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PERSPECTIVE PIECE

Negative mixing enthalpy approach for advanced multi-component alloys: a perspective for high strength yet ductile alloy development

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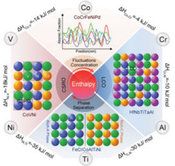
ABSTRACT
In high-entropy alloys (HEA), mixing entropy governs element distribution, while mixing enthalpy dictates interatomic interactions, influencing the formation of solid solutions or intermetallic compounds. Negative mixing enthalpy emerges as a pivotal factor in achieving high yield strength and ductility by driving local chemical fluctuations, short-range ordering, and second-phase formation, thereby optimizing the microstructure. However, excessive negativity in mixing enthalpy can trigger a brittle fracture in metallic materials during tensile deformation, reducing mechanical performance. To optimize HEA design, we propose: (1) introducing controlled 'negative enthalpy genes' to promote SRO via non-equilibrium heat treatments; (2) balancing strength and ductility by fine-tuning enthalpy negativity; and (3) innovating heat treatment techniques to prevent brittle intermetallic growth. These strategies provide a transformative approach to strengthening and toughening M/HEAs, encourage deeper fundamental research to unlock their full potential for advanced material applications.



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1. Overview of multi-component alloys

1.1. Development of high entropy alloys

High-Entropy Alloys (HEAs), also referred to as multi-component alloys, have emerged as a promising class of materials distinct from conventional alloys, offering substantial advantages in mechanical properties that have captivated the attention of researchers. The origins of multi-component alloy research can be traced back to the late eighteenth century, when Franz Karl Achard synthesized alloys containing five to seven elements, laying the groundwork for future explorations [1–3]. In 1993, Greer et al. introduced the 'Confusion Principle', proposing that the diverse elemental composition of multi-component alloys induces high disorder (or mixing entropy) in the liquid state, which favors the formation of disordered amorphous glass structures at high temperatures [4]. This marked an important milestone in alloy theory. In 2004, Yeh et al. formally coined the term 'high-entropy alloys' and outlined the 'four core effects'—high entropy, lattice distortion, sluggish diffusion, and the cocktail effect—significantly advancing the theoretical understanding of these materials [5]. Concurrently, Cantor et al. explored multi-component amorphous alloys, observing the formation of brittle crystalline structures rather than the expected amorphous phases, further validating the feasibility of HEA synthesis [6]. These pioneering studies ignited a wave of interest in HEAs. By

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combining elements such as Co, Cr, Ni, Fe, Al, and Mn in near-equimolar ratios, researchers designed Medium- and High-Entropy Alloys (M/HEAs) with exceptional mechanical properties, high-temperature stability, and radiation resistance [7–9]. The HEA design paradigm breaks traditional alloy research, expanding the material landscape and offering new directions for alloy development [10,11]. Advances in the field are driven by the strategic selection and optimization of elemental compositions and microstructures, underscoring the need for a refined theoretical framework to guide the complex and diverse design of HEAs.

1.2. Critical factors affecting the phase formation in HEA

1.2.1. Entropy

Entropy, a core concept in thermodynamics, quantifies the degree of disorder in a system. As the number of components increases, the system's entropy rises, reflecting greater disorder. Boltzmann's entropy equation expresses this relationship as [12]:

$$S = k_B \ln W \tag{1}$$

where k_B is the Boltzmann constant, and W represents the degree of disorder. In alloy systems, mixing entropy plays a crucial role in determining phase stability and composition.

Traditional alloy theories suggest that high concentrations of mixed elements can lead to the formation of intermetallic compounds, which typically cause brittleness and reduced toughness. However, recent research reveals that cast HEAs, despite containing high proportions of diverse elements, can form single-phase, supersaturated solid solutions, a phenomenon attributed to the 'high entropy effect'. According to thermodynamics, the Gibbs free energy (ΔG) is related to enthalpy (ΔH) and entropy (ΔS) as [13]:

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

In this equation, T is the absolute temperature. HEAs are characterized by high entropy (ΔS), and as the number of alloying elements increases, so does ΔS [14]. When ΔH remains constant, an increase in entropy reduces ΔG, enhancing system stability. At elevated temperatures, the entropy effect becomes even more pronounced, allowing the system to maintain lower energy states and avoid the formation of brittle intermetallic phases. HEAs can crystallize into various structures—face-centered cubic (FCC), body-centered cubic (BCC), and hexagonal close-packed (HCP)—depending on their elemental composition. FCC structures often consist of elements like Co, Cr, Ni, and Fe, while BCC structures are more commonly associated with refractory metals such as Zr, Hf, Ta, and Nb, which favor the formation of single-phase solid solutions [15,16]. Entropy serves not only as a fundamental thermodynamic parameter but also as a critical factor in HEA material design.

In addition to the high entropy effect, successful alloy design must account for other factors such as mixing enthalpy (ΔH_{mix}), valence electron concentration (VEC), melting points (T_m), and atomic size differences (δ) [17,18].

1.2.2. Mixing enthalpy (ΔH_{mix})

ΔH_{mix} represents the interaction between different elements within an alloy. The formation of intermetallic compounds or amorphous phases is governed by the interplay between mixing entropy and mixing enthalpy, making ΔH_{mix} a key factor in alloy phase design. The ΔH_{mix} can be calculated as follows [19]:

$$\Delta H_{mix} = \sum_{i=1, i\neq j}^{n} \Omega_{ij} c_i c_j \tag{3}$$

where $\Omega_{ij} = 4\Delta H_{mix}^{AB}$, and ΔH_{mix}^{AB} represents the mixing enthalpy of binary liquid AB alloys. This equation considers the interactions between different elemental pairs, and the magnitude of these interactions determines the alloy's phase structure. When ΔH is slightly negative or zero or positive, single-phase solid solutions are more likely to form. In contrast, increasingly negative values of ΔH_{mix} favor the formation of intermetallic compounds or amorphous structures. In thermodynamic alloy design, ΔH_{mix} reflects the interaction between constituent elements. Strong interactions promote local atomic ordering, resulting in short-range ordered structures. If sufficiently stable, these structures may evolve into long-range ordered intermetallic compounds [14]. When ΔH_{mix} is negative, a trend can be realized for the formation of short-range atomic clusters or long-range ordered compounds, with the outcome depending on the magnitude of ΔH_{mix} [15,20,21]. Current experimental and computational studies indicate that M/HEAs exhibiting a propensity for single-phase solid solution formation typically possess ΔH_{mix} values in range of -15 to 5 kJ/mol. Within this window, tailored heat treatment effectively stabilizes the solid-solution phase while suppressing the formation of brittle intermetallic compounds. Notably, extensive evidence shows that further reductions in ΔH_{mix} lead to the formation of intermetallic phases, and in some cases, bulk metallic glasses (BMGs) [14,22,23]. Present data suggest that $\Delta H_{mix} \approx -15$ kJ/mol represents a critical threshold demarcating the ductile-to-brittle transition in M/HEAs.

