temperature mechanical properties [21]. The tensile strength of these CoCrNi wires was 1.8 GPa at liquid nitrogen temperature, with an elongation of 37.4%. The high-entropy wires with excellent comprehensive mechanical properties show great development potential in various applications.

5.2. Casted high-entropy alloys

Lu *et al* have successfully developed eutectic HEAs, namely $AlCoCrFeNi_{2.1}$ alloy [72]. The novel eutectic alloys effectively solve the obstacles for their technological applications, such as inferior castability and compositional segregation of HEAs. The microstructure of $AlCoCrFeNi_{2.1}$ alloy is composed of soft fcc and hard bcc phases, which is in the form of fine lamellar fcc/B2 microstructure, as shown in figure 10. Results showed that the $AlCoCrFeNi_{2.1}$ alloy possessed pretty good compressive mechanical properties at room temperature, with a true fracture strength and ductility of 1186 MPa and 22.8%, respectively. Wani *et al* have investigated the cold-rolled and annealed treatment of the $AlCoCrFeNi_{2.1}$ eutectic alloy [73]. The alloy successfully suffered from a severe cold rolling with a reduction of 90%. The strength of rolled alloy reached 1800 MPa, but at the expense of elongation (∼6%). Overall, the eutectic HEAs is quite suitable for the casting process due to its good fluidity and formability, and can be readily adapted to large-scale industrial production of HEAs.

5.3. High-entropy alloys for additive manufacturing

Additive manufacturing has provided new opportunities for fabricating geometrically complex HEAs with the possibility of *in situ* tailoring of their microstructure features. Zhou *et al* have proposed a precipitation-strengthened $Ni_{2.1}CoCrFeNb_{0.2}$ alloy which was particularly easy to print for use in additive manufacturing [74]. The $Ni_{2.1}CoCrFeNb_{0.2}$ alloy showed an excellent combination of strength and ductility. Especially after heat-treatments, the tensile strength of the alloy is 1127 MPa with a tensile elongation of 17%, which is the best performance in the reported additive manufactured HEAs. Moreover, Chew *et al* have fabricated the CoCrFeMnNi alloy by laser aided additive manufacturing [75]. Results proved that graded microstructures were obtained, in which the dendritic columnar grains formed close to the melt-pool boundaries and transited to equiaxed grains further away from the boundaries. The mechanical properties of additive-manufactured CoCrFeMnNi alloy are better than conventionally cast HEAs, with a yield strength of 518 MPa and ultimate tensile strength of 660 MPa, which can be attributed to finer grains obtained by the additive manufacturing process. In fact, many efforts have been carried out to verify the feasibility of additive manufacturing technology to prepare HEAs [76], which is expected to open up new possibilities for the further development of additive manufacturing fabricated HEAs.

5.4. Electrodeposited high-entropy alloys

Electrodeposition is an effective method for obtaining nanocrystalline HEAs, but has seen little attention to date. In comparison to the most commonly-used techniques, such as

