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High-Entropy Alloys and Compounds: Fundamentals

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1.1 Introduction (Historical Background and Development)

High-entropy alloys (HEAs) were first conceptualized and introduced in the early 2000s (Figure 1.1), pioneered by J.W. Yeh and his colleagues in 2004 [1]. Traditional alloy design typically revolves around a single principal element, supplemented with smaller amounts of secondary elements as dopants to achieve desired property enhancements. However, HEAs challenge this paradigm by combining five or more elements in nearly equal proportions, creating a fundamentally distinct multicomponent system characterized by high configurational entropy and complex microstructures or atomic coordination. The elevated entropy arising from the random distribution of multiple principal elements can stabilize simple solid-solution phases, such as face-centered cubic (FCC) or body-centered cubic (BCC) structures rather than the formation of more complex intermetallic compounds. This stabilization is a direct consequence of entropy-driven thermodynamics, where the high configurational entropy counteracts enthalpic contributions that typically drive phase separation.

The initial HEAs, often consisting of transition metals like Fe, Ni, Co, Cr, and Mn, exhibited outstanding properties [3–5], including high hardness, excellent wear resistance, and remarkable thermal stability. These properties stem from the synergistic combination of elements, which collectively enhance the material's performance under extreme conditions. The high configurational entropy in these alloys plays a key role in suppressing the formation of brittle intermetallic phases but instead promoting ductile and tough solid solutions [6].

Building on the foundational work of Yeh and others, the field of HEAs rapidly expanded in scope and application. Researchers began exploring diverse

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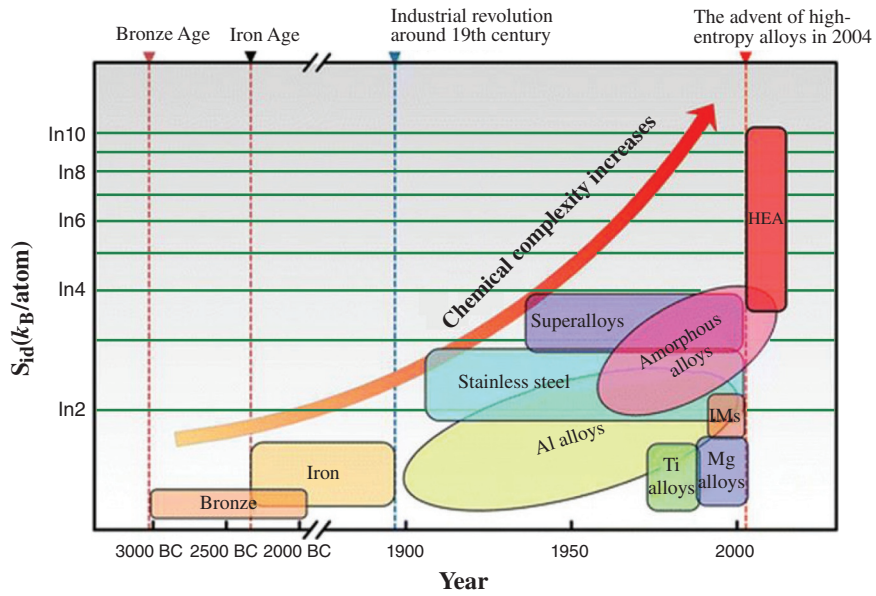


Figure 1.1 Rising trend of alloy chemical complexity versus time (IMs: intermetallics, HEA: high-entropy alloy) [2]. *Source*: [2] / with permission of Springer Nature.

compositional systems, incorporating elements from various groups of the periodic table, including refractory metals (e.g., Mo, W, Ta), lightweight elements (e.g., Al, Mg, Li), and even nonmetallic elements (e.g., Si, B, C) [7]. This diversity allowed for the tailoring of HEA properties to meet the specific demands of various applications. For instance, refractory HEAs demonstrated exceptional high-temperature strength and oxidation resistance, while lightweight HEAs became promising candidates for aerospace applications requiring materials with low density and high strength. HEAs have also shown remarkable potential in harsh environments, such as those encountered in aerospace, nuclear reactors, energy generation, and deep-sea exploration. These environments demand materials that can withstand extreme temperatures, radiation, corrosion, and oxidation. For example, corrosion-resistant HEAs have been developed for marine and chemical processing industries, while high-strength refractory HEAs are being evaluated for use in hypersonic vehicles and fusion reactors [8, 9].

The continued exploration of HEAs is fueled by advancements in computational modeling, materials processing techniques, and experimental characterization. Computational tools such as high-throughput simulations and machine learning algorithms are enabling the design and optimization of novel HEA compositions with tailored properties [10, 11]. These tools allow researchers to predict phase stability, mechanical performance, and environmental resistance with unprecedented accuracy, significantly reducing the time and cost associated with traditional trial-and-error approaches. In parallel, innovations in materials processing techniques, including additive manufacturing (AM), powder metallurgy, and advanced casting methods, are facilitating the scalable production of HEAs with

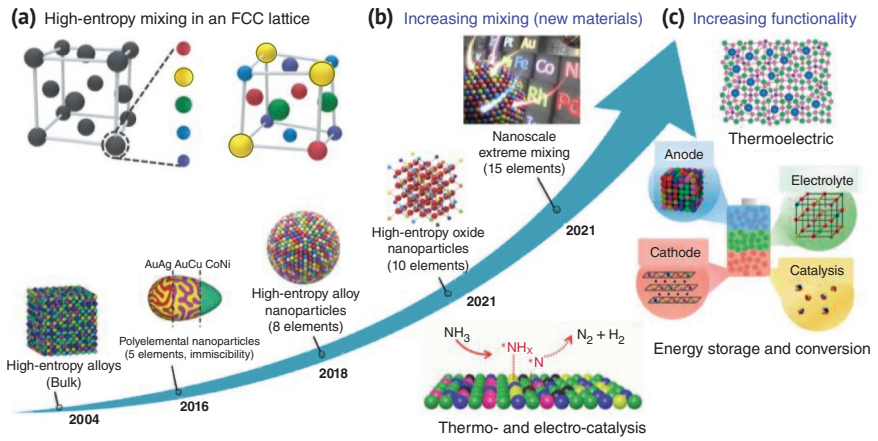


Figure 1.2 Schematic diagram of the development of high-entropy nanoparticles with multielemental composition and enhanced functionality [17]. *Source*: [17] / with permission of American Association for the Advancement of Science.

complex geometries and microstructures [12–14]. Moreover, state-of-the-art characterization tools, such as atom probe tomography (APT), transmission electron microscopy (TEM), and synchrotron-based techniques, provide deep insights into the atomic-scale structure and properties of HEAs, driving a better understanding of the underlying mechanisms that govern their exceptional performance [15, 16].

HEAs hold great promise for addressing critical challenges in materials science and engineering. Their unique combination of properties—including high strength, excellent thermal stability, superior corrosion resistance, and exceptional wear resistance—makes them highly attractive for applications in next-generation technologies. Furthermore, HEAs are poised to play a pivotal role in sustainable development by enabling materials with enhanced durability, reduced resource consumption, and improved energy efficiency. As research continues to advance, the integration of interdisciplinary approaches, combining theoretical modeling, experimental validation, and industrial-scale implementation, will be essential to unlocking the full potential of HEAs. The development of HEAs tailored to specific applications will not only expand the boundaries of materials science but also contribute to the creation of environmentally resilient and economically viable technologies. These advancements position HEAs as key enablers of innovation and sustainability across a broad range of industries (Figure 1.2).

1.2 Definition of HEAs and Compounds

The concept of high-entropy materials (HEMs), which are composed of at least five elements or components, represents a shift in how materials are designed and understood, leveraging entropy as a key factor in their creation. Typical examples are HEAs and high-entropy compounds (HECs), offering a wide array of unique properties derived from their multicomponent systems. While the effects of entropy

have long been recognized in traditional materials and could be explained through thermodynamic principles, the impact of entropy in systems with multiple principal elements was historically overlooked or considered insignificant. This changed with the development of HEAs, which prompted a new focus on multicomponent systems and introduced a paradigm shift in materials science.

Composition Definition. Alloys containing five or more elements with an atomic percentage of each element greater than 5% and less than 35% are defined as HEAs. The idea behind HEAs is to take advantage of multielement mixing and the large configurational entropy (discussed later) that results from the mixing of these elements into a single-phase alloy. HEMs are a broader category of materials that, like HEAs, are composed of multiple elements in near-equal or equimolar proportions to replace the used one/few components position. The term "HEMs" extends beyond just metallic alloys, which also include nonmetallic systems, such as ceramics and polymers, that exhibit the same principle of high entropy. For example, high-entropy ceramics are ceramic materials wherein multiple metal or nonmetal elements are mixed to create a stable phase with desirable properties such as high hardness, thermal stability, and oxidation resistance, as in complex oxide ceramics of (Ti, Zr, Hf, Nb, Ta)O_2. In the later text, we will use HEA as the most important example in HEMs to illustrate those basic concepts.

Entropy Definition. The key defining characteristic of HEAs is their "high-entropy" composition, where the term "entropy" refers to the number of ways atoms can be arranged in a system. By mixing several elements in nearly equal amounts, the number of possible atomic arrangements increases, leading to a higher-entropy state, which can stabilize the solid-solution phase at room temperature, resulting in improved properties. This definition specifies the kinds and ratios of components and introduces the concept of high entropy, which aims to overcome the formation of intermetallic phases through high mixing entropy, thereby obtaining a single-phase solid-solution structure. According to Boltzmann formula, the entropy of a system is related to a given state as the following relationship:

$$S = k_B \ \ln \omega$$

where k_B is the Boltzmann constant and ω is the probability that a given state exists. The entropy of the system includes four parts: configurational entropy $\left(\Delta S_{mix}^{conf}\right)$, vibrational entropy $\left(\Delta S_{mix}^{vib}\right)$, magnetic entropy $\left(\Delta S_{mix}^{mag}\right)$, and electronic randomness entropy $\left(\Delta S_{mix}^{elec}\right)$. The total mixing entropy of HEAs is depicted by the equation:

$$\Delta S = \Delta S_{mix}^{conf} + \Delta S_{mix}^{vib} + \Delta S_{mix}^{mag} + \Delta S_{mix}^{elec}$$

But compared with vibrational entropy, magnetic entropy, and electronic entropy, configurational entropy plays a dominant role, in general. Therefore, to avoid the difficulties caused by the calculation of vibrational entropy, magnetic entropy, and electron entropy, the configuration entropy of the system is generally regarded as the mixing entropy ΔS_{mix} of the ideal solid solution, which can be expressed as:

$$\Delta S_{mix} = -R\sum x_i \ \ln(x_i)$$

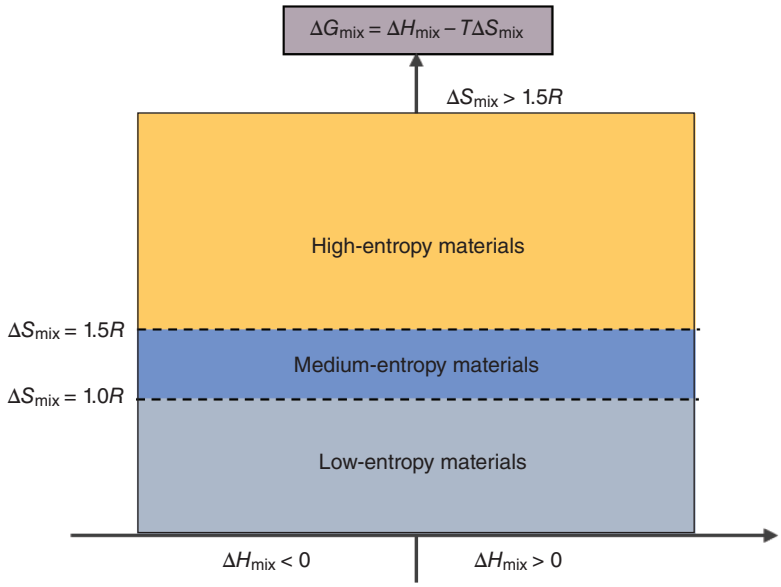


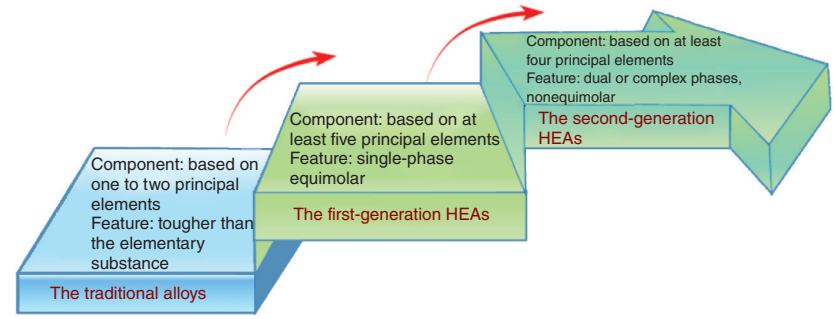
Figure 1.3 Basic definition of HEAs, in which ΔG_{mix}, ΔH_{mix}, ΔS_{mix}, and T are the Gibbs free energy of mixing, the enthalpy of mixing, the entropy of mixing, and the temperature, respectively. The increase in total entropy as the separate systems of different compositions are mixed without chemical reactions. ΔS_{conf} is the configurational entropy, a portion of a system's entropy related to discrete representative positions of its constituent particles.

where R is the molar gas constant ($R = 8.314\ \mathrm{J \cdot mol \cdot K^{-1}}$), x_i is the mole fraction of each constituent element. The mixing entropy of the alloy can be maximized by designing the alloy with equimolar ratios of multiple elements, $x_i = 1/n$, that is:

$$\Delta S_{mix} = -R\left(\frac{1}{n}\ \ln\frac{1}{n} + \frac{1}{n}\ \ln\frac{1}{n} + \ldots\ \frac{1}{n}\ \ln\frac{1}{n}\right) = R\ \ln(n)$$

Based on $\Delta S_{mix} = R\ \ln(n)$, Figure 1.3 clearly shows the relationship between the number of equimolar elements (n) and the mixing entropy (s) of the system. When the number of HEA elements n is greater than or equal to 5, the system's mixing entropy s is greater than or equal to $1.61R$. Therefore, entropy ($1.61R$) can be used as a criterion for distinguishing HEAs/medium-entropy alloys.

