Chapter 2

LITERATURE REVIEW

2.1 Concept of high entropy alloys

Conventionally, metallic alloys are formulated by selecting a primary metal to meet specific property requirements. Subsequently, additional alloying elements are incorporated into the primary metal to customize the microstructure and characteristics for particular applications. This approach has been employed in developing various alloy families such as steels, aluminum alloys, magnesium alloys, cobalt alloys, titanium alloys, and many others. These alloys typically concentrate their composition near the edges and apexes of their phase diagrams rather than the central portion. In response to this conventional method, a novel category of metallic alloys emerged, intending to explore the central region of multicomponent alloy phase diagrams. In 2004, the synthesis of a few alloys composed of equal atomic fractions of 5 or 6 elemental metals was first reported [45, 52, 53]. Despite of their complex composition, some of these alloys exhibited a single face-centered cubic (FCC) or body-centered cubic (BCC) solid-solution phase in their as-cast condition, such as equiatomic Cu-Co-Ni-Cr-Fe [52, 53] and equiatomic Fe-Cr-Mn-Ni-Co [45]. These alloys are called multi-principal element alloys (MPEAs) to highlight the complexity of their composition. Alternatively, they may be termed high entropy alloys (HEAs) or medium entropy alloys (MEAs) to underscore the impact of their high mixing entropy on the formation of a single solid solution phase in their microstructure [45, 52, 53]. The terms MPEAs, HEAs, and MEAs have become widely accepted in the literature to describe this particular class of metallic materials.

Probably, the lack of multi-principal component phase diagrams has led to an inconsistent and undefined definition of HEAs. Initially, HEAs are characterized as alloys comprising 5 or more elements with concentrations of each element ranging from 5 to 35 atomic %. This definition was primarily established to explore alloys in the central region of their multicomponent phase diagrams, a space typically avoided in conventional alloy designs. According to the Gibbs phase rule, the equilibrium phase number in an alloy system is proportional to the number of components [53, 54]. Consequently, it was anticipated that HEAs would exhibit numerous phases, such as solid-solution and intermetallic compounds. Surprisingly, HEAs displayed a lower-than-expected number of phases, with some solidifying into a single BCC or FCC solid-solution phase, as mentioned earlier. This unexpected behaviour was attributed to the significantly high mixing entropy in the liquid or random solid-solution states of HEAs, facilitating the formation of solid-solution phases and preventing segregation into intermetallic compounds. Hence, the term "HEAs" was coined to underscore the influence of entropy on the formation of solid-solution phases in this class of materials [55, 56]. Additionally, Yeh [55] suggested employing Boltzmann's hypothesis for calculating the configurational mixing entropy (ΔS_{mix}) change per mole of an alloy, as presented in Eq. (2.1). This calculation enabled the classification of all metallic alloys into three groups: low entropy alloys (conventional alloys), MEAs, and HEAs. It is noteworthy that certain alloys, designed with equiatomic fractions of four principal elements, have been categorized as HEAs despite having ΔS_{mix} of ~1.38R (J/K mole) [49, 57-59]. According to Yeh's classification, ΔS_{mix} = ~1.38R (J/K mole) falls within the MEAs category [55]. This discrepancy in terminology, particularly the use of "MEA," can be contentious, but in the literature, HEAs, MEAs, and multi-principal element alloys (MPEAs) have often been used interchangeably. Generally, when the number of alloying elements is restricted to 3 or 4, researchers frequently opt for the term MEAs. However, it is acknowledged that there is an

on-going debate and diverse definitions, as extensively discussed in the critical review paper by D.B. Miracle and O.N. Senkov [60].

$$\Delta S_{\text{mix}} = -R \sum_{i=1}^{n} (c_i \ln c_i) \tag{2.1}$$

Where R denotes the gas constant having a defined value of 8.314 $JK^{-1}mol^{-1}$, c_i represents the atomic percentage of i^{th} element.

2.2 Four core effects of high entropy alloys

HEAs exhibit a complex composition; their microstructure normally consists of either solid-solution phases or a combination of primary solid-solution phases with a minor presence of intermetallic compounds. The distinctive microstructure of HEAs has led to the identification of four fundamental core effects:

i. High entropy effect
ii. Severe lattice distortion effect
iii. Sluggish diffusion effect
iv. Cocktail effect

These fundamental effects are briefly outlined below.

2.2.1 High entropy effect

The high entropy effect elucidates the formation of multi-principal atomic solid-solution phases. The increased configurational entropy in equimolar or near-equimolar alloys with at least 5 elements is proposed to reduce the free energy of solid-solution phases, thus favouring solid-solution formation instead of intermetallic compounds. It is observed from Eq. (2.1) that as the number of principal elements is increased from 3 to 9, ΔS_{mix} is enhanced from 1.1R to 2.2R. According to Richards' rule, the fusion entropy of pure metals is ~1.0R at their melting point. Furthermore, the ΔS_{mix} of alloy systems with more than 5 principal elements

significantly surpasses the fusion entropy of pure metals. This suggests that the propensity for ordering and segregation is reduced due to the increased mixing entropy. Consequently, alloys with more principal elements are more prone to forming solid-solution phases than intermetallic compounds [52].

It is important to note that the preceding discussion solely considered the configurational mixing entropy as the primary driving force for forming a solid-solution phase in HEAs. However, the configurational mixing entropy is an idealized measure, estimated by assuming the formation of a disordered solid-solution in the liquid state or at elevated temperatures [52, 61]. This approach fails to account for the fact that an alloy's mixing entropy can significantly reduce with decreasing temperature and the occurrence of segregation [60]. Consequently, research has demonstrated that the impact of configurational mixing entropy on the formation of solid-solution phases in HEAs is not as pronounced as that of other parameters, such as mixing enthalpy (ΔH_{mix}, kJ/mole) and atomic mismatch (δ, %) [62-64]. This suggests that predicting the formation of a solid-solution phase in HEAs should not solely rely on the ideal configurational mixing entropy. The methodology for calculating mixing entropy needs enhancement to illustrate better its effect on forming solid-solution phases in HEAs. In the literature, principal elements are strategically selected to minimize the differences in mixing enthalpy between dissimilar atom pairs to achieve single solid-solution alloys in equilibrium. For e.g., the Fe-Co-Cr-Mn-Ni alloy has shown the ability to form a stable, simple FCC solution at all annealing temperatures [65, 66]. However, secondary phase segregations may lead to the development of alternative disordered solid solutions or intermetallic phases [67, 68]. Additionally, during heat treatments, the largest atomic element in a system tends to segregate out of the solid-solution phase. For e.g., in a Ta-Zr-Nb-Ti MEA alloy, Zr, the largest atom, exhibited segregation into Zr-rich phases following annealing [46]. Analogous phenomena have been documented in various other alloys [69-71].

2.2.2 Severe lattice distortion effect

Traditionally, when alloying elements are introduced into an alloy, they dissolve into the lattice of the host element or alloy, forming a substitutional or interstitial solid-solution, or reacting with alloy components to create intermetallic compounds [72, 73]. The atomic size disparity between the host and alloying elements induces lattice distortion around the alloying element in the solid-solution phase, strengthening the parent material, a phenomenon known as solid-solution strengthening [72, 74]. In HEAs, the solid-solution phase comprises different elemental atoms, randomly dispersed in a lattice, making it difficult to differentiate between solute and solvent atoms. This random distribution results in severe lattice distortion due to atomic size discrepancies among constituents, leading to high hardness and strength, an essential distinguishing feature of HEAs compared to conventional alloys [75-77]. This lattice distortion, often denoted as δ, is the primary strengthening mechanism for HEAs and is crucial for designing the solid-solution phase [62, 78]. A higher value of δ corresponds to more severe lattice distortion, which typically confers greater hardness, strength, and resistance to annealing softening [76, 79, 80]. Additionally, severe lattice distortion reduces X-ray diffraction (XRD) intensity and lowers thermal and electrical conductivity compared to pure metals [81-84]. Experimental evidence of local lattice distortion has been observed in the microstructure of equiatomic Nb-Mo-Ta-W HEA using high-resolution transmission electron microscopy (HR-TEM) by Zou et al. [48].

