The development of Light-weight High Entropy Alloy (LWHEA) composites Al₃₅Ti₃₅Si_(20-x) Be₁₀B_x (x=1,2,3) wt.% prepared by powder metallurgy route

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I declare that this dissertation submitted for the degree M Eng.: Metallurgical Engineering at the Vaal University of Technology was written entirely by myself. It has not been presented in any previous application for a degree or in part. Unless otherwise stated by reference or acknowledgement, the work offered is all my own.

CAP Li.

S.M Dlamini

10 May 2022

DEDICATION

"I love you, Lord, for your mercy has never failed me in all my days I have been held in your hand". "From the moment that I wake up until I lay my head, I will sing of the goodness of God". "For all my life, you have been faithful even in this journey of M Eng., and amid the pandemic, you have been faithful. You have been so good through this journey, and every step I was able to, I will sing of your goodness."

"For your goodness is running after me."

According to Psalms 23: 6

"Surely goodness and mercy and unfailing love shall follow me all the days of my life, And I shall dwell forever in the house and the presence of the Lord."

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ABSTRACT

High entropy alloys (HEAs) are novel alloys with five or more primary elements in an equiatomic or near-equiatomic proportionate ratio. The configuration entropy in HEAs tends to stabilize the development of solid solutions like body-centred-cubic (BCC), face-centred-cubic (FCC), and hexagonal-closed-pack (HCP). Compared to traditional alloys, the increased number of primary elements present in HEAs causes severe lattice distortion, resulting in higher mechanical properties. HEAs are seen as a radical transformation for the next generation of high-temperature alloys in extreme conditions like aircraft, cutting tools, and bearings. The main objective of this dissertation was to develop new types of $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3 wt.%) lightweight high entropy alloys using mechanical alloying and Spark plasma sintering to understand better how microstructures evolve during sintering and secondary

The first part of the project involved subjecting the elemental powders (aluminium, titanium, silicon, beryllium and boron) chosen for this work to mechanical alloying for 45 hours. Subsequently, applying plasma sintering to produce all the three fully densified alloy composites: $Al_{35}Ti_{35}Si_{19}Be_{10}B$, $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$, and $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ at 1000 °C with densities 3.48, 3.40 and 3.51 g·cm⁻³, respectively. The sintered alloys showed the formation of BCC and FCC solid solutions as well as ordered solid solution phases such as Ti₄Si₈/ Ti₁₆Si₃₂, $Al_4Ti_8O_2$, and B_2N_2 , with a microhardness of 957, 989, and 1093 HV, respectively.

processing, as well as the mechanical properties that can be derived.

The three developed alloys also showed remarkable corrosion resistance in a 3.5 wt.% NaCl solution. Tribological characteristics of the developed $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3 wt.%) alloys were examined under dry sliding wear conditions with stainless steel as the static friction partner under a 10 N load and a sliding duration of 60 min. The results indicated that the increase of silicon in the alloy has an impact on the friction coefficient and wear rate. High-temperature oxidation test was also conducted for $Al_{35}Ti_{35}Si_{19}Be_{10}B$, $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$, and $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ alloys at 700 and 900 °C for 400 hours and 200 hours, respectively. These alloys showed good resistance to high-temperature oxidation at 900 °C as compared to oxidation at 700 °C. The resistance to oxidation was indicated by low weight gain and low rate constant.

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Chapter 1

1.1 INTRODUCTION

1.1.1 BACKGROUND

In the metallurgical culture, alloying is proclaimed to be an immeasurable skill to humanity. The alloy selection, its design, and production have been solely dependent on one principal element concept for the basic production of conventional alloys. Most alloys that exist today were produced based on that concept, and it has always been trusted since it made materials applicable to everyday life. However, some limitations were encountered with the degree of freedom of the compositions, which led to constraints in developing unique microstructures, mechanical properties and applications. As more discoveries unfolded, researchers like Jien-Wei Yeh and Brian Cantor (Yeh *et al.* 2004; Cantor *et al.* 2004b) independently presented a solution by introducing a new class of materials called High-entropy alloys (HEAs) which are characterized by their unconventional compositions based on multi-principals element concept, instead of one principal element like in the case of conventional alloying (Pickering & Jones 2016). These alloys were discovered to give ease and allowance for possible applications resulting from their exceptional structures and properties.

HEAs are composed of at least five or more principal elements whereby each principal element has a concentration of between 5 and 35 at.% in equimolar ratios or near-equimolar ratios (Tsai & Yeh 2014; Cantor 2011). The name-calling of HEAs was given owing to the high configurational entropy of mixing possessed by the liquid or random solid-solution phases exceeding those of conventional alloys. Based on existing research outcomes, it showed that multi-principal element alloys are prone to the development of different kinds of phases and intermetallic compounds that lead to brittle microstructures making the processing of alloys impossible. On the contrary, some other experimental results revealed that the higher configurational entropy of mixing in HEAs generates the formation of simple structured solid solution phases. Therefore, microstructural stability is one of the characteristics shown by HEAs, which is highly crucial in the development and applications of such alloys.

One of the factors that has attracted attention toward HEAs is their remarkable properties which include their great room temperature strength/hardness, excellent strength and thermal stability at elevated temperatures, incredible wear resistance, outstanding corrosion and oxidation resistance, astounding structural durability, exclusive fatigue and fracture resistance (Zhang *et al.* 2018b; Tsai 2016; Maulik *et al.* 2016) etc. To add more, most properties possessed by HEAs are not found in conventional alloys which makes them unique in certain aspects of applicability. Also, the fact that they are favourable to high temperatures makes them even more attractive, leading to an increased spectrum of application.

The extraordinary physical and chemical properties of HEAs are influenced by four major factors (Miracle & Senkov 2017; Kim *et al.* 2018). First and foremost, the high entropy effect, characterised by configurational mixing entropy, mixing enthalpy, atomic size difference and valence electron configuration of the elements results in the formation of multi-component solid-solution phase alloy. Secondly, the lattice distortion, which typically suppresses dislocation movement, increases strength and hardness properties and lessens thermal conductivity. Additionally, sluggish diffusion, which results in slower diffusion and phase transformation kinetics as compared to conventional alloys, is generally used to clarify the incredible high-temperature properties (strength and structural stability). Lastly, the cocktail effect sums up the relationship between the constituent elements and the resulting high-temperature properties.

As research on HEAs deepened, the newly developed materials named Light-weight high entropy alloys (LWHEAs) were noticed to have garnered extensive attention in both the transportation and defence industries. That is why the scientists have expanded their research in the development and design of these immense lightweight materials. The main highlight of these lightweight materials is that they are weight saving and cost-saving when it comes to their applicability, which explains the demand in the transportation industry. Lightweight development aims to simultaneously preserve or enhance a product's functionality while decreasing the total weight of the product (Fan & Njuguna 2016).

Lightweight material/alloy design and development for industrial applications is quite a challenging aspect of research especially now that the sustainability of the ecosystem is of

importance (Kumar & Gupta 2016). The sectors such as aerospace, automotive and energy depend on the research conducted in this particular aspect to replace high-density alloys with new lightweight alloys without compromising the structural properties while avoiding an increase in cost.

LWHEAs are defined based on their density, according to Tian *et al.* (2019), and in most cases, the density of titanium ($4.51 \text{ g} \cdot \text{cm}^{-3}$) is used as a limit (Li & Zhang 2019), but others define LWHEAs as having the density less than 7.00 g $\cdot \text{cm}^{-3}$ which are mostly made of solid solutions and intermetallics, with only limited compositions forming just a single-phase solid solutions. For one to be certain of LWHEAs, high concentrations of aluminium (Al) and titanium (Ti) will be noticed or be present in the composition of most LWHEAs. Therefore, the composition of LWHEAs must be adjusted in the design of these alloys to achieve the desired microstructure which will later result in excellent mechanical properties, with the density kept very low. Another factor that needs to be considered and well understood when it comes to the development or design of LWHEAs is the empirical phase-formation rules, even though they are not quite conclusive in predicting the solid-solution formation.

These empirical rules may greatly underestimate the free energies of solid-solution phases by not considering the enthalpy contribution of solid-solution phases. This is due to the strong interatomic interactions between individual elements found in Al-containing LWHEAs. It is quite challenging to form Al-containing equimolar LWHEAs with a density of less than 5.5 $g \cdot cm^{-3}$. For this research study, the elements which are used include titanium (4.51 $g \cdot cm^{-3}$), aluminium (2.70 $g \cdot cm^{-3}$), silicon (2.33 $g \cdot cm^{-3}$), beryllium (1.85 $g \cdot cm^{-3}$) and boron (2.46 $g \cdot cm^{-3}$). These elements tend to possess higher chemical activity, with larger atomic radius, also with a large difference in melting point and boiling point. But because they are not included in the new alloy system for design, their development normally shows challenges (Feng *et al.* 2016). When processing LWHEAs, the physical properties may solely not always promote difficulties, but also the selected processing route can affect the desired structure and properties. Typically, HEAs are manufactured by conventional melting (vacuum arc melting, skull induction melting) and casting into ingots. Nevertheless, the cast products are too defective (typically exhibiting voids and porosity) which results from thermal expansion and contraction. Moreover, the casting method is a challenging and complicated process to control (Qiu 2013; Joo *et al.* 2017). The large scale (kilogram scale) casting of HEAs is regularly tricky, as most HEAs have weak liquidity and castability, and substantial chemical inhomogeneity, which makes them unfavourable for industrial application (Lu *et al.* 2017). Additionally, as-cast HEAs have low hardness (Colombini *et al.* 2018).

An alternative route which stands to improve the shortcomings of the casting method is the powder metallurgy (PM) technique (Kang *et al.* 2018b). The PM approach is a solid-state processing technique which includes mechanical alloying (MA) and rapid consolidation of powders by spark plasma sintering (SPS). MA aids to fabricate the HEA powders consisting of homogeneous morphologies and solid solution, chemical composition distribution and control (Veronesi *et al.* 2017; Colombini *et al.* 2018; Yurkova *et al.* 2019). Also, MA helps attain nano-sized starting powder particles before sintering. Spark plasma sintering (SPS) is described as a rapid consolidation process utilised to form bulk high-density HEAs (Veronesi *et al.* 2017). SPS technique is quick, energy-efficient and pressure aided technique that makes use of pulse current to develop a volumetric joule heating between contacting powder particles resulting in their consolidation (Laurent-Brocq *et al.* 2019).

An additional advantage of PM is that it is a trusted processing method for producing complex shapes and nanocrystalline alloys (Sluzalec 2015), and for lessening the metal removal processes, which result in low production costs as compared to conventional casting (Joo *et al.* 2017). Moreover, this metallurgical process is increasingly suitable for producing small and exact HEA parts that are subjected to very high temperatures (Kang *et al.* 2018b).

1.1.2 RESEARCH PROBLEM(S)

Most studies that have been conducted on High Entropy Alloys (HEAs) and Light-weight High Entropy Alloys (LWHEAs) showed that melting and casting is a typical synthesis route that has been utilised by researchers worldwide. However, there are some limitations associated with this melting and casting route. One of the significant constraints is the development of heterogeneous microstructure or dendritic and interdendritic microstructures formed in HEAs and LWHEAs due to segregation resulting from the slow rate of solidification (Cheng *et al.* 2018).

Furthermore, less than five percent of reports on LWHEAs so far deals with the synthesis route of these alloys by solid-state processing, which includes mechanical alloying (MA) followed by spark plasma sintering (SPS). Since materials properties are closely linked with the processing route and microstructures, it is imperative to understand the fundamentals of the sintered LWHEAs for the replacement of Ni-based alloys to produce compacts that will meet lightweight applications requirements, which are currently in demand.

1.1.2.1 Sub- research problem

Generally, high-temperature turbine engines are made of Ni-based superalloy material. The superalloys, primarily Ni-Co based, have a high density. In this case, Ni-base material can be replaced with lighter alloys without compromising the mechanical properties of the turbine blade. These alloys tend to reduce fuel efficiency and overall the density or weight of turbine blade hence LWHEAs, will be a good substitute for Ni-Co based alloys. The replacement of Ni by other elements could reduce cost and density.

1.1.3 RESEARCH PURPOSE (S)

Given the constant interest in lightweight materials for a basic application, for example, in the transportation sector, endeavours have been made to develop lightweight, high-performance HEAs with the focus being the lightweight applications to alleviate greenhouse gas emissions. The principal advantage of modern lightweight materials is either their restricted properties or high manufacturing cost. Consequently, persistent efforts are made by researchers to develop new types of lightweight alloys, which are cost-effective and meeting properties requirements.

This study will, therefore:

- a. Provide scientific knowledge to the development of lightweight alloys, by keeping density as low as possible to satisfy the needs of the transportation sector, for their application.
- b. Provide detailed information on the development of LWHEAs using the powder metallurgy route since it is quite limited for researchers wanting to explore other processing methods other than the conventional ones.

- c. Weight reduction, by using light elements that are cost-effective for the replacement of high-density alloys used in the transportation sector.
- d. Lead to cost reduction and attainment of efficient and effective high-temperature applications.

1.1.4 RESEARCH OBJECTIVE(S)

1.1.4.1 The aim of the study

The main objective of this research study is to develop lightweight high-entropy alloys $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3) wt.% by mechanical alloying and spark plasma sintering to attain relatively low density compared to existing nickel-based superalloys. A secondary goal is to achieve remarkable mechanical and high-temperature properties that are comparable to nickel-based alloys and that possess a microstructure with potentially high oxidation and corrosion resistance.

1.1.4.2 Specific objectives

The following specific objectives will be employed for the development of lightweight highentropy alloys through the powder metallurgy route:

- a. To optimise and fully characterise the effect of mechanical alloying on the synthesis and microstructural development of Al₃₅Ti₃₅Si_(20-x)Be₁₀B_x (x=1,2,3) wt.% lightweight highentropy alloys.
- b. To fully characterise the sintered $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3) wt.% lightweight highentropy alloys to evaluate the microstructural homogeneity, formed phases and compositions, and the effectiveness of the SPS process in the consolidation of the composites.
- c. To evaluate the effect of boron content on the formation of phases, density and hardness of the compacts.
- d. To evaluate high temperature oxidation and corrosion resistance of the developed $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3) wt% lightweight high-entropy alloys.
- e. To evaluate the wear behaviour of the developed $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3) wt% lightweight high-entropy alloys.

1.1.5 RESEARCH QUESTION(S)

- a. Can the selected composition for the newly developed lightweight high-entropy alloys prepared by mechanical alloying and spark plasma sintering lead to the desired microstructure that will yield good mechanical properties for the replacement of Ni-based superalloys?
- b. Can the newly developed lightweight high-entropy alloys high-temperature properties surpass those of Ni-based superalloys?
- c. How does the addition of boron content affect the density, mechanical properties, final microstructure and thermal stability of the developed lightweight high-entropy alloys?
- d. Do the newly developed lightweight high-entropy alloys meet the requirements of the transportation (aerospace and automotive) and the energy sectors which is weight-saving and cost-saving?

1.1.6 REFLECT ON THE SCOPE

The research focuses on alloying powder selection, composition design, and the development and optimization of appropriate Mechanical Alloying and Spark Plasma Sintering processing parameters. Density, microstructure, microhardness, corrosion, and wear-resistance of the developed LWHEAs were all examined.

1.1.6.1 Structure of the dissertation

The first chapter provides an overview of the entire project. It introduces the dissertation's topic, difficulties, goals, and contents. The definitions and discussion of significant topics are covered in the second Chapter, as well as a review of published articles that are pertinent to the current study. The experimental design, process, and materials and procedures employed in the tests are all outlined in third Chapter. The findings of the experiments, as well as their analysis and complete discussions, are reported in fourth Chapter. The fifth chapter contains summaries of the complete research project as well as recommendations for future research. Finally, a list of all the references used in this study is provided.

Chapter 2

2.1 LITERATURE REVIEW

2.1.1 INTRODUCTION

This chapter delineates a brief review of the development of high-entropy alloys (HEAs), with particular emphasis on lightweight high-entropy alloys (LWHEAs); their discovery into the metallurgical culture, the concept behind these alloys, their structural and property behaviour when subjected to standard and elevated temperatures, and also their processing techniques through the powder metallurgy route (Mechanical Alloying and Spark Plasma Sintering), which is the core of this research study. This chapter intends to give an understanding of LWHEAs, their prominence, why they have garnered significant attention and are currently in demand for weight and cost savings in the transportation and defence sectors, and how that positively impacts society. The drive is necessary to replace the Ni-base superalloys due to their high cost and density. It has been evident that the efficiency of heat engines, irrespective of the types, is directly proportional to temperature, meaning it increases with increasing temperature.

In the case of the energy sector, which includes nuclear, coal-fired and oil-fired, a rise in operating temperatures drops fuel consumption, pollution and operating costs. The escalated working temperature will lead to improved performance in the transportation sector, including groupings of heavier payloads, more incredible speed, and more excellent range (Pineau & Antolovich (2009)). The dominant engine component material customarily used is Ni-base superalloys. Ominously, Ni-base superalloys can only withstand the application temperature between 1160 °C and 1277 °C due to the emerging melting point at around 1300 °C (Pollock & Tin 2006; Karaköse & Keskin 2012). Therefore, it becomes critical to develop the engine component material with more superior high-temperature properties, which is LWHEAs. This new strong and low-density material set holds great potential due to a remarkably high strength-to-weight ratio.

2.1.2 HIGH ENTROPY ALLOYS

2.1.2.1 Discovery of High Entropy Alloys

In the history of alloy design, the addition of one principal element with other minor contents of alloying elements has been a norm for many years in conventional and speciality alloys. (Murty *et al.* 2019a). Various alloying elements are typically added to the principal element to improve their properties, leading to an alloy family based on the principal element. Steel, for example, is made of Fe, while aluminium alloys are made of Al. However, because the periodic table has a finite amount of elements, the alloy families that can be formed are also finite. What can be obtained if the thought is outside the box and construct alloys from numerous components rather than just one or two 'base' elements? This concept was quite helpful in producing an enormous amount of alloys for practice during civilization and daily life. Nevertheless, the degree of freedom in the alloy composition becomes limited and prevents the development of new alloys.

The first study on the multi-component alloy in equi-mass composition alloy with at least five elements was conducted by Karl Achard back in the 18th century (Gao *et al.* 2016). He published his work on binary, ternary, and quaternary alloys, but he also published about quinary, sexinary, and septenary alloys, which were only in equi-mass proportions (Achard 1788). All the material he worked on was in the as-cast condition, and various tests were conducted.

As more studies unfolded, it was precisely 1981 when Brian Cantor and his student Alain Vincent explored their research in a multi-component field. (Gao *et al.* 2016). They blended different alloys to make several equiatomic alloys. They also hold a world record for producing a multi-component alloy having 20 elements containing individual components of 5 at.% (Cantor *et al.* 2004a). That alloy was observed to be crystalline, brittle and multiphase in the as-cast condition and after melt spinning, yet the alloy comprised a single FCC primary phase. The multiple phases observed in the alloy were below the highest equilibrium number acceptable by the Gibbs phase rule and entirely below the highest equilibrium number

acceptable under a non-equilibrium solidification state (Cantor *et al.* 2004a). Brian went further with his research and explored metallic glasses by applying the method of equiatomic substitution, which was the idea he came up with within the early 2000s.

Another incredible researcher, Jien-Wei Yeh, independently explored the field of multicomponent alloys since 1995 and later conceptualised that high entropy of mixing could affect the number of phases by causing a reduction in a high order of mixing and lead to desired properties (Yeh *et al.* 2004). The total number of equiatomic alloys Yeh *et al.* (2004) studied was 40; 9 out of 40 alloys were synthesised via arc melting. Further tests were performed on the alloys, such as microstructural examination, mechanical testing (hardness) and corrosion resistance test.

The area of multicomponent alloys was researched considerably by Prof. Ranganathan; he explored this area of study by simply engaging in discussions with Yeh, and later published a research paper by introducing three distinct areas, namely: Metallic Glasses, Superelastic & Superplastic alloys, as well as HEAs (Ranganathan 2003). The published article became the first open publication in journals on HEAs, which resulted in the instigation of these alloys.

2.1.2.2 Concept of High Entropy Alloys

There is no worldwide definition for HEA; however, there are unquestionably numerous definitions. So, since there was no universal definition, the researchers have consequently given definitions that have stirred up a misperception. The well-known interpretation that is distinguishable from the main definitions is that HEAs are thought to have a single-phase solid solution (SS) even though it is a part of it (Miracle & Senkov 2017). This interpretation drives the urge to produce single-phase SS structures even though it is not applied by the main definitions. The definitions that are .commonly used are highlighted below.

Yeh *et al.* (2004) gave an early definition, and then later Cantor *et al.* (2004a) gave it a name and it states that HEAs are composed of at least five principal elements in equimolar ratios and

near-equimolar ratios, and the concentration of each element is between 5 and 35 at% (Yeh *et al.* 2004). Henceforth, from this definition, it can be drawn that the concentration does not have to be in equimolar ratios, increasing the number of HEAs significantly (Miracle & Senkov 2017). This composition-based definition only highlights elemental concentrations and not the magnitude of entropy. And it further places no condition on the presence of a single-phase SS.

Jien-Wei (2006) proposed another definition but this time about configurational entropy. The term 'high-entropy' crafts a definition based on the magnitude of entropy. Before getting into details about the definition, it is crucial to start with entropy. Entropy is a thermodynamic term used to determine the energy available for valuable work in the thermodynamic process in energy-conservation devices, machines, or even engines, as Zhang et al. (2014b) stated. The entropy equation is given by:

$$dS = \frac{\Delta Q}{T} \tag{2.1}$$

where *S*, *T*, and *Q* are the entropy, the absolute temperature and the heat flow, respectively. The thermodynamic entropy has the dimension of energy divided by temperature resulting in a unit of Joules per Kelvin($J \cdot K^{-1}$) used by the International System of Units (Zhang *et al.* 2014a).

So, according to Boltzmann's hypothesis (Gearhart 1990), the system's entropy is linearly linked to the logarithm of the frequency of occurrence of a microstate or the number W which provides the possible microstates equivalent to the macroscopic state of the system.

$$S = k \ln W \tag{2.2}$$

where k is Boltzmann's constant = $1.38 * 10^{23} \text{ J} \cdot \text{K}^{-1}$, and the logarithm is considered a natural base "e" (Zhang *et al.* 2014a). Regarding alloy systems, the Gibbs free energy of mixing is expressed as:

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \tag{2.3}$$

where ΔG_{mix} is the Gibbs free energy of mixing, ΔH_{mix} is the enthalpy of mixing, *T* is the absolute temperature, and ΔS_{mix} is the entropy of mixing. A conclusion can be drawn from equation (2.3) that if ΔH_{mix} _is kept constant, a higher entropy of mixing will result in a lower Gibbs free energy, making the alloy system relatively stable.

The mixing entropy from equation (2.3) comprises a total of four major parts contributing to the entropy, which includes configurational entropy, vibrational entropy, magnetic dipole and electronic randomness, and their relation is given by:

$$\Delta S_{mix} = \Delta S_{conf} + \Delta S_{vib} + \Delta S_{elec} + \Delta S_{mag}$$
(2.4)

The configurational entropy is the most dominant of all the mixing entropies in equation (2.4) (Fultz 2010). Hence, in most times, configurational entropy is used to the mixing entropy to make it easy to find solutions for complex calculations and resolve the remaining contributions (Gao *et al.* 2016). Therefore, the configurational entropy of mixing derived from equation (2.4) for a random solid solution with *N* number of components is given by (Zhang *et al.* 2014a):

$$\Delta S_{conf} = -R \sum_{i} c_{i} ln c_{i} \tag{2.5}$$

where *R* is gas constant = $8.31 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and c_i is the molar content of i^{th} component. Regarding equimolar of equiatomic ratio alloys, the configurational reaches its peak value and the equation (2.5) is extended to be (Jien-Wei 2006; Yeh *et al.* 2004):

$$\Delta S_{conf} = R \, lnN \tag{2.6}$$

Henceforth, by applying the equation (2.6), results to the definition of low entropy ($\Delta S_{conf} < 1R$), medium entropy ($1R < \Delta S_{conf} < 1.5R$) and lastly, high entropy ($\Delta S_{conf} > 1.5R$) alloys (Jien-Wei 2006). But this entropy definition does not consider the compositional definition when describing the range of HEAs.

Based on each definition, HEAs possess a more comprehensive range of alloys, however, both the composition-based and entropy-based often overlap for a majority of alloys (Zhang *et al.* 2018b). Nevertheless, the compositions not in the overlapping region are also considered HEAs. For instance, an equimolar quaternary alloy is now and then regarded as HEA in literature; its composition, and configurational entropy is close to the least limits of the two definitions.

That is why there is no actual definition for HEAs, just basic approximate guidelines (Zhang *et al.* 2018b). Since the early years, HEA's field has primarily been about configurational entropy and searching for single-phase solid SS alloys (Gorsse *et al.* 2018). Regarding the HEA definition that has been widely used, it is evident that there are some constraints which include alloys having a minimum of 5 or more principal elements, even though the ones with just 3 or 4 principal elements had satisfactory results (Zhang *et al.* 2018b).

