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# Design and High-Throughput Screening of High Entropy Alloys

*Yaqi Wu and Yong Zhang*

## Abstract

A balanced parameter was proposed to design the high entropy alloys (HEAs), which defined by average melting temperature $T_m$ times entropy of mixing $\Delta S_m$ over enthalpy of mixing $\Delta H_m$, $\Omega = T_m \Delta S_m / \Delta H_m$, if $\Omega$ is larger than 1.1, we can predict that the entropy is high enough to overcome the enthalpy, and solid solution is likely to form rather than the intermetallic ordered phases. The composition can be further refined by using high-throughput screening by preparing the compositional gradient films. Multiple targets co-sputtering is usually used to prepare the films, and physical masking can separate the samples independently, chemical masking can also applied if possible. One example is the self-sharpening screening by using nanoindentations, the serration behaviors may related to the self-sharpening compositions.

**Keywords:** designs of high entropy alloys, parameter criterion, high-throughput screening, Multiple targets co-sputtering, chemical masking

## 1. Introduction

In the process of exploring the formation rules of bulk metallic glasses, Greer put forward the "Confusion Rule", believing that the more components that make up the alloy system, the more favorable it is to form metallic glass. Then Professor Cantor synthesized more than 20 components of alloys and obtained alloys in solid solution state instead of metallic glasses in order to verify the effectiveness of this principle. On the basis of this development, professor Yeh J. W. from National Tsing Hua University believed that it is the high mixing entropy that stabilizes the solid solution, and thus, the concept of a new kind of alloy, which was called the high-entropy alloy, was put forward. High entropy alloy is an alloy system with five or more equal atomic ratio compositions, providing a new idea for the development of new alloy system, which shows four outstanding effects: high mixing entropy effect, hysteresis diffusion effect, lattice distortion effect and cocktail effect. With the in-depth understanding of HEAs, the non-equimolar complex phases (the matrix is a solid solution) HEAs have been an important part of HEAs. Therefore, the HEA can be divided into the first and the second generations [1]. The first-generation high-entropy alloy is composed of at least five components of equal atomic ratio, and the phase structure is a single-phase solid solution. The second-generation high-entropy alloy is composed of at least four non-equal atomic ratio principal elements, and the phases structure are dual and complex phases. Through composition designing and reasonable preparation and processing technology, high entropy alloys can form a simple structure and show excellent properties, such as high hardness, high strength, high temperature softening resistance, good wear resistance, corrosion resistance and so on, which make the high entropy

alloys have a broad application prospect, which has been widely concerned and studied by researchers at home and abroad.

## 2. Designs of high entropy alloys

When designing alloys, people prefer to get solid solutions. For binary alloys, an element will bring lattice distortion when it enters the lattice of solvent elements as solute atoms, so the form of solid solution can change the properties of the alloy, for example, the strength of the alloy is improved due to the lattice distortion caused by different atomic sizes. The most popular criteria to decide whether two metals are soluble, and form a solid solution, are the classical Hume-Rothery rules. Crystal structure, atomic size difference, electronegativity and valence electron concentration will affect the formation of solid solution. The rules can predict the phase composition of the alloy from the intrinsic characteristic cs. but this is not the case for HEAs: examples exist of concentrated solid solutions of elements having different crystal structures before alloying. For instance, $AlCoCrCu_{0.5}Ni$ forms a single body-centered cubic (BCC) lattice [2].

The formation of alloys is inevitably related to the energy of the system, so when discussing the formation of high-entropy alloys, thermodynamic factors are a basis for the study of high-entropy alloy design. Due to the increase of components, the thermodynamic Gibbs free energy, enthalpy change and entropy change of high-entropy alloys become complicated. In addition to considering the essential issues of alloy formation, the element composition of the alloy is designed to obtain the required properties, such as refractory and high temperature resistance, high strength and toughness, corrosion resistance, and magnetic properties. Various elements have different characteristics, and the interaction between different elements makes the performance of the high-entropy alloy show a compound effect, that is, the "cocktail" effect [3]. Therefore, starting from the essence of the elements, selecting the required properties and forming the alloy system.

The discovery of high-entropy alloys has broken through the limitations of traditional alloy systems, and more alloy systems with better performance have been discovered. At the same time, because the number of elements in high-entropy alloys is greater than that of binary alloys, it also brings a huge workload for alloy design. Generally speaking, High-entropy alloys (HEAs) are broadly defined as alloys containing 5 or more main elements, and the content of each main element is between 5% and 35%. The increase in the types and quantities of constituent elements and the changes in the content of each element combine to form a huge number of alloy systems. Take a multi-component alloy containing 5 main elements as an example, assuming that every 10% content change will produce a different alloy system, then there will be 906 types; take a multi-component alloy containing 3–6 main elements as an example, will produce 592 billion new alloys [4]. How to efficiently design high-entropy alloys and predict phase formation in advance is one of the important factors that promote the development of high-entropy alloys. The factors of phase formation of high-entropy alloys are considered from the perspective of thermodynamics and solid solution formation, and corresponding parameters are proposed to comprehensively reflect phase formation.

