High Entropy Alloys: The Materials of Future

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Abstract

High Entropy Alloys (HEAs) have recently attracted the researchers' attention as a new track in materials design. Research on HEAs has stimulated new ideas and inspired the exploration of the enormous composition space offered by multi-principal element alloys. HEAs can be simply described as alloying systems that are composed of multi-elements in equimolar or near equimolar ratio. Therefore, HEAs have unique properties which significantly differ from the traditional alloy systems. The current review article is concerned with the definition of HEAs, their development history, and their four core effects which make them different from the traditional alloys. Fabrication routes of HEAs with special emphasis on processing via casting technique are surveyed. The innovative microstructure of HEAs that lead to extraordinary mechanical properties is also discussed. Finally, the promising industrial applications and the future insights of these multi principal alloys are covered.

1. Introduction

Metals have been the most essential materials for thousands of years; however, their utilization is influenced by monetary and environmental concerns. For example, few weight percentages of Cu were added to Ag to produce an alloy for coinage a long time ago, because pure Ag is too soft, and also Cu was added to Fe in historical instances to enhance its strength. This means that the approach of compositional adjustment of alloys has been used for a long time to lend desirable properties to materials. Except for some cases, the basic alloying concept of small elemental additives as secondary elements to a primary element has remained fixed over millennia [1]. Typically, at the beginning of the modern era, classical alloys such as aluminum alloys or steels involved the addition of relatively small amounts of secondary elements to a primary element (e.g., Fe plus C or Al plus Cu). Later on, stainless steels, Ni-based superalloys, Ti-alloys, and composites have been introduced and widely applied in different industries. However, with these extensive efforts on developing these traditional alloys, the development process is approaching its limits. On the other hand, the continued development of high-performance materials is necessary to increase energy efficiency and sustainability [2]. Recently, a new alloying design that combines several principal elements in high concentrations to have new materials named high-entropy alloys (HEAs) has been emerging. High-entropy alloys have significantly extended the compositional space for alloys design. This variety of elemental selection in HEAs can alleviate some of the concerns that are related to increasing strength while maintaining good ductility [3, 4].

In the current review, the historical background of HEAs, their definitions, their design strategies, and their unique properties are introduced. This is followed by presenting the fabrication routes of HEAs with special emphasis on casting technique and finally, the industrial applications and future insights of these multi principal alloys are discussed.

2. Historical background of HEAs

The initial study on multi-principal element crystalline alloys (MPECAs) began as an undergraduate project in the late 1970s and was followed by another undergraduate thesis in 1998. These studies were modified and expanded further and

published in 2002 as conference proceedings. Research on HEAs, as a group of MPECAs, started as a series of projects and theses in 1996 [5]. From the results of these projects, Yeh et al. [6-8] and Cantor et al. [9-11] independently published the first papers on high HEAs in 2004, introducing HEAs as alloys of five or more metals in near-equimolar/ equimolar concentrations.

Yeh and co-workers [6-8] thought to increase the configurational entropy of mixing by an amount sufficient to reduce Gibbs free energy, thereby preventing the formation of harmful intermetallics and forming solid solutions (SS) instead. This was an intuitive idea because the conventional view based on binary phase diagrams is that the probability of reaction and compound formation increases if the number of elements in the concentrated alloys increases. The reasoning of this was given by Yeh et al [7] as follows: if the elements in an alloy increased, the contribution of entropy to the total free energy would exceed the enthalpy contribution and, thereby, solid solutions are stabilized.

Nowadays, the HEAs field has emerged quickly and is not only limited to single-phase solid solution microstructure. HEAs have then been upgraded to complex concentrated alloys that have multi phases. Several pieces of research have been devoted to reviewing HEAs from a thermodynamics point of view [12-15]. Others [16,17] focused on their fabrication techniques based on gas, liquid, or solid processing methods. Some recent works have been concerned with the microstructure features and mechanical properties of HEAs, hence demonstrating their potential applications where they can outperform conventional alloys [18-20]. Gao et al [21] in their published book showed that the number of publications on HEAs increased significantly from six papers in 2004 to 371 in 2015. This clearly reflects the worldwide growing trend of research on HEAs.

3. Definitions of HEAs

High-entropy alloys which have recently grasped the attention due to their unique microstructures, compositions, and controllable properties can be defined in different ways. Simply, HEAs can be defined as solid solution alloys that have equal to or more than five main elements in equal or near-equal atomic percent [22]. Yeh et al. [7,8], and Cantor et al. [9] named HEAS as multi-component alloys. There are also some similar names, such as equimolar alloys, multi-principal-elements alloys, equiatomic ratio alloys, and substitutional alloys [23]. Figure 1

explains the difference between HEAs with multi-principal elements and conventional alloys.
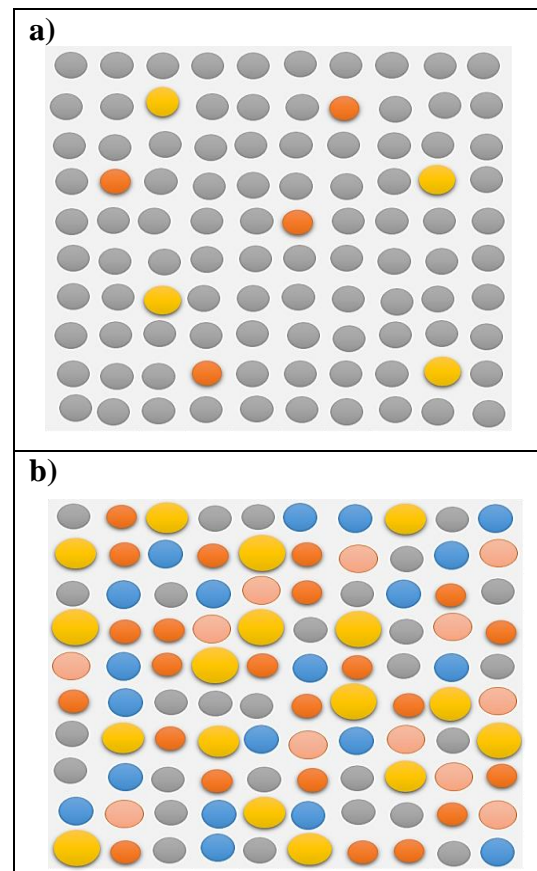
Fig. 1 Illustration of a) Conventional alloys and b) high entropy alloys.

All the prementioned names refer to the same concept which is the composition-based definition. This kind of definition, however, prescribes elemental concentration ns only and does not take into consideration the magnitude of entropy. Moreover, this definition further neglects the presence of a single-phase SS [3- 5]. Another way of defining HEAs is an entropy-based concept. This alternate definition divides the alloys based on their entropy into low, medium, and high entropy alloys [24]. Yeh et al. [25] categorized the alloys as a function of ΔS_{conf} (the configurational entropy). According to this approach, alloys can be considered as HEAs when their ΔS_{conf} at a random state is higher than 1.5R (R: gas constant), regardless of whether they are single/multiphase at room temperature (RT). When the values of ΔS_{conf} fall in the range from 1R to 1.5R, alloys are classified as Medium Entropy Alloys (MEAs). Finally, commercial aluminum (7075) and magnesium (AZ91D) alloys that have ΔS_{conf} less than 1R are defined as low entropy alloys (LEAs).

The entropy-based definition is challenging, however, can cause confusion if the composition is considered along with the entropy. These challenges become more complicated if the prementioned definitions are mixed with the targeted outcome of producing single-phase SS alloys [22, 23]. Some researchers [26], restricted the definition by considering HEAs is the alloy that contains (single-phase or be equimolar) and others broadened the definition scope (to include 4 component systems and alloys with SSS, ideal > 1.36R or SSS, ideal > 1.5R). Earlier definitions prefer atom configurations at the highest temperatures and thus including the liquid state, while later interpretations emphasize lower temperatures [27]. Concluding, there is no correct or mistaken definition, and the appropriate approach will be related to the work being performed. Considering, the different principal elements system of HEAs, some effects that are much less important in the conventional alloys are considered essential in HEAs. These effects are called the four 'core effects' of HEAs.

