Book Chapter

Mechanical Alloying of High-Entropy Alloys

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Abstract

The trajectory of high-entropy alloys (HEAs) from their birth in 2004 to their current popularity demonstrates a dynamic interplay between scientific research and technical innovation, acquiring substantial speed around 2010 due to the attractiveness of their distinctive characteristics and varied compositions. The shift from equiatomic to non-equiatomic formulations has broadened the area of investigation and shown the crucial roles of significant configurational entropy, sluggish (very slow) diffusion, cocktail property effect, and distortion of lattice as the fundamental features forming the exceptional characteristics of HEAs. In an array of manufacturing techniques, mechanical alloying (MA) followed by sintering has emerged as a convincing approach, using mechanical energy for atomic-scale mixing to produce unique microstructures and characteristics. Followed sintering imparts macroscopic integrity, yielding materials with specialised properties and prospective uses.

The present study emphasises the development of mechanically alloyed HEAs, their extraordinary functionality, and the difficulties presented by the process, which necessitate rigorous control and creative solutions. As scientists investigate the relationship between materials science and creativity, the prospect of mechanically alloyed HEAs beckons. This possibility exceeds properties to widen up opportunities for cutting-edge new materials at the forefront of scientific investigation.

1. Introduction: Over the span of several epochs, metals and alloys have shaped a variety of aspects of human existence. Their use has changed from manufacturing agricultural and hunting instruments to advancing the energy, transportation, and defence industries [1]. In materials science and engineering, alloying is a fundamental concept that involves mixing primary elements in higher concentrations with additional elements in less quantities [2], [3].

Numerous alloys including nickel, iron, titanium, magnesium, zinc and aluminium have been produced as a result of research efforts, and studies into their mechanical, thermal, and tribological characteristics have been thoroughly recorded [4]–[8]. Although the chemical composition of alloys has altered recently, for instance, nickel alloy is now utilised with Inconel 718 superalloy and other components [9]. Researchers have been much more interested in HEAs as a result of their better qualities to those of the more common alloys [10]. These characteristics are not just limited to better resistance to localised plastic deformation [11], but these alloys also exhibit promising strength, enhanced endurance limit under cyclic loading [12], a considerable plastic deformation in terms of plasticity [13], stability at high temperatures softening resistance, and outstanding corrosion resistance [14], wear as well as oxidation resistance [15]. As a result, high entropy alloys are recognised as promising class of material with the greatest prospects for innovation, with potential applications ranging from the maritime to the automotive industries [16], [17]. The impact of Mechanical Alloying (MA) and its related factors on the performance of High-Entropy Alloys (HEAs) is not fully explored in the present debate. As a result, an effort has been made to carefully evaluate the crucial part that mechanical alloying plays in the creation of HEAs, taking into account both its current limitations and potential future advantages. To support and promote existing and prospective research, recommendations are also offered with relation to several MA-related process factors. This chapter's summary may be organised as follows:

1.) An overview of HEAs and their stages of development

2.) The definition of HEAs, an explanation of their primary impacts, and a look at phase progression

3.) The brief introduction of many processing methods along with mechanical alloying and the influence of its process parameters on HEAs,

4.) A discussion of the distinct mechanical and operational characteristics displayed by HEAs,

5.) Suggestions for different attributes of mechanical alloying,

6.) Intended utilisation,

7.) scope as well as difficulties

2. High-entropy alloys

High-entropy alloys (HEAs) were the subject of independent investigations by Cantor et al. [18] and Yeh et al. [19] that year, both of which showed a departure from conventional alloy design techniques. In the past, alloying tactics focused on adding two or three elements; however, HEAs presented a paradigm change by including five or more main elements in their composition, and in some cases as much as thirteen elements in equiatomic ratios [19]. The presence of many components would often result in complex phase growth and development, contrary to the widespread understanding of binary and ternary phase diagrams, which was contradicted by this modification. The configurational entropy that exists within HEAs,

according to Yeh et al. [19], was shown to be significant enough to encourage the emergence of stabilised single or multi phases with unambiguous crystal structures. While the phrase "high-entropy alloys" was frequently employed when referring to this promising class of materials, other terminology, such as "multi-principal element alloys" and "compositionally complex alloys," also appeared in the scientific discourse [13]. This trend drove scientists away from the search for ideal HEAs and shifted their attention to exploiting entropy to create precise combinations with desired mechanical and structural characteristics.

