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Phases and Applications of High Entropy Alloys, an Advanced Material - A Review

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Abstract

Properties exhibited by high entropy alloys are globally influenced by the phases present in the alloys, among other factors. Incidentally, their applications are principally determined by the properties they possess. In this study, we look at the phases present in HEAs and the properties exhibited by these alloys. Studied further are their prospective applications. The resource materials were sourced from Scopus database and google scholar website of articles published in the last five years, laying more emphasis on the most recently published works. In the study, it was concluded that double-phase HEAs are more useful than single-phase counterparts because of the synergy existing between the double phases. It was also found that single-phase HEAs are useful in automotive springs and electronic transistors, while double-phase HEAs are applied in biomedical implants.

Keywords:
High entropy alloys, body-centered phase, face-centered phase, hexagonal-centered phase, intermetallic compounds.

1. Introduction
The origin of high entropy alloys (HEAs) dates back to the beginning of 2000s when scholars were seeking for the development of alloys that have more than one principal elements as is the case of traditional alloy. Recall that traditional alloys like Zn-Cu (brasses), Sn-Pb (solders), Cu-Sn (bronzes), nickel-chromium alloys, or iron-carbon steel

contain one or two main principal elements. Nevertheless, researchers postulated that increasing the number of principal elements in an alloy could generate a material with improved characteristics. So, in 2004, Cantor and Yeh, in an independent research developed what was referred to as HEAs by mixing five principal elements in equal or near-equal proportions (Cantor et al. 2004, Yeh et al. 2004b). Schematic representation of traditional alloys and high entropy alloys are shown in Figure 1. This invention led to a birth of new category of alloys with exceptional characteristics and properties with prospective advanced applications. The discovery of HEAs was motivated by the prediction that by raising the number of principal elements in an alloy, new material with novel properties would evolve. Fortunately, the multiple principal elements interact with each other to form a complicated and unpredictable microstructure. The complexity of the microstructure gave rise to exceptional strength without compromising ductility, high wear and corrosion resistance, high fracture toughness and etc (Pan et al. 2021, Yang et al. 2019, Wang et al. 2021b, Qi et al. 2020, Chen et al. 2021).

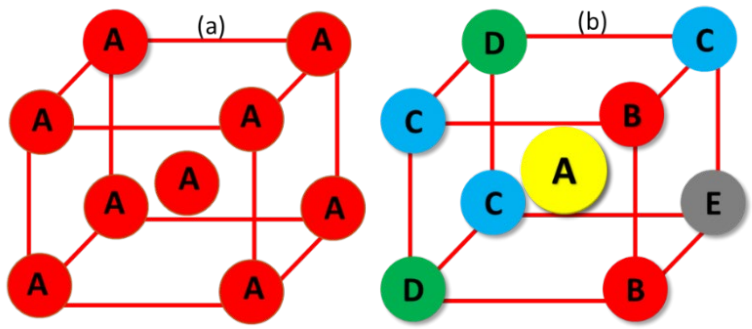

Figure 1: Schematic Diagrams of Alloys: (a) Traditional BCC Alloy with one Principal Element, (b) BCC High Entropy Alloy with 5 Different Elements

Meanwhile, the evolution of a particular phase or combination of phases in HEAs has its own peculiar advantages and disadvantages. For instance, HEAs with single BCC phase possess high hardness and strength but poor ductility with high susceptibility to corrosion. Those with single FCC structure possess excellent plasticity but weak strength. But those HEAs with HCP phase are rarely found and have high work hardening and ductility (Zhang et al. 2020).
One of the principal effects in HEAs is cocktail effect which states that HEAs display unpredictable properties. It is as a result of this postulation, and for the fact that phases present in high entropy alloys dictate their properties that the conceptualization of this study took place. So, this research is important because sound knowledge of the phases present in HEAs will expose probable properties and prospective applications of this all important alloy.
Ni-based alloys, Ti-based alloys and Al-based alloys have been observed to be susceptible to high temperature oxidation, weak in strength at elevated temperatures and poor in creep resistance. Hence, most applications of these alloys in aerospace, automotive, marine and military devices are being replaced with HEAs.