2.2.3 Sluggish diffusion effect

As HEAs consist of solid-solutions of different elements, the atomic diffusion within their matrices follows a unique pattern. Various types of atoms in the lattice result in distinct lattice potential energies (LPE) at each site. This disparity in LPE leads to hindered diffusion and increased activation energy [66]. The sluggish diffusion primarily stems from the barrier

effect created by low LPE regions within the lattice. Consequently, the nucleation and growth of new phases rely on diffusion, directly influencing HEAs' microstructure and final properties. The sluggish diffusion observed in HEAs is advantageous for developing solid-solution within the alloy. This assertion implies that disordered solid solutions, formed at high temperatures or in the liquid phase, persist at lower temperatures due to the impediment of segregation by sluggish diffusion. This phenomenon has been invoked to elucidate various characteristics of HEAs, including the formation of nanostructured configurations, remarkable phase stability, slowed grain growth, resistance to softening at high temperatures, and effective diffusion barriers [85-88].

2.2.4 The cocktail effect

The term "cocktail effect" was initially introduced by Ranganathan [89], referring to synthesizing HEAs using a combination of multiple component metals. This concept suggests that the constituent elements influence the properties of HEAs. For instance, Senkov et al. [57, 90] developed HEAs using refractory metals, known as refractory HEAs (RHEAs), which exhibited superior resistance to softening at high temperatures compared to Ni-based and Co-based super alloys. This enhancement is attributed to the high melting points of the individual refractory metals. Additionally, the density of RHEAs can decrease significantly when alloyed with lighter metals such as Al, Si, and Cr. Furthermore, interactions among the constituent elements may lead to unexpected properties. For example, adding Al to certain Zr-containing RHEAs reduces their density and enhances their resistance to softening at high temperatures [91, 92] and oxidation resistance [93]. This improvement is due to the formation of coherent disordered BCC solid-solution nano precipitates in an ordered B2 (Al_x-Zr_5) matrix through the interaction between Al and Zr, thereby enhancing the mechanical properties of the resulting RHEAs at both ambient and high temperatures.

2.3 Formation of solid-solution phases in HEAs

2.3.1 Motivation for solid-solution phases and/or intermetallic compounds

The microstructure plays a pivotal role in determining the properties of metallic materials. Due to the absence of a phase diagram for HEAs, it is challenging to predict their microstructure and mechanical characteristics. Hence, it becomes essential to forecast the potential phases, such as solid-solution or intermetallic compounds, that may emerge for a given composition of MEAs or HEAs. Intermetallic compounds are known for alloy embrittlement and often complicate machining and processing. Solid-solution contributes to high damage tolerance in the alloys compared to intermetallic compounds [52, 61, 94]. Consequently, efforts are directed toward designing HEAs that exclusively exhibit solid-solution phases. However, it is noteworthy that while intermetallic compounds often induce brittleness in metallic alloys, they can also significantly enhance their strength. For instance, intermetallic compounds like TiB and TiC can reinforce titanium, forming Ti-TiC/TiB metal matrix composites characterized by excellent strength and ductility [95, 96]. In this regard, HEAs containing intermetallic compounds should also be explored, emphasizing the need to control their shape, size, and quantity to achieve the desired mechanical properties.

2.3.2 Empirical rule

To anticipate phase formation in HEAs, Zhang et al. [78] initially introduced an empirical rule. This rule incorporated the Hume-Rothery principles and thermodynamic parameters for analyzing phase formation in a broad spectrum of multi-component HEAs, encompassing bulk metallic glasses (BMGs) and HEAs. The empirical rule was originally formulated based on a set of parameters, including mixing entropy ($\triangle S_{mix}$), mixing enthalpy ($\triangle H_{mix}$), and atomic size difference (δ). These parameters can be determined using Eqs. (2.1, 2.2, and 2.3).

$$\Delta H_{\mathrm{mix}} = \sum_{\mathrm{i=1,i\neq j}}^{n} \Omega_{ij} c_i c_j = \sum_{\mathrm{i=1,i\neq j}}^{n} 4\Delta \mathrm{H}_{\mathrm{mix}}^{AB} c_i c_j \tag{2.2}$$

$$\delta = \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \tag{2.3}$$

Where $\Delta \mathrm{H}_{\mathrm{mix}}^{AB}$ denotes the enthalpy of mixing of the binary alloy system, c_i, and c_j correspond to the atomic percentage of the i^{th} and j^{th} elements, respectively, $\bar{r} \left(= \sum_{i=1}^{n} c_i r_i\right)$ is the average value of the atomic radius of the alloy system, and r_i corresponds to the atomic radius of the i^{th} element.

HEAs consistently exhibit lower δ and higher ΔH_{mix} values compared to BMGs, indicating a distinct separation between HEAs and BMGs. Additionally, it is observed that HEAs demonstrate disordered solid-solution phases when δ is ≤ 4.5 %, aligning with the principles of the Hume-Rothery rules, where low δ values facilitate the formation of substitutional solid solutions. Within the δ range of 4.5 to 8.5 %, the microstructure of HEAs may consist of either a sole solid-solution phase or a combination of solid-solution phases and intermetallic compounds. Conversely, when ΔH_{mix} ≤ -22 kJ/mole or ≥ 7 kJ/mole, even if the δ value is ≤ 4.5 %, intermediate phases may form instead of a solid-solution phase. As stated by Miedema et al. [97], ΔH_{mix} significantly influences the phase formation in binary alloy systems, with highly negative or positive ΔH_{mix} values favouring the formation of intermetallic compounds over disordered solid solutions. Several studies [62, 64, 98] have employed the empirical rule to examine the phase formation in HEAs and BMGs. Their findings reveal that despite exhibiting high mixing entropy, certain alloys possess microstructures incorporating intermetallic compounds and/or solid-solution or amorphous phases. This shows that ΔS_{mix} cannot be used as a sole criterion for predicting phase formation in the MPEAs system.

Therefore, for the formation of a solid solution in HEAs, the parameters should satisfy: 11 $\leq \triangle S_{mix} \leq$ 19.5 J/K.mol, $0 \leq \delta \leq 8.5$, and $-22 \leq \triangle H_{mix} \leq 7$ kJ/mol respectively [78, 99].

As previously discussed, ΔH_{mix} plays a significant role in the phase formation of binary alloy systems. Extremely negative or highly positive values of ΔH_{mix} can lead to the elemental segregation and formation of intermetallic compounds. Conversely, solid-solution phases tend to form when the absolute value of ΔH_{mix} approaches zero. According to the phase rule, if a solid-solution phase exhibits the lowest Gibbs free energy, it will be the most stable phase during solidification. As per the Gibbs equation, the Gibbs free energy is influenced by both ΔH_{mix} and $T\Delta S_{mix}$. The high absolute value of ΔH_{mix} may impede solid-solution formation, indicating its significance in describing the resistance to solid-solution formation. Conversely, ΔS_{mix} always has a positive value, which increases with increasing temperature. Consequently, $T\Delta S_{mix}$ can attain significant values at higher temperatures, leading to a substantial decrease in Gibbs free energy and promoting solid-solution formation by enhancing disorder in the alloy system. Thus, to integrate the effects of both $T\Delta S_{mix}$ and ΔH_{mix} in predicting solid-solution phase formation in HEAs, a dimensionless parameter Ω was introduced by Yang and Zhang [63, 100]. This parameter can be calculated using Eq. (2.4), as the initial phase transformation typically occurs at the liquidus/melting point.

$$\Omega = \frac{T_m \Delta S_{\text{mix}}}{|\Delta H_{\text{mix}}|} \text{where,} \qquad T_m = \sum_{\text{i}=1}^{n} c_i (T_m)_i \tag{2.4}$$

Where T_m is the melting temperature of an n-element alloy system and $(T_m)_i$ is the i^{th} element melting temperature of the alloy system.

The determination of empirical parameters, such as ΔS_{mix}, ΔH_{mix}, δ, and Ω [62, 63, 78, 98, 101], suggest whether solid-solution phases are feasible for a given composition of HEAs or not. However, it does not provide direct insight into the crystal structure of such phases.