### 2.1 Thermodynamic parameters

#### 2.1.1 Proposal of mixed entropy ($\Delta S_{mix}$)

Professor Yeh [5] believes that in a multi-component alloy, as the number of components increases, its mixing entropy (mainly configuration entropy) also gradually increases. The higher mixing entropy reduces the Gibbs free energy of the

solid solution phase and promotes the formation of the solid solution phase (especially at higher temperatures), thus forming a high-entropy alloy. The calculation formula of high-entropy alloy mixing entropy is shown in Eq. (1),

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

In the formula, R is the molar gas constant, R = 8.314 J/(mol · K); n is the number of components of the multi-component material; $c_i$ is the content of the i-th component (at.%). From the calculation formula of mixing entropy, it can be found that when the atomic ratio of n kinds of components is 1, the mixing entropy value formed by the alloy system is the largest. Therefore, the formula for calculating the mixing entropy of a multi-component alloy with equal atomic ratio is shown in Eq. (2)

$$\Delta S_{mix} = R \ln n \qquad (2)$$

Early research believed that $\Delta S_{mix} = 1.5R$ is a necessary condition for the formation of high-entropy alloys, so $\Delta S_{mix} = 1.5R$ is the criterion for dividing high entropy and medium entropy, and $\Delta S_{mix} = 1R$ is the boundary between middle entropy and low entropy. However, subsequent research found that some multi-component alloys have high entropy values, but high-entropy alloys are not formed. Although the configuration entropy of any solid solution will definitely increase with the increase of the elements in the composition, the introduction of additional alloying elements will also increase the possibility of forming a stable intermetallic compound phase. From this point of view, the mixed entropy is a necessary factor affecting the formation of high-entropy alloys, and other parameters are needed to assist in the judgment to comprehensively reflect the law of phase formation.

If kinetic factors are not considered, the choice of phase is controlled by thermodynamics, namely Gibbs free energy. The Gibbs free energy formula is shown in (3)

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \qquad (3)$$

It can be seen from the formula (3) that in addition to the mixing entropy ($\Delta S_{mix}$) has an effect on the phase selection, the mixing enthalpy ($\Delta H_{mix}$) is also one of the factors that need to be considered.

It can be seen from the formula (3) that in addition to the mixing entropy ($\Delta S_{mix}$) has an impact on the phase selection, the mixing enthalpy ($\Delta H_{mix}$) is also one of the factors that need to be considered. Therefore, in 2008, Professor Zhang Yong [6] proposed the $\Delta H_{mix}$ parameter, whose formula is shown in (4)

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^{n} c_i c_j \Omega_{ij} \qquad (4)$$

Among them, $\Omega_{ij} = 4 \Delta H_{mix}^{AB}$, $\Delta H_{mix}^{AB}$ is the mixing enthalpy of a two-element (A-B) liquid alloy calculated based on the Miedema model, and is a parameter that represents the chemical compatibility between components.

## 2.2 Proposal of structural parameters

### 2.2.1 Proposal of the Delta (δ) parameter

For traditional binary solid solutions, the classic Hume-Rothery criterion can predict the phase composition of alloys from the intrinsic characteristics such as

atomic size, crystal structure, valence electron concentration, and electronegativity. However, since the components of high-entropy alloys are mostly 3 to 5, this criterion is no longer applicable. Professor Zhang Yong proposed the Delta ($\delta$) parameter. The Delta ($\delta$) parameter is combined with the mixing entropy ($\Delta S_{mix}$) and the mixing enthalpy ($\Delta H_{mix}$) to jointly predict the phase formation of the multi-component alloy. The formula of Delta ($\delta$) parameter is shown in (5)

$$\delta = 100\sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \tag{5}$$

Among them, $\bar{r} = \sum_{i=1}^{n} c_i r_i$, ci and ri are the atomic percentage and atomic radius of the i-th element, respectively. Therefore, the phase formation law of multi-component alloys is proposed. **Figure 1** shows the relationship between $\Delta H_{mix}$-$\delta$-$\Delta S_{mix}$ and phase selection.

*2.2.2 Proposal of $\Omega$ parameter*

With the development of more and more new multi-component HEAs, in order to obtain more accurate multi-component HEAs phase formation rules. Entropy and enthalpy cannot independently control the formation of amorphous phase. In the Gibbs thermodynamics equation, only the formation of amorphous is expressed as the synergy and competition of entropy and enthalpy. Considering the factors of mixing entropy, mixing enthalpy and melting temperature, the $\Omega$ parameter is proposed [7], and its expression is:

