High-Entropy Alloys for Advanced Energy-Related Applications

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Abstract. Presently, as newborn electrode materials, high entropy alloys (HEAs) have intrinsic physicochemical properties, unique merits and significant application potential in various energy storage and conversion technology fields. Recently, various potential high entropy materials have appeared both domestic and foreign and have developed into one of the essential research hot topics in the field of material science. Based on this overview, the aim of this study supplies fundamental insights into combining the unique concept of HEAs with different latest energy-related applications. In this article, the research state of HEAs will be examined, summarized from many areas of the theoretical foundation, composition, special features, preparation methods, and possible energy-related applications.

Keywords: High entropy alloys, Energy storage, Battery, Hydrogen storage, Supercapacitor.

1. Introduction

Nowadays, with the rapid development of aerospace, aviation, communication, electronics, chemical, energy machinery and other industries. The great challenge facing modern materials science is to develop high-performance materials that can fulfill the rapid growth of technology demands [1, 2]. However, the traditional alloy design concept and system are now close to saturation point, and it seems increasingly hard to create a new alloy system. One way to break through the bottleneck of alloy development is to innovate in the traditional alloy design concept.

Conventional alloy is based on one or two kinds of metal elements, improving the performance of materials by adding different alloy elements. It has been widely applied in aluminum, magnesium, titanium, etc. Additionally, in 2004, Ye Junwei, a Taiwanese scholar, made a breakthrough in alloying theory for the first time by proposing multi-component high-entropy alloys (HEAs) [3]. Since then, high entropy alloy with adjustable properties and special microstructures has gradually entered the field of vision of new materials. In recent years, HEAs have obtained profound interest owing to their powerful performances and properties by developing potential technological applications and scientific understanding [2]. The initial definition of HEAs states that they typically have more than five principal elements with equimolar or nearly equimolar ratios, and the atomic proportion of each element ranges from 5% to 35% [5].

In the dual crisis of environment and energy consumption, various effective technologies, such as batteries, have been utilized to achieve energy storage and conversion [2]. To reach the demands of the commercialization of clean source applications, more functional materials and new concepts for alloy design would be explored [1]. In the last two decades, many scholars have accumulated many research results on HEAs. HEAs are a significant energy storage material [2].

According to the above research situations, a systematical discussion on the latest achievements of high-entropy alloys would be demonstrated. This article presents a comprehensive overview of the unique and remarkable performances of HEAs, their preparation methods, and their perspective applications for energy conversion and storage.

2. The intrinsic physicochemical properties and unique merits of HEAs

In terms of composition, HEA refers to the alloy system containing five or more metal elements mixed by equal atomic ratio; In terms of structure, the initial HEAs mainly refer to the form of solid
metal solutions with normal crystal structures to achieve the optimization of alloy microstructure and properties, such as bcc, fcc, hcp and C14 hcp structures [1, 6, 7], as shown in Figure 1. Conceptually, compared with traditional alloys (such as titanium and aluminum alloy). Being considered to have a high degree of configuration entropy and chemical disorder because HEAs lack a single dominant element in their chemical composition [8, 9].

2.1. Four Core Effects of HEAs

To meet the requirements for either industrial applications or academic research, it is essential to have well-organized alloy design strategies. HEAs showed considerable numbers of combinations of properties and potential compositions [5]. Unlike conventional materials, the high-entropy alloy has a complex composition, and the constituent atoms are distributed randomly and disordered in lattice positions [7]. As a result, HEAs have a severe lattice distortion effect in structure (alter properties to a certain degree), sluggish diffusion effect in kinetics (slow down the phase transformation), and high entropy effect in thermodynamics (meddle in the creation of complex phases), cocktail effect in properties (it means a synergistic mixture, and the result is unpredictable) [3, 5, 10]. This section will further explain the four core effects.

2.1.1 Lattice Distortions Effects

The severe lattice distortion effect is strongly associated with high entropy alloys' mechanical properties and structure. Lattice distortion is caused by the distinctive atomic sizes and the random distribution of atoms in the high entropy phase [10, 11]. As illustrated in Figure 2, each atom is surrounded by various atoms, suffering from lattice stress and strain [5]. Every lattice position's displacement is defined by the atoms in the position and the type of atoms in the local environment. These distortions are far worse than in conventional alloys.