2.1 Four major effects of HEAs.

Four basic characteristics give HEAs their individuality, making them fundamentally different from traditional alloys [20] which is elucidated in figure 1.

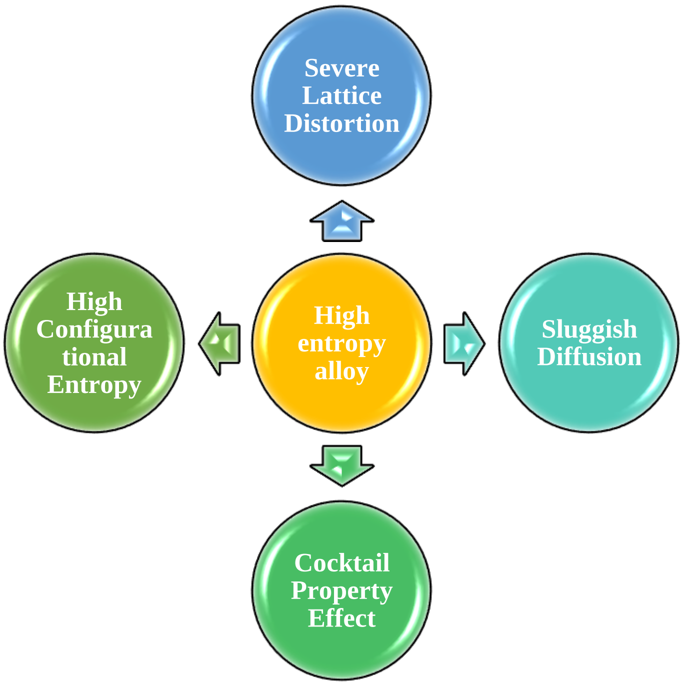

Fig. 1 – Four core effects associated with HEAs.

2.1.1 Effect of High Configurational Entropy: The thermodynamics of alloys is entwined with the high entropy effect, one of the four fundamental effects. The lowest Gibbs free energy defines equilibrium states according to the second rule of thermodynamics [10]. This action plays a crucial role in improving the stability of the solid-solution phase development and preventing the production of intermetallic compounds, which are notorious for their brittleness and difficult analysis [21].

2.1.2 Sluggish (very slow) Diffusion: As a barrier to atomic diffusion, the sluggish diffusion effect promotes the growth of fine precipitates, amorphous structures, controlled grain size, high recrystallization temperatures, low coarsening rates, and increased creep resistance [22]. It also inhibits phase transformations. This result not only permits careful control of microstructure morphology but also enhances HEAs' overall effectiveness.

2.1.3 Severe Distortion of Lattice: Multiple major components seen in the solid solution matrix of HEAs cause significant lattice deformation. Lattice stress and strain are caused by the existence of several distinct atoms with different atomic sizes surrounding each atom. Due of the non-symmetrical binding and distinctive electronic structure of various lattice sites, variations in crystal structure and bonding energies result in severe lattice distortion. By imparting significant solution hardening inside the distorted lattice and eventually increasing strength and hardness, this distortion helps to attenuate thermal impacts [23].

2.1.4 Cocktail Property Effect: The cocktail effect, which was first delineated by Ranganathan et al. [24], is the main focus of HEAs and is caused by the addition of at least five major ingredients to enhance material qualities. Single or many phases may result from the varied composition and processing of HEAs. Phase distribution, shape, and individual phase attributes interact to produce the final qualities. Similar to atomic-scale composites, these solid solutions include several components inside each phase, giving rise to characteristics resulting from complex interactions, reciprocal interactions, and considerable lattice deformation[25].

2.2 Processing methods for HEAs

The acquisition of finely powdered metals is a necessary step in the first stage of HEA processing, which is especially important for HEAs that include five or more key metallic elements. According to a literature review, there are two main ways to process HEA: using pre-alloyed powder as a precursor material and using metal powders mixed conventionally, then spark plasma sintering to mold into the appropriate form [26], [27]. Two main techniques are often used in completely pre-alloyed powder scenarios: atomization and Mechanical Alloying