$$\Omega = \frac{T_m \Delta S_{mix}}{\Delta H_{mix}} \tag{6}$$

Among them, $\Delta S_{mix}$ is the entropy of mixing, $\Delta H_{mix}$ is the enthalpy of mixing, and $T_m$ is the melting point of the mixture. It can be seen from the **Figure 1** that when $\delta \geq 1.1$ and $\Omega \leq 6.6\%$, the multi-component alloy easily forms a solid solution phase.
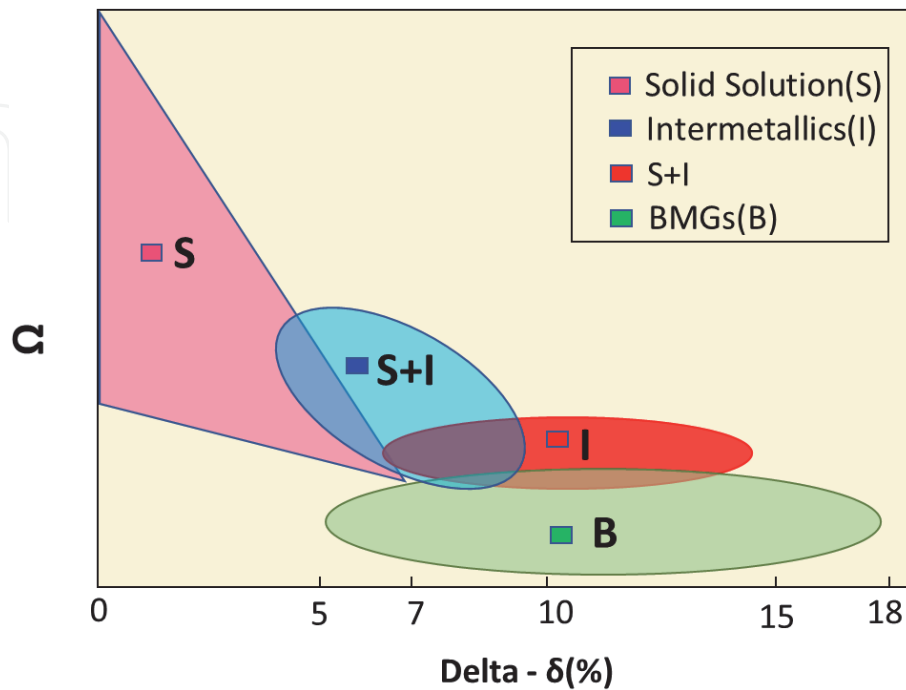


**Figure 1.**
*The relationship between parameters $\delta$ and $\Omega$ for multi-component alloys [7]. This figure reproduced by the paper "Prediction of high-entropy stabilized solid-solution in multicomponent alloys".*

The biggest advantage of this criterion is the combination of size difference, mixing enthalpy and mixing entropy, and the calculation is simple and convenient.

### 2.2.3 Proposal of electronic structure related parameters (VEC, $e/a$, $\Delta X$, $M_d$)

The Hume-Rothery law describes the influence of atomic size, crystal structure, valence electron concentration, and electronegativity on the formation of solid solutions between elements and their laws. Based on the parameters such as $\delta$ proposed by this law, the phase formation law of high-entropy alloys was successfully summarized. Can the electronic structure parameters also make a judgment on the solid solution phase?

The related parameters of electronic structure mainly include $VEC$, $e/a$, $\Delta X$, $M_d$. It should be emphasized here that both e/a and $VEC$ (Valence Electron Concentration) can be called electron concentration. More precisely, e/a is each the average number of electrons flowing in an atom; and $VEC$ is the concentration of valence electrons: the total number of valence electrons per atom (including all electrons in the valence band including d electrons).

Guo et al. [8] proposed a relationship between $VEC$ and solid-solution stability for multi-component alloys. It should be noted that the $VEC$ parameter can only predict phase stability of either FCC or BCC solid-solution in multi-component alloys; But it cannot be used for predicting the formation ability of the solid-solution phase. On the basis of "$\Omega$-$\delta$" rules predicting the formation ability of the solid-solution phase, the $VEC$ rule is used to test and verify which type of solid-solution phase is stable in these alloys. When $VEC \geq 8$, it is easy to form solid solution phase of FCC structure; when $VEC < 6.87$, it is easy to form solid solution phase of BCC structure; when $6.87 \leq VEC < 8$, FCC + BCC mixed solid solution phase. $VEC$ can also be used to predict the precipitation of $\sigma$ phase (a TCP phase). The $VEC$ criterion is not limited to the determination of the phase stability of as-cast high-entropy alloys. Alloys that have undergone heat treatment or aging treatment can also pass this criterion, but are limited to HEAs containing Cr or V elements [9] (**Figure 2**).

The related parameters of electronic structure can not only predict the law of phase formation, but also guide the design of high-entropy alloy hardness according to the requirements of mechanical properties. When $4.33 \leq VEC \leq 7.55$, HEAs have a single-phase BCC structure, and when $7.80 \leq VEC \leq 9.50$, HEAs have a single-
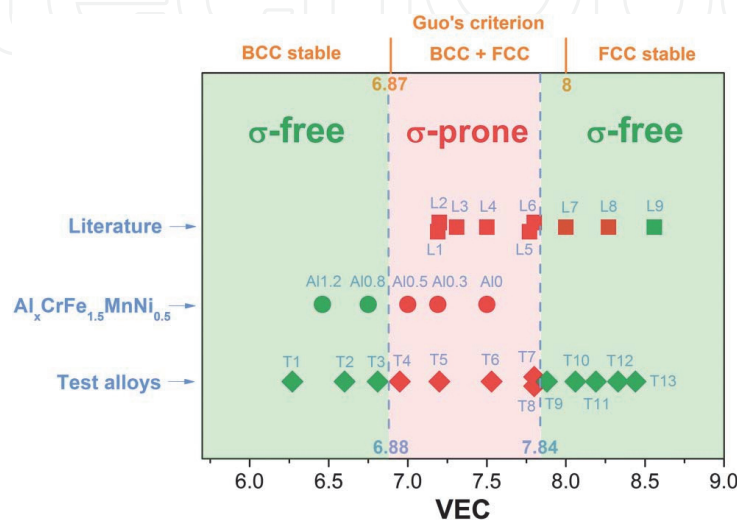


**Figure 2.**
*Relationship between the VEC and the presence of σ phase after aging for a number of HEAs. Green and red icons indicate the absence and presence of σ phase after aging, respectively [9].*

phase FCC structure. The study also found that the hardness varies with *VEC* into a Gaussian distribution. When *VEC*≈6.8, the hardness is the highest, reaching 650*Hν*. According to the empirical criteria proposed above, HEAs with the required hardness can be designed [10].

