CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Historical Sketch

The ever-evolving saga of human civilization started with the use of metals, especially, of copper. Nowadays, we have materials in the pure and alloyed form. Alloying was an accidental and greatest gift of metallurgy to the human civilization. Mixing of tin with copper gave birth to Bronze, an alloy which is first discovered by mankind in 3000 BC [1]. Alloyed materials helped in circumventing the weaknesses of the base material by providing the desired properties. For instance, the most advanced and master of all alloys is steel - an alloy of iron with carbon. The 20th century has explored the science of alloying and established the correlation between microstructure and properties of these alloys with the help of microscopic examination. This helped in developing the several advanced alloys required for critical applications in aerospace, nuclear, defence industries and many other industries. Besides the modern engineering alloys, several novel materials have been developed i.e. intermetallics [2], quasicrystals [3] and metallic glasses [4, 5]. Intermetallics are basically a compound consisting of two or more metallic elements. These intermetallic compounds have attracted enormous interest and still being researched with respect to their high-temperature applications as a new class of structural materials. Most of the intermetallics are brittle in nature [2]. Thus, the alloys containing major amount of intermetallic compounds are also brittle in nature. Many structural alloys are also strengthened by presence of precipitates of intermetallic phases, i.e. Ni-based super alloy contains Ni_3Al based intermetallic [2]. A quasicrystal is another class of intermetallics which belongs to a family of aperiodic crystals and demonstrate the quasiperiodic translation and forbidden rotational symmetries. These were discovered by Shechtman in 1982, as he found the 10 fold electron diffraction pattern in a rapidly solidified Al-Mn alloy. Following the discovery, several other systems were studied, i.e. Al-based, Mg-based, Ti-based, Pd- based and Li-based alloys [5]. Quasicrystals are known to exhibit high hardness, good wear and corrosion resistance and low coefficient of friction etc [6,7].

The metallic glass of composition $Au_{80}Si_{20}$ was first reported by Pol Duwez and his research group [8]. This was obtained by solidifying the molten metal at a high rate of cooling (~10^6 K/s), in order to achieve the glass-like structure. These alloys were classified by adopting the different ways of designing viz. metal-metalloid (B, C, P and Si) and metal-metal types non-crystalline phases. Some well established compositions of metal-metalloid and metal-metal are i.e. $Pd_{80}Si_{20}$, $P_{d77}Cu_6Si_{17}$, $Fe_{40}Ni_{40}B_{20}$, $Fe_{70}Cr_{10}P_{13}C_7$, $Ni_{49}Fe_{29}B_6P_{14}Si_2$, $Ni_{60}Nb_{40}$, $Cu_{57}Zr_{43}Mg_{70}Zn_{30}$, $La_{80}Au_{20}$, $Fe_{90}Zr_{10}$ respectively (subscript represents the atomic % of the elements in the alloy). Among the different metallic glasses the soft magnetic glass of Fe, Ni, P and B, known as Metglas, was first commercially used in the early 80s for low-loss power distribution transformers. Following this, several compositions have been tried and developed the BMGs of different length scale [9].

It may be rationalized in the above mentioned alloys that they are based on one or two principal alloying elements. The discovery of the crystalline multicomponent alloys in the year of 1981 by Brian Cantor with his undergraduate student Alain Vincent [10], ushered a new era in alloy design and development. This group has made several equiatomic alloys consisting of 20 different components. During their study, they found the only composition of $Fe_{20}Cr_{20}Ni_{20}Mn_{20}Co_{20}$ crystallizes in a single phase FCC (face-centered cubic) structure. The alloy composition is known as Cantor alloy [11]. Based on this composition, several other wide ranges of six to nine component alloys have been developed and found to be primarily rich in FCC phase.

In the same line, another group from Taiwan led by J.W Yeh had independently started working on these multicomponent alloys [12]. They have primarily used the common elements of the periodic table, i.e. Ti, Fe, V, Cr, Co, Cu, Ni, Pd, Mo, Zr and Al. From these elements, 20 alloys were produced by melting/casting route with 40 different compositions. It was observed that the effect of configurational entropy plays a significant role in minimizing the number of phases in these multicomponent alloys, Yeh and co-workers had advocated the term 'high entropy alloys' (HEAs) for this new class of material. They have published the first article in the year of 2004 with the title of "Nanostructured high entropy alloys with multi-principal elements - novel alloy design concepts and outcomes" [12]. It has been noticed that the above-mentioned multicomponent alloys are different from conventional alloys. The conventional/ traditional alloys are designed on one or two major principal elements, and other minor elements are added in order to attain the required properties. This has been symbolized in Fig. 1.1 by the representation of the size of the circles. In conventional alloys, the major principal element is termed as solvent, and the minor proportion of elements are solutes. Steel is the best example of the conventional alloys in which iron (Fe) is considered as solvent and C as solute. The mutual solubility of substitutional binary alloys is primarily governed by Hume-Rothery (H-R) rules. Their limited solubility is based on terminal solid solutions and can be obtained through phase diagrams. These terminal solid solutions could exist in binary, ternary, quaternary or higher order alloy systems. This has been schematically shown in Fig. 1.2 for ternary and quaternary systems. It can be seen that there are immense scopes to explore the central regions of phase diagrams. In a significant achievement towards this direction, HEAs were discovered.

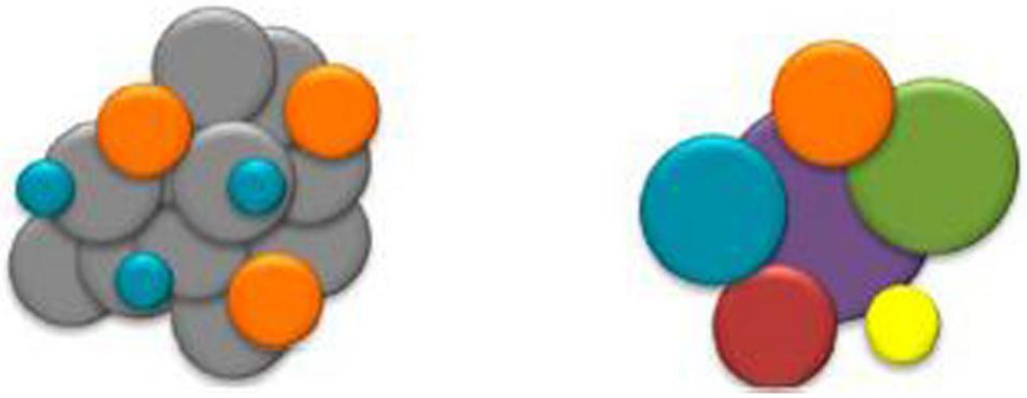

Figure 1.1: The symbolic representation of alloy design in conventional and in HEAs [13].

