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# Fundamentals and Properties of High–Entropy Alloys

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## Summary

High–entropy alloys (HEAs) are alloys with high configurational entropy at the liquid state. The high entropy contribute to making the disordered phases stable, such as disordered solid solution phase and amorphous phases. The first generation of HEAs is defined as alloys with more than five components in equi– and/or near equi–atomic ratio. In these kind of alloys, single phase structure is obtained, including face–centered cubic (FCC), body–centered cubic (BCC), hexagonal–close–packed (HCP), and amorphous structures. The recent advances in HEAs mainly focus on the second generation of HEAs, e.g., the non–equiatomic ratio and dual phase HEAs, which include 8 kinds of HEAs: (1) Lightweight HEAs, e.g., AlLiMgZnCu, which have low density than Titanium alloys and better properties; (2) nano–sized precipitation hardening HEAs, which is potentially the next generation of superalloys; (3) eutectic HEAs, which have excellent casting properties; (4) phase transformation induced plasticity (TRIP) HEAs; (5) nano or ultrafine grain HEAs; (6) soft magnetic HEAs, potentially filling in gaps between the silicon steels and amorphous alloys, e.g., CoFeNiAlSi; (7) low activation HEAs, potentially the next generation of nuclear materials, e.g., WTaFeCrV; (8) high–entropy films, NbTiAlSiN thin films. The HEAs are potentially the breaking property limits of the traditional alloys.

*Keywords*: High–entropy alloys; magnetic properties; serrated flow; high–entropy films; phase formation rules

## 1. Introduction

High–etropy alloys are developed based on the conception of configurational entropy, which is defined by Boltzman:

$$S=k\ln\Omega \quad (1)$$

where, $S$ is configurational entropy; k is Boltzmann constant, $k$=1.38; $\Omega$ is the number of real microstates corresponding to the macrostate. Sometimes, $\Omega$ is called the "thermodynamic probability", since it is an integer greater than one, while mathematical probabilities are always numbers between zero and one.

The materials developments are also like the second law of thermodynamics, obeying the “entropy increase” principle. From the bronzing age to the ironing age, to aluminum alloys, to stainless steel superalloys, the configurational entropy is increasing. In 2004, Professor Yeh first proposed the concept of high entropy alloys [1]. Subsequently, a series of high–entropy alloys appeared. In addition, high–entropy alloys also exhibit excellent overall properties such as high strength, high toughness, wear resistance, corrosion resistance, high temperature oxidation resistance, excellent high temperature and low temperature mechanical properties, Meanwhile, they also exhibit excellent soft magnetic properties and the catalytic properties. Fig. 1 shows the entropy–increasing in the developments of materials [2~4].

At the regular liquid state, the entropy can be simplified as:

$$\Delta S_{mix} = -R\sum_i C_i \ln C_i \quad (2)$$

where $R$ is gas constant, $C_i$ is molar percent of ith component. From Eq. (2), we can see that in the equi–atomic or equi–molar ratio alloys, the configurational entropy of mixing reaches its maximum and Eq. (2) can be simplified as follows:

$$\Delta S_{mix}=R\ln N \quad (3)$$

Unlike conventional alloys, the composition of HEAs is complex due to the definition of high entropy alloys. Four core effects of HEAs are summarized [2–5]: (1) Thermodynamics: high–entropy effects; (2) Kinetics: sluggish diffusion; (3) Structures: severelattice distortion; and (4) Properties: cocktail effects. To some extent, these four effects explain the excellent properties of high entropy alloys.

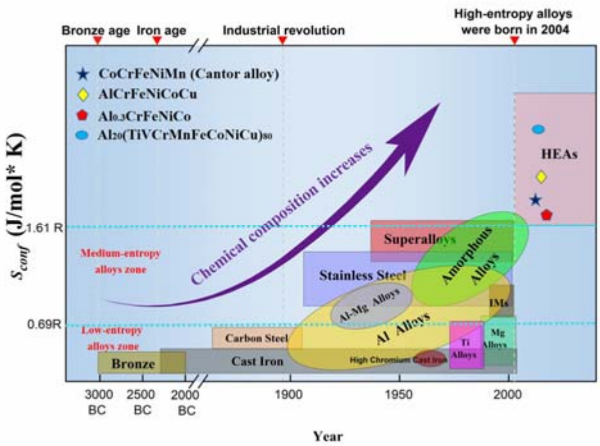


**Figure 1.** Entropy increasing in the developments of materials [4]

## 2. Classifications

HEAs can now be divided into three categories.

i). Conventional alloys, with the main constituent elements rarely exceeding 2;

ii). The first generation of high–entropy alloys, which have 5 or more major component and equal atomic ratio;

iii). Second generation high–entropy alloys, with non–equal atomic ratio; as shown in Fig. 2.