In 2014, Wang Zhijun [11] proposed the phase formation criterion of heat-treated HEAs using *VEC* parameters. When *VEC* > 7.8, FCC phase is easy to form, which is less different from the as-cast formation criterion; when *VEC* < 6.0, BCC phase is easy to form, and this area is obviously smaller than as-cast HEAs. Therefore, heat treatment can narrow the range of the BCC solid solution phase.

In addition to the typical body-centered cubic and face-centered cubic phases, there are also TCP phases and Laves phases in high-entropy alloys. These types of phase structures can be predicted by the theories of electronegativity and orbital capacity. Electronegativity $\Delta X$ [12] describes the ability of atoms to attract electrons The criterion is not easy to distinguish solid solution phase, intermetallic compound and metallic glass. But it is effectively applied to the formation law of TCP phase in high-entropy alloy. Studies have shown that: when $\Delta X$ is small, a solid solution phase is easily obtained, but at the same time intermetallic compounds and metallic glasses can also be formed. Lu Yiping [13] found that: Pauling's electronegativity $\Delta X$ has a good correlation with the stability of TCP phase, when $\Delta X > 0.133$, TCP phase is easily formed in HEAs (except those containing a large amount of Al), (Including the σ phase), when $\Delta X < 0.117$, no TCP phase is generated, and when it is between 0.117 and 0.133, the formation of TCP is uncertain.

Different from Pauling's electronegativity above, Polettti [14] proposed electronegativity $\Delta X_{Allen}$, and together with the atomic size difference parameter δ to predict the law of solid solution phase formation, the criterion shows: when δ is between 1% and 6%, and when $\Delta X_{Allen}$ is between 3% and 6%, only solid solution phase is formed. Yurchenko [15] used the above two parameters ($\Delta X_{Allen}$ and δ) to predict the Laves phase. Through the study of the Laves phase formation law of about 150 kinds of HEAs, it was found that when δ > 5% and $\Delta X_{Allen} > 7\%$, there is the Laves phase is generated, and this criterion is not satisfied in only a few cases.

Yurchenko also found that Allen's electronegativity is more accurate than Pauling's electronegativity prediction.

This parameter was first used as a criterion for the formation of TCP phase in Fe-based, Co-based, and Ni-based superalloys. Because HEAs contain a large amount of transition metals, similar to high-temperature alloys, it is used in high-entropy alloys [16] to predict the formation of TCP (including σ phase) phases. $(M_d)$ has a great relationship with the radius and electronegativity of the metal element: it increases with the increase of the radius of the metal element, and decreases with the increase of the electronegativity. As shown in **Figure 3**, this criterion shows that when $M_d$ is greater than 1.09, TCP structure can be generated, but it is not applicable to HEAs containing more Al and V elements, and the related mechanism still needs further study.

In summary, physical and chemical parameters play an important role in phase prediction. It can also be found that configuration entropy is not always the main parameter, there are also mixing enthalpy, atomic size difference, electronic structure, etc. Effective combination of various parameters can improve the accuracy of phase prediction. The physicochemical parameters have certain reference significance, and can roughly estimate the formation phases of multi-component alloys, but because they are derived from experimental data in a certain system, they may not be applicable to other systems, hence a more comprehensive method is needed to overcome system changes. At present, there are more researches on FCC and BCC, but less research on the structure of HCP and orthorhombic crystals.
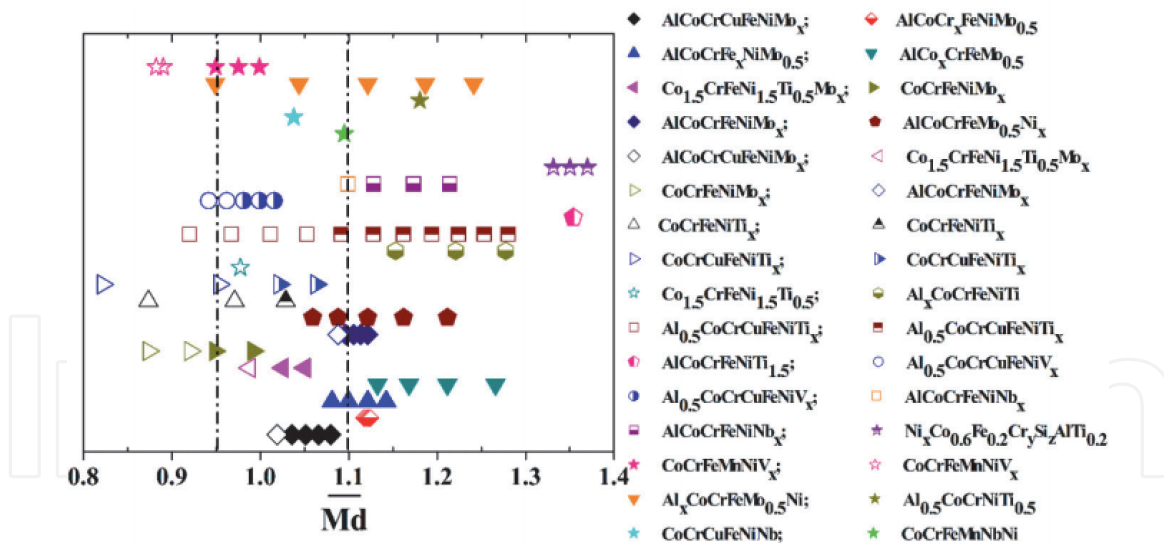
**Figure 3.**
*Relationship between the Md and the TCP phase stability for the HEA systems containing Al, Co, Cr, Cu, Fe, Ni, Mo, Si, Ti, V, Nb, and etc. elements [16].*

