

Review

The Evolution of Intermetallic Compounds in High-Entropy Alloys: From the Secondary Phase to the Main Phase

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Abstract: High-performance structural materials are critical to the development of transportation, energy, and aerospace. In recent years, newly developed high-entropy alloys with a single-phase solid-solution structure have attracted wide attention from researchers due to their excellent properties. However, this new material also has inevitable shortcomings, such as brittleness at ambient temperature and thermodynamic instability at high temperature. Efforts have been made to introduce a small number of intermetallic compounds into single-phase solid-solution high-entropy alloys as a secondary phase to their enhance properties. Various studies have suggested that the performance of high-entropy alloys can be improved by introducing more intermetallic compounds. At that point, researchers designed an intermetallic compound-strengthened high-entropy alloy, which introduced a massive intermetallic compound as a coherent strengthening phase to further strengthen the matrix of the high-entropy alloy. Inspired from this, Fantao obtained a new alloy—high-entropy intermetallics—by introducing different alloying elements to multi-principalize the material in a previous study. This new alloy treats the intermetallic compound as the main phase and has advantages of both structural and functional materials. It is expected to become a new generation of high-performance amphibious high-entropy materials across the field of structure and function. In this review, we first demonstrate the inevitability of intermetallic compounds in high-entropy alloys and explain the importance of intermetallic compounds in improving the properties of high-entropy alloys. Secondly, we introduce two new high-entropy alloys mainly from the aspects of composition design, structure, underlying mechanism, and performance. Lastly, the high-entropy materials containing intermetallic compound phases are summarized, which lays a theoretical foundation for the development of new advanced materials.

Keywords: intermetallic compounds; high-entropy alloy; intermetallic compound-strengthened high-entropy alloy; high-entropy intermetallics



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1. Introduction

The developments of transportation, energy, and aerospace are highly dependent on the availability of new structural materials that can offer light weight, high-temperature strength, creep resistance, and oxidation resistance [1–5]. Nickel-based superalloys are commonly used materials that offer most of these properties; however, there is an issue where it is easy for nickel-based superalloys to form unwanted precipitates or harmful phases during high-temperature applications, and these can reduce the strength significantly [6]. Therefore, it is necessary to develop new high-temperature structural materials with better performance and stronger stability.

In order to develop new alloy materials with excellent properties, in 2004, Yeh et al. [1] and Cantor et al. [2] broke the traditional alloy design mold and proposed a new alloy design strategy. They combined five or more elements in an equimolar or nearly equimolar ratio, and finally obtained a new type of alloy material—high-entropy alloy [3–5]. In the early days when this concept was proposed, researchers generally believed that high-entropy alloys were a new type of single-phase solid-solution high-entropy material [1–5]. The most common solid-solution structures included face-centered-cubic (FCC) [2,7–24], body-centered-cubic (BCC) [25–34], and hexagonal close-packed (HCP) [35–39] (as shown in Figure 1). A lot of research has been devoted to the development of single-phase solid-solution high-entropy alloys with excellent properties. However, due to the inherent high-temperature instability of single-phase solid-solution high-entropy alloys, it has been unable to achieve practical applications in the field of high-temperature structures [40–44]. Nevertheless, with the deepening of the understanding of high-entropy alloys and with the further optimization of analysis processing and testing methods, substantial experimental results have shown that almost all high-entropy alloys are not pure solid-solution structures (except for very few components) [45–50]. There is always a certain number of intermetallic compound phases in the high-entropy alloy, which affects the performance of the material [46–48].

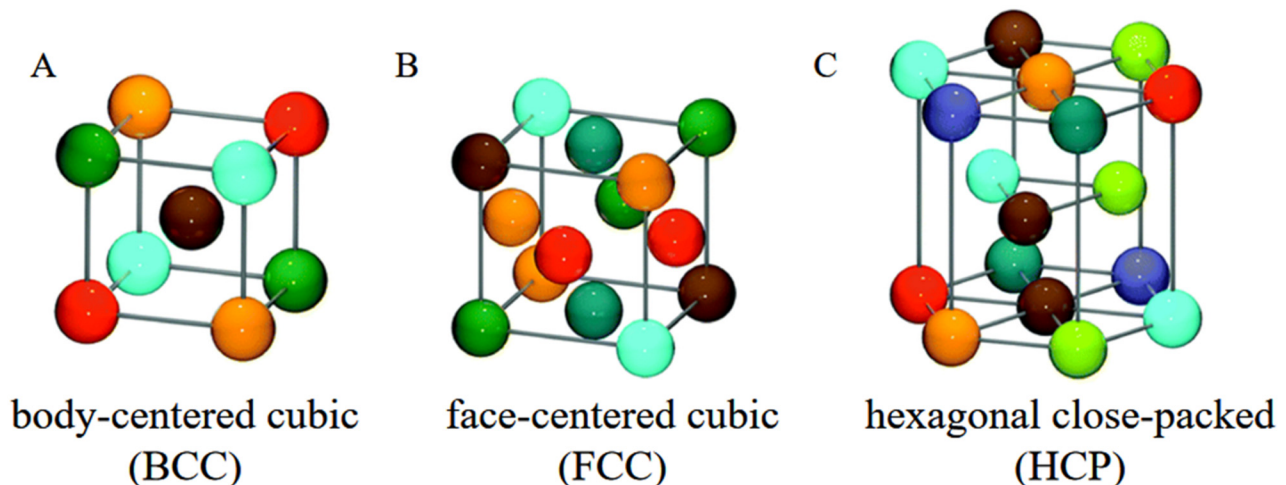


Figure 1. The identified crystal structures of high-entropy alloys adapted with permission from ref. [51] Copyright 2021 Elsevier. (A) Body-centered cubic (BCC) structure. (B) Face-centered cubic (FCC) structure. (C) Hexagonal close-packed (HCP) structure.

Recently, significant attention has been given to high-entropy alloys containing a small number of intermetallic compound phases as a secondary phase. Unlike the traditional alloy, the presence of intermetallic compounds in high-entropy alloys does not necessarily destroy the overall performance of alloys [40,42,45–50]. As shown in Figure 2, the morphology of intermetallic compounds in high-entropy alloys is very similar to that of the γ' phase in nickel-based superalloys. By adjusting the number, density, size, and distribution of intermetallic compounds using appropriate processing methods, the effect of strengthening and stabilizing high-entropy alloys can be achieved [52–54]. It has been reported that increasing the volume fraction of the specific structure intermetallic compound phase significantly improves the strength and ductility at ambient temperature, high temperature, or even at cryogenic temperature of the high-entropy alloy [45–50]. Therefore, more recently, researchers began to introduce a large number of intermetallic compounds intentionally as coherent strengthening phases to improve the overall performance of high-entropy alloys [52–55]. A large amount of mechanical data obtained for these new types of alloys confirm that the performance is far better than those of the traditional alloy materials, meaning these newly developed alloys are suitable for more severe extreme service conditions [52–54]. Inspired from this, in order to introduce more intermetallic

compound phases into the high-entropy material system and improve the comprehensive performance, Fantao and his group changed their mind to take intermetallic compounds with excellent performance as the main phase and to use multiple elements to gradually multi-principalize the sublattice [55]. A new class of ordered high-entropy materials was obtained in 2017, which was named high-entropy intermetallics (HEIs) [55]. It mainly contains three series: $(X_1, X_2, \dots, X_n)_3\text{Al}$ ($X = \text{Fe, Co, Ni}$ and Cr)-series HEIs (the main phase is B2 structure), $\text{Ni}_3(X_1, X_2, \dots, X_n)$ ($X = \text{Al, Si, Ti, Mn, Fe, V}$ and Cr)-series HEIs (the main phase is L_{12} structure), and $(\text{Co, Ni})_3(X_1, X_2, \dots, X_n)$ ($X = \text{Al, Si, Ti, Mn, Fe, V}$, and Cr)-series HEIs (the main phase is L_{12} structure). In addition, there are also some HEIs whose main phase is a simple crystal structure that needs to be explored [55]. In this new type of material, the volume fraction of the intermetallic compound phase reaches more than 75%, which perfectly expands the high-entropy material system from the perspective of the number of intermetallic compound phases.

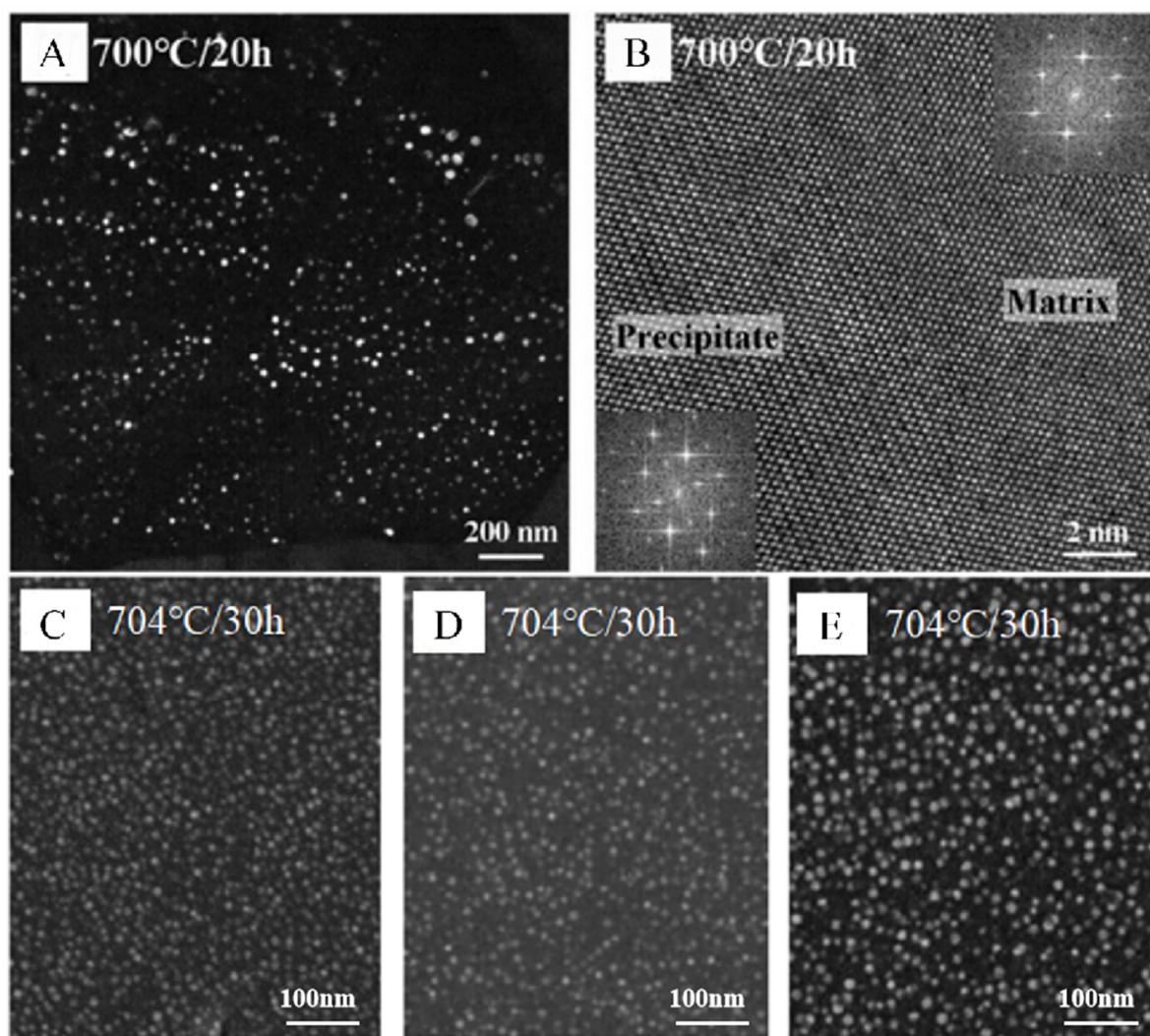


Figure 2. The comparison of the microstructure between high-entropy alloys and nickel-based superalloys. (A) The morphology of γ' phase in $\text{Al}_{0.2}\text{CrFeCoNi}_2\text{Cu}_{0.2}$ HEA adapted with permission from ref. [54]. Copyright 2021 Elsevier. (B) TEM images of the $\text{Al}_{0.2}\text{CrFeCoNi}_2\text{Cu}_{0.2}$ HEA containing γ and γ' phases adapted with permission from ref. [54]. Copyright 2021 Elsevier. (C) The morphology of γ' phase in nickel-based superalloy that contains 1.5 wt.% Ti adapted with permission from ref. [6]. Copyright 2021 Elsevier. (D) The morphology of γ' phase in nickel-based superalloy that contains 10 wt.% Mo [6]. (E) The morphology of γ' phase in nickel-based superalloy that contains 12 wt.% Mo adapted with permission from ref. [6]. Copyright 2021 Elsevier.

In this review, we start with the intermetallic compound phase in high-entropy alloys, combined with the existing research results to explain the inevitability of intermetallic compounds in high-entropy alloys, and illustrate their role in improving the overall performance. The advantages of high-entropy alloys containing intermetallic compound phases as secondary phases compared with single-phase solid-solution high-entropy alloys is also discussed. After providing the significance of intermetallic compounds in high-entropy materials, two new high-entropy materials containing more intermetallic compounds are introduced from the aspects of composition design, microstructure, properties, strength, and toughness mechanism. Finally, existing problems of the two new materials are summarized prior to stating the potential future development and application prospects.

2. Intermetallic Compounds in High-Entropy Alloys

High-entropy alloys, as a new type of alloy created with a new design concept, show unique characteristics different from traditional alloy materials in many aspects, for example, the high-entropy effect in thermodynamics, the delayed diffusion effect in kinetics, the lattice distortion effect in the crystal structure, and the cocktail effect in performance. Due to these characteristics, high-entropy alloys have received extensive attention from scholars all over the world. In these early development stages, excellent properties such as high strength and ductility [56–60], high fracture toughness [61], irradiation resistance [62,63], fatigue resistance [64], corrosion resistance [52,65], and excellent cryogenic or high-temperature properties have been achieved that cannot be matched by traditional alloys. Figure 3 shows the comparison of yield strength and fracture toughness of high-entropy materials and other traditional alloy materials. It is clear that CrCoNi-based medium-entropy and high-entropy alloys are among the most damage-tolerant materials ever produced. Additionally, recent studies have shown that high-entropy alloys had outstanding mechanics and electromagnetics behavior, which makes them ideal materials that are expected to solve the bottleneck problem of material performance in the current engineering field [66–69].

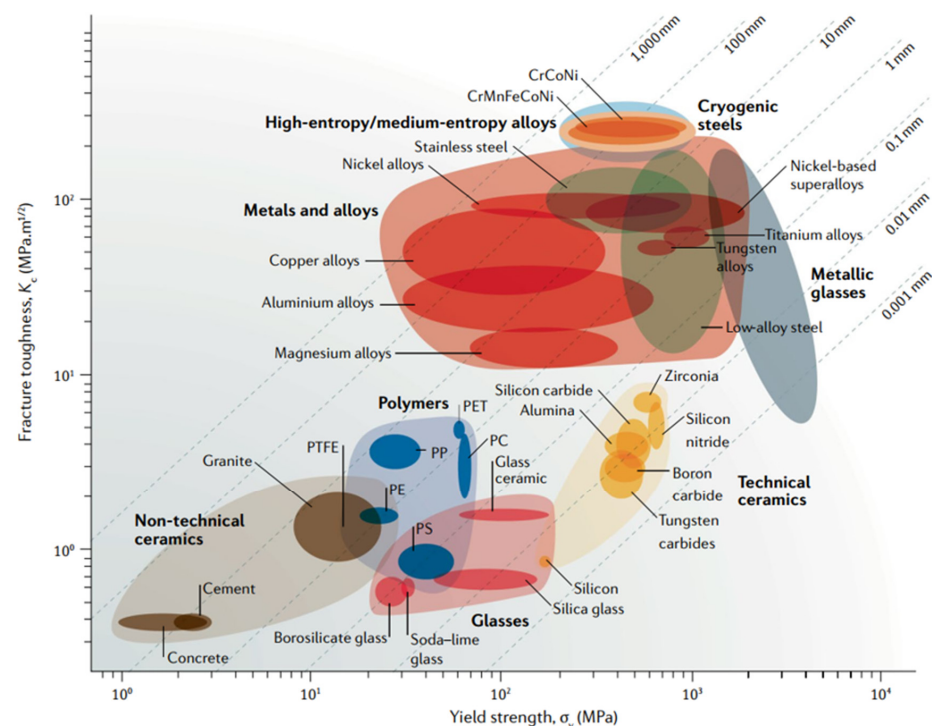


Figure 3. Ashby plot of strength versus fracture toughness showing that CrCoNi-based, medium-entropy, and high-entropy alloys are among the most damage-tolerant materials on record adapted with permission from ref. [70]. Copyright 2021 Springer Nature.

The original definition of high-entropy alloys is a single-phase solid-solution material obtained by combining five or more elements in an equimolar ratio or nearly equimolar ratio. However, it obviously contradicts with traditional alloy design theory, because the addition of multiple elements will inevitably lead to the formation of intermetallic compound phases and other brittle phases. Surprisingly, high-entropy alloys obtain a solid-solution phase with a simple structure to a large extent. Yeh and his colleagues provided a reasonable explanation [70]; they believed that the multi-component mixing of high-entropy alloys maximizes the mixing entropy of the material. This unique high-entropy effect is sufficient to overcome the enthalpy of formation of intermetallic compounds, thereby inhibiting the formation of intermetallic compound phases. At the same time, as number of elements increases, the contribution of mixing entropy will exceed the contribution of enthalpy to the total free energy, which is beneficial to the stability of the solid solution. Therefore, high mixing entropy becomes an important basis for determining whether or not the high-entropy alloy can form a single-phase solid solution.