Extended Definition. HEAs, initially defined as alloys with a single-phase solid-solution structure and containing more than five principal elements in near-equiatomic ratios, have been a focus of research for decades. Over time, this strict definition has evolved, breaking traditional constraints and paving the way for the development of more versatile materials. This progression has allowed researchers to shift from rigidly adhering to classic definitions to prioritizing tailored compositions that address specific functional needs. The so-called second generation of HEAs, often characterized by non-equimolar compositions and multiphase structures, exemplifies this shift (Figure 1.4): at least mixing of four elements would be good, and even multiple phases are allowed in the extended definition of HEAs. By



(a)

Classification	Component	Feature	Composition	Atoms arrangement	Typical alloys
The traditional alloys	One to two principal elements	Tougher than the elementary substance			Fe-Ni, Fe-C, Cu-Al, Al-Mg
The first-generation HEAs	At least five principal elements	Single phase, equimolar			CoCrFeNiMn, AlCoCrFeNi
The second-generation HEAs	At least four principal elements	Dual or complex phases, nonequimolar			NbMoTaW, $Al_{0.3}CoCrFeNi$, $Fe_{50}Mn_{30}Cr_{10}Co_{10}$

(b)

Figure 1.4 (a) The evolution of traditional alloys and HEAs [18]. (b) Characteristics for the traditional alloys and two generations of HEAs [18]. *Source*: [18] /with permission of Springer Nature.

carefully adjusting the proportions of components and introducing minor elements, these materials can be optimized to stabilize specific phases or enhance performance through mechanisms such as precipitation or composite strengthening. For example, alloys like $Fe_{50}Mn_{30}Cr_{10}Co_{10}$ demonstrate transformation-induced plasticity effects, while $(FeCoNiCr)_{94}Ti_2Al_4$ leverages precipitation hardening, and eutectic HEAs such as $AlCoCrFeNi_{2.1}$ combine exceptional phase stability with high mechanical strength.

This evolution reflects a broader trend in material design, where compositional or phase complexity is used as a tool to unlock novel properties, transcending the boundaries of traditional single-phase alloys. By embracing this expanded perspective, researchers are exploring not only alloys but also other high-entropy systems, creating opportunities for materials tailored to specific high-performance applications, from extreme environments to advanced structural and functional technologies. This holistic approach is driving the next wave of innovations, emphasizing adaptability and multifunctionality over rigid adherence to initial definitions.

1.3 Characteristics, Structures, Phase Transformations, and Microstructures

Expanding beyond alloys, the high-entropy concept has been applied to ceramics, carbides, nitrides, oxides, and intermetallic compounds, creating materials with superior mechanical, thermal, and particularly functional properties. The shared underlying

principle of configurational entropy plays a critical role in stabilizing crystalline phases in both metallic alloys and compounds. This section explores the characteristics, crystal structures, phase transformations, and microstructures of these HEMs in detail.

1.3.1 Characteristics of HEAs and Compounds

The four core effects for HEAs are high entropy, severe lattice distortion, sluggish diffusion, and the cocktail effect—each corresponding to four key aspects of material behavior: thermodynamics, structure, kinetics, and performance. The high-entropy effect promotes the formation of stable multielement solid solutions, especially at high temperatures. Severe lattice distortion arises from varying atomic sizes, affecting structural properties and altering thermodynamics and kinetics. Sluggish diffusion slows down atomic movement, delaying phase transformations and enhancing stability. The cocktail effect refers to the synergistic improvement in properties like strength, toughness, and conductivity, surpassing predictions from traditional alloy theory. Together, these effects define the unique behavior and superior performance of HEAs compared to conventional alloys.

High-Entropy Effect. The concept of the high-entropy effect, initially introduced by Yeh, posits that an increase in entropy results in a reduction in the Gibbs free energy of solid-solution phases. High-entropy systems are driven by the concept of maximizing configurational entropy, which arises from the random distribution of multiple principal elements, as discussed in Section 1.2. In contrast to conventional materials where one or two elements dominate, the presence of multiple elements in nearly equal concentrations promotes the formation of simpler phases (e.g., solid solutions in alloys or basic crystal structures in compounds) rather than complex, brittle intermetallic or ordered phases [19, 20]. Rost et al. found an endothermic reaction upon cyclic heat treatment of rock salt (CoCuMgNiZnO high-entropy oxide [HEO]) [21]. They attributed this to the enthalpic penalties of Zn and Cu for the crystallization of a rock salt structure. To lower the barrier of formation of a single solid solution, these two elements were excluded from HEO. However, this was not the case; the exclusion of Zn and/or Cu led to the formation of multiphases. This was a strong indication that the role of mixing entropy was prominent since it decreased when one cation was removed. Besides, the overall degrees of order in HEAs are expected to decrease with the increase in temperature. Therefore, even as-cast alloys containing ordered phases can also be transformed into disordered solid-solution phases at elevated temperatures. However, it is noted that a single solid solution in HEAs is less likely to form as the number of constituent elements increases, which contradicts the high-entropy effect. As they have articulated, the configurational entropy rises slowly with the number of the increasing elements, whereas the probability of the formation of IMs increases more rapidly [22].

While the high-entropy effect is crucial for the formation of HEMs, it is not the sole determinant of phase formation in multicomponent alloys and ceramics. However, it remains a fundamental influence on HEM formation, minimizing the number of phases, as indicated by Gibbs phase rule, which allows for an increase in the number of equilibrium phases with the addition of components [23, 24] (Figure 1.5).

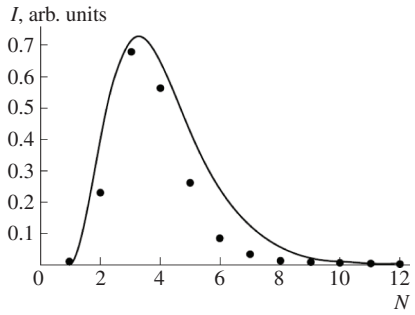


Figure 1.5 High-entropy effect in reducing the number of inorganic crystal structures. Points denote the numbers of inorganic crystal structures with 1, 2, 3, … *N* different elements. *N* = 3 has a maximum of 19,000 [24]. *Source*: [24] / with permission of Springer Nature.

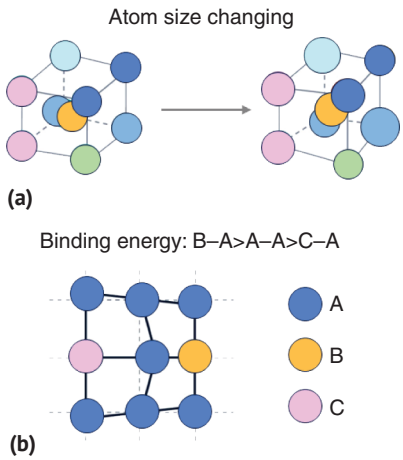


Figure 1.6 (a) Schematic representation of atomic size difference-induced distortion: introducing multiple different elements into the same crystal structures leads to severe lattice distortions. (b) Schematic representation of bonding energy difference-induced distortion. The bonding interaction between A and B is stronger than between A and A and between A and C, so the distance between A and B will be smaller than between A and C, which creates the lattice distortion.

Severe Lattice Distortion. Severe lattice distortion in HEAs is primarily caused by the presence of multiple principal elements with differing atomic sizes, bonding characteristics, and random distribution throughout the crystal lattice [25, 26] (Figure 1.6). The significant atomic size mismatch among these elements results in irregular stretching and compression of the lattice, as atoms of different sizes struggle to fit into the same crystallographic positions. This size disparity disrupts the regular arrangement of atoms, causing considerable strain on the lattice structure. Additionally, the bonding differences between the various elements, which have distinct electron configurations and bonding strengths, further contribute to this disruption. These nonuniform bonding forces lead to uneven interactions between

atoms, creating additional strain and preventing the formation of a smooth, ordered lattice (Figure 1.6).

Moreover, the random atomic distribution of elements in HEAs, where each element is distributed randomly across lattice sites, increases the disorder [27]. Unlike traditional alloys, where a single principal element typically dominates, HEAs have near-equal concentrations of multiple elements, leading to greater structural complexity. This random placement of atoms of different sizes and bonding energies increases lattice distortion, as the structure cannot easily accommodate the varying atomic characteristics.

This lattice distortion has important effects on the properties of HEAs. The distorted lattice hinders the movement of dislocations, which are defects in the crystal structure that allow materials to deform. By impeding dislocation movement, the distorted lattice increases the strength and hardness of HEAs [28]. Additionally, the severe distortion enhances the alloy's resistance to deformation, improving its toughness and wear resistance. Overall, the severe lattice distortion in HEAs, caused by atomic size mismatch, bonding differences, and random distribution, is a key factor contributing to their superior mechanical properties [29].

Sluggish Diffusion. The random arrangement of atoms with varying sizes and bonding preferences in HEAs and HECs disrupts atomic mobility, leading to lower diffusion rates, particularly at high temperatures. This phenomenon of sluggish diffusion arises from two key factors [30].

First, each lattice site in HEAs and HECs is occupied by atoms with different neighboring atoms, creating unique local environments. When an atom moves into a vacant site, the surrounding atoms and bonding energies differ from its original location. Due to these varying local configurations and bonding energies, an atom that moves into a site with lower energy becomes "trapped," making it difficult to transition to a higher-energy site (Figure 1.7). Conversely, if an atom is

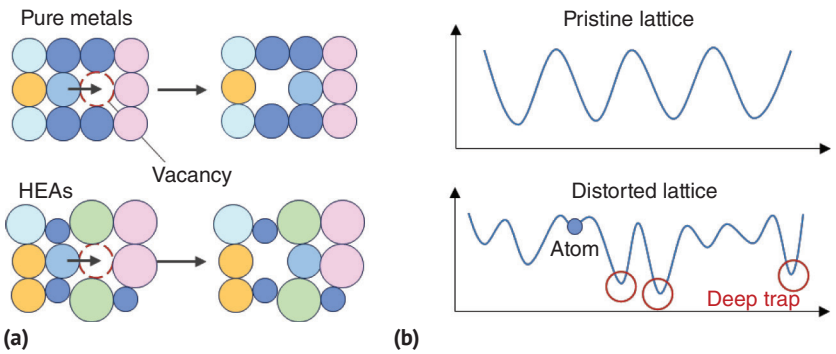


Figure 1.7 (a) Schematic representation of the neighbors an atom interacts with before and after jumping into a vacancy in different matrices. (b) Regular (top) and irregular (bottom) fluctuations of lattice potential energies along the diffusion path for an atom in pure element and HEA lattice. The potential energy of each lattice site in pure elements is nearly identical. By contrast, HEAs are present sites in which the configuration of bonding is preferable for the diffusing species to others; these sites act as traps, and their presence lowers the diffusion rate.

in a higher-energy site, it has a higher likelihood of returning to its original position. These energy differences slow the rate of diffusion. This sluggish behavior, combined with the high activation energy of diffusion in HEAs, is attributed to the significant variation in lattice potential energy (LPE) across different sites within the crystal lattice. Low LPE sites act as obstacles that impede atomic movement, contributing to what is known as the diffusion retardation effect (Figure 1.7b).

Second, the various components in HEAs diffuse at different rates. Some elements move less actively than others, making it more difficult for those components to fill vacancies compared to faster-moving elements. However, processes such as phase changes require the simultaneous diffusion of all components to achieve the desired composition. For example, forming a new phase or facilitating grain growth demands the collective diffusion of all elements to allow effective migration of grain boundaries. In such cases, the slow diffusion of certain components becomes a limiting factor, slowing down the overall transformation process.

Despite this, the sluggish diffusion phenomenon offers several advantages [31], which include the formation of supersaturated states, increased recrystallization temperature, delayed grain growth, reduced grain coarsening, and the formation of fine precipitates. These benefits enhance microstructure and property control, leading to improved material performance.

The Cocktail Effect. The "cocktail effect" refers to the synergistic interaction between different elements in an alloy, resulting in superior material performance. While this effect is also seen in conventional alloys, it is more significant in HEAs due to the complexity of their compositions. The cocktail effect describes the deviation from the simple rule of mixtures and encompasses all factors and mechanisms that contribute to this deviation. In HEMs, the cocktail effect can lead to unexpected and highly beneficial properties, such as increased strength, wear resistance, and stability at high temperatures.

For instance, a heat-treated HEA coating $\left(NiCo_{0.6}Fe_{0.2}Cr_xSiAlTi_\gamma\right)$ demonstrates superior hardness and wear resistance compared to various steels and non-heat-treated HEA coatings [32] (Figure 1.8a). This improvement is due to silicon, which promotes the formation of wear-resistant Cr_3Si precipitates, hardening the coating. Another example involves increasing the aluminum (Al) content in an $Al_xCoCrCuFeNi$ HEA, leading to solution hardening because of Al's larger atomic radius and stronger bonding with other elements [33]. This results in a structural shift from an FCC to a mixed FCC and BCC and ultimately to a purely BCC structure as the Al content rises, enhancing the alloy's hardness. Additionally, multielement synergy in materials arises from the complex interplay of multiple elements rather than from the individual contributions of each element in isolation. This synergy allows the material to harness the diverse properties of the constituent elements, leading to enhanced overall performance. In the context of material design, electrochemically inert elements—such as Zn and Ti—are often chosen to stabilize the host structure, improving its structural integrity. These elements act as stabilizers, preventing phase degradation under operational stresses. On the other hand, electrochemically active elements like Co, Mn, Ni, Fe, and others serve as redox-active centers, facilitating charge transfer and improving the material's

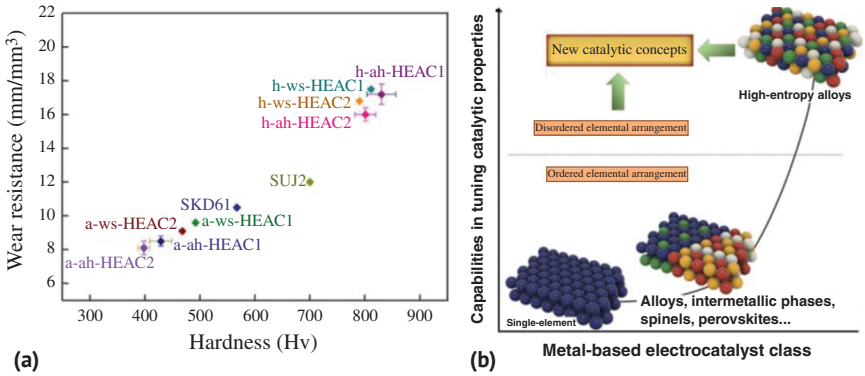


Figure 1.8 (a) The wear resistance of an as-prepared HEA, tool steel SKD61, bearing steel SUJ2, and a thermal-sprayed HEA coating is compared [32]. *Source*: [32] /with permission of IOP. (b) The cocktail effect increases the synergy effects of a vast number of different multielement active sites and expands the capabilities of tuning catalytic properties in HEMs [38]. *Source*: [38] /with permission of John Wiley & Sons.

electrochemical capacity [34–36]. An example of this synergistic approach can be found in the work of Wang et al. [37], who designed a novel O3-type cathode material, $NaNi_{0.2}Fe_{0.2}Mn_{0.35}Cu_{0.05}Zn_{0.1}Sn_{0.1}O_2$. In this material, Mn, Zn, and Sn are critical in mitigating interlayer slipping during the charge–discharge process, effectively reducing the structural degradation that can occur due to irreversible phase transitions. Meanwhile, Ni, Fe, and Cu contribute as redox-active elements, providing additional charge compensation during electrochemical reactions. As a result, this high-entropy cathode material exhibits significant improvements, including enhanced cycling stability (87% capacity retention after 500 cycles at 3C) and a superior discharge capacity of 128 mAh g^{-1} at 0.1C [38].