Of course, this range reflects current research findings, future advances in heat treatment strategies may extend the viable enthalpy range to more negative values, potentially broadening the compositional design space.

1.3. Criteria for the design of high-entropy alloys

1.3.1. Crystal structure

VEC serves as another critical parameter for predicting the crystal structures of metals and HEAs. VEC is determined by averaging the number of valence electrons per atom in the alloy. Guo et al. proposed that VEC can effectively forecast the crystal structure in HEAs: alloys with VEC values exceeding 8 tend to form FCC structures, while those with values below 6.87 preferentially adopt BCC structures [24]. For VEC values between 6.87 and 8, a coexistence of FCC and BCC phases tends to form. So VEC plays a pivotal role in governing phase stability in HEAs. Chen et al. investigated the $(AlCoCrFeNi)_{100-x}Ni_x$ (FCC) and $(CoCrCuFeNi)_{100-x}Mo_x$ (BCC) alloy series, proposing design criteria to balance strength and ductility by tailoring elemental VEC. Specifically, elements with lower VEC than the matrix enhance strength, while those with higher VEC promote ductility [25]. Jin et al. systematically tuned the Al content in $(FeCoNiCrMn)_{100-x}Al_x$ ($x = 0$–20 at.%), revealing a structural evolution from single-phase FCC to FCC + BCC dual-phase, and eventually to single-phase BCC [26]. FCC-dominated alloys exhibited high ductility and low strength, while dual-phase compositions displayed composite-like behavior, with sharply increased strength but reduced ductility. Full transition to the BCC phase resulted in pronounced brittleness [27]. While the VEC criterion predicts the predominant lattice type, it does not capture the potential formation of minor phases or intermetallic compounds, underscoring the need for complementary approaches in identifying single-phase solid solutions [28].

1.3.2. Phase composition

- Binary Regular Solution Model

Chen et al. demonstrated that binary enthalpy interactions can precisely reproduce the ΔH_{mix} in multicomponent random solid solutions, such as quaternary and quinary systems [29,30]. By analyzing more than 40 elements, they constructed a formation enthalpy map for binary solid solutions, relative to their lowest-energy crystal structures at 0 K. In this map (Figure 1), red and blue regions indicate element pairs that either promote or inhibit mixing, respectively. This map provides a robust framework for selecting element combinations capable of forming stable solid solutions in FCC, BCC, and HCP structures, guiding the design of HEAs by optimizing their microstructural and mechanical properties.

- Multi-Component Materials

The Ω parameter offers a valuable thermodynamic metric for predicting the formation of solid solutions or intermetallic compounds in HEAs. Zhang et al. defined an Ω parameter, calculated from the melting temperature (T), mixing entropy (ΔS_{mix}), and ΔH_{mix} of the constituent elements [31]. The parameter is defined as $\Omega = (T_m \Delta S_{mix}) / |\Delta H_{mix}|$. Note that, the Ω parameter here represents the product of entropy and temperature divided by the enthalpy value. Although it shares the same symbol as the Ω_{ij}parameter in Equation (3), it embodies an entirely different physical meaning. Figure 2 presents key thermodynamic parameters influencing phase stability. Statistical analysis (Figure 2(a,b)) shows that HEAs with δ_r between 0 and 8.5%, ΔH_{mix} between −22 and 7 kJ/mol, and ΔS_{mix} between 11 and 19.5 J/(K·mol) tend to form stable solid solutions. When $\Omega \geq 1$ (Figure 2(c)), entropy dominates, favoring solid solution formation. Conversely, when $\Omega < 1$, enthalpy effects lead to intermetallic or BMG. Additionally, atomic size difference ($\Delta\delta_r$) significantly influences phase stability. Therefore, predicting the phase stability and microstructural evolution of HEAs requires a comprehensive consideration of parameters such as ΔH_{mix}, ΔS_{mix}, $\Delta\delta_r$ *and* Ω. Among these parameters, ΔH_{mix} stands out as a key thermodynamic factor governing phase evolution. In the next section, we explore current developments in negative ΔH_{mix} alloy systems.

1.4. Negative mixing enthalpy alloys

Recently, negative ΔH_{mix} solid solution and negative ΔH_{mix} alloys were proposed [33]. In early investigations of metallic glasses (amorphous alloys), the addition of alloying elements with negative ΔH_{mix} was shown to modulate the inhomogeneity of the amorphous matrix, significantly influencing both the plasticity and glass-forming ability (GFA) of BMGs [34,35]. These findings revealed the central role of ΔH_{mix} as a critical thermodynamic parameter governing the formation and stabilization of metallic glasses. Indeed, ΔH_{mix} has been widely used in thermodynamic calculations and is a fundamental thermodynamic parameter together with entropy, valence electron concentration, electronegativity and others for phase diagram establishment and phase stability and phase control calculations [36–39]. For instance, Lu et al. utilized ΔH_{mix} to identify the eutectic point in eutectic high-entropy alloys (EHEAs), streamlining the discovery of novel EHEA compositions [40]. Jin et al.