According to the above ideas, a large number of single-phase solid-solution high-entropy alloys with excellent performance have been developed. Among them, the five-element CrMnFeCoNi (Cantor) high-entropy alloy is one of the first single-phase FCC-type solid-solution alloys reported [2]. Extensive research had been carried out around the structure and properties of Cantor alloys and the deformation mechanism. From the results accumulated to date, it is clear that heat treatment above 800 °C kept the alloy as a stable single-phase solid-solution structure, while heat treatment below 800 °C resulted in the appearance of intermetallic compound phases in the alloy. For example, as shown in Figure 4, after 500 days of holding at 900 °C, the alloy had a single solid-solution phase; after 500 days of holding at 700 °C, a Cr-rich σ phase appeared in the alloy. Similarly, after 500 days of holding at 500 °C, three different phases formed: L1₀-NiMn, B2-FeCo, and a Cr-rich BCC phase [42]. These results show that the single-phase solid-solution state of the high-entropy alloy is a metastable state. After heat treatment under certain conditions, a stable intermetallic compound phase will appear in the high-entropy alloy. In fact, the initial experiment of Yeh and his colleagues was performed near the melting point of the high-entropy alloy, while subsequent researchers tested the microstructure and properties of the high-entropy alloy at ambient temperature [70]. The microstructure is different because of different diffusion rates and cooling rates at ambient temperature and high temperature. This high-temperature instability of phase composition is common in most high-entropy alloys, so the appearance of intermetallic compound phases in the microstructure of solid-solution high-entropy alloys is inevitable [70]. Even in high-entropy alloys that are initially single-phase after solidification, a variety of intermetallic compound phases are easily formed after intermediate temperature annealing [40–44].

More importantly, the high-entropy alloy with intermetallic compound phases has a better comprehensive performance at ambient temperature and high-temperature stability compared with single-phase solid-solution high-entropy alloy [70–72]. For example, He et al. [71] found that by adding an appropriate number of Al and Ti elements into the FeCoCrNi high-entropy alloy, a high-entropy alloy containing a small number of intermetallic compound phases can be formed. After thermomechanical treatment to refine the grains, the alloy has a high tensile strength of 1273 MPa and a considerably high ductility of 17%. This performance is significantly better than most single-phase solid solutions or any other advanced structural materials with excellent performance, as shown in Figure 5. In addition, when studying BCC-type refractory high-entropy alloy TiZrHfNbTa, it was found [72] that, although a metastable solid-solution structure can be obtained in high-entropy alloys after a series of treatments, it only has an effect at ambient temperature. Therefore, it is necessary to introduce dispersive distributed stable intermetallic compound particles into the high-entropy alloy to improve its creep properties and high-temperature stability. For high-temperature structural materials, the alloy must have thermodynamic stability to ensure the reliability of the material during application, rather than solely relying on dynamic stability [70].

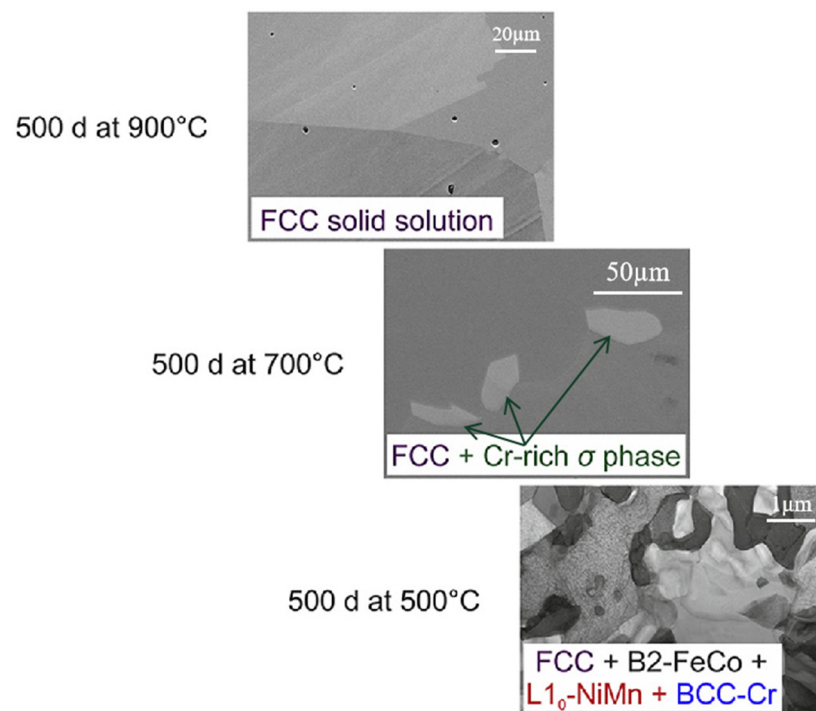


Figure 4. Scanning electron microscopy (SEM) image of CrMnFeCoNi HEA after heat treatment under different temperatures for 500 days adapted with the permission from ref. [42]. Copyright 2021 Elsevier.

The research focus gradually shifted from the initial single-phase solid-solution high-entropy alloy to the high-entropy alloy containing an intermetallic compound phase as secondary phases [73]. The intermetallic compound has many advantages such as the presence of a strong atomic bonding force (existence of covalent bonds), low density, high specific strength and specific stiffness, and good high-temperature resistance. It is anticipated that intermetallic-phase-reinforced high-entropy alloys can replace nickel-based superalloys in aerospace, aviation, transportation, and other industrial fields and become more potential high-temperature structural materials [74,75]. On the other hand, first-principles calculations based on density functional theory (DFT) have shown that the intermetallic compound phase will have a profound impact on the key properties of high-entropy alloys such as stacking fault energy and dislocation mobility. Therefore, it can effectively tailor the overall mechanical properties of high-entropy alloys [76]. In general, the presence of an intermetallic compound phase in any shape or form can greatly improve the mechanical properties of high-entropy alloys (for example, the $L1_2$ -type intermetallic compound phase in CrCoNi can increase its yield strength to 800 MPa and maintain more than 40% tensile plasticity); however, further enhancement can be achieved through optimization of the amount, density, size, and distribution of the precipitated intermetallic compound phases.

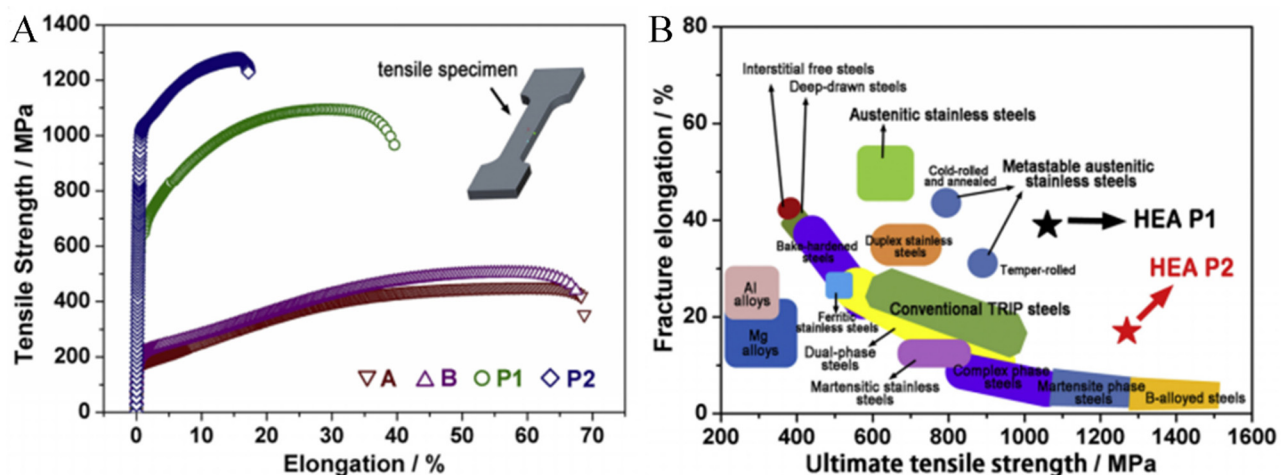


Figure 5. (A) Tensile properties of alloys alloy A (as-homogenized FeCoNiCr), alloy B as-homogenized (FeCoNiCr)₉₄Ti₂Al₄, P1 (alloy B after first treatment), and P2 (alloy B after second treatment) at room temperature. (B) The map of ultimate tensile strength-ductility combinations of various advanced steels including P1 and P2 HEAs adapted with the permission from ref. [71]. Copyright 2021 Elsevier.

3. Intermetallic Compound-Strengthened High-Entropy Alloy

To further enhance the performance of high-entropy alloys and explore new materials with excellent properties, imitating nickel-based superalloys, efforts have been made to introduce as many intermetallic phases as coherent strengthening phases into high-entropy alloys [77–86]. This method has been proven to be one of the most effective methods for strengthening structurally applied alloy materials at ambient temperature and high temperature [77,78]. Therefore, a new type of high-entropy material—intermetallic compound-strengthened high-entropy alloy—has been developed. For these new alloy systems, a single-FCC solid-solution high-entropy alloy is widely used as the matrix alloy of the intermetallic compound-strengthened high-entropy alloy because of its extremely high ductility and excellent work hardening ability. For the strengthening phase, a variety of intermetallic compounds are included in the consideration, such as σ , μ , Laves, B2 (ordered BCC), and L₁₂ (ordered FCC) [41,79–85]. Based on many experimental studies, it can be stated that only the coherent precipitation of L₁₂-type nanoparticles can effectively strengthen single-phase solid-solution high-entropy alloys to provide a good balance of ductility and strength [52,53,71,85–93]. Therefore, in this section, most of the discussion focuses on the research progress of L₁₂-strengthened high-entropy alloys, including their composition design, structure, performance, and underlying mechanism responsible for superior performance.

Prediction of alloy phase composition using physical and chemical parameters

In order to develop the intermetallic compound-strengthened high-entropy alloy with excellent comprehensive properties, it is necessary to introduce more intermetallic compound phases as a coherent strengthening phase into the alloy. As we all know, the phase composition of the alloy is usually closely related to the composition of the alloy; therefore, the key first step in designing such a new alloy is to determine the type and quantity of the alloy elements. Ideally, the alloy should retain a high-volume fraction of the intermetallic compound phase as a coherent strengthening phase after processing so that significant strengthening of the alloy and improvement in the performance would be achieved. For traditional alloy composition design, the phase diagram plays an important role in the selection of alloy composition as it provides a relationship between the alloy phase structure and element content at different temperatures. However, for intermetallic compound-strengthened high-entropy alloys containing five or more elements, the use of well-established binary and partial ternary phase diagrams is not very productive [94–102]. In other words, there is no accurate multiple-principal-element alloy phase diagram that can be used for high-entropy material design. Therefore, it is a significant challenge to

rapidly design the composition of an intermetallic compound-strengthened high-entropy alloy with a high-volume fraction of ordered phases.

Fortunately, the extensive research results attained so far have proven that some physical and chemical parameters can be used to predict the phase composition of multiple-principal-element alloys, meaning that these can be used to assist the composition design of alloys. There are several suitable parameters that have been discovered to predict the phase composition of intermetallic compound-strengthened high-entropy alloys with relative accuracy. A summary of the relationship between the value range of each parameter and phase composition is presented in reference [94]. For example, according to the Hume–Rothery law, there are three criteria for the formation of a single solid-solution phase in a multiple-principal-element alloy: (1). There are at least five main elements. (2). The maximum atomic radius difference between the principal elements does not exceed 12%. (3). The mixing enthalpy of the alloy is between -40 and 10 kJ/mol [95]. Further consideration of the relationship between δ , ΔH_{mix} , and the alloy phase composition reveals that a single solid-solution phase or a structure dominated by a solid-solution phase can only be obtained when the difference in atomic radius is small enough and the mixing enthalpy tends to 0 [96]. The relationship between δ , ΔH_{mix} , and the alloy phase composition can be seen from Figure 6.

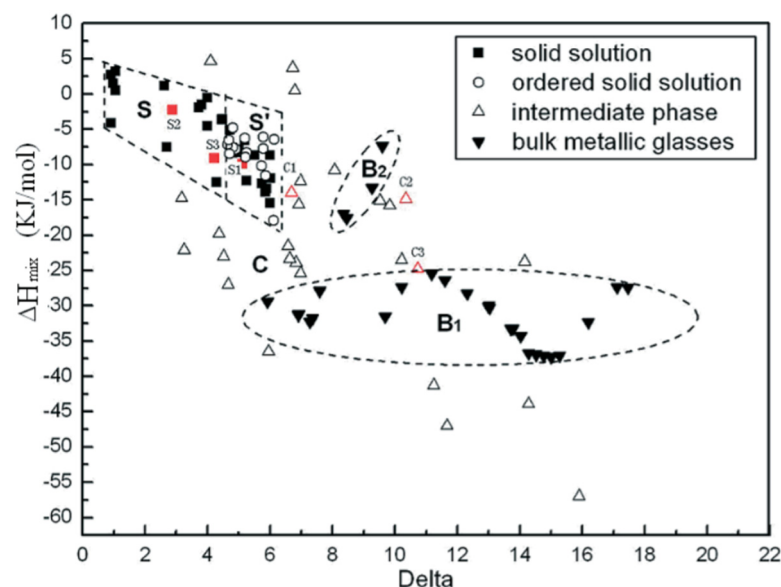


Figure 6. The relationship between δ , ΔH_{mix} , and the alloy phase composition adapted with permission from ref. [96]. Copyright 2021 Wiley Online Library.

To make the more accurate prediction, some researchers have defined a new parameter Ω , which combines the effects of ΔS_{mix} and ΔH_{mix} to predict the phase composition of various multiple-principal-element alloys. It is believed that only when $\Omega \geq 1.1$ and $\delta \leq 6.6\%$ can a solid-solution phase be formed, and the above standards have been verified through a series of experiments [97]. In addition, studies have found that the atomic size difference parameter α_2 can be used to predict the phase composition of multiple-principal-element alloys [98]. Figure 7 shows the relationship between the phase composition of high-entropy alloys and the α_2 value. It can be seen that high-entropy alloys can be divided into solid-solution-phase (SS) alloys, solid-solution-phase and intermetallic-compound-phase (SS + IM) alloys, and metallic glass (MG) high-entropy alloys according to the value of α_2 [98]. Similarly, SINGH et al. [99] proposed that the geometric parameter Λ can be used to predict the formation of a high-entropy-alloy solid-solution phase. Only when $\Lambda \geq 0.96$ of a certain alloy system can the alloy form a single-phase solid-solution phase; when $0.24 < \Lambda < 0.96$, the alloy forms a two-phase mixed structure; when $\Lambda \leq 0.24$, the alloy forms a multiphase structure with intermetallic compound phases [99].

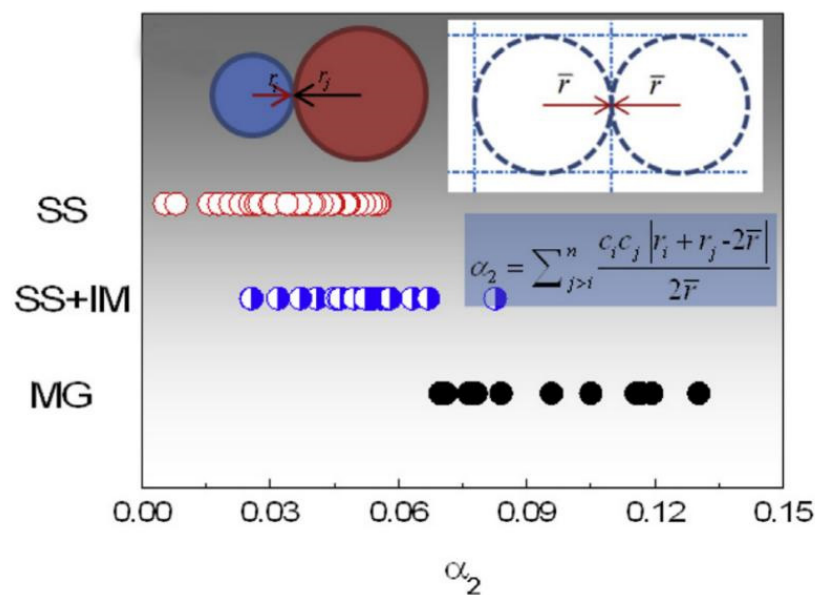


Figure 7. The relationship between high-entropy alloy phase composition and α_2 value adapted with permission from ref. [98]. Copyright 2021 Elsevier.

In summary, the formation of a solid-solution phase and intermetallic compound phase is a competitive and balanced process in the multiple-principal-element alloy system. Only when certain parameter conditions are met will the alloy form a single-phase solid-solution structure, while in the remaining range, the alloy will form an intermetallic compound phase or a mixture of intermetallic compound phase and solid-solution phase [96–98]. The relationship between the physical and chemical parameters and the phase composition of the multiple-principal-element alloys proves the rationality of the existence of the intermetallic compound-strengthened high-entropy alloys. This also provides a new idea for the composition design of this new type of alloy. However, as with most other structural materials, the phase composition of intermetallic compound-strengthened high-entropy alloys shows a strong temperature dependence. Therefore, the above physical and chemical parameter calculation method can only provide alloy information in a certain state, or even phase composition information in the as-cast state. This limits the composition design and optimization of intermetallic compound-strengthened high-entropy alloys to a certain extent [73].