Importantly, the synergy effect in these materials is not just the simple summation of the individual properties of the elements involved. Instead, it results from a complex interaction where changes in element concentrations and types can dramatically influence the material's overall behavior. This highlights the considerable flexibility offered in customizing material performance, as adjusting the composition and proportions of the constituent elements can fine-tune the material's properties for specific applications, offering new pathways for innovation in electrochemical devices and other technologies (Figure 1.8b).

While some researchers argue that the cocktail effect is redundant, this is a misconception. The overall properties of an alloy are the result of the combined contributions of all related factors. Therefore, understanding the interactions at play when elements are mixed and processed is key to improving or developing new alloy designs. The cocktail effect influences many aspects, including composition, atomic interactions, crystal structure, and microstructure. For materials scientists, it is essential to comprehend the factors that affect a material's properties to select optimal compositions and processing techniques for creating new materials with enhanced characteristics. By minimizing negative factors and amplifying positive ones, better materials can be engineered.

1.3.2 Crystal Structures of HEAs and Compounds

HEMs exhibit a variety of crystal structures, depending on the type of material and the elements involved. Both HEAs and HECs tend to form simple crystal structures, although HEAs, particularly ceramics, can display more complex behaviors. From the concept of HEMs, although having multiple elements, they should possess the same (at least similar) phase with the parent structure but in a high-entropy configuration. Severe phase separation or a very complex mixture of multiple phases will fail the definition to be HEMs.

HEAs primarily crystallize into simple solid-solution phases (Figure 1.9). FCC structures based on 3d transition metals (Co, Cr, Cu, Fe, Mn, Ni), with possible additions of Al and other elements, are common, which offer good ductility and toughness, especially at low temperatures, and are suitable for applications requiring high toughness and moderate strength [40]. The arrangement of atoms in the FCC structure is highly symmetrical, with atoms positioned at each corner and the center of each face of the unit cell. This configuration allows for numerous slip systems, which enhances the material's ability to deform plastically, contributing to its toughness. Moreover, the high-entropy effect in FCC HEAs suppresses the formation of brittle intermetallic phases, stabilizing the alloy in a homogeneous solid-solution form, which leads to improved toughness and resistance to cracking.

In contrast, some HEAs, particularly those incorporating refractory metals such as Nb, Mo, Ta, and W, crystallize into the BCC structure. The BCC structure is typically harder and stronger than FCC but exhibits lower ductility, which makes BCC HEAs suitable for high-temperature applications that require high strength and stability [41]. BCC structures are characterized by a single atom at the center of the unit cell and additional atoms at the cube's corners. These structures tend to have fewer slip systems compared to FCC, leading to lower ductility but increased strength due to stronger atomic bonds and a more compact atomic arrangement. BCC HEAs can also exhibit enhanced thermal stability, which is vital for their use in environments that involve extreme temperatures, such as aerospace, power plants, and nuclear reactors. Hexagonal close-packed (HCP) structures can form in alloys containing elements such as Ti or Zr. HCP structures are often more brittle, but they can offer advantages in specific mechanical or corrosion-resistant applications [42]. The HCP structure consists of layers of atoms arranged in a repeating ABAB pattern, where each layer is tightly packed. The fewer slip systems in HCP structures make these materials more prone to brittle fracture under stress; however, the ordered atomic

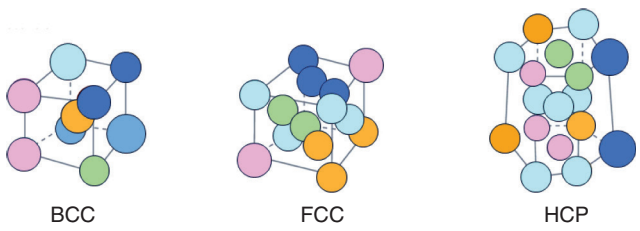


Figure 1.9 Graphic illustration displaying different lattice structures of HEAs.

arrangement can confer specific properties that are advantageous for applications that demand high wear resistance, such as cutting tools or coatings.

Besides, high-entropy intermetallic compounds are a main part of metallic materials, formed from combinations of elements that favor ordered atomic arrangements, that often crystallize in structures such as B2 (CsCl-type), L12 (Cu_3Au-type), or sigma phases. The B2 phase exhibits a simple cubic structure with alternating metal atoms occupying the corners and center of the unit cell. This structure tends to provide good mechanical strength and resistance to thermal degradation, though it is typically more brittle compared to FCC or BCC structures. The B2 structure is often favored in HEAs that involve elements with a large size difference, which helps stabilize the ordered arrangement of atoms. The L12 structure is characterized by an FCC lattice with a more complex atomic arrangement than the simple FCC structure. This phase is often found in HEAs that involve elements such as Ni, Al, or Ti, and it imparts superior strength and creep resistance at elevated temperatures. The L12 phase can enhance the high-temperature stability of alloys, making them suitable for applications in aerospace and high-performance engineering. The sigma phase is an ordered, high-temperature phase that typically forms in HEAs with certain combinations of transition metals. This phase exhibits complex crystal structures that not only often lead to increased brittleness but also provide exceptional resistance to oxidation and thermal damage [43, 44].

HEOs exhibit various crystal structures [45, 46], including rock salt, fluorite, perovskite, spinel, bixbyite, pyrochlore, and layered O3-type (Figure 1.10). Rock salt HEOs [47, 48], identified first, are the most extensively studied due to their facile formation. This structure features a single Wyckoff site for cations, facilitating a homogenous arrangement with superior chemical stability, thus enhancing their electrochemical application potential. Perovskite [49] and spinel-type HEOs are also of significant interest in energy conversion, possessing multiple cation sites that allow for complex atomic arrangements and greater compositional tunability. Other structures such as fluorite, bixbyite, pyrochlore, and O3-layered [50] have

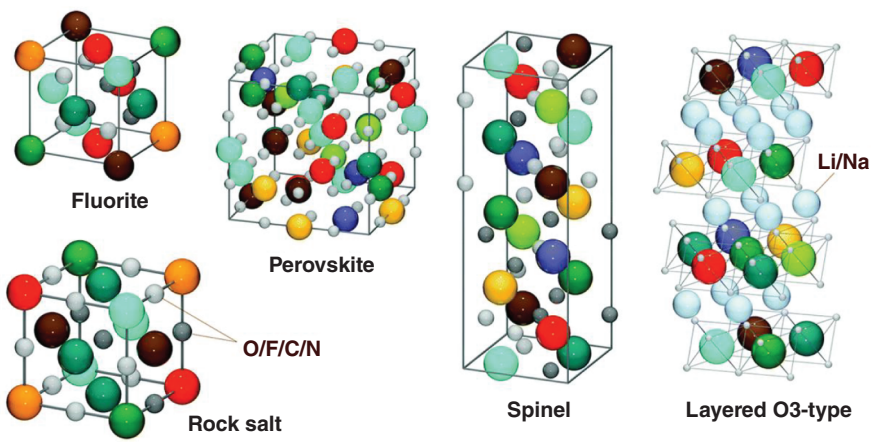


Figure 1.10 Graphic illustration displaying different lattice structures and compositions of HECs [58]. *Source*: [58] /with permission of The Royal Society of Chemistry.

been less explored in electrochemistry but exhibit excellent thermal stability. The phase-formation mechanisms for these HEOs vary significantly due to differences in crystal structures, elemental combinations, and compositions. Nevertheless, all demonstrate enhanced high-temperature stability, attributed to the random distribution of metals within the cation sublattice, leading to uniformly dispersed metal oxide solid solutions.

Bulk high-entropy borides [51], carbides [52], nitrides [53], carbonitrides [54], borocarbides [55], and silicides frequently exhibit enhanced hardness that exceeds predictions based on the rule of mixtures. This phenomenon can be attributed to solid-solution hardening or alterations in the availability of lattice slip systems. Similar to (MgCoNiCuZn)O, both carbides and nitrides generally crystallize in a rock salt structure. In contrast, borides predominantly adopt the AlB_2 hexagonal structure, characterized by alternating two-dimensional boride and high-entropy cation layers. Silicides, on the other hand, typically display relatively low-symmetry structures, with $(MoNbTaTiW)Si_2$ [56] adopting the C40 crystal structure and $(MoNbTaWZr)Si_2$ [57] exhibiting a hexagonal configuration.

1.3.3 Phase Transformations in HEAs and Compounds

As mentioned in Section 1.3.2, there are numerous HEA types and crystal structures, and, similarly, these structures are capable of transforming into each other under certain circumstances and external stimuli. Phase transformations in HEMs are complex and highly dependent on composition, temperature, and external conditions. These phase transformations influence the mechanical properties, microstructure, and stability of the material. Particularly, the phase structure transformation of HEA can be modified using two main approaches. The first approach is chemical tuning, which involves five key physical parameters: mixing entropy, mixing enthalpy, electronegativity difference, valence electron concentration (VEC), and atomic size difference. These parameters significantly influence the atomic arrangement and lattice parameters of HEAs [59]. High mixing entropy in HEAs facilitates the formation of a solid-solution phase [60]. The VEC affects the stacking character of the HEAs' phase structure, determining whether they exhibit FCC or BCC characteristics. The electronegativity difference is associated with phase segregation while mixing enthalpy and atomic size difference are crucial for predicting whether the HEAs will form a solid-solution phase, intermetallic compound phase, or amorphous phase [61, 62]. The second approach is physical field tuning, which also has considerable potential for inducing phase transitions in HEAs. For instance, temperature can cause atomic rearrangement, alter stacking fault energy, and help prevent phase separation. Strain can reduce the magnetic moment, modify dislocation glide, and trigger transitions to metastable phases [63]. Additionally, applying a magnetic field provides energy for atomic movement and alignment while decreasing the Gibbs free energy difference between phases, such as FCC and HCP [64]. In summary, effective property modification of HEAs can be achieved by tailoring their phase structures. This modification not only enhances performance but also offers significant opportunities to attain desired phases with predictable characteristics.

From Solid-Solution to Solid-Solution Phase. The transitions from one solid-solution phase to another demonstrate the complex interplay of many factors in determining the structural phases of HEAs. This ability to switch between various phases under different conditions reveals that solid-solution HEAs can exhibit a much broader range of structural behaviors than might be expected from the simple combination of their constituent elements. Wang et al. studied the $Al_{0.6}CoCrFeNi$ HEA and observed several interesting phase transitions [65] (Figure 1.11). They found that the BCC phase transforms to an orthorhombic phase under pressure, starting at about 10.6 GPa and completing around 21.4 GPa. Upon pressure release, a body-centered tetragonal phase emerges alongside the orthorhombic phase, suggesting that the orthorhombic phase may be metastable at ambient conditions due to a significant energy barrier. Additionally, annealing at 1000 °C for 2 hours converts the initial BCC phase into a stable FCC phase. Under compression, the FCC phase can transform into an HCP phase, similar to Cantor's alloy. The study highlights that lattice distortion, influenced by pressure or temperature, plays a crucial role in the formation and transition of different phases in the HEA.

Form Solid-Solution Phase to Intermetallics. The transition from solid-solution alloys to intermetallic phases marks a significant change in atomic structure, profoundly affecting the material's mechanical and thermal properties. In solid

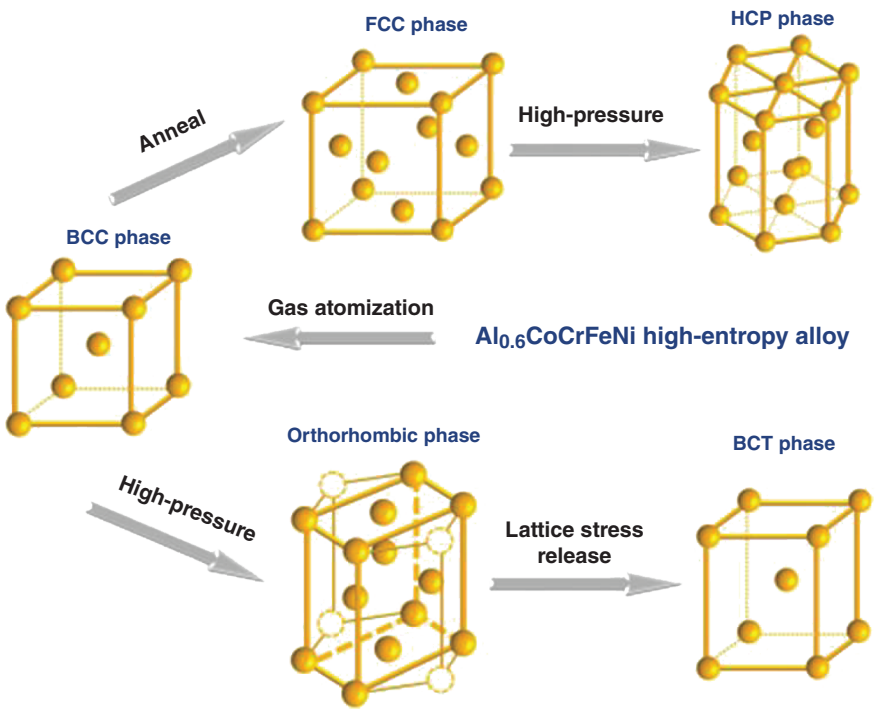
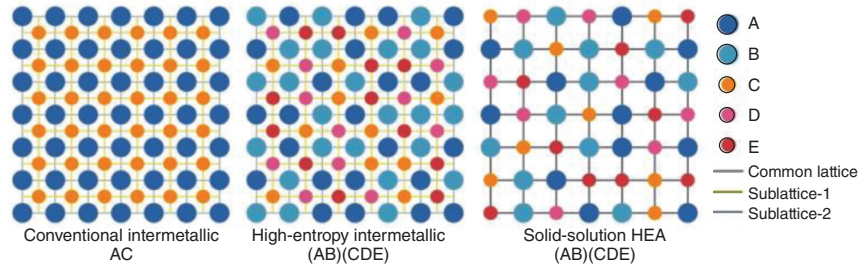
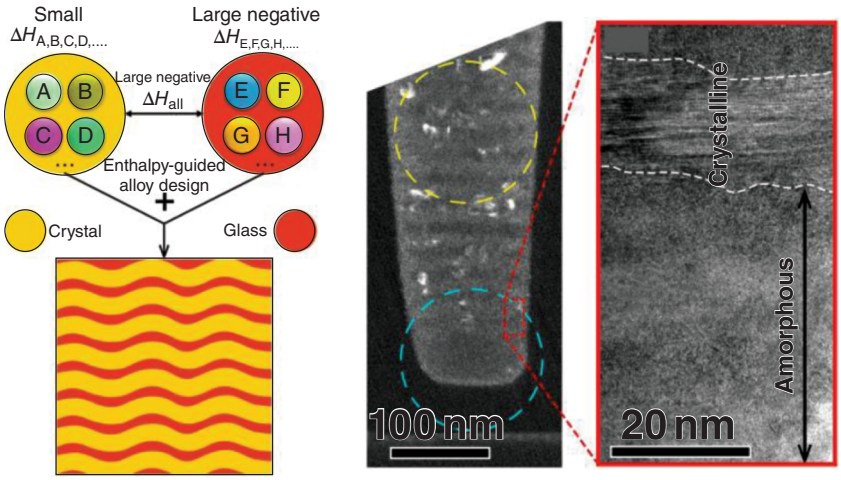


Figure 1.11 A schematic illustration of the atomic structure for five polymorphs observed in the $Al_{0.6}CoCrFeNi$ HEA and the transition paths between them [66]. *Source*: [66] / with permission of Elsevier.

solutions, the atoms of different elements are randomly distributed across the crystal lattice, which provides a good balance of ductility and strength. In contrast, intermetallics are ordered phases where atoms of different elements occupy specific lattice positions, forming compounds with defined stoichiometric ratios and more complex crystal structures, such as B2 (CsCl-type), L12 (Cu_3Au-type), or sigma phases. These ordered structures are generally more chemically stable due to their strong atomic bonds but tend to be more brittle than solid solutions. The transformation to intermetallics is often triggered by thermal treatments, such as annealing or long-term aging, where atoms diffuse and segregate into ordered patterns (Figure 1.12a).