(MA); alternate approaches include producing HEAs by melting followed by high-energy milling to produce powder [28], [29]. Typically, MA and gas atomization are used to create pre-alloyed HEA powder, which is then condensed using a variety of methods. For the manufacture of bulk HEA, the synergy of MA with spark plasma sintering proves to be quite effective[30]. Pre-alloyed powder may be produced via MA, which gives researchers the freedom to achieve a variety of compositions within reasonable energy and time constraints. While minimising excessive grain growth, Spark Plasma Sintering (SPS) ensures quick temperature exposure and little dwell time. Although they need higher temperatures and longer processing times, other methods including hot pressing and hot isostatic pressing also produce dense structures, leading to increased grain growth. The traditional press and sintering process becomes a popular choice for large-scale HEA production after SPS. While most attempts focus on traditional uniaxial pressing, certain articles [31], [32] explore the use of cold isostatic pressing. Traditional techniques like vacuum arc melting (VCM) followed by mechanical alloying and spark plasma sintering (SPS), are frequently used to treat HEAs. To deal with element non-uniformity, the melting process [33] calls for several warming cycles. Both processes take a long time, and some HEAs require intense cooling rates to avoid precipitating undesired hard and brittle intermetallic compounds in the disordered random solid solution phase. The manufacturing of certain HEAs via traditional procedures also becomes difficult as a result of the aforementioned discussions, especially when dealing with complex geometries [11].

3. Mechanical alloying of high entropy alloys:

S. Vara Lakshmi et al. [34], who pioneered the production of a nanocrystalline AlCrCuFeTiZn HEA, conducted the initial investigation of HEA manufacture using Mechanical Alloying (MA). After that, a definite rising trajectory in research articles centred on MA appeared. Some review studies that examine mechanically alloyed HEAs are currently available in the literature [35]–[37]. This study covers both mechanical and functional features with an eye towards prospective applications, illuminating the most recent developments in the field of mechanically alloyed HEAs. A suitable method for dealing with alloys including elements with different melting points is MA, a non-equilibrium process. It extends the range of solid solubility and makes it easier to create nanocrystalline materials with consistent microstructures and compositions. MA plays a significant role in the creation of complex and intelligent materials as a solid-state manufacturing technique. Particle size reduction, efficient mixing and blending, and particle reshaping are the main goals of milling. Through repeated cycles of welding, fracturing, and rewelding, the reinforcement phase particles get ingrained in the matrix during the MA process. Metal powder particles caught between the milling balls or ball-wall surfaces during milling can deform, fracture, or weld depending on the mechanical properties of the metallic powder [38]. Between the speeds of welding and fracturing, a steady-state equilibrium is eventually reached. This equilibrium demands that the strengthening process be distributed evenly and that super-saturated solid solutions be produced. Following aligning, there is particle deformation, which results in a return to the initial morphologies. Equiaxed development of particles prevails during the welding phase and is distinguished by obvious, oriented welding streaks. The shift from this stage into the appearance of spontaneously aligned welding lines that control particle production defines the balance between welding and fracture. The conclusion of the procedure includes a steady-state phase that starts the microstructure refinement process while keeping the particle size and dispersion largely constant. A few of MA's unique characteristics include the development of an amorphous phase, the extension of mutual solid solubility limits, a reduction of grain size to the nano-meter range, the generation of novel crystalline and quasi-crystalline structures, and fostering of low-temperature chemical reactions [39]. MA process depends on a number of important variables, each of which is essential to the synthesis of homogenous atomic particles. These elements interact to affect the final product's characteristics, including stoichiometry, amorphization, and degree of disorder. To create powder with precision, these elements need to be controlled in a subtle way.

3.1 Important Characteristics of Mechanical Alloying

1. MA exhibits faster processing times, less energy consumption, strong coating adhesion, and versatility for producing different structural coatings.

2. It guarantees improved compositional accuracy, overcoming segregation difficulties.

3. MA excels in creating composites or alloys with perfect chemical homogeneity that are nanostructured.

4. It enables a faster diffusion rate.

5. MA is skilled in producing a wide range of material classes, including amorphous and quasicrystalline materials as well as materials that are strengthened by oxide dispersion [40].

6. While attaining a nanocrystalline nature with HEA alloy powder is preferred, maintaining this property in bulk materials offers difficulties [40].

Essentially, the combination of MA and HEAs paves the way for novel materials with broad application, mixing mechanical brilliance with functional perfection.

3.3 Various attributes of mechanical alloying

In order to get fine-grained particles, exact morphology, and controlled microstructures, one must carefully optimise the process parameters. In the following we briefly describe how process variables interact with one another and how this affects the mechanical alloying (MA) process by displaying dependence of various process parameters on mechanical alloying. Moreover, various attributes associated with mechanical alloying are schematically illustrated in Figure 2.