HEAs have elements in equiatomic or near equiatomic composition ranges, so the concept of solvent and solute may not be valid. These alloys have gained significant attention due to their unique ability to produce solid solutions with a simple crystal structure by controlling configurational entropy.

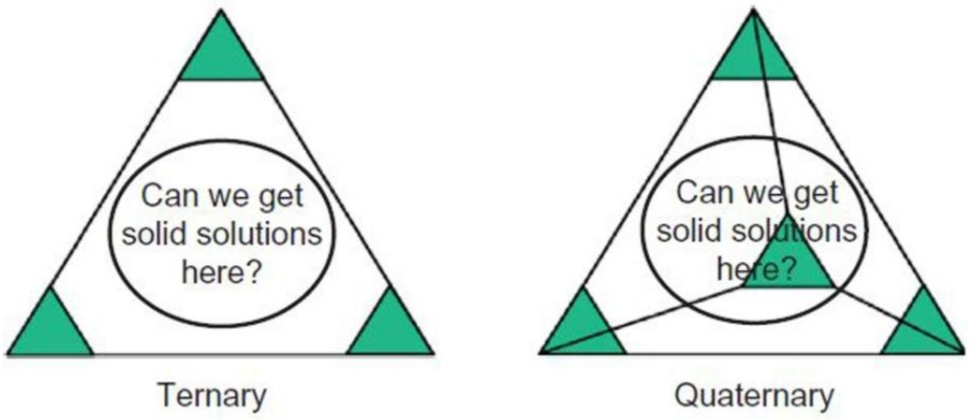

Figure 1.2: The schematic representation of phase diagrams of ternary and quaternary systems with their less known central regions [5].

In literature, there are several terms that have been introduced in order to understand the vastness of the compositional flexibility of these alloys without any implication on the entropy and type of phases present. These terms are complex concentrated alloys (CCAs), multi-principal elemental alloys (MPEAs) and baseless alloys [14]. However, the word ‘HEAs’ have been used throughout the text. The design of the multicomponent alloys could be understood in the more elaborate way in the following sections.

1.2 Alloy design and basic concepts

1.2.1 Bulk metallic glasses (BMGs)

The seminal work of Klement et al. [8] have opened the wide window for the research community to think of the new ways of alloy design. Early reports showed that the glassy structure in metallic alloys could be obtained only in some binary and ternary alloys, which did not have high glass forming ability (GFA). Glassy phase could be obtained upon application of high cooling rate of the order of 10^6 K/s, which further limits the thickness of the metallic glasses [9]. Inoue et al. [15] had breathed a fresh life on the formation of glassy structure in larger sized (up to 3 inch) specimens by enunciating the three empirical rules :-

(1) Multicomponent alloys with at least three components which is related to the kinetic suppression of crystal formation from liquid.

(2) Mixing enthalpy should be high and negative among the major constituent elements, which pertains to thermodynamic stabilization of the liquid.

(3) Atomic radii difference must be larger than 12 % among the major constituent elements which is associated with the topological aspect of the formation of dense random packing.

Out of these three rules, the last two are not favorable to form a solid solution in the HEAs. High negative mixing enthalpy among the elements will lead to the ordering and cannot stabilize the random crystalline solid solution. Similarly, a large atomic size difference is against the Hume-Rothery rules, and it destabilizes the crystalline solid solution and enhances the GFA. In terms of compositional space, BMGs are closer to the HEAs. BMGs are based on the single major element with an amorphous structure, i.e. Zr-base BMGs, Fe-base BMGs and Pd-base BMGs, Mg-based BMGs to name a few.

1.2.2 High-entropy alloys (HEAs)

The alloy design principles of the HEAs are distinct from the conventional alloy systems. Unlike conventional alloys, HEAs are based on equiatomic or non-equiatomic proportion with or without addition of the minor alloying elements. Usually, HEAs are defined to have five or more principal elements with their varying concentration in the range of 5-35 at% [12,16]. This composition-based definition of the HEAs is the earliest one reported so far. It has been understood that these compositional ranges of elements will increase the configurational entropy of alloys, which will overcome the negative enthalpy effect and will help in forming simple and stable solid solutions. Later on, an alternate entropy based definition separated the alloys on their configurational entropy. The configurational entropy (ΔS_{conf}) of an alloy system can be calculated by Boltzmann's equation:

$$\Delta \mathrm{S}_{\text{conf}} = \mathrm{k} \ln \omega \qquad \text{………………………......... (1.1)}$$

where k is Boltzmann's constant and ω is the number of different ways of arranging the atoms at the atomic sites. Thus the change in configurational entropy per mole for n elements system with (X_i) mole fraction is given as:

$$\Delta S_{\mathrm{conf}} = -\mathrm{R}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{X_i} \ln \mathrm{X_i} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.2)$$

where R is the gas constant (8.314 J/K-mol). For an equiatomic alloy composition, this equation can be rewritten as:

$$\Delta S_{\mathrm{conf}} = \mathrm{R} \ln \mathrm{n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.3)$$

where n is a number of elements. From the above expression, the configurational entropy for the equiatomic alloys could be calculated. Based on the calculated entropies for a different type of alloys, the low entropy ($\Delta S_{\mathrm{conf}} < 0.69\mathrm{R}$), medium entropy ($0.69\ \mathrm{R} < \Delta S_{\mathrm{conf}} < 1.61\mathrm{R}$) and high entropy ($\Delta S_{\mathrm{conf}} > 1.61\mathrm{R}$) are categorized. The plot of increase in configurational entropy with a number of constituent elements for an equimolar alloy is given in Fig. 1.3.