Reported solid-solution phases in HEAs can have BCC, FCC, HCP structures, or a combination of these. HEAs with FCC structures typically exhibit favourable ductility but comparatively lower strength [102], while BCC HEAs tend to possess higher strength but limited ductility at room temperature. Consequently, efforts have been made to establish criteria for predicting the crystal structure of solid-solution phases. Guo et al. [99] proposed valence electron concentration (VEC) as a predictive tool for determining BCC and FCC phases in HEAs. VEC represents the total number of electrons, including d electrons, in the valence band and can be computed using Eq. (2.5). Guo and Liu [99] reveal that the formation of a BCC phase occurs when VEC < 6.87. On the other hand, when 6.87 < VEC < 8, both BCC and FCC phases are formed. Finally, if VEC > 8 only the FCC phase is stabilized.

$$\mathrm{VEC} = \sum_{i=1}^{n} c_i (\mathrm{VEC})_i \tag{2.5}$$

Where, $(\mathrm{VEC})_i$ corresponds to the i^{th} element valence electron concentration.

2.3.3 CALPHAD

The empirical rule has found extensive application in HEA design due to its simplicity and efficiency in quickly evaluating potential candidates. Successful predictions of phase formation in the as-cast condition have been documented for various HEAs using the empirical rule [40, 41, 46, 47, 103, 104]. However, its accuracy proved inadequate when predicting phase formation in the equilibrium (annealed) condition. For instance, the Ta-Nb-Hf-Zr HEA shows a single BCC solid-solution phase in the as-cast state, but secondary phase precipitation occurred during annealing [69]. Consequently, computational methods such as computer-aided phase predictions were introduced to address this limitation to support problem resolution and experimental design. One such method is the CALPHAD approach,

commonly employed to predict alloy phase diagrams, and it has been adapted for calculating HEA phase diagrams. However, a significant challenge using this method is the lack of a suitable database available for HEAs, though this may be addressed in the future.

2.4 Classification of High Entropy Alloys

Several distinct HEAs have been formulated using basic metals, non-metals, transition metals, alkali metals, alkaline earth metals, and lanthanides [60]. The majority of HEAs have been formulated by incorporating 3d and 4d transition metals. Broadly speaking, HEAs can be categorized into three distinct groups: those containing 3d transition metals, RHEAs, and lightweight HEAs.

2.4.1 HEAs-containing 3d transition metals

The initial introduction of HEAs containing 3d-transition metals was made by Cantor et al. [45] and Yeh et al. [52] in 2004. Following this milestone, extensive research has been carried out to investigate the microstructure and mechanical properties of equiatomic HEAs composed of 3d transition metals, such as Cu, Cr, Co, Fe, V, Ni, and Mn [66, 103, 105-108] Subsequently, additional alloying elements, including Al, Ti, B, Si, Mo, Nb, and C, were incorporated into these alloys to tailor their microstructure and properties [93, 109-112].

2.4.2 Refractory high entropy alloys

In 2010, Senkov et al. [90] introduced RHEAs with the aim of novel HEAs suitable for high-temperature applications, such as in thermal power plants and the aerospace industry. These RHEAs are typically composed of an equiatomic or near-equiatomic composition of refractory metals, including Ti, Nb, Hf, Mo, V, W, Zr, Cr, and Ta [30, 41, 49, 69, 113-119]. This alloy family often demonstrates superior strength, hardness, and resistance to softening at elevated temperatures compared to Ni-based superalloys [57]. However, they exhibit high

density and limited ductility at room temperature, constraining their processing and applications. Consequently, numerous efforts have been made to decrease their density while maintaining or enhancing their properties. Adjustments to the composition of RHEAs have involved substituting heavy metals like W and Ta with lighter metals such as V, Cr, Al, and Si to reduce density. Nevertheless, the formation of intermetallic compounds in these modified RHEAs has frequently been observed, leading to a significant reduction in ductility at ambient temperature [92, 93, 120-123].

2.4.3 Lightweight HEAs

Numerous research endeavours have aimed to develop lightweight HEAs using light metals such as Al, Li, Mg, Be, Sc, and Ti [124-126]. However, due to significant differences in their melting points, conventional methods such as melting and casting face challenges in their fabrication. As a result, solid-state techniques like MA have been used to fabricate lightweight HEAs. For e.g., Youssef et al. [124] produced a lightweight HEA with a nominal composition of Al_{20}-Li_{20}-Mg_{10}-Sc_{20}-Ti_{30} (at. %) through ball milling. This alloy is characterized by a 2.67 g/cm^3 density, with a single FCC phase and a hardness of 5.9 GPa.

2.5 Fabrication methods of HEAs

Three different methods have been employed for synthesizing HEAs:

- The liquid route (melting and casting)
- The solid-state route (powder metallurgy)
- The vapour-state route (deposition methods)

The advantages and disadvantages associated with each method are discussed below.

2.5.1 Liquid-state Route

The liquid-state route has emerged as the most widely adopted method for synthesizing HEAs. Various techniques fall under this category, including arc melting [103, 105, 127, 128], Bridgman technique [129-132], laser-engineered net shaping (LENS) [133, 134], and induction melting [135-137]. Arc melting, in particular, has been extensively used for HEA fabrication due to the high-temperature capabilities of arc furnaces, which can exceed 3000 °C, enabling the melting of nearly all metals. Moreover, metals are typically melted under an argon atmosphere during arc melting, reducing contamination risks during the melting and casting processes. However, the torch temperature in arc-melting furnaces can surpass 3000 °C, leading to the evaporation of low-melting point metals during the process. Consequently, controlling the composition of alloys containing such metals becomes challenging. Another drawback of the liquid-state route is the occurrence of segregation during solidification, resulting in uneven chemical distribution, coarse dendrite structures, shrinkages, and porosities [57, 108]. These microstructural imperfections can adversely affect the alloy's properties. Therefore, post-processing treatments such as hot and cold working and heat treatment have been employed to refine and homogenize the microstructure of as-cast HEAs, enhancing their mechanical properties [80, 106, 113, 135].

2.5.2 Solid-state route

The solid-state route involves the alloying reaction occurring at temperatures which is below the element's melting point. MA is a material processing technique that entails the repetitive welding, fracturing, and re-welding of a mixture of powdered metals, typically within a high-energy ball milling. This method has been widely used to produce HEA powders, which are consolidated through compacting and sintering processes [138-153]. MA offers several advantages not found in conventional methods. For instance, it enables the incorporation of

alloying elements that are challenging or impossible to combine using conventional techniques. It can produce nanostructured, supersaturated solid solutions and amorphous alloys. Despite its advantages, MA does present certain drawbacks. Obtaining high-purity powdered metals and preventing contamination during the MA process can be challenging. However, the impact of these issues can be mitigated through careful selection of milling jar and ball composition and conducting milling in a high-purity inert gas environment, wet medium (toluene or acetone), or both [141, 154]. Researchers have used an advanced consolidation method known as SPS to consolidate HEA powder synthesized via MA. The SPSed product produces nanostructured HEAs with high compressive strength [140, 155].

2.5.3 Vapour-state route

Concerning the vapour-state route, two techniques, magnetron sputtering, and plasma nitriding, have been used to fabricate thin films of HEAs on substrate surfaces. For instance, an Al-Mo-Nb-Si-Ta-Ti-V-Zr HEA layer was successfully produced to investigate its efficacy as a diffusion barrier between copper and silicon [156]. Furthermore, (Ti-Zr-Nb-Hf-Ta)-N and (Ti-Zr-Nb-Hf-Ta)-C HEAs were deposited onto C45 and M2 steel substrates to enhance their wear resistance. The resulting coatings demonstrated significantly superior wear resistance compared to a binary coating of TiC [157].

2.6 Characterization of corrosion and tribological properties in HEAs

2.6.1 Corrosion

Corrosion is defined as an irreversible chemical or electrochemical reaction occurring at the junction between a metal and its surrounding environment. Corrosion is the progressive, rapid, or slow deterioration of material properties, such as mechanical strength, surface quality, and appearance, caused by the surrounding environment [158]. When a metal is

exposed to a corrosive environment, it can exhibit one of three responses, depending on the metal and the surrounding conditions. Firstly, some metals remain immune to corrosion. Secondly, in an active state, metals are prone to corrosion, resulting in loss of metal or dissolution of the corrosive elements into the metal. Lastly, metals can enter a passive state where they develop a protective oxide film on their surface, thereby mitigating the corrosion rate. Metals are susceptible to a wide variety of corrosion when they are placed in corrosive environments. The following is a short overview of some of the most typical forms of corrosion:

- **Uniform corrosion** also called "General corrosion," occurs when the entire surface of a material is uniformly attacked by corrosion with consistent intensity. This type of corrosion is primarily caused by direct chemical attacks, such as exposure to acids, resulting in uniform metal etching across the surface. General corrosion is easily visible to the naked eye and can be effectively protected through methods such as painting or coating.

