Chapter

Composition Design of High-Entropy Alloys: A Brief Review

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Abstract

High-entropy alloys (HEAs) have attracted significant interest since their conceptualization in 2004, owing to their exceptional properties such as high strength, low-temperature fracture toughness and corrosion resistance. HEAs typically comprise solid solution phases, intermetallics, and/or amorphous phases, with solid solutions being particularly desired for their superior mechanical properties. Accurately predicting phase constituents in HEAs remains a formidable challenge due to their infinite composition space. During the past decade, various strategies have been proposed to design the composition of HEAs. This review aims to provide a brief overview of these strategies, including physical modeling, computational approaches and self-optimizing strategies, thereby providing researchers with current insights and knowledge in this rapidly advancing field.

Keywords: high-entropy alloys, composition design, phase prediction, physical modeling, phase diagram calculation, first-principles calculations, machine learning, self-optimizing strategy

1. Introduction

High-entropy alloys (HEAs), also known as multicomponent alloys or multi-principal element alloys (MPEAs), were first proposed by Jien-Wei Yeh and Brian Cantor in the same year of 2004 [1–3]. HEAs are initially defined as those composed of over five principal elements in equiatomic ratios [1]. Due to the high mixing entropy, single-phase solid-solution (SS) structures tend to form in HEAs, including the FCC (face-centred cubic), BCC (body-centred cubic) and HCP (hexagonal close-packed) phases [4–9]. Recently, the definition of HEAs has been extended to those with a composition of each element between 5 and 35 at.% [6, 10]. Moreover, HEA is not strictly limited to single-phase SS alloys with over five principal elements. To avoid confusion, in this review, the term “HEAs” encompasses both single-phase and multi-phase alloys with equiatomic or non-equiatomic compositions involving multiple principal elements. At present, certain equiatomic quaternary alloys and non-equiatomic multicomponent alloys with multi-phase structures are also classified as HEAs. Examples include NbMoTaW,

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$Fe_{50}Mn_{30}Co_{10}Cr_{10}$, $Ta_{0.6}HfZrTi$, TiZrHfNb and CoCrFeNi alloys [11–17]. These alloys with multi-phase structures are often referred to as complex concentrated alloys or compositionally complicated alloys (CCAs) [11, 17–19].

Up to now, more than 400 HEA systems with diverse compositions have been reported. Researchers have shown considerable interest in developing HEAs with either single-phase SS structures or SS matrix containing nano-sized intermetallic phases due to their exceptional properties. These SS structures commonly adopt FCC, BCC, or HCP crystal structures [4–9]. The mechanical properties of HEAs are primarily dictated by their phase constituents and microstructures. For example, BCC-structured HEAs tend to exhibit high strength but low ductility, whereas FCC-structured HEAs demonstrate high ductility with relatively lower strength [20, 21]. In addition, HEAs combining disordered FCC with coherent intermetallic phases display extraordinary mechanical properties. A notable example is the 6-component $Ni_{32.8}Fe_{21.9}Co_{21.9}Cr_{10.9}Al_{7.5}Ti_{5.0}$ HEA, which features a dual-phase nanoscale lamellar architecture structure comprising FCC and $L1_2$ phases. This alloy exhibits exceptional strength (yield strength >2 GPa) and ductility (uniform elongation >16%) [22]. Therefore, accurately predicting phase constituents in HEAs holds significant implications both theoretically and for practical applications [23]. However, designing HEAs with desired phase constituents remains a formidable challenge due to the vast compositional space of these alloys. To tackle this challenge, various strategies have emerged, including physical modeling, computational methods and self-optimizing strategies [23–26]. The following sections briefly summarize these methods, providing researchers with updated insights and knowledge in this field.

2. Physical model methods

Currently, at least eight physical models have been proposed for predicting the phase structure of high-entropy alloys. These models can be categorized into two groups: parameter-based and free energy-based models [24]. Here, we primarily introduce the most commonly used parameter rules due to their simplicity and relatively high accuracy. These include the ΔH_{mix} (mixing enthalpy) and δ (difference in atomic radius) rules [27–29], the Ω (the ratio of mixing entropy to mixing enthalpy) and δ rule [27], and the VEC (valence electron concentration) rule [6, 30, 31]. The calculation methods and criteria for phase prediction are discussed in the following sections.