The element constraints led to unproductive ways of excluding new results in alloy systems based only on the number of elements present and the phase formations, which ranged to be effectively defined by a single microstructure or phase, and this led to new terms being introduced such as complex, concentrated alloys (CCAs), complex multi-component alloys (CMAs), compositional complex alloys (CCAs), baseless alloys (BAs), metal buffets (MBs), and so on. The terms do not have any suggestions about the magnitude or significance of configurational entropy, and they also include each alloy that satisfies HEA definitions and the ones not benefiting the definition. Thus, due to all these, terms develop the HEA field by including concentrated ternary and quaternary alloys, by permitting elemental concentration in addition of 35 atomic percentage, and also by including single-phase intermetallic compounds (IC) alloys with any number of SS and IC phases (Zhang *et al.* 2018b).

2.1.2.3 Four Core Effects of High Entropy Alloys

Fourteen years ago, an attempt was made in the newly developed studies to elucidate the appearance of simple solid solution phases and their stability in HEAs by introducing the four core effects of multi-principal element composition(Miracle 2017; Miracle & Senkov 2017). These effects are the primary influence of HEAs' exceptional chemical and mechanical properties. As more data was accumulated and results presented on experiments conducted on HEAs broadened in the research field, there was sufficient proof to substantiate the effectiveness of the four cores. The first effect, the High-entropy effect, intends to expound a more straightforward random solid solution phase and the resultant microstructure observed at equilibrium due to increased entropy of mixing (ΔS_{mix}) that suppresses the Gibbs free energy of mixing (ΔG_{mix}). The second one, the Severe lattice distortion effect, is characteristic of a random solid solution in which multi-principal elements involved result in quite increased lattice strain and stress owing to variances in the physical properties of each element. The third one, the Sluggish diffusion effect, is more about kinetics that stabilises the nanocrystalline and the phase transformation. And lastly, the Cocktail effect, unlike the other three, is not regarded as hypothesised but possesses a philosophical impact on HEAs turf. This effect typically considers HEAs as a composite material for elements chosen for specific properties preferred.

2.1.2.3.1 High entropy effect

The high entropy effect generated the name-giving of HEAs. The supposition of the high entropy effect refers to configurational entropy. As per Gibbs Free energy of mixing equation, Eq. 2.3, the formation of a solid solution phase is favoured over the intermetallic phase due to an increased ΔS_{mix} that results in a decreased ΔG_{mix} . Nevertheless, the influence of the ΔS_{mix} to form stable solid solutions seems to decline with declining temperature, *T*, meaning there is a high possibility of phase transformation. In contrast, research later confirmed that the formation of a solid solution phase is not solely dependent on the high entropy effect but on other factors, viz., the enthalpy of mixing (ΔH_{mix}), atomic size difference (δ) and the valence electron concentration (VEC) (Chen et al. 2018a).

Furthermore, Boltzmann's equation, Eq. 2.5 is used to model the configurational entropy ΔS_{config} , of an ideal solution. This equation stipulates that when the number of constituents adds up in a system, the ΔS_{config} of the solid solutions escalates and subdues the enthalpy of the possible formation of intermetallic phases, leading to a stable solid solution. The focus should be restricted to achieving simple solid solution phases and appreciating the appearance of intermetallic phases as they contribute to the improvement of HEA properties (Chen *et al.* 2018).

2.1.2.3.2 Severe lattice distortion

The severe lattice distortion effect results from variances associated with individual atoms present in a multi-element matrix in the solid solution of HEAs, in which each atom is encircled by other dissimilar atoms, leading to increased lattice strain and lattice stress. The principal contributing factor to the severely distorted lattice is the atomic size difference, shown in figure 2.1.



Figure 2.1 A multi-elemental matrix of a solid solution comprising ten different components (Murty *et al.* 2019b)

Moreover, other factors that cause the severity of the distorted lattice, shown in Figure 2.2, include; varying bonding energy of the atoms and the crystal structure. These distortions

observed in HEAs are said to be quite intense as compared to conventional alloys. The unpredictability of positioning of atoms caused by distortions has a significant impact on properties, in which substantial solution hardening increases hardness and strength efficiently(Chen *et al.* 2018; Ye *et al.* 2016). Still, other properties such as thermal effect, electrical and thermal conductivity resulting from increased scattering of propagating electrons and phonons, the temperature dependence of properties decrease, and even the intensity of the X-Ray diffraction peak seems to reduce.



Figure 2.2 A distorted matrix of HEAs (Chen *et al.* 2018)

Therefore, with extensive knowledge about this phenomenon, HEAs consist of the utmost lattice strain associated with identical but less complicated compositions in the alloy system. Based on the quantitative analysis, it should not be substantial. (MacDonald *et al.* 2017). Figure 2.3 (Yeh *et al.* 2004)1 shows another example of how the distortion effect affects the hardness attribute due to the high atomic size of Al.



Figure 2.3 Al_xCoCrCuFeNi alloy hardness as a function of Al content (Yeh et al. 2004)

2.1.2.3.3 Sluggish Diffusion effect

The sluggish diffusion elucidates slower diffusion and higher activation energy in HEAs due to lattice potential energy (LPE) fluctuations within lattice sites. The more low- LPE sites impede atoms' diffusion and then sluggish diffusion results(Gupta 2017). The diffusion rate of individual elements in HEAs is different, and it requires a coordinated movement, meaning slow diffusion is a determining factor for kinetics. So the number of elements present in a matrix impacts diffusion rate; a more significant number suggests a slower diffusion rate. Thus, sluggish diffusion slows down the nucleation of phases, evolution and distribution, and morphology of secondary phases via diffusion-controlled phase transformation. A positive impact is observed on the resultant microstructure and properties. Meaning an allowance for easily achievable supersaturated state and nano-sized precipitates and improved properties such as strength and toughness and creep resistance for the longevity of HEA materials subjected to elevated temperatures.

To analyse the diffusion data of each element in the matrix, (Tsai *et al.* 2013) created diffusion couples from a nearly perfect solution system of Co-Cr-Fe-Mn-Ni. According to their findings (Figure 2.4), the Q/Tm values in HEAs are the greatest, followed by those in the Fe-Cr-Ni(-Si)

alloy, and finally, those in pure metals (Murty *et al.* 2019a). This research concludes that as the number of elements increases, the diffusion rates drop.



Figure 2.4 The melting point normalized activation energy of diffusion for Cr, Mn, Fe, Co, and Ni in various matrices, including pure metals, stainless steels, and the high-entropy alloy CoCrFeMnNi (Tsai *et al.* 2013)

2.1.2.3.4 Cocktail Effect

The cocktail effect provides prominence on the improvement of properties by a minimum of five principal elements. Its range is from the atomic-scale to micro-scale multi-elemental combined effect, where the individual phase acts as a multi-elemental composite. Meanwhile, the mean properties of elements and extra quantities formed by inter-elemental reactions and lattice distortion lead to HEAs' macroscopic properties.

Undoubtedly, these *core effects* have caused quite a positive stir in research. Nevertheless, a piece of contradicting information has confirmed with experiments that the phase stability and various properties found in HEAs do not necessarily adhere to the *core effects*. Observations

revealed that no matter how high configurational entropy is, complex multi-phases still appear in HEA's system. Also, precipitates are spotted, proving the diffusion not to be sluggish. Even better, the concept of structural stability expounded by some of the cores, which include lattice distortion and cocktail effect, seems inadequate, which is why researchers presently need clarity on the instability of phases in HEAs.

2.1.2.4 Prediction of Phase Stability from Basic Thermodynamic Principles

Numerous factors affect the microstructure and properties of HEAs, but as mentioned above, only four factors dominate, and they are the core effects of HEAs (Yeh 2013). The thermodynamics of HEAs is crucial in predicting the generation and stability of solid solution phases. Atomic size differences (δ), enthalpy of mixing (H_{mix}), the entropy of mixing (S_{mix}), valence electron concentration (VEC), and electronegativity difference (ΔX) are all documented structural characteristics that influence the stability of a solid solution (Yang *et al.* 2012b; Zhang *et al.* 2008; Yang *et al.* 2012a; Sheng & Liu 2011; Guo *et al.* 2011)

The Hume-Rothery rules (Zhang *et al.* 2008; Guo *et al.* 2011; Zhou *et al.* 2007b; Tong *et al.* 2005b; Mizutani 2012) were developed in the 1950s and 1960s to establish the criteria for obtaining a high degree of solubility between two elements in a binary alloy. The following four conditions must be satisfied to stabilize a solid solution according to the *Hume-Rothery rules* (Zhou *et al.* 2007b; Mizutani 2012):

- The electronegativities of the elements involved differ just slightly.
- Each element's atomic size difference must be within 15%.
- The chemical valence of the elements must not differ by more than 1
- The elements' crystal structures must be identical.

These rules influence the interaction of distinct elements, causing the enthalpy of mixing to be either negative where IMs develop, positive where clustering or segregation occurs, or near zero where disordered SS develop (Svensson 2015). Competition between the enthalpy of mixing and the entropy of mixing affects the solubility of two components even more. Forming solid solutions at any composition is difficult because the conditions for their formation are quite rigorous, but an isomorphous system results when they do. The classical AlCoCrCuFeNi HEA system of Tong *et al.* (2005b) demonstrates the validity of these laws. In this scenario, the Hume-Rothery rules do not explain why diverse crystal structures of individual elements create a single-phase solid solution of a particular crystal structure, such as face-centred cubic (FCC) or body-centred cubic (BCC), in this case, depending on the content of Al (Yeh *et al.* 2007b; Wu *et al.* 2006; Tong *et al.* 2005b; Tung *et al.* 2007). Additional elements, such as high mixing entropy and multi-component alloying, are needed to explain this effect since they are likely to loosen the limits of the Hume-Rothery rule, allowing for the stability of a single-phase solid solution of this multi-component alloy (Tong *et al.* 2005b; Zhou *et al.* 2007b).

Compared to other potential phases, such as intermetallic compounds, a solid solution has lower free energy of mixing. As a result, using the Gibbs free energy equation (2.3) (Yang *et al.* 2012b; Zhang *et al.* 2008), calculations may be done to predict the tendency to produce a solid solution. However, the free energy of mixing that is used in this calculation of ΔG_{mix} is complicated and difficult to calculate accurately and a study by Takeuchi *et al.* (2001) hypothesized that ΔG is proportional to ΔG_{mix} of the liquid phase in a HEA system, allowing the latter to be used as shown in equation (2.3).

The free energy calculation for HEA systems (Yang *et al.* 2012b) can be simplified using a regular solution model, which assumes that the entropy of an ideal solution of the same composition is equal to the entropy of mixing, yielding the following equations for ΔH_{mix} and ΔS_{mix} (shown in equation (2.5))(Yang *et al.* 2012b; Guo *et al.* 2011):

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^{n} \mathcal{Q}_{ij} c_i c_j \tag{2.7}$$

 $\Delta H_{AB}^{\text{mix}}$ is the enthalpy of mixing between binary A and B elements, c_i , c_j are molar content of *i*th and *j*th elements, where $\Omega_{ij} = -4\Delta H_{AB}^{\text{mix}}$ is the consistent solution interaction parameter between the *i*th and *j*th elements. Miedema's semi-empirical model is one of the techniques utilised to determine the enthalpies of binary A-B alloys. Since Miedema's model is based on
a 50/50 binary alloy (Miedema *et al.* 1980), the value of the enthalpy of mixing in HEA systems where the elements are not equiatomic would differ significantly because the individual binary constituents will no longer be in a 50/50 ratio. Experimental data has been compared to Miedema's model, which shows that for low mixing enthalpies, i.e. < -20 kJ·mol⁻¹, the observed values are typically lower than predicted (Boom *et al.* 1976). Miedema *et al.* (1980) described this as establishing short-range order in the liquid alloy when $\Delta H < -RT$.

As Miedema *et al.* (1980) experimentally demonstrated, the enthalpy of mixing in binary alloys can affect phase formation. The solid solution is stabilized when the mixing enthalpy approaches zero; this is because the elements can be distributed randomly(Yang *et al.* 2012b).

In HEAs, the enthalpy of mixing forms a miscibility gap in the liquid phase, which prevents the development of a solid solution due to the segregation of the individual elements. Other phases in the system become more stable as H_{mix} decreases. As H_{mix} decreases, the binding force between components increases; the solid solution's stability decreases as the binding force between components increases.

Furthermore, in HEAs, the entropy of mixing is always positive and most significant when the constituents' molar percentages are equal (Yang *et al.* 2012b; Sheng & Liu 2011). Figure (2.5) depicts the decrease in entropy as the number of equimolar components increases. The effect of high entropy, based on the free energy formula (Eq. (2.3)), is crucial to maximising the entropy in the system, and the free energy will be reduced as a result of Boltzmann's hypothesis. This would result in stabilised solid solution at lower temperatures, relaxed Hume-Rothery conditions, and balanced lattice strains in the solid solution. The varied sized atoms in the structure that stabilises the solid solution over the ordered intermetallics induce lattice stresses (Cantor *et al.* 2004a; Sheng & Liu 2011; Tong *et al.* 2005b). Nevertheless, calculating the Gibbs free energy of mixing for each phase in these HEAs is exceptionally challenging.



Figure 2.5 The alloy system's entropy of mixing affected by the number of equimolar elements(Kumar & Gupta 2016)

The entropy of mixing ΔS_{mix} , which is determined using equation (2.5), is another parameter from the ΔG_{mix} equation (2.3). The value ΔS_{mix} is always positive in multi-component alloys, and the entropy is always at its maximum in equiatomic alloys. Higher ΔS_{mix} values and lower temperatures in HEA systems promote element confusion, resulting in various elements being randomly dispersed in the crystal lattice and diminishing the tendency of ordered and segregated elements. Consequently, HEAs with a high value of ΔS_{mix} forms random SS and are also more stable than IMs or the other ordered phases during solidification (Kumar & Gupta 2016).

HEAs aid the formation of SS with a high $T\Delta S_{mix}$ value because the value of ΔS_{mix} rises as temperature rises, implying that the high entropy of mixing effect will stabilize the effect of enthalpy of mixing for generating SS at specific temperatures. The T_m is used because phase change normally occurs at the alloy's melting temperature (T_m). Because phase transformations commonly occur at the melting temperature (T_m)of an alloy, T_m is represented with the entropy term $T\Delta S_{mix}$, and another parameter Ω is defined as a result of entropy and enthalpy competition (Kumar & Gupta 2016; Svensson 2015). Yang *et al.* (2012b) described Ω as a predictor of SS formation.

$$\Omega = \frac{T_m \Delta S_{mix}}{\Delta H_{mix}} \tag{2.8}$$

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

where $(T_m)_i$ is the melting point of *i*th element.

As previously stated, both positive and negative values of the enthalpy of combustion are possible. The stability of SS decreases when mixed, and as a result, the absolute value of SS decreases. The mixing enthalpy is employed (Kumar & Gupta 2016). It can also be deduced from the equation (2.8) that if $\Omega < 1$, then the ΔH_{mix} will be prime, leading to a formation of intermetallic compounds. For the HEA alloy to completely have solid solution phases, the contribution of ΔH_{mix} has to be exceeded by $T\Delta S_{mix}$, but only if $\Omega > 1$ (Zhang *et al.* 2014b; Kumar *et al.* 2017b).

Although the Ω value suggests the establishment of SS, another crucial criterion known as atomic size mismatch (δ) aids in establishing stable SS. Since the element concentrations in HEAs are the same, the atoms are predicted to inhabit crystal lattices randomly. By so doing, each element is viewed as a solute element for the formation of SS; however, when there is a considerable atomic size difference between elements, substantial lattice distortion in the alloy can occur, increasing free energy and a decrease in SS stability(Kumar & Gupta 2016). It is defined as follows:

$$\delta = \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \tag{2.10}$$

where $\overline{r} = \sum_{i=1}^{n} c_i r_i$ is the alloy's average atomic radius, *n* is its total number, and each element has an atomic fraction c_i and an atomic radius r_i . And this $\delta \le 6.6\%$ criterion must be met for the simple solid solution to develop (Feng *et al.* 2016; Qiu *et al.* 2017a). Substantially, δ contributes to the average effect of all present elements' atomic size difference in an alloy. Nonetheless, the instability of solid solutions may still occur due to the most significant and smallest atoms of the HEAs. Although Wang et al. (Wang *et al.* 2015a; Wang *et al.* 2015b) replaced δ with another parameter to measure the atomic size difference, disputing that δ does not differentiate exceptionally between alloys that only form solid solutions and those that decompose and strive to form intermetallic compounds.

Guo *et al.* (2013) pointed out that the ΔH_{mix} , ΔS_{mix} , and δ parameters should be utilized jointly to detect SS formation, and they also recommended parameters that will form SS, which are - $22 \leq \Delta H_{mix} \leq 7 \text{ kJ} \cdot \text{mol}^{-1}$, $11 \leq \Delta S_{mix} \leq 19.5 \text{ J} \cdot \text{K} \cdot \text{mol}^{-1}$, and $0 \leq \delta \leq 6$. Using the functions ΔH_{mix} and δ Guo *et al.* (2013) conducted a study (Figure 2.6 (a)) to determine the conditions for the formation of SS, IMs, and amorphous phases, and discovered that SS occur when $\delta \leq 6.6$, -11.6 kJ·mol⁻¹ $\leq \Delta H_{mix} \leq 3.2 \text{ kJ} \cdot \text{mol}^{-1}$ and in the case of amorphous $\delta > 6.4$, $\Delta H_{mix} < -12 \text{ kJ} \cdot \text{mol}^{-1}$.

Yang *et al.* (2012b) used the δ - Ω parameter to determine the conditions under which SS, ICs, and Bulk Metallic Glasses (BMGs) develop. Figure 2.6 (b) depicts the relationship between phases and BMGs.



Figure 2.6 (a) δ - ΔH_{mix} plot illustrates HEAs' phase selection process (Guo *et al.* 2013). (b) The relationship between parameters δ and Ω for multicomponent alloy systems (Yang *et al.* 2012b).

Another parameter, valence electron concentration (VEC), was presented by Guo *et al.* (2013) to determine the formation of FCC or BCC phases. It was discovered that it also influences the stability of the SS phase. The other two methods for calculating electron concentration are the average number of valence electrons per atom (e/a) and valence bonds with a d-electron. (Mizutani 2012). And they are given by:

$$\frac{e}{a} = \sum_{i=1}^{n} c_i (e/a)_i$$
(2.11)

$$VEC = \sum_{i=1}^{n} c_i (VEC_i)$$
(2.12)

Where c_i is the atomic percentage of the *i*th element and $(e/a)_i$ and (VEC), *i* are the VEC of the *i*th element. It has been concluded that for a BCC to be stable, VEC ≤ 6.87 , and for the FCC to be stable, then VEC ≥ 8 (Kang *et al.* 2018a; Kumar *et al.* 2017b; Youssef *et al.* 2014). However, when both faces exist, then $6.87 \leq VEC \leq 8$. Figure 2.7 explains this relationship.



Figure 2.7 Relationship between *VEC* and the FCC, BCC phase stability for some HEA systems (Guo *et al.* 2011)

Eq. 2.13 expounds on the effect of electronegativity on the resultant stable phase in HEAs. Electronegativity is an attraction of elements by atoms. The high electronegativity of solute elements leads to the formation of intermetallic compounds. Dong et al. (Dong *et al.* 2014a), when considering the topological close-packed (TCP) structure, confirmed that for the stability of a solid solution to be observed, then $\Delta X > 0.133$ (Maulik *et al.* 2018). The following equation defines the parameter ΔX :

$$\Delta \chi = \sqrt{\sum_{i=1}^{n} c_i (\chi_i - \bar{\chi})^2}$$
(2.13)

 $\bar{\chi} = \sum_{i=1}^{n} c_i \chi_i$ is the average electronegativity, and *Xi* is the Pauling electronegativity for the *i*th element.

Those prior prediction techniques are useful for determining whether HEAs could form for a specific alloy system, but they cannot distinguish between different phases and single or multiple combinations of phases. Guo found that electronegativity does not affect the creation of solid solution phases. Poletti & Battezzati (2014) displayed the effect of electronegativity in both the experimental and theoretical Allen scales (related to the average energy of the valence electrons in a free atom), instead of the empirical Pauling scale, and VEC on the differentiation between simple and complex phases, as well as identify either bcc or fcc alloys on the map (see Figure 2.8). This implies that electronegativity plays a significant role in the creation of HEAs.



Figure 2.8 Mapping of several HEAs according to their Allen electronegativity and atomic size difference grouped by their crystalline structure (Poletti & Battezzati 2014)

2.1.2.5 Phases

In conventional or traditional alloys, the phases are often divided into three categories: terminal or elemental phases, intermetallic compounds, and solid solution phases (Zhang *et al.* 2014a). Phases based solely on one primary element are terminal or elemental phases. Solid solution phases are based on both simple FCC-BCC structure and complex structure, and intermetallic compounds are stoichiometric compounds with a fixed composition ratio (Zhang *et al.* 2014a). High entropy alloy phases, on the other hand, are classed differently.

The phases in high entropy alloys are ordered solid solution, random solid solution, and intermetallic compounds, which could be categorized as ordered solid solutions. Rather than creating an intermetallic phase, high entropy alloys generate random or ordered solid solution phases with simple body-centred cubic (BCC), face-centred cubic (FCC), and hexagonal closed pack (HCP) structures, according to Zhang *et al.* (2014a). This makes sense since the more significant the number of components in a high entropy alloy, the higher the configurational entropy, which lowers the Gibbs free energy and stabilizes the solid solution. This, however,

only applies when the temperature is high. When high entropy alloys are cooled, the temperature drops, resulting in a rise in Gibbs free energy, and the alloy may phase transition.

2.1.2.5.1 Intermetallic Compounds

a. B2 Phase

The ordered structure of the B2 phase is based on the body-centred cubic (BCC) crystal structure. B2 phase is observed as a primary or minor phase in several high entropy alloys, according to studies (Murty *et al.* 2019a). It has also been reported to precipitate during the aging process of high entropy BCC-structured alloys (Murty *et al.* 2019a). B2 phase is found in high entropy alloys containing 3d transitional elements, and all of them include one of Fe, Co, or Ni, as well as Al (Murty *et al.* 2019a). The interaction of Al with these elements is thought to be responsible for the occurrence of B2 phases.

b. Sigma (σ) Phase

The sigma phase has been reported on high entropy alloys containing Cr. Sigma phase production has been seen in various high entropy alloys containing Fe and Co and significant levels of Cr and Mo (Murty *et al.* 2019a). Furthermore, the sigma phase indicates that a variety of solid solution types may be possible and that this is dependent on interaction and atomic size differences.

2.1.2.6 Crystal Structure

It's difficult to predict what crystal structure will be present in high entropy alloys because of the different components that are mixed. Most high entropy alloys have BCC, FCC, or a combination of these crystal structures (Murty *et al.* 2019a).

2.1.2.6.1 Single-phase high entropy alloys with FCC and BCC structures

Dislocation characteristics influence the mechanical properties of metals. Metal dislocations necessitate slip planes in a specific slip direction. The (111) plane is the face-centred cubic (FCC) structural slip plane, which is all densely packed (Callister *et al.* 2007) and makes the slide simpler.



Figure 2.9 (a) (111) slip system shown within FCC unit cell (b) the (111) plane from (a) (Callister *et al.* 2007)

The critical resolved shear stress forces the dislocation to migrate in a specific direction if stress is applied. Because the energy barrier for dislocation is lower in an FCC structure, the amount of energy required to move (from A to C) to induce dislocation is lower, making it ductile. In an FCC crystal structure, the critical resolved shear stress required to move dislocations is two orders of magnitude lower than in a BCC crystal structure (Callister *et al.* 2007). This ductility is crucial for structural applications since plastic deformation is visible before complete failure. On the other hand, Brittle materials have no plastic deformation, making them risky since fractures can develop without warning.

On the other hand, this ductility comes at a cost in terms of strength. Several FCC-structured high entropy alloys, such as (Ye *et al.* 2016) Al_{0.5}CoCrFeNi, CoCrFeNi, CuNiCoFe,

FeCoNiCrCu, FeNiCrMo, VCuFeCoNi, have been created to produce exceptional mechanical properties. The novelty of high entropy alloys stems from the fact that elements with diverse crystal structures can form a single-phase solid solution, such as CoCrFeNi (Murty *et al.* 2019a), which has a single-phase FCC structure. However, not all constituents have the same FCC structure.

The body-centred cubic (BCC) crystal structure, on the other hand, has a greater number of slip systems that obstruct each other, making slip movement extremely difficult. They become brittle as a result of this. BCC-structured high entropy alloys, on the other hand, are better for high-strength applications than FCC-structured high entropy alloys because they have higher tensile and yield strength. Furthermore, high entropy alloys with a BCC structure are stable at high temperatures (Senkov *et al.* 2011b).

2.1.2.6.2 Mixture of FCC and BCC high entropy alloys

The existence of two or more phases is likely in high entropy alloys prepared by liquid metallurgical processes (Murty *et al.* 2019a). Recent research by Murty *et al.* (2019a) has discovered that when the AlCrCuFeNi alloy is mechanically alloyed, it possesses a single-phase structure. On the other hand, the alloy has a multiphase structure of (FCC + BCC) when treated via arc melting. This effect could be due to the slow pace of solidification, which allows for the growth of distinct phases. Several multiphase (FCC + BCC) alloys have been synthesised including AlCoCrCuFeNi (Yeh *et al.* 2004), AlCrCuFeNi (Li *et al.* 2009), and AlCoCuNi (Yeh *et al.* 2007a). With a fracture strength of 1624 MPa and a fracture strain of 21%, AlCrCuFeNi has good mechanical properties (Joseph *et al.* 2018). The alloy has a lot of potential for high-strength applications in the future.