- **Galvanic corrosion** is a type of corrosion that occurs when dissimilar materials come into contact and are exposed to a conductive solution. Their disparate potentials accelerate the corrosion rate in the more active material. The galvanic cell determines how well something resists oxidation and corrosion when exposed to air. In a galvanic cell, the metal with the highest potential is the anode, and its corrosion rate is lower or higher, respectively than that of the other metals.

- **Pitting corrosion** is a localized corrosion that causes the formation of small cavities or holes on the surface of the metal. The oxidation reaction in the pit causes the pH to drop, which in turn causes chloride ions to migrate and neutralize the metal ions'

positive charge. This results in a more hostile local environment, which speeds up the corrosion process and causes it to penetrate rapidly.

- **Crevice corrosion** is a type of localized corrosion that occurs when the environment partially covers a metal surface, for instance, in small openings, joints, or deep cracks. Anodic reactions occur preferentially in the crevice because of the difference in aeration with the bulk environment. Crevice corrosion can be reduced by design optimization or selecting suitable materials.

- **Fretting corrosion** occurs at the interface of contacting surfaces when there is a small amount of relative motion between them. Fretting corrosion can also be caused by moisture. Fretting corrosion can cause damage, weakening the oxide layer that protects passive metals, leading to increased corrosion.

- **Tribocorrosion** is the corrosion caused by mechanical and chemical attacks on the surface of a metal. The wear disrupts the protective passive layer, and the chemical reaction between the environment and the surface quickly attacks the surface. This corrosion typically happens when the surface is exposed to wear and corrosion at the same time.

The metallic implant inside the body is always in contact with surrounding body fluid. The body fluid behaves like an electrolyte and causes corrosion to the implant's surface. The different phases of Ti-based HEAs lead to galvanic, pitting, and fretting corrosion. So, the newly developed HEAs must be checked for corrosion attack confrontation in a suitable body fluid to use as an implant material.

2.6.2 Corrosion of titanium and its alloys

Titanium and its alloys show excellent corrosion resistance due to the presence of a passive oxide film composed of TiO_2. A good surface finish on the implant enhances its corrosion resistance and durability. The wear and corrosion resistance of an alloy is primarily determined by its microstructure, grain size, and composition [159]. The electrochemical behaviour of Ti alloys is significantly influenced by the microstructure formed and the redistribution of the alloying elements during heat treatment. According to reports, Ti-6Al-4V alloy has good corrosion resistance due to the formation of TiO_2 and Al_2O_3 [23]. The literature survey shows that the anti-corrosive property of Ti and its alloys can be improved by adding alloying elements, which are incredibly stable in corrosive environments. For instance, adding Nb, Mo, Ta, Cr, Fe, and Zr can improve the corrosion response of Ti. Reports have shown that these alloying elements can stabilize the oxide layers in biological media and form a protective stable oxide. Some examples of this oxide type include Nb_2O_5, Ta_2O_5, Cr_2O_3, Fe_2O_3, and ZrO_2 [4-9]. It has been asserted that the corrosion resistance offered by Ti and its alloys with the aforementioned alloying elements is superior to that offered by Co-Ni-Cr alloy and 316L SS.

Based on the preceding review, Ti alloys are expected to possess exceptional environmental stability due to the formation of a passive film on their surfaces. Achieving a surface with superior corrosion resistance hinges on a meticulous selection of alloying elements and precise heat treatment. Thus, the primary objective of this study was to investigate the electrochemical characteristics of different Ti alloys, aiming to elucidate how corrosion might impact the alloy surface.

2.6.3 Tribology

Tribology is the science that deals with friction, wear, and lubrication. Consequently, tribology encompasses the physical and chemical properties of surfaces, including topography, the interactions of surfaces under load, and the modifications of these interactions when tangential motion is introduced. This section will briefly discuss friction, wear, and lubrication.

2.6.3.1 Friction

Friction is the resisting force that occurs during the relative motion of two objects. The asperities on the surface of mating objects resist the motion when coming in contact with each other. The response of any material to friction is determined by the material's structure, the state of the material's surface, and the nature of the contact, which might be corrosive, dry, or lubricated. Friction results in mechanical wear or degradation of the mating surfaces, so it is essential to control the friction to function the materials properly.

2.6.3.2 Wear

Wear is the gradual loss of material from solid bodies in relative motion. This material loss occurs when the bodies are in contact with one another. The chemical interactions, mechanical properties of the rubbing surfaces, and testing conditions influence the wear process. During the wear process, material degradation will occur, which can ultimately fail. The rate of material degradation is primarily related to the surface of the two contact materials and the conditions of the surrounding environment. Material wear has been classified based on the operative mechanisms, with the significant types of wear being (i) abrasive, (ii) adhesive, (iii) fatigue, and (iv) corrosive.

- **Adhesive wear** occurs due to micro-junction formation caused by welding between opposing asperities of two rubbing surfaces. In other words, adhesive wear occurs due to material transfer when two bodies slide against or press against each other. Asperities support the applied load on a body. Because the asperities have a smaller apparent area, the load is high enough to deform and adhere to each other, forming the micro-joints. The body's movement causes the joints to rupture, and the rupture occurs from the non-deformed region. Material is transferred from the counter-body in this manner.
- **Abrasive wear** happens when hard parts that stick out hit the soft parts, causing the soft parts to wear away. It depends on the type of contact and where it takes place. When two parts rub against each other, this is called two-body wear. In this type of abrasive wear, sharp edges on the harder body force the soft body to lose material as it slides. When hard particles get stuck between two surfaces and wear away the material, this is called third-body abrasion.
- **Fatigue wear** is the repeated stressing and relaxing of the material, resulting in micro-cracks formation at or below the surface. These micro-cracks are increased due to the cyclic loading and finally detach from the surface, resulting in material loss.
- **Corrosive wear** occurs when a corrosive medium contributes to surface deterioration through corrosion or oxidation during the sliding process. An overabundance of anti-wear agents or other chemical interactions results in corrosive wear. Dry sliding can also result in this type of wear. Additionally, it can also be caused by exposure to extreme environmental conditions, such as high heat, salt water, or a highly acidic or basic medium.

2.6.4 Tribology of titanium and its alloys

Titanium and its alloys have been studied extensively over the past few decades because of their unique properties, including high strength, lightweight, biocompatibility, and excellent corrosion resistance. Dong et al. [160], have revealed in their findings that there are many factors involved in the friction component of Ti. Titanium shows a high friction coefficient, which is the primary reason for its poor wear resistance. Metal with low tensile and shear strength exhibits a higher friction coefficient than higher-strength material [161]. Different studies on the tribological properties of different types of Ti alloys have shown that the wear resistance and friction coefficient can be improved in different ways. Titanium alloys' tribological behaviour can be significantly changed by the passivity and repassivation that happen when an oxide film forms during rubbing. Alam and Haseeb [162] have reported that α+β microstructure of Ti-24Al-11Nb alloy can form a protective oxide layer during wear, which results in a much lower wear rate. Choubey et al. [163], studied the tribological behaviour of the cp-Ti, Ti-6Al-4V, Ti-5Al-2.5Fe, Ti-13Nb-13Zr, and Co-28Cr-6Mo alloys. They found that Ti-5Al-2.5Fe had the lowest coefficient of friction among all the alloys they studied. Ti-Zr-Nb-Ta-Mo HEAs showed enhanced wear resistance against both dry and wet conditions compared to the Ti-6Al-4V alloy. As the Ti content in Ti_x-Zr-Nb-Ta-Mo (x = 0.5, 1, 1.5, and 2, molar ratio) decreases, the wear resistance of these HEAs improves. Additionally, the wear rates of these HEAs in wet friction conditions are lower than those observed in dry friction. Notably, among the four HEAs studied, the $Ti_{0.5}$-Zr-Nb-Ta-Mo alloy shows the highest resistance to corrosive wear [164]. In dry friction conditions, the wear resistance of the Ti-Zr-Hf-Nb-Fe_x(x = 0, 0.25, 0.5, 0.75, 1, 1.5, and 2.0) HEAs enhances as the Fe content increases, primarily due to the increased hardness. Despite experiencing corrosive wear when sliding in the phosphate buffer saline (PBS) solution, the Ti-Zr-Hf-Nb-Fe HEAs exhibit superior wet-wear resistance compared to the Ti-6Al-4V alloy [9].