At present, accurately determining ΔG for multi-element systems for specific compositions and temperatures is challenging. To address this, Takeuchi and Inoue [32] proposed a hypothesis: ΔG at a given composition is proportional to the ΔG_{mix} (mixing free energy) of the liquid phase, which can be expressed as the following equation:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{1}$$

where ΔH_{mix} is the mixing enthalpy, T is the absolute temperature, ΔS_{mix} is the mixing entropy. The mixing enthalpy of a multicomponent alloy with n-elements can be expressed as eq. (2) [32]:

$$\Delta H_{mix} = \sum_{i=1,\, i\neq j}^{n} \Omega_{ij} c_i c_j \tag{2}$$

where c_i or c_j is the atomic percentage of the ith and jth component, and $\Omega_{ij} = 4\Delta H_{AB}^{mix}$ is the regular solution interaction parameter between the ith and jth elements. The values of ΔH_{AB}^{mix}AB (mixing enthalpy of binary liquid alloys) can be obtained in Ref. [33].

Based on Boltzmann's hypothesis, the mixing entropy of solution n-elements with can be expressed as follows:

$$\Delta S_{mix} = -R\sum_{i=1}^{n} c_i \ln c_i \tag{3}$$

where c_i is mole percent of component, $\sum_{i=1}^{n} c_i = 1$, and $R\left(= 8.314JK^{-1}mol^{-1}\right)$ is gas constant. For alloys with equiatomic ratios, the mixing entropy is the maximum. Thus, equiatomic or near-equiatomic HEAs generally show higher mixing entropy than their conventional counterparts.

According to Sheng et al. [31], the formation of solid-solution phases in HEAs can be assessed by comparing the values of ΔH_{mix} and ΔS_{mix}. But, the ΔH_{mix} and ΔS_{mix} values for HEAs with different phase constituents often significantly overlap. To improve phase prediction accuracy, the atomic size mismatch effect of constituent elements has been considered [34, 35]. This is justified by two main reasons. First, large differences in atomic size ratios cause substantial lattice distortion in HEAs, increasing strain energy. Such significant atomic radius differences elevate the free energy of alloys, destabilizing solid solutions. Second, large atomic size disparities can raise diffusion activation energy, leading to sluggish diffusion in alloys. Consequently, phase transformation rate decreases, potentially causing elemental segregation, nano-sized precipitates, or even amorphous phases. Therefore, to comprehensively describe the impact of atomic radius differences in HEAs, the parameter δ is expressed as follows:

$$\delta = \sqrt{\sum_{i=1}^{n} c_i\left(1 - \frac{r_i}{\bar{r}}\right)^2} \tag{4}$$

where c_i is the molar ratio of the ith component, $\bar{r} = \sum_{i=1}^{n} c_i r_i$ is the average atomic radius and r_i is the atomic radius. In the calculation, the values of $r_i$can be obtained in the Ref. [36]. According to the ΔH_{mix}-δ rule and **Figure 1** [31, 34, 35], solid solution

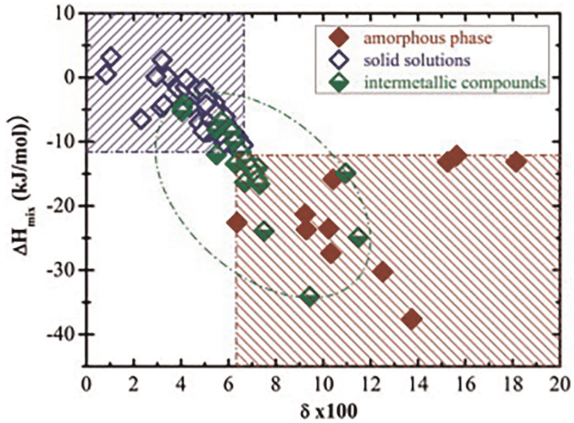

Figure 1.
A δ-ΔH$_{mix}$ plot illustrating the phase selection in HEAs [34].

phases usually form when ΔH_{mix} and δ (%) are in a range around: -11.6 KJ/mol $\leq \Delta H_{mix} \leq 3.2$ KJ/mol and $\delta(\%) \leq 6.6$ [34].