## 2.3 Calculation and simulation methods

### 2.3.1 First principles and molecular dynamics calculations

First-principles refers to the prediction of physical properties without experimental parameters, only calculations by charge, electronic mass and Planck's constant. The first principles mentioned here refer to the first principles based on Density Functional Theory (DFT). This calculation method can systematically study high-entropy alloys from the perspective of theoretical calculations, which is useful for deepening the understanding of HEAs and understanding is very necessary. The exact muffin-tin orbitals (EMTO) based on the framework of density functional theory describes the single-electron potential function and the total energy of the calculation system by using the optimized overlapping potential sphere configuration and the full charge density. This method can not only improve the calculation efficiency, but also ensure sufficient calculation accuracy. The coherent potential approximation (CPA) can solve the problem of the disorder model of multi-principal element replacement solid solution in the first-principles calculation process. Therefore, the combined method of EMTO-CPA is one of the effective methods to solve the first-principles calculation problem of complex alloys with multiple principal elements.

Ab initio molecular dynamics (AIMD) based on quantum mechanics can predict the structure of liquid atoms and better understand the solidification behavior of complex alloys. The AIMD simulation results of Santo Donato et al. [17] showed that during the solidification of the Al1.3CoCrCuFeNi high-entropy alloy, the short-range ordered pairs (Al-Ni, Cr-Fe, and Cu-Cu) in the liquid phase may be B2 ordered phases. At the nucleation point, AIMD can predict the formation trend of short-range ordered phases. Compared with traditional molecular dynamics (MD) simulation, AIMD simulation does not require experiments to obtain the interaction potential between atoms, which is more feasible and more convenient to use. Feng et al. [18] used the DFT calculation method to predict the enthalpy of formation of the actual components in the binary, ternary and quaternary systems. For the $L2_1$ phase, the calculated enthalpy of formation of $AlFe_2Ti$ is $-44$ kJ/mol, the enthalpy of formation of $AlMn_2Ti$ is $-19$ kJ/mol, and the enthalpy of formation of $AlCr_2Ti$ is $-4$ kJ/mol. The $AlFe_2Ti$ phase is a stable ternary phase; When Fe or Mn is used to

replace Cr, the corresponding enthalpy of formation increases linearly, and the DFT calculation results are consistent with the experimental results. Ding Xinkai [19] used first-principles methods to predict the phase and structure of NbMoTaWVx high-entropy alloys. The research results show that when $0 \leq x \leq 1.5$, the most stable configuration of NbMoTaWV$_x$ high-entropy alloy in equilibrium is BCC structure; as the component V increases, its density, lattice size and stability of the body-centered cubic phase gradually decrease.

### 2.3.2 CALPHAD phase diagram calculation

The biggest advantage of the CALPHAD method is to predict and derive the phase diagram of the multi-element system through the binary system or the ternary system composed of it. Unlike traditional thermodynamic databases that only focus on one or two main component regions, HEAs thermodynamic databases need to cover almost the entire component space of a multi-component system. A large number of research results show that the calculation results obtained by the CALPHAD method are basically in agreement with the experimental results, which can be used as a reference for the design of high-entropy alloys [18, 20]. The phase diagram vividly shows the relationship of the various phases in the system. It provides some detailed information of the phase as a function of composition, temperature and pressure. It is a guide diagram for materials science engineering in alloy design and development. The CALPHAD method can be used to study the formation of FCC and BCC phases in multi-component alloys. Since FCC has a greater dynamic effect than BCC structure, the accuracy of using CALPHAD method to predict FCC phase composition is less accurate. The CALPHAD method can also predict the FCC/BCC phase transition of AlxCoCrFeNi high-entropy alloy as cast and heat-treat [21]. Recently, Gao and Senkov used CALPHAD phase diagrams to design a large number of high-entropy alloys. Such as the new HCP structure high-entropy alloys: CoFeMnNi, CuNiPdPt, CuNiPdPtRh [22] and single-phase BCC refractory high-entropy alloys: HfMoNbTiZr, HfMoTaTiZr, NbTaTiVZr, HfMoNbTaTiZr, HfMoTa TiVZr and MoNbTaTiVZr [23]. Therefore, scholars Gao and Senkov believe that CALPHAD is the most direct method for designing HEAs.