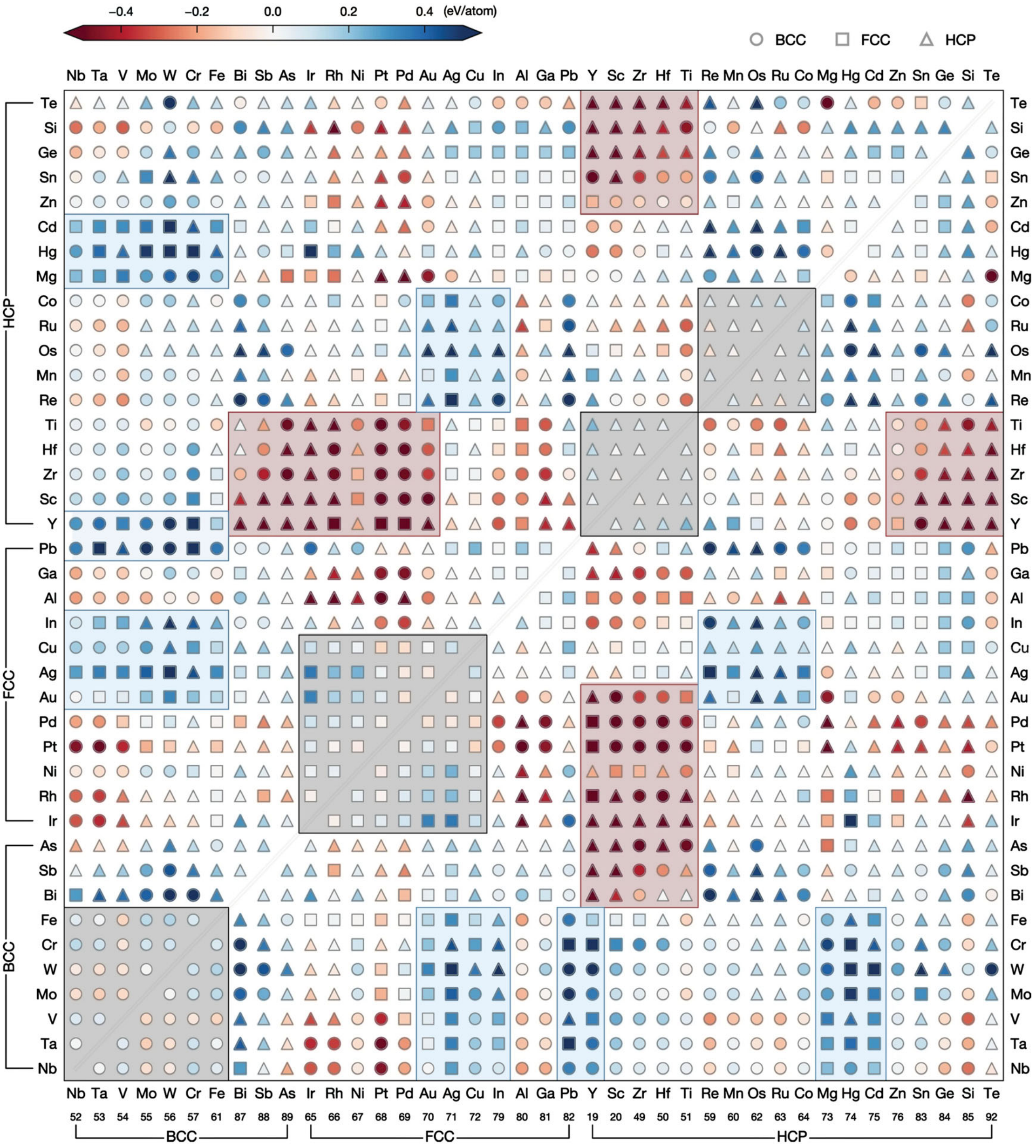


Figure 1. Formation enthalpy map of binary solid solutions based on density functional theory calculations. Element pairs with the same crystal structure are represented by gray shading. Pairs with a strong tendency to mix ($\Delta Hf < -0.2$ eV/atom) are highlighted by red shading, while those with a strong tendency against mixing ($\Delta Hf > 0.2$ eV/atom) are marked with blue shading [29].

combined VEC with ΔH_{mix} to develop nanostructured EHEAs featuring ordered body-centered cubic and FCC phases [41]. However, negative ΔH_{mix} has not been used as general guidance to design alloys with synergy of strength and ductility until recently Han et al. introduced the concept of negative ΔH_{mix} solid solutions in BCC $(\mathrm{HfNbTiV})_{90}\mathrm{Al}_{10}$ HEAs, highlighting 'negative ΔH_{mix} alloying' route to induce multi-scale local chemical ordering (LCO) in cast $(\mathrm{HfNbTiV})_{100-x}\mathrm{Al}_x$ ($x = 0, 5, 10, 12, 15$). This approach enhanced dislocation interactions and improved work-hardening capacity, offering new routes for designing high-strength with high-toughness materials [33,38]. Further advancements involved the design of cast $\mathrm{Co}_{40-x}\mathrm{Cr}_{20}\mathrm{Fe}_{20}\mathrm{Ni}_{20}\mathrm{Al}_x$ ($x = 6$, 11, 13, 15) HEAs, with ΔH_{mix} ranging from −10.6 to −6.57 kJ/mol. These alloys exhibited hierarchical heterogeneous structures across multiple scales—from micron-scale (BCC + FCC) to nanoscale (local chemical fluctuations, LCFs)—resulting in high yield strength and excellent ductility [42]. In FCC M/HEAs, ΔH_{mix} could influence alloy development as implied by the effects of negative ΔH_{mix} from research in the literature, for example, in VCoNi MEA, heat treatments facilitated the formation of precipitate phases (e.g. σ, κ, μ, and Heusler phases), these

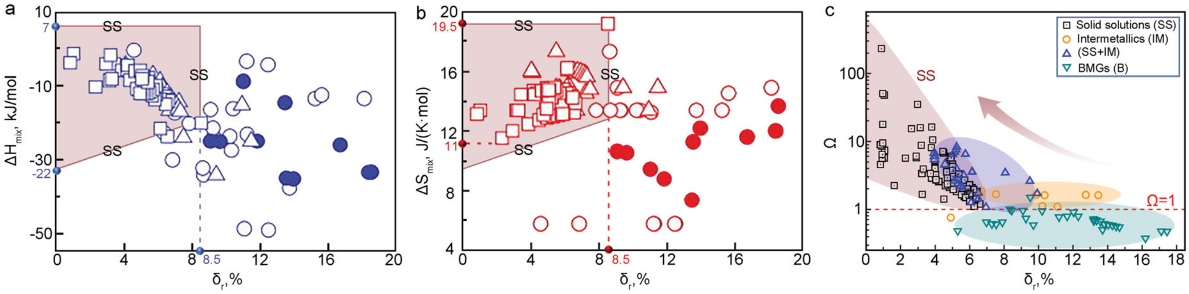


Figure 2. Thermodynamic parameters affecting phase stability. (a) Effect of the mixing enthalpy (ΔH_{mix}) and atomic size difference ($\Delta\delta_r$) on phase stability in multi-component alloys and bulk metallic glasses; (b) Influence of mixing entropy (ΔS_{mix}) and atomic size difference ($\Delta\delta_r$) on phase stability in multi-component alloys and bulk metallic glasses. The symbols in figure a and b, ○ represents equiatomic amorphous phase forming alloys; ● represents non-equiatomic amorphous phase forming alloys; □ represents solid solution phases and Δ represents intermetallic phases [23]; (c) Correlation between $\Delta\delta_r$ and the Ω parameter [31,32].

could possibly be driven by the strong negative enthalpy interactions between V and Ni/Co [43–45].