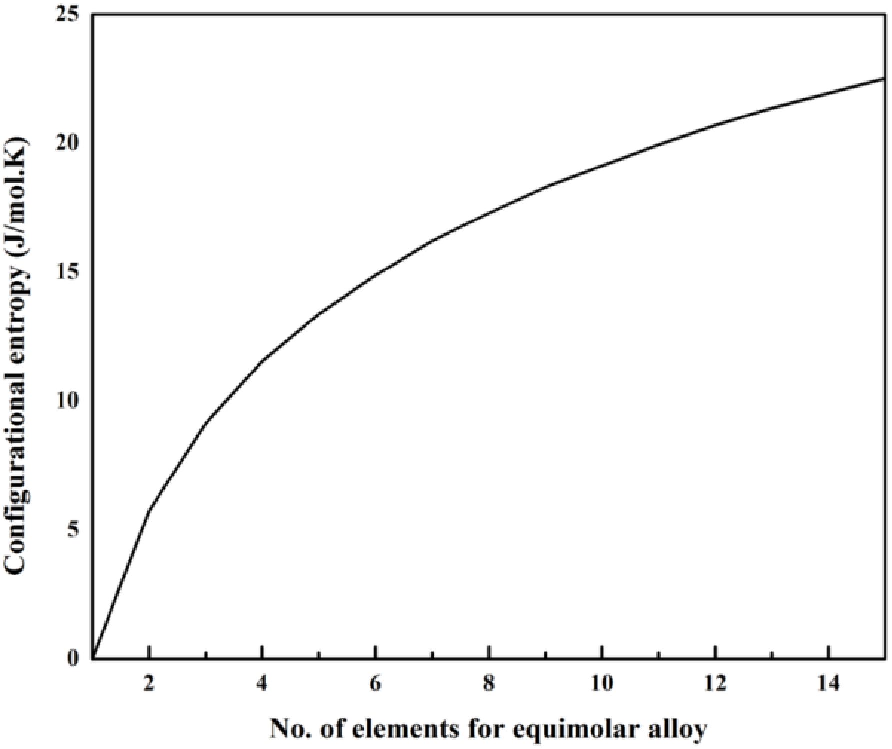

Figure 1.3: The variation of configurational entropy (ΔS_{conf}) for an equimolar alloy with a number of elements.

It could be observed that the contribution of configurational entropy is maximum at the initial level. Adding more number of elements will increase the complexity of the alloy making experimental synthesis difficult. However, it does not increase the configurational entropy that steeply. Yeh et al. [12,17] have suggested the practical limit of number of elements i. e. n = 5-13.

The compositional & entropy based definition, as discussed above, are not the only guidelines for stabilizing the HEAs. Miracle et al. [14] have concluded that the primary definition of HEA is to form simple solid solution phases with simple microstructures in the multicomponent alloys, which make them more attractive.

1.3 Core effects of HEAs

The better properties with simple microstructures of HEAs are basically governed by their four core effects. These core effects are known as founding principles of HEAs and categoriesed as “High-Entropy Effect”, “Lattice Distortion Effect”, “Sluggish Diffusion Effect” and “Cocktail Effect” [17,18].

1.3.1 High-entropy effect

The “High-Entropy Effect” is a signature effect of the HEAs. It proposes that the disordered solid solution phases may be formed when the effect of entropy is significant. Through physical metallurgy concepts, one could expect that these alloys will form a multiphase structure with intermetallic compounds. Here, the concept of high mixing entropy has been neglected. Contrary to conventional metallurgy concepts, the high configurational entropy of HEAs lowers the free energy of solid solution phases. This will further result in reducing the formation of the number of phases by increasing the mutual solubility among constituent elements. From Gibbs free energy rule, ΔG_{mix} =

$\Delta H_{mix} - T\Delta S_{mix}$ (where ΔG_{mix} is the Gibbs free energy, ΔH_{mix} & ΔS_{mix} are mixing enthalpy & entropy, T is temperature), it could be deduced that the higher value of ΔS_{mix} leads to a substantial decrease of ΔG_{mix} [19]. Sufficient experimental data support that the high configurational entropy can stabilize solid solution phases over intermetallic phases [20]. Fig. 1.4 shows the effect of 'high-entropy' by adding the number of elements (upto 7) in a binary alloy of CuNi. These alloys showed the formation of simple structure such as BCC and FCC. However, the misconception that the high-entropy effect will guarantee the formation of simple solid solution phases (BCC/FCC) is not always true, although the role of configurational entropy is significant [21].

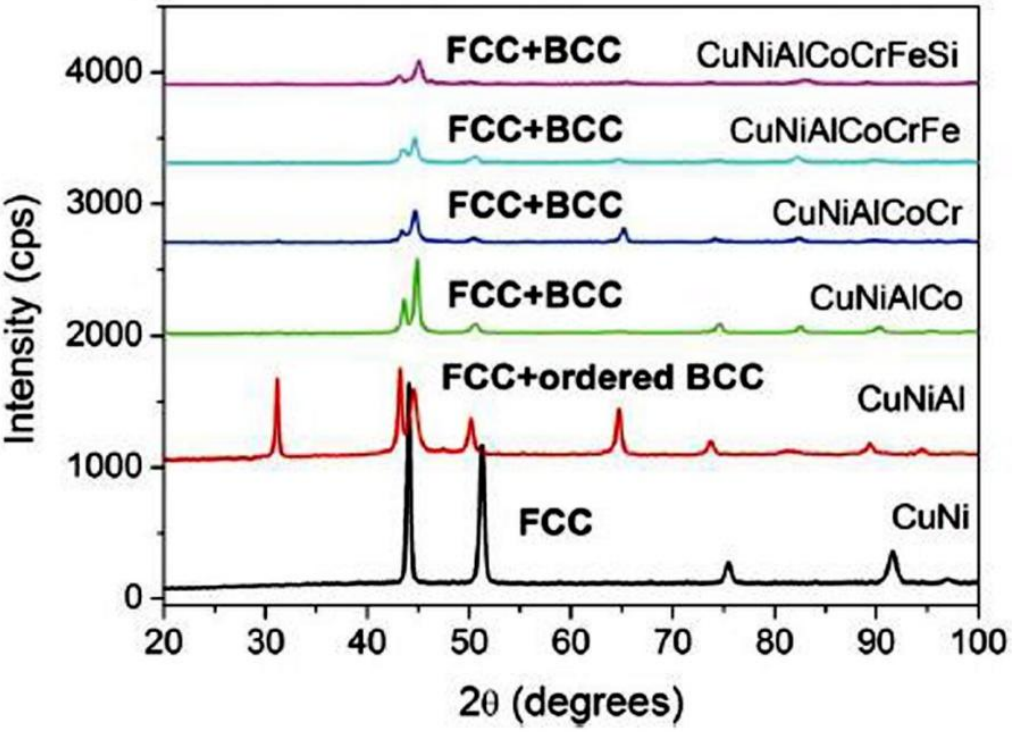

Figure 1.4: The display of XRD patterns of binary to septenary alloys on the addition of one extra element sequentially showed the formation of one or two major phase structure [22].

The possibility of formation of compound phases was already mentioned by J.W Yeh in the very first paper [12]. Although the formations of simple solid solution phases are always desirable, the intermediate phases are also having a great potential for specific applications. So, the advancement of HEAs should not be restricted to solid solution phases alone [23].

1.3.2 Severe Lattice Distortion Effect

Unlike traditional alloys, in the HEA matrix, every atom is surrounded by different kind of atoms. These atoms have different electronic configuration, size and bonding properties, which leads to the displacement in the lattice. This average distortion in the lattice is more severe compared to the conventional alloys. The schematic representation of strained lattices in HEAs is given in Fig.1.5.