1.1 Objectives
The objectives of this study were to investigate different phases present in HEAs and how they influence their applications. The objectives are summarized as follow: (a) to investigate the various phases present in HEAs, (b) the properties of these phases and, (c) their applications.

2. Literature Review
This section discussed in summary various phases obtainable in high entropy alloys, their formations, and examples of some works carried out on them.
2.1. Single-phase HEAs
This type of HEAs possess a mono crystal configuration in the entire alloy. So, atoms are organized in a uniform repetitive manner in the entire material. It manifests in three major forms, namely, FCC, BCC or HCP. To ensure the formation of a single phase structure, there must be strict monitoring of the process and careful selection of the type and volume of elements to be used.

Examples of single-phase HEAs include: $FeCoNiCrMnAl_{0.2}$ (FCC) (He et al., 2014), CuCoNiCrAl0.5Fe (FCC) (Yeh et al., 2004a); AlCoCrCuFeNi (BCC) (Singh et al., 2011), Cu0.5CoNiCrAl (BCC), CuCoNiCrAl0.5Fe (FCC) (Yeh et al., 2004a); $(Ti_{0.11}Zr_{0.11}Hf_{0.11})Nb_{0.11}Re_{0.56}$ (HCP) (Marik et al., 2019).

2.2. Multi-phase HEAs

Multi-phase HEAs are those type that possess crystal phases that are more than one. They include those with a mixture of BCC and FCC, BCC and HCP, FCC and HCP, BCC and Laves phase, FCC and some intermetallic compounds, and even combination of three different phases. The good thing about multi-phase HEAs is that they have properties that are unique, which cannot be obtained in single-phase HEAs. For instance, FCC phase structure can only be good at ductility, but when there is a combination of BCC and FCC in an alloy, the alloy will have good strength and ductility at the same time. The high strength will be accentuated by the BCC phase while the ductility will be produced by the FCC phase. So, the synergy will equip the alloy with both strength and ductility. Examples of multi-phase HEAs include: AlCoNiFeTiSi (Ti2Co3Si-like HCP and Al-rich B2 phases), Ti20-Al20-V20-Fe20-Ni20 (BCC rich in Ti and FCC rich in Ni)(Ujah et al., 2023a), AlCrCoNiCu-Fe-Mn (BCC+FCC).

2.3. Nano-Structured HEAs (NHAs)

Nano-structured high-entropy alloys consist of a special type of HEAs that possess highly refined and fine-grained microstructure which lies between 1-100 nm. They are produced by advanced production processes like severe plastic deformation (SPD), powder metallurgy (PM) and mechanical alloying (MA). NHAs possess more improved properties than the traditional HEAs. This is because their fine grains tend to have a higher grain boundaries' energy density that can perform as the barrier to block dislocation movement of atoms, thereby increasing the strength and integrity of the alloy. The high energy density of the grain boundaries can equally highjack dislocations and prevent their transmission, resulting in increased strength and plasticity of the alloy (Hou et al. 2022). Examples of NHAs include AlCoCrFeNi (FCC + BCC phases) (Mansouri and Khorsand 2023), CrMnFeCoNi (BCC phase) (Fu et al.2021).

2.4. Amorphous High Entropy Alloys (AHEAs)

Amorphous high entropy alloys are non-crystalline high entropy alloys. In crystalline HEAs, the atoms are arranged in a regular pattern. However, in amorphous HEAs, the atoms are arranged in a disordered form, following non-regular pattern. They do not possess specific crystal structure, rather, their structure is irregular. Their structure closely resembles that of glass. The outstanding properties of AHEAs are high hardness (Wang et al., 2018), good thermal stability and excellent corrosion resistance (Zheng et al. 2021). Examples of AHEAs include: VAlTiCrSi, $Zr_xFeNiSi_{0.4}B_{0.6}$, CrMnFeCoNi (Wang et al.2021a).