Excessively negative ΔH_{mix} is detrimental to mechanical properties, as it suppresses the formation of single-phase solid solutions and promotes brittle intermetallic phases, ultimately compromising toughness and ductility [38]. Using $\text{Al}_x(\text{CoCrCuFeNi})_{100-x}$ ($x = 0$, 0.1, 0.5, 0.8, and 1.0 in molar ratios) HEAs as a model system, Xu et al. demonstrated that increasing Al content leads to a more negative ΔH_{mix} (from −3.2 to −4.78 kJ/mol), leading to a structural transition from FCC to BCC. This increase in negative enthalpy also enhances phase separation and facilitates the formation of ordered intermetallics in BCC-rich alloys. Similarly, Kim et al. reported that prolonged annealing of $\text{V}_{16}(\text{CoNi})_{74}\text{Mo}_{10}$ HEA ($\Delta H_{\text{mix}} = -9.5$ kJ/mol) increased yield and tensile strengths from 504 to 923 MPa and 1027 to 1189 MPa, respectively. However, after 48 h, the alloy exhibited complete embrittlement due to the formation of 48.2% intermetallic phases (M_3V and μ), leading to catastrophic brittle fracture in the elastic stage prior to plastic yielding [46]. Based on current experimental and computational findings, a ΔH_{mix} range of −15 to 5 kJ/mol is favorable for the formation of stable solid solution structures [14,22,41,47]. However, when ΔH_{mix} becomes too negative, the strong chemical interactions result in high binding energies between different elements, promoting the formation of long-range ordered atomic arrangements rather than random solid solutions. As a result, the alloy system tends to form intermetallic compounds [14,32]. In addition, Liu et al. found that in a stable single-phase CoCrFeNi HEA, the addition of Al accelerated compositional decomposition, leading to the appearance of a second FCC phase with a different lattice constant in $\text{CoCrFeNiAl}_{0.1}$ HEA after long-term annealing. This induced phase separation at intermediate temperatures (750°C for 800 h), as the Al addition destabilized the metastable CoCrFeNi HEA (−3.75 kJ/mol) [48]. Therefore, the introduction of 'negative enthalpy genes' can promote the formation of LCO regions or even intermetallic compounds within the alloy, leading to structural instability. As a result, subsequent heat treatment processes also play a crucial role.

In summary, the negative enthalpy alloying route, rooted in atomic affinity and thermodynamic principles, can serve as a tool for tailoring alloy microstructures and properties. This approach is effective for optimizing complex multicomponent alloys [42]. By controlling ΔH_{mix}, a balance between single-phase solid solutions and multiphase composite structures can be achieved, introducing multi-scale chemical composition fluctuations. This strategy offers transformative opportunities for developing next-generation high-performance alloys. Mechanical performance in metallic materials is fundamentally governed by the strength–ductility trade-off. Since ΔH_{mix} influences both phase stability and microstructural evolution, the next section presents a statistical analysis of its role in influencing mechanical behavior in M/HEAs.

2. Influence of enthalpy on strength and toughness enhancement

The strength and ductility of metallic materials are two critical mechanical properties. In multi-component M/HEAs, these properties are also influenced by factors such as grain size [49,50], precipitates [11,51,52], and dislocation density [53,54]. Besides these, LCO is a key structural feature that governs the deformation mechanisms of M/HEAs. By introducing structural heterogeneity at the atomic scale, LCO enables an exceptional synergy between strength and ductility [38,55,56]. Based on the **Ω** parameter formula, it is evident that the design of alloy composition through enthalpy has a substantial impact on mechanical properties. Following the studies, Figure 3 illustrates the relationship between yield strength (σ_y) and the enthalpy of HEAs. By summarizing and analyzing BCC and FCC single-phase M/HEA systems with superior mechanical properties, it was found that as the enthalpy becomes more negative, the σ_y of the alloy increases roughly by 10–30 MPa/negative enthalpy. This indicates that negative ΔH_{mix} contributes to enhancing the overall mechanical properties of the alloy. However, excessively negative enthalpy values can also lead to the formation of intermetallic compounds, causing embrittlement and loss of ductility. Therefore, within a certain range, negative ΔH_{mix} can improve yield strength, large values result in the formation of intermetallic compounds. For instance, in the BCC $(HfNbTiV)_{100-x}Al_x$ (x = 0, 5, 10, 15) alloy series, the addition of Al lowers the enthalpy, leading to a gradual increase in yield strength [38]. In other FCC alloys, such as VCoNi, which has a more negative enthalpy, mechanical properties can be further enhanced through processing adjustments [46]. As one of the key thermodynamic indicators, ΔH_{mix} influences atomic affinity and phase stability. Materials with negative ΔH_{mix} are often used in their metastable states, rather than in stable equilibrium, which makes them less unique or consistent in behavior. As a result, establishing a unified quantitative relationship across various material systems remains a significant challenge. For example, in the VCoNi MEA, short-time annealing at temperatures as high as 1000°C can induce the formation of a metastable κ phase, which gradually disappears with prolonged annealing. The introduction and density control of the coherent κ phase can enhance both strength and ductility of the material [43,57]. Currently, efforts have already been made to establish quantitative relationships in certain specific material systems. Wang et al. investigated Ni-W-based HEAs with the addition of Ta, W, Mo, Al, Ni, and Co, and found that Ta, W, Mo, and Al have significantly more negative mixing enthalpies with Ni and Co. Correspondingly, Ni-W-based alloys with these elements exhibited higher yield strength. Using a multiple linear regression model, they predicted that the yield strength of HEAs is negatively correlated with ΔH_{mix} [58,59]. Han et al. designed a series of $Co_{40-x}Cr_{20}Fe_{20}Ni_{20}Al_x$ alloys (x = 6, 11, 13, 15; hereafter referred to as CCFNA-X). For reference, the ΔH_{mix} of CoCrFeNi is −3.75 kJ/mol. With increasing Al content, the ΔH_{mix} decreased further (negative mixing enthalpies of −6.57, −8.97, −9.81, and −10.6 kJ/mol, respectively), and the HEAs' yield strength increased from ∼300 MPa (CCFNA6) to ∼1000 MPa (CCFNA15), while tensile elongation dropped from ∼35% to ∼5%. In CCFNA13 and CCFNA15, the formation tendency of intermetallic compounds became more pronounced, with the B2 structure replacing the LCF structure [42]. Therefore, excessively negative ΔH_{mix} often results in complex phase structures, favoring the formation of hard intermetallic compounds. This enhances the alloy's yield strength but reduces its ductility [38,60].