(a)



(b) (c)

Figure 1.12 (a) Illustration of atomic distribution in a conventional B2-type binary intermetallic, a quinary high-entropy B2-type intermetallic and a quinary HEA in solid solution. It is assumed that A and B occupy one sublattice while C, D, and E occupy the other [71]. *Source*: [71] /with permission of Springer Nature. (b) Schematic presentation of the alloy design strategy. A, B, C, D … and E, F, G, H … are constituent elements of the crystal and the glass phases, having small mixing enthalpy $(\Delta H_{A,B,C,D\ldots})$ and large negative mixing enthalpy $(\Delta H_{E,F,G,H\ldots})$, respectively, while all the constituent elements of the two phases have large negative mixing enthalpy (ΔH_{all}) [70]. *Source*: [70] / Springer Nature / CC BY 4.0. (c) High-Resolution Transmission Electron Microscopy (HRTEM) images of the crystal and amorphous phase [70]. *Source*: Reproduced with permission from [70] / Springer Nature / CC BY 4.0.

This transition reduces configurational entropy but increases the overall chemical stability of the material.

Temperature plays a crucial role in this transformation. High temperatures provide the necessary kinetic energy for atoms in a solid solution to diffuse and segregate, leading to the formation of ordered intermetallic phases. During long-term annealing at elevated temperatures, this diffusion process accelerates, allowing phase transformations to occur more readily. For example, FCC solid solutions can transition into ordered structures like B2 or L12 [66–68]. As the temperature rises, atomic mobility increases, enabling atoms to rearrange into more energetically favorable configurations. Even at lower temperatures, given enough time through aging, intermetallics can still form, although the process occurs more slowly.

The composition of an alloy also strongly influences whether a solid solution will transform into an intermetallic phase. Certain elements, due to their atomic size differences and bonding characteristics, are more prone to forming intermetallics. For instance, aluminum (Al), titanium (Ti), and molybdenum (Mo) have a strong tendency to form intermetallic phases, particularly when combined with transition metals like nickel (Ni) or cobalt (Co). The specific ratio of these elements in the alloy can either stabilize the solid solution or encourage the formation of intermetallic compounds. Therefore, controlling the alloy's composition is critical for tailoring its properties to achieve a desired balance of strength, ductility, and thermal stability.

From Crystal to Amorphous Phases. The transformation from crystalline to amorphous phases in HEMs, including both alloys and compounds, signifies a profound change in atomic structure and material properties [69]. In crystalline phases, atoms are organized in a regular, repeating lattice structure, which provides stability and predictable properties. In contrast, amorphous phases lack this long-range atomic order, creating a disordered atomic arrangement similar to that found in glass. This shift from order to disorder has a marked impact on the material's mechanical, thermal, and chemical behaviors. The transition to an amorphous phase can enhance certain properties, such as hardness, corrosion resistance, and structural stability, though it often comes at the expense of reduced ductility and toughness.

One of the most common methods to induce amorphization in HEMs is through rapid cooling or quenching from the melt. When a material is cooled quickly, the atoms are prevented from rearranging into the stable, ordered lattice typical of a crystalline phase. In HEMs, which already benefit from high configurational entropy, this rapid cooling further delays the formation of ordered structures, making them highly susceptible to forming amorphous phases under these conditions. The complexity of the atomic interactions in HEMs, combined with the rapid solidification, leads to a disordered atomic state, which is often more stable under certain conditions due to the sluggish atomic diffusion characteristic of these materials.

Another method of inducing amorphization is through mechanical processes such as severe plastic deformation (SPD) [70]. When materials are subjected to extreme strain, significant dislocation accumulation and atomic disordering occur, pushing the material toward an amorphous state. In HEAs, this deformation-induced

amorphization can happen under high strain rates, where dislocation movements are restricted, increasing the material's internal free energy. As dislocation density grows and atomic disorder worsens, the crystalline structure collapses, transforming into an amorphous phase. This phenomenon is particularly relevant in HEAs, where the high degree of atomic mixing and entropy promotes such transformations under mechanical stress (Figure 1.12c).

High pressure and shear also play a key role in transforming crystalline structures into amorphous ones. When subjected to high pressure, often in combination with shear forces, the crystalline lattice is forced to collapse, creating an energetically favorable amorphous structure. The applied stresses disrupt the ordered atomic arrangement, causing it to disintegrate into a disordered state. This process is commonly observed in high-entropy ceramics, where high-pressure torsion or ball milling can lead to amorphization. The inherent instability of the crystalline lattice under such conditions, combined with the atomic complexity of HEMs, makes amorphous transformation a likely outcome under high stress.

Composition control is another important factor in promoting the transformation from crystalline to amorphous phases in HEMs (Figure 1.12b). The choice of alloying elements and their concentrations can significantly influence the likelihood of amorphization. Certain elements, such as boron (B), phosphorus (P), and carbon (C), tend to disrupt the atomic ordering in a crystal lattice, thereby encouraging the formation of an amorphous phase. In high-entropy systems, the presence of multiple principal elements creates complex atomic interactions that further favor amorphization, especially under rapid cooling or mechanical stress. The high configurational entropy of these materials, which contributes to the stabilization of disordered phases, makes them more prone to forming amorphous structures when the right conditions are met.

In HEMs, the high configurational entropy further stabilizes the amorphous phase. The sluggish diffusion characteristic of HEMs plays a crucial role, as it inhibits the atomic movements necessary to form ordered crystalline structures during cooling or deformation. This sluggish diffusion delays the formation of stable, ordered phases, allowing the disordered, amorphous structure to persist. As a result, the unique combination of atomic complexity, slow diffusion, and high entropy in HEMs makes them particularly well-suited for stabilizing amorphous phases, which can be exploited in various applications that require high hardness, corrosion resistance, and thermal stability.

1.3.4 Microstructures of HEAs and Compounds

The microstructure of HEAs and HECs is central to their performance and the optimization of their mechanical, thermal, and chemical properties. Microstructural features [72] such as grain size, phase distribution, and defect structures play a pivotal role in determining the material's strength, toughness, hardness, and thermal stability. These microstructures are highly sensitive to processing conditions, including casting, sintering, annealing, mechanical deformation, and post-processing heat treatments. By carefully controlling these processing parameters, the microstructure of HEMs can be tailored to meet the specific demands of various applications (Figure 1.13).

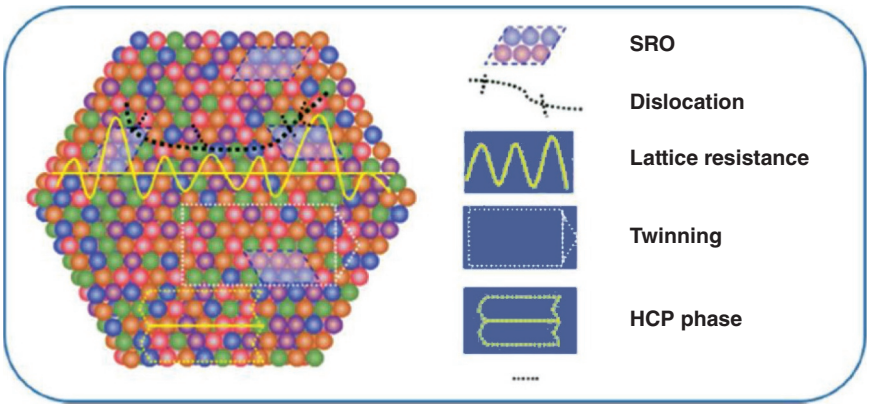


Figure 1.13 Schematic illustration of the interplay between short-range orderings (SROs) and different deformation carriers in a representative FCC HEA [72]. *Source*: [72] / with permission of Elsevier.

Grain Size and Morphology. One of the most influential factors in determining the mechanical properties of HEMs is the size and morphology of the grains. The arrangement and size of the grains significantly impact the material's strength, toughness, and fatigue resistance. Grain refinement can be achieved through various processing methods such as rapid cooling, high-temperature annealing, or SPD. Fine-grained microstructures generally offer enhanced mechanical properties, especially in terms of strength. Fine-grained structures are known to improve mechanical strength through the Hall–Petch effect, which describes the inverse relationship between grain size and yield strength. As the grain size decreases, the number of grain boundaries increases, and these boundaries act as obstacles to dislocation movement. Grain boundaries act as barriers to the motion of dislocations, thereby increasing the material's yield strength and hardness. This effect is particularly pronounced in HEAs, where the solid solution of multiple elements provides additional strength through a combination of solid solution strengthening and grain boundary strengthening [73]. For example, An et al. investigate a multimechanism approach to enhancing the mechanical properties of a CoCrFeMnNi HEA through a combination of non-equiatomic alloy design and innovative processing techniques. By deliberately altering the equiatomic composition of the alloy, the design achieves a single-phase FCC structure while lowering the stacking fault energy (SFE). This modification promotes the formation of deformation twins and stacking faults, contributing to the alloy's enhanced mechanical performance. The processing method applied in this study—rotationally accelerated shot peening (RASP)—was used to create a hierarchical grain size gradient within the material, resulting in a high density of nanotwins. These microstructural features significantly improve the mechanical properties of the HEA. As a result, the non-equiatomic CoCrFeMnNi alloy exhibited impressive mechanical properties, with a yield strength of 750 MPa, a tensile strength of 1050 MPa, and a tensile uniform elongation of 27.5%. Furthermore, the toughness of the alloy was measured at 2.53×10^{10} kJ/m^3, which is approximately twice that of the same alloy without the RASP treatment.

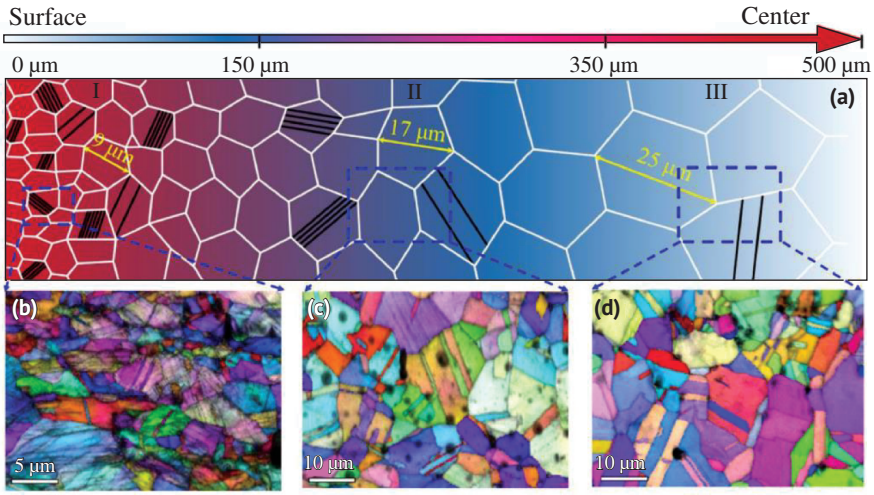


Figure 1.14 Gradient microstructure of the RASP treated $Co_{21.5}C_{r21.5}Fe_{21.5}Mn_{21.5}Ni_{14}$ plate [74]. (a) A schematic of the grain size gradient through the plate thickness. (b)–(d) Electron Backscatter Diffraction (EBSD) micrographs of the alloy at different depths from the surface. *Source*: Reproduced with permission from [74] / Elsevier.

The increase in strength is attributed to several reinforcing mechanisms within the material, including grain boundary strengthening, dislocation strengthening, twin strengthening, and hetero-deformation strengthening, all of which are linked to the heterogeneous microstructure. The simultaneous activation of multiple deformation mechanisms—such as dislocation movement, twinning, and microband formation—contributes to the alloy's remarkable strain hardening. This effect delays early necking and ensures a steady, continuous plastic deformation, which in turn enhances the material's toughness [74]. These findings underscore the potential of multimechanism design strategies for improving the performance of HEAs, offering a promising route for the development of high-strength, tough materials suitable for demanding applications (Figure 1.14).

Fine grains also contribute to better thermal stability and improved resistance to creep, as the grains limit the movement of dislocations at high temperatures. These refined microstructures allow HEAs to maintain their mechanical integrity under extreme thermal cycling and mechanical loading. On the other hand, coarse grains can improve toughness. Larger grains offer fewer grain boundaries, which allows for better dislocation motion, leading to enhanced energy absorption during plastic deformation. This mechanism is especially important in applications where the material needs to absorb impact energy or withstand sudden loading, as larger grains provide fewer barriers to dislocation movement and thus improve the material's ability to deform plastically before failure. While coarse grains may result in a slight reduction in strength, they can offer significant improvements in fracture toughness and ductility [75].

Phase Distribution and Multiphase Microstructures. The phase distribution in HEMs (HEAs and HECs) is a critical factor that influences a broad range

of material properties, extending beyond mechanical strength to include catalytic efficiency, thermal stability, and chemical durability. The ability to tailor and control phase formation through various processing techniques enables the design of high-performance materials for demanding applications in energy systems, aerospace, automotive, and catalysis [76].

Single-phase HEAs, where the constituent elements are uniformly distributed within the lattice, typically exhibit good ductility and toughness, which are vital for mechanical applications. However, the absence of secondary phases does not preclude these materials from being highly effective in catalytic applications. The homogeneous distribution of elements and active sites within single-phase structures can enhance catalytic efficiency, particularly for reactions requiring redox stability or resistance to thermal degradation. For example, oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), critical in water splitting and energy conversion technologies like fuel cells and electrolyzers, benefit from the well-distributed active sites in single-phase HEAs. The electronic configuration of each element within the single-phase structure can influence the binding energy of intermediates and facilitate optimal catalytic behavior. Additionally, the high resistance to corrosion and thermal stability offered by HEAs allow for long-term performance in high-temperature, high-oxidizing environments, such as those found in solar-to-fuel processes or electrochemical cells. For instance, in water electrolysis, a homogeneous solid solution of metals like Ni, Co, and Fe has demonstrated enhanced electrochemical stability and higher reaction rates due to the uniform distribution of cations, which promotes optimal catalytic pathways.