Besides, the Ω rule developed by Zhang and co-workers [27] integrates another two parameters, including ΔS_{mix} (mixing entropy) and T_m (melting temperature of n-element alloy), which can be expressed as follows:

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \tag{5}$$

Disregarding the solid-state phase transitions, phase formation generally takes place near the alloy's melting temperature (T_m). Consequently, T_m is employed for the entropy term $T\Delta S_{mix}$. The melting temperature of n-elements alloys, T_m, is determined using the rule of mixtures:

$$T_m = \sum_{i=1}^{n} c_i (T_m)_i \tag{6}$$

where $(T_m)_i$ is the melting point of the ith component of alloy.

According to eqs. (4) and (5), Zhang et al. proposed a novel solid-solution formation rule for HEAs through the calculation of parameters Ω and δ for equiatomic or near-equiatomic HEAs. According to **Figure 2**, Ω≥1.1, δ≤6.6% is the rough criteria for the formation of SS phase in HEAs [27].

Currently, two-parameter rules (ΔH_{mix} and δ, Ω and δ) are widely used for predicting phase types such as solid solution phases, intermetallics, and amorphous phases in high-entropy alloys (HEAs), due to their simplicity and relatively high accuracy. However, another parameter is necessary for predicting the specific phase structure, such as FCC, BCC, or hexagonal close-packed (HCP). According to Guo et al. [31] and Battezzati et al. [37], the valence electron concentration (VEC) of HEAs is another critical parameter influencing phase formation. The average VEC of an alloy can be calculated using Eq. 7, where $(VEC)_i$is the VEC for the ith element [31].

$$VEC = \sum_{i=1}^{n} c_i (VEC)_i \tag{7}$$

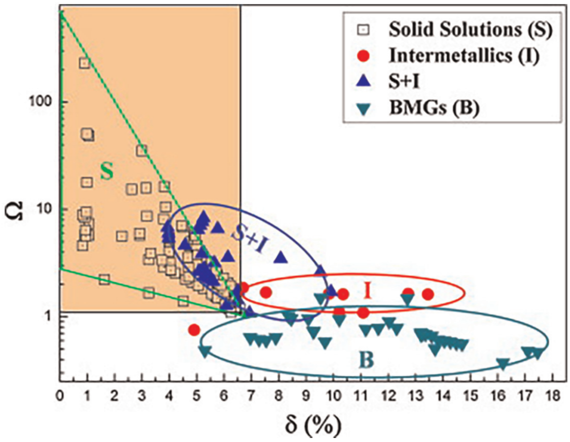

Figure 2.
A Ω-δ plot illustrating the phase selection in HEAs ("S" indicates solid solution; "I" indicates intermetallics; "B" indicates amorphous phase) [27].

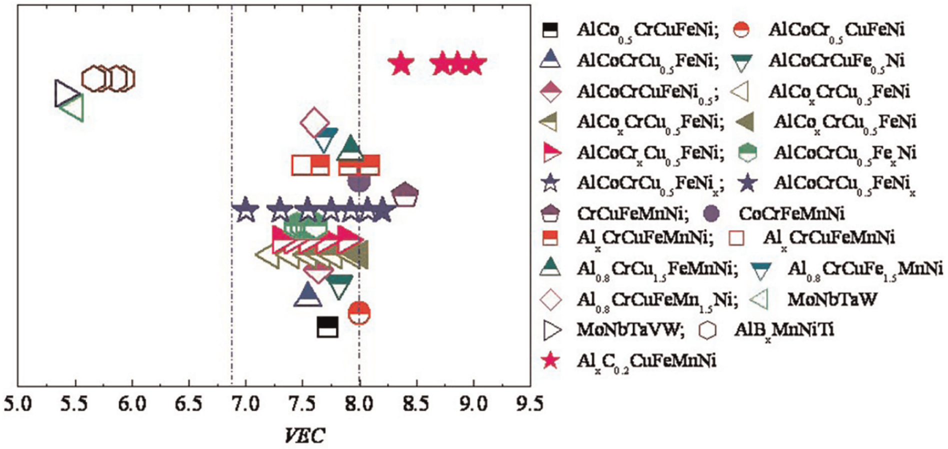

Figure 3.
Relationship between valence electron concentration (VEC) and the stability of FCC and BCC phases in various HEA systems [38].