2.1.2.7 The arrangement of Elements and Lattice Strain in High Entropy Alloys

The arrangement of constituents in a solid solution has received little attention. The organization of elements in multi-component alloys is random or contain short-range ordering based on the probability of occupancy with each element treated as a solute atom (Yeh *et al.* 2007b; Zhang *et al.* 2008; Yeh *et al.* 2007a). As a result, it's difficult to say whether larger or

smaller atoms prefer to occupy specific atomic positions. There is no published information on the effect of the large-to-small atom ratio on the formation or properties of solid solutions. Nevertheless, it has been demonstrated that adding various size elements generates a lattice strain, which increases as the size difference between the size components is bigger (Yeh *et al.* 2007b; Zhou *et al.* 2007a; Tong *et al.* 2005b; Tong *et al.* 2005a; Varalakshmi *et al.* 2010a; Wang *et al.* 2008b). The effect of varied size atoms inserted into a BCC structure is depicted graphically in Figure 2.10. The lattice distortion is exacerbated, as seen in the exaggerated image, resulting in lattice strain.



Figure 2.10 The effect of multicomponent alloying on the lattice deformation of a BCC crystal structure is depicted in this simplified diagram. (Murty *et al.* 2019a)

X-ray diffraction (XRD) intensities have been demonstrated to decrease with increasing lattice strain and an increasing number of elements as a result of this lattice strain (Yeh *et al.* 2004; Tong *et al.* 2005b; Huang *et al.* 2004; Tong *et al.* 2005a; Yeh *et al.* 2007a). In solid solutions, Yeh *et al.* (2007a) found a link between the number of components in a system and the XRD intensity. Peak intensities were found to be much lower with rising component numbers than would be expected based on the well-known Debye-Waller temperature factor. The drop in peak intensity was thought to be caused by crystal structural distortion, which increased the

scattering impact of the beam (Yeh *et al.* 2007a). As a result, a distortion factor was developed. When this distortion factor is combined with the Debye-Waller temperature factor, the peak intensity of the perfect crystal diffraction peak is reduced. Figure 2.11 depicts the decrease in peak intensity as the number of components increases.



Figure 2.11 XRD patterns for the CuNiAlCoCrFeSi alloy with increasing the number of elements (intensity of 500cps/marking). Reproduced with permission from Elsevier (Yeh *et al.* 2007a)

2.1.3 EXISTING ISSUES OF HIGH ENTROPY ALLOYS

2.1.3.1 Cost of high entropy alloys

For structural applications such as aerospace engineering and civil transportation, many sectors are looking for a new material with broad mechanical qualities at a cheaper cost. Excellent entropy alloys can readily acquire these comprehensive mechanical qualities, such as high wear resistance, low-temperature ductility, superparamagnetism, strong corrosion resistance, and high-temperature oxidation resistance (Yeh *et al.* 2004). On the other hand, these

comprehensive mechanical qualities do not come cheap. The concept of having more than one primary element in high entropy alloys approaching equimolar ratios limits their industrial utility because they can be quite costly. Having four or more materials with almost equimolar ratios isn't optimal because the alloys will be quite expensive. These have piqued academics' interest in finding the optimal combination or a novel technique to address the problem, such as combining traditional alloy design techniques with the creation of high entropy alloys.

Furthermore, in the literature, there is minimal information on the evolution of compositional homogeneity in HEAs inherited during synthesizing and processing, as well as strategies to impact it, especially when choosing traditional processing methods. When it comes to mechanical properties of HEAs obtained following various processing conditions and compositional homogeneity levels have never been published before. Nonetheless, such data is critical for gaining a better knowledge of and more robust design recommendations for the synthesis and processing of HEAs, the cost, as well as evaluating appropriate homogenization methods for such complex materials.

2.1.4 LIGHTWEIGHT HIGH ENTROPY ALLOYS (LWHEAS)

2.1.4.1 Simple Definition of LWHEAs

Lightweight HEAs, also known as low-density HEAs, are a word that has only just been coined as researchers seek to broaden the scope of HEAs to include lightweight applications. The highentropy approach offers new opportunities for lightweight alloy development. Several LWHEAs have been developed, and their phase configurations and mechanical properties have been examined. Based on the components, the LWHEAs can be divided into two classes. The LWHEAs in group I are primarily made up of light elements such as Al, Be, Li, Mg, Sc, Si, Sn, Ti, and Zn (Kumar & Gupta 2016; Maulik *et al.* 2018; Feng *et al.* 2016). The Mg_x(MnAlZnCu)100 x LWHEAs (Li *et al.* 2010) with a density of 2.2–4.29 g·cm⁻³ and the AlLiMgSiCa LWHEAs (Jia *et al.* 2019) with a density of 1.4–1.7 g·cm⁻³ are examples of these LWHEAs with an ultra-low density (1–4.5 g·cm⁻³). Group II LWHEAs are primarily derived from pre-existing solid solution (SS) HEAs. As a result, the SS phases in pre-existing HEAs can be inherited by LWHEAs, and phase structures in LWHEAs may be basic. For example, by replacing Hf and Ta (heavy elements) in TiZrHfNbTa HEAs with V and Al (light elements), a series of TiaZrbVcNbdAle LWHEAs (Yurchenko *et al.* 2017; Stepanov *et al.* 2015a) with main body-centred cubes may be obtained. Based on these results, a conclusion can be drawn that the phase structure is crucial in conjunction with the light elements to balance density and mechanical properties (Wang *et al.* 2021).

So far, LWHEAs have been classified according to the specifications above, but with a density of below 3.0 g·cm⁻³ (Kumar & Gupta 2016), while others have indicated a density of less than 7.0 g·cm⁻³ is deemed lightweight (Feng *et al.* 2016). Because there is no unanimity, it is suggested that future lightweight alloys should be equivalent to present alloys such as Al and Ti-based alloys, which have densities of 2.8 and 4.5 g·cm⁻³, respectively. Although Al and Ti have been studied in several HEA systems, they are usually combined with heavier transition metals including Cr, Mn, Fe, Co, and Ni (Zhang *et al.* 2009; Wang *et al.* 2008b; Pi *et al.* 2011; Wang *et al.* 2008a; Wang *et al.* 2007). Because of its low density of 1.738 g·cm⁻³, Mg is an obvious starting element for achieving these lower densities.

2.1.4.2 Existing LWHEAs

Due to the attempt to define the standard CoCrFeNi systems, there is virtually little study on these alloys. Similar methods of determining beginning compositions, such as phase-formation recommendations or the CALPHAD methodology, are employed as in earlier HEAs. Several attempts have been made to synthesise a single-phase LWHEA. Mechanical alloying was used by Youssef *et al.* (2015) to create a single-phase FCC structure of $Al_{20}Li_{20}Mg_{10}Sc_{20}Ti_{30}$ with a density of 2.67 g·cm⁻³. It's worth noting that after 1 hour of annealing at 500°C, this structure converted into an HCP structure. This indicates that the milling phase is not in balance. These alloys provided extraordinarily high hardness with low density, as seen in Figure 2.12 compared to other technical materials. Even though the researchers used a converted hardness measurement to yield strength to compare LWHEAs to other metals, which does not account for the workability of alloys due to lack of ductility, it does show the potential of LWHEAs.

Mechanical alloying has also been used to investigate the equiatomic AlFeMgTiZn system (Hammond *et al.* 2014). However, the workers discovered that the lighter Mg and Al components were depleted in the final alloy due to the ball milling procedure. As a result, when producing alloys by ball milling, this must be considered to get the desired composition. The majority of the material was recognized as BCC, but many intermetallic compounds were also discovered. The mechanical qualities, on the other hand, were observed to improve as the milling time and cooling rate were increased. As Hammond *et al.* (2014) pointed out, there were indicators of insufficient alloy mixing when pure element precipitates were discovered in the final microstructure. As a result, the mechanical characteristics would have been changed, and these data should only be used as a guideline.

Yang *et al.* (2014) used induction melting and suction casting to make MgLiAlZn(Cu &/or Sn) alloys. When the Al and/or Mg content was increased, a variety of phases appeared, including various intermetallic phases. According to the researchers, a thorough examination of the phases present in binary systems is required to establish potential phases and anticipate formation in extended quinary systems. When compared to binary systems, they found no novel structures in the quinary systems. It has been proposed that the enthalpy of mixing of some of the phases contributes more to phase stability than the higher entropy of mixing. This discovery indicates that while the HEA parameters may explain why some solid solutions have developed, the creation of intermetallic compounds may still be a more powerful driving force. In the non-equiatomic compositions, the morphology generated a plate and eutectic structure, but it formed a fine two-phase structure in the equiatomic alloy, as shown in Figure 2.13. This was explained by the fact that when the Mg content increases, the entropy of the composition decreases, resulting in a reduced barrier to the production of intermetallics.



Figure 2.12 Youssef *et al.* (2015)alloy represented by the blue star on the Ashby plot of strength vs density for engineering materials. (Yield strength is used in metals and polymers, tear strength is used in elastomers, compressive strength is used in ceramics, and tensile strength is used in composites.). Reproduced with permission from Taylor & Francis (Youssef *et al.* 2015).

Under the lightweight/low-density banner, certain slightly heavier alloys in the region of 4-5 $g \cdot cm^{-3}$ have also been discussed in the literature. The MgMnAlZnCu system was explored by Li *et al.* (2010; 2011) with changing Mg concentration. HCP and an Al-Mn icosahedral quasicrystal were the major phases produced. According to the researchers, the quasicrystal phase discovered is generated by a rapid heating rate and is particularly unstable during heat treatments. More phases were generated as the Mg concentration increased from 20 (equiatomic) to 50 at.%



Figure 2.13 SEM images of Mgx(MnAlZnCu)100-x, (a) x=20, (b) x=33, (c) x=43, (d) x=45.6 and (e) x=50. Reproduced with permission from Scientific.Net (Li *et al.* 2010).

Compressive strength, hardness, and density all demonstrated a straight linear relationship with Mg content, with all parameters dropping as Mg concentration increased, as would be expected given the reduction in solution strengthening (Kumar & Gupta 2016; Li *et al.* 2010).

As previously indicated, certain research has classified Al-Ti-based alloys as LWHEAs, notably Feng *et al.* (2016). The AlCrFeMnTi system produced two BCC phases and an L2₁ Heusler phase in the equiatomic composition, which was the subject of this research. The researchers looked at alloys with increasing Al content to see whether they could lower density. More intermetallic phases occurred as the Al concentration increased, as measured by XRD. This is in line with prior findings in similar 'standard' HEA systems. Table 2.1 shows roughly LWHEAs that have been developed thus far.

Number	Alloys	Density	Structure	Reference
		(g·cm ⁻³)		
1.	Al _{1.5} CrFeMnTi	5.31	BCC+L21+Laves	(Feng et al. 2016)
2.	Al ₂ CrFeMnTi	5.06	BCC+L2 ₁ +Laves	(Feng et al. 2016)
3.	AlCrFeMnTi _{0.25}	5.87	BCC+L21	(Feng et al. 2016)
4.	Al ₂ CrFeMnTi _{0.25}	5.16	BCC+L21	(Feng et al. 2016)
5.	Al ₃ CrFeMnTi _{0.25}	4.71	BCC+L2 ₁ +Laves	(Feng et al. 2016)
6.	Al ₄ CrFeMnTi _{0.25}	4.40	BCC+L21+Laves	(Feng et al. 2016)
7.	AlCr _{0.5} NbTiV	5.71	BCC	(Stepanov et al. 2015b)
8.	AlCrNbTiV	5.82	BCC+Laves	(Stepanov et al. 2015b)
9.	AlCr _{1.5} NbTiV	5.90	BCC+Laves	(Stepanov et al. 2015b)
10.	AlFeMgTiZn	4.34	BCC+IM	(Hammond et al. 2014)
11.	AlLiMgZnSn	4.23	FCC+IM	(Yang et al. 2014)
12.	AlLi _{0.5} MgZn _{0.5} Sn _{0.2}	3.22	FCC+IM	(Yang et al. 2014)
13.	AlLi _{0.5} MgZn _{0.5} Cu _{0.2}	3.73	FCC+IM	(Yang et al. 2014)
14.	AlLi _{0.5} MgCu _{0.5} Sn _{0.2}	3.69	FCC+IM	(Yang et al. 2014)
15.	$Al_{80}Li_5Mg_5Zn_5Sn_5$	3.05	FCC+IM	(Yang et al. 2014)
16.	Al ₈₀ Li ₅ Mg ₅ Zn ₅ Cu ₅	3.08	FCC+IM	(Yang et al. 2014)
17.	$Al_{20}Li_{20}Mg_{10}Sc_{20}Ti_{30}$	2.67	FCC	(Youssef et al. 2014)
18.	AlNb _{1.5} Ta _{0.5} Ti _{1.5} Zr _{0.5}	6.88	BCC	(Senkov et al. 2014)
19.	AlNbTiV	5.59	BCC	(Stepanov et al. 2015b)
20.	Al _{0.5} NbTiVZr	6.04	BCC+Laves+Zr ₂ Al	(Stepanov et al. 2015c)
21.	AlNbTiVZr	5.79	BCC+Laves+Zr ₂ Al	(Stepanov et al. 2015c)
22.	Al _{1.5} NbTiVZr	5.55	BCC+Laves+Zr ₂ Al	(Stepanov et al. 2015c)
23.	CrNbTiZr	6.67	BCC+Laves	(Senkov et al. 2013a)
24.	CrNbTiVZr	6.57	BCC+Laves	(Senkov et al. 2013a)
25.	NbMoCrTiAl	6.57	BCC+IM	(Chen et al. 2016)
26.	NbTiVZr	6.52	BCC	(Senkov et al. 2013a)

Table 2.1 The density and microstructures for typical and lightweight HEAs, reported and newly-designed HEAs

2.1.4.3 The future direction of LWHEAs

Even though these alloys have begun to demonstrate good strength-to-weight ratios, these figures are based solely on hardness and compressive tests, with only minor elongation observed. Cracks and limited ductility were also reported in lightweight alloys in several studies (Hammond *et al.* 2014; Yang *et al.* 2014; Li *et al.* 2010; Li *et al.* 2011). This could be attributed to various causes, including the presence of brittle intermetallic compounds, severe lattice distortion, and the predominant crystal structure in several Mg-based alloys being HCP (Kumar & Gupta 2016). Because there are fewer slip systems to accommodate the strain in the HCP crystal structure, it is widely acknowledged that it is less ductile than cubic structures (Polmear 2005).

The conventional parameters for HEAs do not apply to LWHEAs, according to Feng *et al.* (2016) and Yang *et al.* (2014), because the lightweight alloys would normally form solid solutions at larger lattice misfits and lower mixing enthalpies. The original guidelines were closely modelled after elements with 3d and/or 4d electron orbitals (Yang *et al.* 2014). As a result, it's only natural that introducing s orbital elements like Mg and Li would have a different effect on bonding and phase formation. According to Yang et al. (2014), the tendency of these alloys to form intermetallics necessitates more conservative parameters, and configurational entropy is insufficient in these alloys where the valence electron concentration is increasing.

The manufacturing of LWHEAs will almost certainly necessitate a different technique. According to Kumar & Gupta (2016), compositions that branch away from equiatomic could produce beneficial results. Non-equiatomic compositions have recently been shown to generate single-phase alloys when the equiatomic composition fails (Yao *et al.* 2014; Tasan *et al.* 2014; Deng *et al.* 2015). Therefore, more research is needed to understand where intermetallics may be avoided and a single-phase alloy can be formed. As a result, discovering these locations free of intermetallics should be a priority.

2.1.5 SOLID-STATE PROCESSING OF LWHEAS

2.1.5.1 Mechanical Alloying (MA)

Powder metallurgy (PM) processing enables the development of ultrafine, submicron, or nano grained microstructures, which can be used to manufacture LWHEA products with a near-net-shape. Because of its application and advancement methods in the metal forming process, PM has been the subject of substantial research (White 2002; Müller 2001; Orban 2004). The ability to manufacture advanced materials that are not achievable with other technological procedures is one of the fundamental features of this approach, which is known as structural components manufacture (Akhtar *et al.* 2018). Traditional metallurgical operations, particularly those dealing with ecosystems, have less of an impact on PM firms (Akhtar *et al.* 2018). PM's simulation is always being developed in the industries because it covers such a broad spectrum.

The first stage of the PM process, which involves blending or mixing elemental metallic powders, increases the likelihood of achieving a homogeneous mixture before sintering. The process is called mechanical alloying (MA) or milling (MM) because it is carried out mechanically (Cobbinah & Matizamhuka 2019b). Mechanical alloying was invented by John Benjamin and his research team. MA was first created to improve the oxide-dispersion strength of nickel- and iron-based superalloys for aerospace applications (Benjamin 1976; Benjamin 1970; Gao *et al.* 2016; Junaid *et al.* 2018; El-Eskandarany 2013). Furthermore, it is a well-known top-down, solid-state, nonequilibrium method for developing nanocrystalline materials. It entails milling elemental particles to achieve atomic-scale alloying. Intermetallics, ordered compounds, solid solution alloys, amorphous structures, quasicrystalline phases, and nanocomposites have all been successfully produced using this technology (Suryanarayana 2001). MA has the added benefit of extending nanoscale processing. Even immiscible solutions have solid solubility. It's owing to the increased diffusion rates of powder components before alloying due to their nano size. As a result, MA improves the stability of solid solution phases in HEAs while also increasing configurational entropy.

MA is defined as the repeated welding and fracturing of powder particles entrapped between milling medium, the extent of which is determined by the mechanical properties of powder ingredients (Suryanarayana 2001). Plastic deformation of powders happens during the MA process as a result of the high energy and extreme mobility of balls impacting each other and the milling container or vial wall. As the deformation progresses, increased defect density, a reduction in diffusion distance, and an increase in powder temperature are observed, all of which contribute to an increase in the diffusion rate. The deformation of powder particles continues until the desired particle size is achieved, as shown in figure 2.14.



Figure 2.14 A schematic for the mechanical alloying or mechanical milling of powder particles (Suryanarayana 2001)

MA is a complicated process that necessitates the optimization of several variables. To produce the required product phase and/or microstructure, some variables are used. The following are some of the key criteria that influence the powder's ultimate composition: type of mill, milling container (vial), milling speed, milling time, type, size, and size distribution of the grinding medium, ball-to-powder weight ratio, milling vial, milling atmosphere, process control agent, and temperature of milling (Suryanarayana 2001). All of these process variables aren't entirely self-contained. The optimum milling time, for example, is determined by the mill type, size of the grinding medium, milling temperature, ball-to-powder ratio, and other factors. Rigorous research of the effects of these parameters on LWHEAs, except for milling time, is lacking in the literature (Salemi *et al.* 2016). The impact of milling time on phase evolution is evident in the majority of MA reports on LWHEA synthesis. X-ray diffraction (XRD) patterns of powders taken at regular intervals are frequently used to determine the extent of alloying during milling. Within 15–40 hours of milling, the majority of the solid solution phases in HEAs develop. While the longer milling period results in a more homogeneous alloy, it also increases the likelihood of contamination during the milling process. As a result, particles are sometimes milled for a short time and then annealed or consolidated to accomplish alloy formation. Mechanical activation is the term for this (Colombini *et al.* 2018).

The milling atmosphere is another parameter that has to be controlled. The atmosphere in which mechanical alloying takes place has an impact on LWHEA powder manufacturing yield. For example, the nitrogen shock method, which involves introducing nitrogen gas after milling in argon for a while, aids in the fracturing of powders by producing brittle a supersaturated -phase solid solution with nitrogen (Cobbinah & Matizamhuka 2019b). When dry milling LWHEAs, an argon environment has been used frequently (Zhang et al. 2018a; Kang et al. 2018b; Ge et al. 2017) to prevent powder oxidation. The use of a mixture of dry and wet milling to make LWHEA powders is becoming more common. Additionally, The size of the grinding balls and the amount of energy imparted by their impact have an impact on the solid-state reactions that occur during the mechanical milling of LWHEAs (Guo et al. 1994; El-Eskandarany 2015). Mechanical milling with balls of varying diameters results in significant collision energy, which has an impact on the structure of MAed LWHEAs. Nonetheless, increasing the quantity of balls negatively influences the performance of the milling operation. Also, increasing the number of grinding balls lowers the degree of fullness of the mill generating limited mobility in the balls and concomitant reduction of kinetic energy transfer and milling efficiency (Ghayour *et al.* 2016).

Additionally to MA parameters, the charge ratio (CR), also known as the weight ratio of the balls to powder (BPR), is an important variable in the milling process. Different researchers have altered this figure from as low as 1:1 to as high as 220:1 (Suryanarayana 2001). When

milling powder in a small capacity mill, a 10:1 ratio is most typically employed. When milling in a large capacity mill, a higher BPR of 50:1 or even 100:1 is used. The BPR has a major impact on the amount of time it takes to accomplish or form a certain phase required in the powder being milled. The less time is necessary the higher the BPR. Longer milling and higher milling intensities are thought to enhance the likelihood of sticking as a result of the heating caused by impacts and friction, making the powder more ductile (Bhattacharya *et al.* 2004). As a result of the strong sticking, the powders' microstructural homogeneity is frequently compromised. Low milling intensity, on the other hand, slows the alloying process (Neikov 2019; El-Eskandarany 2015).

To avoid sticking the powder on the walls of the vial and milling balls during milling, a process control agent (PCA) has to be added. PCAs or surfactants, which are generally organic compounds, are used to modify the surfaces of deforming particles and reduce excessive cold welding. A portion of the PCA decomposes during milling, depending on the type of PCA and milling settings, and can contaminate the milled particles. As a result, small amounts are usually recommended (Cobbinah & Matizamhuka 2019b). Toluene is the most widely used process control agent (PCA), followed by n-heptane (Rogal *et al.* 2017), dodecane (Zaddach *et al.* 2016), ethanol (Fu *et al.* 2014), methanol (Moravcik *et al.* 2016), cyclohexane (Wu *et al.* 2016), and stearic acid (Dwivedi *et al.* 2016). Regarding the milling speed, the faster the mill rotates, the higher the energy input into the powder. The greatest speed that can be used depends on the mill's design. The powders may be contaminated as a result of the high temperatures developed at a high speed. Due to increased dynamical recrystallization during nanocrystal formation, the average crystal size increases and the internal strain reduces at increasing milling intensities (Suryanarayana 2001). Different types of mills reach different maximum temperatures, and the values vary greatly.

Individual components are mixed in the proper proportions in a single stage in the traditional method of forming HEA by MA. As a result, phase formation is determined by the system's inherent thermodynamic and kinetic parameters. Vaidya *et al.* (2019b) presented a new method for producing HEAs via MA that involves adding constituent pieces one at a time. Sequential

alloying is the name for this approach, which is depicted schematically in Fig. 2.15 (a). They demonstrated this by using MA to create nanocrystalline AlCoCrFeNi. Variable proportions of BCC and FCC phases obtained at the end of each sequence revealed the path dependence of phase development (Figure. 2.15(b)).



Figure 2.15 (a) Schematic of conventional alloying versus sequential alloying. (b) Phase fractions of BCC phase obtained in AlCoCrFeNi synthesized through different sequences. (Vaidya *et al.* 2019b)

MA is the ideal processing procedure for producing valid LWHEAs with a density of below 3 g.cm⁻³ (Kumar & Gupta 2016). However, MA, like any other processing technology, has drawbacks, including the possibility of contamination and fire dangers when the particles are small, as well as milling media or the working environment.

2.1.5.2 Powder Consolidation by Spark Plasma Sintering (SPS)

As MA is the first stage of PM, powder consolidation is the next step, which is usually achieved with sintering equipment. The sintering process is commonly chosen to get the best density and nano-crystallinity combination. To consolidate milled LWHEA particles, SPS has been the most extensively employed technology. Vacuum hot pressing sintering (VHPS) (Ge *et al.* 2017; Varalakshmi *et al.* 2010a; Wu *et al.* 2016), microwave sintering (Shivam *et al.* 2018),

and hot isostatic pressing (HIP) (Varalakshmi *et al.* 2010b) are some of the other sintering processes commonly utilized. SPS has many advantages over traditional powder metallurgy processes, including ease of use, high repeatability, precise sintering energy management, high sintering speed, safety, and reliability. (Borkar & Banerjee 2014). When compared to traditional sintering, SPS compaction time is usually shorter while maintaining nanocrystalline properties.