The above literature shows that the wear resistance of Ti alloys can be enhanced with alloying elements under different conditions. Adding elements such as Nb, Co, Fe, etc. can improve the wear resistance of Ti-based HEAs. Therefore, one objective of the present work is to investigate the impact of tribological behaviour of the newly developed Ti-based HEAs.

2.7 Microstructure and mechanical performance of bio-HEAs

2.7.1 Bio-HEAs with single-phase BCC

The examination of HEAs for potential applications in the medical field, such as implants, stents, structural components, and coatings for conventional alloys, reveals that most of these alloys possess a BCC structure. Generally, refractory elements such as Nb, Ta, Mo, W, or V act as stabilizers for the BCC phase [165-167].

Segregation of elements within HEAs presents a challenge, even in the case of single-phase compositions. Addressing this issue, Akmal et al. [168] employed a remelting technique on the $(Mo\text{-}Ta)_x$-Nb-Ti-Zr HEAs to achieve element homogenization and dendritic structure elimination. Their experimentation revealed that a BCC phase was achieved for x values of 0.2, 0.4, and 0.6. However, the presence of two BCC phases was confirmed at x values of 0.8 and 1. The addition of Mo and Ta into the Nb-Ti-Zr alloy results in solid solution strengthening and a decrease in the plastic strain with increased strength. Additionally, it was noted that Young's modulus of the alloy increased with higher concentrations of Mo and Ta, a characteristic deemed undesirable for biomedical applications. A comparative analysis was conducted on the electrochemical characteristics of the $(Mo\text{-}Ta)_{0.2}$-Nb-Ti-Zr HEA, 316 L SS, and cp-Ti. The findings revealed that HEA showed superior passive behaviour in PBS than 316L SS and cp-Ti. The hardness of the single-phase BCC structure lies between 380-430 HV, while elastic modulus values are between 110-125 GPa. Furthermore, in-vivo biocompatibility assessments indicated non-toxicity even after four weeks of implantation.

Yuan et al. [43] fabricated Ta_x-Nb_x-Hf-Zr-Ti (x = 0.2, 0.4, 0.5, 0.8, and 1.0) HEAs using arc melting method. Their study reveals that the increase in the concentration of Nb and Ta in Ta_x-Nb_x-Hf-Zr-Ti alloy results in increased Young's modulus except for the case when x = 0.6 (it shows a decreased value). Elastic modulus values were observed in the range of 73-103 GPa. Among the different concentrations of Nb and Ta investigated, the $Ta_{0.2}$N--$Nb_{0.2}$-Hf-Zr-Ti alloy was the only one that did not show a single BCC phase, resulting in a combination of BCC and HCP phases.

Savin et al. [169] used vacuum arc melting to develop Ti-Mo_{20}-Zr_7-Ta_{15}-Si_x (x = 0, 0.5, 0.75, and 1.0) alloy. It was observed that the inclusion of Si content led to an enhancement in hardness. The hardness values for compositions with x = 0.5, 0.75, and 1 were determined to be 337, 355, and 356 HV, respectively. In contrast, the elastic modulus values corresponding to x = 0.5, 0.75, and 1.0 were found to be 89, 69, and 79 GPa, respectively. Notably, an increase in the Si concentration resulted in a decrease in the elastic modulus for x = 0.5 and 0.75, whereas for x = 1.0, it led to an increase in the elastic modulus.

Motallebzadeh et al. [170] developed Ti-Zr-Ta-Hf-Nb and $Ti_{1.5}$-Zr-$Ta_{0.5}$-$Hf_{0.5}$-$Nb_{0.5}$ RHEAs using the arc melting technique. The study reveals the highly promising attributes as superior metallic biomaterials for both the RHEA. These two RHEAs show desirable wear resistance, wettability, and resistance to pitting and general corrosion, surpassing 316L SS, Co-Cr-Mo, and Ti-6Al-4V. Furthermore, the research illustrates how strategic alloying in RHEAs can be employed to optimize their performance as superior metallic biomaterials, including insights into the relationship between lattice strain and corrosion resistance.

Computational exploration of Ti-Zr-Ta-Hf-Nb and $Ti_{1.5}$-Zr-$Ta_{0.5}$-$Hf_{0.5}$-$Nb_{0.5}$ RHEAs has been conducted by Bhandari et al. [171]. The structural, mechanical, and thermal characteristics were analyzed using First-principles Density Functional Theory (DFT). The computed elastic

constants indicate mechanical stability for both RHEAs. Moreover, the calculated lattice constant, elastic modulus, density, and hardness align closely with experimental data. Notably, the $Ti_{1.5}$-Zr-$Ta_{0.5}$-$Hf_{0.5}$-$Nb_{0.5}$ RHEA exhibits a low Young's modulus, high plasticity, and superior thermal properties, suggesting its potential as a candidate for future biomedical applications. The DFT computational approach emerges as a cost-effective and efficient alternative to explore the structures, mechanical behaviour, and thermodynamic properties of novel bio-RHEAs, complementing experimental investigations.

Gurel et al. [167, 172, 173] investigated three Ti-Ta-Hf-based HEAs, namely Ti-Ta-Hf-Nb, Ti-Ta-Hf-Nb-Zr, and Ti-Ta-Hf-Mo-Zr. The study reveals that introducing Zr and Mo decreases ductility compared to the Ti-Ta-Hf-Nb alloy. Regarding elastic modulus, the Ti-Ta-Hf-Nb, Ti-Ta-Hf-Nb-Zr, and Ti-Ta-Hf-Mo-Zr alloys exhibited values of 112, 132, and 159 GPa, respectively. Additionally, the incorporation of Mo resulted in increased microstructural heterogeneity. Further findings revealed that the Ti-Ta-Hf-Nb alloy demonstrated the highest corrosion resistance against fetal bovine serum (FBS) among the investigated HEAs. This was evidenced by the lowest ion release observed from this HEA into the FBS solution. Additionally, after a 28-day immersion in FBS, bone-like apatite formation was observed on all three HEAs, indicating a potential orthopaedic implant material. The corrosion response in SBF and artificial saliva (AS) indicates that the Ti-Ta-Hf-Nb HEA undergoes pitting corrosion when exposed to SBF, but it retains a healthier surface when subjected to AS. Notably, incorporating Zr and Nb in the samples enhances corrosion resistance, leading to decreased ion release and improved surface properties in the presence of SBF and AS.

Ishimoto et al. [174] emphasize the significance of the selective laser melting (SLM) technique in obtaining a single-phase BCC HEA. Their team produced $Ti_{1.4}$-$Nb_{0.6}$-$Ta_{0.6}$-$Zr_{1.4}$-$Mo_{0.6}$HEA through SLM, exhibiting porosity below 0.5 %. This low level of porosity is

ascribed to the rapid cooling facilitated by SLM during the solidification process. It is believed that this accelerated cooling effectively hinders the segregation of the elements. The resultant sample showed a BCC structure characterized by dendritic phases enriched with Mo, Ta, and Nb, intermingled with interdendritic phases enriched in Ti and Zr. The alloy Young's modulus was reported as 140 GPa, showcasing superior yield strength and comparable biocompatibility to cast counterparts.