It should be noted that among various thermodynamic factors, such as mixing enthalpy, mixing entropy, atomic size difference, valence electron concentration and electronegativity, mixing entropy is the only factor that increases as the number of major elements increases. As a result, according to the value of mixing entropy, alloys can also be divided into the following four categories:

i). The polar material, which is also called 0 entropy alloy. They are the high purity materials, and the theoretical entropy value is close to 0;

ii). Low entropy materials, which have 1~2 kinds of elements;

iii). Medium entropy alloys, containing 2~4 elements;

iv). High–entropy alloys, with 5 or more major components. The four materials classified according to entropy values is shown in Fig. 3.

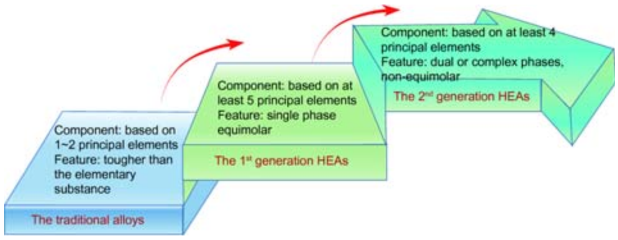


**Figure 2.** The two generations of high–entropy alloys [4]

In terms of the properties, the large amount of optional elements leads to the performance diversity, which in turn determines their broad application in many fields. According to the major properties and their corresponding application fields, the HEAs can be classified into eight categories, as shown in Table 1.

**Table 1.** High–entropy alloys with different application background and performance characteristics

| Category | Performance Characteristic | Representative alloy |
|---|---|---|
| Lightweight HEAs | Low density, excellent mechanical properties | AlLiMgZnCu |
| Nano–precipitation hardening HEAs | Excellent high temperature stability | CoCrFeNi(Al, Ti) |
| Eutectic HEAs | Excellent casting properties | AlCoCrFeNi(1.8–2) |
| TRIP HEAs; | High strength and plasticity | $Fe_{80-x}Mn_xCo_{10}Cr_{10}$ [6]<br>$Co_{20}Cr_{20}Fe_{40-x}Mn_{20}Ni_x$ [7] |
| Nano or ultrafine grain HEAs | High room temperature comprehensive mechanical properties | AlCrFeCoNiCu<br>$AlCrFeCoNi_{2.1}$ |
| Soft magnetic HEAs | Excellent meachical and soft magnetic properties, can fill in gaps between the silicon steels and amorphous alloys | CoFeNiAlSi[8] |
| Low activation HEAs | potentially the next generation of nuclear materials | WTaFeCrV |
| High–entropy films | Excellent thermal stability and high hardness | NbTiAlSiN thin films |

High–entropy alloys can also be called the multiple principle elements alloys (MPEA). Other various names have also emerged with the development of HEAs, such as multi–component alloys (MCA), complex concentrated alloys (CCAs), and baseless alloys (BA) etc. [9]

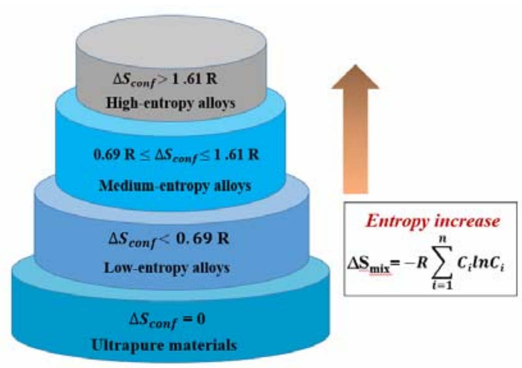


**Figure 3.** Alloys world based on the configurational entropy

## 3. Preparation of High entropy alloys

At present, the main method of HEAs preparation is the vacuum arc melting, induction magnetic suspension melting and powder metallurgy etc. Meanwhile, some high–throughput methods for screening high entropy alloy composition is introduced here, including multi–target co–sputtering, masking method and supergravity method etc. [10].