### 2.3.3 Machine learning

Islam [24] uses artificial neural network (ANN) algorithm to predict phase selection, and the accuracy of the neural network model trained by it is 83% on average. As the learning progresses, the accuracy rate gradually increases. The generalization accuracy rates of the four cross-validation data sets were 86.7%, 83.3%, 86.2%, 75.9%, and the average accuracy rate was 83.0%. Although the prediction accuracy of 83% is an acceptable level, a larger data set can infer a higher generalization accuracy. In addition, the neural network parameters after training show that the valence electron concentration *VEC* plays a leading role in determining the phase. Because density functional theory (DFT) calculations are very time-consuming and there are uncertainties in processing the d orbitals of transition metal atoms, HEAs usually contain transition metals. Therefore, Huang [25] uses machine learning algorithms to explore phase formation criteria. It uses the nearest neighbor algorithm (K-nearest neighbors, KNN), support vector machine (Support vector machine, SVM), artificial neural network (Artificial neural network, ANN) 3 algorithms to calculate, respectively, the detection accuracy of 68.6%, 64.3%, 74.3%. When the artificial neural network algorithm is used to distinguish between solid solution + intermetallic compound phase and intermetallic compound phase, the test accuracy reaches 94.3%, which is the best algorithm among the three

machine learning algorithms. Huang also evaluated the importance of the five parameters $\delta$, $VEC$, $\Delta H_{mix}$, $\Delta S_{mix}$, $\Delta \chi$ and found that the $\delta$ and $VEC$ parameters are more important for phase selection.

## 3. High-throughput screening of high entropy alloys

### 3.1 Mask method for high-throughput screening

Materials science is an experiment-based science. The traditional experimental methods represented by the "trial and error method" are time-consuming and laborious, and far from meeting the requirements of current industrial development for new materials. With the advancement of technology and commerce more dependent on the advanced materials, the rapid design and development of new materials with excellent performance has become one of the most pressing needs.

The establishment of a systematic study on the design and preparation of high entropy alloys is helpful to the further development of high entropy alloys. The establishment of systematic study on the design and preparation is helpful to the further development of high entropy alloys. For this reason, material genetic engineering provides an effective method to accelerate the screening of the excellent alloy systems of high-performance high entropy alloys, so as to obtain the relationship among material composition, structure and properties with high efficiency, low cost and high reliability.

In addition, compared with traditional alloys, the design, preparation and performance optimization of multi-component materials are more complex, and there is no linear relationship between material properties and mixing entropy, that is, mixed entropy cannot be used as an effective criterion to predict material properties. This makes the screening of multi-component materials more complex and lengthy. The preparation of multi-component gradient materials by high-throughput preparation technology can provide a platform for high-throughput screening of multi-component materials and improve the efficiency of material development.

Different from conventional co-sputtering, the substrate stage was fixed during deposition. A physical mask is placed on the substrate, and the mask can be designed into $2^n$ areas with the same area according to the requirements. Variations in the relative position between the targets and substrate can cause non-uniformity of deposition. Utilizing the differences in deposition density on the substrate, compositional gradient materials were obtained. The composition of the high entropy alloy film obtained in each small region is different, so its physical and chemical properties are also different. By testing the mechanical properties or corrosion resistance and other chemical properties of the film, the composition range with excellent performance was selected. The high throughput screening method of physical mask provides an efficient and accurate experimental method for the enrichment of high entropy alloy system, and has been widely used in scientific research.

### 3.2 Serratioins in materials

Serration behavior is a common phenomenon in plastic deformation of materials. For example, serration behavior exists in TRIP steel, amorphous alloys, high-entropy alloys and other materials. The discovery of serration behavior is to explore the relationship between microscopic mechanism and macroscopic properties provides a new way. As the name implies, the stress–strain curve of the material is

different from the common type, showing a serration shape. This special mechanical behavior is called the serration of the material. Research shows that serration behavior has a certain similarity with noise, and compares it with noise. This phenomenon occurs when the material undergoes plastic deformation at a certain strain rate, which is caused by dynamic strain aging (DSA). From a microscopic point of view, lattice distortion during plastic deformation leads to a large number of dislocations in the material. The solute atoms interact with the dislocations, and the dislocations are pinned. After the dislocations break free from the pinning, they continue to move. Releasing the microscopic stress caused by lattice distortion has been reported to have similar behavior in low carbon steel.

Temperature, strain rate, load, phase structure, grain size, etc. It is generally believed that it is related to the flow units inside the material. These units can be dislocations, stacking faults, and grain boundaries. The serration behavior is considered to be caused by the interaction with these flow units [26]. Changes in these influencing factors cause the amplitude of the serration to change.

The HEAs possess very high entropy of mixing in their solution states. we cannot distinguish which is the solvent and which is the solute element. In other words, there is no dominant element in HEAs. The special solid solution structure makes defects, in HEAs may be segregated by solute atoms that grants it special plastic-deformation mechanisms. In high-entropy alloys, under high temperature conditions, as the strain rate increases, the sawtooth amplitude of the stress–strain curve becomes smaller and the fluctuation becomes tighter. This may be related to the fact that when the temperature is higher, the atoms are more active, and the thermal motion causes a rapid change between the effect of the atom pinning the defect and the effect of the defect breaking free of the atomic group [27–29]. At lower temperatures and low strain rate, the magnitude of serrations to dramatically increase with an increase in the compression strain. The serrations are believed to be related to the twinning plastic-deformation mechanism [27, 28]. The sample size also has a certain influence on this, Zou et al. have explored it, Such HEA pillars exhibit extraordinarily high yield strengths of about 10 GPa — among the highest reported strengths in micro−/nano-pillar compression and one order of magnitude higher than that of its bulk form — and their ductility is considerably improved (compressive plastic strains over 30%) [30].