Using enthalpy to design alloys not only helps predict and adjust crystal structures in M/HEAs but also plays a crucial role in determining mechanical performance. The enthalpy-based design of HEA compositions not only enhances mechanical properties but also significantly influences other performance aspects, such as corrosion resistance [75], high-temperature strength [76,77], friction and wear behavior [78], and irradiation resistance [79]. For example, Wang et al. reported that the addition of Al to a HfNbTaTiZrV BCC HEA resulted in excellent compressive yield strengths of 1392 MPa at 800°C and 693 MPa at 1000°C [76]. Similarly, Li et al. developed a non-equiatomic FeNiCoCr HEA exhibits superior corrosion resistance compared to 316L stainless steel [80].

2.1. *Mixing enthalpy in BCC structural materials*

Refractory element-based BCC HEAs have garnered significant attention for their exceptional high-temperature performance, making them promising candidates for applications in high-temperature structural components, protective armor, and nuclear materials [81,82]. However, the inherent hardness and brittleness of BCC HEAs often lead to premature failure under tensile loading, limiting research to compression properties. To improve their mechanical performance, alloy composition can be tailored through the adjustment of ΔH_{mix}, along with control over processing techniques, microstructural design, and the introduction of chemical ordering [33,65,83]. Figure 4 summarizes advances in BCC systems via local chemical ordering or phase transitions to enhance mechanical properties, emphasizing atomistic structure regulation as a promising strategy.

2.1.1. *Local chemical ordering (LCO)*

The incorporation of elements with negative ΔH_{mix} can induce LCO within the alloy, providing a new pathway for tailoring mechanical properties. An et al. introduced the concept of negative ΔH_{mix} solid solutions and designed a series of BCC $(HfNbTiV)_{100-x}Al_x$ alloys ($x = 0, 5, 10, 15$; $-12 < \Delta H_{\text{mix}} < 5$ kJ/mol). Their follow-up studies developed a multi-scale heterogeneous structure in BCC $(HfNbTiV)_{90}Al_{10}$ negative enthalpy solid solution alloys ($\Delta H_{\text{mix}} = -9.07$ kJ/mol) [38]. When the enthalpy dropped to −12 kJ/mol ($(HfNbTiV)_{85}Al_{15}$), the alloy achieved a yield strength of ∼1.5 GPa, but fractured rapidly after yielding. In

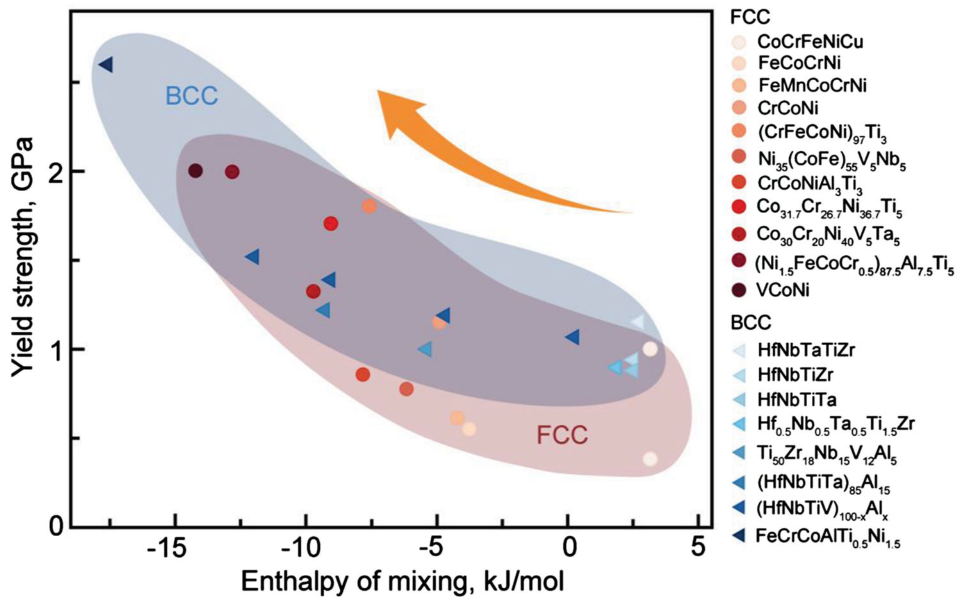


Figure 3. Statistical relationship between the mixing enthalpy (ΔH_{mix}) and yield strength (σ_y) of M/HEAs. The red and blue shading areas corresponding to FCC and BCC structural M/HEA, respectively [33,38,46,61–74].

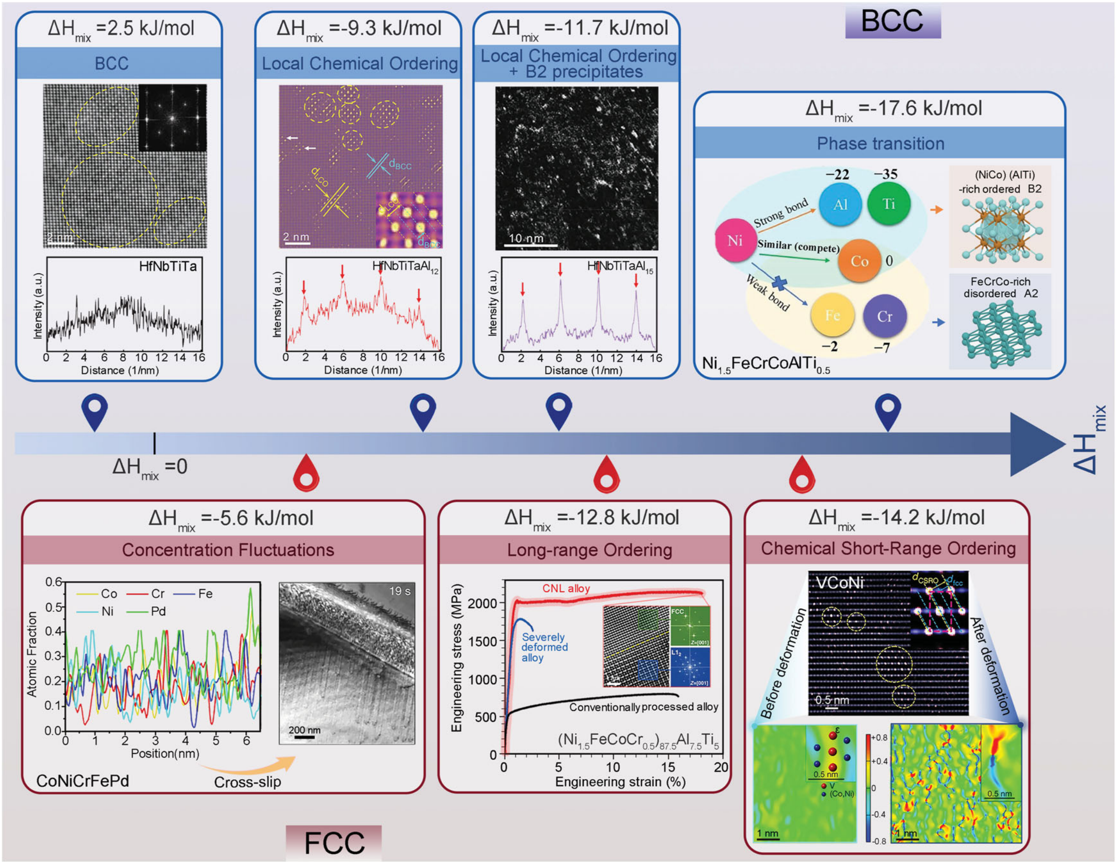


Figure 4. Notable advances in high-performance FCC and BCC structural M/HEA materials, where enhanced performance is typically associated with local chemical composite ordering. The mixing enthalpy values for these materials were calculated, with most falling within the negative enthalpy range [33,56,65,71,84].