In contrast, multiphase microstructures can form when secondary phases, such as intermetallics or other compounds, coexist with the primary solid solution. These multiphase structures often provide increased hardness and wear resistance, as the presence of harder secondary phases reinforces the overall material. However, the trade-off is typically reduced ductility, as the additional phases create localized regions that are more prone to cracking. In HEOs and nitrides, multiphase systems offer a balance between strength and toughness, with different phases contributing to a combination of mechanical properties that are suitable for demanding applications.

The precipitation of secondary phases plays a significant role in the modification of mechanical and catalytic properties in HEMs. Secondary phases, such as carbides, oxides, or intermetallic compounds, form during cooling or aging, influencing both structural integrity and functional properties. In HEAs used in applications like aerospace and power generation, the precipitation of hard secondary phases like carbides or intermetallics can substantially increase high-temperature strength and oxidation resistance. These secondary phases obstruct dislocation movement and grain growth, creating a more robust and stable material. For instance, in Ni-based HEAs, the precipitation of carbides or Ni–Al intermetallics during aging can create a precipitate-hardening effect, which makes the alloy stronger at elevated temperatures and resistant to oxidation. This property is crucial in applications such as jet engine components, where the material must withstand both extreme temperatures and mechanical loading over extended periods. In catalytic applications, the precipitation of secondary phases can significantly influence active site formation and

reaction kinetics. The controlled precipitation of phases can help tailor the electronic structure around catalytic sites, improving their reactivity and selectivity. For example, in CO_2 reduction reactions, where the conversion of CO_2 into useful chemicals is catalyzed, the presence of precipitates in HEA-based catalysts can enhance the electronic properties at the active site, thereby improving catalytic efficiency. The precipitation of phases like oxides or nitrides can also stabilize the active sites under harsh reaction conditions, ensuring consistent performance over long operational periods. In energy storage devices such as supercapacitors and batteries, the precipitation of secondary phases can also play an essential role in optimizing performance. Carbide and nitride precipitates can enhance the thermal stability and cycle life of materials used in these devices. The secondary phases can alter the electrode material's porosity, improving the ion diffusion rates and charge storage capacity. For instance, the precipitation of TiC or NbC in high-entropy carbide-based electrodes can increase the specific surface area, leading to better charge storage and cycle stability. Similarly, the precipitation of oxides in HEOs used in supercapacitors can improve electrical conductivity and charge retention during long-term cycling.

Defects and Dislocations in HEMs. The presence of defects and dislocations in the crystal structure of HEMs also contributes to their mechanical performance [77]. These materials are characterized by a high density of lattice defects, including vacancies, dislocations, and stacking faults (Figure 1.15). These defects arise due to severe lattice distortion caused by the incorporation of multiple elements with different atomic sizes. The high density of dislocations serves as a strengthening mechanism, as these defects impede further dislocation motion, improving both hardness and yield strength. In high-entropy ceramics, grain boundary strengthening mechanisms are further enhanced by the presence of these defects, while crack deflection mechanisms improve toughness. As cracks propagate through the material, they are often deflected at grain boundaries or by secondary phases, reducing the likelihood of catastrophic failure.

The high density of dislocations in HEMs provides additional dislocation hardening and increases strength. In electrocatalysts, dislocations can serve as effective

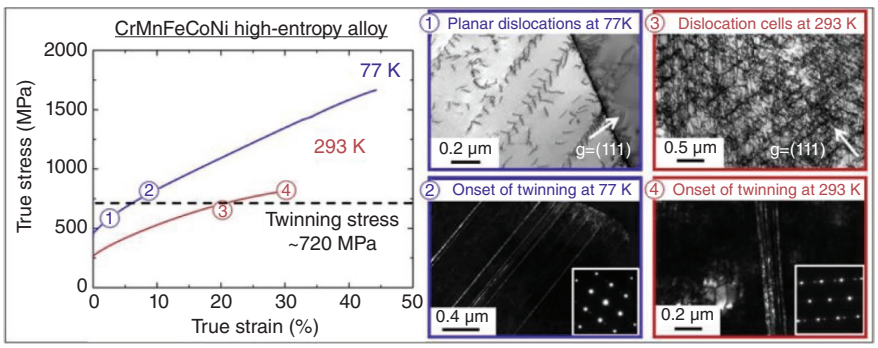


Figure 1.15 Representative true stress–strain curves of tensile tests at 77 K and 293 K, and TEM micrographs showing twin evolution with true tensile strain [77]. *Source*: [77] / with permission of Elsevier.

sites for the adsorption and activation of molecules, improving the material's ability to facilitate redox reactions. The presence of vacancies and stacking faults can also enhance the material's electrochemical reactivity, leading to higher charge transfer rates and catalytic efficiency. The presence of lattice defects and grain boundaries in HEMs contributes to grain boundary strengthening, which not only improves mechanical properties but also enhances the material's thermal stability and resistance to corrosion. In HEOs used for solid oxide fuel cells, defects at grain boundaries enhance ionic conductivity and electrochemical stability, leading to better fuel cell performance. The dislocation strengthening in HEAs can improve the material's resistance to wear and oxidation in demanding energy conversion applications, such as in thermal power plants and gas turbines.

Local Ordering. Local ordering in HEAs is a dynamic and crucial aspect of their structure, influencing many of their mechanical and physical properties. While HEAs are traditionally regarded as disordered solid solutions due to their high configurational entropy, more recent studies have shown that local ordering, specifically short-range ordering (SRO) and medium-range ordering (MRO), plays an important role in shaping the alloy's behavior. SRO refers to atomic pairings that form over short distances, typically a few atomic layers, where elements preferentially cluster together. MRO, on the other hand, refers to atomic arrangements that extend over several nanometers, often forming nanoscale domains or superlattice structures. These ordering phenomena, though not long-range periodic, have a substantial impact on the material's macroscopic properties.

In HEAs, local ordering is primarily driven by atomic size mismatches, differences in atomic radii, and the chemical affinity between constituent elements. For instance, elements with similar atomic sizes tend to cluster, reducing local lattice distortions and minimizing strain energy. This clustering can create short-range ordered regions within the alloy. MRO occurs as these short-range ordered regions coalesce into larger, more structured domains that extend over multiple atomic layers, often leading to the formation of nanoscale heterostructures. These features can significantly influence the material's behavior during deformation. For example, in FCC-based HEAs, local ordering can alter the SFE, making it easier or harder for dislocations to glide. This, in turn, influences the activation of mechanisms like twinning, phase transformations, and work hardening [78].

The presence of both SRO and MRO has significant consequences for the mechanical properties of HEAs. The enhanced dislocation resistance due to local ordering strengthens the alloy by increasing the energy barrier for dislocation motion, which improves the material's yield strength. Furthermore, the coexistence of SRO and MRO promotes more complex dislocation behaviors, such as wavy slip and cross-slip, which are beneficial for achieving high strain hardening and ductility. This interplay between local ordering and dislocation dynamics is particularly important for improving the alloy's performance in demanding conditions, such as at cryogenic temperatures. For example, in FeMnCoCr-based HEAs, MRO domains help the alloy maintain its mechanical integrity under low-temperature deformation, where traditional alloys would typically become brittle. MRO also facilitates

the formation of stable nanostructures, such as nanoscale precipitates, that enhance the alloy's strength without sacrificing ductility. This is particularly useful for tailoring the performance of HEAs for applications requiring high strength and toughness at both ambient and extreme temperatures. The structural stability imparted by MRO allows these materials to withstand severe environmental conditions without undergoing detrimental phase transitions or losing their mechanical properties. As a result, HEAs with well-controlled local ordering can offer a superior combination of strength, ductility, and stability, making them ideal candidates for applications in aerospace, energy storage, and cryogenic technologies [72].

Moreover, the ability to manipulate the degree of SRO and MRO in HEAs opens up new avenues for designing materials with specific properties. This can be achieved through careful control of the alloy's composition, processing conditions, and thermal treatments. For instance, elemental substitutions, such as replacing Rh with Ru in noble-metal-based HEAs, can dramatically change the local atomic arrangement, shifting the material from a random solid solution to one with localized clustering (Figure 1.16a). Similarly, thermomechanical treatments, including annealing or cold working, can modify the extent of local ordering, resulting in alloys with enhanced strength, toughness, and resistance to thermal creep. Additionally, the incorporation of small interstitial atoms like nitrogen or oxygen can further tune the local chemical order, improving both strength and ductility [79].

While significant progress has been made in understanding and manipulating local ordering in HEAs, challenges remain in fully characterizing and quantifying this phenomenon. Advanced techniques such as APT [80], high-resolution STEM (Figure 1.16b) [81], and first-principles simulations [82] are crucial to unraveling the complex relationship between local ordering and alloy properties. These tools will be essential in developing a deeper understanding of how local ordering contributes to the unique performance of HEAs and in guiding the design of next-generation materials with tailored properties for demanding applications in aerospace, energy, and cryogenic environments. Local ordering plays a critical role in determining the mechanical, thermal, and structural properties of HEAs. Understanding and controlling these ordering phenomena provide a pathway to design HEAs with tailored properties for advanced applications.

In summary, the microstructures of HEMs, influenced by grain size, phase distribution, secondary phase precipitation, and the presence of defects, are key determinants of their overall performance. By carefully controlling these microstructural features through processing techniques, it is possible to create materials with a tailored balance of strength, toughness, hardness, and thermal stability, suitable for a wide range of advanced engineering applications. The field of HEMs has expanded from alloys to include a wide range of compounds such as oxides, nitrides, carbides, and intermetallics. The common principles of high configurational entropy, sluggish diffusion, lattice distortion, and the cocktail effect apply to both HEAs and HECs, influencing their crystal structures, phase transformations, and microstructures. These factors contribute to the exceptional mechanical, thermal, and chemical properties of HEMs, making them highly suitable for demanding applications in aerospace, energy, and advanced.

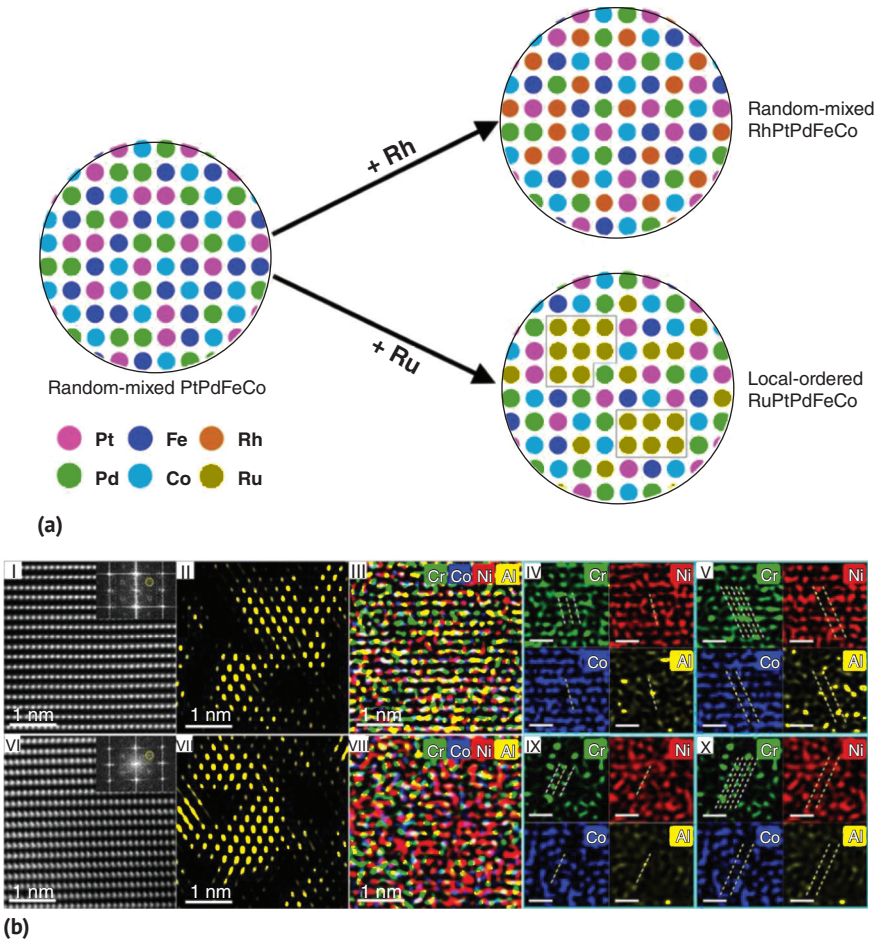


Figure 1.16 (a) Composition-structure relationship in HEAs with one constituent difference [79]. *Source*: [79] / with permission of American Chemical Society. (b) I. HAADF image under [112] z.a. (zone axis) before tensile deformation. Inset: Fast Fourier Transform (FFT) pattern. II. Corresponding Inverse Fast Fourier Transform (IFFT) image showing CMRO regions. III. EDS map. IV and V. Close-up views of Cr, Ni, Co, and Al maps in individual CSRO and CMRO regions, respectively. All dashed white/yellow lines: Cr-enriched and Cr-depleted $\{\bar{3}11\}$ planes. VI–X. Corresponding results after tensile deformation. Scale bars in IV, V, IX, and X: 0.5 nm [83]. *Source*: Reproduced with permission from [83] / Springer Nature / CC BY 4.0.

1.4 Diverse Applications of Functional HEAs and Compounds

HEMs, with their multicomponent structure, have opened new frontiers in materials science, offering a plethora of properties that can be fine-tuned for various applications. This section briefly introduces the functional applications of HEAs and compounds, exploring how their unique characteristics can be harnessed across different industries. More details will be presented in subsequent chapters.

(a) (b)

Figure 1.17 (a) Schematic picture of a space engine. (b) Schematic picture of bulk HEAs in a high-pressure and high-temperature environment. Generated with AI using Doubao.

Extreme Environments. In the aerospace sector, the demand for materials with high strength-to-weight ratios, excellent corrosion resistance, and the ability to withstand extreme temperatures is ever-increasing. HEAs, with their remarkable combination of strength, ductility, and corrosion resistance, are being considered for critical structural components (Figure 1.17). Their potential use in aircraft engines, where materials must endure high temperatures and mechanical stress, is currently a topic of intensive research. Besides, the thermal management capabilities of HEMs are particularly intriguing for industries that require efficient heat dissipation or insulation. In aerospace and automotive applications, HEMs with low thermal expansion coefficients can be used to create thermal barriers that protect sensitive components from extreme temperature fluctuations. Additionally, the radiation tolerance of certain HEMs makes them suitable for use in nuclear reactors, where materials are exposed to high levels of radiation. Their ability to maintain structural integrity and resist radiation-induced degradation is crucial for the safe and efficient operation of nuclear facilities [84–86].