Guo et al. [31] and Battezzati et al. [37] summarized the relationship between VEC and phase structure in HEAs. As shown in **Figure 3**, HEAs with a single FCC phase typically have VEC values greater than 8.0, while those with a single BCC phase have values below 6.87, and HCP phases occur around a VEC of 2.8.

The aforementioned commonly used parameter rules, along with other physical models, offer effective guidelines for predicting phase types in high-entropy alloys (HEAs). However, it is crucial to note that the overall accuracy of existing physical models remains relatively low, with the highest reported accuracy reaching approximately 72% [24]. Thus, experimental methods are often necessary to validate these predictions.

3. Computational methods

The current computational methods for designing high-entropy alloys (HEAs) primarily include phase diagram calculation (CALPHAD), first-principles calculations (e.g., ab initio and density functional theory (DFT)), molecular dynamics (MD), Monte Carlo simulations (MC). CALPHAD has been extensively utilized in traditional alloy composition design, which involves compiling thermodynamic databases, simulating phase diagrams, predicting phases formed, and employing computational techniques [23]. Thermo-Calc stands out as the predominant software for thermodynamic calculation of HEAs, leveraging CALPHAD-based databases. Recently, Thermo-Calc has successfully contributed to designing high-performance HEAs, such as $(FeCoNi)_{92}Al_{2.5}Ti_{5.5}$ [39] and $CoCrFeNiNb_x$ eutectic HEAs [40], known for superior mechanical properties. For instance, in the case of $CoCrFeNiNb_x$ eutectic HEAs, He et al. proposed that adding Nb to CoCrFeNi forms a pseudo-binary eutectic alloy due to the formation of intermetallics [40]. They developed the (CoCrFeNi)-Nb pseudo-binary diagram using Thermo-Calc, identifying a Nb-10 at.% eutectic composition (**Figure 4**). Accordingly, they designed various $CoCrFeNiNb_x$ ($x = 0.1, 0.25, 0.5, 0.8$) alloys, which exhibit hypo-eutectic, eutectic, and hyper-eutectic structures, respectively. The predictions by Thermo-Calc agreed well with the experimental phase

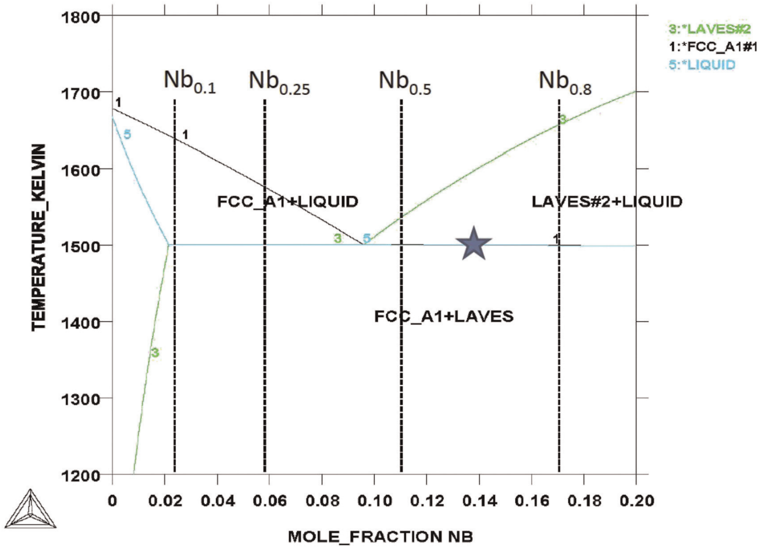

Figure 4.
Phase diagram of the CoCrFeNiNb$_x$ *HEAs [40].*

diagrams. However, the development of thermodynamic databases using CALPHAD relies heavily on accurate experimental phase diagrams and thermochemical data. Extrapolating from binaries and ternaries to multiple component systems may not always match experimental outcomes, such as the quaternary and/or quinary systems. Given the infancy of HEA research, limited experimental data on phase equilibrium and thermochemistry complicate the direct validation of thermodynamic databases [41].