3.1. Composition Design Based on CALPHAD

To better develop intermetallic compound-strengthened high-entropy structural materials, researchers have developed a CALPHAD (Calculation of Phase Diagrams) technique based on thermodynamic calculations, which provides an effective method for predicting the phase relationship of multiple-principal-element alloy materials [85,89,100–102]. Currently, it has been the most widely used tool for the development of structural alloys such as steel, superalloys, and titanium alloys [100–102]. This calculation-assisted method makes it easy to obtain the required microstructure with target phase and composition, and significantly accelerates the rapid design of advanced structural materials [73]. In addition, the method can also intuitively show the effect of the content change of a certain element in the multiple-principal-element alloy on the overall phase structure of the alloy. This provides an efficient way for the composition optimization of the intermetallic compound-strengthened high-entropy alloy. In general, CALPHAD technology as an advanced multiple-principal-element alloy composition design method can provide the relationship between the temperature-composition-phase composition of various materials under different conditions in the early stage of material design. In other words, it facilitates the effective selection of the most suitable compositions for tens of thousands of alloys. It greatly shortens the composition design time of intermetallic compound-strengthened

high-entropy alloys and promotes the development of advanced structural materials. At present, databases of common alloys are all included in CALPHAD. For high-entropy alloys, those of Ni-based superalloy libraries are often used instead [85,90,103,104].

At present, many research results have confirmed the feasibility of this technology, and the use of this many intermetallic compound-strengthened high-entropy alloys with excellent properties has been developed and evaluated [79,84,85,103,104]. For example, as shown in the Figure 8, Zhao et al. [85] used the CALPHAD technology to calculate and develop the L_{12} -strengthened $(\text{CoCrNi})\text{Al}_3\text{Ti}_3$ alloy. This study concluded that after aging at 800 °C, a typical FCC + L_{12} dual-phase nanostructure can be obtained, which is consistent with the software calculation results. Chang et al. [104] evaluated the equilibrium phase composition of the $(\text{Ni}_{1.5}\text{Co}_{1.5}\text{CrFe})\text{Al}_x\text{Ti}_y$ alloy with the change in Al element content through Thermo-Calc software, and their calculation results were completely consistent with the experimental results. In addition, the TCHEA1 thermodynamic database specially designed for multiple-principal-element alloy systems has recently been developed [104]. Using this modified database, the phase composition in alloy materials can be predicted more accurately. It is worth noting that the method using the thermodynamic phase diagram calculation to assist composition design makes it easy to obtain the required alloy materials with target phases and compositions and significantly accelerates the composition design of many advanced structural materials. However, the phase composition of the intermetallic compound-strengthened high-entropy alloy is more complicated than that of the general multiple-principal-element alloy. Therefore, there are still some differences between the simulation results based on the current database and the experimental results directly affecting the processing and design of alloys. Therefore, in order to make more accurate predictions on the composition design of intermetallic compound-strengthened high-entropy alloys in the future, there is still an urgent need for a thermodynamic database specifically designed for intermetallic compound-strengthened high-entropy alloys.

3.2. Unique Structure and Excellent Tensile Properties at Ambient Temperature

Compared with traditional high-temperature structural materials, the new L_{12} -strengthened high-entropy alloy combines the advantages of a plastic high-entropy alloy matrix and a stable intermetallic compound strengthening phase, which can achieve a perfect combination of physical and mechanical properties [83,85,91,100–106]. It can exhibit ultra-high strength and good plasticity at ambient, high, or cryogenic temperature. This cannot be completed by ordinary single-phase solid-solution high-entropy alloys or any other traditional structural materials [83,106–112]. Overall, it is safe to assume that the excellent performance of the unique intermetallic compound-strengthened high-entropy alloy is closely related to its special structure.

To better understand the excellent properties of these new alloys, a lot of research has been focused on exploring the relationship between the microstructure and properties of intermetallic compound-strengthened high-entropy alloys. Liu et al. [105] developed an L_{12} -strengthened high-entropy alloy (MCINPS) with an excellent strength-ductility combination, as shown in the Figure 9. This is a typical polycrystalline structure composed of uniform equiaxed crystals with a grain size of about 40–50 nm. Within a grain, the nearly spherical nano-intermetallic compound phase (about 30–50 nm) is uniformly distributed in the matrix, with a volume fraction of up to 50% to 55%. From the XRD results, it is clear that it is a fcc- L_{12} dual-phase nanostructure. Additionally, the nanoscale intermetallic compound phase in the alloy is perfectly coherent with the matrix phase. This small lattice mismatch effectively enhances the stability of the ordered phase in the alloy and avoids the occurrence of heterogeneous coarsening to offer excellent properties [106–108]. It is noteworthy that this L_{12} -strengthened high-entropy alloy has a tensile yield strength of up to 1 GPa and ultimate tensile strength of close to 1.5 GPa, which is five times that of a single-phase FeCoNi alloy [13]. At the same time, the tensile elongation is up to 50%, which provides a perfect balance of tensile properties. Figure 10 compares the ambient

temperature properties of the L1₂-strengthened high-entropy alloy with those of other high-temperature structural materials [71,83,100,106,108–112].

Similarly, a large number of studies have proved that the L1₂-strengthened high-entropy alloy has excellent mechanical properties at ambient temperature. Yang et al. developed an L1₂-strengthened high-entropy alloy based on FeCoNiAlTi. There are plenty of ductile multi-component L1₂ nanoparticles (about 30–50 nm) with a volume fraction of up to 55% in the multi-component matrix. Its ambient-temperature yield strength and ultimate tensile strength are 1 GPa and 1.45 GPa, respectively. More importantly, the alloy can still maintain a large uniform tensile elongation of 46% with such a high yield strength. Zhao et al. [85] developed an L1₂-strengthened high-entropy alloy (CoCrNi)Al₃Ti₃ based on CoCrNi (Figure 11), which achieved an excellent tensile ductility up to 45% at the ultimate tensile strength of 1.2 GPa. A comparison of tensile properties (at ambient temperature) revealed that the L1₂-strengthened (CoCrNi)Al₃Ti₃ alloy was significantly better than existing nickel-based superalloys. Table 1 below summarizes the tensile properties of various L1₂-strengthened high-entropy alloys at ambient temperature.

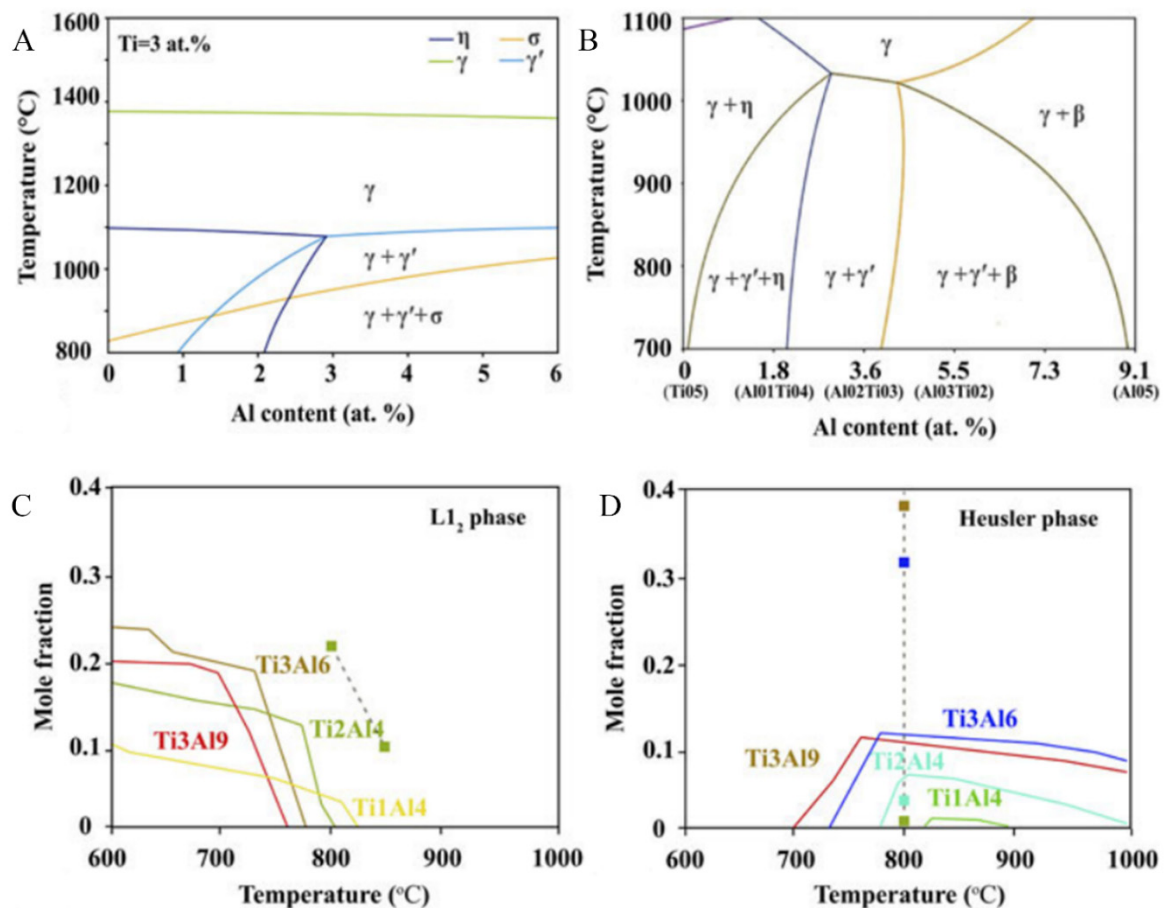


Figure 8. (A) Phase diagram calculations of (CoCrNi)_{97-x}Ti₃Al_x alloy (at.%) using Thermo-Calc software with TTNi8 database. (B) Phase diagram calculations of Al_xCo_{1.5}CrFeNi_{1.5}Ti_y alloy (at.%) using Thermo-Calc software with TTNi8 database. (C) The equilibrium phase mole fraction of the L1₂ phase as a function of temperature calculated using the thermal-calc method for the (FeCoNiCr)_{100-x-y}Al_xTi_y system (at.%). (D) The equilibrium phase mole fraction of the Heusler phase as a function of temperature calculated using the thermal-calc method for the (FeCoNiCr)_{100-x-y}Al_xTi_y system (at.%) adapted with permission from ref. [85]. Copyright 2021 Elsevier.

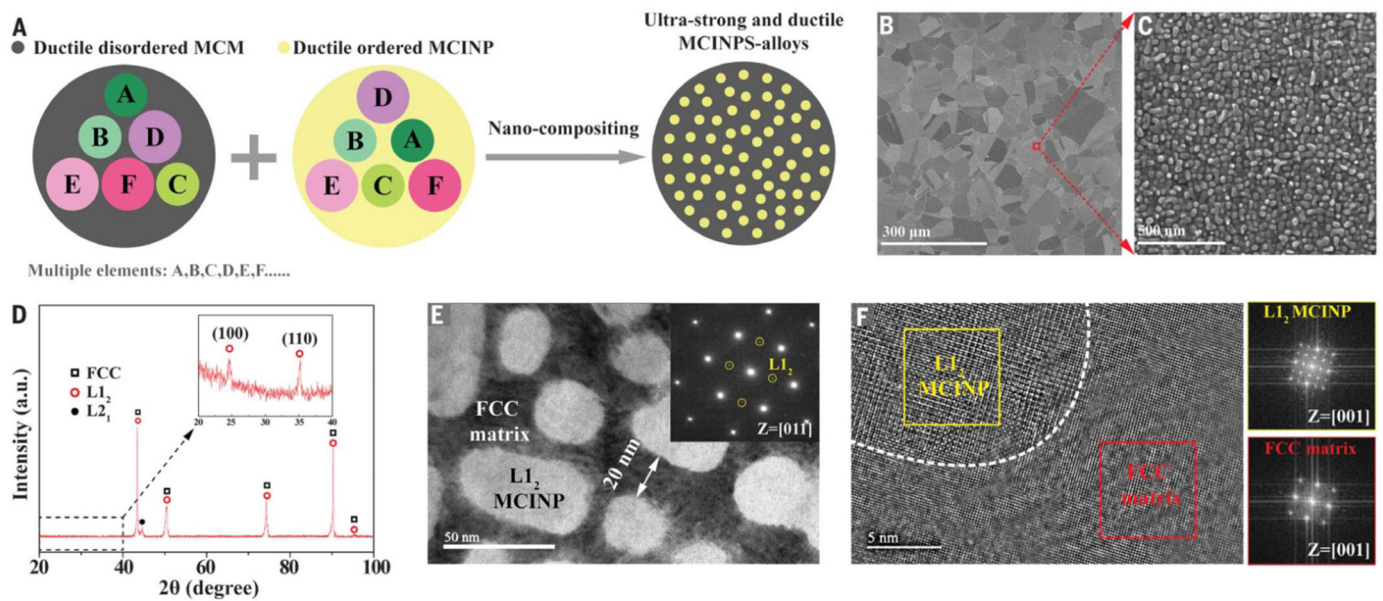


Figure 9. Conceptual design and microstructural characterizations of the MCINPS alloys. (A) Schematic of the design concept of the MCINPS alloys. MCM, multicomponent matrix. (B) Scanning electron microscopy (SEM) image of the Al_7Ti_7 alloy exhibiting the typical equiaxed grain structures. (C) SEM image of the Al_7Ti_7 alloy revealing the uniform distribution of high-density L_{12} MCINP within the grain interior. (D) XRD patterns showing the phase compositions of the Al_7Ti_7 alloy. a.u., arbitrary units. (E) TEM image of the Al_7Ti_7 alloy showing the nanostructured morphology. The inset shows the corresponding SAED pattern. (F) Representative high-resolution TEM image confirming the interfacial coherency. adapted with permission from ref. [105]. Copyright 2021 The American Association for the Advancement of Science.

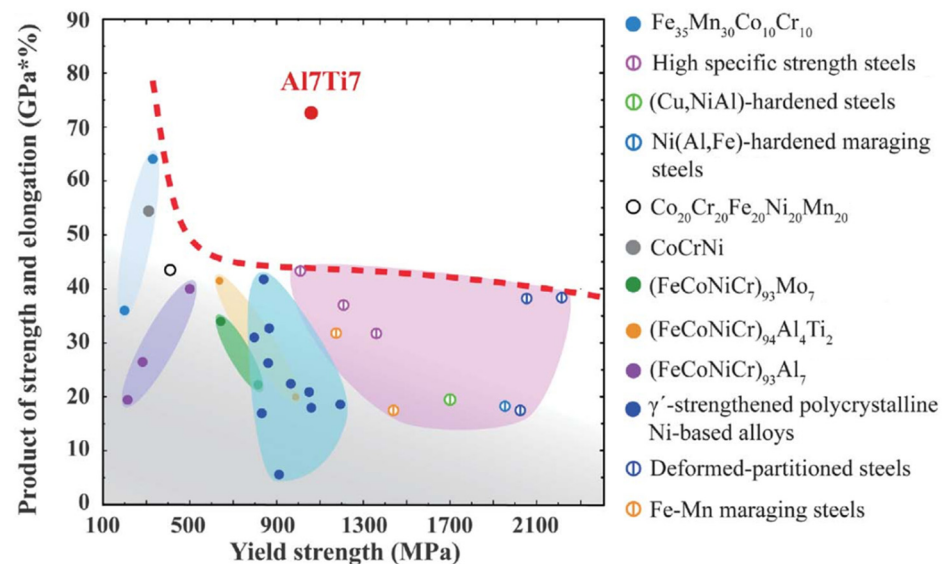


Figure 10. Yield strength versus the product of strength and ductility of the MCINPS alloys compared with those of other high-performing materials showing that exceptional strength-ductility combination can be achieved in the MCINPS alloys at ambient temperature (Al_7Ti_7 is the alloy of interest in this reference) adapted with permission from ref. [105]. Copyright 2021 The American Association for the Advancement of Science.

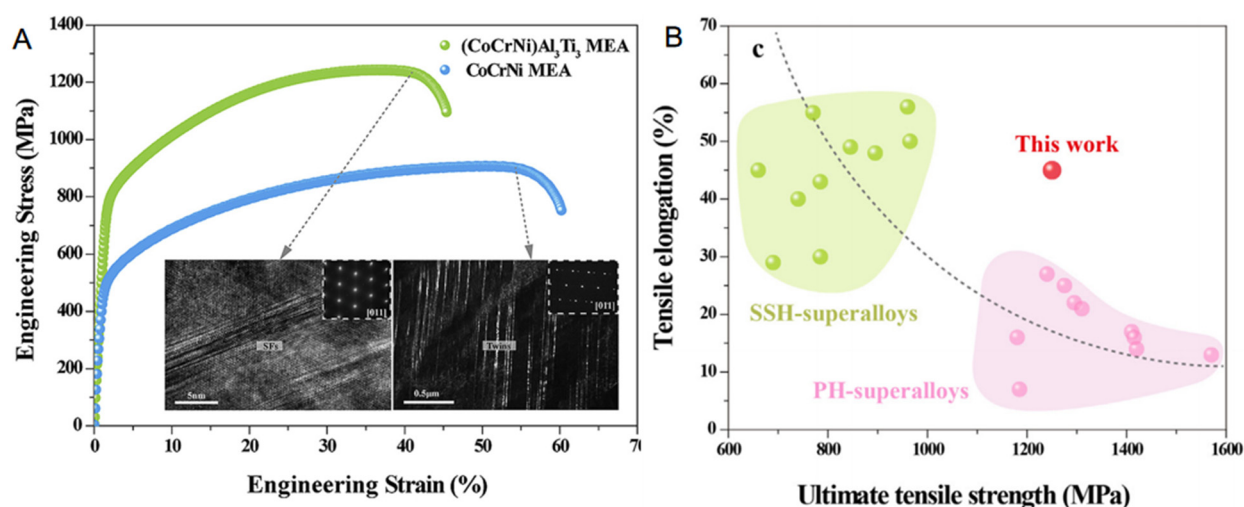


Figure 11. (A) Mechanical properties of the L_{12} -strengthened $(\text{CoCrNi})_{94}\text{Al}_3\text{Ti}_3$ alloy (at.%) compared to those of single-phase CoCrNi base alloy at ambient temperature. (B) Ultimate tensile strength at ambient temperature versus tensile elongation of the present alloy in comparison with commercial superalloys adapted with permission from ref. [85]. Copyright 2021 Elsevier.