Traditionally, bulk high–entropy alloys are mainly prepared by vacuum arc melting with copper mold cooling, and the equipment schematic diagram is shown in Fig. 4. The preparation device is derived from the preparation of bulk amorphous, and 3~5 alloy ingots of about 100g can be prepared at one time. Then a larger rods or sheets can be obtained after rolling or forging, and the mechanical properties can also be tested, through which the composition with excellent performance can be found. Vacuum magnetic suspension smelting method can prepare the larger bulk alloys relative to vacuum arc melting, and an alloy ingot obtained by this method is shown in Fig. 5. For light–weight high–entropy alloys, the melting point is relatively low, and the required ingots can be prepared by induction melting. Some alloys are also prepared by new methods such as directional solidification and powder metallurgy. The effects of different preparation methods on the microstructure and properties of the alloy were investigated.

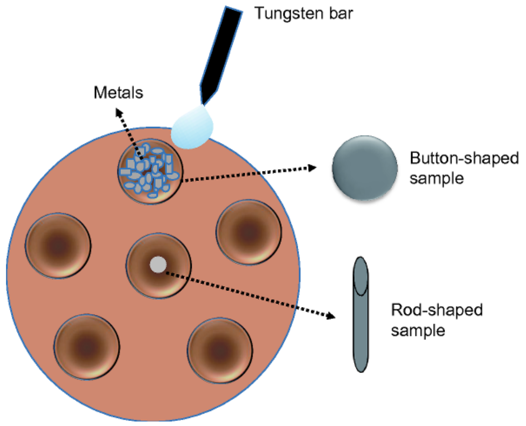


**Figure 4.** Schematic of arc melting [4]

**Figure 5.** An alloy ingot obtained by magnetic suspension melting [19]

In terms of the material design, elements having a FCC or BCC crystal structure are generally considered to be matrix elements. Thereafter, appropriate modifying elements are added to improve the desired properties. The traditional alloying method of "repetitive testing" leads to a large amount of human and material resources consumption, a prolonged research cycle, and low efficiency. These shortcomings become more pronounced in the design of multi–component HEAs. The development of high–throughput experiments can solve these problems well [11]. High throughput experiments have been developed in the preparation of thin films and bulk alloys, particularly for the manufacture of films. In addition, the multi–target co–deposition method is suitable for the preparation of high entropy films with various constituent elements [12]. As shown in Fig. 6, co–deposition uses different distances between the substrate and the target, and different targets provide a concentration gradient on the substrate during deposition to produce a HEA film with a continuous concentration gradient [13]. At the same time, the high–entropy alloy gradient materials with different specific gravity elements can be prepared by using the super–gravity technology, and the suitable high–entropy alloy composition is selected. Subsequently, combined with high–throughput characterization techniques, we can achieve rapid screening of HEA and then prepare a large number of selected components. Depending on the composition of the HEAs, many single element or alloy targets can be prepared, and the atomic percentage of the elements can be controlled by adjusting the target sputtering power. A HEA film having a continuous composition gradient is obtained, and then a block–selected alloy can be produced. Today, high–throughput highways that calculate HEAs are a huge opportunity and challenge for the development of HEAs [14].

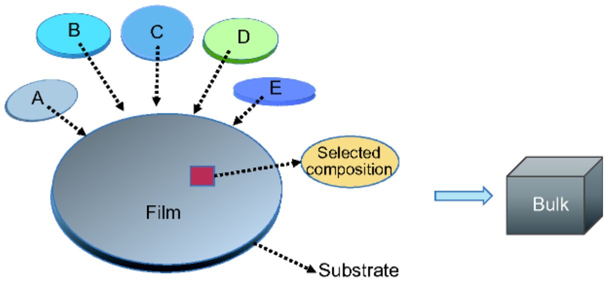


**Figure 6.** Schematic of multi–target co–deposition for HEAs [4]

## 4. Microstructure and properties

The high–entropy alloys obtained by arc melting tend to be a single solid solution phase, and the structure of the alloy tends to exhibit a dendritic structure due to the faster cooling rate. In addition, different preparation processes often have different microstructures, mainly the influence of the direction and speed of grain growth during solidification on the microstructure of the alloy. For example, Zhang et al. studied the effect of directional solidification on $Al_{0.3}CrFeNiCu_2$ alloy [15]. Of course, the alloy composition of different alloys often has a large difference, so the alloy has a large difference in properties. When the alloy composition is changed, the solidification process of the alloy will be greatly changed. The eutectic or peritectic reactions may occur, such as eutectic high–entropy alloy system $Al_xCrCoFeNi_2$ [16].