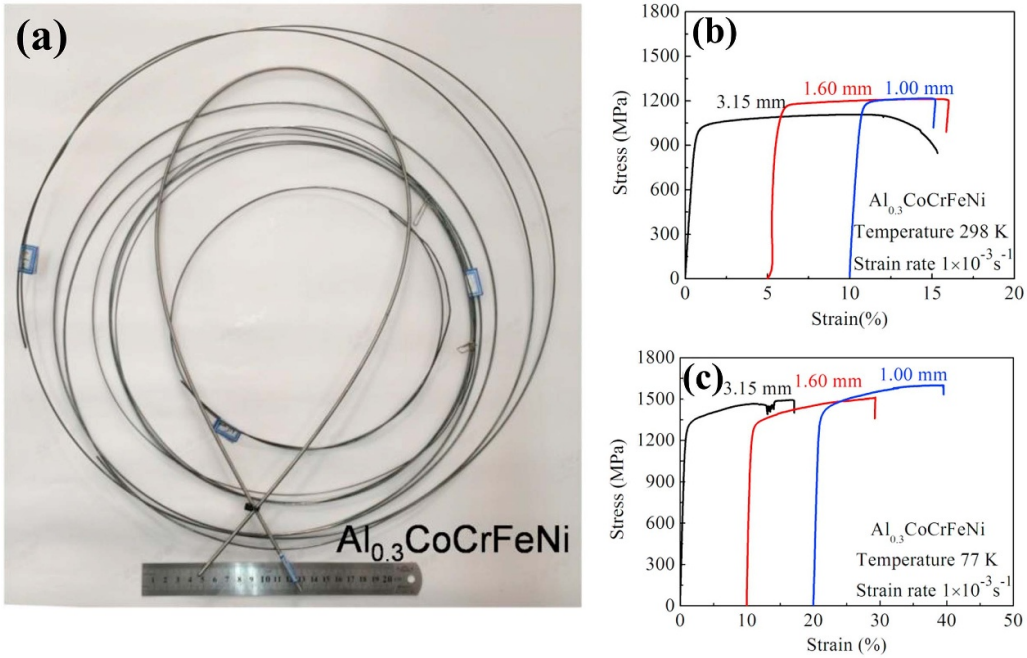


Figure 9. Macroscopic views and mechanical properties of the $Al_{0.3}$CoCrFeNi fibers. (a) Macroscopic views of $Al_{0.3}$CoCrFeNi fibers. Fiber diameters range from 1.00 to 3.15 mm. (b) Engineering stress–strain curves with different diameters at room temperature, respectively. (c) Engineering stress–strain curves at 77 K. Reproduced and adapted with permission from [19]. Copyright 2016 Acta Materialia Inc. Published by Elsevier Ltd.

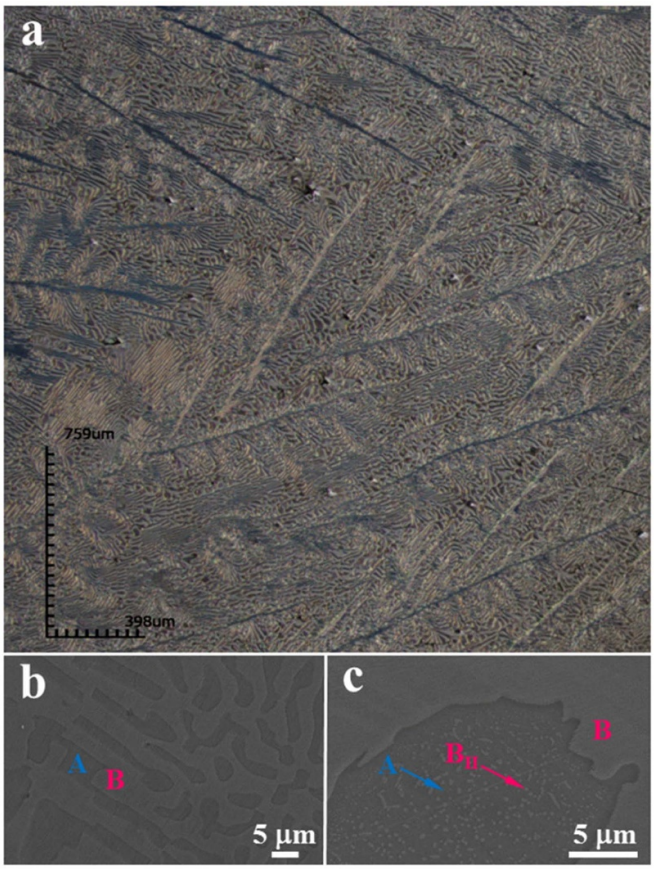


Figure 10. Micrograph of eutectic HEAs. (a) An LSCM image showing the eutectic microstructure of the $AlCoCrFeNi_{2.1}$ alloy. (b) The lamellar dual-phase structure seen under SEM. (c) The enlarged view showing the precipitates in one phase. Reproduced and adapted with permission from [72]. © The Author(s) 2014. Published by CC BY-NC-ND 4.0.

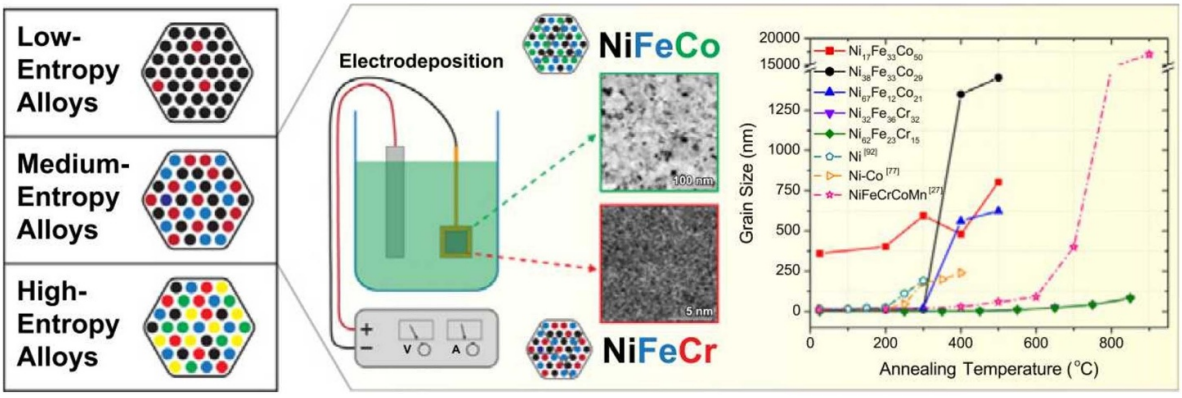


Figure 11. Schematic diagram of electrodeposition synthesis of HEA and its thermal stability. Reproduced and adapted with permission from [77]. Copyright 2021 Elsevier.