Corrosion Resistance. HEMs offer exceptional corrosion resistance, making them ideal for use in harsh environments such as marine structures, chemical processing equipment, and offshore platforms. Their corrosion resistance arises from mechanisms like the formation of stable oxide layers, solid-solution strengthening, and resistance to galvanic corrosion. These features prevent degradation and reduce maintenance costs, enhancing the material's durability and lifespan. In applications like offshore oil rigs, chemical reactors, and nuclear industries, HEMs' ability to resist acidic, alkaline, and oxidative conditions ensures long-term performance. The materials' high-temperature stability further enhances their suitability for extreme environments, where traditional materials would fail more rapidly. The economic benefits of using HEMs include cost-effective solutions through reduced maintenance, extended service life, and fewer material replacements, offering sustainability and reliability in critical [87, 88].

Functional Materials. The magnetocaloric effect (MCE) refers to the reversible change in a material's temperature (T) and entropy (S) induced by the application or removal of an external magnetic field. When magnetization or demagnetization occurs adiabatically, it results in an adiabatic temperature change, ΔT_{ad}, with the total entropy remaining constant. Under isothermal conditions, the magnetization or demagnetization leads to a heat transfer, where the heat transferred is $Q = T \cdot \Delta S_m$, with ΔS_m representing the isothermal magnetic entropy change. The MCE is typically maximized near the phase transition temperature, where an ideal transition should be sharp and nonhysteretic, resembling both first-order and second-order transitions. In an ideal case, the magnetization is initially high and drops at the transition temperature [89].

For energy-efficient and sustainable magnetic refrigeration, the ideal magnetocaloric material should combine a large, reversible MCE in fields around 1 T, along with properties such as nontoxicity, noncriticality, high corrosion resistance, mechanical stability, and machinability. Currently, most magnetic refrigerators use elemental heavy rare-earth (RE) materials like Gd, which are critical and expensive. Gd-based MCEs are governed by a second-order phase transition, limiting the reversible entropy change and heat transfer. Materials such as $La(Fe,Si)_{13}$ alloys, which rely on a first-order phase transition, can enhance heat transfer but often suffer from functional fatigue and poor machinability.

HEMs could address these challenges. Recent studies have explored equiatomic compositions using RE elements or mixtures of transition metals, with some thermoelectric HEMs surpassing conventional materials in properties. However, most HEM-based magnetocaloric materials show gradual changes in magnetization, typical of second-order phase transitions. Engineering HEMs toward first-order transitions remains a major challenge. Promising systems like all-d-Heusler-type, MM′X-type, and Fe_2P-type compounds are already multielement materials that could be further optimized [90, 91].

To enhance the MCE, a deeper understanding of the underlying physical mechanisms—including crystal structure, electronic configurations, microstructure, and configurational entropy—is essential. Corrosion resistance is also crucial, as magnetocaloric materials undergo millions of cycles in contact with heat exchange fluids, typically water. HEMs offer the potential to reconcile these multifunctional requirements, integrating enhanced MCE with durability. Given the complexity of synthesis methods (e.g., conventional melting, nonequilibrium processes, and AM), guidance from theoretical models and machine learning will be invaluable for optimizing these materials.

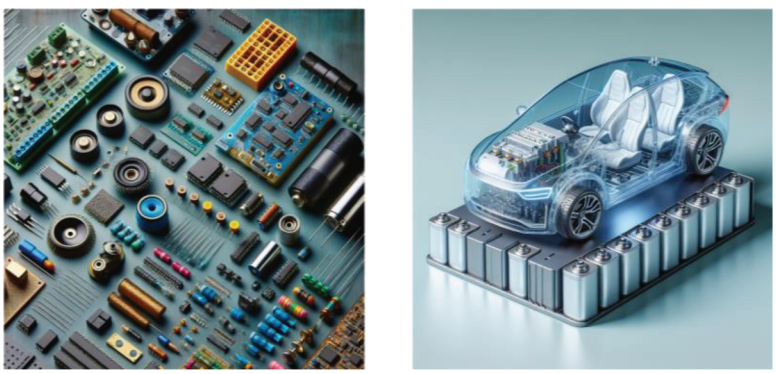
In thermoelectrics, materials convert thermal gradients (e.g., from waste heat) into electricity through the Seebeck effect. Their efficiency is characterized by the figure of merit (ZT), given by $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is electrical conductivity, T is the absolute temperature, and κ is thermal conductivity. To enhance efficiency, two key properties must be optimized: reducing thermal conductivity through phonon scattering to maintain the temperature gradient and increasing charge carrier mobility and density to improve electrical conductivity. Achieving this balance is challenging due to electron–phonon interactions. Additionally, thermoelectric materials must withstand harsh environments, requiring high damage tolerance, oxidation resistance, good mechanical properties, low cost, and thermal stability [92, 93].

HEMs can be used to optimize thermoelectric materials for higher efficiency and safer operation, with potential benefits from entropy engineering and composition modification. Some thermoelectric HEMs have already demonstrated better performance than conventional materials, indicating the promise of this design pathway. For example, increasing configurational entropy can stabilize solid-solution ranges beyond traditional limits, promoting lattice distortion and enhancing phonon scattering to lower thermal conductivity. In Pb—Sb—Se—Te—S thermoelectric HEMs, increasing S and Te content triggers a multiphase state due to phase separation, which is stabilized upon adding Sn. This entropy-driven phase stabilization results in significant lattice strain (~0.45%) and a maximum ZT of 1.8 at 900 K [94]. The high configurational entropy and sluggish diffusion stabilize materials at high temperatures, although further research is needed to assess their long-term performance under thermal cycling.

HEMs can also enhance the Seebeck coefficient by tuning electronic band features close to the Fermi level, such as band degeneracy or convergence, at optimal carrier concentrations. The increased configurational entropy can lead to higher-symmetry crystal structures, which enhance the electronic density of states and effective mass, improving thermoelectric properties.

However, a challenge in using HEMs for thermoelectrics is the potential decrease in electrical conductivity due to Anderson localization in highly disordered systems, leading to a trade-off between thermal and electrical conductivity. Recent research has demonstrated that entropy engineering can enhance thermal conductivity without sacrificing electrical properties, as seen in GeTe-based HEMs with a ZT value of 2.7 at 750 K. This was explained by entropy-induced disorder suppressing transverse phonons, while increased crystal symmetry delocalized the electron distribution, improving electrical properties (Figure 1.18).

Applications in Biomedical Fields. HEMs are emerging as highly promising materials in the biomedical field due to their remarkable combination of mechanical strength, corrosion resistance, and biocompatibility. These alloys, characterized



(a) (b)

Figure 1.18 (a) Schematic picture of HEMs used in electronic components. (b) Schematic picture of HEMs for automotive applications. Generated with AI using Doubao.

by the inclusion of multiple elements in near-equal proportions, exhibit unique properties that make them particularly suited for a range of biomedical applications. For instance, HEAs made from biocompatible elements such as titanium (Ti), nickel (Ni), chromium (Cr), and molybdenum (Mo) demonstrate excellent resistance to corrosion in physiological environments. This resistance is crucial for biomedical implants and prosthetics that are exposed to harsh conditions within the human body. By maintaining their integrity in these corrosive environments, HEMs ensure the long-term durability and reliability of medical devices.

The inherent mechanical properties of HEMs, such as high strength, toughness, and wear resistance, make them ideal candidates for load-bearing applications, particularly in bone and dental implants. These implants are subject to significant stress and strain during daily activities, requiring materials that not only offer superior mechanical performance but also maintain functionality over extended periods. HEAs meet these demands by providing a high-performance solution that resists wear and fatigue, which are common challenges in traditional biomaterials. This makes them particularly suitable for high-stress applications, where material degradation could compromise the structural integrity of implants. Moreover, HEAs offer considerable advantages in promoting osseointegration, the process by which implants bond with bone tissue, an essential factor for the success of orthopedic and dental implants. The flexibility in the composition of HEMs allows for the development of tailored surface properties, enabling better biomolecule adsorption and enhancing tissue integration. This promotes a stronger and more stable bond between the implant and surrounding tissues, which is crucial for the long-term success of implants. In addition, HEAs can be engineered to possess antimicrobial properties, a critical feature for preventing infections that can occur postsurgery. By incorporating specific elements or compounds into the alloy, antimicrobial coatings can be applied to medical devices, reducing the risk of infection and promoting quicker recovery for patients.

Another significant advantage of HEMs in the biomedical field is their compositional flexibility and ability to be precisely engineered for individual needs. With the rise of 3D printing technologies in medicine, HEMs can be tailored to create patient-specific implants, allowing for a perfect match to an individual's anatomical structure. This customization not only improves the fit and function of implants but also reduces the risk of complications that may arise from ill-fitting devices. By incorporating 3D printing, it becomes possible to design complex geometries that would be difficult or impossible to achieve with traditional manufacturing methods, thereby enhancing the surgical outcome and improving the overall quality of life for patients. Furthermore, the unique properties of HEMs also offer potential for the development of advanced drug delivery systems. These materials can be designed to carry and gradually release therapeutic agents, providing targeted treatments for a range of conditions. By engineering the surface properties of the alloys, drug release profiles can be carefully controlled, optimizing the therapeutic effects while minimizing side effects. This combination of mechanical performance, biocompatibility, and versatility makes HEMs an exciting avenue for the development of next-generation biomedical devices that can significantly improve patient care and treatment outcomes.

High-Performance Catalysts. The polyelemental nature of HEMs offers a unique platform for designing catalytically active materials or surfaces. Key reactions in electrolyzers and fuel cells—such as the HER, OER, and oxygen reduction reaction—require multifunctional electrocatalysts. These catalysts must be not only active and stable but, ideally, made from sustainable elements and their oxides. HEM electrocatalysts can meet these conflicting demands by combining multiple functionalities from their diverse constituents, allowing for tunability in properties through composition. Additionally, the complex chemical features of HEM surfaces make them ideal candidates for designing electrocatalysts for other critical reactions like CO_2 reduction and N_2 fixation, as well as more intricate multistep and cascade reactions. While the promising properties of HEM electrocatalysts were only recently recognized, numerous studies have demonstrated their potential across a variety of catalytic processes. The development of HEM surfaces also holds promise for multifunctional materials in broader electrochemical applications (Figure 1.19) [45, 95, 96].

HEMs, formed from compositionally complex solid solutions, offer unprecedented access to a diverse range of surface atom arrangements (SAAs) in the top few atomic layers. These SAAs refer to the spatial arrangement of surface and subsurface atoms, as well as their chemical identities and the binding configurations (on-top, bridge, hollow) for reaction intermediates. The abundance of SAAs on HEM surfaces provides an expansive design space to optimize multifunctionality for a wide array of electrochemical reactions. Through careful tuning of the elemental distribution within these SAAs, the binding energies for reaction intermediates can be adjusted, offering a means to tailor catalytic properties. This dynamic tuning can influence the shape of volcano plots, which illustrate the relationship between catalyst activity and the binding energy of reactants or intermediates. Volcano plots serve as a tool for identifying catalysts with optimal binding energy, which, according to the Sabatier principle, leads to the highest activity [97, 98].

The key difference between conventional single-element or binary catalysts (often composed of scarce and expensive noble metals such as Ir, Pt, and Rh) and HEMs lies in the statistical diversity of SAAs on the surface. In HEMs, the vast array of SAAs increases the likelihood of having active sites on the surface, which are essential for high electrochemical activity. These active sites can be engineered through

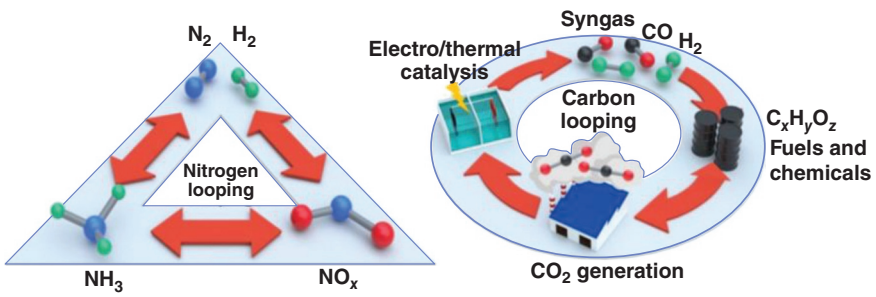


Figure 1.19 The applications of HEMs in nitrogen and carbon looping reactions [102]. *Source*: [102] / John Wiley & Sons / CC BY 4.0.

the manipulation of SAAs, overcoming the limitations of traditional catalysts and paving the way for sustainable materials with excellent multifunctionality—combining high activity, stability, and selectivity. Importantly, certain electrochemical functionalities typically dependent on rare noble metals can now be achieved with compositionally complex solid solutions containing minimal or no noble elements. This reduction or replacement of noble metals allows for finer control over the active site properties by adjusting the binding energy distribution. Moreover, replacing unstable yet highly active elements with more stable, less active ones can enhance overall catalyst performance. Recent research has used both experimental and theoretical methods to identify optimal HEM systems for the OER, demonstrating the potential for significant activity improvements when adjusting the composition of Ru, Pd, and Ir.

The vast abundance of SAAs on the surface of HEMs increases the chances of identifying active sites that remain stable during operation. Rather than relying on a single "perfect" active site, HEMs offer a multitude of potential sites, each close to the desired optimal catalytic activity. This flexibility suggests that such solid solutions might offer robust surface synthesis options and long-term operational stability.

A challenge in utilizing HEMs lies in efficiently exploring the immense surface composition space and identifying the most effective SAAs. High-throughput calculations and experiments, particularly those combining density functional theory and machine learning-enhanced computations, are key strategies for addressing this challenge. These methods allow for the correlation of surface compositions with electrochemical activity, using descriptors like adsorption energy to predict the most promising candidates [11, 99–101]. Another critical factor in the performance of electrocatalysts made from complex solid solutions is the control of surface composition. Surface segregation effects must be carefully considered to achieve the desired surface properties. Stability, which is as crucial as activity in electrocatalysis, is a key strength of HEMs. The entropy stabilization inherent in highly multinary HEMs may help overcome the common trade-off between activity and stability. Additionally, metastable phases in HEMs, achieved through nonequilibrium methods, offer rich possibilities for designing new catalysts. However, metastable materials may eventually demix into competing phases during operation, posing challenges related to long-term stability, such as oxidation state changes, contamination, and material loss during extended use. Addressing these challenges requires in situ monitoring to assess the stability and performance of HEM catalysts over time.

HEMs have also shown promise in photocatalysis, where catalysts must absorb photons to generate electron–hole pairs and drive redox reactions. The diversity of surface elements in HEMs is expected to enhance photocatalytic yields, create new catalytic sites, modify electronic structures, and improve surface properties. These improvements can increase light absorption, promote surface reactions, and ultimately enhance photocatalytic efficiency. Mechanisms that may contribute to these improvements include the generation of new surface reconstruction features, a broader spectrum of active sites, tunable band gaps, and improved charge separation.