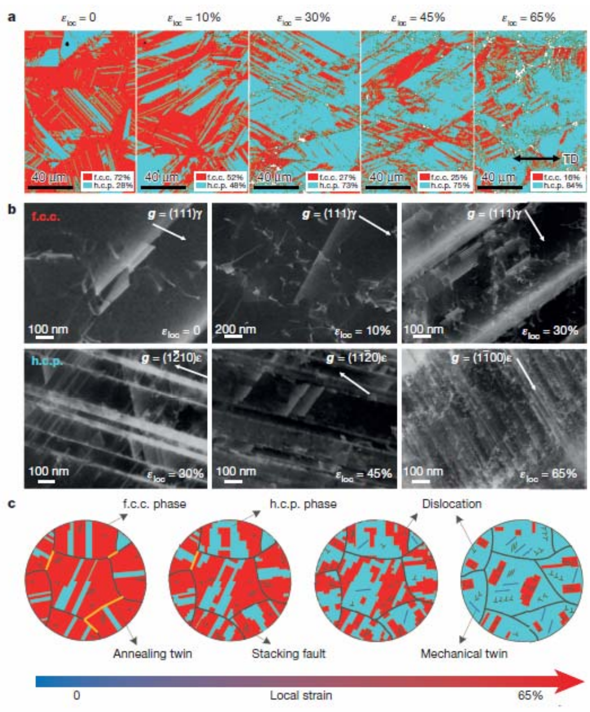


**Figure 7.** Deformation micro–mechanismsin the TRIP–DP–HEA with increasing tensile deformation at room temperature [7, 8]

Moreover, the processing deformation of the alloy also changes the structure of the alloy and even induces the phase transition of the high–entropy alloys. Another example is $Co_{10}Cr_{10}Fe_{50}Mn_{30}$ high–entropy alloys. After deformation processing, the FCC structure changes to HCP structure [7], it is shown in Fig. 7. Therefore, the plasticity and strength of the alloy are greatly increased, and the strength and plasticity are simultaneously improved to achieve the effect of phase transformation and toughening.

HEAs had been studied extensively, not only because there is a unique multicomponent solid solution phase, but also because they have high hardness and strength. High–entropy alloys have good compressive mechanical properties and tensile properties by the mechanical properties testing. By comparing with the high temperature performance of traditional superalloys, it is found that several series of high entropy alloys have excellent high temperature mechanical properties. The high temperature mechanical properties of HEAs were shown in Fig. 8 [17]. Li et al. tested the tensile properties of high–entropy alloys at lower temperatures and found that the high alloys did not exhibit the ductile–brittle transition and exhibited excellent low–temperature mechanical properties, even under 77k conditions. Furthermore, their comprehensive mechanical properties are the best [18].

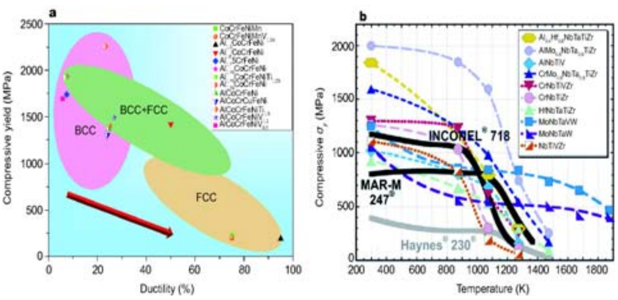


**Figure 8.** (a) Compressive behaviour of various HEAs; (b) compressive yield strength versus temperature [4]

## 5. Conclusion

HEAs have excellent properties such as excellent mechanical properties, high temperature properties as well as corrosion resistance and radiation resistance, which make HEAs become the potential materials under extreme conditions. In recent years, although research scholars from different countries have carried out a lot of research work and obtained some research results, due to the diversity of alloy components, a lot of research works still needs to be done. How to transfer the HEAs from scientific research to industrial production and some other problems still needs to be solved.

## Acknowledgement

The authors would like to thank the financial supports by the National Science Foundation of China (NSFC, Granted Nos. 51471025 and 51671020).

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