In this way, lattice distortions are one of the most characteristic structural features among the four core effects of HEAs [8]. The uncertainties of the positions of these variable atoms lead to higher entropy in the alloy formation [5]. Furthermore, there is a substantial increase in strength and hardness due to the large solution hardening that occurs during the lattice distortion process [8]. Physically, this can reduce the intensity of the X-ray diffraction peak, increase hardness, reduce conductivity, and reduce the alloy's temperature dependence. However, systematic experiments to quantify the value of these changes in performance are still lacking.
2.1.2 Sluggish Diffusion Effects

Compared with traditional alloys and pure metals, the kinetics of diffusion is forbidden due to the sluggish diffusion effect, causing a decreasing value in diffusion coefficients [11]. Because of the slow diffusion rate, the high entropy alloy is less likely to undergo adverse effects such as grain coarsening and recrystallization at high temperatures, resulting in good thermal stability. Furthermore, the slow diffusion effect makes it easy for the HEA to acquire a supersaturated solid solution, leading to the formation of nanoscale precipitates. [10]. Due to the precipitation of the nanophase, the alloy will undergo precipitation strengthening, and the hardness and strength will be significantly improved. As many publications have proved, the sluggish diffusion effect might supply some significant advantages, such as decreasing the particle coarsening rate, promoting the creep resistance ability, increasing the recrystallization temperature, and controlling the speed of grain growth [5].

2.1.3 High-Entropy Effects

As the name implies, the high entropy effect is the most significant and unique of the four core effects of HEAs due to its ability to promote the formation of solid solutions and control the microstructure much more easily [5]. The entropy value of a multi-principal component high-entropy alloy is significantly greater than that of a conventional alloy. The high entropy effect of the multi-principal component high-entropy alloy decreases the free energy of forming solid solution phases and promotes solid solution formation, especially in high-temperature environments [11]. However, with further study, many high entropy alloys contain various intermetallic compounds.

2.1.4 Cocktail Effects

Ranganathan first mentioned the cocktail effect for metallic alloys [12], which subsequently confirmed the mechanical and physical properties [9]. Unlike the other three core effects, the cocktail effect is not hypothetical and does not need to be proven [9]. The definition of the cocktail effect refers to specific material properties and unexpected synergies produced by mutual interactions between the constituent elements. As a result, the excess is averaged and simply predicted by the mixing rule [9, 11]. Additionally, due to the cocktail effect, changing the composition and alloying of HEAs could substantially alter performances [11].

2.2. Performance

Apart from that, recent studies have found significant element fluctuations in the solid solution structure of HEAs. The comprehensive mechanical performances of HEAs could be effectively upgraded by controlling the fluctuations of element concentration in HEAs [13]. As illustrated in figure 3, high entropy alloy has many excellent properties that traditional materials cannot match, such as hardness, corrosion resistance, wear resistance, high elongation, tempering and softening resistance, fatigue, fracture properties, etc. [2, 14]. To be more specific, the quantity of alloying elements and processing conditions significantly affect the microstructure of the alloy. HEAs with different structures demonstrate different structural properties and functional characteristics. The unique structure and wide variety of HEAs provide the foundation for functional and structural applications, thus leading to promising properties [2].

![Advantages of HEAs](image_url)

Figure 3 Properties and advantages of HEAs [14].
3. Preparation Methods of HEAs

The preparation methods of HEAs can be classified based on the initial state of the alloys, such as vacuum arc furnace casting, mechanical alloying, laser cladding, thermal spraying, magnetron sputtering etc. Figure 4 illustrates the categorization of methods for preparing various samples [2].

![Figure 4 Preparation methods of various samples formation [14].](image)

3.1. Vacuum Arc Furnace Casting

The most conventional method is vacuum arc furnace casting [2]. HEAs are prepared by repeated melting various alloy elements at least five times in an arc melting furnace. By controlling the current of the arc melting furnace, the arc can reach non normally high temperature ($\geq 3000 \degree C$) [15]. Therefore, most of the metal elements with a high melting point can be mixed in the melting well in the liquid state in this furnace. However, arc smelting may not be suitable for low melting point elements because these low melting point elements are volatile and difficult to mix well with other elements during heating elements. In addition, it is difficult to adjust the alloy composition and only a small amount of melting each time.