4. The Four Core Effects of HEAs

There are several factors that influence the microstructure and hence the properties of HEAs. Among these, there are four factors that are the most influential and they are known as the 'four core effects' [27]. In terms of properties, the 'cocktail effect' is the governing factor that is related to the mixture rule that includes the interactions of the atoms and the severe lattice distortion. From a thermodynamics point of view, the 'high entropy' effect is the most influential since it interferes with the formation of complex phases. For kinetics, there is an effect called 'sluggish diffusion' which possibly slowdown phase transformation. The fourth effect is the 'severe lattice distortion' which could change the properties to an extent. Following is a detailed description of each effect and how it contributes to the microstructure and properties of HEAs [28].

4.1. Cocktail Effect

This effect relates the properties of HEAs to their composing phases and elements. This effect should be majorly emphasized in HEAs since at least five main elements participate in the properties of the material [29]. As mentioned above, HEAs might be single-phase or multi phases alloys relying on the composition and the processing method. Concluding, the HEAs' properties are from the whole contribution

of the constituting phases by the influence of phase-type, shape, properties, and distribution [27,28]. Further, each phase is a multi-element solid solution and can be considered as an atomic-scale composite. The composite properties rely not only on the properties of the composing elements following the mixing rule but also on the severe lattice distortion and the interactions between all the elements [25]. Therefore, it is important for a material designer to properly correlate all the factors involved before choosing the suitable composition and manufacturing processes for HEAs.

Examples that explain the cocktail effect can be found in different systems such as the addition of Al which is a soft and low-melting-point element that can actually harden HEAs. Figure 2 [28] shows the plot of $Al_xCoCrCuFeNi$ alloy hardness as a function of Al at.%. It is observed that the Al significantly enhances the alloy hardness. This is partly because of the strong cohesive bonding between the existing elements and Al, its larger atomic size, and also due to the formation of a hard BCC phase. Thus, the macroscopic properties of HEA are highly influenced by the excess elemental quantities produced by reactions between elements and lattice distortion and not only by the averaged properties of the constituting elements [30].
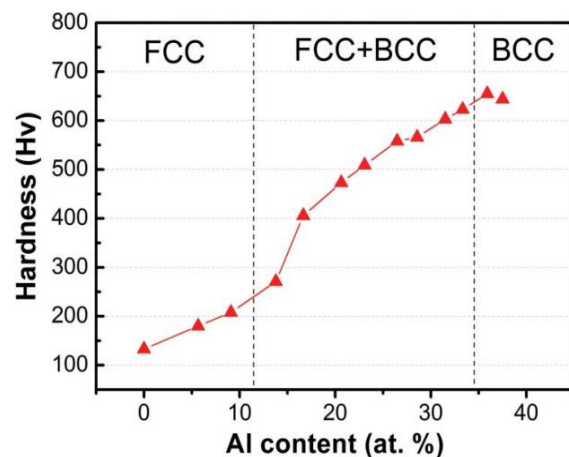
Fig. 2 Hardness distribution in $Al_xCoCrCuFeNi$ alloys vrs. Al content [28].

4.2. High Entropy Effect

The high-entropy effect is founded on the concept that as the mixing configurational entropy increases, the free energy of solid solution phases decreases, and thus they can be easily formed, especially at higher temperatures hence ($G = H-TS$), where H is enthalpy, G is the Gibbs-free energy, S is entropy and T is temperature [31]. However, not all the multi-elements in the equimolar ratio form solid solutions at the

central point of the phase diagram. It has been also reported that only accurately selected compositions that satisfy the HEAs-formation criteria form solid solutions rather than intermetallic compounds [25, 28]. The solid-solution phase as understood from the theoretical physical metallurgy is named a terminal solid solution which is based on one element as a solvent, and other minor elements as solutes. In the case of HEAs, because of the equimolar portions of the elements, it is very hard to differentiate the solute from the solvent. It has also been reported that in the multi-principal-element alloys, the number of phases that can be formed is much lower than the maximum number of phases that are calculated based on the Gibbs phase rule [32] and they are almost simple phases of face-centered-cubic (FCC) or body-centered-cubic (BCC) solid solutions [33]. Based on the above discussion, the design of HEAs can extend the solution limits between the various elements, which confirms the contribution of the "high entropy effect".

4.3. Sluggish Effect

It is well known that in order to form new phases, diffusion of a large number of different atoms should occur to fulfill the partitioning of composition in HEAs. However, in crystalline HEAs, there are limited vacancies that are needed for substitutional diffusion. This is due to the fact that every vacancy is also accompanied by excess mixing entropy and positive enthalpy of formation, which in its turn minimizes the mixing free energy for a certain temperature at a specific equilibrium concentration [34]. In the solute matrix, each vacancy is surrounded by different elemental atoms during diffusion. It has been suggested that higher activation energy and slower diffusion in HEAs are due to the large variation of lattice potential energy (LPE) among lattice sites. The numerous low-LPE sites act as traps and suppress atomic diffusion, which is the so-called 'sluggish diffusion effect' [29].

Yeh [36] calculated the coefficients of diffusion for the elements in HEAs, stainless steel, and pure metals. The values of diffusion rates were as follow: HEAs < stainless steels < pure metals. This comparison emphasizes the role of the 'sluggish diffusion effect' in controlling the phase formation in HEAs. Tsai et al [35] in their work on the near-ideal solution system of Co-Cr-Fe-Mn-Ni single-phase FCC solid solution, proved that the degree of sluggish diffusion is related to the number of elements in that matrix for the same element. Figure 3 shows that the

degree of sluggish diffusion (Q/T_m) is related to the number of elements in that matrix. The Q/T_m (activation energy/melting point) values which refer to the degree of sluggish diffusion are the highest in CoCrFeMnNi HEAs, Fe-Cr-Ni (-Si) alloys are the 2nd and pure metals are the lowest. [35].
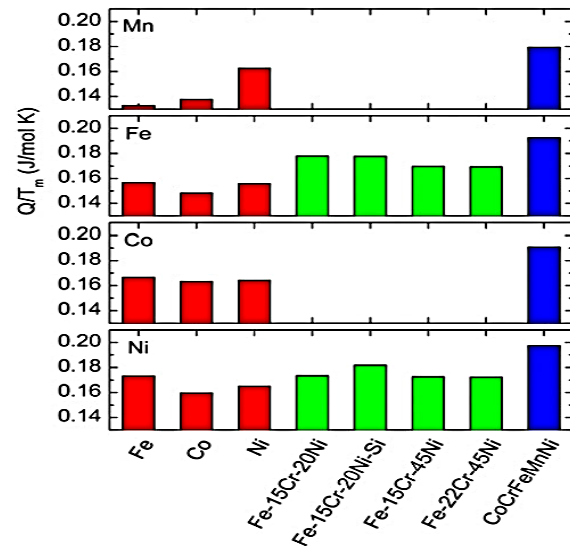
Fig. 3 Melting-point normalized activation energy of diffusion for Cr, Mn, Fe, Co, and Ni in different matrices [35].

4.4. Severe Lattice Distortion Effect

The effect called 'severe lattice-distortion' implies that each atom suffers both stress and lattice strain due to the atomic size differences with the surrounding atoms in the multi-element matrix of HEAs as illustrated in Fig. 4.
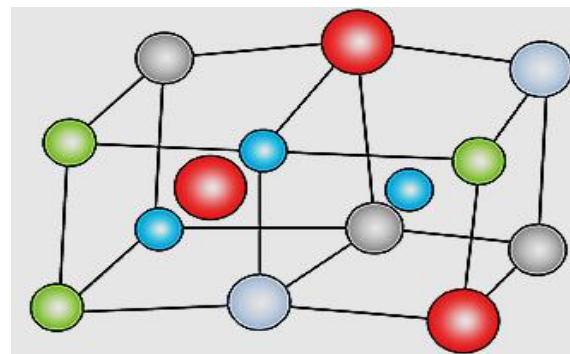
Fig. 4 Severe lattice distortion with elements addition [25].