Based on the literature, Table 2.1 shows the information regarding HEAs intended for biomedical applications, including their Vickers hardness and Young's modulus, specifically those having a single BCC phase. To facilitate comparison, all hardness values which was originally reported in GPa were standardized to HV (Vickers hardness) using Eq. (2.6).

$$HV = \frac{Value\ in\ GPa}{0.009807} \tag{2.6}$$

Table 2.1 Mechanical properties of bio-HEAs with single-phase BCC

Alloy	Route	Hardness (HV)	Young's Modulus (GPa)	Reference
Ti-Zr-Hf-$Cr_{0.2}$-Mo	Arc melting	531	-	[104]
Ti-Zr-Hf-$Co_{0.07}$-$Cr_{0.07}$-Mo		532	-	
Ti-Zr-Ta-Hf-Nb	Arc melting	320	112	[170]
$Ti_{1.5}$-Zr-$Ta_{0.5}$-$Hf_{0.5}$-$Nb_{0.5}$		307	98	
Ti-Ta-Hf-Nb	Arc melting	-	112	[167]
Ti-Ta-Hf-Nb-Zr		-	132	
Ti-Ta-Hf-Mo-Zr		-	159	
Ti-Nb-Zr-Ta-Hf	High-pressure torsion	564	79	[175]
Hf-Nb-Ta-Ti-Zr	Computational method	297	97	[171]
$Hf_{0.5}$-$Nb_{0.5}$-$Ta_{0.5}$-$Ti_{1.5}$-Zr		253	86	
Ta_x-Nb_x-Hf-Zr-Ti	Arc melting	-	73-103	[43]
Ti-Zr-Hf-Nb-Ta	Arc melting	320	79	[176]
Ti_{25}-Zr_{25}-Hf_{25}-$Nb_{12.5}$-$Ta_{12.5}$		293	68	
$Ti_{27.7}$-$Zr_{27.7}$-$Hf_{27.7}$-$Nb_{8.3}$-$Ta_{8.3}$		287	56	

2.7.2 Bio-HEAs with dual-phase BCC

Although powder metallurgy is not as commonly used in bio-HEAs, it remains a vital technique for biomedical applications due to its capability to lower Young's modulus. Another notable benefit is its reduced segregation effect compared to casting HEAs. Akmal et

al. [165] developed Mo-Nb-Ta-Ti-Zr HEA using plasma spheroidization and SPS technique. The HEA produced through plasma spheroidization and SPS showed enhanced mechanical characteristics when compared to arc-melted HEAs. This improvement is attributed to the finer dispersion of the harder phase within the softer phase matrix. Furthermore, it showed outstanding corrosion resistance and lower magnetic susceptibility compared to commercially available alloys, rendering it a promising candidate for biomedical implants.

Different studies have investigated four equimolar HEAs composed of Mo-Nb-Ta-Ti-Zr, with three produced through arc melting [40, 164, 177] and one through the induction method [178]. Wang and Xu [40] and Hua et al. [164] reported a hardness of ~ 500 HV, whereas Li et al. [178] and Shittu et al. [177] observed higher hardness values of 619 and 657 HV, respectively. The reason for this disparity is not fully understood, but it could be influenced by factors such as varying grain sizes due to different cooling rates and the extent of segregation. Wang and Xu [40] noted the segregation of Nb, Mo, and Ta in the dendritic regions. Hua et al. [164] did not disclose elastic modulus values, whereas Wang and Xu [40] and Shittu et al. [177] reported 153 and 164 GPa respectively.

Hua et al. [164] altered the atomic % of Ti in the double BCC Ti_x-Zr-Nb-Ta-Mo HEA (x = 0.5, 1, 1.5, and 2) to investigate its microstructure, corrosion, and mechanical properties. During solidification, the primary dendritic phase exhibited elements with high melting points (Mo and Ta). In contrast, Zr and Ti (elements with lower melting points) were segregated from the dendritic region and accumulated in the interdendritic regions. This distribution pattern is proposed to be influenced by the heat of mixing. There is a positive mixing enthalpy among Ti, Nb, Zr, and Ta, causing Ti and Zr to segregate first into the interdendritic regions. Notably, an increase in Ti concentration resulted in a decreased hardness (for $Ti_{0.5}$ = ~500 and Ti_2 = ~450 HV). Conversely, higher Ti content resulted in

lower yield strength ($Ti_{0.5}$ = ~1580, and Ti_2 = ~1440 MPa). The $Ti_{0.5}$-Zr-Nb-Ta-Mo alloy showed remarkable hardness, higher compressive strength (~2600 MPa), and over 30 % plastic deformation. The Ti-Zr-Nb-Ta-Mo HEAs exhibit an enhanced anti-corrosion behaviour in the presence of PBS solution.

Koval et al. [179] employed computational techniques to investigate the suitability of the Ti-Zr-Nb-Ta-Mo alloy for biomedical applications. Their approach involved DFT to evaluate elastic properties and the Universal Structure Predictor: Evolutionary Xtallography (USPEX) method to forecast crystal structure. The findings suggest that the elastic properties are more affected by the chemical composition and lattice type than by the arrangement of lattice atoms. The calculated elastic modulus values ranged from 122 to 140 GPa, varying with the total number of atoms in the cell.

Perumal et al. [180] used the stationary friction processing (SFP) technique to achieve microstructure homogenization in the Mo-Nb-Ta-Ti-Zr HEA. Their study revealed that 15 min of processing using this method resulted in significant homogenization of elements within the interdendritic and dendritic regions. Numerous cast Mo-Nb-Ta-Ti-Zr alloy compositions [40-42, 181] exhibited Mo, Nb, and Ta segregation within the dendritic regions, whereas Zr and Ti predominantly concentrated in the interdendritic regions. Similar segregation patterns were also observed in the HEA produced by induction [178]. Table 2.2 shows the mechanical properties of bio-HEAs having double BCC phase.

Table 2.2 Mechanical properties of bio-HEAs with dual-phase BCC

Alloy	Route	Hardness (HV)	Young's Modulus (GPa)	Reference
Ti-Zr-Nb-Ta-Mo	Arc melting	500	153	[40]
Ti-Nb-Ta-Mo-Zr	Mechanical alloying	591	62	[182]
Ti-Zr-Nb-Ta-Mo	Computational method	-	122-144	[179]
Mo-Nb-Ta-Ti-Zr	VAM	657	164	[177]
$(Mo-Ta)_{0.8}$-Nb-Ti-Zr	VAM	480	140	[168]
Mo-Ta-Nb-Ti-Zr		510	160	
Ti_x-Zr-Nb-Ta-Mo	Arc melting	430-490	-	[164]

2.7.3 Bio-HEAs with single-phase FCC or dual FCC

Table 2.3 illustrates the methods of fabricating and types of phases (single-phase FCC and double FCC structures) that evolved in the selected HEAs. It is important to highlight that among the referenced studies, only one provided data on hardness and elastic modulus [183], which will be analyzed further in the discussion below.

Gao et al. [184] developed Co-Cr-Fe-Cu-Ni HEA using the SLM method. This HEA exhibits a homogeneous elements distribution and a single-phase FCC structure. Compression testing reveals average yield strength of 516 MPa, surpassing 316L SS and Co-Cr-Mo alloys. Chang et al. [185] used a composition similar to that of Gao et al. [184], differing only in substituting Cu with Pd. They employed the VAR method and found a single-phase FCC

structure in the Fe-Co-Ni-Cr-Pd HEA. The outcomes reveal that the concentration of released metal ions from Fe-Co-Ni-Cr-Pd HEA is significantly lower than observed in Co-Ni-Cr and Fe-Co-Ni-Cr MEAs. This outcome implies that Fe-Co-Ni-Cr-Pd HEA displays a notable selective leaching property.

Alagarsamy et al. [183] developed FCC single-phase $Al_{0.1}$-Co-Cr-Fe-Ni HEA, which underwent a heat treatment process involving annealing at 1000 °C for 24 h, followed by cold rolling, resulting in a hardness enhancement to 143 HV. This treatment also improved tensile strength (570 MPa) and yield strength (212 MPa). Notably, the achieved tensile strength is comparable to that of cortical bone (100-200 MPa), although the yield strength values are lower compared to commonly used biomaterials (such as Co-Cr-Mo, 316L SS, and Ti6Al4V alloys). Despite the thermo-mechanical process, the elastic modulus remained unchanged (203 GPa). Another alloy with a similar composition, $Al_{0.4}$-Co-Cr-Cu-Fe-Ni [186], was developed to balance mechanical and antimicrobial properties, incorporating Cu and a higher Al content. This HEA shows microstructure with two FCC phases, interdendritic regions predominantly containing Cu and dendritic regions enriched in Ni, Cr, Fe, and Co. However, mechanical testing was not conducted for this bio-HEA alloy.

Seven different bio-HEAs (Cu-Co-Cr-Fe-Mn-Ni, Ag-Co-Cr-Fe-Mn-Ni, Co-Cr-Cu_2-Fe-Mn-Ni, Co-Cr-Cu_3-Fe-Mn-Ni, Co-Cr-Cu-Fe-Mn-Ni-$B_{0.2}$, Co-Cr-Cu_2-Fe-Mn-Ni-$B_{0.2}$, and Co-Cr-Cu_3-Fe-Mn-Ni-$B_{0.2}$) underwent assessment for liquid phase separation (LPS) using the heat of mixing and thermodynamic calculations [187]. All these bio-HEAs exhibited a double FCC structure, and there was no phase-separated structure due to LPS in Co-Cr-Cu_x-Fe-Mn-Ni (x = 1, 2, and 3). However, the introduction of B increased the propensity for liquid phase separation.