Furthermore, SPS, also known as field aided sintering technique, is a PM method for consolidating powders when electrical charge and pressure are applied (Mogale & Matizamhuka 2020). The approach (shown schematically in Figure 2.16) uses uniaxial pressure and pulsed high direct current to consolidate powders, according to Xie et al. (2011). The science underlying the successful consolidation of the powders is due to the sufficient development of Joule heating (Ganesh et al. 2020), which was achieved by using voltages below 10V and currents up to 10 kA in conjunction with an electrically conductive tool partner. As a result of the Joule heating at the particle's contact areas, new metal with a higher energy level than the particle's internal energy appears (Cobbinah & Matizamhuka 2019b). This method allows for a temperature of 2000 degrees Celsius to be reached at a heating rate of 1000 degrees Celsius per minute. Despite numerous papers claiming to elucidate the sintering mechanism of SPS, no conclusive evidence has been found to date to unravel the microscopic mechanism of the sintering process. The mechanics of LWHEA densification during sintering have yet to be thoroughly investigated. Additionally, the temperature is the most important regulating parameter in the SPS process for determining microstructural properties such as grain size, grain boundary misorientation distribution, and coincidence site lattice, such as the 3-grain borders (Borkar & Banerjee 2014). However, sintering at high temperatures is not always suggested since it makes it difficult to keep ultrafine or nanostructures (Liu et al. 2007).



Figure 2.16 (a) Diagram of the SPS process, (b) Schematic diagram of a sintered bulk sample in which the pressure direction of SPS processing is along the Z-axis, adopted from (Xie *et al.* 2011)

High angle grain boundaries (including twin boundaries) and multi-grain size distributions, for example, are responsible for high ductility, whereas high dislocation density and refined grain structure are responsible for high strength (Dutel *et al.* 2013; Borkar & Banerjee 2014). As a result, processing factors are critical in improving metal ductility and strength. The quasi-static compressive force applied in SPS (Mogale & Matizamhuka 2020) has mechanical effects that promote densification. This improves particle contact, changing the morphology and number of contacting particles while also improving densification kinetics related to viscous flow, lattice, and grain boundary diffusion. Most LWHEAs undergo SPS at temperatures much below the melting point, resulting in solid-state sintering as the primary method of densification. Sintering of annealed powders is governed by volume diffusion, while densification of milled powders is governed by a complicated mix of ultrafine grains, high grain boundary fractions, and chemical homogeneity, according to Mane & Panigrahi (2018).

The effects of the solid-state processing technique on the microstructure and mechanical properties of LWHEAs has been reported. The structural development and mechanical

properties of the high-entropy AlCuNiFeCr alloy produced by MA and SPS were examined by (Yurkova *et al.* 2019). The nanocrystalline high-entropy AlCuNiFeCr alloy treated during MA was proven to be a supersaturated solid solution with a bcc crystalline structure in this work. The alloy had three phases after SPS at 800 °C: a majority of B2- ordered solid solution, one fcc solid solution, and the (Cr, Fe)23C6 phase. A sintered alloy has a hardness of 8.35 GPa and compressive strength of 1960 MPa at room temperature.

Another study was conducted by Chae *et al.* (2020) fabricated a brand new $Al_{16.6}Cu_{16.6}Fe_{16.6}Mn_{16.6}Mg_{16.6}Ti_{16.6}$ LWHEA using MA and SPS. The findings revealed that milled LWHEA has a BCC base structure, consisting of a dual BCC1/BCC2 matrix with Ti and a few Cu₂Mg precipitates strewn about. The finer secondary phases in the matrix altered the dispersion strengthening in some way. The finer secondary phases in the matrix had an impact on dispersion strengthening. When compared to Al or Ti-based conventional alloys, AlCuFeMnMgTi LWHEA has higher microhardness and density (770 HV and 4.34 g·cm⁻³, respectively).

Furthermore, Kanyane *et al.* (2020) used a spark plasma sintering technique to consolidate TiAlMoSiW, Ti_{0.25}AlMoSi_{0.25}W_{0.1}, and Ti_{0.3}AlMoSi_{0.3}W_{0.1} LWHEAs. The findings revealed the presence of a BCC structure in TiAlMoSiW alloy, as well as W-rich and Si-rich phases and FCC of ordered phases of TiSi₂. The Ti_{0.3}AlMoSi_{0.3}W_{0.1} alloy, on the other hand, had more intermetallic phases such as Mo₂Si₄ and WSi₂. The developed alloys had great microhardness, although TiAlMoSiW had the highest microhardness, with 802.01 HV. The alloys' tribological behaviour, on the other hand, appeared to be low, with a minor average weight loss of 0.00120g. The alloys' corrosion resistance qualities were also investigated.

Regarding the SPS parameters that influence the microstructure and mechanical properties of the material, Borkar & Banerjee (2014) concluded in their study based on the findings that processing temperature is the most critical factor in defining the microstructure and mechanical properties of SPS processed pure nickel, whereas processing pressure appears to have little effect on mechanical qualities. The average grain size in these SPS processed nickel samples grows dramatically as the processing temperature rises.

2.1.6 MICROSTRUCTURE AND PHASE STABILITY OF LWHEAS

Although HEAs are composed of multiple elements, the feature that distinguishes these alloys the most is their apparent simplicity in forming single fcc/bcc crystalline solid solution phases rather than multiple phases FeCoCrNi (Lucas et al. 2012) and FeCoCrNiMn (Cantor et al. 2004a) include a single simple fcc phase, NbMoTaW (Senkov et al. 2010), and TaNbHfZrTi (Senkov et al. 2011a) produce a single simple bcc phase, while others form a mixture of those simple phases, such as FeCoCrNiCu creating two identical fcc phases (Hsu et al. 2005), FeCoCrNiAl developing a combination of bcc and fcc (Yeh et al. 2004), or MoWAlCrTi forming two identical bcc phases (Gorr et al. 2015). Many systems in which the crystalline phase is composed of the simple phases bcc/fcc with the addition of other phases such as Laves (e.g. CrMo_{0.5}NbTa_{0.5}TiZr forming two bcc phases and one laves phase (Senkov *et al.* 2013b)) are also referred to as HEAs simply because they are "alloys composed of multiple elements at near-equiatomic ratio". For example, when the amount of Al in the alloy system FeCoCrNiCu is increased, the crystalline structure changes from fcc single phase to bcc single-phase, passing through a mixture of fcc and bcc (Yeh et al. 2004). In contrast, the amount of intermetallic phases such as Laves phase (intermetallic phases of the form AB₂ such as NbCr₂ and NbFe₂ (Huo et al. 2015)) increases when titanium or niobium is added (Shun et al. 2012). Even though certain alloy systems do not form single phases when Al, Ti, or Nb concentration is increased, they are nonetheless classified as HEAs. When compared to traditional metallic systems, single phase HEAs can attain high mechanical properties, hence some writers focus their study on single phase HEAs (Pi et al. 2011; Senkov et al. 2011a; Tong et al. 2005b). Structures consisting of single phases with a modest quantity of second phases, such as intermetallic compounds, have proved to have considerable promise as well (Lu et al. 2014).

Multiphase microstructures are typical in HEAs. Solid solutions and/or intermetallic phases are examples of this. Due to the action of precipitate hardening, the latter might take the form of nano- to micro-scale precipitates (Zhang *et al.* 2014a), which are frequently desired for mechanical applications. However, complicated brittle microstructures can be formed, which are dominated by ordered compounds and are generally undesirable. Designing microstructures for optimal material qualities necessitates investigating their phase stability and likely changes. The complicated local atomic environment of HEAs, on the other hand, makes understanding

phase stability and transition characteristics difficult. Mechanical properties are influenced by the underlying phase stability and transition behaviours in lightweight HEAs. Nonetheless, due to the complicated elemental-diffusion and atomic-bonding environments in HEAs (Santodonato *et al.* 2015) and strong interatomic interactions between Al/Ti and transition metals (Feng *et al.* 2016), the compositionally complex lightweight HEAs pose a fundamental challenge to the basic understanding of phase stability and transformation behaviours (Feng *et al.* 2017). For future effective development of lightweight HEAs, it is critical to understand phase stability and transformation characteristics to attain appropriate mechanical properties.

Feng et al. (2018) studied the phase stability and transformation behaviours of a newlydesigned lightweight Al_{1.5}CrFeMnTi HEA by integrated experimental and theoretical approaches. The fundamental goal of this research was to create a lightweight HEA with a microstructure similar to that of Ni-based superalloys. It has been established that the Fe-Al-Ti alloy system can produce a body-centred-cubic (BCC) and a body-centred-cubic (BCC) structure. Analogue of the L21 aligned/coherent two-phase microstructure In Ni-based superalloys, γ/γ' coherent microstructure. Furthermore, due to the limited-slip systems available in the alloy, an earlier study reveals that L2₁ has stronger creep resistance than B₂ and L1₂ phases (Strutt et al. 1976; Song et al. 2015; Song et al. 2017). As a result, the newly developed HEA will aim to create similar BCC and L2₁ coherent microstructures by selecting Fe, Al, and Ti components. The BCC, L2₁, and C14-Laves phases make up the Al_{1.5}CrFeMnTi alloy in its as-cast state, with the L21 phase coherently dispersed inside the BCC phase. Growth, coarsening, and/or phase transitions undoubtedly changed the morphology, size, coherency, and spatial arrangement of the L2₁ precipitates during high-temperature service. In addition, the amount of C14- Laves phase inside the microstructure must be regulated for optimal mechanical qualities.

In this study, Scanning electron microscopy (SEM), electron-backscattered diffraction (EBSD), energy-dispersive spectroscopy (EDS), and transmission electron microscopy (TEM) techniques were used to analyze the microstructures. Synchrotron X-ray diffraction (XRD) on the 11-ID-C beamline at the Advanced Photon Source (APS), Argonne National Laboratory, was used to identify the crystal structures. The findings revealed that the novel Al_{1.5}CrFeMnTi light-weight HEA comprises three phases: BCC, L2₁, and C14-Laves, with the L2₁ phase

distributed coherently inside the BCC phase in the as-cast form. After that, annealing treatments at 750 °C and 850 °C were used to change the size, shape, coherency, and spatial distribution of the L2₁ phase. Because of the tiny interfacial energy between the L2₁ and BCC phases caused by the minor lattice mismatch, the L2₁ phase had a significant nucleation advantage. Also, the constituent phases and phase-transformation temperature of the L2₁ phase (837 °C) were accurately predicted by CALPHAD thermodynamic modelling, which matched the actual results. A BCC+L21 two-phase area can be obtained by reducing the Ti content in the projected phase diagram. And finally, the measured compositions of L2₁ and C14 phases were explained by the DFT-predicted enthalpies of forming a range of virtual compositions in binary, ternary, and quaternary systems. The AIMD simulations indicated the potential formation mechanism of L2₁ precipitates based on the preferred bond pairings (AIFe, AITi, and AlMn).

Yang *et al.* (2014) conducted a study on Phase Stability of Low-Density, Multiprincipal Component Alloys Containing Aluminum, Magnesium, and Lithium. This study developed a variety of low-density multicomponent alloys based on the Al-Li-Mg-(Zn, Cu, Sn) system using a previously published high-entropy alloying technique. To investigate the lower density design space, two variations with a greater Al content, Al₈₀Li₅Mg₅Zn₅Sn₅ and Al₈₀Li₅Mg₅Zn₅Cu₅ were investigated. The microstructures, phase compositions, and mechanical behaviours of these materials were detailed. Each alloy's microstructure and characteristics were investigated in their as-cast state. X-ray diffraction (XRD) was used to describe crystal structures using a PHILIPS APD-10 diffractometer with Cu Ka radiation and samples in the form of around 2-mm-thick plates. A ZEISS SUPRA 55 scanning electron microscope (SEM) with energy-dispersive spectrometry was used to study microstructures (EDS).

The findings discovered that the ten constituent equiatomic binary alloy systems (Al-Li, Al-Mg, Li-Zn, Li-Sn) generated single-phase intermetallic compounds at room temperature. The Mg-Zn and Mg-Sn equiatomic binary alloy systems, on the other hand, were made up of one solid solution and one intermetallic compound. Only disordered solid solution phases formed at average temperature in the other four equiatomic binary alloy systems. These (Al-Zn, Al-Sn, and Zn-Sn) comprised two solid solution phases with different crystal structures. The Li-Mg

system was the only one to have a single solid solution phase (BCC crystal structure). As a result, phase selection in the quinary AlLiMgZnSn alloy is driven by the stable phases of binary alloy systems, and no new higher-order phases are visible. In the as-cast condition, the substantial enthalpy contributions for the ordered Mg₂Sn phase outweighed the entropy contributions toward stability of the solid solution phases, and it became the primary phase in AlLiMgZnSn alloy.

Therefore, it was concluded that except for $Al_{80}Li_5Mg_5Zn_5Sn_5$ and $Al_{80}Li_5Mg_5Zn_5Cu_5$, predominately FCC α -Al in the as-cast state, the microstructures of these alloys were dominated by diverse intermetallic compounds in the as-cast condition. The effects of entropy, atomic size, enthalpy effect, electronegativity, and valence electron concentration on phase formation were studied to understand better the mechanisms governing phase stability in these alloys. The findings showed that configurational entropy is insufficient to stabilise the majority of disordered solid solution phases in low-density alloys containing large proportions of Al, Mg, and Li.

2.1.7 MECHANICAL PROPERTIES

The dominating element dictates a conventional alloy's mechanical properties and behaviour with a primary component. A small alloying element is used to achieve specific and distinctive features (Zhang *et al.* 2014a). Steel alloys, for example, require a combination of carbon and iron to produce a lighter and stronger metal than pure iron. In contrast, aluminium alloys combine very softly and light-weighted pure aluminium and alloying elements such as magnesium or copper, resulting in a metal with an excellent strength-to-weight ratio that is now widely used in aerospace applications. On the other hand, high entropy alloys may have mechanical properties that differ from constituents (Zhang *et al.* 2014a). The mechanical properties are controlled by their crystal structure. As previously stated, the crystal structure of a high entropy alloys with FCC structures have higher ductility but lower strength, whereas high entropy alloys with BCC structures have very high strength but restricted ductility (Zhang *et al.* 2014a). The strength and ductility of a mixture of FCC and BCC phases (FCC+BCC) are intended to be balanced. The mechanical properties of designed high entropy alloys have been

superior to structural ceramics, such as increased strength and ultrahigh fracture toughness. High entropy alloys have also been reported to be superconductive and resistant to corrosion (Ye *et al.* 2016). High entropy alloys are a good candidate for structural, aerospace, and energy industry applications, even though they are still being widely explored.

2.1.7.1 Structural Properties

Since HEAs have demonstrated good qualities, they are being examined as a viable candidate for various applications, including high temperature, anti-corrosion, and wear resistance(Murty *et al.* 2019a). In some circumstances, nanoscale precipitates have been found in HEAs, which aid in enhancing some of these alloys' properties (Murty *et al.* 2019a).

2.1.7.1.1 Room Temperature Properties

At room temperature, the yield strength of HEAs ranges from 300 MPa for FCC-structured alloys like CoCrCuFeNiTix to 3000 MPa for BCC-structured alloys such AlCoCrFeNiTix system (Wang et al. 2007; Zhou et al. 2007a). Vickers hardness levels range between 100 and 900 HV (Zhang et al. 2014a). The AlxCoCrCuFeNi alloys were the first HEA system to be thoroughly investigated (Tong *et al.* 2005b; Tung *et al.* 2007; Tsai *et al.* 2009). When x = 0-0.5, the hardness value was 133 HV, but when x=3 (Figure 2.17), the hardness value increased dramatically to 655 HV (Figure 2.17) (Tong et al. 2005b). Because Al is the most significant atom among the constituent elements in the alloy (Callister Jr & Rethwisch 2020), and Al also forms strong bonds with other elements in the alloy, as suggested by the enthalpy of mixing (Takeuchi & Inoue 2010), this rise in hardness value is attributed to an increase in lattice distortion. These factors combine to boost the SS strengthening effect when the Al content rises (Murty et al. 2019a). The alloy transitioned from single-phase FCC to dual-phase FCC+BCC and ultimately to the BCC phase as the Al content increased (Murty et al. 2019a). The BCC and ordered B2 phases are considerably stronger than the FCC phase. Furthermore, the delayed deformation kinetics that leads to the creation of nano-precipitates aid in the material's strength (Murty et al. 2019a).



Figure 2.17 Vickers hardness and total crack length around the hardness indent of Al_xCoCrCuFeNi alloy system with different aluminium contents (x values) (Tong *et al.* 2005b).

It has been shown that alloying elements with greater atomic sizes have a proclivity for forming secondary phases, strengthening precipitation (Murty *et al.* 2019a). When Li *et al.* (2009) studied ten alloy systems, they found that adding Zr and Ti resulted in the maximum hardness (566 HV) because they have bigger atomic sizes and promote the precipitate strengthening of secondary phases. Furthermore, when Ma *et al.* (2012) investigated the AlCoCrFeNb_xNi alloy, they discovered that increasing the Nb content from x=0-0.5 increased the hardness from 500 to 750 HV. By combining Nb and Ti, the hardness can be increased to 797 HV, which is higher than that achieved by adding just one of these two elements (Razuan *et al.* 2013).

In compression, the AlCoCrFeNiTi_x alloys have excellent mechanical properties (Zhou *et al.* 2007a; Zhou *et al.* 2008). When x=0.5, the alloy was found to have a BCC structure and excellent properties (Murty *et al.* 2019a). The yield and fracture strengths of the alloys were found to be 2.26 and 3.14 GPa, respectively, which are significantly higher than those of BMGs (Murty *et al.* 2019a). It had a 23.3 percent elongation as well. The high strength in the alloy

was endorsed by the spinodal decomposition in the DR region, while there was precipitation of BCC phase particles in the ID region (Murty *et al.* 2019a). As a result, in addition to SS strengthening, nanoparticle and precipitation strengthening play a vital role in alloy mechanical properties (Murty *et al.* 2019a).

2.1.7.1.2 High-Temperature Oxidation Properties

The solid solution nature of HEAs allows them to accommodate more Al and Cr than traditional alloys such as Ni-based alloys and stainless steels (Zhang *et al.* 2014a). This should help them withstand oxidation by providing vast Al and Cr reservoirs for sustained oxide development and repair. HEAs with the ability to selectively oxidize to form Al_2O_3 and/or Cr_2O_3 should have better oxidation resistance. With this in mind, only a few studies have looked into the oxidation behaviours of HEAs in depth. As previously noted, the majority of research has been on as-cast microstructures and phase formation requirements as a function of alloying variables. As a result, fundamental research into the oxidation mechanisms in compositionally complex alloys is required.

On thermally sprayed AlSiTiCrFeCoNiMo_{0.5} and AlSiTiCrFeNiMo_{0.5} coatings, Huang *et al.* (2004) conducted one of the earliest HEA oxidation investigations. At 900°C, 1000°C, and 1100°C, their oxidation behaviours were studied. Coatings with disordered BCC microstructures were discovered, but bulk alloys with the same compositions had both B2 and numerous FCC phases. The mass change data from the oxidation tests revealed parabolic oxide growth for the first 50 hours, then a plateau. This behaviour was attributed to microstructurally forming a protective Cr_2O_3 scale beneath a transitory TiO₂ surface layer.

In a similar study, Liu *et al.* (2014) looked at the oxidation behaviour and microstructures of NbCrMoXAl_{0.5} refractory HEAs with X = Ti, Si, and V. Each alloy was discovered to include a parent BCC phase, with secondary phases appearing in several of the alloys. All alloys exhibited linear oxide growth after 20 hours of oxidation testing at 1300°C. To a lesser extent, each alloy formed Al₂O₃, but it primarily formed other oxides. Ti and Si additions significantly improved the oxidation resistance of the alloys, whereas V was found to be detrimental (Liu *et al.* 2014).

Chuang *et al.* (2011) linked the superior oxidation resistance of $Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti$, $Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti_{0.5}$, $Co_{1.5}CrFeNi_{1.5}Ti$, and $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}$ HEAs to their enhanced wear properties. For 24 hours, all of the alloys were oxidized at 600°C and 800°C. Compared to other wear-resistant steels, the HEAs showed significantly reduced mass increases during oxidation. It's also been suggested that the production of oxide scales acts as a barrier between the underlying alloy and the abrasive surface, increasing wear resistance.

At 850°C, Jiang & Luo (2013) investigated the oxidation behaviour of an AlCuTiFeNiCr HEA. Initially, the alloy showed both BCC and FCC phases. Based on previous research, a B2 phase is anticipated in this alloy (Singh *et al.* 2011). However, XRD was the only method of determining structure in this study, leading to some ambiguity in phase determination. The alloy had parabolic oxidation kinetics during oxidation and generated an oxide scale of complex transient oxides with a tiny volume fraction of Al₂O₃ (Jiang & Luo 2013). Because all microscopy was done on the outer oxide surface, it's difficult to say whether the oxides constituted a protective barrier.

Chen *et al.* (2010) investigated the oxidation behaviours of two HEAs, $Al_xCrFe_{1.5}MnNi_{0.5}$, at 800°C, where x = 0.3 and 0.5. FCC and BCC+B2 areas were found in the $Al_{0.3}$ HEA, whereas BCC and BCC+B2 regions were found in the $Al_{0.5}$ HEA. Each alloy exhibited parabolic oxide growth for 50 to 100 hours, followed by a mass change plateau, similar to the AlCuTiFeNiCr HEA mentioned above. A multilayer scale of Cr and Al oxides develops beneath an outer transitory Mn oxide, as detected microstructurally. It was eventually determined that higher Al concentrations resulted in better oxidation resistance, likely due to the development of more Al oxides.

At 900 degrees Celsius, Zhang *et al.* (2013a) investigated the oxidation resistance of $Al_{0.5}FeCoCrNi$, $Al_{0.5}CoCrFeNiSi_{0.2}$, and $Al_{0.5}FeCoCrNiTi_{0.5}$ HEAs. Due to the production of spinel and non-protective Fe-based oxides, the Ti-containing HEA had a complex oxide microstructure and had lower oxidation resistance than the other two alloys. The oxidation resistance of the $Al_{0.5}FeCoCrNi$ and $Al_{0.5}CoCrFeNiSi_{0.2}$ HEAs was equivalent, with both generating exterior Cr_2O_3 scales with inside Al_2O_3 oxides and AlN precipitates. The oxidation

characteristics of all three alloys were non-linear. However, all three HEAs demonstrated some degree of oxidation resistance, as proposed by Zhang *et al.* (2013a).

At 800°C and 1000°C in air, Daoud *et al.* (2015) investigated the oxidation behaviours of highentropy alloys Al₈Co₁₇Cr₁₇Cu₈Fe₁₇Ni₃₃ (FCC- alloy), Al₂₃Co₁₅Cr₂₃Cu₈Fe₁₅Ni₁₅ (BCC- alloy), and Al₁₇Co₁₇Cr₁₇Cu₁₇Fe₁₇Ni₁₇ (reference alloy). An FCC matrix with L1₂ precipitates was discovered in the FCC-alloy. Along grain boundaries, the BCC-alloy was composed of a B2 matrix with a high volume percentage of BCC precipitates and a low volume fraction of Curich FCC precipitates. The reference alloy was discovered to have regions having B2 and BCC phases and Cu-rich regions containing both FCC and BCC phases.

Based on the findings presented in this analysis of the oxidation literature, it can be concluded that HEAs having standard elements like Al, Co, Cr, Fe, Ni, and other transition metals oxidize similarly to conventional alloys containing equivalent contents. This remark is based on the assumption that such alloys include sufficient amounts of protective oxide-forming components. The fact that HEAs with high Al and/or Cr contents tend to oxidize to form Al₂O₃ and/or Cr₂O₃ selectively is a huge plus. On the other hand, refractory-based HEAs tend to have lower oxidation resistance due to the relative stability of refractory-based oxides. Not enough work has been conducted on the oxidation behaviour of LWHEAs. This is also why LWHEAs must be explored, especially regarding high-temperature applications.

2.1.7.2 High Hardness /Strength

The ideal alloy in alloy engineering has a high strength/hardness ratio and a low density (Ashby 2011). This is especially relevant in structural applications like aerospace engineering and civil transportation, where reducing the weight of engineering components is crucial for lowering energy demand. The mechanical characteristics of HEAs can vary significantly due to their vast composition range and a large variety of alloy systems. The following are the essential criteria in terms of hardness/strength: (1) the hardness/strength of each composing phase in the alloy; (2) the relative volume ratio of each composing phase; and (3) the morphology/distribution of the composing phases. Each phase's crystal structure and bonding play a significant role in the first factor. According to the observations, the phases can be
divided into four groups, each with a particular hardness range. Table 2.2 has this information. It's vital to remember that the hardness ranges provided in Table 2.2 are only examples; there may be exceptions. Valence compounds, essentially ceramics, are based on extremely strong covalent bonding.

As a result, they have the highest toughness. Dislocation actions are hampered in non-simple intermetallic phases due to the lack of easily accessible slip systems. Because BCC-based structures have greater directional bonding and lack a fully close-packed slip plane, they are tougher than their FCC counterparts. (Ogata *et al.* 2008; Abbaschian & Reed-Hill 2009). The main rule for estimating the hardness/strength of a HEA is simple: the harder the phase (and the larger the hard phase percentage), the harder the alloy. The phase distribution can also be crucial when two HEAs contain phases with equal hardness and relative percentage. The phase in the alloy affects the ductility of HEA. Harder phases, as one might imagine, have lesser ductility.