Also, the differences in the bonding energy and crystal structure might increase lattice distortion further due to the non-symmetrical bindings and electronic structure that exist between the neighboring atoms

[36]. Moreover, this non-symmetry is not identical which increases the distortion severity compared to the conventional alloys that are based on one principal element [37].

5. Manufacturing Routes of HEAs

The high-entropy alloys are basically prepared in the same way as the conventional alloys. The most common classification of HEAs manufacturing methods is based on the initial state of the material. Liquid state processing includes casting, plasma spray, and laser melting, gas state-based processing comprises the different sputtering techniques while fabrication in solid-state involves mechanical alloying and consolidation [33,38]. Regardless of the fabrication method of HEAs, the most essential issue is to properly mix the different elements to make HEAs with the desired structures and to maximize the contribution of every element to the properties whilst maintaining high entropy of mixing. Zhang et al [39], stated that manufacturing routes of HEAs can be chosen based on the required shape and dimensions. Accordingly, there are four types of HEAs based on their dimension: zero-dimensional HEAs (powders), one-dimension HEAs (fibers), two-dimension HEAs (high-entropy films and coatings), and finally three-dimension HEAs (bulk). Following this classification, of Table 1 shows the manufacturing processes of HEAs based on their dimensions as adapted from [39]. For example, ball milling is used to produce powders, laser cladding deposit coatings while induction melting, arc melting and Bridgeman methods are used to process bulk HEAs.

Table. 1 Manufacturing processes of HEAs based on their dimensions.

HEAs type	Manufacturing processes
Powders	Ball milling-Carbothermal shock synthesis
Fibers	Melt spinning- Taylor/Ulitovsky method
Films	Laser cladding- Magnetron sputtering
Bulk	Bridgeman method- Induction melting-arc melting

Another issue that should be considered while selecting the manufacturing route; is the desired microstructure of HEAs product. If HEAs metal glasses are required then copper-mold suction casting is the suitable method. Gradient structures HEAs are best fabricated by co-sputtering or high gravity casting. Single crystal HEAs are prepared by liquid metal processing using the Bridgman solidification method [37,39].

In the following subsections, separate examples of the most widely used HEAs processing methods are outlined with special focus on processing by melting and casting. **Fig. 8** the manufacturing processes of HEAs based on their dimensions [39].

### 5.1. Processing by Mechanical Alloying (0-D HEAs)

Mechanical alloying is simply three steps process. Firstly, the alloy material is ground in a ball mill, then the produced HEAs powder is consolidated by one of the prementioned methods to be compressed and sintered. Finally, heat treatment is carried out to relieve existing internal stresses produced during cold compaction. The ''MA + SPS'' method is considered the most suitable fabrication method in manufacturing HEAs based on solid-state. SPS process consists of the application of pressure under a high heating rate and under the influence of an electric current [40]. The HEAs prepared by the ''MA + SPS'' method exhibit distinguished mechanical properties. The hardness of CoCrFeNi HEAs prepared by ''MA + SPS'' technique (570 HV), is 5 times greater than that by the conventional casting (119 HV) as reported by Praveen et al [41].

5.2. Processing by melt extraction technique (1-D HEAs)

The melt-extraction technique is a good choice when HEAs fibers are required. Firstly, a quartz glass wherein the rod material is inserted inside the boron nitride crucible, surrounded by an induction coil, and the rods are heated to melt continuously the fed metal bar. The HEAs fiber filament is then pulled out and cooled rapidly as exits from the rotating copper wheel under an argon atmosphere.

5.3. Processing by Sputtering Technique (2-D HEAs)

Processing HEAs using gas state-based method has been developed to produce coatings for tribological applications. It can be done using the gas puttering technique [44, 45]. In this process, a thin film is deposited onto a substrate by sputtering the atoms away from a target under the gas ion bombardment. Excellent coatings could be achieved, Fig. 5 [46], using this technique depending on the gas flow ratio.
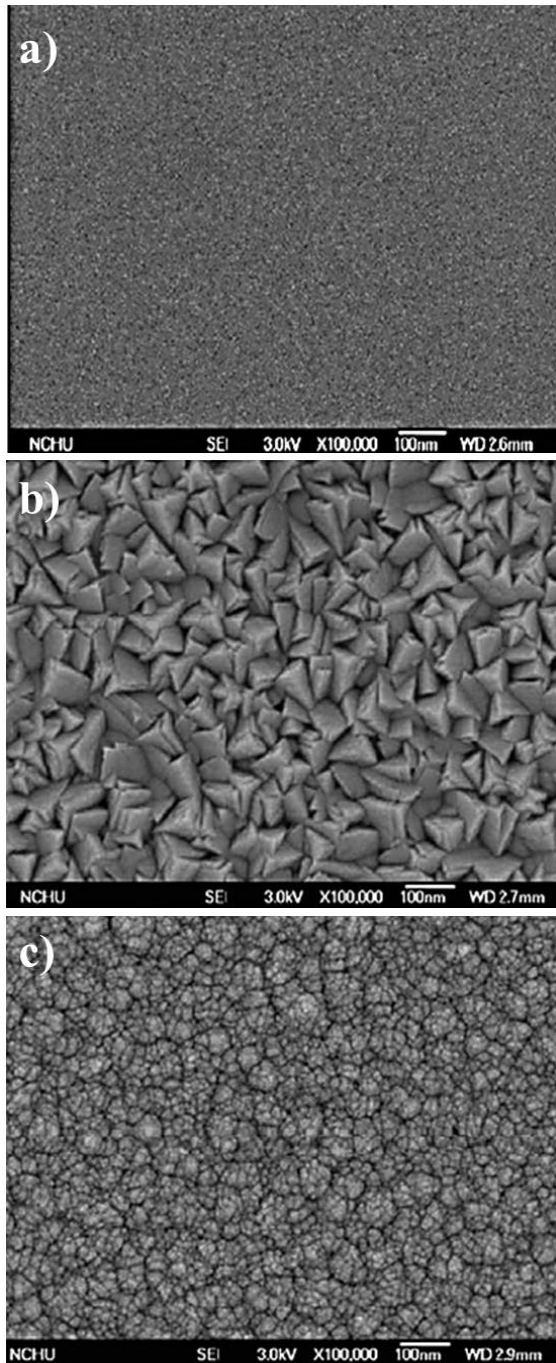
Fig.5 SEM surface morphologies of (AlCrTaTiZr)Nx coatings deposited with different N_2-to-total flow ratios (RN): (a) surface and (b) cross-section for RN = 0%; (c) surface and (d) cross-section for RN = 10% [46].
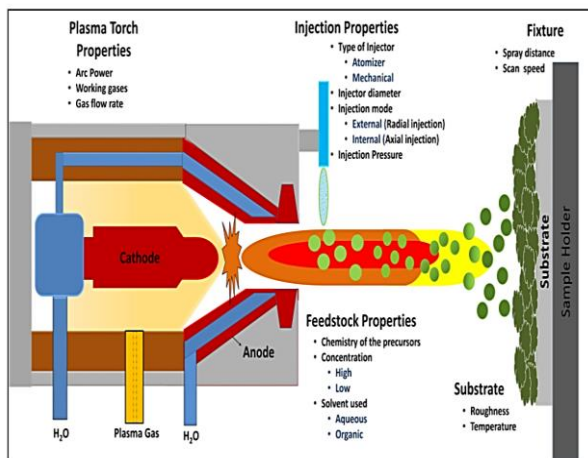
5.4. Processing by cladding (2D -HEAs)

In the surface cladding process, an additive cladding layer is first built to cover the substrate surface then this layer melts with energy heating into a thin layer to form a metallurgical bonding with the substrate [4]. According to the heating sources, cladding can be divided into laser cladding and plasma cladding. For example, alloy Al1.5CrFeNiTi0.5W0.5 was manufactured by Liang et al. [47] using laser cladding on 304 stainless steel, and the HEA coating shows the optimum wear resistance. Figures 6 & 7 [48] show the differences between laser and plasma spray cladding processes respectively.
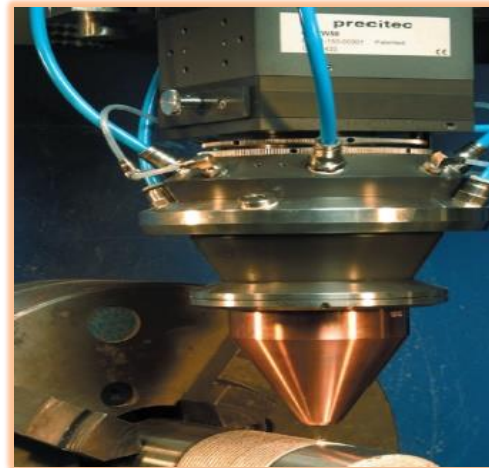
Fig. 6 Laser beam cladding process.