mechanical alloying, high-pressure torsion, and sputtering-based techniques, electrodeposition offers itself as a relatively low-cost and low-energy method for nanocrystalline alloy synthesis that can be applied to various substrates. However, it is truly difficult to deposit multiple elements simultaneously, due to different potential of components and complexity of electrolytes. To date, Haché *et al* have developed two model ternary alloy systems to serve as starting points for the eventual development of five-element HEAs, as shown in figure 11 [77]. In this work, two important issues have been evaluated, including the ability of forming and maintaining a single solid-solution phase and standard reduction potential. Based on these evaluations, ternary NiFeCo and NiFeCr alloys were selected to investigate the electrodeposition behavior, and the ternary alloys show a nano grain size of 1–360 nm. Particularly, these alloys show enhanced thermal stability compared to pure metal and binary alloy electrodeposits, and even nanocrystalline CoCrFeNiMn fabricated by high-pressure torsion. It could be inferred that electrodeposition is a viable route towards the synthesis of strong and highly stable nanocrystalline alloys. The research route to develop suitable ternary alloys as 'stepping-stones' for future design of HEAs is worthy of expectation.

6. Future opportunities and challenges

Recently, much new thinking about HEAs is gradually emerging. One of them is the discussion about entropy. As we all know, Clausius first proposed the concept of entropy in the interpretation of the second law of thermodynamics, and gave the calculation method of 'entropy change' (i.e. $\Delta S = S_A - S_B \geqslant \int_A^B \frac{dQ}{T}$). Based on statistical mechanics, Boltzmann defined entropy by analyzing the relationship between entropy and the number of microscopic states of an isolated system, which is namely microscopic statistical thermodynamic expression of thermodynamic entropy as we know it. The current discussion and physical interpretation of HEAs are mainly based on Boltzmann entropy, which is the mainstream. In fact, Boltzmann's micro definition of entropy can only be regarded as an explanation of Clausius entropy. Moreover, Shannon defined entropy utilizing probability statistics and proposed the 'information entropy', which is a broader research object of thermodynamics. What we now generally recognize is that, based on the ideal solid solution structure, the entropy state of a certain HEA depends only on the chemical composition, ignoring the actual atomic arrangement.

Recently, researchers have used Shannon entropy to explain HEAs, intending to reveal the information that is encoded in various local atomic arrangements [78]. They concluded that the HEA with the higher Shannon entropy is energetically more stable, electrically conductible, and mechanically malleable than its counterpart with the lower Shannon entropy. In the future, introducing Shannon entropy to HEAs could offer a new pathway to describe more atomic details of HEAs, and inspire unknown landscapes.

Furthermore, there are many other attractive efforts and challenges that could be implemented on HEAs, which are mainly summarized in three trade-offs: (a) breaking the trade-off between strength and ductility; (b) breaking the properties limits of traditional materials, such as low temperature plasticity, radiation resistance and self-sharpening;(c) breaking the trade-off between the mechanical properties and the physical properties. Among them, we believe that the trade-off between the mechanical properties and the physical properties will be a future hot spot in HEAs. The ability of HEAs to be designed in unique combinations of mechanical and functional properties in unlimited space of alloy compositions is encouraging. Generally, the functional properties are available from traditional materials. However, traditional materials usually fail to perform well in extreme conditions, and cannot simultaneously possess excellent mechanical properties. Hence, we would like to propose a trade-off between the mechanical properties and the physical properties, such as deformability and soft magnetic properties, thermal stability and mechanical properties stability. These efforts will undoubtedly provide exciting hope for the development of high-quality HEAs to meet the needs of next-generation engineering applications.

7. Conclusions

As an emerging material system, the unique characteristics of HEAs in dynamics, thermodynamics, and structure have aroused great interest in both structural and functional materials. Considerable efforts have been focused on the mechanical properties and related mechanisms of HEAs. Nevertheless, many unique combinations of mechanical and functional properties of HEAs are unique advantages that should not be ignored. Developing HEAs that are suitable for a wide range of preparation and deformation techniques should be one of the future research projects in HEAs, for example, HEAs suitable for casting, deformation processing, additive manufacturing, and electrodeposition. Therefore, we should not only focus on performance-driven HEAs, but also develop HEA systems from the perspective of processing and manufacturing.

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