Table 1	2.2 Hardness	s-based c	classification	of HEA	phases.	There a	are also	examples	and	typical
hardne	ss ranges for	each cat	tegory. (Ogat	a <i>et al</i> . 2	2008)					

Туре	Example	Typical hardness (HV)
Valence Compounds	Carbides, Borides, Silicates	1000-4000
Intermetallics phases with non-simple structures	σ , Laves, η	650-1300
BCC and derivatives	BCC, B2, Heusler	300-700
FCC and derivatives	FCC, L1 ₂ , L1 ₀	100-300

2.1.7.3 Corrosion Resistance

In general, an alloy's composition and microstructure impact its corrosion resistance in certain corrosive conditions (Murty *et al.* 2019a). In both the H_2SO_4 and NaCl solutions, some of the HEAs have demonstrated outstanding performance. In HEAs, constituents such as Cr, Ni, Co, and Ti boost corrosion resistance in acid solutions, and Mo inhibits pitting corrosion. At the same time, Al and Mn have a negative effect, just as they do in traditional alloys. There is still a need for more research into these mechanisms.

The HEA exhibits passivation behaviour, as shown in Figure 2.18, which depicts the potentiodynamic polarization curves of AlCoCrCu_{0.5}FeNiSi alloy and 304 stainless steel in 0.1 M NaCl solution. It can also be noted that the corrosion potential of HEA is larger than that of 304 stainless steel, while the corrosion current potential is lower (Murty *et al.* 2019a). Similar behaviour is observed in 0.1 M NaCl solution (Murty *et al.* 2019a). The average corrosion rates in mpy obtained from polarization curves and immersion tests of as-cast CoCrCuxFeNi alloy (x=0, 0.5,1) in 3.5 percent NaCl solution are listed in Table 2.3 (Hsu *et al.* 2005). Cu addition is detrimental to pitting resistance, as evidenced by the findings provided (Murty *et al.* 2019a). Despite this, CoCrFeNi outperforms 304 stainless steel in pitting resistance (Murty *et al.* 2019a).



Figure 2.18 AlCoCrCu0.5FeNiSi alloy and 304 stainless steel potentiodynamic polarization curves in 0.1 M NaCl solution (Hsu *et al.* 2005).

Table 2.3 Average Corrosion Rate of CoCrCuxFeNi HEAs Obtained from Immersion Testand Polarization Curve in 3.5% NaCl solution (Hsu *et al.* 2005).

	CoCrFeNi	CoCrCu _{0.5} FeNi	CoCrCuFeNi
Immersion test	7.62 x 10 ⁻⁴	8.89 x 10 ⁻³	1.14 x 10 ⁻²
Polarisation test	3.31 x 10 ⁻⁴	7.46 x 10 ⁻³	1.37 x 10 ⁻²

Corrosion resistance has also been studied in certain environments compared to other traditional alloy systems (Yang *et al.* 2012a). The corrosion rates of many materials in two different environments have been compared with HEAs, as illustrated in Figures 2.19(a) and 2.19(b). As a result of the findings, HEAs are a competitive material for specific circumstances, as it has a corrosion rate comparable to most conventional systems.



Figure 2.19 Corrosion rates of various materials (a) tested at 25°C under 3.5wt% NaCl and (b) tested at 25°C under 0.5M H₂SO₄. (Yang *et al.* 2012a)

2.1.7.4 Wear Resistance

Even though limited data is available (Murty *et al.* 2019a), wear properties must be examined from the beginning as the HEAs are produced. Hsu *et al.* (2004) discovered that the volume fraction of (Fe, Cr)-rich boride increases with increasing B content in abrasion wear resistance analysis of $Al_{0.5}B_xCoCrCuFeNi$ (x=0, 0.2, 0.6, and 1) HEAs. Figure 2.20 (Hsu *et al.* 2004) illustrates a comparison of wear resistance of common wear-resistant alloys. The HEA with x=1 has better wear resistance than the SUJ2 bearing steel, as can be observed. V and Ti additions to the same alloy have also been recorded (Chen *et al.* 2006b; Chen *et al.* 2006a). Wear resistance increased rapidly as Ti concentration scaled from 0.6 to 1, followed by a slow reduction as Ti content increased higher (Chen *et al.* 2006a). The wear resistance of V increased by 20% as the content of V increased from x=0.6 to 1.2 and then remained steady beyond x=1.2 (Chen *et al.* 2006b). The formation of the phase, which is a difficult phase, is responsible for this improvement (Murty *et al.* 2019a).



Figure 2.20 Hsu investigated the abrasion wear resistance of Al0.5BxCoCrCuFeNi in a study (Hsu *et al.* 2004).

In research of the adhesive wear resistance of AlxCoCrCuFeNi HEAs by Wu *et al.* (2006), it was discovered that with increased Al content, the worn surface is smooth and yields fine debris with high oxygen content, resulting in a significant improvement in wear resistance, as illustrated in Figure 2.21. This improvement in wear resistance is due to the high hardness, which resists plastic deformation and delamination and causes oxidative wear, which can help with wear resistance (Zhang *et al.* 2014a). It was discovered in this study that alloying could impact the wear behaviour of HEAs (Zhang *et al.* 2014a).



Figure 2.21 Vickers hardness and wear coefficient of AlxCoCrCuFeNi alloys with varying aluminium content. (Wu *et al.* 2006).

2.1.7.5 Strengthening Mechanisms

It's crucial to understand the different sorts of strengthening mechanisms in metals if the aim is to sacrifice ductility for strength. Because plastic deformation depends on dislocations' capacity to move, restricting dislocation mobility increases mechanical strength and necessitates a more considerable effort to commence plastic deformation. Solid-solution hardening, grain-boundary strengthening, dislocation hardening, and dispersion hardening are the four types of strengthening mechanisms found in HEAs. According to some experts, solid solution hardening is the primary cause of HEAs' outstanding mechanical properties. A simple total of the four independent contributions yields the final increment of YS ($\Delta \sigma_{0.2}$), which may be written as (Kamikawa *et al.* 2015; He *et al.* 2016):

$$\sigma_{0.2} = \sigma_0 + \Delta \sigma_s + \Delta \sigma_g + \Delta \sigma_p \tag{2.14}$$

where $\Delta \sigma_s$, $\Delta \sigma_g$, $\Delta \sigma_d$, and $\Delta \sigma_p$ are the incremental YS from solid-solution, grain-boundary, dislocation, and precipitation hardening, respectively, and σ_0 is the lattice friction strength.

2.1.7.5.1 Solid Solution Hardening

When the atoms of the solvent and alloying elements dissolve into each other, a solid phase is formed. The action of impurity atoms in either substitutional or interstitial solid solutions is exploited in solid solution hardening (Callister Jr & Rethwisch 2020). Since the lattice strain on the surrounding atoms is applied, strengthening occurs. When a lattice strain is applied, dislocation mobility is restricted (Callister Jr & Rethwisch 2020), increasing the material's hardness. According to Yeh *et al.* (2004), the explanation for the increased hardness of HEAs is that there is no idea of the matrix, and all atoms are solute atoms, resulting in a higher saturation degree of solid solution. Li (2019) added a small quantity of C atoms to CoCoCrFeMoNi, and the interstitial C atoms increased the stress field, which helped strengthen the solution. The Gypen L A formula (s) (Tian *et al.* 2019) can be used to describe the solid solution strengthening effect caused by various alloying elements:

$$\Delta\sigma_s = \left(\sum_i (k_i * \sqrt{c_i})^{1/p}\right)^p \tag{2.15}.$$

where k_i is the solute *i*'s strengthening coefficient, C_i is the atomic percentage of solute *i* and p are 1/2 (Mishima *et al.* 1986; Tian *et al.* 2019). k_{Al} and *Ci* have 225 MPa/(at. %)^{1/2} (Tian *et al.* 2019; Mishima *et al.* 1986) and 20%, respectively. As a result, the $\Delta \sigma_s$ can be determined to be 101 MPa.

2.1.7.5.2 Grain Boundary Strengthening

Using the rule of mixture described in a study (Sriharitha *et al.* 2014), the 0 values for AlCoCrFeNi HEA may be calculated as 121 MPa. The Hall-Petch equation can be used to calculate the effect of grain boundaries on the YS (G):

$$\Delta \sigma_G = k d^{-1/2} \tag{2.16}$$

d is the average grain size of the alloys; *k* is the strengthening coefficient, and the values can be derived as 182 MPa μ m^{1/2} using the rule of mixture (Sriharitha *et al.* 2014). In the LM-1, LM-2, and AM alloys, the grain boundary contribution was 11.14, 12.74, and 13.38 MPa, respectively.

The increase in yield strength due to the grain size variation in FeCoNiCrMn is insufficient to account for the total strength increase in the HEA (Liu *et al.* 2013). Precipitation and grain boundary strengthening were associated with the CoCrFeNi hardness of 580 HV (Sathiyamoorthi *et al.* 2017). The high tensile strength of 712.5 MPa and the high elongation of 56 % were similarly linked to grain boundary strengthening in the same alloy by Liu et al. (Liu *et al.* 2016). Grain boundary strengthening contributes roughly 85% of flow stress in AlCoCrCuFeNi HEA, according to Ganji *et al.* (2017). The hardness of 8.13 GPa and elastic modulus of 172 GPa were achieved in a dual-phase (FCC + BCC) AlCoCrCuFeNi HEA (Ganji *et al.* 2017), were apparently due to strain hardening and grain boundary strengthening.

2.1.7.5.3 Dislocation Hardening

Dislocation hardening refers to the mutual delivery and entanglement that occurs during dislocation movement, forming an impediment to dislocation movement and making plastic deformation difficult, hence boosting strength. Melting, casting, hot rolling, and homogenization procedures were used by Deng *et al.* (2015) to make $Fe_{40}Mn_{40}Co_{10}Cr_{10}$. The HEA was discovered to have a substantial number of active dislocations. These dislocations crisscrossed and overlapped one another, forming a high-density dislocation wall that slowed dislocation movement. High-density dislocations are formed during the processing of HEA matrix composites due to the differing thermal expansion coefficients of the reinforcement and the matrix, and the reinforcement prevents dislocation slip and grain boundary movement from improving strength. Equation (2.17) (Fu *et al.* 2016; Ganji *et al.* 2017) is used to calculate the dislocation strengthening value:

$$\Delta \sigma_{Dis} = M_{\alpha} G b \rho^{1/2} \tag{2.17}$$

where $\Delta \sigma_{Dis}$ is the dislocation strengthening value, *M* and α are the FCC structure's *M* and 0.2, respectively, *G* is the shear modulus, *b* is the Burger vector, and ρ is the density. He *et al.* (2016) showed that by combining grain boundary hardening, dislocation hardening, and precipitation hardening, a good balance of yield strength and ductility could be attained in FCC HEAs. According to research, tiny interstitial solutes like carbon or boron can also initiate phase change during solid solution strengthening.

2.1.7.5.4 Dispersion Hardening

Dispersion hardening occurs when second phase particles obstruct dislocation movement. The interaction between particles and dislocations can be classified into two types: the Orowan strengthening mechanism, in which the particles are sufficiently strong, their radius surpasses the critical value, and the dislocations bypass the particles. The Ansel-Lenier mechanism, in which the dislocation cuts through the particles, causing them to break, is the other. It can occur when the particles are tiny enough and coherent with the matrix (He *et al.* 2016; Fu *et al.* 2018; Rogal *et al.* 2017). The Fe₂₅Co₂₅Ni₂₅Al₁₀Ti₁₅ crystallized γ' , the HEA and γ' are coherent, and dislocation shear γ' (Fu *et al.* 2018). Fan *et al.* (2014) developed TiC-reinforced (FeCrNiCo)Al_{0.7}Cu_{0.5}, with a yield strength of 630 MPa for the HEA and 1,290 MPa for the composite. Equation (2.18) (Liu *et al.* 2017a; Wu *et al.* 2019) can be used to obtain the Orowan strengthening value of HEA matrix composites:

$$\Delta \sigma_{Orowan} = \left\{ 0.13 \ Gb/d_p \left[(2f_v)^{-\frac{1}{3}} - 1 \right] \right\} ln \left(d_p / 2b \right)$$
(2.18)

where $\Delta \sigma_{Orowan}$ is the Orowan strengthening value, *G* is the HEA matrix's shear modulus, *b* is the Burger vector of the matrix, and f_v and d_p are the reinforcement's volume fraction and size, respectively.

2.1.7.6 Effect of Alloying Elements

Powder metallurgy is recently employed to fabricate the HEAs. The research of the alloying sequence of elements during ball milling has made some progress because the element with a

low melting point in the solid-state has a more significant diffusion coefficient and a faster diffusion rate, which is more favourable to alloying. The alloying rate is inversely related to the melting point. Because the brittleness of the metal is more likely to be broken during ball milling when the melting point is close, the alloying rate is proportional to the brittleness of the pure element, speeding up the alloying process—furthermore, the faster the alloying rate, the lower the component concentration (Chen *et al.* 2013). According to the XRD study of HEA powders, the alloying sequence of the common elements in HEAs is $Al \rightarrow Cu \rightarrow Co \rightarrow Ni \rightarrow Fe \rightarrow Ti \rightarrow Cr \rightarrow Mo$, according to the XRD study of HEA powders with varying milling times (Chen *et al.* 2013; Fu *et al.* 2016). The type and concentration of elements such as Ti, Al, and V that stimulate the development of BCC structure, while Cu and Co promote the formation of FCC structure, are linked to the phase structure of HEAs after alloying (Ferrari *et al.* 2019).

Yang *et al.* made Al_{0.4}FeCrCoNi_{1.2}Ti_{0.3} (2016) and Al_{0.4}FeCrCo_{1.5}NiTi_{0.3} (2018) with nano-Al₂O₃ particles as reinforcement. The first was an FCC + BCC structure, whereas the second was primarily an FCC structure. The amount of Co present mostly determines the difference in microstructure; the lower the Co content, the less likely the FCC structure will form. Incompletely dissolved Al and Ti produce a BCC structure since they cannot be completely dissolved in the FCC structure. CuNi, CuNiCo, and CuNiCoZn were all FCC structures, while CuNiCoZnAlTi nano-HEA was BCC, according to Varalakshmi *et al.* (2010a), proving that Al and Ti enhanced the production of BCC structures. In addition to Ti, pure titanium (Ti) is a theoretically passive metal in most aqueous environments because it produces a protective TiO₂-based coating on its surface (Qiu *et al.* 2017b). In circumstances where Ti is incorporated into the surface film, it is possible that adding Ti to HEAs can improve corrosion resistance (Qiu *et al.* 2017b).

On the other hand, titanium is metallurgically active (in the melt) and forms several intermetallic compounds with the other elements in HEAs (Ren *et al.* 2014; Choudhuri *et al.* 2015). In the AlCoCrFeNiTi_{1.5} and CoCrCuFeNiTi systems, the presence of Ti causes the Fe₂Ti-type Laves phase to develop(Wang *et al.* 2007). As a result of the formation of such incorporating intermetallic compounds, the microstructure of many Ti-containing HEAs can become more heterogeneous, with implications for corrosion resistance.

The alloying behaviour and phase transformation are affected by the type and content of elements. Yeh *et al.* (2004) synthesized CuCoNiCrAl_xFe by increasing the Al concentration from 0 to 2.8 percent and changing the HEA structure from FCC to BCC. As illustrated in Figure 2.22, the influence of Al content on hardness and lattice constant was also presented (a). In addition, as shown in Figure 2.22, the microstructure of Ti_{0.5}CrFeCoNiAlxCu1_x HEA (Wang *et al.* 2009) and (FeCoNiCrMn)_{100x}Al_x HEA (He *et al.* 2014) shifted from FCC to BCC when the Al concentration increased (b). FCC is unstable due to the enormous radius of the Al atom, which increases the lattice distortion energy. BCC has a lower stacking density (68%) than FCC and HCP (74%) than FCC and HCP, making it easier to adapt to larger atoms.

Moreover, with regards to the effect of alloying elements, proper composition design has been proven to improve the characteristics of HEAs in prior research (Dong *et al.* 2014b; Cai *et al.* 2017; Rao *et al.* 2017). Lindner *et al.* (2017) discovered that adding Al to Al_xCoCrFeNiTi HEAs stabilized the high-temperature phase, and Butler & Weaver (2016) found that adding Al to Al_x(CoCrFeNi)100-x HEAs improved the oxidation behaviours. These discoveries are critical for material research and highlight novel aspects of material composition (Zhu *et al.* 2010). Al and the fourth period of transition metal elements have been the most commonly designed elements.



Figure 2.22 (a) CuCoNiCrAlxFe HEA, (b) (FeCoNiCrMn)100xAlx HEA (He *et al.* 2014). Effect of Al concentration on the structure of BCC and FCC in HEAs.

To add more, regarding Al, Because Al is a light metal, it can reduce the density of HEAs. Al has also been shown to improve the mechanical strength of HEAs (Qiu *et al.* 2017b), Al/Al alloys have a lower galvanic series (i.e., are less noble) than the other elements used to make HEAs, such as Fe, Ni, Cr, Co, and Ti. As a result, it's possible that when a solid solution containing more noble elements is exposed to aqueous environments, Al atoms are preferentially liberated, similar to dealloying (Qiu *et al.* 2017b). In depassivating conditions or conditions that encourage dissolution, the corrosion rate of HEAs containing Al may be expected to rise with increasing Al content.

Nonmetallic elements such as Si and C, on the other hand, play a crucial role in traditional alloys due to their strengthening effect. Due to the strengthening effect generated by the Si in HfMo_{0.5}NbTiV_{0.5}Si_x HEAs, Liu *et al.* (2017b) observed that Si-containing alloys showed appealing strength at elevated temperatures. The oxidation rates of FeCoCrNiSi_x HEAs increased with increasing temperature and decreasing Si content, according to Kai *et al.* (2018). Yang *et al.* (2017) used a gas atomization technique to make AlCoCrCuFeNiSi_x HEAs. The fast cooling rate of the gas atomization technique was found to reduce segregation, and the solid solution strengthening effect boosted hardness without diminishing crystallinity with the addition of Si. Additionally, Kumar *et al.* (2017a) and Zhang *et al.* (2013b) indicated that the Si element is preferred for forming the BCC structure. However, the design of AlCoCrFeNiSix has only been documented in a few investigations.

When it comes to one of the secondary phases forming elements, B, it is commonly added to HEAs to improve their hardness and wear resistance due to its capacity to induce the synthesis of borides (Hsu *et al.* 2004). The addition of B to Al_{0.5}CoCrCuFeNi increased its hardness (Vickers hardness with a 5 kg load) to HV 736 (compared to HV 232 for the B-free alloy) (Hsu *et al.* 2004), which is a significant improvement. This B-containing HEA's wear resistance was significantly higher than SUJ2 wear-resistant steel (Hsu *et al.* 2004). The effect of B additions or borides on HEA corrosion has not been thoroughly defined or investigated. Another feature that makes B more favourable is its atomic radius is substantially less than other elements, allowing for easier diffusion during solidification.

2.1.8 APPLICATIONS OF LWHEAS

HEAs can be utilized for a variety of purposes. HEAs can be employed as hydrogen storage materials, radiation-resistant materials, diffusion barriers for electronics, precision resistors, electromagnetic shielding materials, soft magnetic materials, thermoelectric materials, functional coatings, and anti-bacterial materials. Because of their excellent thermal stability, refractoriness, and low density with high strength, HEAs can be used in the aerospace industry. (Murty *et al.* 2019a; Qiu *et al.* 2015). As a result, HEAs are becoming a topic of tremendous academic interest in today's world, and they are attracting a lot of attention due to their novelty. HEAs and other high-entropy materials (e.g. high-entropy ceramics or even polymers) will most likely find uses in disciplines far beyond those listed above, thanks to their distinct design philosophy and distinctive characteristics. More scientists need to investigate this fascinating new virgin field.

Chapter 3

3.1 MATERIALS AND EXPERIMENTAL METHODS

3.1.1 INTRODUCTION

The current chapter delineates the research methods undertaken to develop and synthesise the desired lightweight, high entropy alloys. The methods include:

(a) Theoretical analyses, highlighting the common problems, selecting the powder materials, choosing the operating parameters and the experimental equipment.

(b) Experimental research is the optimisation of working parameters, milling of the powders, pre-characterisation (milled powders), sintering of powders to discs, and density determination of the sintered discs.

(c) Characterisation of sintered samples includes XRD, SEM, micro-hardness, high-temperature oxidation, corrosion, and wear tests.

(d) The analyses of results obtained above

Therefore, the experimental research route is illustrated below in Figure 3.1



Figure 3.1 Experimental research route

3.1.2 MATERIALS

3.1.2.1 Alloying powders

The three compositions of lightweight, high entropy alloys: $Al_{35}Ti_{35}Si_{19}Be_{10}B$, $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$, and $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ (all in wt.%), were prepared and developed from pure constituents (\geq 99% purity) *viz* Al, Ti, Si, and B. Each elemental powder had a starting particle size of 44 microns obtained from Alfa Aesar (Germany). In Beryllium's case, supplied by Sigma Aldrich (South Africa), the as-received flakes were milled down to obtain starting powder particle size (51 microns) in order to be in the same form as other received elemental powders.

The basic principle of developing LWHEAs is selecting principal alloying elements, which determines the alloy's density and are also utilised for the development and design of high-temperature applications. Therefore, the lightweight elements were rationally selected based on their relatively low density. The broad definition of lightweight materials typically utilises the density of titanium alloy as the limit. In this study, the elements included above have a density lower than titanium (4.51 g·cm⁻³). They include aluminium (2.70 g·cm⁻³), beryllium (1.85 g·cm⁻³), and the non-metallic elements such as silicon (2.33 g·cm⁻³) and boron (2.34 g·cm⁻³).

Moreover, the selection was also based on the individual element properties. Aluminium improves oxidation resistance and reduces density; silicon strongly influences the alloys' phase structure, increases strength and hardness, and, like aluminium, has excellent oxidation resistance. On the other hand, titanium is well known for its corrosion resistance, hence used for surgical applications and high-temperature applications. Beryllium is used as a structural component in the defence and aerospace industries. And boron refines the grains and also stabilises the microstructure at elevated temperatures. Table 3.1 shows the physical properties of the selected elements used.

Element	Density (g.cm ⁻³)	Melting Temperature (°C)	Atomic Radius (Å)	Pauling electronegativity	Crystal structure	VEC
Aluminium	2.70	660	1.432	1.61	FCC	3
Titanium	4.51	1670	1.462	1.54	HCP	4
Silicon	2.33	1414	1.153	1.90	A4 (cubic diamond)	4
Beryllium	1.85	1287	1.128	1.57	НСР	2
Boron	2.34	2077	0.820	2.04	A10(simple trigonal)	3

Table 3.1 The physical properties of the selected elements (Scerri & Sciences 2015)

3.1.3 SYNTHESIS OF ALLOYS

3.1.3.1 Mechanical Alloying (MA)

Mechanical alloying is a solid-state, non-equilibrium processing method that involves continuous cold welding, fracturing, and rewelding of powder particles to attain alloying at an atomic scale in a high-energy ball charge (Vaidya *et al.* 2019a). A high energy ball mill (Model: PULVERISETTE 6; Make: FRITSCH) shown in figure 3.2 (a), was used to mix and reduce the particle size of the elemental powders to produce three alloys of different compositions: Al₃₅Ti₃₅Si₁₉Be₁₀B, Al₃₅Ti₃₅Si₁₈Be₁₀B₂, and Al₃₅Ti₃₅Si₁₇Be₁₀B₃ (all the elements in weight percent) under dry milling conditions. This constituted of weighing the elemental powders, masses shown in Table 3.2, for blending and then poured into 250 ml hardened stainless-steel vial together with the 25 mm tempered stainless steel milling medium or balls to mix all the powders, at a speed of 350 rpm and a ball-to-powder ratio of 10:1 for total milling duration of

45 hours. The process control agent used in that powder mixture was 6wt.% stearic acid to avoid agglomeration of the powders which reduced the milling.

Element/PCA	Wt.%	Alloy 1 mass (g)	Alloy 2 mass (g)	Alloy 3 mass (g)
	(x=1,2,3)			
Aluminium	35	6.7660	6.7663	6.7666
Titanium	35	6.7660	6.7663	6.7666
Silicon	20-x	3.6729	3.4798	3.2866
Beryllium	10	1.9331	1.9332	1.9333
Boron	X	0.1933	0.3866	0.5800
Stearic acid	6	2.3941	2.3944	2.3947

 Table 3.2 The elemental powder measurements for blending

Post the addition of the powder and milling medium into the vial, argon gas was injected into the vial, to make it an oxygen-free atmosphere, the goal being to avoid powder contamination. Additionally, handling of the elemental powders and the pouring into the vial was executed in a glove box Easy Lab, MBRAUN with an argon atmosphere to also avoid powder contamination, as shown in figure 3.3. The powder samples were collected for further analyses after milling for 5h, 10h, 20h, 35h and 45h.





Figure 3.2 (a) The milling machine (CLOSED), (b) The milling machine (OPEN), (c) The clamped vial with nozzled lid, (d) The glovebox

3.1.3.2 Spark Plasma Sintering (SPS)

Since Mechanical Alloying (MA) is the first stage of powder metallurgy (PM), consolidation of powder is a subsequent stage, and it is generally accomplished by sintering equipment. The sintering method is usually selected to attain the best combination of density and nano-crystallinity. In this case, a Spark plasma sintering machine (KCE[®]FCT system model H-HP D25 Hybrid Furnace by FCT System GmbH) was used to synthesise LWHEA materials for this study.