Fig. 7 Plasma spray cladding [48].

5.5. Processing by Casting Technique (3D-HEAs)

Processing HEAs in the liquid state is performed by casting. Casting is an advantageous method by being an economical technique that can process HEAs when bulk/3-D HEAs are required [16]. There are three melting methods to process HEAs: arc melting, induction melting, and Bridgman solidification. In the case of HEAs liquid processing, elemental segregation should be considered since there are various principal elements are included. Moreover, the melting process should be repeated 5 times or

more depending on the fluidity of the alloy constituents. Further, the differences in the melting points of the constituting elements will increase with increasing the number of components [27]. Therefore, choosing the cocktail of HEAs elements along with the proper melting process should be considered. The selection of suitable melting methods relies on the type of elements, the desired microstructure, and the product shape. In the following subsections, the different methods to melt HEAs and to control their solidified microstructure are discussed.

5.5.1 Melting Methods

5.5.1.1 Arc Melting

Arc melting is the most popular liquid processing method of HEAs. In the case of melting by arc, the charge that consists of several elements is inserted into the copper melting pot that is cooled by water, and the torch is applied closely. The torch temperature of the furnace can be increased to higher than 3000°C by controlling the electrical power [49]. Arc melting is therefore the ideal method to melt refractory HEAs. The process should be repeated several times to ensure homogeneity of the produced sample. In the case of reactive metals, the open-air arc furnace system, however, is not suitable. For example, titanium-containing HEAs should be melted using a vacuum arc furnace. A schematic representation of the vacuum arc melting process is shown in Fig. 8 [49].
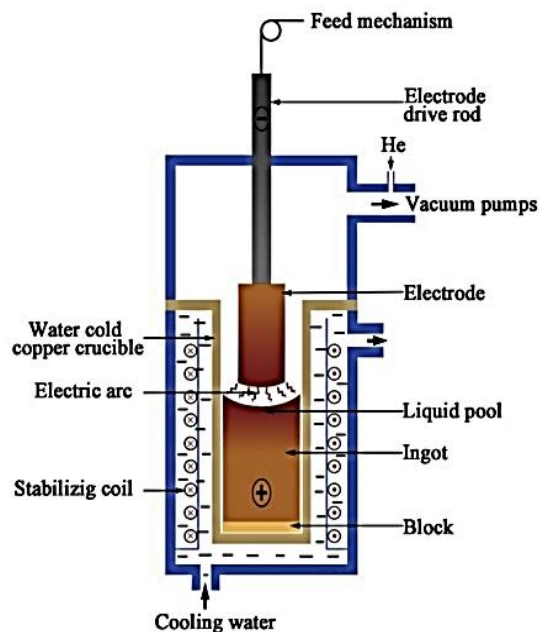
Fig. 8 A schematic representation of the vacuum arc melting process [49].

A photograph of the melting chamber of an arc furnace that works under a vacuum is also shown in Fig. 9. The furnace has three main units: melting chamber, control unit, and chiller. As the first step, the pieces of pure metals are placed in the water-cooled crucible and the melting chamber is evacuated. When the vacuum reaches the required degree, argon gas is injected into the vacuum chamber then the high voltage is applied between the copper crucible and the arc gun. Once the arc touches the copper crucible, the arc is initiated. It is also recommended to apply electromagnetic stirring to ensure homogeneity of the produced HEAs in addition to repeating the melting process. Figure 10 shows the influence of remelting under electromagnetic stirring on the homogeneity of Ti5553 alloy using vacuum arc melting.
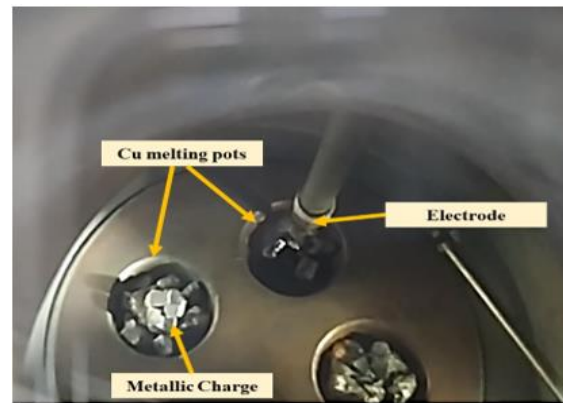
Fig. 9 A photograph of the arc melting chamber.

Fig. 10 Homogenization of an arc melted sample by repeating the melting process.

In regards to the properties of cast HEAs, Zhang et al. [50] prepared $CrFeVTa_{0.2}W_{0.2}$ and $CrFeVTa_{0.1}W_{0.1}$ HEAs by arc melting and the alloy samples showed excellent resistance to heat-softening. The yield stress of these alloys at the temperature range of 600–800°C exceeded that of Inconel 718 and Haynes 230 superalloys. Ma et al. [51] melted $Al_{0.5}CrCuFeNi_2$ HEAs in an arc melting furnace. The cast specimen exhibited FCC solid solution with a dendrite structure. Both of $Nb_{25}Mo_{25}Ta_{25}W_{25}$ and $V_{20}Nb_{20}Mo_{20}Ta_{20}W_{20}$ alloys were obtained with single-phase BCC structures using

arc melting in the work of Senkov et al [52]. Qin et al [53] reported a new equiatomic-ratio CoCrCuMnNi HEAs, which they prepared using vacuum arc melting. The as-cast alloy exhibited excellent mechanical properties with yield strength, tensile strength, and elongation of 458 MPa, 742 MPa and 40 % respectively. They observed that the nanometer precipitates (5–50 nm in size) that are found in dendrite and inter-dendrite zones of HEA are the key factor of these excellent properties.

Arc melting method, however, is not a suitable method for all HEAs systems. Low melting temperatures HEAs containing, e.g., Mg, Zn, and Mn can be evaporated under such high temperatures of the melting torch. Therefore, resistance heating or induction heating are recommended in this case.

5.5.1.2 Resistance Melting

Resistance furnaces can be used to melt HEAs which do not require either high heating power or a vacuum system. In this furnace, a solid charge is positioned inside the crucible and then heated by radiation from the electric-resistance coils. The molten metal can be lifted out through the spout (hole) by tilting the whole furnace. Figure 11 [54] shows a schematic of a resistance furnace that is equipped with a stirrer to ensure homogeneity of the processed HEAs and a degassing system to avoid metals oxidation.
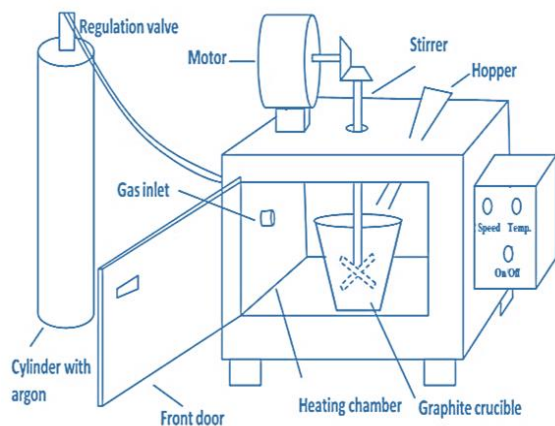

Fig. 11   Schematic of a resistance furnace equipped with a stirrer and degassing system [54].