2.5. Metallic Glassy HEAs (MGHEAs) or High Entropy Bulk Metallic Glass (HE-BMG)

Research shows that a few HEAs possess excellent glass forming ability (GFA) when rapidly cooled to form a hard non-crystalline transparent or translucent structure. The swift cooling inhibits the atoms from evolving into a crystalline microstructure, thus, culminating in a distinctive atomic configuration which is neither similar to crystalline nor HEAs amorphous HEAs. This type of rapidly quenched HEAs are referred to as high entropy bulk metallic glass (HE-BMG) (Wang, 2014). HE-BMG has outstanding properties much better than conventional bulk metallic glass (BMGs). They have more homogenous microstructure, lesser roughness and superior GFA than BMGs (Tong et al. 2019).

2.6. Ceramics-Reinforced HEAs Composite (CR-HEA)

CR-HEA composites consist of composite system where HEAs act as the matrix while the ceramics act as the reinforcing phase. The function of the HEA is to provide the frame work, ductility and toughness, while the ceramics provide the strength and load-bearing role of the system (Zhang et al. 2022). The synergy of the two materials culminate into a system with higher strength, higher wear resistance and toughness than that of either the ceramics or the HEA. An example of CR-HEA include: CoCrFeNi-SiC (FCC + graphite globules/fakes + silicides + chromium carbide platelets quaternary-phase structure) (Mehmood et al.2022).

3. Methods

The methodology was based on PRISMA frame work. A total of 100 journal articles were downloaded on Scopus database. The search keywords included articles on high entropy alloys published from 2019 – 2024. They were screened based on their relevance to the objective of the study. Finally, 35 articles were used for the study.

4. Data Collection

From the selected articles, authors able to obtain the relevant information that we analyzed and presented in the work as shown.

5. Results and Discussion

5.1.1. Properties and applications of single-phase HEAs

Table 5.1 shows the properties of the three main single-phased HEAs

Table 5.1 Comparative Characteristics of Single-Phase HEAs (Huang et al. 2019, Poletaev et al., 2019, Ujah et al. 2022c, Soni et al. 2018, Ujah et al., 2023c, Ujah et al. 2022b)

FCC	BCC	HCP
Its atoms are organized in cubic lattice. Each atom is encircled by 8 other atoms	Its atoms are organized in cubic lattice. Each atom is encircled by 6 other atoms	Its atoms are organized in a hexagonal lattice, with each atom encircled by 12 other atoms
The percentage of space occupied by atoms in the lattice (packing factor) is 74%	The packing factor of BCC is 68%. This implies that BCC has lower density of atoms than FCC and HCP	The packing factor of HCP is variable, sometimes it is 74%. Hence, higher density of atoms.
Plasticity: there are 4 slip planes and 3 slip direction, giving it a total of 12 slip systems with closely packed atoms (high ductility)	Plasticity: there are 6 slip planes and 2 slip directions giving it a total of 12 slip systems with remotely packed atoms (medium ductility).	Plasticity: there is 1 slip plane and 3 slip directions giving a total of 3 slip systems (low ductility).
Coefficient of thermal expansion: it has higher CTE than BCC	Coefficient of thermal expansion: it has lower CTE than FCC	Coefficient of thermal expansion: This lies between FCC and BCC.
Corrosion: FCC phase has higher corrosion resistance than BCC in corrosive media	Corrosion: BCC phase is more readily dissolved by corrosive ions than FCC phase	Generally, corrosion resistance of HCP falls between FCC and BCC but sometimes may deviate due to the elements present
Tribology: FCC has lower wear resistance than BCC and HCP	Tribology: BCC has higher wear resistance than FCC but lower than HCP	HCP has the highest wear resistance amongst the three phases
Mechanical strength: FCC phase is weaker than BCC and HCP in mechanical strength.	Mechanical strength: BCC phase has more superior mechanical strength than FCC phase	Mechanical strength: HCP is strongest of the three phases because of its strength of bonding
Magnetic properties: FCC phase has the lowest magnetic properties	BCC phase has the highest magnetic properties because of its high magnetic moment	HCP has higher magnetic properties than FCC but lower than BCC
Elements that induce the formation of FCC include Co, Ni, Mn, Cu, Al,	Elements that induce BCC: Cr, Fe, Mo, Ti, Nb, Ta, V, W	Elements that induce HCP include Hf, Sc, Zr, Ti,