Figure 3.3 (a) Spark Plasma Sintering machine components, (b) Furnace chamber

Figure 3.3 (a) shows the main components of the SPS machine, like the power control unit and furnace chamber (Figure 3.3 (b). With three power units supplying a direct current of 3000 amps and a potential of 5 V, the machine is capable of generating maximum process temperature up to 2200 °C. Also, the SPS equipment can attain a high heating rate as high as 600 °C /min. Moreover, a vacuum pump can provide a highly evacuated medium inside the furnace up to 0.002-0.003 Torr preventing contamination of power samples. In the low-pressure range (< 100 MPa), graphite dies and punches are appropriate for samples synthesis. The SPS machine is equipped with a punch displacement measurement feature, which permits users to monitor punch movement during the whole sintering process. The punch displacement can be used to study the densification behaviour of synthesised alloy samples.

Compaction of LWHEA samples using SPS is achieved by placing blended elemental/ alloy powder inside graphite die in between two punches at a required temperature and pressure. The chosen sintering temperature and pressure control the selection and design of graphite dies, punches, and spacers. Synthesis of LWHEAs through liquid phase sintering requires a temperature above the melting temperature of Al (> 660 °C). High thermal conductivity mainly at higher temperatures, abundance, and ease of machining makes graphite to be the most broadly used material in the SPS process as dies, punches, and spacers.

3.1.3.2.1 Synthesis of Bulk Samples of Al35Ti35Si(20-x)Be10Bx LWHEA composites

Spark plasma sintering was used to synthesise LWHEA samples, as shown in figure 3.4 (a). Al₃₅Ti₃₅Si_(20-x)Be₁₀B_x LWHEA were sintered at 1000 °C and at a constant pressure of 50 MPa with a heating rate of 100 °C /min and soaking time of 5 minutes. The powder samples were processed under vacuum (10^{-2} torr) during the experiment. A thermocouple (K type) was used to measure the temperature during the experiment, and a pyrometer which is fixed in the SPS apparatus at 3 mm from the top of the sample surface, was used to monitor temperature during the sintering process at 1000 °C. Graphite paper (65 mm x 55 mm) was put in between the die (20 mm dia., 48 mm height and 9mm thickness) and powder sample, and two 20 mm graphite papers put between the two punches (10 mm dia., 34 mm height and 5 mm thickness) and the powder sample to prevent direct contact of the powder with the die and punches and for easy removal of the sample after sintering. Figure. 3.4 (b) shows the die, two punches and a graphite paper that were used during this experiment.



Figure 3.4 (a) Schematic of Graphite die and punches dimensions, (b) Graphite die, two punches and graphite paper

3.1.4 METALLOGRAPHIC SAMPLE PREPARATION

3.1.4.1 Sectioning and Polishing

The size of the sintered discs was approximately 20 mm in diameter and 3 mm in height. Smaller samples were cut from the sintered discs post density measurements for various tests that were conducted later. The Struers Discoplan-TS cutting machine shown in figure 3.5 (a)was used to cut samples of various dimensions. The acrylic cold mounting resin was used to mount the cut samples for subsequent tests and analyses. Mounted samples were then polished with Struers Tegramin-25 automatic polishing machine shown in figure 3.5(b). The finished samples were cleaned up using alcohol (ethanol). The $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ LWHEA samples were etched using Kellers Etch which consists of 2 vol.% HF, 3 vol.% HCL, 5 vol.% HNO₃ and 190 vol.% H₂O



Figure 3.5 (a) Struers Discoplan-TS cutting machine, (b) Struers Tegramin-25 automatic polisher

3.1.5 CHARACTERISATION AND TESTING METHODS

3.1.5.1 Particle Size and Distribution Analyser

The particle size and distribution (PSD) of the as-received elemental powders (Al, Ti, Si, B and Be (after crushing it from flake to powder form)) was determined using Malvern

mastersizer 2000 particle size analyser shown in figure 3.6. The particle size analysis (PSA) measuring device features a dispersion of powder aggregates into subtle elements employing chemical, mechanical, and ultrasonic (Gee & Or 2002). Furthermore, it uses a sieve for the separation of individual particles. It uses diffraction methods to determine the particle size, which includes suspensions of solid particles, droplets of emulsion, and dry powder samples. Additionally, Malvern mastersizer 2000 uses the Fraunhofer model and the Mie theory principles for determining the size of powder particles of a given sample.



Figure 3.6 Malvern mastersizer 2000 particle size analyzer

3.1.5.2 X-Ray Diffraction (XRD)

X-ray diffraction is one of the few techniques widely utilised for determining the crystallographic structure, chemical composition and physical properties of materials on the atomic scale (Asensio Dominguez 2016). The Shimadzu XRD-700 X-Ray Diffractometer, shown in figure 3.7 (a), was used in this study for characterising the as-received powder samples. X-ray diffraction uses Bragg's law ($n\lambda$ = 2dsin θ) (Shimpi 2017). A beam of X-rays incident the sample, and the detector detects the reflected X-rays. The measurements typically taken for X-ray diffraction, phase identification and unit cell dimensions of powder particles and analysis of a sample were recorded on an X-ray diffractometer functioning with Cu ka radiation (1.5406 nm) over the 2 θ range from 10 to 100 degrees in the steps of 0.01 degree at

room temperature and scanning speed of 4 °/min at a voltage and current of 40 kV and 30 mA respectively.

However, the milled and sintered alloys were characterised using The PANalytical EMPYREAN X-ray Diffractometer shown in figure 3.7 (c) as the one used initially was no longer functioning well. For this equipment, the measurements that were taken for X-ray diffraction, phase identification and unit cell dimensions of powder particles and analysis of a sample were recorded on an X-ray diffractometer functioning with Cu k α radiation (λ =1.5406 nm) over the 2 θ range from 5 to 90 degrees in the steps of 0.02 degree at room temperature and scanning speed of 4 °/min at a voltage and current of 40 kV and 45 mA respectively.





Figure 3.7 (a)Shimadzu XRD-700 X-Ray Diffractometer (closed), (b) Interior of the XRD (open), (c) PANalytical EMPYREAN X-ray Diffractometer

3.1.5.3 Scanning Electron Microscope (SEM)

The morphology and microstructure of both the powder samples(as-received and blended) and sintered samples were evaluated using JOEL JSM-IT500 Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray (EDX) shown in figure 3.8(b). SEM uses electron beam scans that captures an image from the signal generated at each scan point. SEM gives information such as crystalline structure, chemical composition and surface topography. The favourable reasons for opting for the SEM is due to the ability to reach a higher magnification, broader information rather than just of the surface is attained. Shorter sample preparation time can also be achieved when using this type of equipment.

In SEM, the electrons are typically accelerated to high energies within 2 and 1000 keV. In most cases, the interactions between the high-energy electron beam and the atom within the specimen are relatively thin. The electrons may go via it not absorbed and result to form an image(Vernon-Parry 2000).



Figure 3.8 (a) Schematic of SEM and labellings, (b) JOEL JSM-IT500 SEM machine

3.1.5.4 Density Determination

Densities of sintered $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ LWHEA composite samples were measured using OHAUS Adventurer Density balance (shown in figure 3.9) which employs Archimedes principle. This method was conducted immediately after the sintering of samples. When applying this principle, density can be measured using equation 1:

$$\rho = \frac{x}{x - y} (\rho_0 - \rho_L) + \rho_L \tag{1}$$

where ρ is the density of the bulk sample; *x* is sample weight in the air; *y* is the weight of sample; ρ_0 is auxiliary liquid density (in this case it is distilled water); ρ_L is the density of air (0.0012 g·cm⁻³) and the water density at room temperature is 0.99804 g·cm⁻³. The theoretical density of Al₃₅Ti₃₅Si_(20-x)Be₁₀B_x LWHEAs composition is 3.24 g·cm⁻³ and was estimated by using the assumptions of a rule of the mixture and can be determined using equation 2, Where, *xi*, ρi , and *Ai* are the atomic ratio, density and atomic weight of the *ith* constituent element present in the given alloy composition. Equation 3 was used to determine the relative density/percentage density of the bulk alloys.

$$\rho_t = \frac{\sum x_i A_i}{\sum_{\rho_i}^{x_i}} \tag{2}$$

Percentage of densification =
$$\frac{\text{density of sinterd sample}}{\text{Theoretical density of powder}} \times 100$$
 (3)



Figure 3.9 OHAUS Adventurer Density Balance used for density measurement

3.1.5.5 Hardness Test

Vickers microhardness of sintered samples was measured by making an indent at a load of 1 kgf with a dwell time of 15s using a microhardness tester (INNOVATEST FALCON 500) using the standard ISO 6508 shown in figure 3.10. Well-prepared and polished surfaces of the Al₃₅Ti₃₅Si_(20-x)Be₁₀B_x LWHEA composite samples were prepared for microhardness testing. Measurements were made with ten indentations to find the average value of microhardness. Average microhardness readings were reported for each alloy sample along with the standard deviation of these readings.



Figure 3.10 Micro-hardness testing machine

3.1.5.6 Corrosion Test

The corrosion resistance of the sintered $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ alloys were evaluated by potentiodynamic polarization. Prior to electrochemical testing, each sintered disc from each alloy was sectioned into a square sample of 10 mmx10 mm x 3mm. and therefore were subjected to mounting, grinding (80, 220,320, 500, 800 and 1200 SiC grit papers) and polishing to 1 µm mirror-like surface finish on one face, then the samples were immediately prepared for electrochemical testing. In the laboratory, mirror surface finish is quite significant because the samples surfaces need to be flat, smooth and free of scratches. A smooth, clean and scratch-free surface reduces the number of corrosion initiation points on the composite surface, which aids in comprehension and improved characterisation behaviours of the sintered samples (Cobbinah & Matizamhuka 2019a).

Potentiodynamic experiments were conducted under the thermostatic condition of +/- 25°C (room temperature). The electrochemical cell used in this study was a 250 ml beaker and about 200 ml of a solution of 3.5 wt.% NaCl. The solution was left in the aerated condition. The electrochemical polarization experiments were accomplished with a conventional three-electrode cell, consisting of a working electrode (sintered LWHEA), a platinum counter electrode, and a saturated calomel electrode (SCE) as the reference electrode (shown in 3.11.b)



Figure 3.11 (a) Potentiodynamic experiment (b) A conventional three-electrode cell

The potential was controlled and the current was measured using a Digi-Ivy DY2300 series potentiostat with a computer-controlled electrochemical interface, permitting for monitoring of

the total current (I), potential (V), and time (t). All experiments were conducted at a scan rate of 0.0002 V/sec from the initial potential of -0.1 V versus the open circuit potential (OCP) and terminated when the current reached 1 mA. Before the experiment, the OCP was recorded for approximately 20 min to acquire a steady-state potential.

Characteristic electrochemical parameters, such as corrosion potential (Ecorr), corrosion current density (*i*corr), primary passive potential (Epp), passive current density (*i*crit), breakdown (Eb) or transpassive potential (Etrans), and repassivation potential (ERP) can be extracted from the evaluation of polarization curves. An average corrosion current density was found by dividing corrosion current I by the working area of the electrode. Eb or Etrans was determined by observing the potential at which a continuous increase of the anodic current initiated, indicating the sustained breakdown of the passive film. To determine duplicability, tests were repeated three times under each condition. Post the polarisation experiments, all the samples were thoroughly washed and then dried.

3.1.5.7 Wear Test

The spark plasma sintered $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ alloys tribological behaviour was analysed using reciprocating–sliding friction experiments on a ball-on-disc tribometer (Anton Paar, TRB3) under dry/lubricated conditions, as shown in Figure 3.12 (b). The tribometer functions with a steel counter-face ball that responds to the specimen using varying loads, as shown schematically in Figure 3.12 (a). The loads are applied vertically downward on the specimens with a carriage facilitated by a motor. The carriage uses a load sensor for feedback to maintain a constant applied load.

A steel ball (6mm in diameter) was used as a counter body of wear test. Testing parameters of the wear test were as follows: 150 rpm speed, 10 N normal force, and 4 mm diameter wear track. The test was carried out for 60 min total sliding time by having test segments of 10 min in a laboratory temperature of 26.22 °C under the atmosphere of 1018 and humidity of 28.58%. Weight loss and the average coefficient of friction as a function of sliding time will be reported for sintered samples.



Figure 3.12 (a) Schematic diagram of a Tribometer Setup, (b) Tribometer instrument

3.1.5.8 High-Temperature Oxidation Test

Discontinuous, isothermal oxidation test of the sintered $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ alloys was conducted at 700 °C for 400 hours and 900 °C for 200 hours under ambient laboratory air in a furnace (Nabertherm GmbH, P310), depicted in figure 3.13 (a-b). Tests were carried out in 50 hours cycles. Before the oxidation tests, the samples were ground to a 1200 grit surface finish using SiC paper, cleaned with acetone, and placed in individual open-topped alumina crucibles as shown in figure 3.13 (c). After each cycle, the samples were removed periodically to record their relative mass changes. The samples were measured on a AND HR-250A microbalance with a sensitivity of $1x10^{-6}$ g. Data collection included only mass change measurements.



Figure 3.13 (a) Closed Furnace, (b) Open Furnace and (C) Alumina crucibles

Chapter 4

4.1 RESULTS AND DISCUSSIONS

4.1.1 DESIGN OF LIGHTWEIGHT HIGH ENTROPY ALLOYS

4.1.1.1 Compositional Design

The initial stage of the design process is utilised to guarantee that the alloy system is capable of forming HEAs. It is accomplished by specifying thermodynamic and electronic parameters for determining the formability of solid solution: mixing enthalpy (ΔH_{mix}), mixing entropy(ΔS_{mix}), atomic size mismatch (δ), ratio (Ω), Pauling electronegativity difference (ΔX), and valence electron concentration (*VEC*). Furthermore, because these characteristics are interrelated, both simple and non-complex parameters can be used to predict alloy stability in HEAs. Table 4.2 summarises the empirical parameters that are defined by their respective equations used for their calculations. The mixing enthalpy ΔH_{AB}^{mix} of different atomic pairs obtained by Miedema's model (Takeuchi & Inoue 2005) is summarised in Table 4.1. The negative ΔH_{AB}^{mix} indicates that the A atom likes the B atoms and prefers to mix with B to form solid solutions or even form intermetallic compounds.

The LWHEAs having Al, Ti, Si, Be, and B as principal elements were selected and the quantity of Al and Ti was kept higher range (35 wt.%) to reduce the density of the systems. Because the Al-Ti and Ti-B pairs have substantial negative mixing enthalpies of $-30 \text{ kJ} \cdot \text{mol}^{-1}$ and $-58 \text{ kJ} \cdot \text{mol}^{-1}$, respectively, and the Si-Ti pair has the biggest negative mixing enthalpy of $-66 \text{ kJ} \cdot \text{mol}^{-1}$, therefore, due to this pair Si-Ti the Si and Ti compounds are expected to develop in equilibrium with the multi-element matrix phase, which has a larger mixing entropy to lower its free energy. Ti seems to have a strong bond with all the selected elements and this might result in groups of laves phases due to atomic size. Previous studies (Zhou *et al.* 2007a; Zhang *et al.* 2009; Zhang *et al.* 2008) have shown that, in addition to solid-solution phases, intermetallic compounds and amorphous phases can develop in multi-component HEAs, but simple solid-solution phases are the most likely to form due to the promising features of multicomponent HEAs.

	Al	Ti	Si	Be	В
Al	-	-30	-19	0	0
Ti	-30	-	-66	-30	-58
Si	-19	-66	-	-15	-14
Be	0	-30	-15	-	0
В	0	-58	-14	0	-

Table 4.1 The values of ΔH_{AB}^{mix} (kJ· mol⁻¹) calculated by Miedema's model for the present atomic pairs(Takeuchi & Inoue 2005)

4.1.1.2 Application of Thermodynamic Prediction Rules

The parameters are calculated for this research study, and their values are listed in Table 4.3. Gibbs free energy for HEA systems has been considered a significant parameter in predicting the solid-solution formation rule in multi-component alloys. However, it is difficult to compute ΔG properly for HEA systems at a given composition and temperature. To calculate the free energy of multi-component HEAs easier, a normal solid solution model was proposed. As a result, the enthalpy of mixing for a five-element Al₃₅Ti₃₅Si₁₉Be₁₀B, Al₃₅Ti₃₅Si₁₈Be₁₀B₂ and Al₃₅Ti₃₅Si₁₇Be₁₀B₃ alloys can be calculated. Thus, ΔH_{mix} obtained for the three alloys was outside the range ($-22 \leq \Delta H_{mix} \leq 7 \text{ kJ} \cdot \text{mol}^{-1}$) defined for the formation of HEA. Negative ΔH_{mix} encourages different elements to combine to form intermetallic compounds. Furthermore, the stronger the binding force between elements, the more negative ΔH_{mix} , the larger absolute value of ΔH_{mix} will make solid-solution difficult to form. Enthalpy mixing promotes the development of solid solutions.

When it comes to mixing entropy ΔS_{mix} , the obtained values for the three alloys were found to be within the range ($11 \le \Delta S_{mix} \le 19.5 \text{ J} \cdot \text{K} \cdot \text{mol}^{-1}$) defined for the formation of an HEA. For the favourable formation of a HEA, the value of ΔS_{mix} is always positive. The high ΔS_{mix} can effectively increase the degree of confusion in the alloy system while lowering the ΔT_{mix} , causing the different elements to randomly distribute in the crystal lattice and lowering the tendency of ordering and segregation of alloy elements. As a result of the high ΔS_{mix} , random solid-solution forms are easier to form and more stable than intermetallic complexes or other ordered phases during alloy solidification. Among all of the criteria described above, the atomic size difference (δ) is critical in phase formation. And for this study, the (δ) values for the three alloys were found to be very high, which is $\geq 6.6\%$ indicating that they were beyond the limit ($0 \leq \delta \leq 6.5$) defined for the formation of solid solution in HEA. A significant value of δ indicates slow element diffusion and phase development, resulting in the separation of nanoparticles or amorphous phases and the breakdown of solid solution stability.

For various HEAs, a parameter (Ω) is defined to predict solid-solution formation. The values of the ratio obtained from the calculations were all < 1. If $\Omega > 1$, $T\Delta S_{mix}$ will contribute more to solid-solution formation than ΔH_{mix} , and multi-component HEAs will be mostly made up of solid solutions. However, for this study, the results of the alloys' Ω values imply that they cannot form solid solutions. In the meantime, the (ΔX) was found to be the most predictable parameter across all of the HEAs. The ΔX values of the three alloys were found to be ≤ 0.175 . According to this criterion $\Delta X \geq 0.175$, the intermetallic compounds are found to be stabilised, however, that seems not to be the case with the three alloys of this study which means that the stability of solid solutions is favoured. The last parameter to be calculated was the *VEC*. The three obtained VEC's were found to be ≤ 6.87 , which indicates the formation of a BCC structure.

Table 4.2	nodynamic parameters	s and their	equations	used for	determining	stability in
LWHEAs						

Thermodynamic	Equation	Reference				
Parameter						
Mixing Enthalpy (ΔH_{mix})	$\Delta H_{mix} = \sum_{i=1,i\neq j}^{n} \mathcal{Q}_{ij} c_i c_j$	(Shao <i>et al.</i> 2018; Guo <i>et al.</i> 2013)				
	$arOmega_{ij}=-4\Delta H_{AB}^{mix}$					
Mixing Entropy (ΔS_{mix})	$\Delta S_{\rm mix} = -R \sum_{i=1}^n c_i \ln c_i$	(Shao <i>et al.</i> 2018; Guo <i>et al.</i> 2013)				
Atomic size mismatch (δ)	$\delta = \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} ,$	(Shao <i>et al.</i> 2018; Yang <i>et al.</i> 2012b; Guo <i>et al.</i> 2013)				
	$\overline{r} = \sum_{i=1}^{n} c_i r_i$					
Ratio (Ω)	$\Omega = rac{T_m \Delta S_{ m mix}}{ \Delta H_{ m mix} }$,	(Shao <i>et al.</i> 2018; Yang <i>et al.</i> 2012b)				
	$T_m = \sum_{i=1}^n C_i (T_m)_i$					
Paulingelectronegativitydifference (ΔX)	$\Delta \chi = \sqrt{\sum_{i=1}^{n} c_i (\chi_i - \bar{\chi})^2} ,$	(Shao <i>et al.</i> 2018; Dong <i>et al.</i> 2014a; Maulik <i>et al.</i> 2018)				
	$\bar{\chi} = \sum_{i=1}^{n} c_i \chi_i$					
Valenceelectronconcentration (VEC)	$\text{VEC} = \sum_{i=1}^{n} c_i(\text{VEC}_i)$	(Shao <i>et al.</i> 2018; Kang <i>et al.</i> 2018a)				
Where, c_i = atomic ratio of the <i>ith</i> element, c_j = atomic ratio of the <i>jth</i> element, ΔH_{mix}						
=enthalpy of mixing between the <i>ith</i> and <i>jth</i> elements, $R = 8.314$ J/K mol (gas constant),						
r_i = atomic radius of <i>ith</i> elem	ent, r⁻=average atomic radius	s,) T _m = hypothetical melting				
temperature of the alloy						

Alloy	ΔH_{mix} ,	ΔS_{mix} ,	⊿, %	<i>T_m</i> , K	Ω	ΔX	VEC
	kJ∙mol ⁻¹	J∙mol ⁻					
		¹ ·K ⁻¹					
Al35Ti35Si19Be10B	-43.57	11.03	20.79	1506.78	0.379	0.138	3.44
Al35Ti35Si18Be10B2	-43.23	11.24	21.10	1513.41	0.393	0.141	3.43
Al35Ti35Si17Be10B3	-42.87	11.40	21.42	1520.04	0.404	0.145	3.42

Table 4.3 Calculated values for ΔH_{mix} , ΔS_{mix} , δ , T_m , Ω , ΔX , and VEC of alloys in this work

4.1.2 MATERIALS CHARACTERISATION

4.1.2.1 As- Received Powders

The chemical composition of the bulk alloy powders utilised in the experiment is shown in Table 4.4. The scanning electron micrographs (SEM), particle size distribution (PSD), and XRD spectrum of the as-received aluminium powder are shown in Figures 4.1,4.2, and 4.3, respectively, whereas the SEM, PSD, and XRD spectrum of the titanium powder are shown in Figures 4.4, 4.5, and 4.6. The SEM, PSD, and XRD of the as-received silicon powder are shown in Figures 4.7, 4.8, and 4.9, respectively and those shown in Figures 4.10,4.11 and 4.12 are of the as-received beryllium flake. Whereas figures 4.13,4.14, and 4.15 are the SEM, PSD and XRD of the as-received boron powder. The as-received powders, namely Al, Ti, Si, and B, as well as the as-received, Be flake, were observed under the SEM shown in Figures 4.1, 4.4, 4.7,4.10 and 4.13. Based on these SEM figures, it can be seen that the powders were agglomerated and free from contamination.

The morphology of the Al powder particles shows a semi-spherical shape with a relatively broad particle size distribution and an average particle size of 44 μ m as quoted by the supplier; however, figure 4.3 shows a measured particle size distribution of 13.216 μ m at D50. The XRD peaks identified the indexing of a majority of an FCC phase which confirms the aluminium structure and the level of purity of the powder, as depicted in figure 4.2. The SEM for the titanium revealed the morphology of irregularly shaped particles of different sizes. The average particle size distribution depicted in figure 4.6 is 39.312 μ m at D50; however, it was supplied

as 44 μ m. The XRD pattern of the titanium identified mostly a BCC deduced from indexes of the peaks. Since there was only titanium identified it also denotes the purity of the powder.

The as-received silicon powder showed the morphology of a mixture of coarse and fine irregular shaped particles in SEM. The XRD pattern revealed the indexing of a simple cubic which denotes silicon at its highest purity. The average particle size distribution of the as-received powder was found to be $5.327 \,\mu\text{m}$ at D50 which is finer than what was quoted by the manufacturer. Beryllium, was purchased as flakes and was milled down to a particle size close to the other starting powders, for 54 hours, in this case, figure 4.12 shows the particle size distribution of 52.801 μm at D50. The SEM micrograph of beryllium shows coarse irregular flakes. Lastly, the SEM, XRD and PSD of the as-received boron powder exhibit non-uniform irregular shaped particles, whereas the XRD pattern indicates the pure boron powder being not fully crystalline based on the indexes. And the particle size distribution of boron was found to be 16.832 μm at D50, respectively.



Figure 4.1 Scanning electron micrograph showing the morphology of the as-received aluminium



Figure 4.2 XRD pattern of the as-received aluminium powder



Figure 4.3 Particle size distribution of the as-received aluminium powder showing an average particle size of $13.216 \,\mu$ m.


Figure 4.4 Scanning electron micrograph showing the morphology of the as-received titanium



Figure 4.5 The XRD pattern of the as-received titanium powder



Figure 4.6 Particle size distribution of the as-received titanium powder showing an average particle size of $39.312 \,\mu$ m.



Figure 4.7 Scanning electron micrograph showing the morphology of the as-received silicon



Figure 4.8 The XRD pattern of the as-received silicon powder



Figure 4.9 Particle size distribution of the as-received silicon powder showing an average particle size of $5.327 \,\mu\text{m}$.



Figure 4.10 Scanning electron micrograph showing the morphology of the as-received beryllium flakes



Figure 4.11 The XRD pattern of the as-received beryllium flakes



Figure 4.12 Particle size distribution of the as-received beryllium flakes showing an average particle size of $52.801 \ \mu m$.