### 3.3 Self-sharpening of materials

Self-sharpening is often used to discuss depleted uranium alloys and grinding wheels. The critical adiabatic shear strain rate and critical adiabatic shear strain value of depleted uranium alloy materials are low, and they are prone to adiabatic shear fracture. They have self-sharpening effects and can penetrate armor. During the armor piercing process, part of the projectile fell off by itself under high-speed collision, exposing a new cutting edge, enhancing the damage. That is a characteristic of the depleted uranium alloy material itself. The self-sharpening of the grinding wheel is the self-sharpening of the structure. During the grinding process, the force acting on the abrasive grains gradually passivates from the sharpness. When the force exceeds the maximum strength of the abrasive grains, the abrasive grains break and form new. When the force exceeds the bonding strength of the bonding agent, the abrasive will fall off the grinding wheel, exposing new abrasive particles, so that it can maintain its own sharpness, which plays an important role in the grinding process.

With the development and progress of modern material technology and the continuous discovery of new materials, many excellent properties of amorphous alloys, such as high strength, corrosion resistance, penetration ability and excellent

ferromagnetic properties, are widely used. Amorphous alloy is a new type of alloy, and its internal structure presents a state where chemical disorder and structural disorder coexist. Therefore, the plastic deformation behavior of amorphous alloys has always been a research hotspot. More mature theories believe that different from an alloy with a crystalline structure, which slips through dislocations, however the plastic deformation behavior of amorphous alloys through flow units. The high strength and penetration behavior of amorphous alloys are favored for the preparation of armor piercing materials. For example, the fracture strength of the zirconium-based amorphous alloy is as high as 60, and it has a very high dynamic fracture toughness under the action of high-speed load. It has excellent self-sharpening properties when penetrating the metal, which is better than depleted uranium alloys. And it is a favorable alternative materials [31]. Then the crystallization behavior and size of the amorphous alloy in the manufacturing process are caused, and although the strength of the amorphous alloy is high, the plasticity is poor, so it is restricted.

As we all known, refractory high-entropy alloys (HEAs) posses outstanding mechanical strength at room and high temperature but lack the room temperature ductility. In recent study, Liu et al. [32] designed a new tungsten HEA WFeNiMo with equimolar ratio to enhance chemical disorder, in contrast, to conventional single-principal-element tungsten alloys, and obtained a multi-phase structured alloy. "Self-sharpening", the capacity of a material maintaining its acute head shape during penetration, is a highly required attribute of materials in armor piercing. Depleted uranium kinetic energy penetrators exhibit superior penetration due to their themo-plastic shear banding induced "self-sharpening" behavior during penetration. While tungsten alloy kinetic penetrators usually form mushroom-like heads, which results in a poorer penetration performance when compared to depleted uranium alloy. The development of high-entropy alloys can be said to have opened up new ideas for exploration in the field of materials. In addition to replacing depleted uranium alloys as a projectile, it can even replace drug-type cover materials. According to the theory of penetration fluid dynamics, a long and stable jet can only be formed by a drug-type cover with high density, high sound velocity, favorable thermal conductivity, and high dynamic elongation at break.

The discovery of tungsten-based high entropy alloy breaks through the passivation behavior of traditional tungsten alloy in the process of armor piercing, and maintains the characteristic of high strength, which is expected to replace depleted uranium alloy in the future. However, when selecting the composition system of tungsten-based high-entropy alloy, the test workload and performance testing need to consume a lot of manpower and material resources, such as the traditional Hopkinson rod test or target verification. And what kind of composition ratio will give full play to the performance of tungsten-based high-entropy alloy is an existing problem at present.

So far promising HEAs have been mostly studied in their bulk forms, but small-dimension HEAs have received much less attention. As demands for micro- and nano-scale devices for high-temperature and harsh-environment applications increase, the fabrication and investigation currently popular HEAs at small sizes become more and more interesting. Focused Ga ion beams (FIB) were used by Zou et al. [33] to mill fine-scale pillars out of the obtained HEA films and micro compression tests were carried out using a nano-indenter. After compression a fraction of large pillars, about 1 um in diameter, it was observed that pillars show single slips with wave morphologies or fracture behavior from the SEM images showing in **Figure 4**.