Applications of single-phase HEAs include: FCC-phased HEAs which have high ductility is employed in production of electric wires, automotive springs and shock absorbers (Figures 2a & b); BCC-phased HEAs with high strength are applied in electronic transistors and diodes (Figures 2c & d) due to their high thermal stability, aerospace components like landing gear, airframe structures, and engine parts due to their high fracture toughness and high strength. HCP-phased HEAs have high strength and hardness at elevated temperatures, so, they are used in aerospace fan and turbine blades (Figures 2e & f) as they can withstand high stress at high temperatures; in automotive piston, piston rings and piston liners because they can withstand high temperature and high wear.

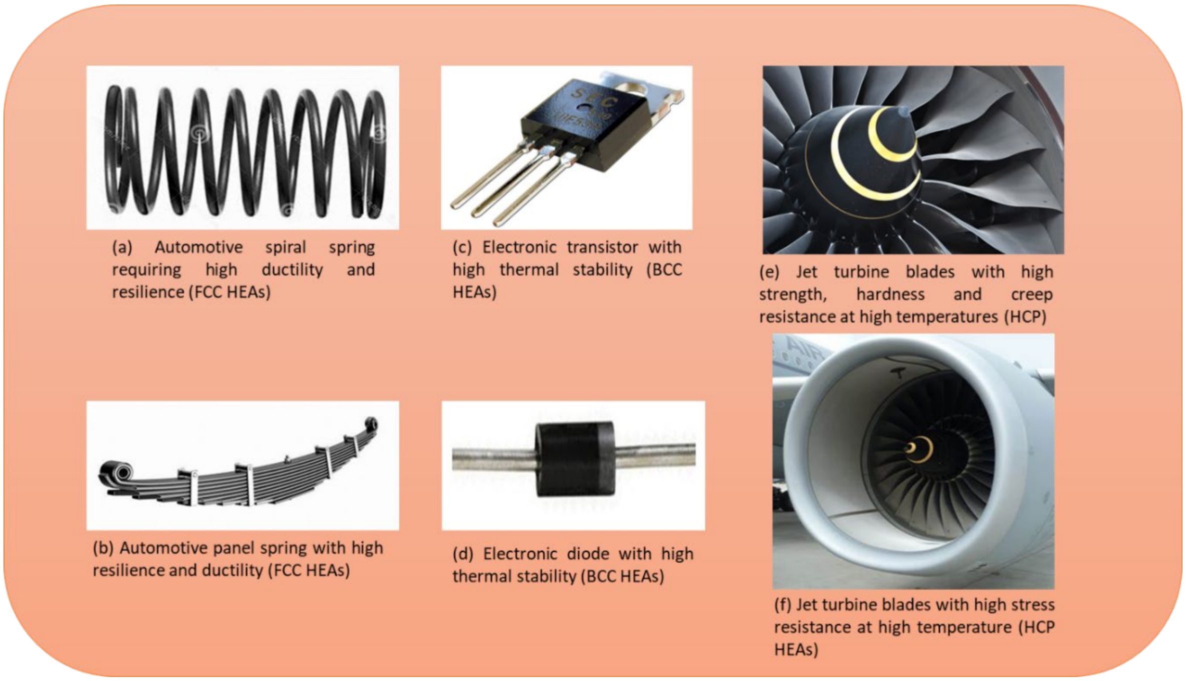

Figure 2. Images of Prospective Applications of Single-Phase HEAs

5.1.2. Properties and Applications of Multi-phase HEAs

Multi-phase HEAs are useful in many strategic applications because of their unique synergistic properties. They are suitable for use in medical implants and prosthetics (Li et al. 2023) as can be seen in Figure 3. Their suitability in medical and biomedical applications is because of their high strength-to-weight ratio. This