3.2. Mechanical Alloying

Mechanical alloying is commonly used to produce HEA powder. [2]. It is mainly divided into three steps. Firstly, the powder metallurgy method is used to prepare the powder of each component element. Then, according to the design of the composition, the elements are proportionally mixed and pressed into the mold into blocks. Finally, it is heated up, hot pressed, or sintered using discharge plasma in a sintering furnace. The choice of sintering mode is figured out by the sintering temperature of high entropy alloy [15]. The main advantage of mechanized alloys is the more uniform distribution of nanoscale structures.

3.3. Laser Cladding

Prefabricated laser cladding is the main method used to prepare HEA coating. The HEA is placed on the cladding part of the matrix material’s surface in advance, then the HEA is melted by laser beam irradiation, and the surface coating is formed after rapid solidification. Rapid heating and solidification are features of this process, and the coating's thickness can approach millimeter levels [15].

3.4. Thermal Spraying

The sprayed material is melted in a heat source and sprayed to the substrate surface by high-speed air flow to form a coating [14]. The advantage is that the base material is not limited. The substrate material's temperature is low throughout the spraying process, and no stress or deformation is produced. The coating might be anywhere between 0.01mm and many mm thick. Generally, the initial HEA is made by an arc melting furnace, and then the alloy ball is ground into particles with a diameter of less than 44 um, [15].
3.5. Magnetron Sputtering

By xenon gas ionization under the action of the electric field, argon ion is accelerated by electric field bombarded target sputtering a huge amount of target atoms deposited on the substrate to form a film. Magnetron sputtering has a high film creation rate, low substrate temperature, good film adherence, and large-area coating. Multi-principal high-function alloy coatings have been successfully prepared by magnetron sputtering [15].

4. Latest achievements of HEAs for energy conversion and storage

The potential uses of HEAs for energy conversion and storage have been greatly promoted by their illustration of numerous enticing traits and capabilities, such as catalysis, hydrogen storage, supercapacitor, and rechargeable batteries (as figure 5 shows). While more research is being done to determine their durability and performance in challenging circumstances [16], this section will comprehensively discuss the latest advanced energy-related applications.

4.1. Catalysis

HEAs have immense potential for energy conversion reactions and catalyzing chemical transformation [17]. As electrocatalytic materials, they could obtain an unexpected and predominant catalytic activity due to geometric configurations and controllable electronic structures of HEAs [18]. Additionally, owing to the brilliant stability, high porosity, and high catalytic activity. HEAs have obtained much promise and widespread concern in this field of catalysis. To realize the practical application of HEAs in catalysis, the combination of experimental methods with computationally assisted theoretical predictions have done to discover novel HEAs catalysts with unique catalytic properties [16]. However, this remains extremely difficult because of the complexity of multi-component HEAs and how they interact. In this section, some suggestions will be put forward for the forthcoming development and application of HEAs.

The various core technologies for energy conversion are oxygen evolution reactions (OER) and oxygen reduction reactions (ORR), such as water splitting and fuel cells [1, 16]. Recently, many studies have focused on how to solve the ineffective slow reaction kinetics that needs to develop and explore catalysts to overcome energy barriers [1]. For example, Pt-based nanomaterials are the most advanced electrocatalysts nowadays due to their superior catalytic activity for the ORR [19]. As Figures 6a and 6b illustrate, compared with the specific activity of commercial Pt/C, 3.8 times enhancement in that toward the ORR, as well as a high level of long-term stability [1]. In contrast, costs are a barrier to the majority of energy-related applications. As newly created electrocatalysts,
HEAs illustrated promising performances toward ORR and OER, which are the potential candidates for both. As the earlier studies proved, HEAs seem to have better stability and catalytic activity by adding tiny amounts of Pt [1, 18].

Figure 6 (a) Nanoporous PtIrRuCuOs and Pt/C at 0.9 V vs. RHE (electrochemical surface area and mass-specific activities). [1]. (b) ORR polarization curves (HEAs) after three different cycles [1]. Pt-based catalysts could benefit from the high entropy method to improve catalytic performance, decrease the proportion of noble metals, and limit the overall cost by adding more elements through synergistic effects [16]. Therefore, by adding active transition metals (non-noble metals) to the entire system, the expected properties would be improved, and a significant decline in the cost of the catalyst. This way, it is possible that the concept of HEAs could be applied in the same reactions by using appropriate elements to upgrade catalytic performances and resolve miscibility problems. [1, 16]. Most importantly, high entropy materials could be one of the most promising approaches to sustainability and cost problems connected with energy [1, 18].