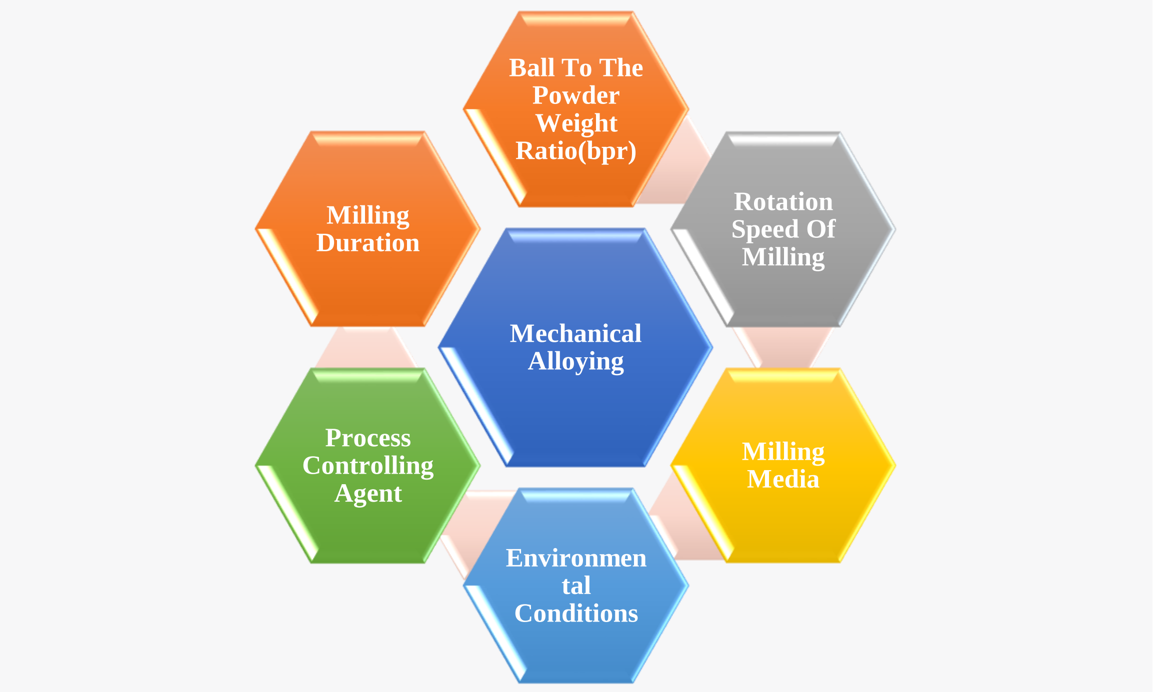

Fig. 2 – Various attributes associated with mechanical alloying.

3.2.1. Influence of the weight ratio of the ball to the powder (BPR)

The rate of amorphization is greatly affected by the ball-to-powder weight ratio (BPR), which is principally controlled by the mechanical energy imparted from the ball to charge, enabling particle reactions and interdiffusion. Amorphization rate augmentation is correlated with BPR augmentation. A noticeable portion of the amorphous phase appears within the first 48 hours of ball milling, however continued milling causes the crystalline phases to form owing to heat production. A downside of using a larger BPR is contamination brought on by excessive weight ratios, which results in coarser particles [41]. A lower BPR, on the other hand, exhibits variations in crystallite size showing the discrepancies in the performance of milling process and improper phase growth and development.

3.2.2 Influence of speed of rotation in milling

Morphology of powder particles is significantly affected by speed of rotation during milling operation; higher speeds promote improved cold-welding between particles because the balls hit the surface of ball or vial more forcefully. Notably, greater particle sizes are correlated with an increase in spinning speed. Maximum energy impact is achieved at higher RPMs, but lower speeds are linked to decreased milling efficiency [42]. High-energy milling for HEA synthesis was first proposed by Mykhailo Semen'ko et al. [43], who accomplished the task of synthesizing CoCrFeNi consisting a stable single phase face centered cubic (FCC) structure HEA in just 2 hours, as opposed to the customary need of milling for a long time. According to research investigation conducted by Salemi et al. [44], Despite milling for 50 hours at 300 RPM, sufficient alloying was not attained; nevertheless, raising the rotational speed to 350 RPM led to the achievement of a single-phase FCC structure. Energy transmission to the powder particles of high entropy alloy is said to amped by 1.7 times with an increase in rotational speed up to 350 RPM [44].