In low-dimensional forms, HEMs are being explored for electrocatalytic applications, particularly in reducing barriers for redox reactions crucial for energy conversion. The advantages of low-dimensional materials—such as high electrical conductivity and multiple active sites—are amplified in chemically complex systems. These materials offer increased charge carrier densities, a wider selection of active sites, and enhanced chemical and thermal stability. However, challenges such as material robustness under cycling, exposure to complex reactants, and stability in real-world environments must be addressed. Furthermore, good electron mobility alone is insufficient for a successful electrocatalyst—other factors, including long-term stability and environmental resilience, must be considered for practical applications.

Energy Storage Applications. HEMs have garnered significant attention for their potential in energy storage applications, particularly in lithium-ion batteries (LIBs) and other advanced energy storage systems. One of the key advantages of HEMs is their high electrochemical stability, which improves performance during repeated charge and discharge cycles. This is particularly critical in applications where materials must endure cyclic stress without significant degradation. The inherent stability of HEMs, combined with their unique structural properties, makes them highly resilient to the degradation mechanisms that often limit the lifespan of conventional battery materials, offering a longer operational lifetime and reduced maintenance needs.

The multiphase microstructures that are often present in HEMs offer several advantages in ion storage and ion diffusion. These materials can accommodate a wide range of ion sizes, facilitating faster ion diffusion and enhanced ionic conductivity. In LIBs, the rapid transport of lithium ions is critical for fast charge–discharge cycles and high energy density. By tailoring the alloy composition, HEMs can optimize ion movement paths, allowing for higher throughput of ions and faster charge rates. This reduces internal resistance and improves the overall efficiency of the energy storage system, enabling faster charging and higher power output without compromising the material's longevity.

Another significant benefit of HEMs in energy storage systems is their mechanical durability, which is particularly valuable for high-performance applications like electric vehicles (EVs) and grid energy storage. The combination of multiple elements in HEAs or HECs can be tuned to resist mechanical degradation under extreme operating conditions, such as high temperatures, large current loads, and stress cycling. These conditions can cause material failure in traditional battery electrodes, but HEMs maintain their structural integrity during repeated charging cycles, significantly reducing the risk of failure due to mechanical stress, cracking, or material fatigue. This durability ensures longer battery life, as the materials retain their structural and electrochemical properties over extended periods of use.

The synergistic effects between various elements in HEMs contribute to increased energy capacity and improved efficiency. Unlike traditional alloys or materials, which are limited by the properties of a few elements, HEMs exploit the diverse combination of metals to achieve enhanced electrochemical performance.

For example, in battery anodes or cathodes, the presence of refractory elements can increase thermal stability, while more active elements can enhance capacity and voltage output. Additionally, the multiphase structures in HEMs are less prone to phase transitions that can adversely affect performance, such as dendrite formation or volume expansion that occurs in conventional materials like graphite or silicon. By minimizing these issues, HEMs offer a more stable and reliable option for high-capacity energy storage.

HEMs are poised to revolutionize next-generation energy storage systems due to their high capacity, long cycle life, and excellent thermal and chemical stability. These materials can be tailored for a range of applications, from EVs requiring fast charging and long-range capacity to grid storage systems that demand high efficiency and long-term performance. Moreover, HEMs' resistance to chemical degradation and their ability to maintain high electrochemical performance under demanding conditions make them an ideal choice for portable electronics, which require both lightweight and high-performance energy storage solutions. The development of HEM-based materials could help overcome some of the major limitations of current battery technologies, leading to more sustainable, efficient, and durable energy storage solutions for a wide range of industries and applications.

In conclusion, the diverse applications of functional HEAs and compounds are a testament to their versatility and potential impact on various industries (Figure 1.20). As research continues to uncover new properties and improve the understanding of HEMs, their applications are expected to expand, leading to innovative solutions in engineering, technology, and science.

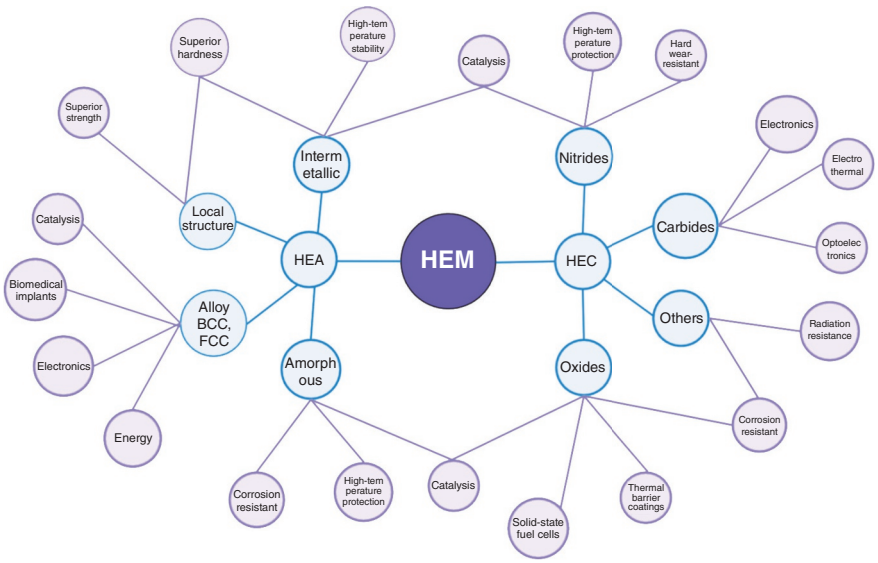


Figure 1.20 Schematic diagram of different classifications and applications of high-entropy functional materials.

References

1 Yeh J W, Chen S K, Lin S J, et al. Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. *Advanced Engineering Materials*, 2004, 6: 299–303. https://doi.org/10.1002/adem.200300567

2 He Q F, Ding Z Y, Ye Y F, et al. Design of high-entropy alloy: a perspective from nonideal mixing. *JOM*, 2017, 69: 2092–2098. https://doi.org/10.1007/s11837-017-2452-1

3 Tong C J, Chen Y L, Yeh J W, et al. Microstructure characterization of Al_xCoCrCuFeNi high-entropy alloy system with multiprincipal elements. *Metallurgical and Materials Transactions A*, 2005, 36, 881–893. https://doi.org/10.1007/s11661-005-0283-0

4 Wu J M, Lin S J, Yeh J W, et al. Adhesive wear behavior of Al_xCoCrCuFeNi high-entropy alloys as a function of aluminum content. *Wear*, 2006, 261: 513–519. https://doi.org/10.1016/j.wear.2005.12.008

5 Wang K, Liu H, Zhang L, et al. Unveiling the nucleation and evolution of twinned intermetallic nanocrystals for CO-tolerant selective hydrogenation. *Inorganic Chemistry Frontiers*, 2023, 10: 1027–1036. https://doi.org/10.1039/d2qi02262a

6 Hsu W L, Tsai C W, Yeh A C. Clarifying the four core effects of high-entropy materials. *Nature Reviews Chemistry*, 2024, 8: 471–485. https://doi.org/10.1038/s41570-024-00602-5

7 Tung C C, Yeh J W, Shun T T, et al. On the elemental effect of AlCoCrCuFeNi high-entropy alloy system. *Materials Letters*, 2007, 61: 1–5. https://doi.org/10.1016/j.matlet.2006.03.140

8 Zhang R, Wang C, Zou P, et al. Compositionally complex doping for zero-strain zero-cobalt layered cathodes. *Nature*, 2022, 610: 67–73. https://doi.org/10.1038/s41586-022-05115-z

9 Yao Y, Huang Z, Xie P, et al. Carbothermal shock synthesis of high-entropy-alloy nanoparticles. *Science*, 2018, 359: 1489–1494. https://doi.org/10.1126/science.aan5412

10 Chen S, Aitken Z H, Pattamatta S, et al. Simultaneously enhancing the ultimate strength and ductility of high-entropy alloys via short-range ordering. *Nature Communications*, 2021, 12: 4953. https://doi.org/10.1038/s41467-021-25264-5

11 Yao Y, Liu Z, Xie P, et al. Computationally aided, entropy-driven synthesis of highly efficient and durable multi-elemental alloy catalysts. *Science Advances*, 2020, 6: eaaz0510. https://doi.org/10.1126/sciadv.aaz0510

12 Wang B, Wang C, Yu X, et al. General synthesis of high-entropy alloy and ceramic nanoparticles in nanoseconds. *Nature Synthesis*, 2022, 1: 138–146. https://doi.org/10.1038/s44160-021-00004-1

13 Nellaiappan S, Katiyar N K, Kumar R, et al. High-entropy alloys as catalysts for the CO_2 and CO reduction reactions: experimental realization. *ACS Catalysis*, 2020, 10: 3658–3663. https://doi.org/10.1021/acscatal.9b04302

14 Zhan C, Xu Y, Bu L, et al. Subnanometer high-entropy alloy nanowires enable remarkable hydrogen oxidation catalysis. *Nature Communications*, 2021, 12: 6261. https://doi.org/10.1038/s41467-021-26425-2

15 Moniri S, Yang Y, Ding J, et al. Three-dimensional atomic structure and local chemical order of medium- and high-entropy nanoalloys. *Nature*, 2023, 624: 564–569. https://doi.org/10.1038/s41586-023-06785-z

16 Liu H, Zhang Y, Zhang L, et al. Unveiling atomic-scaled local chemical order of high-entropy intermetallic catalyst for alkyl-substitution-dependent alkyne semihydrogenation. *Journal of the American Chemical Society*, 2024, 146: 20193–20204. https://doi.org/10.1021/jacs.4c05295

17 Yao Y, Dong Q, Brozena A, et al. High-entropy nanoparticles: synthesis-structure-property relationships and data-driven discovery. *Science*, 2022, 376: eabn3103. https://doi.org/10.1126/science.abn3103

18 Zhang W, Liaw P K, Zhang, Y. Science and technology in high-entropy alloys. *Science China Materials*, 2018, 61: 2–22. https://doi.org/10.1007/s40843-017-9195-8

19 Pickering E J, Muñoz-Moreno R, Stone H J. Precipitation in the equiatomic high-entropy alloy CrMnFeCoNi. *Scripta Materialia*, 2016, 113: 106–109. https://doi.org/10.1016/j.scriptamat.2015.10.025

20 Otto F, Dlouhý A, Pradeep K G, et al. Decomposition of the single-phase high-entropy alloy CrMnFeCoNi after prolonged anneals at intermediate temperatures. *Acta Materialia*, 2016, 112: 40–52. https://doi.org/10.1016/j.actamat.2016.04.005

21 Rost C M, Sachet E, Borman T, et al. Entropy-stabilized oxides. *Nature Communications*, 2015, 6: 8485. https://doi.org/10.1038/ncomms9485

22 Huang H, Wu Y, He J, et al. Phase-transformation ductilization of brittle high-entropy alloys via metastability engineering. *Advanced Materials*, 2017, 29: 1701678. https://doi.org/10.1002/adma.201701678

23 Allmann R, Hinek R. The introduction of structure types into the inorganic crystal structure database ICSD. *Acta Crystallographica Section A*, 2007, 63: 412–417. https://doi.org/10.1107/S0108767307038081

24 Mackay, A L. On complexity. *Crystallography Reports*, 2001, 46: 524–526. https://doi.org/10.1134/1.1387117

25 Yeh J W, Chang S Y, Hong Y D. Anomalous decrease in X-ray diffraction intensities of Cu–Ni–Al–Co–Cr–Fe–Si alloy systems with multi-principal elements. *Materials Chemistry and Physics*, 2007, 103: 41–46. https://doi.org/10.1016/j.matchemphys.2007.01.003

26 Wang H, He Q, Gao X, et al. Multifunctional high entropy alloys enabled by severe lattice distortion. *Advanced Materials*, 2024, 36: 2305453. https://doi.org/10.1002/adma.202305453

27 Lin K H, Tseng C M, Chueh C C, et al. Different lattice distortion effects on the tensile properties of Ni-W dilute solutions and CrFeNi and CoCrFeMnNi concentrated solutions. *Acta Materialia*, 2021, 221: 117399. https://doi.org/10.1016/j.actamat.2021.117399

28 Cao B X, Wang C, Yang T. Cocktail effects in understanding the stability and properties of face-centered-cubic high-entropy alloys at ambient and cryogenic temperatures. *Scripta Materialia*, 2020, 187: 250–255. https://doi.org/10.1016/j.scriptamat.2020.06.008

29 Jien-Wei Y. Recent progress in high entropy alloys. *Annales De Chimie – Science des Materiaux*, 2006, 31: 633–648.

30 Tsai K Y, Tsai M H, Yeh J W. Sluggish diffusion in Co–Cr–Fe–Mn–Ni high-entropy alloys. *Acta Materialia*, 2013, 61: 4887–4897. https://doi.org/10.1016/j.actamat.2013.04.058

31 Zhang C, Zhang F, Jin K, et al. Understanding of the elemental diffusion behavior in concentrated solid solution alloys. *Journal of Phase Equilibria and Diffusion*, 2017, 38: 434–444. https://doi.org/10.1007/s11669-017-0580-5

32 Hsu W.-L, Murakami H, Araki H, et al. A study of $NiCo_{0.6}Fe_{0.2}Cr_xSiAlTi_y$ high-entropy alloys for applications as a high-temperature protective coating and a bond coat in thermal barrier coating systems. *Journal of the Electrochemical Society*, 2018, 165: C524. https://doi.org/10.1149/2.1191809jes

33 Yeh J-W. Recent progress in high-entropy alloys. *European Journal of Control*, 2006, 31: 633–648. https://doi.org/10.3166/acsm.31.633-648

34 Wu D, Kusada K, Yamamoto T, et al. Platinum-group-metal high-entropy-alloy nanoparticles. *Journal of the American Chemical Society*, 2020, 142(32): 13833–13838. https://doi.org/10.1021/jacs.0c04807

35 Wu D, et al. Noble-metal high-entropy-alloy nanoparticles: atomic-level insight into the electronic structure. *Journal of the American Chemical Society*, 2022, 144: 3365–3369. https://doi.org/10.1021/jacs.1c13616

36 Hao J, Zhuang Z, Cao K, et al. Unraveling the electronegativity-dominated intermediate adsorption on high-entropy alloy electrocatalysts. *Nature Communications*, 2022, 13: 2662. https://doi.org/10.1038/s41467-022-30379-4

37 Wang L, Zhang F, Nie Z, et al. Abundant polymorphic transitions in the $Al_{0.6}$CoCrFeNi high-entropy alloy. *Materials Today Physics*, 2019, 8: 1–9. https://doi.org/10.1016/j.mtphys.2018.12.002

38 Wang Y, Chen S, Zhang Y, et al. Effect of multi-element synergistic addition on the microstructure evolution and performance enhancement of laser cladded Al–Mg–Zn-(Mn–Cu–Er–Zr) alloy. *Materials Science and Engineering: A*, 2024, 896: 146256. https://doi.org/10.1016/j.msea.2024.146256

39 Löffler T, Ludwig A, Rossmeisl J, et al. What makes high-entropy alloys exceptional electrocatalysts? *Angewandte Chemie International Edition*, 2021, 60: 26894–26903. https://doi.org/10.1002/anie.202109212