5.5.1.3 Induction Melting

In Induction furnaces, an electric-induction coil is embedded into the furnace walls, Fig. 12 [55]. The induced current in this case heats any metallic object that obstructs the electromagnetic flux. Low and high-frequency induction furnaces are available. Alloys, such as HEAs may favor low frequency to enable the stirring of the different elements. Induction furnaces are speed melting furnaces and therefore, they are widely used in the industry they are ideal to prepare HEAs whether ferrous or nonferrous groups except for those containing refractory metals. Induction melting is generally distinguished by the ability to produce homogeneous compositions, distribute the temperature within the molten metal uniformly and control the furnace atmosphere. Repetition of the melting process in the case of HEAs is necessary to obtain a homogenized sample.

In our previous work [56] a $Fe_{31}Mn_{28}Ni_{15}Al_{24.5}Ti_x$ alloy was melted in an induction furnace and a lamellar microstructure that contains two phases: a lamellar structure (ordered BCC) that consists of mainly Al and Ni with some Fe and Mn and the second phase/lamella (FCC) was composed of Fe and Mn with some Ni and Al. it was observed that adding Ti by 3 wt.% significantly improves the hardness of the alloy from 300 to 500 (Hv) by the combined effect of solid solution strengthening and decreasing the lamellar spacing.
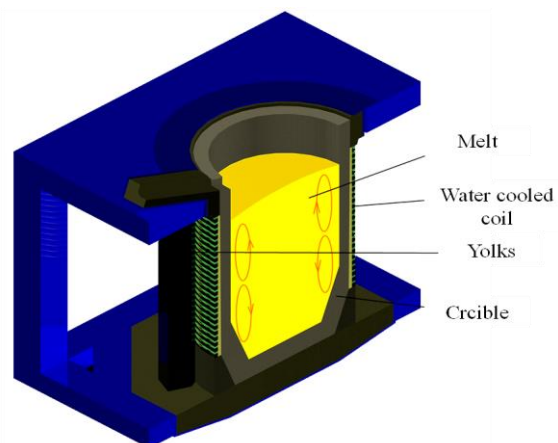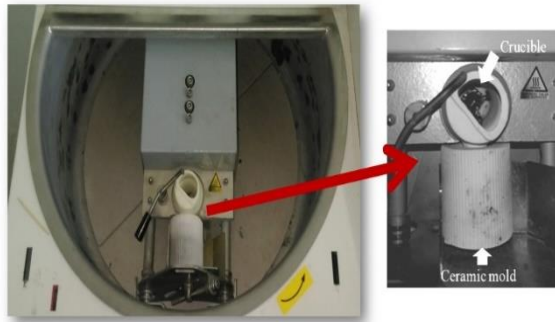

Fig. 12   Induction melting method [55].

As mentioned in section 5.5.1, if reactive metals as Ti will be included as a principal element in the HEAs, vacuum induction melting should be used to avoid the high affinity of Ti to oxygen. Figure 13 shows a small size vacuum induction melting furnace. In this furnace, the ceramic mold that contains the cavity is prepared by investment casting, and the pieces of different metals are inserted into the crucible then the chamber is closed and a vacuum is applied. Once the melting process is completed, pouring into the mold cavity starts by pressing the start button in the control panel. Concluding, HEAs containing

reactive metals can be successfully prepared using vacuum induction melting.

Fig. 13 Vacuum Induction melting furnace.

5.5.1.4 Induction-levitation-melting

Another induction melting technique is called "Induction-levitation-melting" (ILM) has been suggested by Xia et al [57]. In this method, there is a vacuum chamber in which the pure metals are inserted into a copper crucible (water-cooled). High purity argon gas is then supplied to the chamber to melt under a protective atmosphere. After the induction coil that surrounds the crucible is electrified, the charge is heated using the induced current. This process is effective and takes short time due to the good conductivity of metals. Additionally, stirring by the electromagnetic field is applied which is helpful in homogenizing the alloy during melting. Xia et al. [57] reported that AlxCoCrFeNi HEAs prepared by this method have the same structures as those prepared by arc melting. However, this approach has an advantage over arc melting that is larger sized (> 1 Kg) samples can be produced [58]. Figure 14 [59] describes schematically the ILM method.
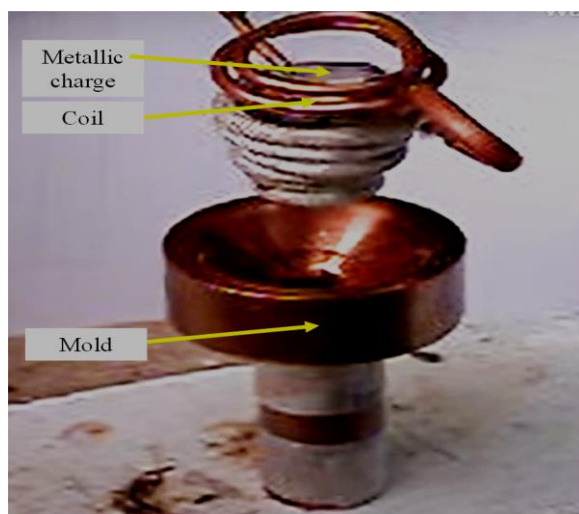
Fig. 14 Schematic of induction-levitation-melting [59].

5.5.2 Solidification methods

The kinetics through which the microstructure of HEAs is formed during processing in the liquid state was described by Singh [60]. This figure shows that the microstructure of HEAs strongly depends on the cooling rate. The low cooling rates favor the formation of dendritic/interdendritic microstructures because of the elemental segregation. On the other hand, high cooling rates result in polycrystalline phases with few nanometers in size. To summarize, in order to obtain HEAs with single solid solution, high cooling rates should be applied to avoid the formation of multiple phases which decreases dramatically the configurational entropy of mixing [21, 23].

Zhang et al [16], stated that the grain growth that occurs during the solidification of HEAs can be controlled by both the gravitational field and temperature field. The gravitational field encourages gravity segregation and hence promotes the formation of microstructural and compositional gradients in the HEAs. The copper-mold suction method, on the other hand, is used to increase the cooling rate during the solidification process. Bridgman method is mainly applied to control the direction of the solidifying melts. The different solidification methods that are used to control the microstructure of HEAs are described below.

5.5.2.1 High Gravity Method

In this method, the centrifugal force is applied to simulate the external gravity field during solidification. This results in pushing the denser elements along the direction of gravity thus creating a compositional gradient from inside the ingot. The alloy ingots are then cut into a series of samples with graded compositions [61]. The AlxCoCrFeNi HEAs that are prepared under high-gravity exhibit dendritic microstructures. The structure of AlxCoCrFeNi changes from single-phase FCC to BCC when x varies from 0 to 1.

5.5.2.2 Copper Mold Suction Method

In this method, HEAs melt is sucked into a copper mold cavity under the driving of negative pressure. The excellent heat conductivity of copper promotes high cooling rates. It has been reported that, even at high cooling rates, HEAs still can form solid solutions due to their stable high mixing entropy [62]. This method is mainly applied when bulk metallic glasses are required to restrain recrystallization [16]. Zhou et al. [63] melt AlCoCrFeNiTix HEAs in an arc melting

furnace, then the ingot was injected into a copper mold (water-cooled) to obtain cylindrical rods with a diameter of 5 mm. Samples that are composed of BCC solid solution, showed excellent compressive mechanical properties.