property is required in leg prosthetic as it requires high strength but less weight so as to be able to carry the weight of the entire body without fracture. Besides their strength, they have good corrosion cum wear resistance (Glowka et al. 2022). Good corrosion resistance of multi-phase HEAs is a necessity for implants because they are in constant contact with the body fluids. Also, high wear resistance of HEAs is a prerequisite because implants or prosthetics are in constant friction with the part of body it is attached to.

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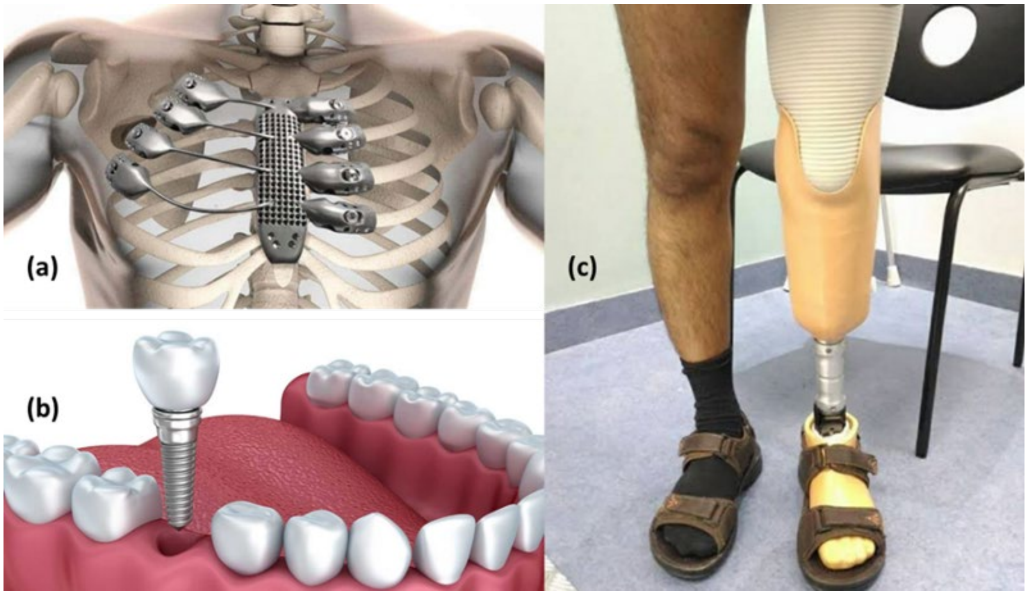

Figure 3. Images of Medical Implants (a) Ribs Implants, (b) Tooth Implant, (c) Leg Prosthetic

5.1.3. Properties and applications of nano-structured HEAs

The overall properties of NHAs include high strength, good formability, excellent wear resistance, high thermal stability and high ductility. These superior properties make them excellent materials for application in structural (aerospace components), wear-resistant (cutting tools) and medical (implants) contrivances. (Holmström et al., 2018) compared the edge deformation of cobalt alloy and HEA and discovered that cobalt alloy deforms far higher than HEA as seen in Figure 4c.