40 Hilhorst A, Jacques P J, Pardoen T. Towards the best strength, ductility, and toughness combination: High entropy alloys are excellent, stainless steels are exceptional. *Acta Materialia*, 2023, 260: 119280. https://doi.org/10.1016/j.actamat.2023.119280

41 Couzinié J P, Dirras, G. Body-centered cubic high-entropy alloys: From processing to underlying deformation mechanisms. *Materials Characterization*, 2019, 147: 533–544. https://doi.org/10.1016/j.matchar.2018.07.015

42 Uporov S, Estemirova S K, Bykov V A, et al. A single-phase ScTiZrHf high-entropy alloy with thermally stable hexagonal close-packed structure. *Intermetallics*, 2020, 122: 106802. https://doi.org/10.1016/j.intermet.2020.106802

43 Wang H, Yang P Y, Zhao W J, et al. Lattice distortion enabling enhanced strength and plasticity in high entropy intermetallic alloy. *Nature Communications*, 2024, 15: 6782. https://doi.org/10.1038/s41467-024-51204-0

44 Zerdoumi R, Ludwig A, Schuhmann W. High entropy intermetallic compounds: a discovery platform for structure-property correlations and materials design principles in electrocatalysis. *Current Opinion in Electrochemistry*, 2024, 48: 101590. https://doi.org/10.1016/j.coelec.2024.101590

45 Aamlid SS, Oudah M, Rottler J, et al. Understanding the role of entropy in high entropy oxides. *Journal of the American Chemical Society*, 2023, 145: 5991–6006. https://doi.org/10.1021/jacs.2c11608

46 Tomboc G M, Zhang X, Choi S, et al. Stabilization, characterization, and electrochemical applications of high-entropy oxides: critical assessment of crystal phase–properties relationship. *Advanced Functional Materials*, 2022, 32: 2205142. https://doi.org/10.1002/adfm.202205142

47 Sarkar A, Velasco L, Wang D I, et al. High entropy oxides for reversible energy storage. *Nature Communications*, 2018, 9, 3400. https://doi.org/10.1038/s41467-018-05774-5

48 Lun Z, Ouyang B, Kwon D H, et al. Cation-disordered rocksalt-type high-entropy cathodes for Li-ion batteries. *Nature Materials*, 2021, 20: 214–221. https://doi.org/10.1038/s41563-020-00816-0

49 Nguyen T X, Liao Y C, Lin C C et al. Advanced high entropy perovskite oxide electrocatalyst for oxygen evolution reaction. *Advanced Functional Materials*, 2021, 31: 2101632. https://doi.org/10.1002/adfm.202101632

50 Cai T, Cai M, Mu J, et al. High-entropy layered oxide cathode enabling high-rate for solid-state sodium-ion batteries. *Nano-Micro Letters*, 2023, 16: 10. https://doi.org/10.1007/s40820-023-01232-0

51 Gild J, Zhang Y, Harrington T, et al. High-entropy metal diborides: a new class of high-entropy materials and a new type of ultrahigh temperature ceramics. *Scientific Reports*, 2016, 6, 37946. https://doi.org/10.1038/srep37946

52 Sarker P, Harrington T, Toher C, et al. High-entropy high-hardness metal carbides discovered by entropy descriptors. *Nature Communications*, 2018, 9: 4980. https://doi.org/10.1038/s41467-018-07160-7

53 Jin T, Sang X, Unocic R R, et al. Mechanochemical-assisted synthesis of high-entropy metal nitride via a soft urea strategy. *Advanced Materials*, 2018, 30: 1707512. https://doi.org/10.1002/adma.201707512

54 Peng C, Gao X, Wang M, et al. Diffusion-controlled alloying of single-phase multi-principal transition metal carbides with high toughness and low thermal diffusivity. *Applied Physics Letters*, 2019, 114: 011905. https://doi.org/10.1063/1.5054954

55 Zhang H, Akhtar F. Processing and characterization of refractory quaternary and quinary high-entropy carbide composite. *Entropy*, 2019, 21: 474.

56 Gild J, Braun J, Kaufmann K, et al. A high-entropy silicide: $(Mo_{0.2}Nb_{0.2}Ta_{0.2}Ti_{0.2}W_{0.2})Si_2$. *Journal of Materiomics*, 2019, 5: 337–343. https://doi.org/10.1016/j.jmat.2019.03.002

57 Qin Y, Liu J X, Li F, et al. A high entropy silicide by reactive spark plasma sintering. *Journal of Advanced Ceramics*, 2019, 8: 148–152. https://doi.org/10.1007/s40145-019-0319-3

58 Ma Y, Ma Y, Wang Q, et al. High-entropy energy materials: challenges and new opportunities. *Energy & Environmental Science*, 2021, 14: 2883–2905. https://doi.org/10.1039/D1EE00505G

59 Chen R, Qin G, Zheng H, et al. Composition design of high entropy alloys using the valence electron concentration to balance strength and ductility. *Acta Materialia*, 2018, 144: 129–137. https://doi.org/10.1016/j.actamat.2017.10.058

60 Guo S, Ng C, Lu J, et al. Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloys. *Journal of Applied Physics*, 109: 103505. https://doi.org/10.1063/1.3587228

61 Liu W H, Lu Z P, He J Y, et al. Ductile $CoCrFeNiMo_x$ high entropy alloys strengthened by hard intermetallic phases. *Acta Materialia*, 2016, 116: 332–342. https://doi.org/10.1016/j.actamat.2016.06.063

62 Guo S, Hu Q, Ng C. More than entropy in high-entropy alloys: forming solid solutions or amorphous phase. *Intermetallics*, 2013, 41: 96–103. https://doi.org/10.1016/j.intermet.2013.05.002

63 Santodonato L J, Zhang Y, Feygenson M, et al. Deviation from high-entropy configurations in the atomic distributions of a multi-principal-element alloy. *Nature Communications*, 2015, 6: 5964. https://doi.org/10.1038/ncomms6964

64 Niu C, LaRosa C R, Miao J. Magnetically-driven phase transformation strengthening in high entropy alloys. *Nature Communications*, 2018, 9: 1363. https://doi.org/10.1038/s41467-018-03846-0

65 Zhang F, Lou H, Cheng B, et al. High-pressure induced phase transitions in high-entropy alloys: a review. *Entropy*, 2019, 21: 239.

66 Cui M, Yang C, Hwang S, et al. Multi-principal elemental intermetallic nanoparticles synthesized via a disorder-to-order transition. *Science Advances*, 2022, 8: eabm4322. https://doi.org/10.1126/sciadv.abm4322

67 Yang T, Zhao Y L, Tong Y, et al. Multicomponent intermetallic nanoparticles and superb mechanical behaviors of complex alloys. *Science*, 2018, 362: 933–937. https://doi.org/10.1126/science.aas8815

68 Xing F, Ma J, Shimizu K.-I, et al. High-entropy intermetallics on ceria as efficient catalysts for the oxidative dehydrogenation of propane using CO_2. *Nature Communications*, 2022, 13: 5065. https://doi.org/10.1038/s41467-022-32842-8

69 He X, Zhang Y, Gu X, et al. Pt-induced atomic-level tailoring towards paracrystalline high-entropy alloy. *Nature Communications*, 2023, 14: 775. https://doi.org/10.1038/s41467-023-36423-1

70 Wu G, Liu C, Yan Y Q, et al. Elemental partitioning-mediated crystalline-to-amorphous phase transformation under quasi-static deformation. *Nature Communications*, 2024, 15: 1223. https://doi.org/10.1038/s41467-024-45513-7

71 Wang H, He Q-F, Yang Y. High-entropy intermetallics: from alloy design to structural and functional properties. *Rare Metals*, 2022, 41: 1989–2001. https://doi.org/10.1007/s12598-021-01926-7

72 Wu Y, Zhang F, Yuan X, et al. Short-range ordering and its effects on mechanical properties of high-entropy alloys. *Journal of Materials Science & Technology*, 2021 62: 214–220. https://doi.org/10.1016/j.jmst.2020.06.018

73 George E P, Curtin W A, Tasan C C. High entropy alloys: a focused review of mechanical properties and deformation mechanisms. *Acta Materialia*, 2020, 188: 435–474. https://doi.org/10.1016/j.actamat.2019.12.015

74 An Z, Mao S, Liu Y, et al. Hierarchical grain size and nanotwin gradient microstructure for improved mechanical properties of a non-equiatomic CoCrFeMnNi high-entropy alloy. *Journal of Materials Science & Technology*, 2021, 92: 195–207. https://doi.org/10.1016/j.jmst.2021.02.059

75 Seol J B, Bae J W, Li Z, et al. Boron doped ultrastrong and ductile high-entropy alloys. *Acta Materialia*, 2018, 151: 366–376. https://doi.org/10.1016/j.actamat.2018.04.004

76 Luan H, Huang L, Kang J, et al. Spinodal decomposition and the pseudo-binary decomposition in high-entropy alloys. *Acta Materialia*, 2023, 248: 118775. https://doi.org/10.1016/j.actamat.2023.118775

77 Laplanche G, Kostka A, Horst O M. Microstructure evolution and critical stress for twinning in the CrMnFeCoNi high-entropy alloy. *Acta Materialia*, 2016, 118: 152–163. https://doi.org/10.1016/j.actamat.2016.07.038

78 Sun L, He Z, Jia N, et al. Local chemical order enables an ultrastrong and ductile high-entropy alloy in a cryogenic environment. *Science Advances*, 2024, 10: eadq6398. https://doi.org/10.1126/sciadv.adq6398

79 Huang Z, Li T, Li B, et al. Tailoring local chemical ordering via elemental tuning in high-entropy alloys. *Journal of the American Chemical Society*, 2024, 146: 2167–2173. https://doi.org/10.1021/jacs.3c12048

80 Yang Y, Zhou J, Zhu F, et al. Determining the three-dimensional atomic structure of an amorphous solid. *Nature*, 2021, 592: 60–64. https://doi.org/10.1038/s41586-021-03354-0

81 Chen X, Wang Q, Cheng Z, et al. Direct observation of chemical short-range order in a medium-entropy alloy. *Nature*, 2021, 592: 712–716. https://doi.org/10.1038/s41586-021-03428-z

82 Zhao S. Effects of local elemental ordering on defect-grain boundary interactions in high-entropy alloys. *Journal of Alloys and Compounds*, 2021, 887: 161314. https://doi.org/10.1016/j.jallcom.2021.161314

83 Wang J, Jiang P, Yuan F. Chemical medium-range order in a medium-entropy alloy. *Nature Communications*, 2022, 13: 1021. https://doi.org/10.1038/s41467-022-28687-w

84 Orhan O K, Hendy M, Ponga M. Electronic effects on the radiation damage in high-entropy alloys. *Acta Materialia*, 2023, 244: 118511. https://doi.org/10.1016/j.actamat.2022.118511

85 Zhang H, Li T, Wang Q, et al. Effects of nitrogen doping on microstructures and irradiation resistance of Ti–Zr–Nb–V–Mo refractory high-entropy alloy. *Acta Metallurgica Sinica (English Letters)*, 2024, 37: 1007–1018. https://doi.org/10.1007/s40195-024-01686-0

86 Kombaiah B, Zhou Y, Jin K, et al. Nanoprecipitates to enhance radiation tolerance in high-entropy alloys. *ACS Applied Materials & Interfaces*, 2023, 15: 3912–3924. https://doi.org/10.1021/acsami.2c17540

87 Duan J M, Jiang Z N, Zeng X Q, et al. Unveiling the underlying corrosion/corrosion-resistance mechanism of a novel corrosion-resistant high entropy alloy by experimental means and AIMD simulations. *Corrosion Science*, 2024, 227: 111782. https://doi.org/10.1016/j.corsci.2023.111782

88 Shi Y, Yang B, Liaw P K. Corrosion-resistant high-entropy alloys: a review. *Metals*, 2017, 7: 43.

89 Gottschall T, Skokov KP, Fries M, et al. Making a cool choice: the materials library of magnetic refrigeration. *Advanced Energy Materials*, 2019, 9: 1901322. https://doi.org/10.1002/aenm.201901322

90 Tegus O, Brück E, Buschow KH, et al. Transition-metal-based magnetic refrigerants for room-temperature applications. *Nature*, 2002, 415: 150–152. https://doi.org/10.1038/415150a

91 Fries M, Pfeuffer L, Bruder E, et al. Microstructural and magnetic properties of Mn-Fe-P-Si (Fe_2 P-type) magnetocaloric compounds. *Acta Materialia*, 2017, 132: 222–229. https://doi.org/10.1016/j.actamat.2017.04.040

92 Snyder G J, Toberer E S. Complex thermoelectric materials. *Nature Materials*, 2008, 7: 105–114. https://doi.org/10.1038/nmat2090

93 Perumal S, Roychowdhury S, Negi D S, et al. High thermoelectric performance and enhanced mechanical stability of p-type $Ge_{1-x}Sb_xTe$. *Chemistry of Materials*, 2015, 27: 7171–7178. https://doi.org/10.1021/acs.chemmater.5b03434

94 Jiang B, Yu Y, Cui J, et al. High-entropy-stabilized chalcogenides with high thermoelectric performance. *Science*, 2021, 371, 830–834. https://doi.org/10.1126/science.abe1292

95 Xin Y, Li S, Qian Y, et al. High-entropy alloys as a platform for catalysis: progress, challenges, and opportunities. *ACS Catalysis*, 2020, 10: 11280–11306 https://doi.org/10.1021/acscatal.0c03617

96 Han X, Wu G, Zhao S, et al. Nanoscale high-entropy alloy for electrocatalysis. *Matter*, 2023, 6: 1717–1751. https://doi.org/10.1016/j.matt.2023.03.034

97 Lu Z, Chen Z W, Singh C V. Neural network-assisted development of high-entropy alloy catalysts: decoupling ligand and coordination effects. *Matter*, 2020, 3: 1318–1333. https://doi.org/10.1016/j.matt.2020.07.029

98 Batchelor T A, Pedersen J K, Winther S H, et al. High-entropy alloys as a discovery platform for electrocatalysis. *Joule*, 2019, 3: 834–845. https://doi.org/10.1016/j.joule.2018.12.015

99 Bell T E, Torrente-Murciano L. H_2 production via ammonia decomposition using non-noble metal catalysts: a review. *Topics in Catalysis*, 2016, 59: 1438–1457. https://doi.org/10.1007/s11244-016-0653-4

100 Xin L, Yongqiang, H, Husheng J. Pt-Rh-Pd alloy group gauze catalysts used for ammonia oxidation. *Rare Metal Materials and Engineering*, 2017, 46: 339–343. https://doi.org/10.1016/S1875-5372(17)30091-7

101 Xie P, Yao Y, Huang Z, et al. Highly efficient decomposition of ammonia using high-entropy alloy catalysts. *Nature Communications*, 2019, 10: 4011. https://doi.org/10.1038/s41467-019-11848-9

102 Yu L, Zeng K, Li C, et al. High-entropy alloy catalysts: from bulk to nano toward highly efficient carbon and nitrogen catalysis. *Carbon Energy*, 2022, 4: 731–761. https://doi.org/10.1002/cey2.228