As another important computational method, the first-principles calculation (e.g. the ab initio calculation using density functional theory (DFT)) augments the CALPHAD method when lacking sufficient thermodynamic data [42–44]. The DFT involves the direct calculation of the electronic structure of atoms through the solution of Schrodinger equations, which can determine formation energies, magnetic states, and lattice parameters for multicomponent phases [23]. However, DFT calculations have uncertainties in handling the d orbitals of transition-metal atoms, which are commonly used in HEAs [45]. Moreover, the DFT calculations require a large amount of numerical computation, which leads to the rapidly increasing computing time with the number of atoms [23]. Other computational methods include molecular dynamics (MD), Monte Carlo (MC), and others. Unlike first-principles calculations, both MD and MC are atomistic techniques. These two methods are mainly used for the prediction of structures of initial cluster formation or the material response to stimuli rather than phase prediction [23].

In recent years, machine learning (ML) has been increasingly employed to accelerate the simulation and phase prediction of HEAs [45–50]. On the one hand, utilizing DFT datasets, machine learning (ML) methods can construct atomic interaction models (AIMs) that effectively describe complex interactions within multicomponent alloys. This approach circumvents the need for time-consuming first-principles thermodynamics simulations. This method eliminates the need for lengthy first-principles thermodynamics simulations. Additionally, machine learning can be utilized to develop models for predicting bulk properties, including phase constituents, crystal structures, yield strengths, etc. These models are built using high-throughput experimental or computational data, demonstrating the versatility of ML in materials science research [51]. For instance, Zheng et al. applied ML methods to design nanoprecipitate-strengthened HEAs using extensive thermodynamic data [46]. The newly developed γ'-strengthened HEA demonstrates enhanced mechanical properties, exhibiting a yield strength of approximately 1.31 GPa and a tensile elongation of about 15%. In addition, Su et al. introduced an optimized ML model that achieved high accuracy rates, reaching up to 88.7% in identifying solid-solution and non-solid-solution HEAs, and further achieving 91.3% accuracy in distinguishing BCC, FCC, and dual-phase HEAs [47]. These studies present an alternative approach to HEA design, accelerating the development of novel HEAs with superior performance.

4. Self-optimizing methods

In contrast to traditional alloys based on a single principal element, the multicomponent approach of HEAs offers an almost limitless range of alloy systems. Experimental testing of all these alloys is impractical. To date, just over 400 HEA systems have been reported, primarily developed through trial-and-error experiments and modeling methods [23]. Consequently, there is a pressing need to devise new strategies that can efficiently identify potential high-performance alloy compositions from the vast HEA compositional space. Tracing back to the origins of the renowned CoCrFeMnNi HEA, Brian Cantor, one of the pioneers in HEA research, has applied a rapid alloy design strategy. This approach, later termed the "self-optimizing strategy" by Yin and co-workers [25], involves identifying the chemical composition of supersaturated single solid-solution phases by directly using the local compositions of specific phase constituents within existing multicomponent alloys containing dual or multiple phases. Brian Cantor et al. initially developed a 20-component alloy with an equiatomic chemical composition of MgAlSiMnCrFeCoNiCuZnGeNbMoAgCdSnSbWPbBi, which exhibited a multi-phase structure (**Figure 5a**). However, one of the phases in this alloy predominantly consisted of five components in nearly equal proportions (i.e. Cr, Mn, Fe, Co, and Ni), confirmed to be a single FCC phase upon producing a new sample using the probed composition. Therefore, while the equiatomic composition of CoCrFeMnNi was not deliberately designed by Cantor