Table 2.3 Bio-HEAs with single-phase FCC or dual FCC

Alloy	Route	Phase	Reference
Fe-Co-Ni-Cr-Pd	VAR	FCC	[185]
Co-Cr-Fe-Cu-Ni	SLM	FCC	[184]
$Al_{0.4}$-Co-Cr-Cu-Fe-Ni	Induction	Double FCC	[186]
$Al_{0.1}$-Co-Cr-Fe-Ni	Arc melting	FCC	[183]
Ag-Co-Cr-Fe-Mn-Ni Cu-Co-Cr-Fe-Mn-Ni Co-Cr-Cu_2-Fe-Mn-Ni Co-Cr-Cu_3-Fe-Mn-Ni Co-Cr-Cu-Fe-Mn-Ni-$B_{0.2}$ Co-Cr-Cu_2-Fe-Mn-Ni-$B_{0.2}$ Co-Cr-Cu_3-Fe-Mn-Ni-$B_{0.2}$	Arc melting	Double FCC	[187]

2.7.4 Bio-HEAs with amorphous phase

The amorphous structure achieved through sputtering results from factors such as high mixing entropy, low enthalpy, slow diffusion, and disparities in atomic radii among the elements [188]. It is anticipated that HEAs with an amorphous phase exhibit notably higher hardness values than conventional FCC and BCC alloys, as shown in Table 2.4. Among the HEAs exhibiting solely an amorphous phase, Ti-Ta-Hf elements are prevalent. It is important to highlight that nearly all the studies with alloys displaying an amorphous microstructure employed a process involving melting and subsequent deposition onto substrates. This

method has gained popularity owing to its ability to form a uniform coating layer with strong adhesion and provide convenient control over the structure and composition of the film [188].

Two studies investigated the sputtering-coating of Ti-6Al-4V alloys with HEAs. The first study used the $Ti_{1.5}$-Zr-$Ta_{0.5}$-$Nb_{0.5}$-$W_{0.5}$ HEA [188] coating, achieving a hardness of 1835 HV and an elastic modulus of 210 GPa. The incorporation of Ag nanoparticles in some samples resulted in a hardness of 1631 HV and an elastic modulus of 200 GPa. The second study analyzed the tribological properties of the Ti-Ta-Hf-Nb-Zr [189] alloy. The findings revealed a protective surface against wear and cracks, a crucial aspect for implants in long-term and load-bearing applications, such as hip or knee joints. Nanoindentation testing yielded a hardness of 1276 HV and Young's modulus of 181 GPa.

Two additional studies investigated the application of Ti-Ta-Hf-Nb-Zr HEA coating onto Ni-Ti substrates. Motallebzadeh et al. [190] observed increased grain size and surface roughness with enhanced film thickness. They noted a higher hardness of 1285 HV and Young's modulus of 183 GPa for the thinner film (0.750 μm), while the thickest film (1.5 μm) showed a hardness of 1132 HV and an elastic modulus of 173 GPa. Aksoy et al. [191] reported elastic modulus and hardness values similar to those obtained by Motallebzadeh et al. [190] for their thinner films. They highlighted the similarity between elastic moduli and microstructures, promoting strong adhesion at the interface and evenly distributing applied stresses to minimize or eliminate delamination risk [191].

Three commonly used medical alloys, such as Ti-6Al-4V, 316L SS, and Co-Cr-Mo, were coated with $Ti_{1.5}$-Zr-$Ta_{0.5}$-$Nb_{0.5}$-$Hf_{0.5}$ HEA [192] to assess the film's hardness compared to the substrate and the coating's microstructure via nanoindentation. All three alloys displayed increased hardness after applying the HEA coating. The hardness of 316L SS enhanced from

248 to 1165 HV, Co-Cr-Mo exhibited an increase from 419 to 1172 HV, and the Ti-6Al-4V alloy, which initially measured 338 HV, reached 1168 HV.

Table 2.4 Mechanical properties of amorphous phase bio-HEAs

Film	Route	Substrate	Hardness (HV)	Young's modulus (GPa)	Reference
$Ti_{1.5}$-Zr-$Ta_{0.5}$-$Nb_{0.5}$-$Hf_{0.5}$	Arc melting	Co-Cr-Mo	1172	185	[192]
		316L SS	1165	180	
		Ti-6Al-4V	1168	183	
$Ti_{1.5}$-Zr-$Ta_{0.5}$-$Nb_{0.5}$-$W_{0.5}$	Arc melting	Ti-6Al-4V	1835	210	[188]
HEA-9Ag-NPs		Ti-6Al-4V	1661	200	
Ti-Ta-Hf-Nb-Zr	VAM	Ti-6Al-4V	1276	181	[189]
Ti-Ta-Hf-Nb-Zr	Arc melting	Ni-Ti	1285	183	[193]
		Ni-Ti	1132	173	
Ti-Ta-Hf-Nb-Zr	VAM	Ni-Ti	1285	183	[191]

2.7.5 Bio-HEAs with other phases

A number of publications highlight additional constituent phases, such as BCC and FCC, BCC and amorphous, BCC and HCP, and cubic phase. Table 2.5 provides a summary of some studies discovered with microstructures containing these combinations of phases. Liu et al. [194] use a non-equiatomic Fe-Co-Ni-Ti-Al HEA coating on porous Ti-6Al-4V alloy substrates. The duration of spraying was kept between 0.5 and 3 h to evaluate the changes in mechanical properties and coating quality. All the coated samples exhibited both BCC and

FCC structures. For different spraying times, the elastic modulus was reported as 100 GPa (0.5 h), 132 GPa (1 h), 120 GPa (2 h), and 112 GPa (3 h). Further, the hardness was reported as 867 HV (0.5 h), 2294 HV (1 h), 1754 HV (2 h), and 1479 HV (3 h). Notably, samples sprayed for 1 and 2 h exhibited higher Young's modulus and hardness values than others, possibly due to increased accumulation of spatter particles with prolonged spraying time, potentially decreasing the coating quality. Consequently, the HEA coated for 1 h showed better quality and enhanced mechanical properties.

Guo et al. [195] produced a non-toxic $(Ti\text{-}Zr\text{-}Nb)_{14}$-Sn-Mo RHEA showing a BCC structure and HCP dendrites. In this study, a pure Ti substrate underwent laser coating with $(Ti\text{-}Zr\text{-}Nb)_{14}$-Sn-Mo RHEA. The rapid solidification during the process resulted in reduced dendritic segregation and suppression of the HCP phase. The hardness of the RHEA-coated sample was enhanced due to grain refinement and the supersaturated solid solution formation. The reported hardness of the RHEA-coated sample was 584 HV and an elastic modulus of 89 GPa. Conversely, the hardness and elastic modulus of RHEA in its raw solidification state were reported to be 551 HV and 110 GPa, respectively.

Rios et al. [196] investigated the effects of Ni concentration in Al-Co-Cr-Fe-Ni_x alloys (x = 1.0, 1.4, and 1.8). The alloys were fabricated using the VAR technique. Their study reveals a decrease in hardness with the increase in the Ni content (Table 2.5), attributing to precipitate dissolution in a Ni-rich matrix forming a solid solution. They also noted increased interdendritic regions with higher Ni proportions and reported an unconventional primitive cubic phase in the equiatomic alloy, contrasting with a fractional second-phase FCC in the other composition of the alloys. Conversely, Socorro et al. [197] investigated the effects of Al content in Al_x-Co-Cr-Fe-Ni HEAs (x = 0.6, 0.8, and 1.0). They reported a decrease in Al content leads to changes in solubility limits within the solid phase. Ni and Co show increased

solubility, Cr exhibits decreased solubility, while the solubility of Fe remains unaffected. These alterations reflect how Al levels influence the composition and interactions of the alloy's constituent elements.

The presence of Ta and Nb plays a vital role in stabilizing the BCC phase. Yuan et al. [43] reported the effects of Ta and Nb content in the Ta_x-Nb_x-Hf-Zr-Ti HEAs. At x = 0.2, the HEA showed both BCC and HCP phases, accompanied by a low elastic modulus of 71 GPa and a yield strength of 480 MPa. However, only the BCC phase was observed as the Ta and Nb contents increased (x = 0.4, 0.6, 0.8, and 1.0).