4.2. Hydrogen Storage

It is well known that the development of current society is actuated by energy. To decrease the carbon emissions caused by fossil fuels and satisfy the future energy demands, environmentally benign energy has become an essential issue worldwide [20].

Under such status, the “power-to-gas” strategy has been proposed, including energy conversion of surplus electricity into gaseous fuel [21]. Hydrogen is a promising clean energy carrier with zero-carbon emissions, high energy density, high efficiency, and a long storage period [1, 21]. As the previous studies demonstrated, hydrogen has been confirmed as a guiding fuel based on the above features. HEAs have attracted comprehensive attention in various fields, especially in hydrogen storage under the diversity in the structural composition of HEAs [21]. Many studies have been devoted to applying various structures of HEAs in hydrogen energy [1]. Additionally, the phase transition of HEAs has been proposed [15]. As figure 7 shows, there are three routes during the phase transition: (1) the BCC route, from BCC (H/M=0) to BCT, then partially hydrogenated to FCC (H/M=2). (2) the RE route, from dHCP (H/M=0) to FCC (H/M=2), then up to BTC (H/M>2.3). (3) the HEA routes illustrate a combination of the BCC and RE routes, from BCC to BCT [22]. In this section, the present research situations will briefly summarize HEAs in the field of hydrogen storage.

Figure 7 Various routes for hydrogen absorption in metals [22]
Nevertheless, the utilization of hydrogen still has drawbacks, including the low gaseous density and safety problems caused by the property of ready-to-flame [1]. Therefore, safe, reasonable cost, and efficient storage are the bottlenecks hindering commercialization and critical factors in promoting sustainable hydrogen energy systems [21]. At present, Metal hydrides are an alternative method. By comparing HEAs with the conventional binary or ternary alloys, the properties could be easily changed and upgraded by the compositional design [1]. It is proved that the severe lattice distortion effects of the HEAs resulted in surprising hydrogen storage performances.

On the other hand, the lattice strain (distortions) in the HEA supplies much more beneficial and suitable diffusion pathways and interstitial sites for hydrogen atoms [23]. Additionally, the tetrahedral and octahedral interstitial sites could be occupied by the hydrogen atoms in the tetragonal crystal, and the hydrogen could be absorbed in both sites by the big lattice distortion in the HEAs [1, 24]. Therefore, HEAs are an excellent method to upgrade the hydrogen storage performance of traditional metal hydrides.

4.3. Supercapacitors

Compared with batteries, supercapacitors are considered a well-studied, effective and the most prospecting high-power alternative energy storage devices due to the nearly unlimited number of cycles (4106 cycles) [1].

As a promising class of energy storage device, supercapacitors display exceptional performance sitting between traditional capacitors and batteries, which could store enormous energy by polarized electrolyte [14, 25]. Because of their long lifespan, short charging time, high power density and brilliant safety properties, supercapacitors have attracted substantial attention in energy storage. They have been extensively applied in devices requiring fast charge or discharge cycles in the past few decades [22, 25]. However, the practical applications have been hampered because of their complex manufacturing, low energy density and soaring prices. For instance, carbon-based electrode materials have a fast charge/discharge rate and significant life cycle, but the low energy density restricts their practical applications [14].

Thus, producing high-power energy density supercapacitors remains a huge challenge and improving and optimizing electrode materials for supercapacitors are one of the critical strategies to modify the properties of supercapacitor devices [14]. To increase capacity, improved electrode materials should have adjustable pore size, high surface area, and significant conductivity [2]. Due to their excellent capacitive properties, HEAs and nanostructured HEAs have been identified as potential electrode materials.