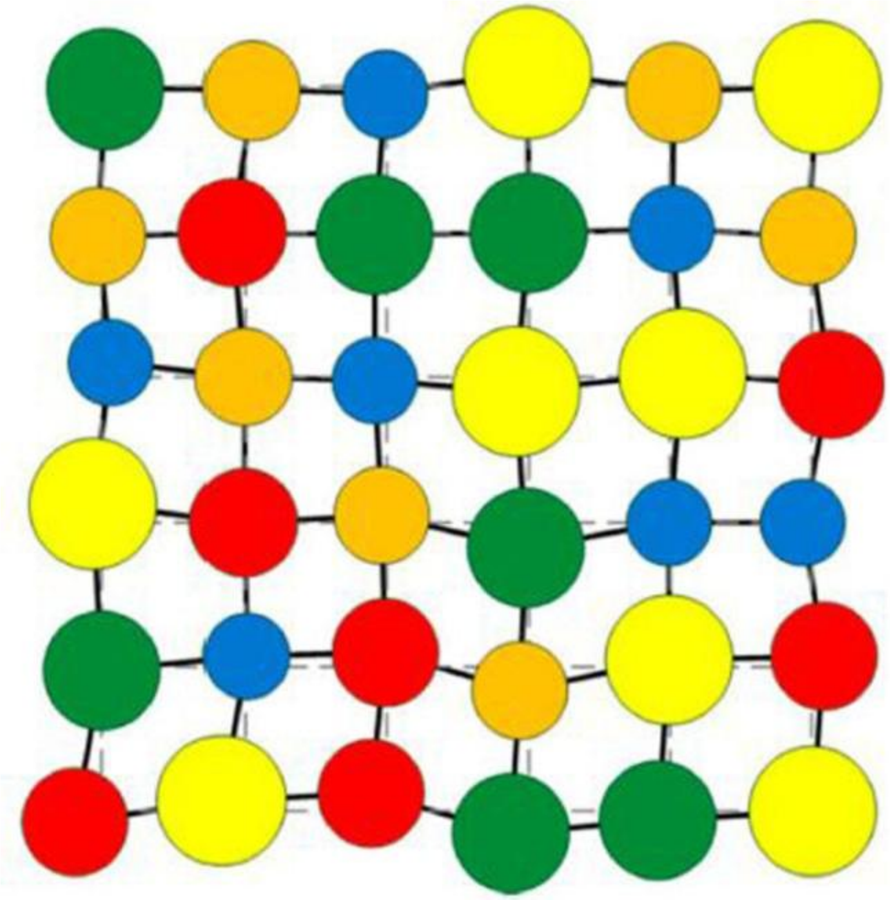

Figure 1.5: The schematic representation of strained lattices in HEAs [17]

The uncertainty of the atomic positions in the HEAs contributes to an increase in the configurational entropy, which results in decrease in intensity of diffraction peaks due to the diffuse scattering [5]. The lattice distortion effect significantly affects the HEA properties, i.e. strength, hardness, electrical and thermal conductivity [5,18]. This effect has been assessed by using the pair distribution function (PDF) analysis. Evidence of lattice distortion was found in neutron scattering data of $Al_{1.3}CrFeCoNiCu$ HEA by PDF analysis [24]. Other evidence of this effect could also be observed in the atomic column contrast- in which column will appear blurred in a highly strained region compared to the unstrained region. Yeh et al. [25] have suggested that although the high-resolution TEM (HRTEM) images can show lattice distortion, the localized strain is not consistent with the long-range distortions effect due to the presence of dislocations. The presence of lattice distortion could also be predicted by the density functional theory (DFT) approach and a spring model based on quadratic potentials [26].

1.3.3 Sluggish Diffusion Effect

The hypothesis of sluggish diffusion effect in HEAs is the most debated issue. It has been assumed that the rate of diffusion in HEAs is very slow due to the presence of different kind of atoms compared to that of the conventional alloys [12,14]. The mechanism of slow diffusion could be understood by Fig.1.6 (a - d). In Fig.1.6 (c), it can be seen that in HEAs, atom A is surrounded by different kind of atoms. This will lead to larger fluctuation in lattice potential energy (LPE), which affects the activation energy of diffusion in these alloys by hindering the movement of atoms as shown in Fig.1.6 (d) [27]. The seven bond model was used to understand the effect of local potential energy fluctuation on diffusion in CoCrFeMnNi HEAs by Tsai et al. [28].

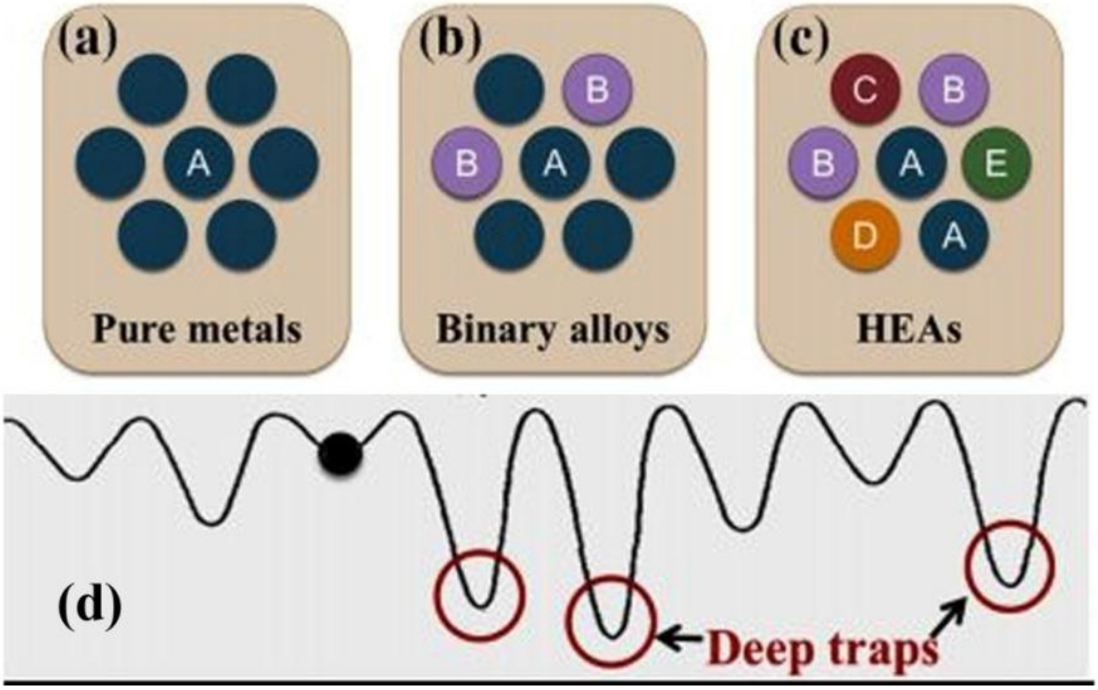

Figure 1.6: Models of nearest neighbours around atoms in (a) Pure metal (b) Binary alloys (c) HEAs and (d) schematic representation of the diffusion path for an atom in HEAs [27].