Table 1. Tensile properties of representative single-fcc and L_{12} -strengthened HEAs at ambient temperature adapted with permission from ref. [73]. Copyright 2021 Springer Nature.

Composition (at.%)	Aging Condition	Strengthening Phase	YS (MPa)	UTS (MPa)	EL(%)	Ref.
$\text{Fe}_{25}\text{Co}_{25}\text{Ni}_{25}\text{Cr}_{25}$	800 °C/1 h	Nil	~276	~705	~39	[12]
$\text{Fe}_{20}\text{Co}_{20}\text{Ni}_{20}\text{Cr}_{20}\text{Mn}_{20}$	800 °C/1 h	Nil	~265	~460	~47	[12]
$\text{Al}_7\text{Co}_{23.26}\text{Cr}_{23.26}\text{Fe}_{23.26}\text{Ni}_{23.26}$	550 °C/150 h	L_{12}	~285	~540	~50	[113]
	630 °C/50 h	$B2 + L_{12}$	~490	~835	~48	[113]
$(\text{Fe}_{25}\text{Co}_{25}\text{Ni}_{25}\text{Cr}_{25})_{94}\text{Ti}_2\text{Al}_4$	700 °C/18 h	$L_{12} + L_{21}$	~551	~982	~42	[82]
	800 °C/18 h	$L_{12} + L_{21}$	~645	~1094	~39	[82]
	900 °C/18 h	L_{21}	~301	~715	~46	[82]
	Coldroll					
	+700 °C/4 h	$L_{12} + L_{21}$	~1005	~1273	~17	[69]
$\text{Al}_{3.7}\text{Cr}_{18.5}\text{Fe}_{18.5}\text{Co}_{18.5}\text{Ni}_{37}\text{Cu}_{37}$	700 °C/20 h	L_{12}	~719	~1048	~30.4	[95]
	800 °C/1 h	L_{12}	~460	~732	~31.7	[95]
$\text{Al}_{3.64}\text{Co}_{40.9}\text{Cr}_{27.27}\text{Fe}_{27.27}\text{Ni}_{40.9}\text{Ti}_{5.45}$	750 °C/50 h	L_{12}	~640	~830	~10	[114]
$\text{Al}_{3.31}\text{Co}_{27}\text{Cr}_{18}\text{Fe}_{18}\text{Ni}_{27.27}\text{Ti}_{5.78}$	Hotforging	L_{12}	~952	~1306	~20.5	[85]
$\text{Al}_8\text{Co}_{17}\text{Cr}_{17}\text{Cu}_8\text{Fe}_{17}\text{Ni}_{33}$	700 °C/5 h	L_{12}	~365	~365	~0.1	[115]
	1150 °C/5 h	L_{12}	~215	~489	~59	[115]
$\text{Al}_{10}\text{Co}_{25}\text{Cr}_8\text{Fe}_{15}\text{Ni}_{36}\text{Ti}_6$	900 °C/5 h	L_{12}	~568	~786	~12	[86]
	900 °C/50 h	L_{12}	~596	~1039	~20	[86]
$\text{Ni}_{47.9}\text{Al}_{10.2}\text{Co}_{16.9}\text{Cr}_{7.4}\text{Fe}_{8.9}\text{Ti}_{5.8}\text{Mo}_{0.9}\text{Nb}_{1.2}\text{W}_{0.4}\text{C}_{0.4}$	800 °C/20 h	L_{12}	~847	Nil	Nil	[116]

3.3. Outstanding Thermal Stability at High Temperatures

In addition to its outstanding comprehensive mechanical properties at ambient temperature, the L_{12} -strengthened high-entropy alloy also has excellent performance at high temperatures. As mentioned earlier, this strategy of strengthening the alloy by introducing a large number of coherent intermetallic compounds as the strengthening phase on the multiple-principal-element alloy matrix is the same as that of the nickel-based superalloys. Studies have also observed that the role of the L_{12} phase in the L_{12} -strengthened high-entropy alloy is the same as that of strengthening phase γ' in the nickel-based superalloys. Therefore, it is hoped that the new alloy will be a good candidate in the field of high-temperature structural application [89,117,118].

There are many studies that have proven that the L₁₂-strengthened high-entropy alloy does perform well in terms of high-temperature thermal stability. For instance, a variety of L₁₂-strengthened high-entropy alloys, including (NiCoCr)₉₄Al₃Ti₃ [119], (NiCoCrFe)₉₄Al₄Ti₂ [114], and Al_{0.5}CuCrFeCoNi [120], can have a reinforcing phase even after prolonged high-temperature heat treatment. The coarsening rate of the reinforcing intermetallic compound phase in the alloy is much slower than that of the traditional superalloys. Therefore, the new superalloys have good creep resistance and high-temperature stability, making them more suitable for use as high-temperature structural materials. The above characteristics are the attribute of two aspects. First, the matrix of the L₁₂-strengthened high-entropy alloy is a multiple-principal-element alloy. It can prevent the coarsening of L₁₂ nanoparticles by inhibiting the migration of atoms because of its unique lattice distortion effect and slow diffusion [121–123]. On the other hand, the intermetallic compound phase itself has a high stacking fault energy, which increases the activation energy of atom diffusion and provides softening resistance [73]. However, most L₁₂-strengthened high-entropy alloys have shortcomings when used as high-temperature structural applications. The main reason is that the intermetallic compound phase in the alloy will dissolve at high temperatures. When the volume fraction of L₁₂ in the alloy is too small, it will not be able to stabilize the alloy at high temperatures. To solve the above problems, a large number of L₁₂-strengthened high-entropy alloys with a higher volume fraction at high temperature have been developed, as shown in Figure 12. There is still a 45% volume fraction of the L₁₂ phase in the Ni_{44.7}Co_{23.7}Fe₈Cr₁₀Al_{8.6}Ti₅ alloy after 1000 °C aging treatment [114]. This is much higher than other L₁₂-strengthened high-entropy alloys. The solid-solution temperature and solidus temperature of the L₁₂ phase in the Ni_{47.9}Al_{10.2}Co_{16.9}Cr_{7.4}Fe_{8.9}Ti_{5.8}Mo_{0.9}Nb_{1.2}W_{0.4}C_{0.4} alloy are 1199 °C and 1276 °C, respectively [118]. Therefore, the alloy can have enough strengthening phases to improve the thermal stability at higher temperatures. It is worth mentioning that Zhao et al. [124] suggested a new type of (Ni₂Co₂FeCr)₉₂Al₄Nb₄ alloy where the addition of the Nb element provides a large lattice mismatch of 0.78%. This results in excellent tensile properties in a large temperature range from ambient temperature to 870 °C (especially at 760 °C). From the data, it is clear that a yield stress of more than 720 MPa can be achieved, which exceeds most L₁₂-strengthened high-entropy alloys.

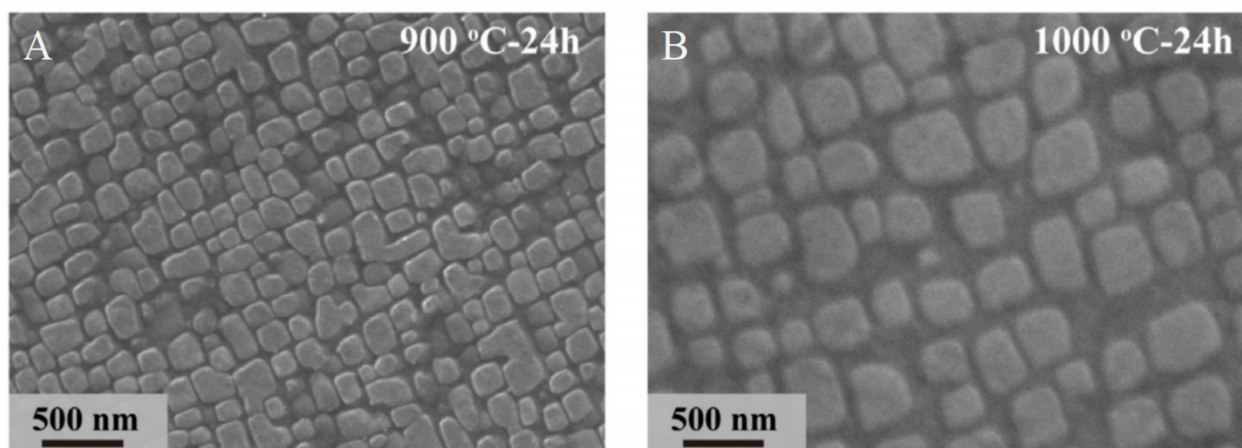


Figure 12. Microstructures of the Ni_{44.7}Co_{23.7}Fe₈Cr₁₀Al_{8.6}Ti₅-based (at.%) high-entropy superalloys aged at (A) 900 °C for 24 h and (B) 1000 °C for 24 h adapted with permission from ref. [114]. Copyright 2021 Elsevier.

For some high-temperature structural materials, another thorny issue is the inherent intermediate-temperature embrittlement of the material. Most nickel-based superalloys are prone to the formation of brittle precipitate or unwanted phases at high temperatures, which reduces the high-temperature performance of the material. Similarly, in L₁₂-strengthened high-entropy alloys, complex chemical interactions of multiple elements greatly increase the possibility of the formation of unwanted precipitation phases, especially

at grain boundaries, e.g., Heusler, η , and Laves phases [84,125]. The presence of a small number of precipitation phases will not cause much damage to the ambient-temperature performance of the material. However, it will cause severe grain boundary embrittlement of the alloy at the intermediate temperature (usually about 600–800 °C), which is the so-called intermediate-temperature embrittlement [126,127]. To address this issue, Yang et al. [128] obtained the solidification path of the intergranular heterogeneous precipitation phase by analyzing the evolution of the solidification structure at the grain boundary during the aging process, and thus proposed a duplex-aging strategy, as shown in Figure 13. Using this strategy can eliminate the brittle precipitation at the grain boundary and stabilize the intergranular structure, thereby improving the intermediate-temperature embrittlement of the L_{12} -strengthened high-entropy alloy and improving the performance of the material.

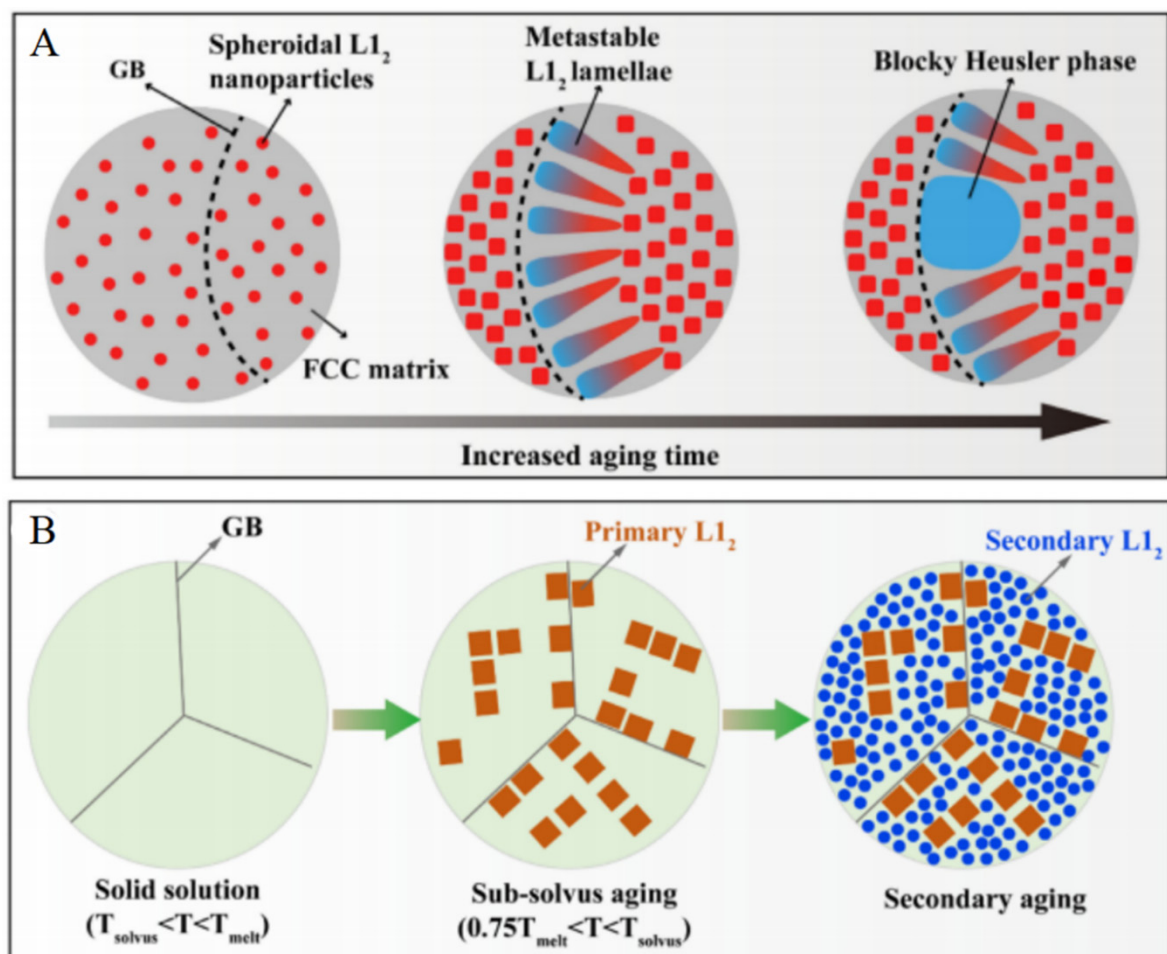


Figure 13. (A) Schematic illustration showing the complex precipitation pathway from the metastable L_{12} to the Heusler phase at the GBs. (B) Schematic illustration of the duplex-aging design for the GB stabilization adapted with permission from ref. [128]. Copyright 2021 Elsevier.

In summary, compared with traditional alloys, these L_{12} -strengthened high-entropy alloys constitute a new type of structural material with a unique structure. A large number of studies have shown that they have excellent mechanical properties in a wide temperature range [124]. This is due to the unique “dual-high-entropy synergy” [114]. The multi-component matrix and intermetallic compound particles essentially have better comprehensive properties than their chemically simple counterparts. For example, the tensile strength of single-phase FeCoNiCr HEA is much higher than that of pure Ni, while still maintaining an excellent ductility of up to 40% at 293 K [12]. At the same time, unlike other intermetallic compounds, some L_{12} -type intermetallic compounds generally do not exhibit

a ductile-to-brittle transition at cryogenic temperatures, but have surprisingly excellent properties on the contrary. For FeCoNiCrTi_{0.2}, when the temperature is reduced from 293 K to 77 K, the tensile strength increases from 1.24 GPa to 1.58 GPa, and the ductility increases from 36% to 46% [128]. This makes L1₂-strengthened high-entropy alloys more attractive for many cryogenic applications or services involving other extreme service conditions [84]. The tensile mechanical properties of single-phase solid-solution high-entropy alloys and intermetallic compound-strengthened high-entropy alloys at different temperatures are compared in Figure 14.