5.5.2.3 Bridgeman Solidification Method

Bridgman solidification is a technique that is used to grow single-crystal ingots. In this method, the polycrystalline material is heated to a temperature that is above its melting point and then cooled down slowly from the end of the container, where a seed crystal is placed. A single crystal (with the same crystallographic orientation as the seed material) grows on the seed, and forms progressively along the length of the container [64]. The thickness of this spiral (seed) should be close to the grain size in order to allow one grain only to enter the mold cavity. Figure 15 shows a photograph and a simple schematic of the Bridgeman method [65].
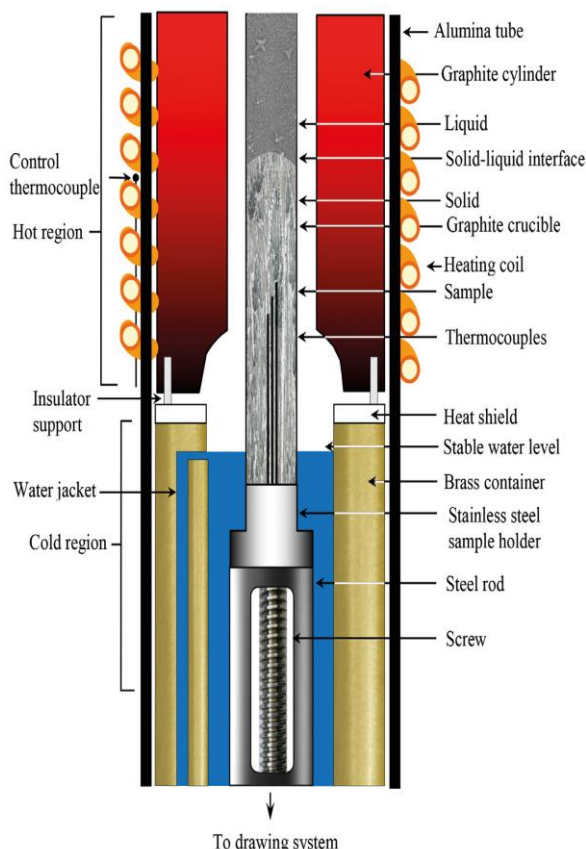
Fig. 15 A photograph and schematic representation of Bridgeman solidification [65].

Ma et al. [66] compared the morphology of AlCoCrFeNi alloy solidified by Bridgman under extremely low withdrawal velocity to the same alloy that was produced by the copper mold method and found that in the former case, equiaxed grains was obtained while in the latter, a dendritic structure was observed. This difference was owed to the ratio of a temperature gradient to that of growth velocity (G/V). In the case of Bridgman solidification, G/V is much higher than in the copper-mold method. This is translated to lower constitutional undercooling of the alloy which in turn restrain the dendrite formation. Zuo et al. [67] also produced FeCoNiAlSi HEAs via the Bridgman solidification method. The soft magnetic properties obtained were better than those prepared by arc melting. In another research for Ma et al [68], they could process single-crystal CoCrFeNiAl0.3 HEAs with superior elongation under Bridgman solidification conditions. They referred to such excellent ductility to the presence of low-angle grain boundaries so less distance to dislocation motion and also their single <001> crystallographic orientation which decreases plastic-strain incompatibility.

6. Microstructure Design Strategy of HEAs

HEAs are complex alloys that contain several principal elements and hence a very wide range of microstructures exists. Nanocrystalline, amorphous, single/ multi phases are all expected in HEAs [6]. This section discusses the phase and crystal structure of HEAs. This is followed by, answering a question about the prediction of phases in HEAs and their structure. Finally, the type of phases which possibly form at high temperatures is also discussed.

6.1 Phase and Crystal Structure

In traditional alloys, phases are categorized into three types: intermetallic compounds, terminal solutions, and intermediate solutions. The intermetallic compounds have fixed compositions and are stoichiometric. Terminal phases are the phases that are based on one principal element. In the case of HEAs, the situation is completely different due to the existence of several principal elements. Therefore, the presence of intermetallic compounds is not common in HEAs [69].

HEAs have solution phases, which do not belong to the above-mentioned categories. Simple solid solutions such as random BCC and FCC ordered solid solutions (e.g., B2 and L12)   are the common phases in HEAs and also complex structures (e.g. Laves phase) might present [5, 7].

6.2 How to predict phases in HEAs?

One fundamental question concerning HEAs is: what phases can be obtained when these different main elements melt together? Though complex structures are expected here, the literature [25] reported that the simple structures are the most commonly seen in cast HEAs, Fig. 16 [28]. This figure shows how elemental addition increases the system entropy and affects the type of solid solution phases. The high-entropy effect discussed in section 4.2, has been reported as responsible for the formation of simple phases in HEAs systems.
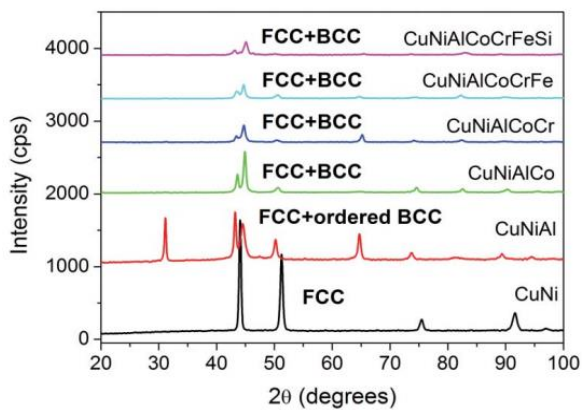
Fig. 16 XRD patterns of some designed alloys that are based on increasing the number of constituting [28].
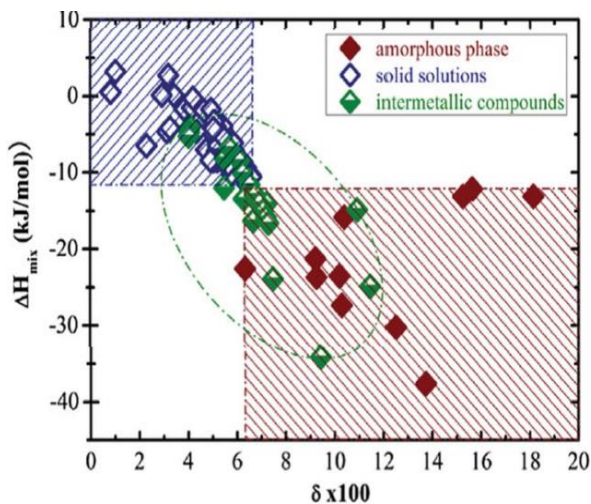
Fig. 17 Plot of δ-H_{mix}, the dash-dotted area determines the region of simple solid solutions, amorphous phases, and intermetallic.[46].

Phases such as Laves, etc., can also be observed in HEAs. In order to understand phases formation in HEAs, Hume-Rothery rules should be considered [7]. In these rules, the formation of binary solid solutions is controlled by several factors: the atomic size of the different elements, their electronegativity, and electron concentration [28]. Other thermodynamic factors can also play essential roles.

In HEAs, enthalpy and entropy are the most important phase formation parameters. It has been reported by Guo et al. [13, 14] that the formation of phases in HEAs depends mainly on the mixing enthalpy (H_{mix}), entropy (S_{mix}), and also on the atomic size differences (δ). In order to obtain simple phases (i.e., BCC, FCC, etc.) and their ordered versions, it is necessary that different conditions be simultaneously achieved: $-22 \leq H_{mix} \leq 7$ kJ/mol, $\delta \leq 8.5$, and $11 \leq S_{mix} \leq 19.5$ J/(K mol) [29,31]. Ming et al [46] explained this by presenting the simple illustration shown in Fig.17.