contrast, HfNbTiVAl$_{10}$ exhibited ~20% tensile ductility and ultrahigh yield strength (~1.39 GPa). The relatively negative enthalpy of Al-(Hf, Nb, Ti, V) atomic pairs (−39 to −16 kJ/mol) enhanced chemical affinity, introducing multi-scale chemical composition fluctuations ranging from sub-nanometer to several hundred nanometers, which improve the strength-toughness balance. Additionally, a study of refractory high-entropy alloys (RHEAs) $(\mathrm{HfNbTiTa})_{100-x}\mathrm{Al}_x$ ($x = 0$, 5, 10, 12, and 15) with ΔH_{mix} values of 2.5, −2.8, −7.5, −9.3, and −11.7 kJ/mol (Figure 4), respectively, showed that the $(\mathrm{HfNbTiV})_{88}\mathrm{Al}_{12}$ alloy achieved 24.5% ductility, while $(\mathrm{HfNbTiV})_{85}\mathrm{Al}_{15}$ lost its plasticity. Microstructural characterization of these alloys revealed the presence of LCO, confirming that negative enthalpy drives LCO formation. The multi-scale heterogeneity of LCO disrupts the randomness of solid solution structures, forming chemically biased negative enthalpy solid solutions [33].

2.1.2. Phase transition

Tuning the composition of BCC HEAs via ΔH_{mix} adjustment is an effective approach for achieving a balance between strength and toughness. By carefully controlling phase transitions, it is possible to significantly enhance toughness while maintaining high strength. For instance, Guo et al. introduced Ni into FeCrCoAlTi$_{0.5}$ ($\Delta H_{\mathrm{mix}} = -16.9$ kJ/mol) to design a new HEA, Ni$_{1.5}$FeCrCoAlTi$_{0.5}$ ($\Delta H_{\mathrm{mix}} = -17.6$ kJ/mol, Figure 4) [65]. Enthalpy analysis and simulations revealed that the addition of Ni promoted an entropy-driven order–disorder transformation during cooling, resulting in phase separation. Two distinct phases emerged: a hard, ordered B2 phase enriched in (Ni, Co)(Al, Ti), which had a stronger ΔH_{mix}, and a soft, disordered A2 phase enriched in FeCrCo, with a weaker enthalpy. The original FeCrCoAlTi$_{0.5}$ alloy had a compressive strength of ~1.19 GPa with negligible plasticity, while the designed Ni$_{1.5}$FeCrCoAlTi$_{0.5}$ alloy, with a heterogeneous nanostructure (A2 nanostructure precipitates (~12.5 nm) + B2 matrix phase), achieved a compressive strength of ~2.60 GPa and a plasticity of ~15.8%. While high configurational entropy can mitigate phase separation in HEAs, strongly negative mixing enthalpies may still drive compositional segregation. In particular, Laves-type intermetallics—characteristically hard and brittle—frequently form under such conditions. Their formation is governed by electronic parameters (e.g. electronegativity, valence electron concentration) and geometric factors (e.g. atomic size mismatch, packing density), and is often linked to Cr- or Mo-enriched regions [85–88]. Computational modeling by Yin et al. predicted that Laves phases in FCC HEAs precipitate predominantly at lower temperatures (900–1200°C) [89]. Experimentally, Liu et al. observed that Nb addition to CoCrFeNi alloys induces HCP-structured Laves phase formation, enhancing yield strength but sharply reducing ductility—indicating the need for careful control over the volume fraction and distribution of such brittle phases [90]. Similarly, Cai et al. demonstrated that the strong negative enthalpy between Ni and Zr in CoCuFeNi alloys promoted the formation of a Ni-Zr C14-type Laves phase; within a tailored Zr concentration range, a balance strength-ductility synergy was achieved [91]. This result reveals that more negative enthalpy values are not always beneficial; reasonable control of ΔH_{mix} allows for the prediction and adjustment of phase transitions during heat treatment, leading to beneficial phase structures that improve the trade-off between strength and toughness.

2.2. Mixing enthalpy in FCC structural materials

Despite excellent tensile ductility and good processability, FCC HEAs often suffer from relatively low yield strength, limiting their broader application. To address this issue, researchers have explored various strategies, including compositional design and microstructural control, to enhance mechanical performance. Notable approaches include adjusting element distribution, promoting chemical short-range order (CSRO), and forming long-range Ordering (LRO). Figure 4 shows representative FCC-based alloys strengthened by local ordering. The calculated ΔH_{mix} values fall within a negative range, supporting the link between enhanced properties and ordering tendencies.

2.2.1. Element distribution tuning

Due to differences in atomic properties (such as size, mass, and electronegativity), HEAs often exhibit non-uniform element distribution at the atomic scale [92]. For example, in the CoCrFeMnNi HEA, which has a mixing enthalpy of $\Delta H_{\mathrm{mix}} = -4.2$ kJ/mol, the substitution of Mn with larger Pd atoms in CoNiCrFePd HEA induces significant concentration fluctuations (amplitudes up to 60%, wavelengths 1–3 nm), altering the slip mechanism from planar to cross-slip, thereby enhancing work hardening [84]. Calculations show that the ΔH_{mix} of CoNiCrFePd is further reduced to $\Delta H_{\mathrm{mix}} = -5.6$ kJ/mol (Figure 4), leading to noticeable elemental fluctuations on the microscale. These fluctuations improve mechanical properties, demonstrating how compositional changes can introduce concentration fluctuations that regulate slip mechanisms and hardening behavior.