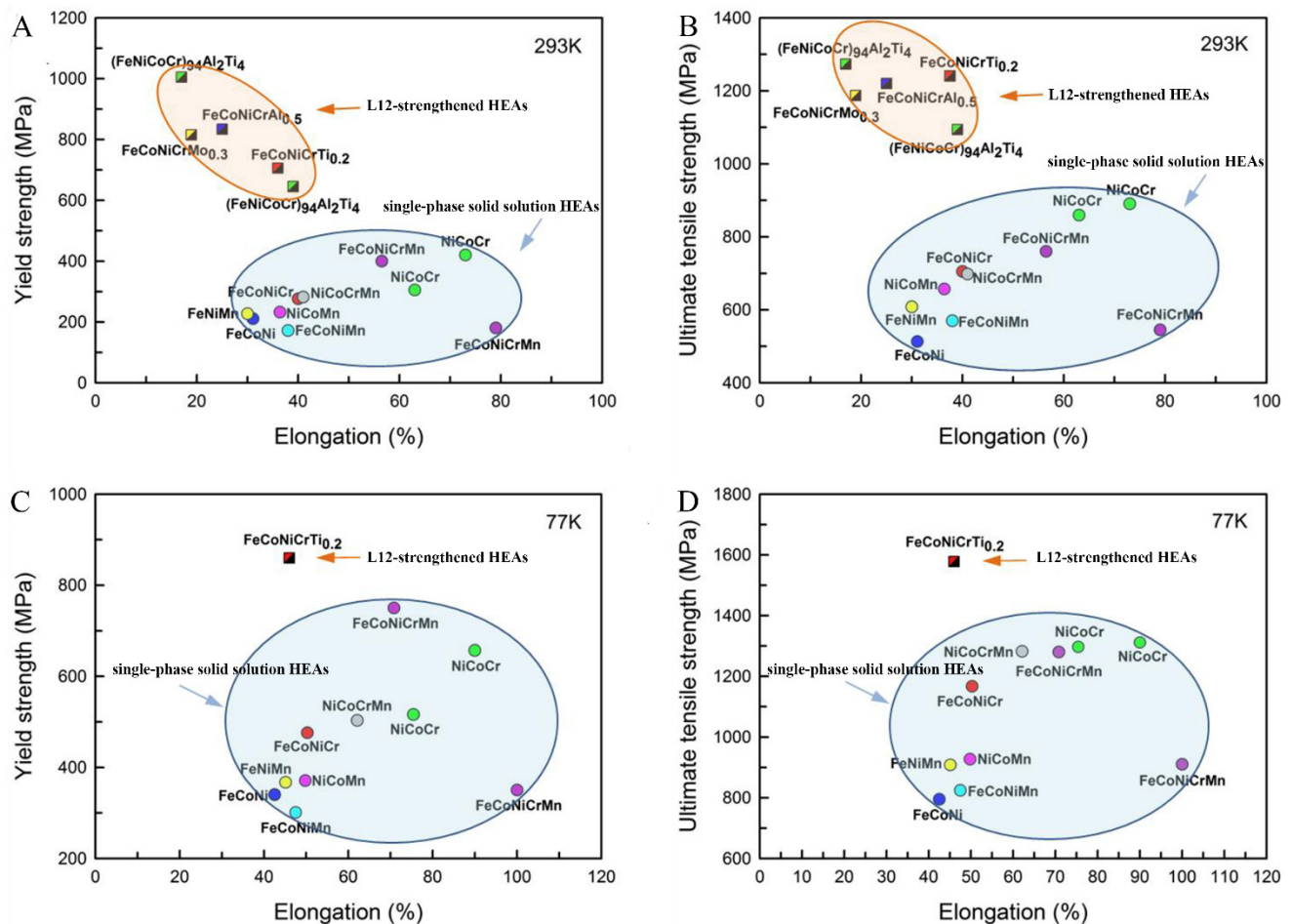


Figure 14. (A) Elongation versus yield strength of the L1₂-strengthened HEAs compared with the single-phase solid-solution HEAs at 293 K. (B) Elongation versus ultimate tensile strength of the L1₂-strengthened HEAs compared with the single-phase solid-solution HEAs at 293 K. (C) Elongation versus yield strength of the L1₂-strengthened HEAs compared with the single-phase solid-solution HEAs at 77 K. (D) Elongation versus ultimate tensile strength of the L1₂-strengthened HEAs compared with the single-phase solid-solution HEAs at 77 K adapted with permission from ref. [128]. Copyright 2021 Elsevier.

3.4. The Effect of Different Strengthening Mechanisms on the Properties of Alloys

The ultra-high strength of the intermetallic compound-strengthened high-entropy alloy comes from its unique strengthening mechanisms. Traditionally, the strengthening mechanisms in polycrystalline materials are summarized into four categories: solid-solution strengthening, fine-grain strengthening, dislocation strengthening, and precipitation strengthening [129]. For single-phase solid-solution high-entropy alloys and most other traditional alloy materials, their strength comes from only one or two strengthening mechanisms, and it would not be sufficient for many engineering applications. Therefore, scientists consider applying more or even all types of strengthening mech-

anisms to intermetallic compound-strengthened high-entropy alloys to achieve greatly improved strength.

Many studies have confirmed that all strengthening mechanisms can be introduced into the intermetallic compound-strengthened high-entropy alloy through appropriate processing methods to greatly improve the properties of the alloy. He et al. [71] perfectly combined the four strengthening mechanisms in the intermetallic compound-strengthened high-entropy alloy through thermomechanical processing and microstructure control, which achieved extraordinary tensile properties at ambient temperature. The in-depth analysis in such studies shows that among the four strengthening mechanisms, precipitation strengthening plays a major role. This also provides the reasoning why the strength of the intermetallic compound-strengthened high-entropy alloy is better than that of the single-phase solid-solution high-entropy alloy. There is no strengthening phase in the single-phase solid-solution high-entropy alloy to initiate the precipitation strengthening mechanism. Figure 15 shows the contribution of different strengthening mechanisms to the overall strength of the two intermetallic compound-strengthened high-entropy alloys after different thermomechanical treatments. At the same time, Zheng et al. [130] also carried out a similar study to provide the same conclusion.

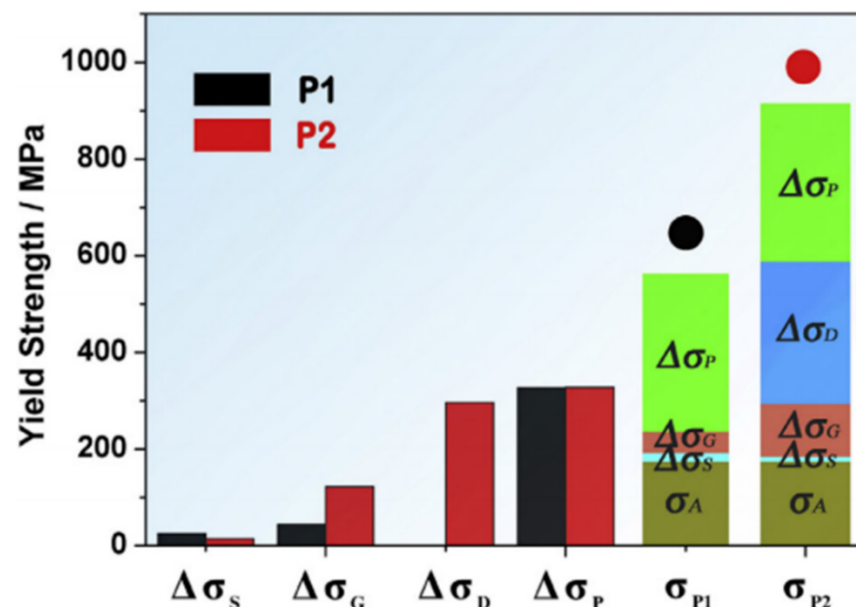


Figure 15. The strength contributions from different hardening mechanisms adapted with permission from ref. [71]. Copyright 2021 Elsevier.

Peng et al. [131] also studied the ripening of the nano-intermetallic compound phase and its effect on the overall performance of the intermetallic compound-strengthened high-entropy alloy. It is well known that the intermetallic compound phase in the alloy can provide strong precipitation strengthening. As shown in Figure 16, precipitation strengthening can be divided into the Orowan dislocation looping mechanism and dislocation cutting through the particle mechanism [71,132], which is closely related to the size of the intermetallic compound phase. For ordered phases that are not coherent with the matrix or when the size of the ordered phase exceeds a critical value, the Orowan dislocation looping particles mechanism plays a dominant role [133,134], and when the ordered phase particles are sufficiently small and coherent, the dislocation shearing particles mechanism [134] dominates. It is very apparent that the size of the intermetallic compound phase has a great influence on the alloy strengthening mechanism, and thus the strength of the alloy. The growth of crystal grains is dependent on the ripening of the intermetallic compound phase. Due to the growth of the intermetallic compound phase, the pinning pressure of the grain boundary is reduced, resulting in the growth of crystal grains. In addition, the yield

strength and microhardness of the alloy first increase and then decrease with the aging time, reaching the peak at 24 h, which is obviously related to the precipitation strengthening mechanism of the alloy. From calculations, it is clear that the dislocation shear particles are the main precipitation strengthening mechanism in the range of 0–24 h, while the Orowan dislocation looping particles are the main precipitation strengthening mechanism after 24 h.

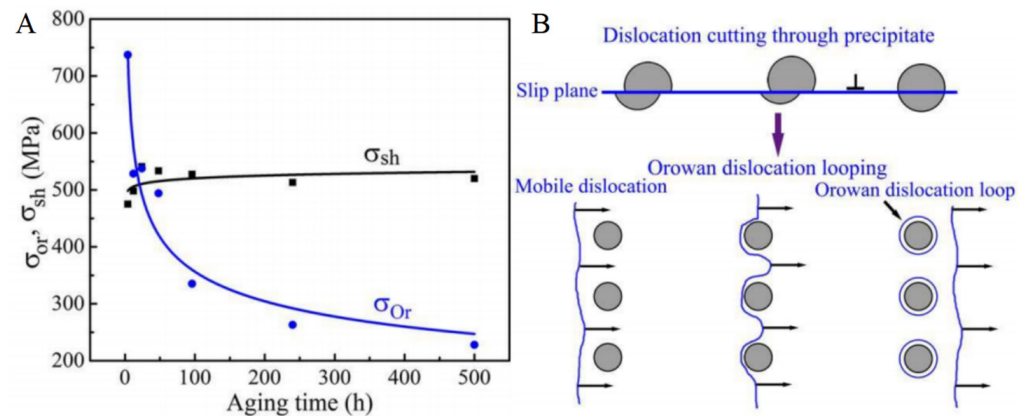


Figure 16. (A) Variations in precipitate shearing stress (σ_{sh}) and Orowan dislocation looping stress (σ_{Or}) as functions of the aging time. (B) Schematics of the Orowan dislocation looping and dislocation shearing mechanisms adapted with permission from ref. [131]. Copyright 2021 Elsevier.

In summary, the development of intermetallic compound-strengthened high-entropy alloys is of great significance for improving the performance of high-entropy alloys. As for the initial single-phase solid-solution high-entropy alloy, the most common means to improve the strength is preventing the movement of dislocations through refining the grains and increasing the number of boundaries in the alloy. However, it has been proven that the effect of this strengthening method is very limited. For example, Otto et al. [135] attempted to enhance the strength of the FeCrNiCoMn high-entropy alloy by refining the grain. The result suggested that as the grain size decreased from 155 nm to 4.4 nm, the ambient-temperature yield strength of the alloy was only increased from the original 200 MPa to 350 MPa. This increase was even smaller for higher temperature, as shown in Figure 17. Therefore, it can be stated that to activate more strengthening mechanisms, it is necessary to introduce a strengthening secondary phase into the single-phase solid-solution high-entropy alloys. However, for high-entropy alloys containing only a small number of intermetallic compound phases, most precipitates in alloys are often too large in size and nonuniform in distribution, so they cannot have a significant effect [71], such as the mixed FCC + BCC structure of CuCr₂Fe₂NiMn [136] and the single-phase BCC structure of Al_{0.5}CrFe_{1.5}MnNi_{0.5} [137]. Therefore, the emergence of intermetallic compound-strengthened high-entropy alloys is an inevitable result in the process of exploring high-performance high-entropy materials.

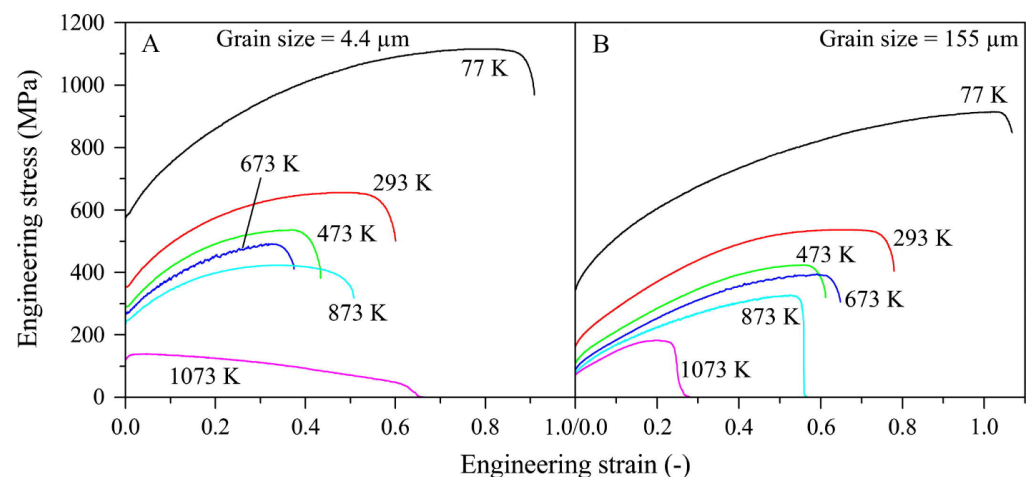


Figure 17. (A) Engineering stress–strain curves of the CoCrFeMnNi alloy at the six testing temperatures for the fine-grained (grain size 4.4 μm). (B) Engineering stress–strain curves of the CoCrFeMnNi alloy at the six testing temperatures for the coarse-grained (grain size 155 μm) adapted with permission from ref. [135]. Copyright 2021 Elsevier.

4. High-Entropy Intermetallics (HEIs)

The development of intermetallic compound-strengthened high-entropy alloy points out the direction for the further exploration of high-temperature structural materials. To some extent, intermetallic compound-strengthened high-entropy alloys solve the problem that traditional structural materials cannot possess both high strength and good plasticity at ambient temperature. However, it has to be admitted that these new alloys still have unoptimized structures and unavoidable defects. There is a study showing that these intermetallic compounds as strengthening phases can only be stable at temperatures below 900 °C [114]. In other words, these new types of materials can only be used at temperatures below 900 °C, which is not sufficient in many applications such as engines, turbines, and other heat-resistant components. Therefore, significant efforts are underway to address this issue and to create alloys that can be used reliably at even higher temperatures (higher than 850 °C) and to meet the urgent need for high-performance structural materials through new science and technology developments. To make ordered phases with high-volume fractions existing in multiple-principal-element alloys, a new type of high-temperature structural material—high-entropy intermetallics (HEIs)—was invented.

Unlike the idea of introducing ordered phases into high-entropy alloys, the HEIs start with the existing intermetallic compound using a variety of elements to multi-principalize the sublattice of intermetallic compounds and gradually form a new high-entropy material with a long-range ordered structure. The specific definition of HEIs is a kind of intermetallic compound with a long-range ordered crystal structure, in which at least one sublattice is randomly occupied by 3 or more kinds of atoms in (near) equimolar ratio, and the volume fraction of the intermetallic compound phase (main phase) is at least 75% [138–140]. The crystal structure model of typical high-entropy intermetallics is shown in the Figures 18 and 19.

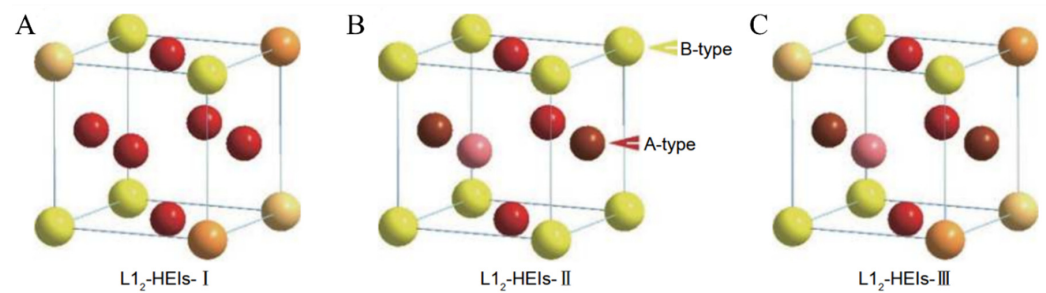


Figure 18. Crystal structure model of $L1_2$ structure high-entropy intermetallics simulation adapted with permission from ref. [54]. Copyright 2021 Elsevier. (A) I type high-entropy intermetallics. (B) II type high-entropy intermetallics. (C) III type high-entropy intermetallics.

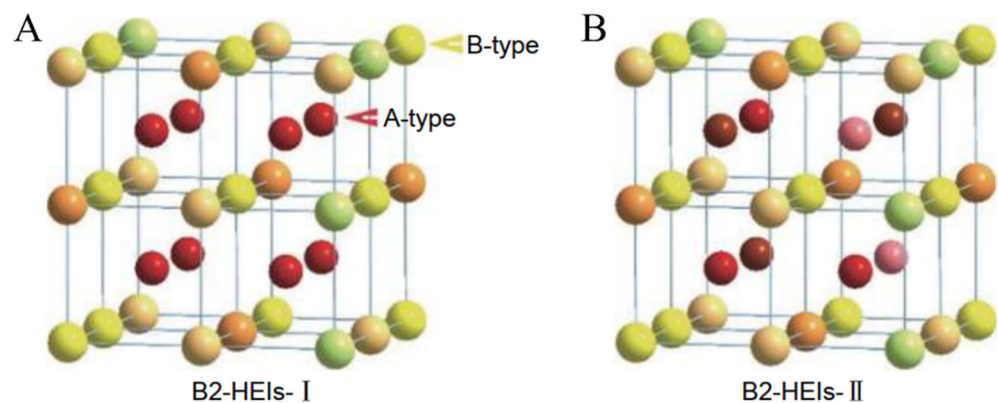


Figure 19. Crystal structure model of B2 structure high-entropy intermetallics adapted from [55]. (A) I type high-entropy intermetallics. (B) II type high-entropy intermetallics.

This multi-component strategy can lead to a significant increase in the entropy of high-entropy intermetallics to meet their intrinsic requirements as high-entropy materials. In HEIs, the content of each component in the same sublattice is mostly in an equimolar ratio, while the total content ratio of each component in the different sublattice depends on the stoichiometric ratio of the chemical formula. Moreover, the components have a tendency to occupy specific sublattices, so they are completely different from the random occupancy of each component in the high-entropy alloy lattice [138–140]. This complex and unique arrangement of atoms makes HEIs become a new type of alloy material that is substantially different from high-entropy alloys and intermetallic compounds.