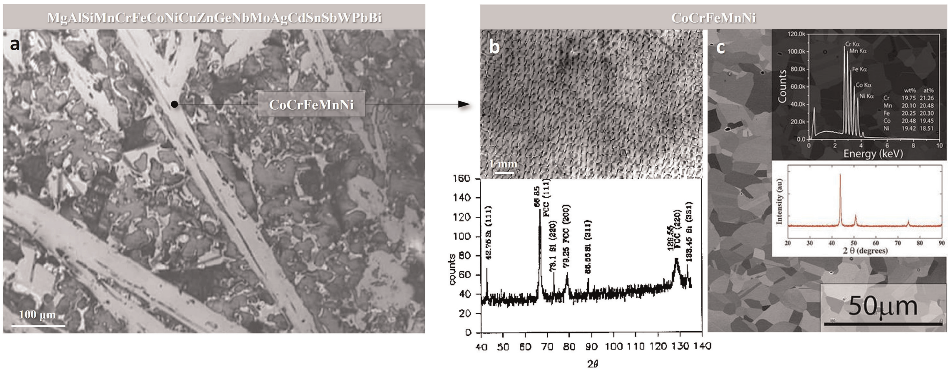

Figure 5.
a. Optical micrograph of the equiatomic 20-component alloy MgAlSiMnCrFeCoNiCuZnGeNbMoAgCdSnSbWPbBi [52]; b. Microstructure and XRD patterns of the as-cast CrMnFeCoNi alloy [2]; c. SEM image, EDS analysis, and XRD patterns of the fully recrystallized CrMnFeCoNi alloy [53].

et al., it emerged naturally from the alloy itself through the inherent solute partitioning or diffusion processes among its constituent elements [2]. As shown in **Figure 5b**, the as-cast Cantor alloy, which has a single FCC solid-solution phase, exhibits a typical dendritic microstructure with Cr, Fe, and Co segregation along the dendrites. Thermomechanical processes, such as annealing after cold rolling, can transform the dendritic structure of the as-cast Cantor alloy into a homogeneous microstructure with equiaxed grains and annealing twins (**Figure 5c**). Cantor et al. not only ushered in the research era of high-entropy alloys but also pioneered a rapid alloy design strategy. However, since the advent of CoCrFeMnNi Cantor alloy, researchers appear to have been solely focused on the novel concept of HEAs, overlooking this innovative rapid alloy design strategy.

In 2024, inspired by the intermediate-temperature instability of HEAs, Yin et al. proposed a novel approach for rapidly designing Nanostructured Multicomponent (NM) alloys [25]. Using the FeAlTiVCrMoW HEA as a model, Yin et al. firstly destabilized the BCC matrix into two phases by increasing the Fe content (**Figure 6b-d**). This led to the development of a new Fe5AlTiVCrMoW HEA with dual