2.2.2. Long-range ordering (LRO)

LRO refers to the long-range, ordered arrangement of atoms in a crystalline structure [93,94]. Unlike CSRO, LRO describes the specific atomic positions within the lattice, leading to ordered structures. For example, in the FCC $(CoCrNi)_{100-x}Ti_x$ series HEAs, the high affinity between Ni and Ti ($\Delta H_{\mathrm{mix}} = -38$ kJ/mol) leads to the formation of Ni_3Ti-rich phases, while Cr, with lower enthalpy, remains non-segregated [72,95]. Fan et al. designed a $(Ni_{1.5}FeCoCr_{0.5})_{87.5}Al_{7.5}Ti_5$ HEA with ~2 GPa yield strength and ~16% uniform elongation ($\Delta H_{\mathrm{mix}} = -12.8$ kJ/mol, Figure 4) [71]. Subsequent heat treatment induced discontinuous precipitation of $L1_2$ phases (30–40 nm). Due to differences in ΔH_{mix} between Al, Ti, and Ni ($\Delta H_{\mathrm{Al,Ti}} = -30$ kJ/mol, $\Delta H_{\mathrm{Ni,Ti}} = -38$ kJ/mol, $\Delta H_{\mathrm{Ni,Al}} = -38$ kJ/mol), variations in chemical affinity resulted in differing elemental concentrations within the multi-component $(Ni, Co, Cr, Fe)_3(Al, Ti)$ $L1_2$ phase. The fully coherent, high-density interfaces between the FCC and $L1_2$ phases promote dislocation movement while preventing dislocation pile-up, facilitating long-range dislocation slip. This enhances both strength and ductility, offering superior mechanical performance.

2.2.3. Chemical short-range ordering (CSRO)

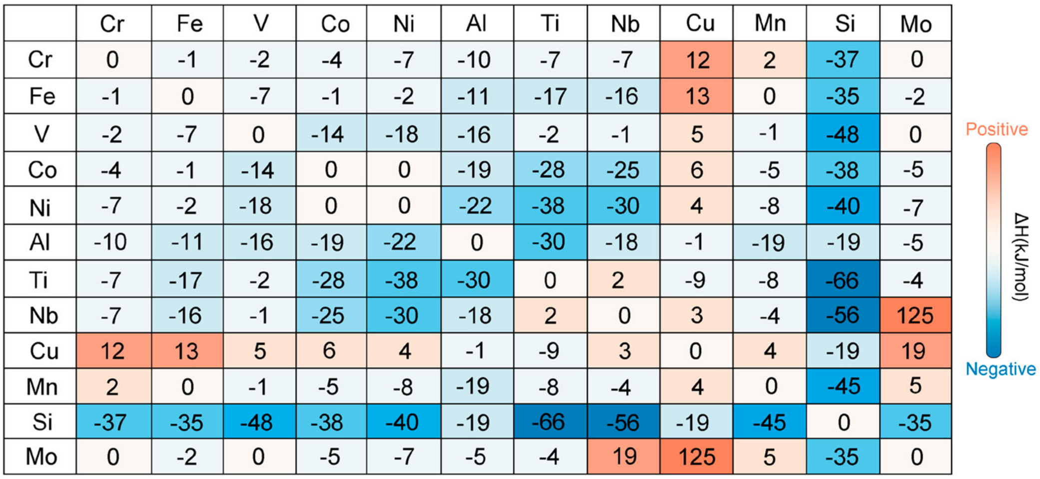
The affinity between elements, as influenced by ΔH_{mix}, can introduce elemental segregation, resulting in CSRO. CSRO refers to the arrangement of atoms within a few atomic distances, significantly affecting mechanical properties, diffusion behavior, and phase stability [96]. In the VCoNi MEA, $\Delta H_{\mathrm{mix}} = -14.2$ kJ/mol (Figure 4), with V showing strong affinity for Ni and Co ($\Delta H_{\mathrm{v,Co}} = -14$ kJ/mol, $\Delta H_{\mathrm{v,Ni}} = -18$ kJ/mol). This affinity promotes chemical short-range ordering, as confirmed by Chen et al. through high-angle annular dark-field (HAADF) and atomic-scale EDS-Mapping [56]. Analysis showed that V-V atoms tend to avoid each other, while V-Co and V-Ni prefer adjacency, driven by differences in enthalpy. Further process modifications introduced sub-nanoscale CSRO and a secondary $L1_2$ phase, yielding exceptional properties of 2.0 GPa yield strength and 16% tensile ductility [46]. CSRO thus not only governs microstructural evolution but also enhances alloy performance, highlighting the pivotal role of enthalpy in element affinity and subsequent material properties.

3. Future perspective of designing HEA using mixing enthalpy

Composition design has always been an essential aspect of the materials field, as only with validated design principles can one make rational choices regarding elemental selection and enthalpy adjustment. By fine-tuning the ΔH_{mix}, M/HEA compositions can be further optimized to endow the material with superior mechanical properties and complex microstructures. Analyzing commonly used elements in M/HEAs reveals that in FCC M/HEAs, enthalpy regulation helps stabilize the FCC crystal structure, and the addition of elements such as Si, Ti, Nb, and Al reduces the alloy's ΔH_{mix} (Table 1) [97]. BCC HEAs, characterized by their non-close-packed lattice structure and limited slip systems, often exhibit constrained plasticity. This limitation is further exacerbated by severe lattice distortions arising from the multi-principal element design, which increases resistance to dislocation motion. In RHEAs, additional challenges to ductility result from elemental segregation, intermetallic formation, and phase separation [98]. Recent advances in BCC M/HEAs demonstrate that tuning enthalpy to promote LCO and induce pronounced compositional fluctuations can significantly enhance work-hardening capability and uniform plasticity during deformation [38,64]. In the Ti–Zr–V–Nb–Al system ($\Delta H_{mix} = -5.4$ kJ/mol), Ma et al. achieved exceptional tensile ductility by exploiting the synergistic effects of Zr and Al—both exhibiting large atomic size mismatch and negative mixing enthalpies—and introducing B2-type LCO [64]. In BCC M/HEAs, introducing elements with highly negative ΔH_{mix}, such as Al and V, similarly decreases the mixing enthalpy (Table 2) [97]. Notably, both BCC and FCC structures exhibit an optimal enthalpy range (-20 kJ/mol $< \Delta H_{\mathrm{mix}} < -10$ kJ/mol) during tensile deformation. An important statistic result is that the tensile yield strength does not continuously improve with increasing of enthalpy value negativity. Once the enthalpy drops below a critical threshold, both BCC and FCC structures tend to display brittle fracture behavior during tensile tests. Ultimately, the relationship between elemental chemical affinity and ΔH_{mix} allows the formation of composition fluctuations, local ordering, and phase separation within HEAs, enabling spacious room to control over microstructure and mechanical properties on a microscopic scale. Through elaborated negative mixing enthalpy design and control, appropriate elements can be selectively introduced to achieve optimal mechanical properties and microstructural characteristics.