HEIs not only have similar characteristics to high-entropy alloys, but also have its unique internal characteristics. Specifically, in addition to the high-entropy effect, lattice distortion effect, and slow diffusion effect similar to high-entropy alloys, HEIs also have unique electronic structure diversification effects [138–140]. As each sublattice of HEIs contains a variety of alloy elements with different types and amounts, the electronic environment of atoms is quite different from each other. In addition, HEIs not only form a variety of nondirectional metallic bonds in the same sublattice, but also form a variety of directional covalent bonds through hybridization between different sublattices, so the type of bond is far more than those of traditional solid-solution alloys and intermetallic compounds. Overall, HEIs are appearing as a new generation of new materials that are most promising for high-temperature structural applications. Thus, in this section, we start with the existing research results on HEIs, and then make a detailed and systematic overview of the research progress in its atomic occupancy rules, performance characteristics, plasticization mechanism, and other aspects.

4.1. Experiments Combined with Calculations to Accelerate the Study of Atomic Occupancy

In the previous section, we mentioned that HEIs are obtained by the multi-principalization of intermetallic compounds. Compared with high-entropy alloys, one of the most obvious

characteristics of HEIs is that each component has a specific tendency to occupy different sublattices in the alloy, rather than being randomly arranged in a lattice. Therefore, when designing HEIs, we need to understand the position of each component in the alloy sublattice. As different atoms have different electronic structures and atomic radii, this means that the occupancy of atoms is closely related to the crystal structure of the alloy, and the crystal structure directly affects the properties of the alloy material [141]. Therefore, in the composition design process of HEIs, we must understand the position of each atom in the crystal lattice in order to determine the type and quantity of the added alloying element to obtain the best comprehensive performance.

The most commonly used strategy to analyze the rule of atomic occupancy of components in HEIs is the method combining experiment and theory. More precisely, it is three-dimensional atom probe technology (3D-APT) combined with first-principles calculations. The 3D-APT is a measurement and analysis method with atomic-level spatial resolution. Complex structures such as the surface of the sample and interface of various compound materials can be reconstructed by analyzing different element atoms one by one to reconstruct three-dimensional distribution patterns of different element atoms at the nanoscale and provide accurate analysis of element spatial content [142]. As shown in Figure 20, Yang et al. [143] obtained the distribution of atoms of different elements in superlattice materials that have nanoscale disordered interfaces (NDI-SMS) using 3D-APT technology. It is apparent that the 3D-APT can be used to accurately obtain the distribution of each element atom in different phases of HEIs, thus providing accurate crystallographic information for further analysis of the position of element atoms in the lattice. It is worth remembering, as with any other characterization technique, that the 3D-APT has its reliability issues at times. These are much more evident when we want to analyze the trace element atoms in alloy materials. In other words, this technology sometimes fails to provide accurate enough results. Therefore, further improved results can be achieved by the first-principles calculation.

First-principles calculation can provide the total energy, enthalpy of formation, relative stability of various crystal structures of compounds, lattice parameters, and the energy of point and planar defects based only on the atomic number of the constituent elements of the material and their positions in the unit cell of a given crystal structure [144]. That is to say, 3D-APT can provide the elemental distribution in the different phases of the alloy, and several possible unit cell models can be constructed based on the ratio of moles of elemental atoms, the ratio of stoichiometric numbers between different sublattices, and the known atomic occupancy information. The total energy of different models can be obtained using first-principles calculation and the information from 3D-APT. Generally, the unit cell model with the lowest total energy should be the most stable crystal structure in practice, and its corresponding atomic occupancy situation should be the most reasonable. Using this calculation method, the occupancy of many components in HEIs can be ascertained. For example, Zhang et al. [141] studied $(\text{Ni,Co,Fe})_3(\text{Al,Ti,Fe})$ and its six derived L_{12} subsystems based on the first-principles calculation. Here, they determined the site preference of different elements in multicomponent intermetallics (MCIs) using Monte-Carlo simulations with the energies obtained from DFT calculations (DFT-MC). It is clear that Ti tends to occupy the Al sublattice, while most Co and Fe atoms tend to occupy the Ni sublattice. This provides a theoretical basis for the subsequent composition design of HEIs. Figure 21 is one structural model of the studied alloys based on the simulation results.

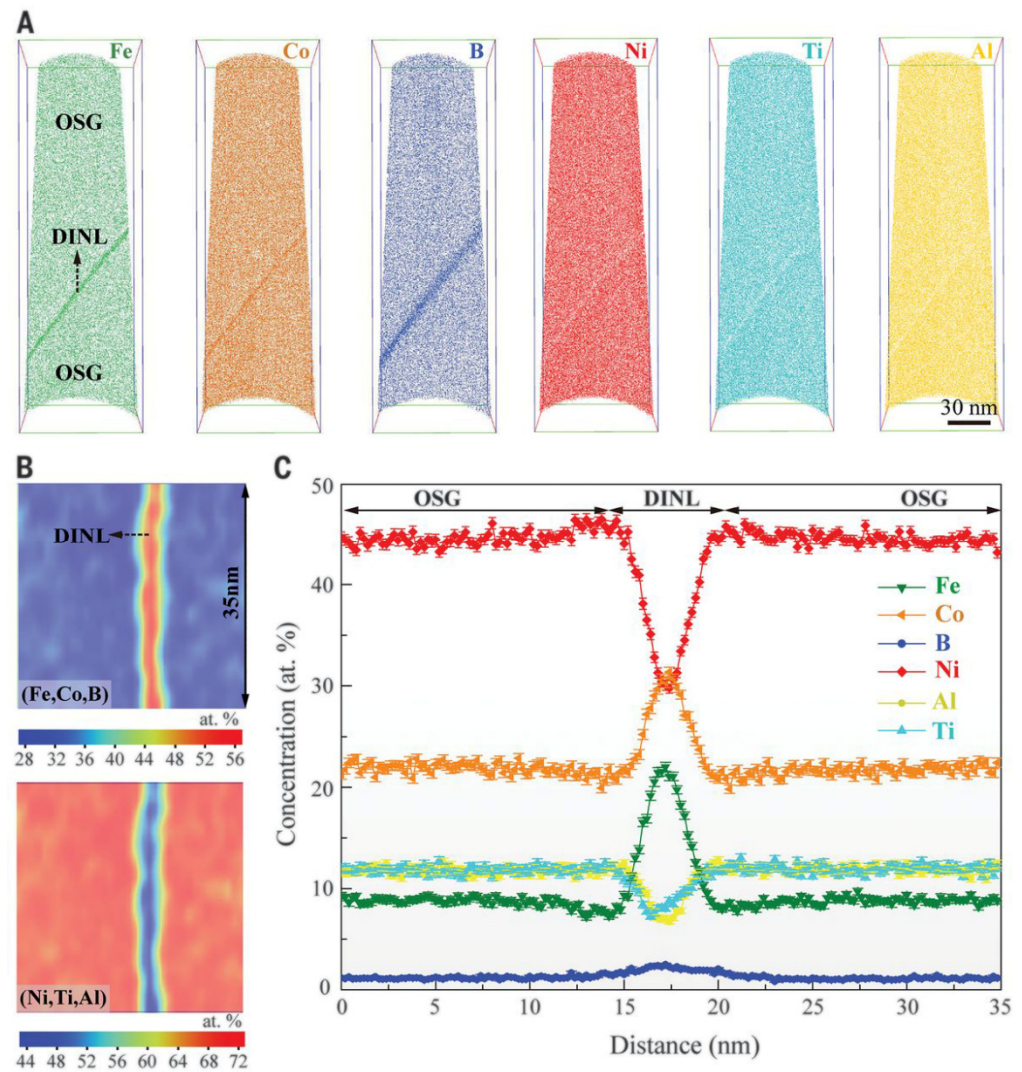


Figure 20. Three-dimensional compositional distributions and nanoscale interfacial cosegregation of the NDI-SMs. (A) Atom maps reconstructed using 3D-APT that show the distribution of each element. (B) Two-dimensional compositional contour maps revealing the multielement cosegregation behaviors of different elements within the disordered interfacial nanolayer (DINL). (C) One-dimensional compositional profile that quantitatively reveals the elemental distributions across the micrometer-scale ordered superlattice grain (OSG) and disordered interfacial nanolayer (DINL) adapted with permission from ref. [143]. Copyright 2021 The American Association for the Advancement of Science.

Research in recent years has shown that first-principles calculation is a promising tool for designing materials from scratch. Coupled with improvements in theoretical and computational methods, it is possible to theoretically anticipate the crystal structure, thermodynamic properties, and defect behavior of a multiple-principal-element alloy before actually synthesizing it. The calculation can be used to screen alloy materials with more advanced properties than existing materials, and find ways to improve the preparation of alloys with practical value [143,144]. The combination of 3D-APT and first-principles calculation can more efficiently assist the composition design and optimization of HEIs, and further accelerate the development of this new type of material.

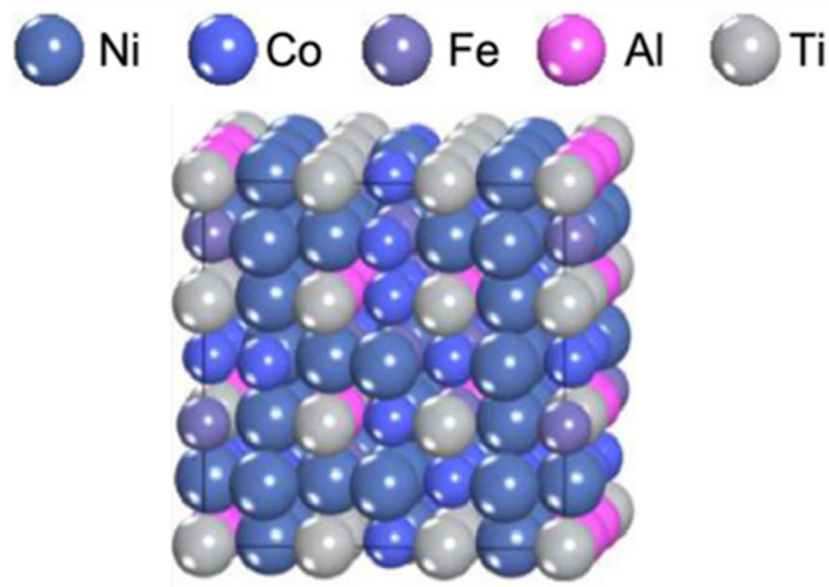


Figure 21. Structure models of $\text{Ni}_{44}\text{Co}_{23}\text{Fe}_{11}\text{Al}_8\text{Ti}_{14}$ based on the results of MC simulation adapted with permission from ref. [141]. Copyright 2021 Elsevier.

4.2. Unique Atomic Structure Provides Remarkable Comprehensive Mechanical Performance

As a new type of high-temperature structural material, HEIs have unique performance characteristics that many existing alloys do not have. From a thermodynamic point of view, the unique arrangement of atoms makes the enthalpy of mixing/enthalpy of formation of HEIs lower than those of high-entropy alloys and other multiple-principal-element alloys. Additionally, sublattice multi-principalization makes the configuration entropy of HEIs significantly higher than those of other traditional intermetallic materials. According to the thermodynamic Gibbs–Helmholtz equation $\Delta G = \Delta H - T\Delta S$, it can be seen that a higher configuration entropy and lower mixing enthalpy/enthalpy of formation will inevitably lead to a decrease in Gibbs free energy, which is conducive to the formation and structural stability of HEIs. From a dynamic point of view, the diffusion mechanism of HEIs is composed of both solid solution and compound diffusion methods. It can be carried out by the random jumping of vacancies and interstitial atoms within the same sublattice. There may be a vacancy diffusion mechanism between the two types of sublattices, including the divacancy diffusion mechanism and the annular diffusion mechanism. This complicated diffusion mechanism coupled with the hindrance of lattice distortion and other factors make it more difficult for atoms to diffuse in HEIs. Therefore, the crystal structure of HEIs is more stable than other alloys, including the intermetallic compound-strengthened high-entropy alloys mentioned above, and is more suitable for high-temperature structural materials from the perspective of thermodynamics and kinetics [54]. Zhou et al. [145] obtained B2 and D0_{22} -type HEIs through mechanical alloying and spark plasma sintering. After experimental analysis, it was found that most of the alloys exhibited a single B2 phase and D0_{22} phase when annealed at a temperature higher than 1300 °C; however, when annealed at a temperature lower than 1100 °C, there will be a small number of secondary phases, as shown in Figures 22 and 23. Importantly, these secondary phases are reversible and they will disappear when temperatures rise above 1300 °C again. In general, it can be stated that HEIs have the potential to broaden the range of temperature used for high-temperature structural materials and maintain a stable microstructure under higher-temperature conditions.

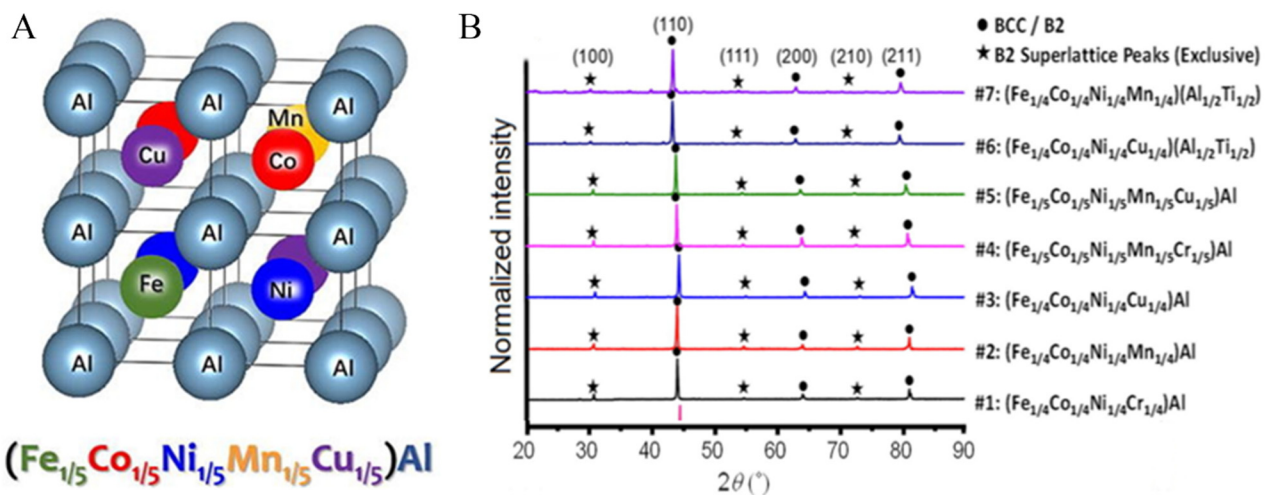


Figure 22. (A) Schematic illustrations of the HEIs with the B2 structure. (B) XRD patterns for seven HEIs specimens that exhibit primarily or completely single B2 phases after annealing at 1100 °C for 10 h adapted with permission from ref. [145]. Copyright 2021 Elsevier.

The HEIs can also have ultra-high strength and good plasticity at the same time. We know that strength and plasticity are two important indicators for measuring whether structural materials can be put into actual production and application. However, as shown in Figure 24, due to the inherent conflict between strength and plasticity, so far, it is still a significant challenge to develop a material with excellent strength and plasticity that can be put into practical commercial use [146]. For example, for single-phase alloys including high-entropy alloys, they generally show good ductility, but most of the materials suffer from relatively cryogenic strength. To solve the lack of strength problem, the researchers introduced the intermetallic compound-strengthened high-entropy alloy. However, due to the dissolution of the ordered phase at high temperatures, its use of extremely high temperature is limited. As described previously, the nickel-based superalloy is reasonably good at providing comprehensive performance in the higher-temperature range, but inevitably, the formation of brittle precipitate will result in premature cracks and final failure of the material.

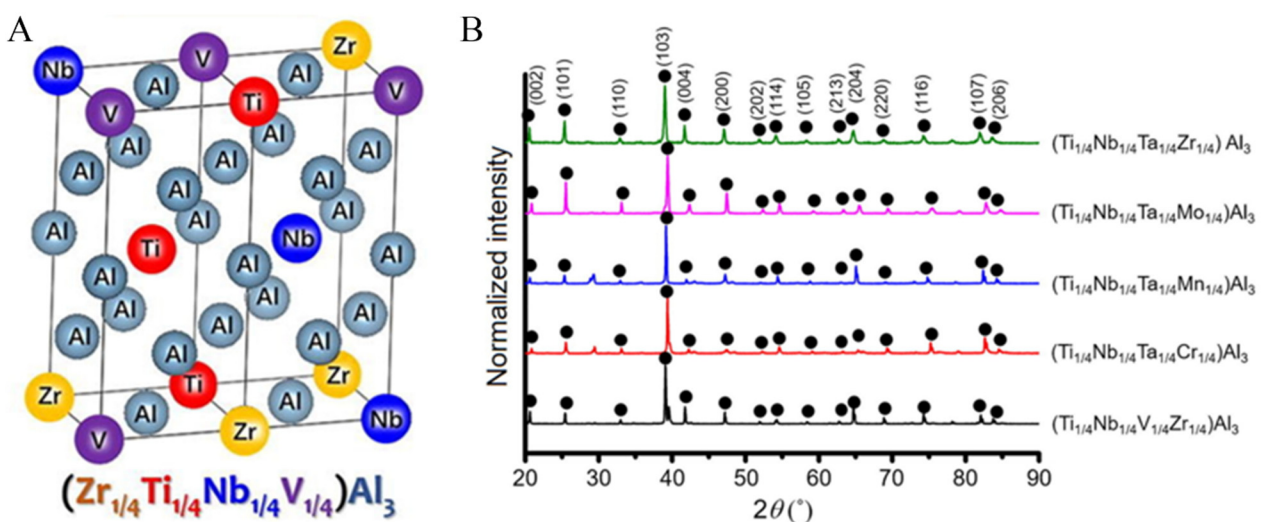


Figure 23. (A) Schematic illustrations of the HEIs with the D0₂₂ structure. (B) XRD patterns of five HEIs specimens with primarily the D0₂₂ phase after annealing at 1300 °C for 10 h. The D0₂₂ phase is indexed, and the unindexed peaks with low intensity correspond to the secondary phases. The D0₂₂ phase is dominant in all five cases (albeit some minor secondary phases) adapted with permission from ref. [145]. Copyright 2021 Elsevier.