3.2.3. Influence of milling duration

A mechanism involved both repeated cold-welding and fracturing occurs during the milling process. The primary rise in particle size is mostly caused by cold-welding. The fracture mechanism takes control as the milling process advances, resulting in a reduction in particle size. An X-ray diffraction plot is used at various milling speeds to evaluate the degree of alloying. Cold welding and fracturing eventually get to a dynamic equilibrium where they are balanced. Avoiding excessive milling time is crucial because extended duration reduces the appearance of diffraction peaks. It is difficult to distinguish the stages in the powder as a result of the prolonged milling time. Additionally, crystal size decreases and lattice strains rise with milling time. Long-term grinding can also result in contamination problems and the formation of undesirable phases. On the other hand, shorter milling times do not produce the desirable features[45].

3.2.4. Influence of process Control Agent (PCA)

Particle shape and size must always be precisely controlled, and milling conditions must constantly be taken into consideration. One technique used is the use of surface active agents or organic solvents known as process controlling agents (PCAs) to prevent excessive cold welding [46]. These substances soak onto particle surfaces and have surface activity, which reduces surface tension [47]. They aggressively interfere with the cold-welding process to prevent agglomeration. A variety of control agents, including n-heptane, toluene, ethanol, stearic acid, hexane, methanol, poly-ethylene glycol, and ethyl propyl alcohol, have been regularly reported in the context of mechanical alloying (MA) [48]. PCAs influence the intrinsic properties through interacting with the material's surface particles, affecting solubility levels, adjusting crystal dimensions, and ultimately altering the final mechanical properties.

3.2.5. Influence of environmental Conditions

The milling air conditions are one of the key variables influencing elemental powder. The ultra-fine powder that is created as a result of milling has a large surface area, which makes it extremely reactive with oxygen and sensitive to the creation of oxides as well as reactive with other gases like nitrogen, sulphur, or hydrogen [49].

3.2.6. Recommendations

Optimal modifications to process variables are essential to achieving the most favourable characteristics. Mechanical Alloying (MA), which depends on a number of variables, gradually changes the originally spherical shape of elemental powder. For the defined optimised time, they include maintaining a intermediate ball-to-powder weight ratio (10:1) and an adequate speed of about 300 RPM, which significantly retains the powder's morphology [50]. It is preferable to avoid using an excessive amount of milling time since this lengthens the diffraction peaks' ability to stand out. The powder's phase identification suffers because of the prolonged duration. Stearic acid stands up as the most suited surface-active chemical to create equilibrium between welding and fracturing in the context of the continuous welding-fracturing process in MA. Additionally, a number of safety measures are advised for the Mechanical Alloying (MA) procedure:

1. It is advisable to fully mix various particles before adding them to the vial rather than simply placing metallic particles there.
2. To avoid particle settling, it is crucial to only apply a little amount of processing control agent since too much addition might make milling less efficient.
3. In light of the materials being processed, RPM, vial composition, and ball materials, it is advised to stop a milling run after a certain amount of time. This helps to reduce vial temperature and jar motor wear [51].

4. To prevent the accumulation of powder particles, which might provide subpar milling results, routine inspections are essential.
5. The powder blend should be kept in a container for a considerable amount of time after the grinding process since it is in a highly heated condition and might cause unanticipated events.

It is essential to use a micro-wave oven or induction furnace to remove moisture in vacuum and processing control agents from High-Entropy Alloys, maintaining their purity from any impurities, before compaction and sintering.

3.3. Thermodynamic criteria for phase evolution in high entropy alloys

The evolution of phases and high temperature stability of HEAs are thoroughly discussed on the basis of thermodynamic parameters in this section. It is commonly known that the HEAs' high configurational entropy helps to stabilise them. The formation of solid solution in a multi-component system involves a change in configurational entropy (ΔS_{conf}), which is represented by the following equation:

$$\Delta S_{conf} = -R \sum_{i=1}^{n} (X_i \, ln \, X_i)$$

The magnitude of ΔS_{conf} has been determined to be 1.61 times R in a system composed of five equiatomic elements in the configuration of an alloy where component i contributes a mole fraction x_i and R indicates the universal gas constant. It's interesting to note that for the majority of metallic elements, this number exceeds even the entropy change caused on by fusion (ΔS_f). Notably, the increased ΔS_{conf} in the world of multi-component High-Entropy Alloys (HEAs) serves to effectively reduce the Gibbs free energy of mixing ($\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$) within solid solution phases. This is significant since the enthalpy of mixing (ΔH_{mix}) often stays low in metallic materials. Stable random solid solution phases develop as a result of this complex interaction [34]. Small differences in atomic radius and a large negative value of the enthalpy of mixing are two crucial factors for the production of a stable random disordered solid solution in HEA. Other characteristics can also contribute to the creation of disordered random solid solution phases in multi-principal element systems. The typical expression for the difference in atomic radius or atomic size mismatch (δ) is:

$$\delta = 100\sqrt{\sum_{i=1}^{n} c_i\left(1-\frac{r_i}{\bar{r}}\right)^2}$$

where $\bar{r}$ is the mean value of the atomic radius and c_i is the percentage of the ith component. The macroscopic Miedema approach for binary liquid compositions served as the foundation for obtaining the ΔH_{mix}.

$$\Delta H_{mix} = \sum_{i=1,i\neq j}^{n}(\Omega_{ij}C_iC_j)$$

ΔH_{mix} is known as enthalpy of mixing of a system consisting n-component, wherein

$$\Omega_{ij} = 4\Delta H_{ij}^{mix}$$

The mixing enthalpy of a binary alloy consisted of the element i and j is ΔH_{ij}^{mix}, while the mixing entropy ΔS_{mix} is ($\approx\Delta S_{conf}$). Additionally, it has been postulated that the thermodynamic parameter ($\Omega \geq 1.1$) and the mismatch in atomic size may both be used to account for the stability of multi-principal elements HEAs. The thermodynamic parameter (Ω) is presented mathematically by

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|}$$

where

$$T_m = \sum_{i=1}^{n} C_i(T_m)_i$$

T_m is the melting temperature of the multi-principal elements system made of n-components [52]. Additionally, Guo et al. [42] observed that the formation of the solid solution phase in the multi-principal elements alloy is not significantly caused by the difference in Pauli electro-negativity ($\Delta\chi$). The valence electron concentration (VEC) may be utilised to quantitatively anticipate the emergence of stable Face-Centered Cubic and Body Centered Cubic phases in these alloy systems is expressed as

$$VEC = \sum_{i=1}^{N} C_i(VEC)_i$$

According to reports, the VEC has a significant effect on the synthesis of stable disordered random solid solution phases because (i) the FCC phase can occur for VEC ≥ 8.0; (ii) the FCC and BCC phases is permitted for $6.87 \leq VEC < 8.0$; and (iii) the BCC phase may only exist for $VEC < 6.87$; concluding that the VEC has strong impact on synthesizing stable random solid solution phases.

Alloys with multi-principal elements are made up by combining several different elements. By adjusting configurational entropy of mixing and other crucial parameters, such as differences in atomic radii or atomic size mismatch (δ), valence electron concentration (VEC), mixing enthalpy (ΔH_{mix}) and electro-negativity ($\Delta\chi$), it has been possible to produce simple random disordered solid-solution phases as opposed to hard intermetallic compounds. The wide variety of compositions awaiting inquiry in the centre portions of the composition space is what draws researchers to study HEAs in the first place. As a result, a variety of compositions are now possible to explore to achieve intended properties.

4. Properties and proposed applications of high entropy alloys

4.1. Mechanical characteristics

The mechanical characteristics of the material, particularly its phases, are the key drivers for assessing its quality and robustness. For instance, HEAs based on the FCC structure have high plasticity and poor yield strength, whereas HEAs based on the BCC structure displays high yield tensile strength and low ductility. The micro-hardness for mechanically alloyed HEAs ranges from 375 to 699 HV. When mechanical alloying and specialised consolidation procedures are applied to HEAs, several advantages become apparent, including the development of nano-twins, numerous hardening processes, and precipitate formation, all of which increase the HEAs' strength.

For instance, CoCrFeNi exposed to mechanical alloying followed by SPS displayed a hardness (570 HV) [53], which is approximately four times larger than the hardness (150 HV) of the as-cast alloy [54]. AlCoCrFeNi produced with Mechanical Alloying and SPS, on the other hand, attained a compressive yield strength of 2.6 GPa [55], which is approximately two times as strong as its as-cast counterpart [56]. The creation of nano-precipitates helped AlCoFeNiMoTi HEAs treated with Mechanical Alloying to have better strength in comparison to as-cast HEAs [156]. Mechanical alloying and SPS were used to create a NbMoTaW HEA that had outstanding yield compressive strength (2612 MPa) and 8.8% ductility. On the other hand, the same HEAs created using arc melting showed significant strength of 1246 MPa and 1.7% flexibility, respectively [57].