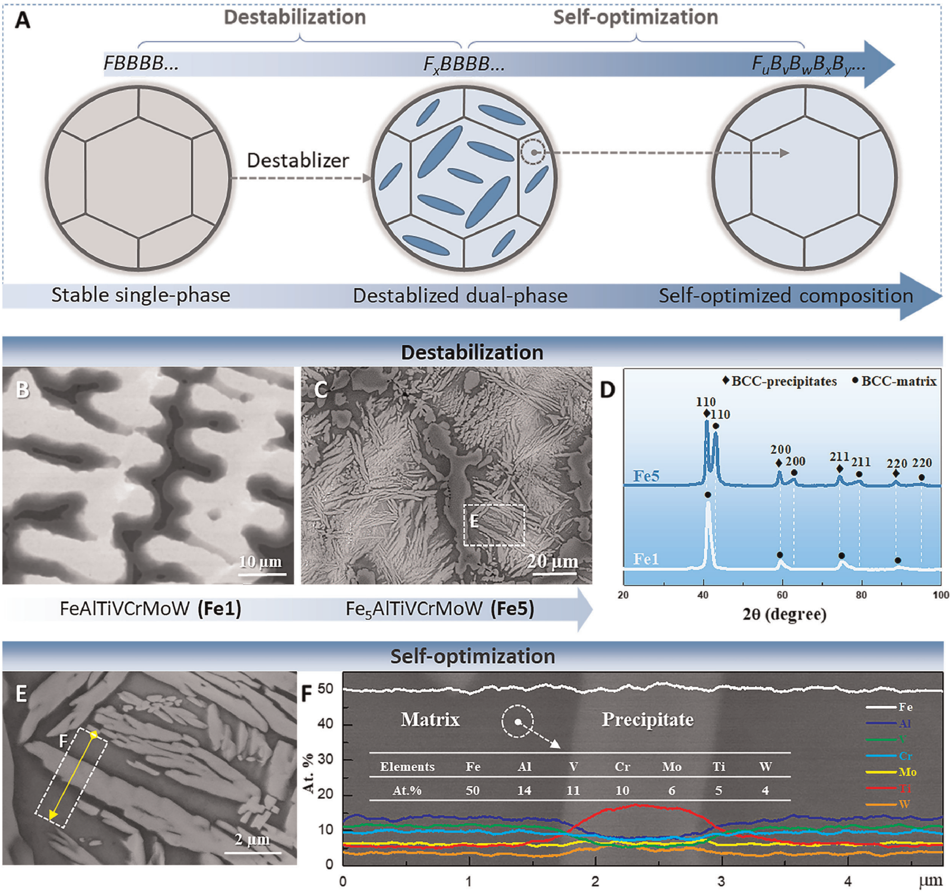

Figure 6.

A. Schematic illustration of the alloy design strategy; B. Microstructure of the as-cast FeAlTiVCrMoW HEA; C. Microstructure of the as-cast $Fe_5AlTiVCrMoW$ HEA. D. XRD patterns of the FeAlTiVCrMoW; E. Magnified SEM image of the as-cast $Fe_5AlTiVCrMoW$ HEA; F. EDS spectra of the BCC matrix and precipitates in $Fe_5AlTiVCrMoW$ HEA [25].

BCC phases. Next, the "self-optimizing" method was applied by directly leveraging the local composition of the metastable phase within the destabilized dual-phase Fe5AlTiVCrMoW HEA (**Figure 6e-f**). The novel self-optimized alloy with a composition of Fe50Al14V11Cr10Mo6Ti5W4 exhibited a two-stage phase decomposition behaviour at 600°C, showcasing a strong ageing response. The peak-aged hardness can be up to ~1378 HV. This was attributed to the formation of a distinctive multiphasic nanostructure, consisting of two BCC phases and one B2 phase, which significantly increased the density of phase boundaries and enhanced the strengthening effect [25]. This approach enables the effective design of large-scale NM alloys based on HEAs, which can be synthesized using conventional techniques such as casting and heat treatment. In contrast to the conventional focus on attaining a single solid-solution phase in HEAs, this study introduces an alternative method for designing bulk nanostructured alloys with complex compositions and multiple phases, thereby achieving superior properties.

5. Conclusions and outlook

In recent decades, several strategies have emerged to explore the vast composition space of HEAs and identify compositions that result in superior properties. These include physical modeling, computational approaches, and self-optimizing strategies. Among the physical modeling methods, parameter rules such as the ΔH_{mix} and δ rules, the Ω and δ rule, and the VEC rule have been widely utilized due to their simplicity and relatively high accuracy in predicting solid solution phases. These rules have proven effective in composition design and phase prediction. However, the overall accuracy of existing physical models remains relatively limited, particularly in predicting the phase constituents of precipitates.

In contrast, computational methods offer potentially higher accuracy in predicting phases of HEAs. Among these methods, CALPHAD are extensively employed. However, their accuracy diminishes as alloy complexity increases beyond binaries and ternaries, owing to limited experimental phase diagrams and thermochemical data. First-principles calculations, such as DFT, complement CALPHAD when thermodynamic data is insufficient. Nevertheless, DFT calculations introduce uncertainties, particularly in handling d orbitals of transition-metal atoms prevalent in HEAs. Moreover, the DFT calculations involve intensive numerical computations, with computational demands escalating with system size. To accelerate simulations and enhance phase prediction accuracy for HEAs, machine learning (ML) has gained prominence. ML sidesteps the need for time-consuming first-principles simulations, directly predicting bulk properties such as phase formations, crystal structures, and mechanical properties.

In addition to traditional physical modeling and computational methods, a novel composition design concept has emerged: the "self-optimizing strategy". Inspired by the discovery of the Cantor alloy, this approach involves identifying the chemical composition of supersaturated single solid-solution phases by directly utilizing the local compositions of specific phase constituents within existing multicomponent alloys containing dual or multiple phases. This "self-optimizing" alloy design strategy circumvents both experimental and computational "trial-and-error" processes. It can be applied to conventional or multicomponent alloys with dual or multiple phases, facilitating the rapid design or optimization of compositions, customized microstructures, and improved mechanical properties.

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Conflict of interest

The authors declare no conflict of interest.

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