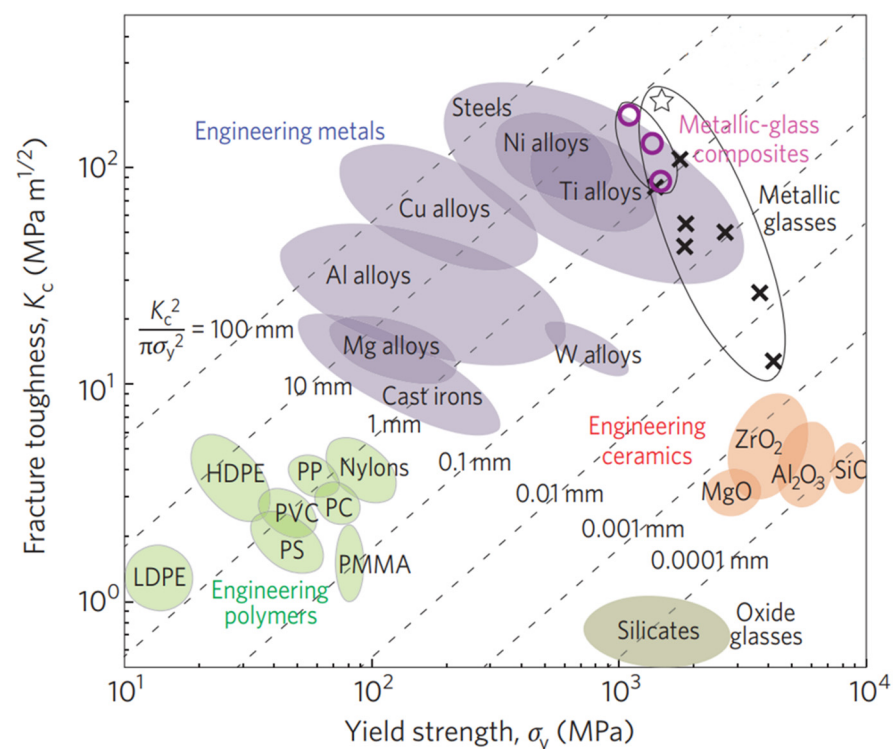


Figure 24. Ashby plot showing strength–toughness relationships for engineering materials. Diagonal lines show the plastic-zone size, $K_c^2 / \pi \sigma_y^2$, where K_c is the fracture toughness and σ_y is the yield strength adapted with permission from ref. [146]. Copyright 2021 Springer Nature.

The emergence of HEIs seems to solve all of the above problems. As a new type of high-temperature structural material with a similar structure to nickel-based superalloys, HEIs have excellent strength and toughness. More importantly, it is worth noting that HEIs are expected to replace nickel-based superalloys in a higher-temperature range due to their better stability at high temperatures. Shi et al. [147] developed a new eutectic HEI named EHEA, which precipitated the $L_{12} + B_2$ phase with a hierarchically organized herringbone structure inside the material through directional solidification technology. The microstructure and XRD analysis of such a material are shown in Figure 25. It is apparent that the volume fraction of the L_{12} phase is 59%, and the volume fraction of the B_2 phase is 41%. This new type of material combining a soft phase and hard phase effectively induces the crack buffer mechanism. Additionally, it can provide an ultra-high ambient temperature tensile elongation of 50% without sacrificing strength. Its overall performance is significantly better than any other as-cast eutectic and near-eutectic high-entropy alloy materials. Figure 26 shows the tensile properties of EHEA at ambient temperature and the comparison with other as-cast eutectic and near-eutectic HEAs. The results show that EHEA is the best eutectic high-entropy material reported in recent years with superior tensile properties at ambient temperature.

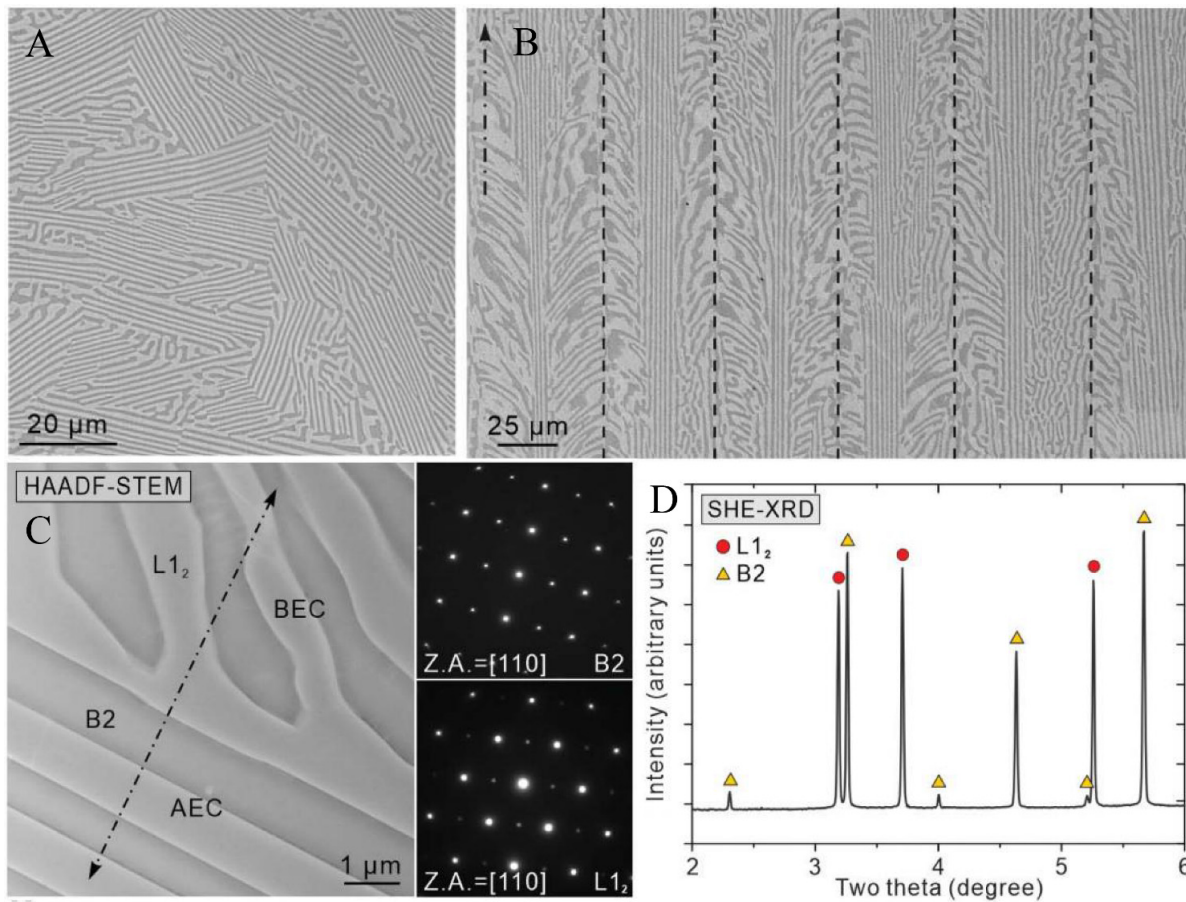


Figure 25. (A) SEM backscattered electron image of conventionally cast EHEA. (B) SEM backscattered electron image of directionally solidified EHEA with a hierarchical herringbone microstructure. The black arrows in (B) indicate the DS direction, and also the tensile loading direction in Figure 26A. (C) HAADF-STEM image and related SAED patterns of B2 and L1₂ phases. (D) SHE-XRD of B2 and L1₂ phases adapted with permission from ref. [147]. Copyright 2021 The American Association for the Advancement of Science.

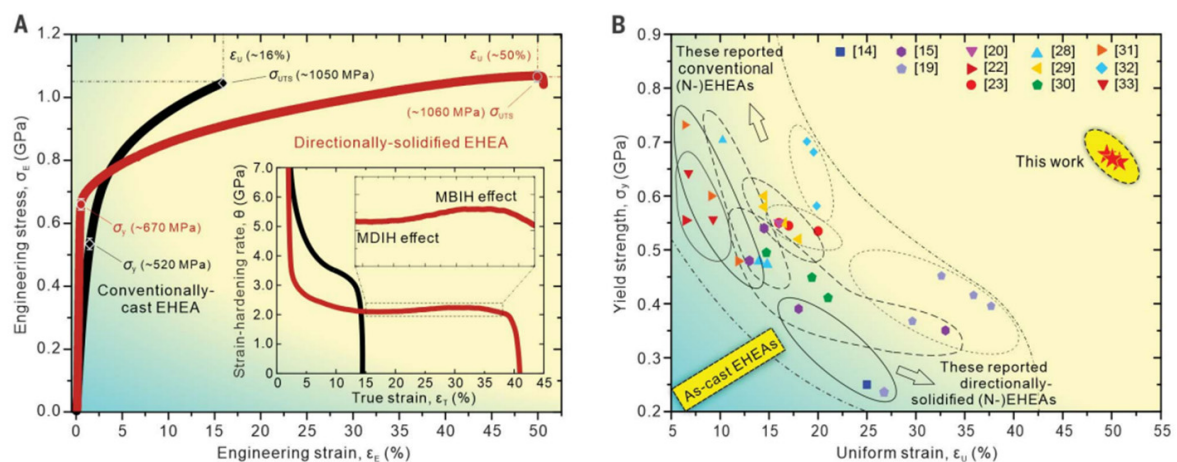


Figure 26. Tensile response at ambient temperature. (A) Engineering stress–strain curves of the directionally solidified EHEA compared with the conventionally cast EHEA. Inset shows the corresponding strain-hardening curves. MDIH and MBIH refer to multi-slip dislocation-induced hardening and microband-induced hardening, respectively. (B) Yield strength versus uniform strain of the directionally solidified EHEAs compared with those of previously reported as-cast eutectic and near-eutectic HEAs. (N-) EHEAs refer to eutectic and near-eutectic HEAs. The conventional (N-) EHEAs include directly cast and arc-melting eutectic and near-eutectic HEAs adapted with permission from ref. [147]. Copyright 2021 The American Association for the Advancement of Science.

4.3. Ingenious Structure Improves Grain Boundary Properties of Alloy

In polycrystalline materials, the grain boundary is usually the weak spot. The grain boundary is usually the location where unwanted brittle phases result in the initiation of site of cracks. It is also the most basic part of the alloy to fail under load, and HEIs are no exception. Although attempts have been made to introduce single-crystal technology to solve this problem, it is impossible to apply this technology to HEIs because of long production periods and high manufacturing costs. Therefore, in order to solve the problem of grain boundary brittleness in polycrystalline alloys and to further improve the comprehensive performance of HEIs, Yang et al. [143] prepared a HEI $\text{Ni}_{43.9}\text{Co}_{22.4}\text{Fe}_{8.8}\text{Al}_{10.7}\text{Ti}_{11.7}\text{B}_{2.5}$ with nanoscale disordered interfaces, and used EDX technology to accurately obtain the position of different element atoms in the ordered superlattice structure $(\text{Ni,Co,Fe})_3(\text{Al,Ti,Fe})$. Figure 27 highlights the nanoscale interfacially disordered structure of this material.

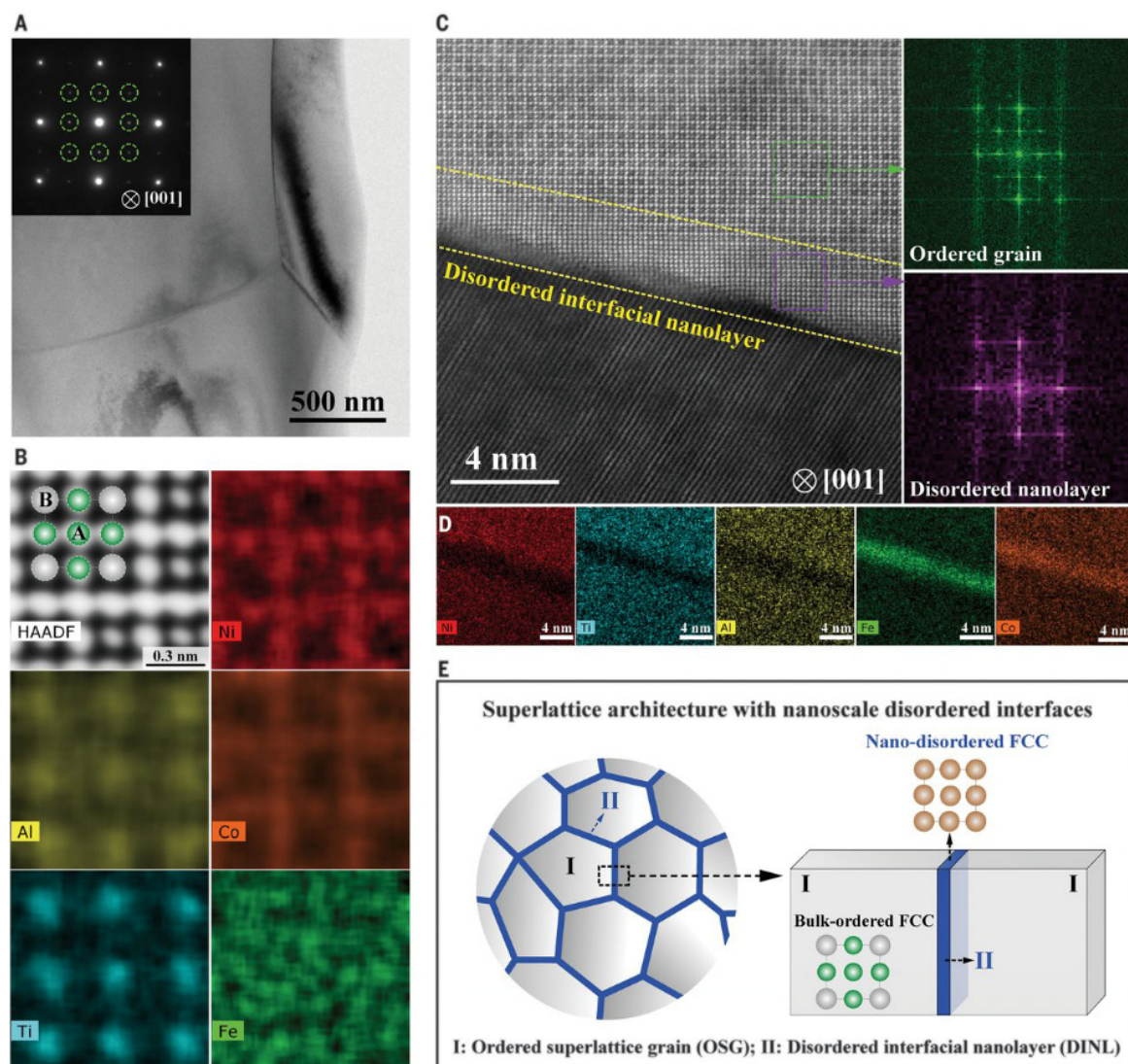


Figure 27. (A) Bright-field TEM image showing the polycrystalline morphology. (Inset) A corresponding selected-area electron diffraction pattern collected from the grain interior, which shows the L_{12} -type ordered structure. (B) Atomic-resolution HAADF-STEM image and corresponding EDX maps taken from the inner L_{12} -type OSG, revealing the sublattice occupations. (C) High-resolution HAADF-STEM image revealing the ultrathin disordered layer at the grain boundaries with a nanoscale thickness. The images on the right show the corresponding fast Fourier transform (FFT) patterns. (D) EDX maps showing the compositional distribution of the DINL. (E) Superlattice architecture with nanoscale disordered interfaces. © Schematic illustration highlighting the nanoscale interfacially disordered structure adapted with permission from ref. [143]. Copyright 2021 The American Association for the Advancement of Science.

The results show that the unique interfacial disordering is driven by multi-element cosegregation, which creates a distinctive nanolayer (5 nm) between adjacent micrometer-scale superlattice grains with an $L1_2$ structure. This nanolayer can serve as a source of sustainable ductility because of its excellent ductility and work hardening ability under tensile deformation [83,145,148]. In addition, this nanoscale disordered interface can also accommodate a large number of dislocations and allow dislocations to migrate across the grain boundaries to other grains, thereby effectively preventing brittle intergranular fractures by enhancing dislocation mobilities in polycrystalline alloys. This HEI has good comprehensive performances at ambient temperature. It has an ultra-high yield strength of 1040 ± 61 MPa, which is 2.6 times that of a binary Ni_3Al alloy (320 MPa) with similar grain size [149]. It also has a large tensile elongation of $25 \pm 1\%$ and work hardening ability along with an ultimate tensile strength of 1611 ± 2 MPa, as shown in Figure 28A. The performance comparison of this HEI with other existing high-performance-ordered alloys is shown in Figure 28B [150–161], which further illustrates the excellent comprehensive performance of this HEI.