Table 2.5 Mechanical properties of bio-HEAs

Alloy	Route	Structure	Hardness (HV)	Young's modulus (GPa)	Reference
$Al_{0.6}$-Co-Cr-Fe-Ni	VAR	BCC and FCC	245	-	[197]
$Al_{0.8}$-Co-Cr-Fe-Ni			427	-	
Al-Co-Cr-Fe-Ni			562	-	
Al-Cr-Fe-Co-Ni	VAR	Cubic	562	-	[196]
Al-Co-Cr-Fe-$Ni_{1.4}$		FCC and cubic	455	-	
Al-Co-Cr-Fe-$Ni_{1.8}$			316	-	
Ag-Al-Nb-Ti-Zn	Powder metallurgy	BCC and FCC	-	-	[198]
Ti-Nb-Mo-Mn-Fe	Powder metallurgy	BCC and amorphous	-	-	[199]
$Ta_{0.2}$-$Nb_{0.2}$-Hf-Zr-Ti	Arc melting	BCC and HCP	-	71	[43]
$(Ti\text{-}Zr\text{-}Nb)_{14}$-Sn-Mo	VAM	BCC and HCP	551	110	[195]

2.8 Biological and Chemical Properties

2.8.1 Cell viability of the HEAs

Different studies were carried out to explore HEAs cell density and viability. Overall, HEAs showed either similar [28, 174, 200, 201] or superior performance [41, 180] compared to cp-Ti, 316L SS, and Co-Cr-Mo alloys. The presence of Zr, Ta, Nb, and Ti in the alloys might be responsible for establishing a favourable microenvironment for cell adhesion and attaining good density outcomes. In the assessment of cell density, Todai et al. [41], Ishimoto et al. [174], and Iijima et al. [201] conducted comparisons between bio-HEAs and widely used implant alloys. They observed that HEAs showed positive performances, either comparable to or surpassing cp-Ti. Iijima et al. [201] reveal that $Ti_{28.3}$-$Zr_{8.3}$-$Hf_{28.3}$-$Nb_{6.7}$-$Ta_{6.7}$-$Mo_{1.5}$ HEA achieved a cell density >7000 cells/cm². In the study by Ishimoto et al. [174], the SLM-HEA $Ti_{1.4}$-$Nb_{0.6}$-$Ta_{0.6}$-$Zr_{1.4}$-$Mo_{0.6}$ exhibited a density >8000 cells/cm², which was higher than the cast alloy with the same composition that yielded around 7500 cells/cm². Todai et al. [41] emphasized that heat treatment improved the cell density results for the Ti-Nb-Ta-Zr-Mo alloy, increasing from 100 to 150 cells/mm².

Additional studies have explored the cell viability % concerning bio-HEAs. Yang et al. [28] reveal comparable cell viability between Ti-Zr-Hf-Nb-Ta and Ti-6Al-4Valloy during cell cultivation, with both alloys achieving ∼100 % viability after 7 days of incubation. Perumal et al. [180] noted that Mo-Nb-Ta-Ti-Zr HEA processed by stationary friction processing (SFP) and friction stir processing (FSP) performed better than cast alloys, showing >90 % viable cells after 48 h of incubation. These observations highlight the superior cell viability of HEAs in contrast to Ti-6Al-4V and 316L SS alloys.

2.8.2 Anticorrosive performance of the HEAs

Among the assays and tests that evaluated the biocompatibility for bio-HEAs, anticorrosive performance is the most studied. The importance of evaluating this parameter is because it is a key factor for biocompatibility, in which corrosion resistance directly affects the functionality and durability of an implant material. Several studies have compared HEAs with conventional alloys Ti-6Al-4V, Co-Cr-Mo, and 316L. Regarding the corrosion potential, Motallebzadeh et al. [170] evaluated two Ti-Zr-Ta-Hf-Nb-based alloys with different compositions. These alloys presented a lower performance compared to Ti-6Al-4V, but with better polarization resistance. The authors argue that it may have been due to the higher content of electronegative elements, such as Ti and Zr. In contrast, the work by Yang et al. [28] showed a lower corrosion potential for HEA Ti-Zr-Ta-Hf-Nb in relation to Ti-6Al-4V and lower resistance to polarization. Wang and Xu [40] and Navi et al. [181] studied a similar HEA replacing Hf with Mo (Ti-Zr-Nb-Ta-Mo) and reported lower corrosion potential compared to conventional alloys. Furthermore, Navi et al. [181] analyzed the polarization resistance and current density, indicating better performance of the HEA. When comparing with the SS304, Shittu et al. [177] confirms better corrosion resistance for the HEA, both for corrosion potential and current density. With the three HEAs Ti-Ta-Hf-Nb, Ti-Ta-Hf-Nb-Zr, and Ti-Ta-Hf-Mo-Zr [173], it was possible to observe that the presence of Zr and Nb improved the corrosion resistance performance of the samples. Through SEM micrographs after immersion in SBF and AS, it appears that there was no significant corrosion on the surface of Ti-Ta-Hf-Nb-Zr. On the other hand, the alloy without Zr (Ti-Ta-Hf-Nb) showed corrosive behaviour in SBF. For HEA with Mo, there was a large amount of the release of ions of this element. The analysis of the concentration of ions after immersion for 1, 7, 14, 21, and 28 days, demonstrate values much higher of release for the alloy with Mo, while the alloys with Nb and Zr proved to be more stable and with lower release of ions [173]. The

good anticorrosive performance of HEA compared to conventional alloys may also be related to the formation of a protective oxide layer, as reported in several works. Some examples are the HEAs Al_x-Co-Cr-Fe-Ni (x = 0.6, 0.8 and 1) [197], Ti-Zr-Ta-Hf-Nb [28], Mo-NbTa-Ti-Zr [180], (Ti-Zr-Nb)14Sn-Mo [195], Ti-Ta-Hf-Nb, Ti-Ta-Hf-Nb-Zr and Ti-Ta-Hf-Mo-Zr [173].

2.9 Summary and remarks

In summary, the concept of HEAs emerged from exploring multi-principle element alloys positioned within the central region of the multi-component phase diagram. Despite their complex composition, HEAs exhibit a simple microstructure, typically comprising a single solid-solution phase or a mixture of solid-solution phases with a small amount of intermetallic compounds. Consequently, four core effects of HEAs have been acknowledged: (i) high entropy effect, (ii) lattice distortion effect, (iii) sluggish diffusion effect, and (iv) cocktail effect. While the first three effects are hypothesized metallurgical attributes, efforts have been made to quantify these core effects, necessitating further empirical validation. HEAs are commonly divided into three categories: those containing 3d transitional metals, RHEAs, and lightweight HEAs. HEAs can be manufactured using various methods such as arc melting, induction melting, solid-state, and vapour-state routes. The choice of fabrication method depends on the properties of the constituent metals.

Drawing from existing literature, significant emphasis has been made on single solid-solution phase HEAs to overcome challenges faced by intermetallic compounds. The intermetallic compounds lead to embrittlement and processing difficulties. Many reported HEAs are formulated with equiatomic or near-equiatomic compositions to maximize configurational mixing entropy and encourage the formation of a single solid-solution phase. However, the literature suggests that configurational mixing entropy is not the only parameter that can

decide the formation of the solid solution phase. Other parameters such as δ, Ω, and ΔH_{mix} hold equal importance in predicting solid solution phase formation in HEAs. The empirical approach is a widely accepted tool for predicting solid solution phase formation in multi-component HEAs.

The bio-HEAs should be highly corrosion and wear-resistant. The literature shows that adding Nb, Mo, Ta, Cr, Fe, and Zr can improve the corrosion behaviour of Ti alloys. These alloying elements stabilize the oxide layers in biological media and form a protective stable oxide (such as Nb_2O_5, Ta_2O_5, Cr_2O_3, Fe_2O_3, and ZrO_2). The wear has been classified based on operative mechanisms, such as (i) abrasive, (ii) adhesive, (iii) fatigue, and (iv) corrosive. Literature has shown that incorporating Co, Fe, and Mo in Ti alloys produces high corrosion resistance. The bio-HEAs should be biocompatible. The reported bio-HEAs possess single-phase BCC/FCC, dual-phase BCC/FCC, amorphous and other phases. The microstructure and mechanical properties of each phase of HEAs have been discussed in detail.