5.1.4. Properties and Applications of Amorphous High Entropy Alloys (AHEAs)

The outstanding properties of AHEAs are high hardness, good thermal stability and excellent corrosion resistance (Zheng et al., 2021). In terms of their production technique, additive manufacturing, like 3D printing is one of the most prominent processes. AHEAs are useful in applications where strength and high thermal stability are of essence, such as cutting tools. The high hardness required in cutting tools is embedded in AHEAs' random and disordered structural configuration. One of the applications of AHEAs is in self-healing coating in houses and bridges to avoid corrosion attack on the underlining metals, used in microelectronics for sensors and memory chips because of their high electrical conductivity and high storage density.

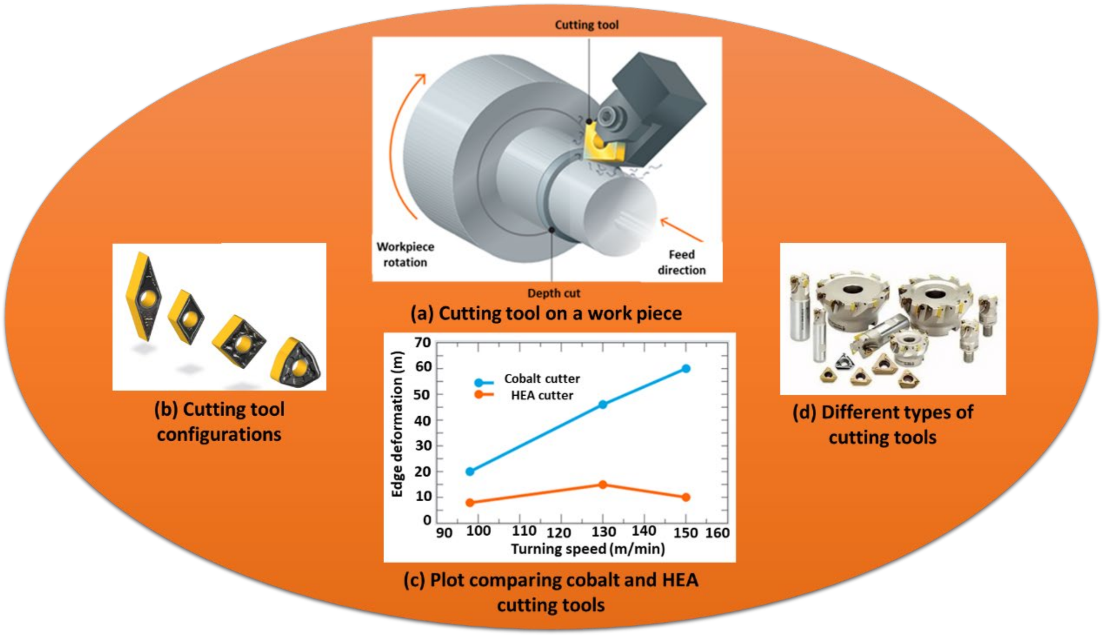

Figure 4. Images of Nano-structured HEA in comparison with Cobalt Cutting Tool. (a) Materials being removed from work piece by HEA cutting tool, (b) Different configurations of HEAs cutting tool, (c) Plot of edge deformation of cutting tool made from HEA and cobalt alloy, (d) Different shapes of cutting tools made from HEAs (Holmström et al.2018)

5.1.5. Properties and Applications of High Entropy Bulk Metallic Glass (HE-BMG)

One of the outstanding properties of this alloy that expanded its potential application is the lower Young's modulus (Takeuchi et al., 2016). Hence, it can accommodate a lot of energy or stress before breaking. More so, HE-BMGs' lower thermal conductivity/expansivity (Li et al., 2019) endear them as excellent player in development of fuel cells, batteries, supercapacitors and solar cells (Figure 5). This is because they rarely contract and expand when temperature fluctuates. There is very heightened research on their possible use in biomedical devices and implants as a result of their high corrosion resistance and good strength-to-weight ratio.