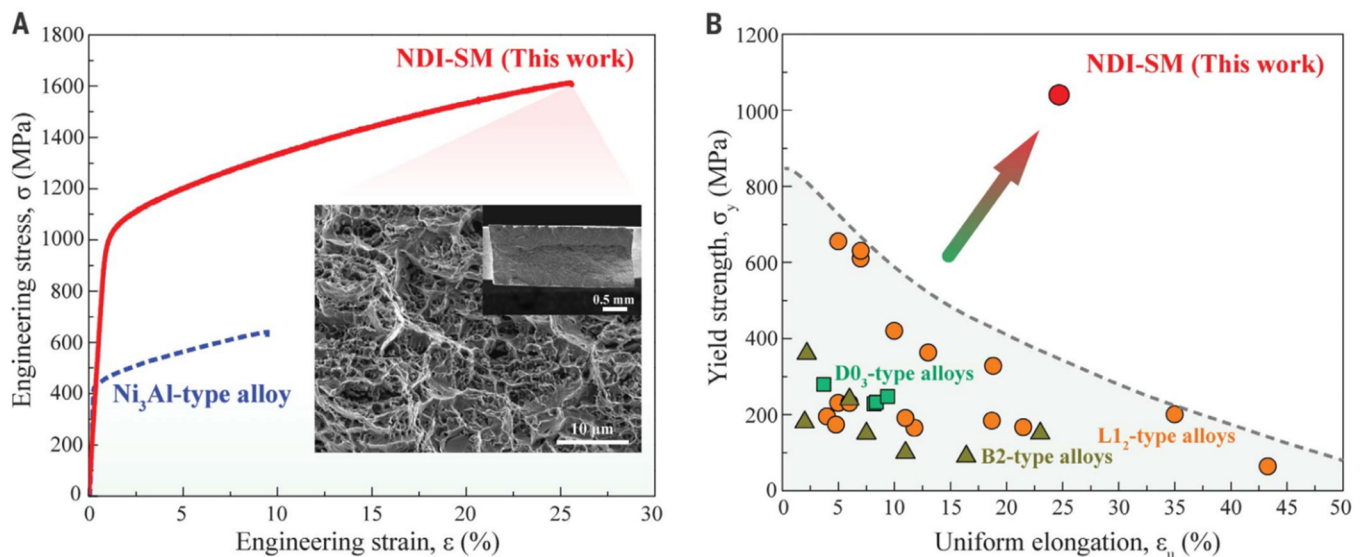


Figure 28. Mechanical properties and thermal stability of the NDI-SMs. (A) Tensile stress–strain curve of the NDI-SM tested at 20 °C in air. The stress–strain curve of the high-strength Ni_3Al -type (Ni_3Al -2.5 at.% B) alloy is also plotted for a direct comparison. (Inset) Tensile fractography showing the ductile dimpled structures. (B) Yield strength (σ_y) versus uniform elongation (ϵ_u) of the present NDI-SM compared with various conventional bulk-ordered alloys adapted with permission from ref. [143]. Copyright 2021 The American Association for the Advancement of Science.

4.4. Various Plasticizing Mechanisms Effectively Improve Alloy Plasticity

The good plasticity of HEIs results from their unique atomic arrangement. The coexistence of multiple components in high-entropy intermetallic compounds leads to the diversification of the electronic structure inside the material. Therefore, the combination of specific alloying elements becomes more complicated and diverse, which is likely to increase the symmetry of the crystal structure of the alloy. As a result, the directionality of the directional bonding in the alloy is reduced, and the Burgers vector of the dislocation movement is reduced. More slip systems are activated because the overall slip system of the alloy is changed and the plasticity of the material is improved. On the other hand, periodic holes in the alloy grain boundary will be reduced or even disappear because of the diversification of the types of elements that make up the alloy. The use of a nanoscale disordered interface to improve material plasticity mentioned above [142] is the best proof of this mechanism. In addition, the grain size of the materials is usually small because of slow atomic diffusion within HEIs, which also improves the material properties and results in improved plasticity of the alloy at ambient temperature.

To date, many studies have demonstrated that most HEIs have excellent strength-plasticity synergies over a wide temperature range of 77 to 293 K [73,85,127,160]. Based on the excellent properties of HEIs, researchers have also explored the deformation methods of this new material. In terms of the influence of stacking fault energy (SFE), a recent study revealed the deformation behavior induced by stacking fault (SF) in a high-performance $L1_2$ -type HEI [85,160]. In this alloy, a large amount of high-density SF was induced through mechanical treatment. This eventually led to the widespread formation of sessile Lomer-Cottrell locks and allowed the material to produce an excellent combination of strength and ductility at ambient temperature. The balance of mechanical performance is attributed to the activation of hierarchical SFs upon loading, which provides continuous work hardening of the material and delays the occurrence of plastic instability. In general, previous studies have shown that various effective plasticizing mechanisms can be initiated in HEIs, such as microband-induced plasticity (MBIP) and SF-induced plasticity (SFIP), among which SFIP is more common [127,161,162].

4.5. Distinctive Electronic Structure Produces Attractive Catalytic Performance

It is worth mentioning that HEIs have the potential to become unique and attractive functional materials in addition to their exceptional structural performance. According to Fantao Kong, the application of this new material is not only limited to the field of advanced structural materials. This newly developed material can have a very broad expansion in superconductivity, catalysis, magnetism, hydrogen storage, etc. [54]. The research results in recent years have gradually confirmed some of these potentials. Jia et al. [163] recently reported a HEI FeCoNiAlTi with an unusual periodically ordered structure containing multiple nonnoble elements as a highly efficient electrocatalyst for hydrogen evolution, naming it D15h HEI (Figure 29). It not only has the same hydrogen evolution reaction (HER) performance as precious metal Pt, but it is also easy to operate and is suitable for large-scale production. As shown in Figure 29B, the excellent catalytic activity of the new material is derived from the special $L1_2$ -type ordered structure of the alloy, which is the important characteristic of HEIs, unlike other traditional alloys. The atomic structure diagram and spatial topography of D15h HEI are shown in Figure 30. The development of this new type of catalyst provides new ideas for the preparation of high-efficiency heterogeneous catalysts, and at the same time, opens up the possibility of HEIs in the field of functional materials.

In summary, the unique atomic arrangement of HEIs and the composition design strategy of coexistence of multiple elements enable a variety of strengthening and plasticizing mechanisms to coexist in the materials, thus enabling HEIs to have excellent properties incomparable to traditional materials in a wide temperature range. A large number of scholars' in-depth research on the composition-structure performance of HEIs and the in-depth exploration of the various mechanisms behind the excellent performance will surely lay an important theoretical and technical foundation for the subsequent research and development of HEIs with more excellent properties. At the same time, HEIs will become a new generation of amphibious high-entropy materials spanning the fields of structural materials and functional materials due to their distinctive electronic diversity structure and other properties. Table 2 lists the structure and mechanical properties of high-entropy intermetallics that have been reported so far.

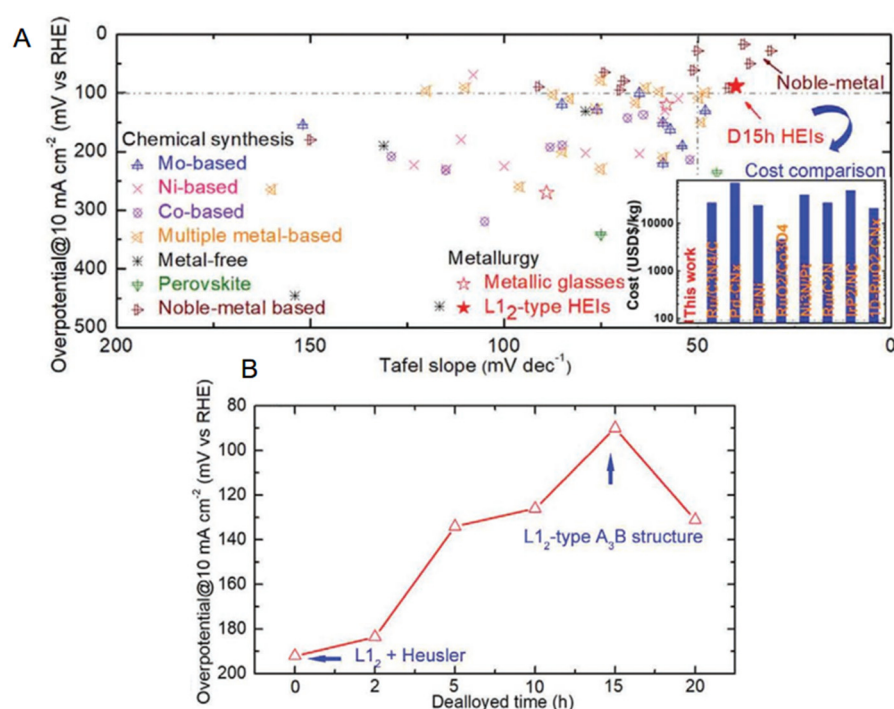


Figure 29. Electrocatalytic performance of the HEI for HER in 1.0 m KOH solutions. (A) Comparison of overpotentials at 10 mA cm⁻² versus Tafel slopes for ≈60 different catalysts in 1.0 m KOH, showing that the L₁₂ HEI represents a low-cost alternative to compete with noble metal catalysts (inset is the comparison of raw materials costs). (B) Relationship between dealloying time-dependent structural evolution and catalytic performance variation, showing the significant improvement for hydrogen evolution reactions (HER) performance as the dealloying process isolated the L₁₂ phase adapted with permission from ref. [163]. Copyright 2021 Wiley Online Library.

Table 2. Microstructure and ambient-temperature tensile properties of HEIs have been reported.

Composition (at.%)	Processing Technic	Phase	YS (MPa)	UTS (MPa)	EL(%)	Microstructure Characteristic
Ni _{43.9} Co _{22.4} Fe _{8.8} Al _{10.7} Ti _{11.7} B _{2.5} [142]	arc melting and thermomechanical processing	L ₁₂ + 0.13 vol%FCC	1040	1600	25	disordered interfaces
Al ₁₉ Fe ₂₀ Co ₂₀ Ni ₄₁ [146]	Conventional casting	55 vol%L ₁₂ + B2	520	1050	16	eutectic herringbone
Al ₁₉ Fe ₂₀ Co ₂₀ Ni ₄₁ [146]	directional solidification	59 vol%L ₁₂ + B2	670	1060	50	eutectic herringbone
Fe _{12.5} Co _{12.5} Ni _{12.5} Cu _{12.5} Al ₅₀ [144]	anneal at 1100 °C for 10 h	B2	-	-	-	dendritic-like structure
Fe ₁₀ Co ₁₀ Ni ₁₀ Mn ₁₀ Cu ₁₀ Al ₅₀ [144]	anneal at 1100 °C for 10 h	B2	-	-	-	
Ti _{6.25} Nb _{6.25} V _{6.25} Zr _{6.25} Al ₇₅ [144]	anneal at 1300 °C for 10 h	D0 ₂₂	-	-	-	
FeCoNiAlTi [163]	dealloying for 15 h	L ₁₂	-	-	-	
Ni ₆₂ Co ₃₄ Fe ₁₅ Al ₁₂ Ti ₂₁ [140]		L ₁₂	-	-	-	

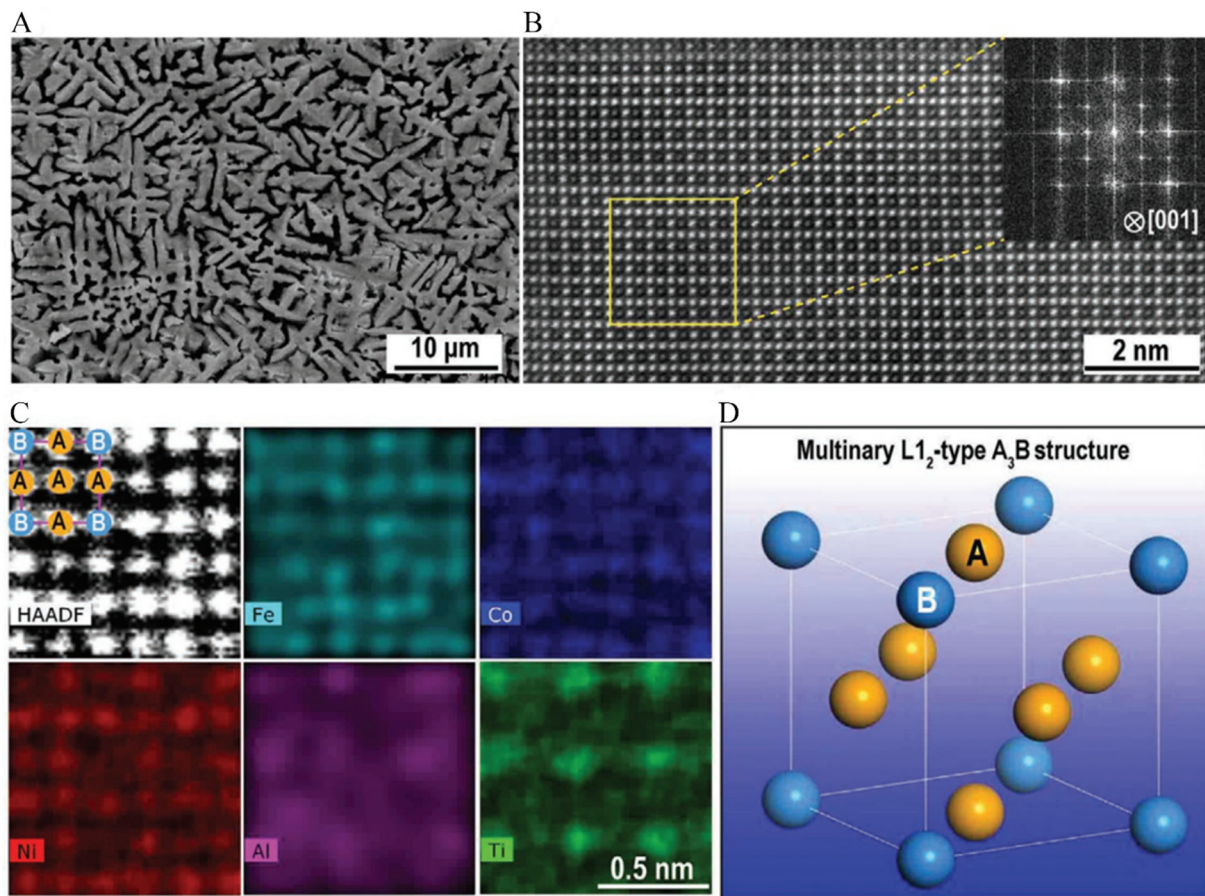


Figure 30. Spatial morphology, structural, and multicomponent nature of the D15h HEI. (A) SEM image of the D15h HEI with a dendritic-like morphology. (B) Aberration-corrected HAADF-STEM image viewed along the [001] zone axis showing the L_{12} -type A_3B structure. The inset shows the corresponding SAED pattern. (C) High-magnification HAADF-STEM image accompanied by atomic-resolution elemental maps clearly showing the ordered crystallographic structure and site occupancy of the L_{12} -type structure (AlTi atoms on the vertices and FeCoNi atoms on the face center in an L_{12} unit cell). (D) DFT modeling of the atomic ordering and site occupancy of the L_{12} HEI, emphasizing the site-isolated structure (A: AlTi, B: FeCoNi) adapted with permission from ref. [163]. Copyright 2021 Wiley Online Library.

5. Conclusions

The intermetallic compound plays a key role in improving the performance of multiple-principal-element alloys. The high-entropy materials enhanced by intermetallic compounds have attracted significant attention because of excellent comprehensive properties and have been used in many fields such as transportation, energy, and aerospace. In this review, we elaborated the importance of intermetallic compounds in high-entropy materials relative to the overall properties and focused on two new types of high-entropy materials containing intermetallic compounds. We also systematically analyzed the microstructure and underlying mechanism responsible for enhanced performance, which is crucial to understand these new materials.

It can be seen from the above report that the intermetallic compound-strengthened high-entropy alloy and HEIs have excellent tensile properties at ambient temperature, high temperature, and even cryogenic temperature. This is achievable via introducing a certain number of intermetallic compounds as the secondary phase to enhance properties including strength, plasticity, thermal stability, and creep resistance. In particular, HEIs have the potential to become a new advanced structural material and solve the inherent strength–plasticity trade-off problem of traditional alloys because of their unique atomic arrangement and electronic structure. In addition, HEIs are also expected to take the place of existing functional materials due to their novel performance characteristics. It is clear

that HEIs can be used as low-temperature superconducting materials, hydrogen evolution reaction (HER) catalysts, magnetic materials, and hydrogen storage materials to replace NbTi, single Pt, ferrite, and other commonly used functional materials [164–167].

These newly developed alloys have their own changes and shortcomings that need to be resolved to explore the full potential of these materials. A key issue is that there is no special database to support the thermal simulation calculation of the new material, which undoubtedly sets up obstacles for the development and optimization of the material. In addition, the development of new materials is inseparable from the progress of processing technology. In order to further improve the performance of materials, it is necessary to discover new processing technology in the future to improve the existing defects, promote the development of materials, and lay a foundation for the progress of a new generation of high-performance high-entropy materials.

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