Zou's method provides a new way to solve the problem of "self-sharpening" screening. Combined with the high-throughput screening method of physical mask,
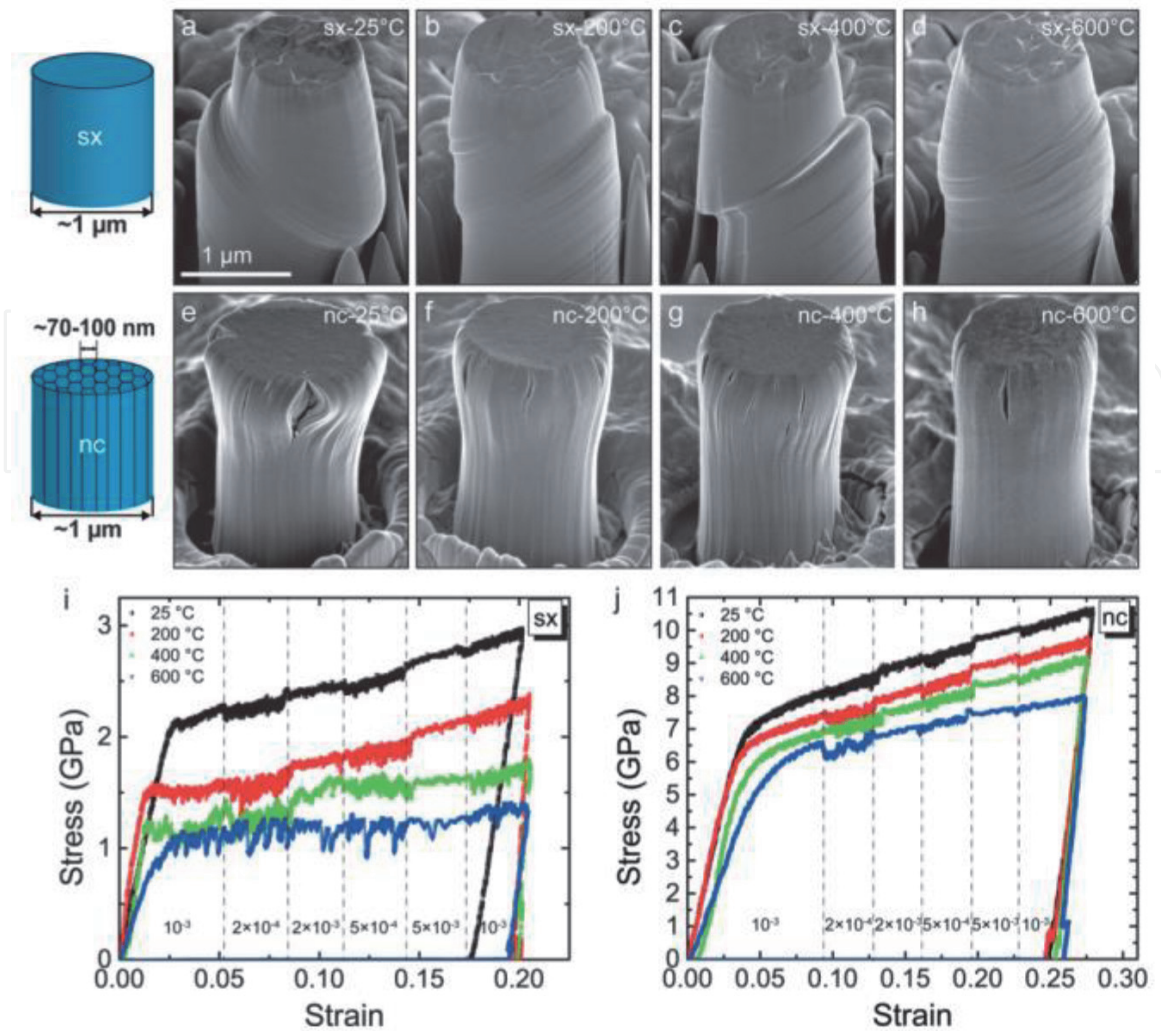
**Figure 4.**
*Compression results for the single-crystalline(sx)- and nanocrystalline(nc)-HEA pillars from room temperature to 600 °C. representative SEM images of the deformed sx-HEA pillars (a − d) and nanostructured columnar-grained HEA pillars (e − h) ([34] copyright@2017 American Chemical Society).*

the composition gradient thin films are prepared by magnetron sputtering and high-throughput preparation, and the excellent "self-sharpening" materials can be screened effectively by using Zou's method for reference.

High-throughput screening and nanoscale performance testing can also be used in the design of materials with special needs, such as corrosion-resistant materials. After the corrosion resistance test, the corresponding optimum composition range of the prepared gradient film can be determined, and the film can be prepared in multiple batches and gradually narrow composition range until determined. And combining the above-mentioned zigzag behavior and self-sharpening, there is a certain connection between the two, which may become a hot topic of research in the future.

## 4. Summary

This section summarizes the parameters for predicting the formation of high-entropy alloy phases and the method of machine learning to predict the formation of high-entropy alloy phases, combined with experimental verification, establishes related databases, and provides data and empirical support for subsequent research on high-entropy alloys. Under continuous research and verification, there are other criteria that continue to emerge, such as: distinguishing single-phase solid solution

and multiple solid solution parameters ($\phi$) [35], parameters of reaction atom filling mismatch and topological instability ($\gamma$), residual stress root mean square $(\varepsilon^2)^{\frac{1}{2}}$ [35, 36], interatomic distance mismatch ($S_m$) and bulk modulus mismatch ($K_m$) [37] and other parameters, but these parameters are more practical for some specific alloys, and $\Delta H_{mix}$, $\delta$, $\Omega$, *VEC* et al. parameters are the more mainstream phase criteria, and the range of use is relatively wide. The application of simulation calculation methods such as first principles and machine learning to the research of high-entropy alloys has also achieved remarkable results, providing more accurate and scientific guidance for the composition design of high-entropy alloys. The composition and structure of the material determine the performance of the material. The multi-principal component design makes the phase composition of the high-entropy alloy more complicated. Accurately predicting the formation phase of the alloy with a given composition is very important for the design of high-entropy alloy materials. The current phase prediction requires comprehensive judgment of multiple parameters and multiple methods. The high-throughput screening of high-entropy alloys is also described and the performance of high-entropy alloys in terms of self-sharpening and serrations behavior. Regarding the high-throughput screening method, only the reticle method is described. This method is more practical for the onlooker size. For the screening of the block, the existing research has shown that the method is through hot isostatic pressing. At the same time, matching screening also has high-throughput characterization and high-throughput testing. The description in this chapter is limited. Promoting the development of high-entropy alloys requires more new methods and theories to keep pace with the times.

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