### 6.3 Phase crystallization in HEAs

Almost all solid solutions in HEAs have either FCC or BCC simple structures. It has been reported that valence electron concentration (VEC), is the essential factor that determines whether an alloy crystallizes into FCC or BCC structure [30, 31]. VEC is the average VEC of the constituting elements. Guo et al. [70] plotted the relationship that shows the dependency of HEAs structure on the value of VEC in Fig. 18. They stated that if the VEC of the HEA is lower than 6.87, then the structure is BCC and if larger than 8, the FCC structure is then stabilized. It is also possible that both FCC and BCC coexist in case VEC fall between 6.87 and 8.
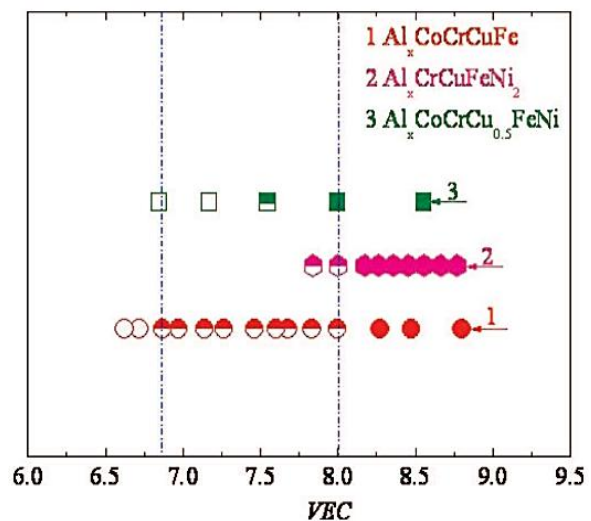
Fig. 18 Relationship between VEC and stability of phases in HEAs systems: fully closed symbols for sole fcc phases; fully open symbols for sole bcc phase; top-half closed symbols for mixed fcc and bcc phases. [70].

6.4 Elevated Temperature phases of HEAs

Cast state is known to be thermodynamically unstable. If we look at Fig. 19 [35], in the alloys that exist in either BCC or FCC, phase transformation is less significant. An example has been reported in [35], where no phase was formed in Co–Cr–Fe–Mn–Ni alloys (FCC) during high-temperature annealing. In alloys that are located in (BCC+FCC) region, however, phase transformation occurs at higher temperatures. In Al-Co-Cr-Cu-Fe-Ni, annealing at 800°C or lower increases the fraction of BCC while at temperatures that are higher than 800°C, FCC phase fraction increases. This phase selection ability in HEAs is very beneficial in terms of mechanical properties control via annealing as the BCC phase is relatively brittle while FCC is ductile. However, in some HEAs, some intermediate stable phases exist upon annealing, e.g. η and σ, which are detrimental to the mechanical properties due to their brittleness [4-7]. Fortunately, this type of phase is predictable based on VEC as explained in ref. [70].
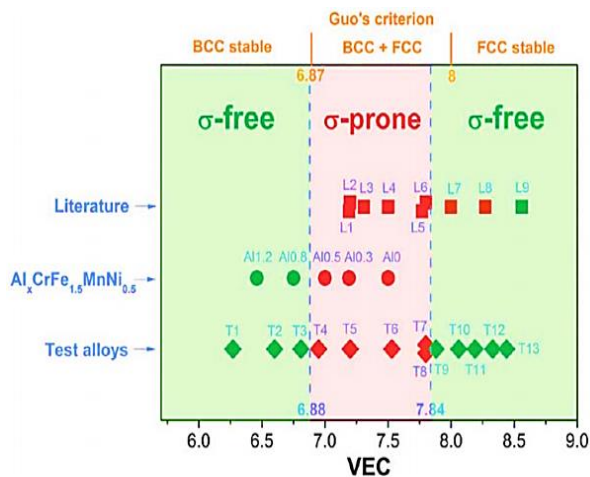
Fig. 19 Relationship between VEC and phases formation in HEAs [35].

7.   Mechanical Properties of HEAs

Unlike conventional alloys, the mechanical properties of HEAs as multi principal elements alloys cannot be simply predicted. This is because every element in the cocktail of HEAs participates in the total strength of the alloys. In terms of strength, the most essential factors are the strength of each phase, the volume ratio of the phases to each other, and the morphology/distribution of the constituting phases [28]. In the following subsections: the strengthening mechanisms in HEAs are discussed and their mechanical properties are compared to the classical alloys.

7.1 Strengthening Mechanisms in HEAs

In order to understand the strengthening mechanisms in HEA, some cases from the literature are given herein. Yeh [27] compared Young's modulus of the conventional alloys where mainly one basic element controls the properties to that of HEAs with multi principal elements. Ex. In Al-, Ti- and Fe-based alloys, Young's modulus are 75 GPa, 110 GPa, and 200 GPa respectively, which are close values to the modulus of their main elements. Contrasting, in HEAs, Young's modulus may differ significantly from any of the constituting elements, therefore selecting the composing elements is of great importance to control the strength in HEAs [71,72]. Wang et al. [73] reported that Young's modulus of $(CoCrFeNiCuAl0.5)$ alloy is ~ 24.5 GPa, while the lowest modulus of the constituting elements is that of Al which equals 69 GPa.

In some reported studies [74-77], HEAs with FCC structure showed high plasticity and low strength, while BCC-structured alloys exhibited low plasticity and high strength at room temperature. So, the dominant factor that controls the strength/ hardness of HEAs is their constituting phases. For the fracture toughness of the HEAs, only one paper in the literature [74] discussed the fracture toughness of $(Al_{0.2}CrFeNiTi_{0.2})$ and $(AlCrFeNi_2Cu)$ HEAs that were prepared by vacuum arc melting. Both the two alloys consisted of two phases (BCC & FCC). Alloy $AlCrFeNi_2Cu$, showed lower strength and higher toughness relative to $Al_{0.2}CrFeNiTi_{0.2}$.

Heat treatment which plays a vital role in many classical alloys can also significantly alter the strength. In the two phases (BCC/FCC) HEAs, the selected annealing temperature determines the alloy's property. The alloy becomes harder and more brittle if the annealing temperatures increase the BCC phase while the temperatures that increase the fraction of the FCC phase result in a more ductile alloy [21].

7.2 Mechanical Properties of HEAs Vs. Conventional Alloys

In classical alloys, there is one major element that controls the mechanical properties of the whole alloy. Ex., Fe (BCC) in the low-carbon ferritic steels is the main reason for their mechanical properties [75]. C is used as an interstitial solute element for solid-solution strengthening; however, the main strength is from Fe.

Similarly, in Ti-based alloys and Al- alloys, their properties are related to the dominance of Ti and Al, respectively. In the case of HEAs, the structure types are the controlling factor of the hardness/strength of HEAs [46] since there is no one dominant element. Based on this concept, BCC-HEAs can be chosen if high yield strengths are required while FCC-HEAs are preferred when low yield strength (high plasticity) is targeted. Mixing both of the structures, results in balanced properties, e.g., high strength along with good ductility can be achieved in the two phases HEAs. Zhang et al [29] showed that, unlike the conventional alloys, the cocktail effect in HEAs can dramatically enhance the hardness by altering the alloy composition. HEAs like the CoCrFeNiCu system are very soft alloy (200 HV) while alloy MoTiVFeNiZrCoCr shows a hardness value of 800 HV. Concerning high-temperature strength, refractory HEAs have high melting point elements and can sustain yield strength to ultrahigh temperatures. The strength of HEAs can be maintained at higher temperatures compared with Inconel and Haynes superalloys.

HEAs are also characterized over conventional alloys by having a strong age-hardening phenomenon. Gao et al [39], reviewed the response of different HEAs to annealing. Based on this review, HEAs can be divided into (a) weak aging hardening and (b) strong aging hardening. The strong age-hardening is owed to the formation of precipitates, as a (Ni, Al)-rich B2 phase in $Al_{0.3}CoCrFeNi$ alloy and ρ ($Cr_5Fe_6Mn_8$) phase in $Al_xCrFe_{1.5}MnNi_{0.5}$ (x ¼ 0.3 and 0.5) alloy, However, when the temperature increases above 900 K, the grain size of these precipitates increases and softening occurs leading to hardness decreases [76, 77].