The mean potential difference of Ni atoms diffusing in CoCrFeMnNi HEAs is 50 % higher than that in FeCoNi alloys (Fig.1.7). However, in recent reports of sluggish diffusion in CoCrFeNi and CoCrFeMnNi HEAs measured by diffusion techniques have demonstrated that the diffusion in HEAs is not so sluggish as to be assumed [29, 30]. Chen et al. [31] studied the competition among elements during mechanical alloying from binary to octanary alloy system and observed that the melting point of the element is one of the governing parameters of alloying rates. Sluggish diffusion effect will provide various advantages in controlling microstructure and properties, i.e. increase in recrystallization temperature, grain growth kinetics, particle coarsening and creep resistance etc.

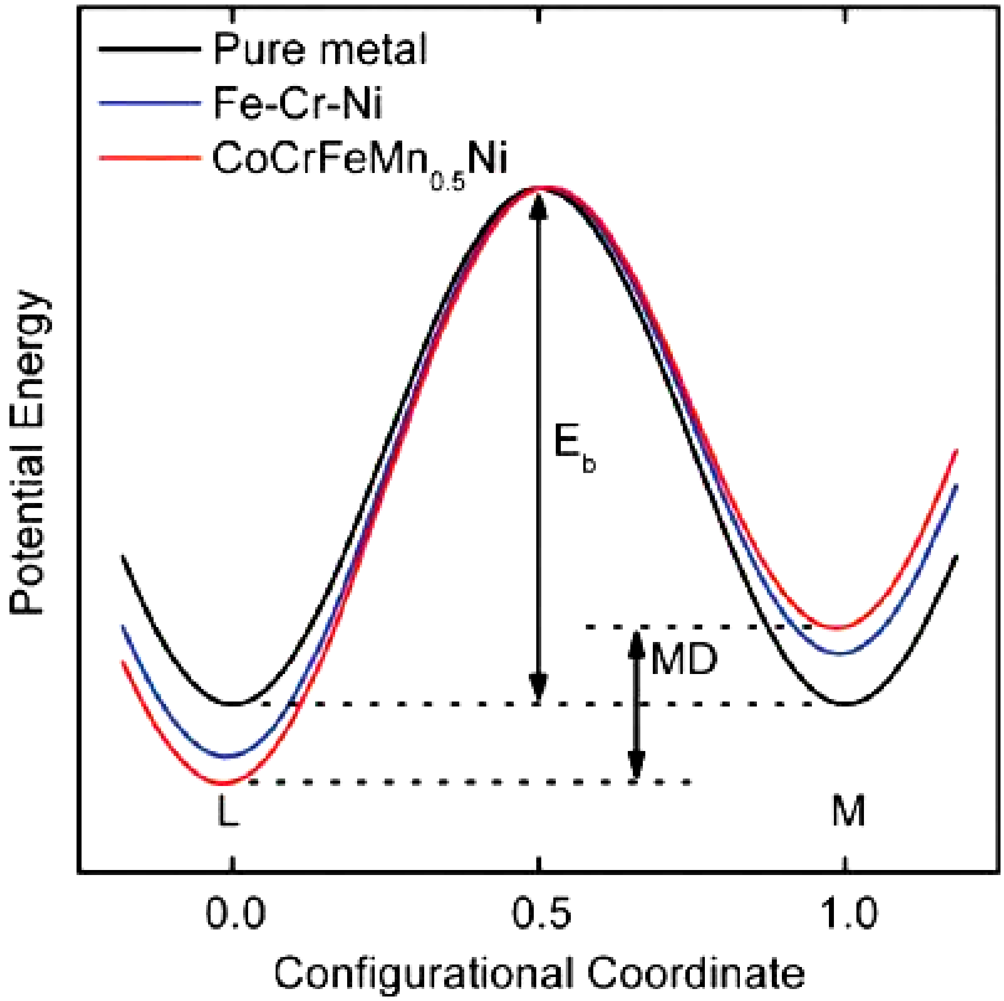

Figure 1.7: Schematic representation of the change in potential energy required for the movement of the Ni atom. For pure metals migration, the mean difference (MD) in potential energy is zero, whereas for HEA is the largest [32].

1.3.4 Cocktail Effect

The unusual and interesting properties of HEAs are arising from the combined effect of all the constituent elements not only form the basic properties of elements. The concept of the multi-metallic cocktail was first introduced by Ranganathan in 2003 in his famous article, “Alloyed pleasures: multimetallic cocktails” [1]. He has mentioned that each phase in HEAs is resultant of mutual interaction of elements at the atomic scale. This atomic-scale composite effect will transfer to micro-scale multiphase composite effect.

Yeh et al. [18] reported the cocktail effect in CuCoNiCrAl$_x$Fe HEAs by varying the Al concentration, as shown in Fig.1.8. It implies that the alloy properties and phase transformation could be adjusted by varying the elemental composition. Alloy showed the change in phases from FCC to FCC+BCC and then BCC structure along with lattice parameter and hardness on varying the Al concentration.