Figure 4.13 Scanning electron micrograph showing the morphology of the as-received boron powder



Figure 4.14 The XRD pattern of the as-received boron powder



Figure 4.15 Particle size distribution of the as-received boron powder showing an average particle size of $16.832 \,\mu$ m.

4.1.2.2 Phase Formations and Structures of Milled Alloys

4.1.2.2.1 Alloy 1(Al₃₅Ti₃₅Si₁₉Be₁₀B)

The results of this alloy's X-ray diffraction and corresponding scanning electron microscope micrographs and the EDS analysis conducted at 45 hours of milling time are shown in Figures 4.16,4.17 and 4.18, respectively. Figure 4.16 shows the XRD pattern of mechanically alloyed powders at different milling times. It can be observed from the initial XRD pattern (5 h) that the peaks are attributed to the elements incorporated in the alloy. The diffraction peak of the Titanium and Boron elements was quite pronounced. These elemental peaks reveal that the shorter milling time was insufficient for completing the alloying process in the LWHEA. After milling for 10 h, all the elemental peaks are still observed, and now an intermetallic compound, Titanium diboride (TiB₂), which is a BCC, is observed at this point. However, the elemental peak that seemed to dominate was that of titanium which showed appearance in most diffraction peaks.

As the milling progressed to 20 h, the elemental peaks and the TiB_2 intermetallic were still present. However, only the elemental peaks were starting to fade away, but the titanium peak had the strongest intensity in this pattern; this appearance of a BCC solid solution phase is attributed to the high entropy of mixing (Jhong *et al.* 2020; Raza *et al.* 2019). No new intermetallic compounds seemed to have formed after 35 h of milling. However, this pattern shows that the elements have dissolved, and the sign of refinement of particles has taken place. The 45-hour XRD pattern indicates that microstructural refinement has occurred.

The majority of a phase observed in most peaks is BCC, followed by an FCC phase. And also, the TiB_2 intermetallic compound is still present. However, it was the least observed pattern. Therefore, the majority of the phase structure formed for this alloy after 45h of milling is BCC. The XRD patterns of this alloy show the phase makeup that is significantly more familiar than previously published HEAs that usually contain only FCC and/or BCC phases. Because the intensities of the diffraction peaks of intermetallic phases are less substantial than those of solid solution phases, the volume fractions of the FCC and/or BCC phases appear to predominate.



Figure 4.16 XRD patterns of ball-milled samples at 5, 10, 20, 35, and 45 hours of Al₃₅Ti₃₅Si₁₉Be₁₀B LWHEA



Figure 4.17 SEM micrographs of ball-milled samples at 5, 10, 20, 35, and 45 hours of $Al_{35}Ti_{35}Si_{19}Be_{10}B LWHEA$

The SEM micrographs of the powders mechanically alloyed for 5,10,20,35, and 45 hours at 100X magnification are shown in figure 4.17. As milling time increased from 5 to 45 hours, the particle size became less coarse but was still in the micron meter range. Nonetheless, higher agglomeration and morphology change of the Al₃₅Ti₃₅Si₁₉Be₁₀B alloy powder was noticed after 35 hours of milling. The blow marks from compression gas during SEM sample preparation for non-conductive samples are evidence of how fine the powder has become. As the milling time increased, the resultant powder showed a flat spongy and little agglomeration for 35 and 45 hours. The change in particle morphology is related to a rise in milling energy, which produces an increase in the contact area between the grains and an increase in the amount of coalesced particles and a decrease in particle deformation.

After 45 hours of milling, it is observed that increased milling time generates greater particle fracture, resulting in increased deformation and fragmentation by the steel balls. Because of the increased surface area, the flat and spongy structure obtained due to extended milling time will be difficult to compact. As a result, a higher compaction pressure will be necessary to avoid high porosity and attain high density for as-sintered alloys. Figure 4.18 shows the compositions of the constituents, as measured by the energy dispersive spectroscopy (EDS) analysis. Be and B are not included in the analyses due to inadequate EDS peak intensity. However, the presence of oxygen is identified, which might result from sample exposure to the air during preparation. The Al peak intensity seems to be quite pronounced after 45 hours of milling.



Figure 4.18 EDS analysis of Al₃₅Ti₃₅Si₁₉Be₁₀B LWHEA after a total of 45 hours of milling

$4.1.2.2.2 \text{ Alloy } 2 (Al_{35}Ti_{35}Si_{18}Be_{10}B_2)$

The XRD patterns of the equiatomic Al₃₅Ti₃₅Si₁₈Be₁₀B₂ LWHEA powders with different milling times are shown in Figure 4.19. For 5h milling, all the elemental peaks are identified, and intermetallic phase diffraction peaks in the initial blend. The intermetallic compound identified here is Titanium Silicide (Ti₄Si₈). The diffraction peak of titanium together with Ti₄Si₈ is quite pronounced compared to the other peaks in the pattern. The peak intensities of Beryllium decline more quickly at the start of ball milling. Another intermetallic phase, TiB₂, was observed after 10h of milling. However, the Ti₄Si₈ intermetallic compound seems to disappear at 10 h of milling, this might be attributed to extended milling hours. Subsequently, all the other elemental peaks are present, and aluminium is included this time, but with no sign of boron, meaning it has completely dissolved. Al-Ti peak intensity is observed to be quite pronounced than other peaks. As milling time progressed to 20 h, only three elements were still present: silicon, aluminium and beryllium alongside the TiB₂ intermetallic phase.



Figure 4.19 XRD patterns of ball-milled samples at 5, 10, 20, 35, and 45 hours of Al₃₅Ti₃₅Si₁₈Be₁₀B₂ LWHEA

In this pattern, the intensity diffraction of aluminium is stronger than in other peaks. After 35 h of milling, fineness in grains is observed. And also, the BCC phase seems to be predominant in this pattern. To obtain alloy powders with homogeneous composition, the milling time is prolonged to 45 h. The equiatomic Al₃₅Ti₃₅Si₁₈Be₁₀B₂ LWHEA powders after 45 h of milling show still show the BCC phase to be quite predominant in this pattern. Traces of an FCC phase were also observed in the 45 h milling pattern and reduced grain size. The FCC peak seems to be quite pronounced in this pattern compared to other peaks. The three factors that cause the decrement in intensity and broadening of the peak during the milling process are refined crystal size, high lattice strain, and decreased crystallinity caused by the MA process (Yeh *et al.* 2007a; Suryanarayana *et al.* 2001). Crystal refinement, lattice distortion, and solid solution cause the diffraction peak's disappearance (Zhang *et al.* 2010). Therefore, the majority phase structure observed for this alloy is still BCC after 45h milling.

Scanning Electron Microscopy (SEM) of Al₃₅Ti₃₅Si₁₈Be₁₀B₂ LWHEA powders was performed to compare the morphology, agglomeration and particle size at different milling times. The SEM micrographs of the 5, 10, 20, 35 and 45 hours milled Al₃₅Ti₃₅Si₁₈Be₁₀B₂ LWHEA at 350X magnification are shown in Figure 4.20. Based on these micrographs, at 5 h of milling, Be and Ti elemental powder particles are observed, which shows that the time for blending was not enough. Agglomeration and the sponginess appearance of the powder are observed after 20 h of milling, which shows the reduction of powder particles upon milling. More agglomeration was observed as the particle size was reduced to the nano-scale. After 45 hours of milling, fine nano-sized powder particles are achieved. And particle deformation and fragmentation are observed. The existence of nano-scaled crystallite indicates that the ball-milled micro-scaled alloy particles observed in SEM micrographs are agglomerations of nano-sized grains. On the other hand, the EDS analysis shown in Figure 4.21 only reveals the intensities of Al, Ti and oxygen. Still, no traces of other elements like Si, Be and B were picked up.



Figure 4.20 SEM micrographs of ball-milled samples at 5, 10, 20, 35, and 45 hours of $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$ LWHEA



Figure 4.21 EDS analysis of Al₃₅Ti₃₅Si₁₈Be₁₀B₂ LWHEA after a total of 45 hours of milling

4.1.2.2.3 Alloy 3 (Al₃₅Ti₃₅Si₁₇Be₁₀B₃)

The X-Ray Diffraction pattern of $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ LWHEA powder samples that were sequentially collected after the predecided interval is shown in Figure 4.22. It can be observed that alloy formation begins after 5 h of milling. In this pattern, all the elemental peaks except for boron only appear for this diffraction pattern. And the aluminium peaks seem to dominate. And the Al-Ti peak intensity was observed to be stronger than the others. As the milling time progresses to 10 h, the same diffraction pattern is observed; however, at this time, the intensity of the peaks is reduced, and there is a trace of an ordered phase, TiB₂, which is BCC.

Nonetheless, the peak intensities of most elemental phases seem to have reduced, indicating a reduction in grain size. As 35 h of milling was reached, the diffraction peaks of only three principal elements remained visible, but peak density and intensity decreased. The peak intensities gradually decreased and broadened with prolonged milling, indicating a decrease in particle size. The diffraction peaks of titanium partially disappeared completely, which could be attributed to the mixing enthalpies between Ti and other elements. Finally, 45 h of milling was attained with a sign of an intermetallic phase, TiB_2 , for this alloy. The dual phases (BCC + FCC) diffraction peaks appear in most peaks. A dual-phase is expected to give enhanced

mechanical properties in an alloy. The BCC phase was observed in most peaks, making it the dominant phase, still in this alloy after 45h milling.



Figure 4.22 XRD patterns of ball-milled samples at 5, 10, 20, 35, and 45 hours of $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ LWHEA



Figure 4.23 SEM micrographs of ball-milled samples at 5, 10, 20, 35, and 45 hours of $Al_{35}Ti_{35}Si_{17}Be_{10}B_3LWHEA$

Even though the powders were high-energy milled for 45 h, no diffraction peak of a new phase was observed. Figure 4.24 shows the compositions of the constituents, as measured by EDS analysis. Be and B are not included in the analyses due to inadequate EDS peak intensity. However, the presence of oxygen is identified, which might result from sample exposure to the air during preparation. The EDS analysis presented for this alloy matches the identified XRD phases.



Figure 4.24 EDS analysis of Al₃₅Ti₃₅Si₁₈Be₁₀B₂ LWHEA after a total of 45 hours of milling

4.1.3 SPARK PLASMA SINTERING

4.1.3.1 Powder consolidation of $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}Bx$ (x=1,2,3 wt.%) alloys

To investigate the effect of sintering temperature on phase evolution, spark plasma sintering of composite powders $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}Bx$ (x=1,2,3 wt.%) alloys was carried out at the temperature of 1000 °C. Typical SPS-fabricated discs with their appropriate diameters are illustrated in Figure 4.25. The discs were almost irregularly shaped. This might have been attributed to the melting of Al in all the sintered alloyed samples. During the fabrication of the alloys, as the SPS temperature approached the melting point of Al, punch displacement fluctuation was detected, resulting in various densification phases. Figure 4.26 shows the heating rate and punch displacement curves as a function of processing time at a sintering temperature of 1000 °C. These curves are categorised into stages to examine the alloys'

densification reaction effectively. The primary stages (I) and (II) are more concerned with powder particle rearrangement and contacting particle coarsening with distinctive neck growth inside the sintering die. Intermediate shrinkage and pore collapsing at grain boundaries occur during stages (III) and (IV). In practice, this can be explained as follows: When the temperature falls below 660 degrees Celsius, the punches begin to compress (densify). After that, as Al melts, punches retrace (expand) due to the low temperature. Finally, solid-state diffusion and solidification occur with no further changes in punch distribution. As observed in Figure 4.26, alloys 2 and 3 exhibited higher punch displacement than alloy 3, which showed lower punch displacement and experienced a more extended stage II. To add more, B additions seem to limit punch displacement, attributed to the fact that B retards grain growth.



Figure 4.25 Typical spark plasma sintered disc shapes of Al₃₅Ti₃₅Si_(20-x)Be₁₀Bx (x=1,2,3 wt.%) alloys



Figure 4.26 Temperature and punch displacement as a function of processing time during spark plasma sintering of composite $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}Bx$ (x=1,2,3 wt.%) alloys.

4.1.3.2 Characterisation of sintered Al₃₅Ti₃₅Si_(20-x)Be₁₀Bx (x=1,2,3 wt.%) alloys

4.1.3.2.1 Alloy 1(Al35Ti35Si19Be10B)

The X-ray diffraction pattern of spark plasma sintered Al₃₅Ti₃₅Si₁₉Be₁₀B alloy at 1000 °C is presented in Figure 4.27. The diffraction pattern of the bulk Al₃₅Ti₃₅Si₁₉Be₁₀B alloy is entirely different from the patterns observed in the milled bulk. The unanticipated phenomena could be linked to the crucial conditions of SPS's non-equilibrium quick sintering process. The SPS's high pulsed electric current could potentially cause phase evolution to be unclear. The predominant peak shows a combination of the FCC phase and face centred ordered phase, Titanium Silicide (Ti₄Si₈), which appeared to be present in most peaks. The ordered phase diffraction peak was also the second-highest peak in the diffraction pattern. The developed compound was made possible by the high entropy of binary component mixing (Ti, Si). The compound's outstanding features include increased strength, melting point, and low density. These characteristics, along with the density and superior oxidation resistance, make it a viable aerospace engineering material (Kanyane *et al.* 2019). The diffraction peaks observed show an equal amount of FCC and BCC phases present in the pattern. However, the ordered phase, Ti_4Si_8 , dominated this pattern for this sintered alloy.

SEM micrographs of Al₃₅Ti₃₅Si₁₉Be₁₀B LWHEA sintered at 1000 °C taken at different magnifications are presented in Figure 4.28. The surface morphology of the sample indicates no significant presence of pores or cracks with no signs of stress initiation. However, this sample exhibited a few cavities, which may be due to Al's low melting point (660 °C) and high-pressure sintering conditions, which led to the forcing out of some proportion of Al from the alloy system. The microstructure is divided into four phases: light grey, dark grey, and dark and dark dots on the microscope. The dark shaded area represents Si. The light grey irregular patches dominate the microstructure, implying that these phases make up a more significant volume fraction of the alloy's composition, indicating that the phase is quite hard. Furthermore, some white dots are observed as Au contamination traced by the EDS shown in Figure 4.29 (b).



Figure 4.27 XRD pattern of sintered Al₃₅Ti₃₅Si₁₉Be₁₀B LWHEA



Figure 4.28 SEM micrographs showing the microstructure of Al₃₅Ti₃₅Si₁₉Be₁₀B LWHEA. a) Higher magnification at X800 and b) Lower magnification at X500.



Figure 4.29 SEM spot analysis results of sintered Al₃₅Ti₃₅Si₁₉Be₁₀B LWHEA sample: (**a**) SEM image showing the locations for the EDS spot analysis; (**b**) EDS spectrum for Spot 001; (**c**) EDS of Spot 002; (**d**) EDS of Spot 003, and (**e**) EDS of Spot 004.

As illustrated in Figure 4.28, a spot analysis was conducted on these features and phases to obtain some typical morphological features and phases' composition information. In Figure 4.29 (a), four representative locations for the spot analysis are shown as Spot 001, Spot 002, Spot 003 and Spot 004. Figure 4.29 (b)-(d) depicts the qualitative results obtained at each site. Table 4.4 shows the relative mass percentage composition details for each element from the four spots. The diffraction peaks from three key elements are depicted in the spectra in these four sub-figures. One is Ti, and another is Al; still, another is Si. At spot 001, the highest peak of Si is observed because it is one of the major elements. The Ti peak is the second highest one. The Al signal follows them, resulting in the third-highest peak. The Au peak contaminants from the surface coating of the sample before SEM analysis were observed. This indicates that the sample is highly oxidised, which might also impact the mechanical properties of the alloy. At spot 002, the O element shows the highest peak, indicating that the dark shaded region is due to the rapid formation of the oxide layer on the Al surface.

The presence of O is a common issue faced when working with Al due to the high affinity of Al towards O. The C element was observed to have the second-highest peak. This C contamination may be due to various reasons, viz., the mounting resin, carbon tape or even improper sample handling. At Spot 003, Si appears as one of the major elements, having a pronounced peak, followed by Ti, the second-highest peak. The presence of C and O residues is still observed. At spot 004, Si'speak still appears to be strong. This indicates that the intense electron discharge aggregates represent the developed alloy's microstructures. The carbon signal comes from Spot 002 and 003, revealing the carbon residues. It is believed that the qualitative and quantitative elemental results from EDS spot analysis at the 004 location also provide information that the oxidation state of the coating should be prevented. The values of oxygen and carbon usually observed through EDS can sometimes be misleading due to the limitations in the technique when it comes to identifying elements of lower atomic numbers. Therefore, the phases observed here are Ti₂O₃ and Ti₄Si₈. The primary phase is the Titanium silicide (Ti₄Si₈), an intermetallic compound.

Element	Mass %					
	Spot 1	Spot 2	Spot 3	Spot 4	Average	
С	9.50	23.13	14.44	9.28	14.09	
0	12.86	39.70	9.69	9.10	17.84	
F	1.69	0	0	0	0.42	
Al	6.45	4.46	14.02	8.42	8.34	
Si	17.68	9.37	21.03	28.15	19.06	
Ti	41.67	23.33	40.82	45.05	37.72	
Au	10.16	0	0	0	2.54	
Phase	(Ti ₄ ,Si ₈),	(Ti ₂ ,O ₃)	(Ti4,Si8),	(Ti ₄ ,Si ₈),		
	rich	rich	rich	rich		

Table 4.4 Quantitative results of elemental composition from spot analysis of sinteredAl35Ti35Si19Be10B LWHEA sample.

4.1.3.2.2 Alloy 2 (Al₃₅Ti₃₅Si₁₈Be₁₀B₂)

Figure 4.30 shows a diffraction pattern of a sintered bulk of Al₃₅Ti₃₅Si₁₈Be₁₀B₂ LWHEA, which exhibits a combination of disordered phases (BCC and FCC) and an ordered phase, titanium silicide (Ti₁₆Si₃₂), which is consistent with the EDS analysis. Both BCC and FCC phases appeared in equal amounts in the diffraction peaks. However, face-centred Ti₁₆Si₃₂ dominated just like it was observed in alloy Al₃₅Ti₃₅Si₁₉Be₁₀B. A dual-phase appeared with an intermetallic phase in one of the diffraction peaks. The intensities of all the peaks were observed not to be high. The presence of minor phases means that Al, Si, and Ti have surplus amounts that are not dissolved in the matrix phase and are instead segregated as silicide compounds.

It should be noted that this alloy's phase number is significantly lower than the projected maximum phase number of the 6 Gibbs rule of phases. The high-entropy effect is to blame for this. This facilitates the formation of simple solid solutions.

SEM micrographs of Al₃₅Ti₃₅Si₁₈Be₁₀B₂ LWHEA, also sintered at 1000 °C taken at different magnifications, are presented in Figure 4.31. The sample's surface morphology shows no substantial presence of cracks and no indicators of stress start, but minor cavities are observed, and black dots indicate them. This is still due to forcing some proportion of Al from the alloy system. The microstructure of this alloy is quite different from that of Al₃₅Ti₃₅Si₁₉Be₁₀B LWHEA, which is still divided into three separate phases, which are represented on the microscope as light grey dark grey and dark dots. However, a needle-like structure is also observed in an irregular grey matrix. Furthermore, some white dots are observed as Au contamination traced by the EDS shown in Figure 4.32 (a)- (d).



Figure 4.30 XRD pattern of sintered Al₃₅Ti₃₅Si₁₈Be₁₀B₂ LWHEA



Figure 4.31 SEM micrographs showing the microstructure of Al₃₅Ti₃₅Si₁₈Be₁₀B₂ LWHEA. a) Higher magnification at X800 and b) Lower magnification at X500.

Figure 4.32 depicts the EDS spot analysis conducted on the sample $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$ LWHEA. In Figure 4.32 (a), three representative locations for the spot analysis are shown: Spot 001, Spot 002, and Spot 003, whereas Figures 4.32 (b)-(d) depict the qualitative results obtained at each of the three sites. The relative mass % composition details for each element from the three spots are shown in Table 4.5. These three sub-figures depict the diffraction peaks of the three primary constituents: the main elements viz., Ti, Al and Si. At spot 001, the highest peak is Si, followed by the second highest peak of O and the Ti peak being the third highest.

Along with the C residues, Au impurities were found in this sample. The O element has the largest peak at spot 002, representing the dark shaded region caused by the rapid growth of the oxide layer on the Al surface, as shown in $Al_{35}Ti_{35}Si_{19}Be_{10}B$ LWHEA. The second-highest peak belongs to the Si element, which is still followed by the Ti element. Si emerges as one of the significant elements at spot 003, with a prominent peak. Ti comes in second with the second-highest peak. Only C residues were found, and the existence of the Fe element was also noted. The EDS spot analysis of this sample appears to correspond with the phases that the XRD detected; however, the phases observed here are Ti_2O_3 and $Ti_{16}Si_{32}$. Therefore, the primary phase observed for this alloy is the Titanium III oxide (Ti_2O_3).



Figure 4.32 SEM spot analysis results of sintered Al₃₅Ti₃₅Si₁₈Be₁₀B₂ LWHEA sample: (**a**) SEM image showing the locations for the EDS spot analysis; (**b**) EDS spectrum for Spot 001; (**c**) EDS of Spot 002, and (**d**) EDS of Spot 003.

Element	Mass %					
	Spot 1	Spot 2	Spot 3	Average		
С	8.74	6.88	10.24	8.62		
0	39.00	48.78	0	29.26		
Al	5.84	2.55	5.10	4.50		
Si	10.28	10.36	23.87	14.84		
Ti	32.64	31.43	59.31	41.13		
Au	3.51	0	0	1.17		
Fe	0	0	1.48	0.49		
Phase	(Ti ₂ ,O ₃),	(Ti ₂ ,O ₃),	(Ti ₁₆ ,Si ₃₂),			
	rich	rich	rich			

Table 4.5 Quantitative results of elemental composition from spot analysis of sinteredAl35Ti35Si18Be10B2 LWHEA sample.

4.1.3.2.3 Alloy 3 (Al₃₅Ti₃₅Si₁₇Be₁₀B₃)

Figure 4.33 presents the X-ray diffraction (XRD) pattern of the sintered $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ at 1000 °C. The bulk consists of disordered solid solutions, and an ordered phase is observed even in this alloy. However, no silicides are observed here, but the presence of Aluminium Pentaoxotitanate (Al₄Ti₈O₂) and Boron Nitride (B₂N₂). Only two intermetallic phases are recognised in the diffraction pattern and are more body-centred than the other two alloys, where only one ordered solid solution phase was observed. Transition metal borides have better chemical stability in ambient settings (Hamayun *et al.* 2018). The appearance of B₂N₂ is attributed to the increase of boron content observed in this bulk alloy. When boron content increases, boride with high hardness and thermal stability is formed in the microstructure (Ren *et al.* 2021). The Al₄Ti₈O₂ intermetallic compound was observed in each peak, making it dominant in this diffraction pattern. Even though the EDS does not correspond to this, it can be inferred that the increase of boron content positively affected the phase pattern of this alloy.



Figure 4.33 XRD pattern of sintered Al₃₅Ti₃₅Si₁₇Be₁₀B₃ LWHEA

The morphological and microstructural features of the sintered $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ LWHEA at 1000 °C taken at different magnifications are presented in Figure 4.34. Only three phases are observed: a needle-like structure that is light and dark grey, tiny black dots scattered all over the needle-like matrix and the dark shaded area. The presence of dark dots, which are believed to be borides intermetallic phases, is associated with an increase in boron content. The microstructure appears to still exhibit a hard phase. The major phase is BCC, which is highly associated with the presence of ordered solid solution phases.

A spot analysis was performed on some typical morphological features and phases, as shown in both Figures 4.34, to gather composition information on these features and phases. Spot 001, Spot 002, Spot 003, and Spot 004 are four example locations for the spot analysis in Figure 4.35 (a). The qualitative results obtained at each spot are depicted in Figure 4.35 (b)-(d). Table 4.6 shows the relative mass % composition details for each element from the three spots. The diffraction peaks of the three major constituents are depicted in these three sub-figures. Ti, Al,

and Si are the primary constituents. At spot 001, the dominant peak is that of Al, and the second-highest peak is that of Ti. The presence of the B element is also identified in substantial amounts, even though the peak is not that pronounced. At spot 002, an increased number of elements detected by the spectrum is observed. Additional elements such as Mn. Cr, and Fe. Si has the highest peak, which is followed by the Ti peak.



Figure 4.34 SEM micrographs showing the microstructure of Al₃₅Ti₃₅Si₁₇Be₁₀B₃ LWHEA. a) Higher magnification at X800 and b) Lower magnification at X500.



Figure 4.35 SEM spot analysis results of sintered $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ LWHEA sample: (**a**) – (**b**) SEM image showing the locations for the EDS spot analysis; (**c**) EDS spectrum for Spot 001; (**d**) EDS of Spot 002; (**e**) EDS of Spot 003, and (f) EDS of Spot 004.