5.1.6. Properties and Applications of Ceramics-Reinforced HEAs Composite (CR-HEA)

CR-HEA has high resistance to wear and fracture (Liu et al., 2022) so, they are applied in automotive and aerospace exhaust system, engine blocks, crankshafts, and etc. For the production of engine blocks, CR-HEA composites are suitable as they can decrease the weight of the vehicle and provide the requisite strength and resilience. In the case of exhaust systems, CR-HEA helps to diminish the noise of the system. This is achieved by dampening the vibration of the exhaust system. It is vibration that brings about greater percentage of noise in exhaust system. So, while HEA matrix acts as the absorber and dissipater of the energy of vibration, the ceramic phase acts as a sound blocker. More so, the low thermal conductivity of the CR-HEA composites helps in reducing the thermal noise of the exhaust. In automotive brake pads, CR-HEA composites are suitable for dissipating heat from the pads, thereby improving the durability and performance of the brake system.

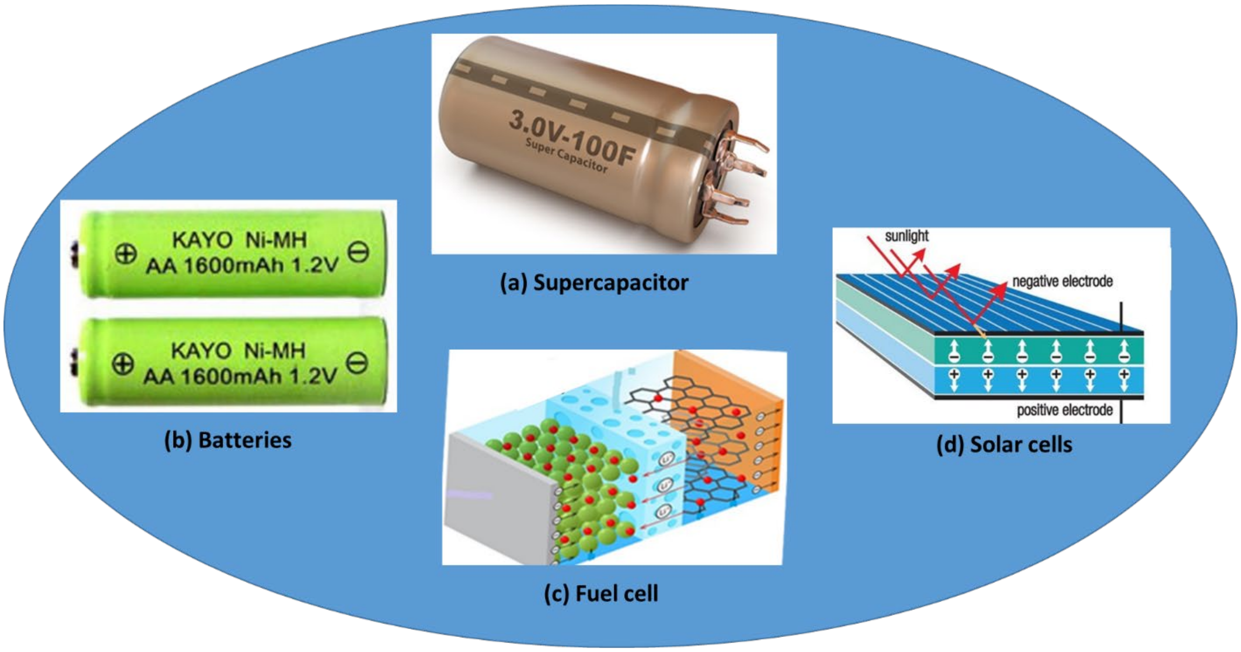

Figure 5. Images of Prospective Applications of HE-BMG

In summary, it is worthy to take a look at a comparison between HEAs and traditional alloys

Table 5.2. Comparison of HEAs and Traditional Alloys (Ujah et al., 2023b, Ujah et al., 2024, Ujah et al., 2022a)