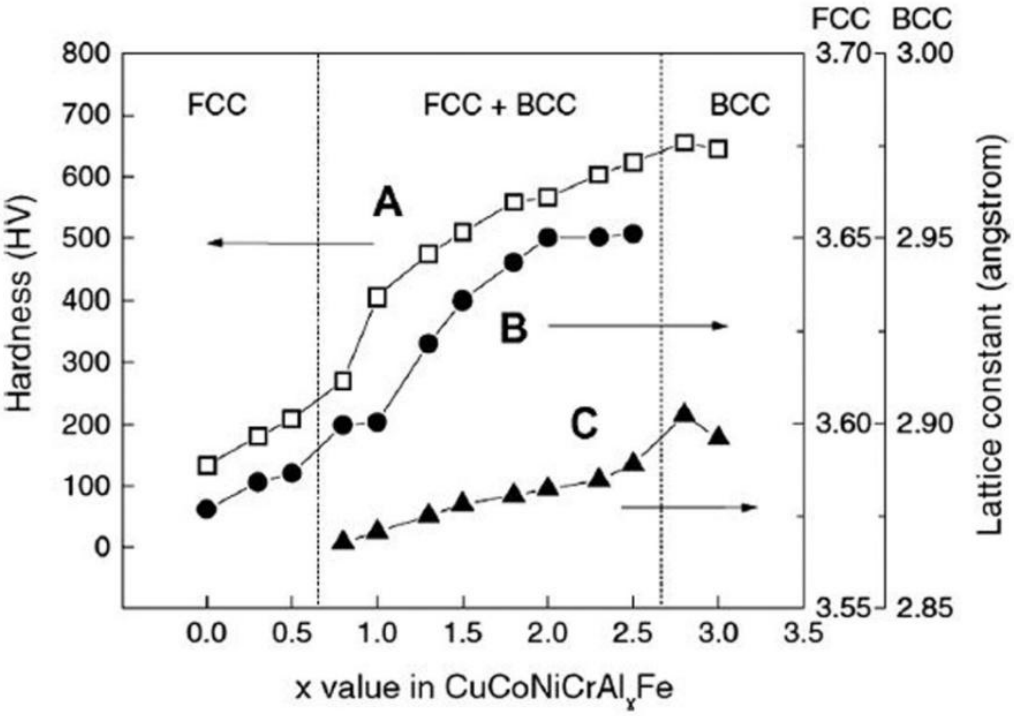

Figure 1.8: Variation in hardness and lattice constants of a CuCoNiCrAl$_x$Fe alloy system with different x values for Al: **(A)** change in hardness **(B)** Variation in lattice constant of an FCC phase **(C)** lattice constant of a BCC phase [18].

1.4 Phase selection rules in HEAs: - A theoretical approach

The phase forming ability of the binary alloys is based on the Hume-Rothery (H-R) rules for a substitutional solid solution. H-R rules have given a simplified connection among factors like atomic size mismatch, crystal structure, valency and electronegativity for binary alloys to form substitutional solid solution phases [33]. These rules are stated as:-

1. The atomic radii of solute and solvent must not differ by more than 15% and for complete solid solubility, it should be less than 8%.
2. The crystal structure of the two elements must be the same.
3. Two elements must have the same valency for extended solid solubility.
4. To avoid the formation of intermetallic compounds, the electronegativity difference of two elements should be similar.

The above-mentioned rules are required to be modified for the HEAs. In HEAs, the concept of solute and solvent is not valid. HEAs are known to form simple solid solution to some extent by proper selection of elements and processing route. In this context, several attempts have been made to predict the phase forming criterion for HEAs. Zhang et al. [34] have introduced three thermodynamic parameters to represent the collective behaviour of constituent elements in these alloys: atomic size difference (δ), mixing enthalpy (ΔH_{mix}) and mixing entropy (ΔS_{mix}). Out of these three parameters, the role of mixing entropy (ΔS_{mix}) has been already discussed in the section (1.2.2). The other parameters could be defined as follows:-

The atomic size mismatch (δ) for the n-elements alloy is expressed as

$$\delta = \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \quad \text{………………………………} (1.4)$$

Here, n is the no. of elements in the alloy system, c_i & r_i is the concentration and atomic radii of i^{th} component and $\bar{r}$ is the average value of atomic radii. The mixing enthalpy is used to characterize the chemical compatibility of the alloying elements in the HEAs. The mixing enthalpy (ΔH_{mix}) of a solid solution is determined as follows:-

$$\Delta H_{mix} = \sum_{i=1, i\neq j}^{n} \Omega_{ij} c_i c_j \quad \text{…..…… ……………} (1.5)$$

where $\Omega_{ij} = 4\Delta H_{ij}^{mix}$ is the regular solution interaction parameter between ith and jth elements, c_i and c_j is the atomic percentage of the ith and jth components and ΔH_{ij}^{mix} is the enthalpy of mixing of the binary equiatomic alloy as calculated using Miedema's semi-empirical model.

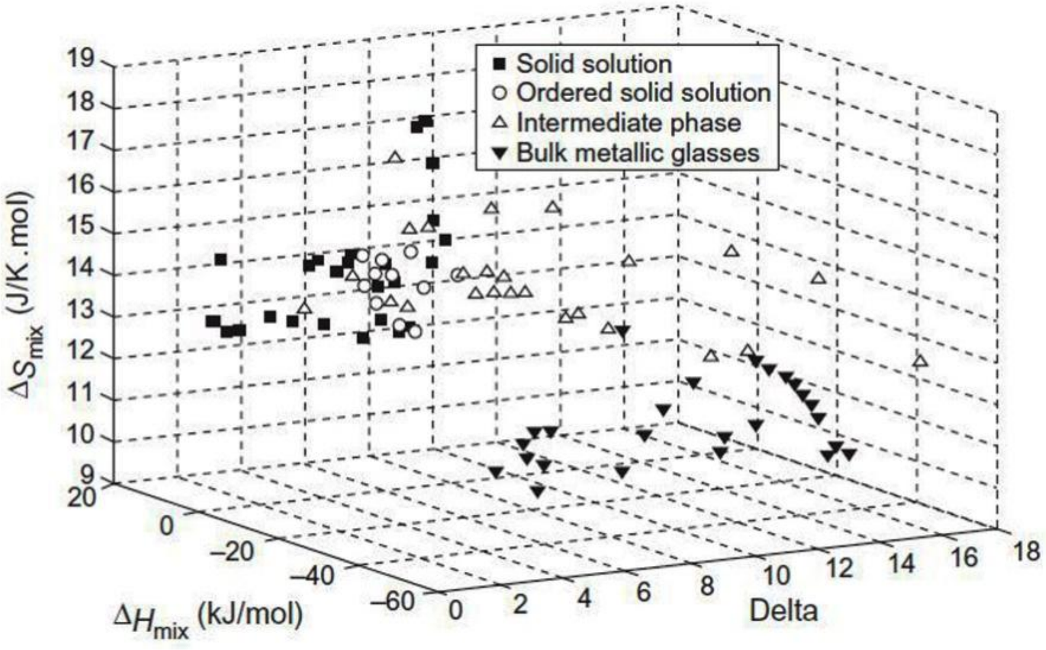

Figure 1.9: The superimposition of entropy of mixing (ΔS_{mix}),enthalpy of mixing (ΔH_{mix}) and atomic size difference, delta (δ) on the solid solution formation in HEAs [34].

Zhang et al. [35] and Guo et al. [36] have studied the effect of these parameters on the solid solution phase formation of HEAs. They have proposed that solid solution phases will be formed when ΔH_{mix}, δ and ΔS_{mix} lie in the range of $-22 \leq \Delta H_{mix} \leq 7$ KJ/mol, $0 \leq \delta \leq 8.5$ and $11 \leq \Delta S_{mix} \leq 19.5$ J/(K.mol) respectively. The superimpositions of these parameters have been shown in Fig.1.9.

Apart from the above-mentioned parameters, Zhang et al. [35] have introduced another thermodynamic parameter (Ω).