Notably, a non-equiatomic $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}$ multi-component alloy outperformed conventional as-cast HEAs in terms of mechanical parameters, showing outstanding bend strength of 2.6 GPa, hardness of 4.4 GPa, plastic strain of 4% and yield tensile strength of 1.4 GPa [58]. Another instance is the creation of an AlCoFeNiTi HEA using Mechanical Alloying and SPS, which produced a dominating FCC phase with precipitation of ordered Al-Ni rich B-2 phase and Al_3Ti particles [59]. The HEAs had a high compressive strength of 2.9 GPa and a plastic strain of 5.9% because to the existence of twin boundaries inside the solid solution-strengthened Face Centered Cubic phase [59]. Additionally, FCC phase of $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}$ showed enhanced strength (1460 MPa) and ductility (14.5%) after the addition of Ni_3Ti precipitates and TiO_2 particles [60].

4.2 Functional properties

The study on HEAs, a unique class of materials, has mainly focused on its simple micro-structure and mechanical characteristics. An in-depth study has not been reported on the developments of functional characteristics of high entropy alloys. The peculiar structural component of multi-principal element solid solutions seen in HEAs is closely entwined with these characteristics.

4.3. Preferred applications of high entropy alloys

The search for substitutes for traditional superalloys has been prompted by the spike in demand for structural and functional materials in a variety of industries, including mining, transportation, marine, and aviation, among others. Different HEAs show promise for a wide range of possible applications in various areas as follows:

1. The random disordered solid solution phases FCC and BCC form with HEAs, which have great thermal stability and can sustain extremely high temperatures[14]. HEAs are great candidates for use in steam turbine blades, engine parts, boiler pipes, chemical plants and heat exchanger tubes that withstand high temperature and pressure because of their stated hardness, which is close to 110 HV.
2. Due of its excellent cold formability and high strength-to-weight ratio, $Ti_{15}V_3Cr_3Sn_3Al$ HEA is used in aviation components [61]. Similar to how $Ti_3Al_8V_6Cr_4Zr_4Mo$, which combines high strength, plasticity, fatigue durability, and exceptional fracture toughness, finds use in aviation [62]. Notably, the gear system of landing of the A-40-500/600 aircraft and Boeing-777 aircraft have successfully used $Ti_{10}V_2FAl_3Fe$, recognised for its outstanding ductility and lightweight attributes [63].

3. Demanding qualities including mechanical characteristics at elevated temperatures, resistance to oxidation and corrosion are crucial for the correct function of ultra-supercritical boilers [64], [65]. The $Al_XCoCrFeNi$ HEA provides an appealing option that can endure supercritical settings whereas HR3C steel is often employed [66].
4. Materials that are designed for maritime applications must have their antifouling, tribological behaviour, anti-corrosion, and mechanical qualities thoroughly evaluated. $AlCoCrFeNiCu_{0.5}$ has exceptional antifouling properties along with outstanding wear and corrosion resistance, according to studies [67]. $CoCrFeNiCu_X$ showed improved tribological behaviour with increasing Cu content, whereas $Al_{0.4}CoCrFeNiCu_X$ has demonstrated antibacterial characteristics [68].
5. Nanocrystalline HEAs have the potential to be used to create tiny devices that can withstand extreme environmental conditions, making them appropriate for the energy, aerospace, nuclear, medicinal, and tool industries [69].
6. In HEAs, extraordinary magnetic features (super-magnetic, ferro-magnetic, soft-magnetic) have been discovered recently.
7. HEAs are excellent choices for materials used for nuclear application including nuclear fuel cladding due to their increased irradiation and corrosion resistance.
8. HEAs might provide coatings that are heat- and wear-resistant, but new techniques are needed to improve their uniformity and cohesiveness with substrates.
9. It is worth investigating how refractory metallic HEAs may be used as thermal barrier coatings.
10. Hard coatings, diffusion barriers, and biomedical coatings may be made from the characteristic carbides and nitrides found in HEAs due to their outstanding hardness and strength and amorphous or solid solution structure [70].
11. $Al_{2.08}CoCrFeNi$ has peculiar properties that position them for potential electronic applications and demand more study, such as their nearly constant resistivity [71].
12. Lightweight HEAs are the subject of research because they may be used as battery anode materials, mobile facility enclosures, and in the transportation industry.