High Entropy Alloys	Traditional Alloys
One of the major features of HEAs is huge compositional space; this permits for discovery of many new properties which do not exist now.	The compositional space of TAs is limited; no new properties can be discovered bedsides the existing ones.
It is easy to manipulate and tailor the properties of HEAs; for example, to have HEA with low coefficient of expansion (CTE), select elements with low CTE, like Ni, Al, Fe, etc. and alloy them.	Manipulation and tailoring the properties of TAs is not as flexible as that of HEAs; their properties are always fixed and consistent.
HEAs can be conditioned to be magnetic for their use in electrical, electronic or satellite applications by alloying magnetic elements like Fe, Ni and Co together.	TAs that have no magnetic properties cannot be tailored to be magnetic. Their properties are always consistent.
Production of HEAs can simply be by using powder metallurgy method that permits the alloying of multiples elements in a well-ordered method. Flexibility in production.	Some TAs may need sophisticated equipment and process in order to melt and achieve their specific properties. There is complexity in fabrication method.
Cocktail effect can induce unanticipated novel properties in HEAs because the multiple elements involved can react in sophisticated ways to generate exceptional properties that were non-existent before.	TAs usually generate material with consistent and known properties. There is no cocktail effect in TAs.
In HEAs, high thermal stability can be induced by alloying elements like W, Cr, V, Nb or Mo which has high melting points	TAs have specific temperature ranges which cannot be manipulated.
HEAs are relatively less dense than TAs because they contain more pores than TAs and this can be an advantage.	TAs are more densely configured and so heavier than HEAs which increases their fuel consumption capacity when used in aerospace or automobile applications.
Lattice distortion effect in HEAs induces fracture toughness with high resistance to plastic deformation.	There is no such lattice distortion effect in TAs, hence, they are prone to plastic deformation.

High entropy of mixing and lattice distortion induce solid solution strengthening with high resistance to deformation in HEAs.	Mixing reaction in TAs form ordered structure like precipitates or grain boundaries, which has lesser level of strengthening.
High entropy effect in HEAs does not permit formation of intermetallic compounds easily in the alloy.	In TAs, formation of precipitates and intermetallics is common.
Sluggish diffusion effect reduces grain growth and phase separation	There is usually swift diffusion of atoms in TAs, hence, there may be grain growth.
Severe lattice distortion retards the evolution of defects like loose grain boundaries or helps in pinning them.	There is no severe lattice distortion, so, there can be evolution of weak grain boundaries and loss of strength
High entropy and lattice distortion effects in HEAs improve their resistance to corrosion	In TAs, these effects are absent, so, rate of corrosion may be higher

6.0. Conclusion and Recommendation

Study of the characteristics of different phases formed in HEAs and their production techniques have been conducted. The following conclusions were drawn:

A) Single-phase HEAs have their unique properties, like high strength in BCC and high ductility in FCC; but a dual-phase HEAs enjoy a combination of those properties.
B) Tailoring of phases can be achieved by selection of elements during the development of HEAs
C) Applications of HEAs are influenced by the type of phases present in them. So, careful selection of elements is necessary in developing specific HEAs for particular applications since elements which make up the alloys contribute to the type of phase generated.

D) Prospective applications of the different-phased HEAs include: Single-phase HEAs ae applied in automotive springs, electronic transistors, aerospace turbine blades. Multi-phase HEAs are useful in biomedical implants, aerospace and automobile applications; nanostructured HEAs are useful in cutting tools; amorphous HEAs are useful in self-healing coating, microelectronics for sensors and memory chips. High entropy bulk metallic glasses are useful in fuel cells, batteries, supercapacitors and solar cells; and ceramics-reinforced HEAs composite is useful in automotive and aerospace exhaust system and engine block.

E) We recommend future research on the following: Effect of stacking faults on the properties of HEAs, use of HEAs as reinforcements in composite materials, influence of irradiation on HEAs, and the relationship between twinning and texture of HEAs and their properties.

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