This can be determined as follows-

$$\Omega = \frac{T_{\mathrm{m}}\Delta S_{\mathrm{mix}}}{|\Delta H_{\mathrm{mix}}|} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1.6)}$$

where (T_m) is the average melting point of the alloy system. The other two parameters have already been discussed in the above paragraphs. It has been analyzed that the value of (Ω) is positive, and ($\Omega = 1$) is considered to be critical for solid solution phase formation. If the value of ($\Omega > 1$) then the HEAs are mainly composed of solid solutions and ($\Omega<1$), then the alloy is more prone to form intermetallic compounds and shows the segregation effect. In the same line, Zhang et al. [35] reported that values of δ and Ω parameters are larger for multicomponent bulk metallic glasses (BMGs) compare to HEAs. The representation of the phase map of solid solution, intermetallics and BMGs are given in Fig. 1.10. Guo et al. [36] have reported that the calculation of valence electron concentration (VEC) of these alloys gives a general idea of simple structures. It acts as a critical parameter in determining the BCC and FCC phase forming abilities in HEAs. VEC of an alloy could be calculated as follows-

$$\mathrm{VEC} = \sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{c_i}\,(\mathrm{VEC})_{\mathrm{i}} \qquad \ldots\ldots\ \ldots\ldots\ldots\ldots\ldots\ldots \text{(1.7)}$$

where $(\mathrm{VEC})_{\mathrm{i}}$ is for the i$^{\mathrm{th}}$ element. An alloy will stabilize an FCC structure if the VEC ≥ 8 whereas BCC if VEC ≤ 6.87. On the other hand, both the structures (BCC+FCC) will form in between the range.

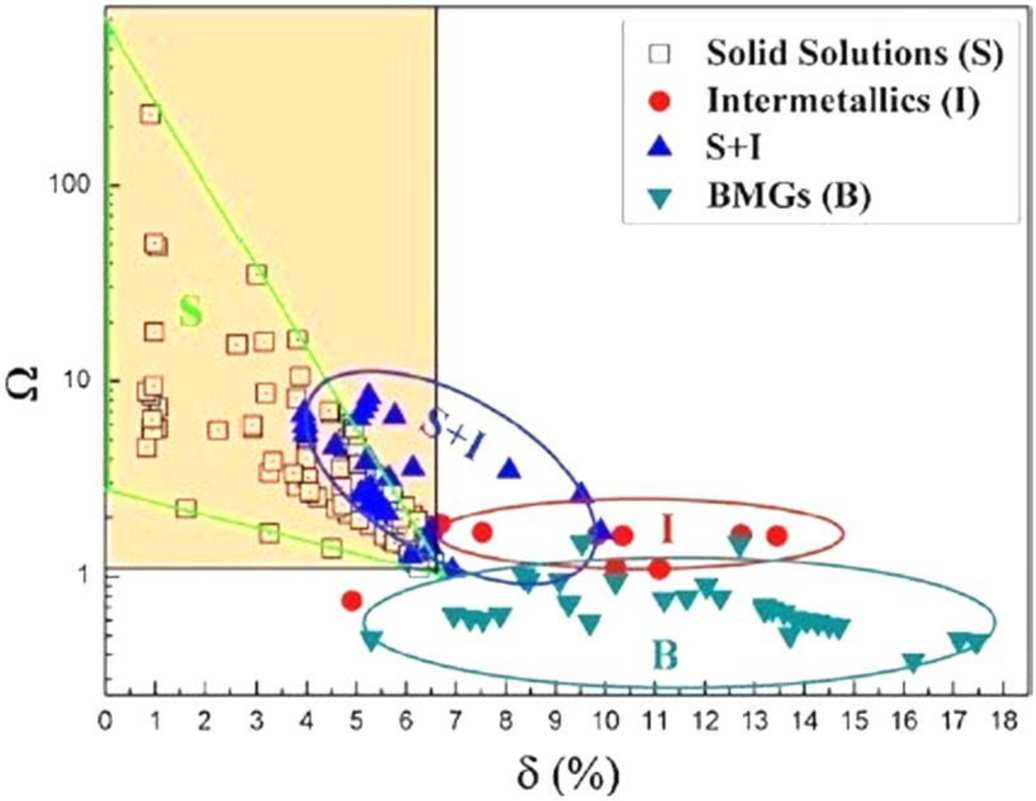

Figure 1.10: Representation of phase maps for solid solution (SS), intermetallics (IM), solid solution + intermetallics (S+I) and BMGs (B) based on δ (%) and Ω parameters for multicomponent alloys [35].

Following the above approach, Tsai et al. [37] have collected the data of phases formed after ageing for a number of HEAs from literature along with the $Al_xCrFe_{1.5}MnNi_{0.5}$ HEA aged at 700 ºC for 20 h. They have proposed the criterion for the σ phase formation when VEC is between 6.88 and 7.84. Formation of phases in HEAs based on VEC calculation has been depicted in Fig. 1.11.