5. Challenges and the opportunities

1. **Limited practical applications**: Despite having exceptional mechanical capabilities, HEA materials find it difficult to replace well-known conventional alloys like steel, titanium, and nickel-based superalloys. The potential of HEAs is still being fully used,

with a focus on application-based development frequently limited to microstructure and mechanical characteristics.

2. **Advanced Functional properties**: The success of future HEA development depends on obtaining outstanding mechanical qualities while combining advanced functional characteristics as magnetic behaviour, stress corrosion resistance, weldability, shape memory effect, and more. For this, HEAs must be specifically designed to be both mechanically strong and versatile.

3. **Role of Interstitial Elements**: Interstitial elements, in particular C, B, H, O, and N, play an important function in HEAs but are not fully investigated. It is vital to look into how they affect mechanical characteristics, phase stabilisation, microstructure, and compound formation.

4. **Application-Centric development**: While earlier research mostly focused on morphology, microstructure, and mechanical characteristics, the focus now has to be on the creation of HEAs that are tailored to certain applications. It is crucial to design HEAs for certain functional characteristics and requirements of future generations.
5. **Nano-crystalline HEAs and catalyst**: Catalyst applications utilising nanocrystalline HEAs have a tremendous amount of promise. However, obstacles to synthesis and a concentration on bulk forms prevent advancement. High-temperature stability may be predicted with the use of computational design, and nanoscale synthesis has to be addressed.
6. **Cost-Effectiveness and Durability**: In order to replace current materials, HEAs must be both affordable and long-lasting. For the actual deployment of HEAs, handling waste, recyclability, and material durability in hostile settings are critical factors.
7. **Weldability and joint optimization**: Research gaps exist in HEA-HEA and HEA-non-HEA material weldability. Joint optimisation. It is crucial to improve joint performance, mechanical characteristics, and microstructural uniformity. Exploration of impurity effects on joint characteristics is necessary.

8. **Diverse Powder Processing Methods**: Although mechanical alloying (MA) is often used, alternative techniques including gas atomization and electrolytic processing are still being researched for use in the creation of HEA powder.
9. **Industrial material improvement**: Businesses are looking for materials that perform better in challenging circumstances. There is a critical need for the creation of materials with enhanced high-temperature performance, wear resistance, and dynamic mechanical stresses.

These difficulties lead the development of novel materials to fulfil the needs of the aviation, marine, energy, and transportation sectors.

6. Conclusion

High-Entropy Alloys (HEAs) are created by a process known as mechanical alloying (MA), which is frequently used. This in-depth analysis explores the usage of MA in the creation of HEAs and focuses on all of its many elements. This chapter's main objective is to offer a thorough examination of the phase development seen during the MA of HEAs.

MA produces a new result, defying the traditional wisdom that HEAs, with their several primary constituents, form complicated and multiphase crystal structures. With the incorporation of numerous key constituents, it makes it easier to obtain single-phase crystal formations. Hardness, high-temperature strength, thermal stability, corrosion resistance, oxidation resistance, and wear resistance are all greatly improved by the MA process. The exact management of HEAs' delicate structure is credited with this improvement. The homogenous solid solutions produced by the careful management of HEAs' fine powder dispersion are credited with this improvement.

Due to its excellent retention and densification properties, spark plasma sintering (SPS) is emerging as a preferred method for consolidating HEA metal powder. The resulting high hardness endows HEAs with noteworthy wear-resistant properties. Additionally, investigations on the behaviour of corrosion consistently show increased corrosion resistance with HEA coatings.

A key factor affecting crystal formations and subsequent attributes is the length of MA. The ideal milling time is crucial because insufficient time prevents correct alloying and too much time prevents precise phase identification in the metal powder. Long-term milling lowers the crystal size of the particles while enhancing the lattice strain inside the particles.

Stability in phases or powerful strengthening processes are required in order to produce HEAs with high mechanical characteristics under various environmental conditions. The results highlight the fact that MA mostly produces solid solution phases, occasionally containing numerous phases and complex structures. The development of metastable phases throughout the MA process is highlighted by the observation of the shift from phases to complex structures during consolidation and annealing.

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