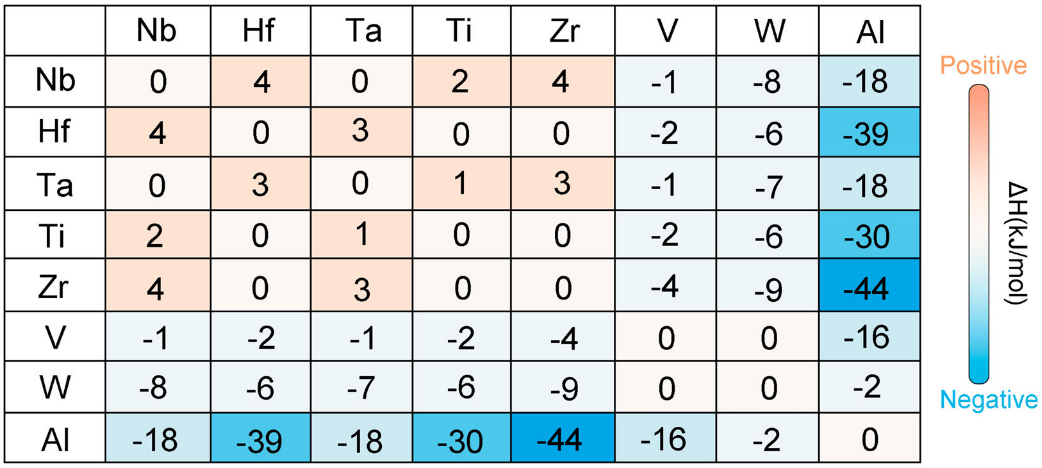
Element addition and compositional adjustments influence the ΔH_{mix}, introducing chemical composition fluctuations across different scales within the alloy. The unique effects of HEAs (e.g. high entropy, slow diffusion, lattice distortion) caused by the multiple-element systems can effectively regulate the microstructure [3,99,100]. In M/HEAs, prolonged heat treatments (aging at 1000°C for 120 h) can induce CSRO structures in CoCrNi MEAs [55]. The introduction of elements with negative enthalpy increases the likelihood

Table 1. The values of ΔH in FCC (kJ/mol).



	Cr	Fe	V	Co	Ni	Al	Ti	Nb	Cu	Mn	Si	Mo
Cr	0	-1	-2	-4	-7	-10	-7	-7	12	2	-37	0
Fe	-1	0	-7	-1	-2	-11	-17	-16	13	0	-35	-2
V	-2	-7	0	-14	-18	-16	-2	-1	5	-1	-48	0
Co	-4	-1	-14	0	0	-19	-28	-25	6	-5	-38	-5
Ni	-7	-2	-18	0	0	-22	-38	-30	4	-8	-40	-7
Al	-10	-11	-16	-19	-22	0	-30	-18	-1	-19	-19	-5
Ti	-7	-17	-2	-28	-38	-30	0	2	-9	-8	-66	-4
Nb	-7	-16	-1	-25	-30	-18	2	0	3	-4	-56	125
Cu	12	13	5	6	4	-1	-9	3	0	4	-19	19
Mn	2	0	-1	-5	-8	-19	-8	-4	4	0	-45	5
Si	-37	-35	-48	-38	-40	-19	-66	-56	-19	-45	0	-35
Mo	0	-2	0	-5	-7	-5	-4	19	125	5	-35	0

Table 2. The values of ΔH in BCC (kJ/mol).



	Nb	Hf	Ta	Ti	Zr	V	W	Al
Nb	0	4	0	2	4	-1	-8	-18
Hf	4	0	3	0	0	-2	-6	-39
Ta	0	3	0	1	3	-1	-7	-18
Ti	2	0	1	0	0	-2	-6	-30
Zr	4	0	3	0	0	-4	-9	-44
V	-1	-2	-1	-2	-4	0	0	-16
W	-8	-6	-7	-6	-9	0	0	-2
Al	-18	-39	-18	-30	-44	-16	-2	0

of forming intermetallic compounds, and the enhancement of annealing temperature and duration may further promote the development of short-range ordered atomic clusters. In multi-principal element alloys, the incorporation of elements with strongly negative mixing enthalpies drives the solid solution into a metastable state, amplifying atomic-scale compositional fluctuations that favor the emergence of SRO. This chemically driven tendency can be further tuned through post-synthesis heat treatment, offering additional control over SRO formation. SRO has been experimentally shown to form in H/MEAs over a broad temperature range of 400–1200°C. Han et al. investigated the SRO density in CoCrNi MEA and reported that neither cooling rate nor thermal treatment protocols significantly alter SRO density. Notably, CoNiV MEA exhibits a substantially higher degree of SRO than its CoCrNi counterpart. This enhancement can be attributed to enthalpic interactions arising from the preferential affinity of V for elements such as Cr, Fe, or Mn. Vanadium readily forms stable or metastable intermetallic compounds with Ni and/or Co, thereby increasing its propensity to induce SRO. From the perspective of ΔH_{mix}, the incorporation of V drives a marked reduction in enthalpy to negative values, further facilitating SRO formation [101]. These findings highlight the critical role of elemental selection in modulating SRO formation in HEAs. In contrast, the development of second-phase precipitates in H/MEAs is largely governed by thermal treatment, typically within the 600–900°C range [102–104]. For instance, Xue et al. examined the phase stability of an $Al_{0.5}Cr_{0.9}FeNi_{2.5}V_{0.2}$ HEA and identified coherent $L1_2$ and semi-coherent BCC precipitates exhibiting exceptional coarsening resistance at intermediate temperatures (500–700°C). These observations indicate the interplay between thermal history and alloy composition in governing second-phase evolution [102]. Combined with traditional alloy strengthening mechanisms, such as grain refinement, precipitation hardening, and TWIP/TRIP effects [105], these strategies are expected to improve the long-standing inverse relationship between strength and toughness in alloys. Despite their attractive properties, HEAs with strongly negative mixing enthalpies pose significant challenges in fabrication. Strong chemical affinities between certain elemental pairs can induce segregation, phase separation, and the formation of intermetallic compounds during solidification or annealing. These phenomena complicate phase control and microstructural stability, thereby requiring precisely tailored processing strategies—such as vacuum melting, rapid solidification, or advanced powder metallurgy—combined with non-equilibrium heat treatments to regulate phase evolution and suppress undesired transformations. A deeper understanding and analysis of the negative enthalpy concept will facilitate the development of novel M/HEAs with superior comprehensive performance, significantly influencing the design of microstructures and the enhancement of mechanical properties in multi-component alloys.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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