**Table 1.** Electronic conductivity and capacitance of metal-based electrodes [14].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Capacitance (F g⁻¹)</th>
<th>Electronic conductivity (S cm⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>MnO₂</td>
<td>1370</td>
<td>~10⁻⁶ to 10⁻⁵</td>
</tr>
<tr>
<td>RuO₂</td>
<td>1358</td>
<td>3 × 10²</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>2299</td>
<td>~10⁻² to 10³</td>
</tr>
<tr>
<td>NiO</td>
<td>2584</td>
<td>~10⁻³ to 10⁻²</td>
</tr>
<tr>
<td>Ni(OH)₂</td>
<td>2082</td>
<td>~10⁻¹⁷</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>3560</td>
<td>~10⁻²</td>
</tr>
<tr>
<td>CoO</td>
<td>4292</td>
<td></td>
</tr>
<tr>
<td>Co(OH)₂</td>
<td>3460</td>
<td></td>
</tr>
</tbody>
</table>

According to the previous studies, Scopus illustrated around 18% of the supercapacitor’s publications related to cobalt and/or nickel materials in the past 15 years [14]. Compared with other metal-based electrode materials, cobalt/nickel-based materials have demonstrated significant
competitiveness due to the higher theoretical capacitance (Table 1) [2, 14]. Due to the multi-component concept and properties of HEAs, various cheaper metals could be combined to be HEAs. Furthermore, the performance of each material in the composition would play a crucial role, such as adding extra metals could lead to better mechanical properties, thermal stability and so on. Thus, it is a clever way to obtain better supercapacitor electrode materials [14].

4.4. Rechargeable Batteries

Rechargeable batteries have been widely used for various energy applications as a power source, from portable electronics to electric vehicles [1]. As for the e-mobility application, there is a huge demand for energy and power densities. High entropy materials, especially HEOs, were originally employed in rechargeable batteries because of their superionic conductivity [1, 16]. As earlier studies showed, HEOs is the promising electrode materials in the application of rechargeable batteries. The most typical representative is called conversion-type (CoMgCuNiZn)O anode for LIBs, showing significant long-term cycling performance (Figure 8) [1, 16]. However, these conversion-type materials remain inherent limitations, such as (1) poor energy efficiency due to the sizable voltage hysteresis, stability and (2) cycling properties may be affected by the continuous electrolyte decomposition.

Figure 8 Cycling number property and Coulombic efficiency of (CoMgCuNiZn)O (200mA g⁻¹) [1].

There are some basic approaches and strategies that may be utilized to solve these problems, such as (1) altering the anion could improve energy efficiency, which would potentially lead to better power density, and (2) stabilizing the interface (electrode/electrolyte) and prevent the electrolyte decomposition, making passivation on the surface of highly reactive particles may be a good way to mitigate such problems [1]. Until recently, layered HEOs illustrate attractive and potential lithium storage performances, a promising research direction for rechargeable battery technologies. For instance, the HEO (layered O3-type NaCu₀.₁₂Ni₀.₁₂Mg₀.₁₂Co₀.₁₅Fe₀.₁₅Mn₀.₁₅Ti₀.₁₅Sn₀.₁₅Sb₀.₀₄O₂) cathode for batteries, demonstrated long cycle life stability and great rate capability [1, 2]. In addition, lithium battery storage and conversion by alloying reaction mechanism is currently a vacant field for high entropy materials in the applications of rechargeable batteries [1].

5. Conclusion

HEA is a new field of alloy system which can be synthesized, controlled and analyzed. The concept of HEAs enlarges the composition range of alloy design, leading to various superior performances. Multi-principal element high-entropy materials have many excellent properties that functional and traditional structural materials do not, such as corrosion resistance, tempering and softening resistance, wear resistance, electrical properties, fatigue properties, etc. Moreover, people must develop high-performance electrode materials based on the demand for upgrading the energy conversion and storage systems. HEAs could keep up with these requirements because of exhibiting specific characteristics, such as good cycle stability, controllable structure, high porosity, etc. In this article, the recent development of HRAs would have a discussion and outline, just as the following illustrated.
(1) There are four special core effects for HEAs, cocktail effects, sluggish diffusion effects, high entropy effects and severe lattice distortion effects, which are the basis for supplying a variety of promising properties.

(2) To obtain better physical, chemical and mechanical performances, more fundamental scientific research on the HEA system is required and ought to have continuous improvement of existing functional materials. Thus, the ultimate aim is to save energy, resources, and cost for the world by acquiring better properties and preparation methods.

(3) Exploiting the performance of HEAs should get closer to fulfilling the requirements in the field of advanced energy-related applications, such as catalysis, hydrogen storage, supercapacitors and batteries, and finally reach commercial standards.

Although HEAs' mechanical properties and preparation process have tremendous achievements, composition design still faces an imperfect theoretical system. In addition, some obvious restrictions and challenges should be considered for energy-related applications. As a new promising material, the research on HEA is far from in-depth and systematic.

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