8. Applications of HEAs

As discussed in the previous section, HEAs have distinguished mechanical properties that made them widely applied in the different sectors of industry. Wang et al [3] reported that HEAs can maintain their stability and withstand the surrounding conditions in various harsh environments (corrosive, high temperature, etc.). The type of application dictates the alloy composition and fabrication route of HEAs. Following are some examples of applications where HEAs can be the ideal choice:

- Transportation and energy industries that require high strength with low density and durability at high-temperature conditions are the ideal applications of HEAs [80, 81]. Highly alloyed stainless steels are used in aircraft for their resistance to oxidation, and erosion and their ability to tolerate high temperatures. However, in order to decrease the component weight, higher strength is required for the steel. Aluminum alloys are also aero-engine materials but are not able to perform perfectly at high temperatures. Even nickel superalloys, titanium alloys, and rare earth metallic alloys which are fascinating due to their high strength to weight ratio fail at extreme temperature conditions [29, 64]. HEAs are excellent candidates and can replace titanium alloys and steel in the compressor blade of an aero-engine. This is due to their high specific strength, oxidation resistance, fatigue resistance, elevated temperature strength, and also because of being lightweight, wear and creep resistant.

- HEAs can be used in cryogenic applications such as storage of liquefying gases and can retain mechanical properties at temperatures as low as 77K. Rob et al [78] examined a five-element HEA, CrMnFeCoNi, which forms a single-FCC solid solution, and found that it has an exceptional damage tolerance of tensile strength that exceeds 1 GPa and toughness values above 200 MPa.m$^{(1/2)}$, Fig. 20 These toughness values are the highest reported for any other material and also do not show a decrease at lower temperatures, which does not occur at conventional alloys.
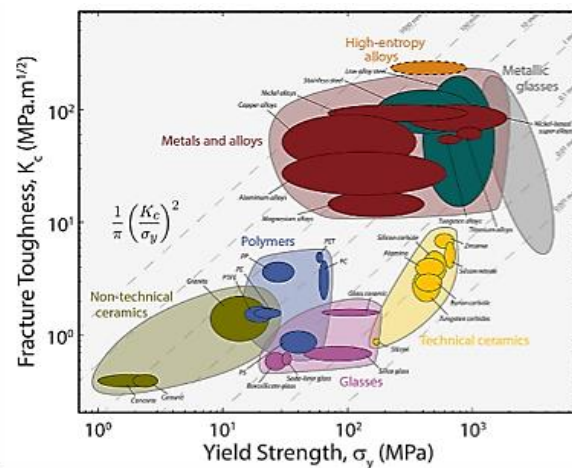
Fig. 20 Fracture toughness of some HEAs reported in [81].

- HEAs with their corrosion resistance and improved irradiation can be typically used for cladding the high-pressure vessels and nuclear fuels materials [17]. Pickering [82] showed that HEAs can be successfully used as oxidation-resistant coating and anti-burst refractory cladding alloys.

- HEAs are also applied recently in biomedical fields. Ceramic HEAs proved excellent

biocompatibility as implant biomaterials. Yuan et al. [83] prepared several biocompatible TiZrHfNbTa HEAs with low magnetic susceptibility and low elastic modulus. In addition, they systematically analyzed and summarized the performance of HEAs with the addition of any element. It is remarked that the modulus of elasticity in HEAs is easily controlled compared to the traditional metallic materials; see Fig.21 [84] for a comparison between HEAs and Ti-based alloys.
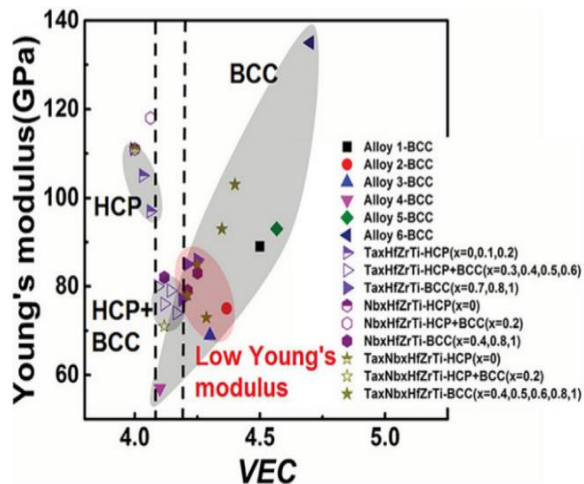
Fig. 21 Performance of Ti-based HEAs and other metallic alloys [84].

- HEAs are also ideal for hard-facing of molds, dies, tools and nozzles, wherein HEAs are fabricated as powders and then thermally sprayed or plasma arc onto the surface of the different components.

- HEAs are employed as a transitional layer between two types of alloys, so solder and brazing fillers of HEAs can be used for welding pure titanium and chromium–nickel-titanium stainless steel, cemented carbide, and steel, respectively [17].

- These alloys also find a wide range of applications as binders. AlCoX and CoCrX as examples can replace the conventional binders as they have low contents of expensive cobalt and are composed of an FCC phase [85].

- The special physical properties of the HEAs, e.g., AlCoCrFeNi, with near-constant resistivity would make them useful for electronic applications [17].

- Light-weight HEAs could be used as casings for mobile facilities, battery anode materials.

- With their excellent corrosion resistance, HEAs containing rare earth can be used to coat different materials for various applications and replace the old traditional coats [83].

Figure 22 [87] presents a comparison between the corrosion resistance of Hf0.5Nb0.5Ta0.5Ti1.5Zr and the other alloy systems in NaCl solution.
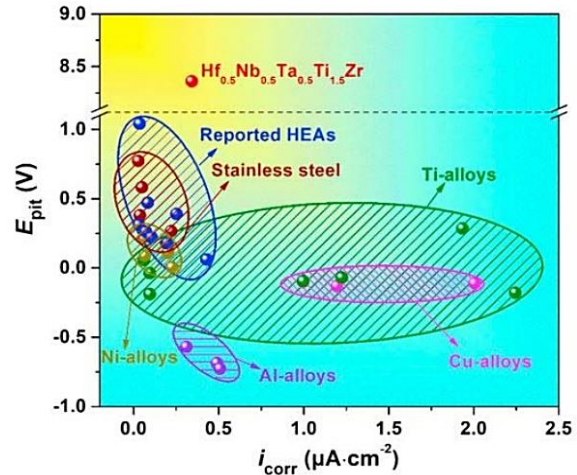
Fig. 22 Compare the corrosion of an Hf0.5Nb0.5Ta0.5Ti1.5Zr RHEA with other HEAs and other alloys in a 3.5 wt% NaCl solution [87].

9. Future Insights & Conclusions

The excellent properties of some promising HEAs presented in the previous sections should direct the materials science community to further develop HEAs and direct their efforts toward more economical and lower weight HEAs. In the following points, future insights into the development of HEAs are summarized:

- Upon surveying the published articles, it was observed that limited research exists about fatigue, creep, wear, and deformability of HEAs which are very important properties for the functional use of HEAs in load-bearing applications [17].

- Tuning the atomic order of HEAs to achieve the best mechanical properties needs more experimental investigation. There is only one research that studied the structure of CrCoNi using XRD and showed that Cr atoms display less affinity to bonding to Cr atom than to Ni and Co atoms. So, further experiments are required [37, 1]

- Other manufacturing routes should be explored to widen the application range of HEAs. Processes such as hot/cold working, homogenization, and annealing should be tried to alter the microstructure and eliminate casting defects [3, 16].

- Another interesting research point relates to the function of interstitial elements as N, O, H in HEAs. These elements can be used for doping in HEAs. For example, O, which is considered a harmful

element in alloys and metals, has been reported to form clusters that are rich in ordered O-Ti-Zr-in TiZrHfNb HEA and hence enhance the strength and ductility [25]. Moreover, H, which is the most deleterious interstitial element in metallic alloys, has been discovered to improve resistance to hydrogen embrittlement in HEAs. This is due to the fact that H minimizes the stacking-fault energy and thus provides high local strain hardening [3]. However, C is the only interstitial element that is well covered in the literature.

- Careful assessment of the relationship between microstructure, heat treatment, and properties of the promising HEAs is required, otherwise, these alloys will be early dismissed [30]

- Concluding, there is still undiscovered wealth in HEAs alloys which can be revealed with a careful combination of the alloy composition along with customization of the microstructure, and hence multi functionalities and unlimited potential can be achieved.

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