At spot 003, the presence of additional elements seen in spot 002 is still observed. And Si's intensity peak still takes the lead. However, Al now has the second-highest peak and the third highest one being that of Ti. And at spot 004, Al's peak is dominant, just like it was observed in spot 001. Si has the second-highest peak. The presence of the Fe element is still identified, like in spots 002 and 003. The EDS spot analysis for this alloy shows quite a variation, especially in the number of elements observed compared to alloys 1 and 2. Therefore, the

phases observed here are Ti_2B , TiO_2 and Ti_4Si_8 . The major phase is the Titanium silicide (Ti_4Si_8), an intermetallic compound.

Element	Mass %					
	Spot 1	Spot 2	Spot 3	Spot 4	Average	
В	28.46	0	0	0	7.12	
С	8.55	5.77	10.44	11.86	9.16	
0	0	0	0	18.93	4.73	
Al	17.18	3.53	15.74	13.71	12.54	
Si	3.90	24.79	20.97	13.39	15.76	
Ti	41.91	57.59	43.05	35.43	44.50	
Cr	0	4.67	2.99	0	1.92	
Mn	0	0.64	0.47	0	0.28	
Fe	0	3.00	6.33	6.69	4.01	
Phase	(Ti ₂ ,B), rich	(Ti4,Si8),	(Ti4,Si8),	(Ti,O ₂), rich		
		rich	rich			

Table 4.6 Quantitative results of elemental composition from spot analysis of sinteredAl35Ti35Si17Be10B3 LWHEA sample

4.1.3.3 Density Determination of sintered $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3 wt.%) alloys

The theoretical densities (ρ_t) of the developed Al₃₅Ti₃₅Si_(20-x)Be₁₀B_x (x=1,2,3 wt.%)alloys were estimated using a rule of mixtures assumption of a disordered solid solution and listed in Table 4.4, as given by:

$$\rho_t = \frac{\sum x_i A_i}{\sum \frac{x_i A_i}{\rho_i}} \tag{4.1}$$

where x_i , A_i , and ρ_i denote the weight fraction, atomic weight, and density of each constituent element, respectively, and *t* denotes the total number of elements. The densities measured by

the Archimedes method for these alloys (ρ_{exp}) are also listed in Table 4.4. The measured density for the developed Al₃₅Ti₃₅Si_(20-x)Be₁₀B_x (x=1,2,3 wt.%) alloys deviated significantly from the theoretical density, meaning it was greater than the theoretical density, indicating the presence of ordered phases as observed in XRD results. When Yang *et al.* (2014) conducted a study on Phase Stability of Low-Density, Multiprincipal Component Alloys Containing Aluminum, Magnesium, and Lithium. Density discrepancies were also identified, and it was concluded that it was due to the presence of the intermetallic compounds. This leads to quite abnormal relative density values; as shown in Table 4.7, high relative densities of more than 100% were attained for all samples produced under 1000 C. The relative densities of the developed alloys were obtained using equation 4.2.

$$\rho(\%) = \frac{\rho_{Bulk}}{\rho_{Theoretical}} \times 100 \tag{4.2}$$

Table 4.7 Theoretical (ρ_t), measured densities (ρ_{exp}) and relative densities of Al₃₅Ti₃₅Si₁₉Be₁₀B, Al₃₅Ti₃₅Si₁₉Be₁₀B, and Al₃₅Ti₃₅Si₁₇Be₁₀B₃ LWHEAs

Developed Alloys	Theoretical Density	Experimental	Relative
	(g·cm ⁻³)	Density (g·cm ⁻³)	Density (%)
Al35Ti35Si19Be10B	3.24	3.48	107
Al35Ti35Si18Be10B2	3.25	3.40	105
Al35Ti35Si17Be10B3	3.26	3.51	108

4.1.3.4 Micro-Hardness of sintered $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3 wt.%) alloys

The mechanical parameters of sintered $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3 wt.%) alloys were determined using a Vickers microhardness test at a maximum load of 1 kgf, as indicated in chapter three. Each sample was subjected to ten different tests or indentations, with the average being used to determine the strength. To avoid spatial variations in hardness, each sample was polished. It was noticed that as boron content increased, the hardness values of the sintered alloys increased, as shown in Figure 4.36.

The developed Al₃₅Ti₃₅Si_(20-x)Be₁₀B_x (x=1,2,3 wt.%) alloys exhibited hardness values that are higher than those of quartz, HV 700-900 (Tseng *et al.* 2017). The high overall hardness suggests that the major solution-type matrix phase is hard. Particle rearrangement and homogenous distribution of a secondary phase, which is preferred at high temperatures, may also contribute to an increase in microhardness values. Microhardness levels have been associated with high relative densities. The OPM of the microhardness indentions of the developed LWHEAs sintered at 1000 °C is shown in Figure. 4.37. After etching the alloys, the indentations were examined, and micrograph pictures were used to assess the manufactured LWHEAs' mechanical properties qualitatively. In all of the synthesised alloys, no cracking around the indentation surfaces was seen in micrographs. Figure 4.38 shows a comparison of the three developed alloys in this study. It can be shown from the scatter plot that the highest relative density is proportional to the microhardness obtained for Al₃₅Ti₃₅Si₁₇Be₁₀B₃ LWHEA as compared to Al₃₅Ti₃₅Si₁₉Be₁₀B and Al₃₅Ti₃₅Si₁₈Be₁₀B₂.



Figure 4.36 A relationship between microhardness values and boron content in the developed $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3 wt.%) alloys



Figure 4.37 Indentation mark obtained after Vickers microhardness test on the consolidated $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3 wt.%) alloy samples. (a) $Al_{35}Ti_{35}Si_{19}Be_{10}B_3$ (b) $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$, and (c) $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$


Figure 4.38 Microhardness vs relative density of the developed Al₃₅Ti₃₅Si₁₉Be₁₀B, Al₃₅Ti₃₅Si₁₈Be₁₀B₂, and Al₃₅Ti₃₅Si₁₇Be₁₀B₃ alloys

4.1.3.5 Electro-chemical Analysis of sintered Al₃₅Ti₃₅Si_(20-x)Be₁₀B_x (x=1,2,3 wt.%) alloys

The dynamic potential polarization curves of the developed $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3 wt.%) alloys in 3.5 wt% NaCl solution is shown in Figure 4.39. These polarisation curves of the three alloys exhibit the same corrosion behaviour with minor differences observed in $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$. However, the passive zone ($E_{pi}t$ - E_{corr}) of the LWHEAs is slightly wide and straight as observed for alloys $Al_{35}Ti_{35}Si_{19}Be_{10}B$ and $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$, indicating that the passive film performance of LWHEAs is good and steady. Alloy $Al_{35}Ti_{35}Si_{18}Be_{10}B$ shows a slightly wide but curved passive zone ($E_{pi}t$ - E_{corr}). Tafel extrapolation analysis derived the corrosion potentials (E_{corr}) and corrosion current densities (I_{corr}), utilising both anodic and cathodic branches of the curves, as shown in Table 4.8.



Figure 4.39 Potentiodynamic polarization curves of (a) $Al_{35}Ti_{35}Si_{19}Be_{10}B$, (b) $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$, and (c) $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ LWHEAs in 3.5 wt% NaCl solution at 25 °C.

More positive potential and low current densities characterise the polarisation curves. This finding demonstrates the formation of a passivating layer during the interaction of the corrosive media with the elements present in the alloy. Aluminium and titanium have been shown to create a stable, protective layer, and their inclusion in an alloy has been linked to increased corrosion resistance. This layer establishes a barrier between the corrosive media and the alloy, preventing further corrosion (Chou *et al.* 2010). Notably, the LWHEAs have low corrosion current densities (5.065×10^{-5} , 5.24×10^{-5} and 5.263×10^{-5} A·cm⁻²) and slightly wide passive zones (1.41, 1.28, and 1.32 V_{SCE}), implying that the LWHEAs have a low corrosion rate. Alloy Al₃₅Ti₃₅Si₁₇Be₁₀B₃ shows a very low corrosion rate compared to the other two alloys. The

current density of the alloys increased with increasing the potential in the active zone, where metal oxidation is the dominant reaction. Because the passive zone is frequently linked to the stability of the passive film, a wide passive zone on the LWHEAs' surfaces implies a relatively stable passive film. Regarding the boron content, in 3.5 wt% NaCl solution, the anodic polarisation data of the developed Al₃₅Ti₃₅Si₁₇Be₁₀B₃ alloy demonstrated that the general corrosion resistance diminishes due to the formation of Fe and Cr borides as the content of boron increases.

The OCP readings in the 3.5 wt% NaCl solution are shown in Figure 4.40. Each alloy's OCP was measured for 22 minutes. All three alloys exhibited different behaviour. Alloy $Al_{35}Ti_{35}Si_{19}Be_{10}B$ (OCP = -0.487 V) showed a fluctuating potential behaviour over time, whereas alloy $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$ (OCP = -.0363 V) showed a rapid increase in potential over time, indicating passive behaviour. As for alloy $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ (OCP = -0.409), the behaviour was somewhat abnormal in which initially, there was an increase in potential. Still, after the maximum potential was reached, there was a rapid decline indicative of metastable pitting at the OCP.

Alloy	Ecorr	Icorr	Corrosion	Epit	Epit-Ecorr
	(V _{SCE})	(A·cm ⁻²)	rate	(V _{SCE})	(V _{SCE})
			(mm/year)		
Al35Ti35Si19Be10B	-0.410	5.065 x 10 ⁻⁵	2.32 x10 ⁻²	0.997	1.41
Al35Ti35Si18Be10B2	-0.280	5.24 x 10 ⁻⁵	2.02 x10 ⁻²	0.999	1.28
Al35Ti35Si17Be10B3	-0.332	5.263 x 10 ⁻⁵	3.38 x10 ⁻³	0.985	1.32

Table 4.8 Alloy properties derived from potentiodynamic polarisation curves by a linear fit.



Figure 4.40 22 min OCP of the LWHEAs:(a) Al₃₅Ti₃₅Si₁₉Be₁₀B, (b) Al₃₅Ti₃₅Si₁₈Be₁₀B₂, and (c) Al₃₅Ti₃₅Si₁₇Be₁₀B₃ in 3.5 wt% NaCl solution at 25 °C

4.1.3.6 Tribological Analysis of sintered Al₃₅Ti₃₅Si_(20-x)Be₁₀B_x (x=1,2,3 wt.%) alloys

Tribological characteristics of the developed $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3 wt.%) alloys were examined under dry sliding wear conditions with stainless steel as the static friction partner. Figure 4.41 depicts the variation in coefficient of friction (COF) for the developed LWHEAs during sliding under a 10 N load and a sliding duration of 60 min. The results indicated that the alloy's increase in silicon impacts the friction coefficient and wear rate. Table 4.9 shows that the maximum COF and wear rate are found in the high-silicon alloy ($Al_{35}Ti_{35}Si_{19}Be_{10}B$). Due to the brittle nature of the alloys, observation of the wear tracks with a scanning electron microscope indicated that these alloys lead to an intense removal of the silicide particles from the surface (Figure 4.42). The grey area represents the worn surface compared to the unworn surface. The extracted hard silicide particles act as abrasive in all tested alloy composites, causing the wear to be mostly abrasive. The alloys in the wear track have visible signs of oxidation. Furthermore, hard and oxidised wear debris moving in the sliding region, resulting in third body wear, might also explain the rise in COF.

Jin *et al.* (2018) studied the phase evolution and wear mechanism of AlCoCrFeNiSi_x highentropy alloys. The wear results showed that the COF of the alloys could be affected by the presence of Si content. From Si $_0$ to Si $_{1.5}$, the alloys showed considerable oscillations, which gradually diminished, while the Si $_{2.0}$ alloy showed fewer tiny fluctuations. The friction coefficient gradually decreased as Si increased. The coefficient of friction was 0.3 at x=2.0, which is nearly half of the alloy without Si. The coefficient of friction is affected by the amount of wear debris on the surface, and the coefficient of friction rose as huge debris accumulated on the wear surface. Also, it was observed that with variable Si concentration, the mass loss of the AlCoCrFeNiSix HEAs appeared to be sensitive to hardness, and there was a substantial association between hardness and transition from FCC to BCC phase. Therefore, it was also found that the increase in wear resistance can be attributed to changes in organisation and structure.

Alloy	Friction Coefficient (µ)				Wear rate
	Min	Max	Mean	Std dev.	(mm ³ /N/m)
Al35Ti35Si19Be10B	0.002	0.751	0.624	0.080	3.646E-005
Al35Ti35Si18Be10B2	0.002	0.649	0.511	0.133	1.081E-006
Al35Ti35Si17Be10B3	0.001	0.584	0.491	0.106	2.733E-007

Table 4.9 Tribological properties of tested $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3 wt.%) alloys.



Figure 4.41 Coefficient of friction of all the three alloy composites :(a) $Al_{35}Ti_{35}Si_{19}Be_{10}B$, (b) $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$, and (c) $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$



Figure 4.42 SEM micrographs of the worn surfaces: :(a) $Al_{35}Ti_{35}Si_{19}Be_{10}B$, (b) $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$, and (c) $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$

4.1.3.7 High-Temperature Oxidation of sintered $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3 wt.%) alloys

The mass change versus time curves of $Al_{35}Ti_{35}Si_{19}Be_{10}B$, $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$ and $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ under isothermal exposure in air at 700 °C and 900 °C are shown in Figures 4.44 (a) and (b), respectively and the corresponding *n* and *k* values are listed in Table 4.10. The mass change that occurs during isothermal exposure can be explained by:

$$(\Delta W/A)^n = k \cdot t \tag{4.3}$$

where $\Delta W/A$ is the mass change per unit area, *t* is the exposure time, *n* is the oxidation rate exponent, and *k* is the oxidation constant. The oxidation constant *k* is the straight-line slope when $(\Delta W/A)^n$ vs *t* is plotted linearly. The rate exponent (*n*) can be calculated using a logarithmic representation of this relationship.

$$\ln \Delta W/A = \frac{1}{n} \ln k + \frac{1}{n} \ln t \tag{4.4}$$

as the slope of a mass change with a time double logarithmic plot.



Figure 4.43 Isothermal oxidation tests results of $Al_{35}Ti_{35}Si_{(20-x)}Be_{10}B_x$ (x=1,2,3 wt.%) alloys (weight gain versus oxidation time curves) at (a)700 °C for 400h and (b) 900 °C for 200 h

Figure 4.43 (a) shows that the developed alloys exhibited a maximum mass gain during the third oxidation cycle (t= 100-150h). Alloys $Al_{35}Ti_{35}Si_{19}Be_{10}B$ and $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$ showed 151

similar oxidation behaviour compared to alloy $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ with a parabolic rate (n = 0.3969) which in this case is higher than the two other alloys which showed parabolic rate (n = 0.0382 and 0.0631), respectively. After the third cycle, alloys, $Al_{35}Ti_{35}Si_{19}Be_{10}B$ and $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$, the mass gain was observed to have drastically decreased, yielding a shallow mass gain up to 400 h. The mass gain of alloy, $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$, fluctuated up to 400h. Figure 4.43 (b) exhibited the alloys to have the lowest mass gain during oxidation at 900 °C as compared to oxidation at 700 °C.

Interestingly, the second batch of samples was 200 h shorter than the first batch tested for 400 h at a lower temperature. Alloys, $Al_{35}Ti_{35}Si_{19}Be_{10}B$ and $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$ still showed similar oxidation behaviour with the oxidation rate (n = 0.1397 and 0.1602), respectively. However, alloy $Al_{35}Ti_{35}Si_{18}Be_{10}B_2$ showed the highest oxidation rate, but alloy $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ showed the second-highest oxidation rate.

Low weight gain and a low rate constant suggest that the alloy is resistant to oxidation at working temperatures. This is owing to the alloy's high Si and Al concentration which aids in the production of protective oxide against further oxidation. Aside from that, the presence of Ti, which causes TiO₂, aids in the formation of the protective oxide layer. Therefore, the exceptional oxidation resistance was observed at 900 °C, which showed almost no mass gain. The different origin points are due to the weighed samples' different initial masses. No residual metal substrate could be found for all the samples post cyclic oxidation tests.

Table 4.10 Oxidation rate exponents (n) with regression coefficient (R^2) and oxidation constants (k) calculated from the curves shown in Figures. 4.44 (a) and (b).

Temperature 700 °C for 400h					
Alloy	Intercept	Oxidation rate	Regression	Oxidation rate	
		exponent (<i>n</i>)	coefficient (R^2)	constant (K)	
Al35Ti35Si19Be10B	0.0282	0.0382	0.4812	-2.9333 x10 ⁻⁶ mg·cm ⁻	
				² ·h ⁻¹	
Al35Ti35Si18Be10B2	0.0277	0.0631	0.4102	-1.6333 x 10 ⁻⁶ mg·cm ⁻	
				² ·h ⁻¹	
Al35Ti35Si17Be10B3	0.0308	0.3969	0.1042	-3.3333 x 10 ⁻⁷ mg·cm ⁻	
				² ·h ⁻¹	

Temperature 900 •C for 200h

Alloy	Intercept	Oxidation rate	Regression	Oxidation rate
		exponent (n)	coefficient (R^2)	constant (K)
Al35Ti35Si19Be10B	0.0324	0.1397	0.5708	$4.40 \text{ x} 10^{-6} \text{ mg} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$
Al35Ti35Si18Be10B2	0.0331	0.1602	0.5349	$1.18 \times 10^{-5} \text{ mg} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$
Al35Ti35Si17Be10B3	0.0361	0.1586	0.5376	$4.38 \ge 10^{-5} \text{ mg} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$

Chapter 5

5.1 CONCLUSIONS AND RECOMMENDATIONS

5.1.1 CONCLUSIONS

Materials engineers face an expanding number of harsh and aggressive situations in which they must perform to meet the demands of modern technological advancement. As a result, materials engineers are frequently faced with the task of selecting the right material for a certain application as well as designing novel materials that can handle a wide range of uses. The goal of this study was to develop lightweight high-entropy alloys by mechanical alloying from elemental powders to spark plasma sintering of Al₃₅Ti₃₅Si₁₉Be₁₀B, Al₃₅Ti₃₅Si₁₈Be₁₀B₂, and Al₃₅Ti₃₅Si₁₇Be₁₀B₃ composites. Also, the impact of mechanical alloying and SPS sintering on density, microstructural uniformity and produced phases were evaluated. The influence of boron content on microstructure and mechanical properties (hardness), and properties such as wear, corrosion, and high-temperature oxidation, was studied and the major conclusions were drawn and summarised below.

- i. Despite a large number of components, the Hume-Rothery laws have been utilized to describe the solid solubility of LWHEAs, where the influence of mixing entropy, mixing enthalpy, atomic size difference, electronegativity, and valence electron concentration has been taken into account. Furthermore, based on the findings, it can be stated that the entropy cannot be increased any further to avoid the development of IM phases.
- The presence of the elements utilized to form the alloy is confirmed by EDS analysis. The mechanical alloying of the alloys, Al₃₅Ti₃₅Si₁₉Be₁₀B, Al₃₅Ti₃₅Si₁₈Be₁₀B₂, and Al₃₅Ti₃₅Si₁₇Be₁₀B₃, was conducted for 45 hours and the XRD analysis revealed two solid solution phases (BCC and FCC) and intermetallic compounds (TiB₂ and Ti₄Si₈) for all the alloys. However, the Ti₄Si₈ was only observed in alloy 2, Al₃₅Ti₃₅Si₁₈Be₁₀B₂. The findings of this study support previous research that shows that increasing the

milling time of powder particles reduces the average particle size due to a high rate of particle fragmentation. The particle size reduction rate was caused by increased milling energy, which increased the contact surfaces between grains, resulting in particle welding. Increased milling time resulted in morphological changes and increased agglomeration of powder particles. SEM also showed a spongy appearance for all three alloys. Because of the greater surface area, which increases internal friction between particles, the morphology (flat and spongy) change observed with increased milling can obstruct compaction. Therefore, achieving a good dense compact was achieved by a higher compaction pressure.

Due to higher sintering pressure of 50 MPa and temperature at 1000 °C, non-porous, iii. and fully densified compacts were achieved with relative densities above 100% for all the three developed alloys. The unexpected relative densities resulted from the high presence of intermetallic compounds and the high oxygen content present in the alloys. The experimental densities $(3.48, 3.40 \text{ and } 3.51 \text{ g} \cdot \text{cm}^{-3})$ of the developed alloys were found to be lesser than that of titanium (4.51 g·cm⁻³). The solid solutions phases (BCC and FCC) and the ordered solid solution phases (Ti₄Si₈/Ti₁₆Si₃₂) were identified by the XRD for alloys 1 and 2, and the intermetallic compounds were dominant in both developed alloys. Aluminium Pentaoxotitanate (Al₄Ti₈O₂) and Boron Nitride (B₂N₂) were only observed in alloy 3, $Al_{35}Ti_{35}Si_{17}Be_{10}B_3$ and the appearance of B_2N_2 is attributed to the increase of boron content. The EDS on the other hand showed major phases to be Titanium silicide (Ti_4Si_8) , an intermetallic compound for Al₃₅Ti₃₅Si₁₉Be₁₀B and Al₃₅Ti₃₅Si₁₇Be₁₀B₃, Titanium III oxide (Ti₂O₃) for Al₃₅Ti₃₅Si₁₈Be₁₀B₂. The SEM showed no significant presence of pores or cracks with no signs of stress initiations. Minor cavities observed resulted from the forcing out of some proportion of Al from the alloy systems. A needle-like structure was observed with the increase of boron content for both Al₃₅Ti₃₅Si₁₈Be₁₀B₂ and Al₃₅Ti₃₅Si₁₇Be₁₀B₃. The overall microstructure of all the alloys was observed to be extremely hard, this is due to very strong attractive interaction between Al/Ti and 3d-transition metals, brittle intermetallic compounds form readily.

- The synthesised alloys exhibited extremely high microhardness values 957, 989, and iv. 1093 HV, this is attributed to the high sintering temperature employed and the increase in boron. With high microhardness values reached at 1000 °C, there is a direct proportionality between sintering temperature and microhardness. The formation of the BCC phase, which has been shown to have outstanding mechanical properties, is responsible for this result. With increasing sintering temperature, the formation of the BCC phase increases, and its presence in the microstructure causes significant lattice distortion. The high overall hardness suggests that the major solution-type matrix phase is hard a content. The addition of titanium and boron led to the formation of intermetallic bonds (TiB₂, Ti₄Si₈/ Ti₁₆Si₃₂, Al₄Ti₈O₂ and B₂N₂) in the alloys which resulted to increased hardness. No cracking was identified on the indentation surfaces of all the samples. The strength to weight ratios estimated from the hardness values of the synthesised alloys (957, 989, and 1093 HV) reveal that strength to density ratios of the alloys processed in this work is better than that of conventional light-weight Al, Mg, and Ti alloys.
- v. Al₃₅Ti₃₅Si₁₉Be₁₀B, Al₃₅Ti₃₅Si₁₈Be₁₀B₂, and Al₃₅Ti₃₅Si₁₇Be₁₀B₃ LWHEAs show outstanding corrosion resistance properties in a 3.5 wt.% NaCl solution as compared to AISI 316L austenitic stainless steel and Ti-6Al-4V commercial alloys. Regarding the boron content, in 3.5 wt% NaCl solution, the anodic polarization data of developed Al₃₅Ti₃₅Si₁₇Be₁₀B₃ alloy demonstrated that the general corrosion resistance diminishes due to the formation of Fe and Cr borides as the content of boron increases.
- vi. The resistance to wear increased with high contents of silicon observed in alloy 1, Al₃₅Ti₃₅Si₁₉Be₁₀B. The results indicated that the increase of silicon in the alloy has an impact on the friction coefficient and wear rate. High densities can also significantly increase wear resistance.
- vii. All the three developed alloys, Al₃₅Ti₃₅Si₁₉Be₁₀B, Al₃₅Ti₃₅Si₁₈Be₁₀B₂, and Al₃₅Ti₃₅Si₁₇Be₁₀B₃ showed good resistance to high-temperature oxidation at 900 °C as compared to oxidation at 700 °C. At operating temperatures, the alloy's low weight gain and low rate constant indicate that it is resistant to oxidation. This is due to the

alloy's high Si and Al content, which helps to produce a protective oxide to prevent further oxidation.

5.1.2 RECOMMENDATIONS

Based on the findings presented in this research work, it is recommended that:

- i. Physical parameters were researched to understand how they play an essential part in predicting SS. Based on the findings, it can be stated that the values supplied by various researchers for physical characteristics are not conclusive and should be further evaluated.
- ii. To reliably anticipate single solid solution phases in various systems, more research using CALPHAD method is needed. The typical parameters employed in the prediction of LWHEAs, such as lattice misfit, enthalpy of mixing, the entropy of mixing, and electronegativity, are beneficial once identified for a certain alloy system, but not transferable to completely new systems.
- iii. Increase the number of primary elements (up to eight lightweight elements) in alloy development to determine if the increase in configurational entropy can stabilize the ensuing solid solution and produce a single-phase crystal structure.
- iv. More mechanical properties need to be explored for the newly developed LWHEAs such as tensile strength, ductility and fracture toughness.
- v. Electrochemical analysis should be performed in different corrosive media to see if these newly developed alloys are highly resistant to corrosion in various environments.
- vi. The development of new LWHEAs should be developed using CALPHAD-based models which can accurately anticipate the phases that develop in compositionally complicated LWHEAs similar to the ones developed for this work.

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