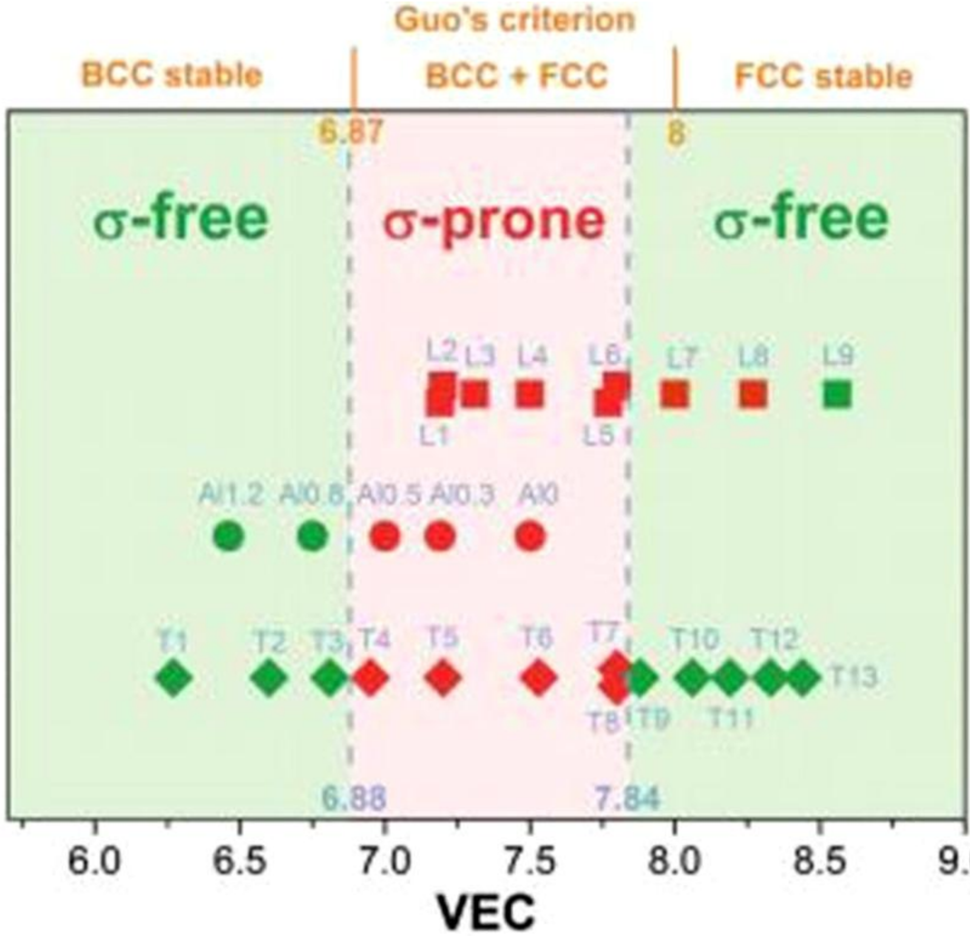

Figure 1.11: Representation of proposed VEC phase map for BCC, FCC and σ based phases in HEAs [37].

1.5 The Miedema Model

Miedema model is a semi-empirical method used for the calculation of enthalpy of formation for the binary system [38]. The constants used for an element has been derived from the properties of the elements and later on adjusted to give the best possible fit to known experimental data along with their physical significance. Therefore, the classification of the model as semi-empirical is justifiable. In order to find out the heat of formation of alloys, Miedema considered atoms as a piece of metal, or in other words, atoms, as they are embedded in pure metals, are considered as a reference system. When two macroscopic piece of metals are brought together to form an alloy, there will be a discontinuity of electron density n_{ws} at the boundary of their (Wigner-Seitz) atomic cell [39]. This discontinuity will be eliminated by providing the required positive energy, which can be determined by n_{ws}. Values for the n_{ws} for transition metals is calculated by taking the ratio of the experimental bulk modulus (K) and molar volume (V). For non-transition metals, values of n_{ws} can be calculated by considering the acceptable assumption of superposition of the charge distribution of free atoms placed at the lattice points. On the other side, a negative contribution to the enthalpy of formation or mixing which is stabilizing with respect to constituent elements arises from the equalization of the chemical potential of the electron charge, ϕ between dissimilar atomic cells. This term is also known as Miedema electronegativity, which is derived from the work function of the pure metals. The relationship between the interaction energy of two blocks of atoms and the heat of alloying of their corresponding binary system assumed to be linear. Miedema et al. [38] called this approach to reflect macroscopic atomic picture.

The generalize equation of heat mixing for ith, and jth binary solution can be described as

$$\Delta H^{ij}_{mix} = \frac{V_i^{2/3}}{(n_{ws}^{-1/3})_{avg}}\left\{- P\,(\Delta\phi)^2 + Q(\Delta n_{ws}^{1/3})^2\right\} \quad \text{..............} \quad (1.8)$$

$$(n_{ws}^{-1/3})_{avg} = \frac{1}{2}\left(\frac{1}{(n^{i}_{ws})^{1/3} + (n^{j}_{ws})^{1/3}}\right) \quad \text{......................} \quad (1.9)$$

where V, ϕ and n_{ws} represents the molar volume, work function and electron density of the constituents. P and Q are two empirical constants. The average value of Δn_{ws} enters the expression as a measure of the difference in electron density at the boundary of the

Wigner-Sietz cell of pure metals; (Δϕ) represents electronegativity difference. The values of the V, ϕ and n_{ws} used for the present work are provided in Table 1.1.

Table 1.1: Parameters used in Miedema's model for calculation of mixing enthalpy (ΔH^{ij}_{mix})

Elements	**n_{ws}**	**$(n_{ws})^{1/3}$**	**ϕ**	**V**	**$(V)^{2/3}$**
Al	2.7	1.387	4.2	10	4.645
Co	5.36	1.740	5.1	6.7	3.556
Cr	5.18	1.720	4.65	7.23	3.741
Fe	5.55	1.760	4.93	7.09	3.693
Mn	4.17	1.601	4.45	7.35	3.782
Ni	5.36	1.740	5.2	6.6	3.520
Ti	3.51	1.513	3.8	10.58	4.823

1.6 Synthesis and processing routes for HEAs

HEAs have been synthesized by various processing routes. These routes can be classified into three major categories: melting/casting route, solid-state processing route and deposition techniques. Out of these three processing routes, melting/casting route is widely used for the synthesis of the HEAs. A large number of HEAs have been produced by vacuum arc melting [40]. It utilizes the arc for melting of different metals at higher temperature. This technique is not suitable to melt the metals of low melting temperature (T_m<600 °C) because of their high vapour pressure, i.e. Mg, Zn and Mn etc. Low melting point metals are usually melted by vacuum induction melting (VIM). VIM utilizes the heat generated by the eddy current induced through electromagnetic induction to melt the charge material. The major drawback associated with the melting/casting route is the formation of the heterogeneous microstructure [41]. This heterogeneous microstructure is the outcome of the slow rate of solidification. This will result in the formation of dendritic (DR) and inter-dendritic (ID) segregations in the microstructure [42]. The typical microstructure of AlNiCo (Cu-Fe) HEA at as cast and annealed state is given in Fig.1.12 with dendrite and interdendritic region. Faster cooling rates can suppress the formation of secondary phases in the microstructure [43]. However, in some cases, it is difficult to avoid the formation of interdendritic regions. Alternatively, annealing at higher temperature and then followed by quenching can produce a single phase at room temperature. In order to get the single-phase microstructure by melting/casting route a faster solidification process, i.e. suction casting, injection casting, drop casting, splat quenching, and melt spinning should be used [44]. Compared to melting/casting route a small fraction of HEAs have been produced by the solid-state processing route [45]. This route basically involves the mechanical alloying (MA), a top-down approach to produce nanocrystalline materials [46]. The mechanism of alloying involves repeatedly flattening, cold welding, fracturing and re-welding of powder particles trapped between the balls [47]. This can be understood as the high impact forces from the balls plastically deforming the powder particles, which ultimately leads to work hardening and fracture. The new surfaces those are created on the fractured particles allow them to weld together and form larger sizes (due to the nature of softness). At the end of milling, particles will have a layered structure of the various combination of starting materials. On further deformation, the powders will become work hardened and fractured. This cycle continues until a stage when the fracture dominates over the cold welding. To this end, particle sizes will remain constant and the structure of the particles is refined steadily. After certain time frame, a steady state condition is attained between the rate of welding and rate of fracturing.

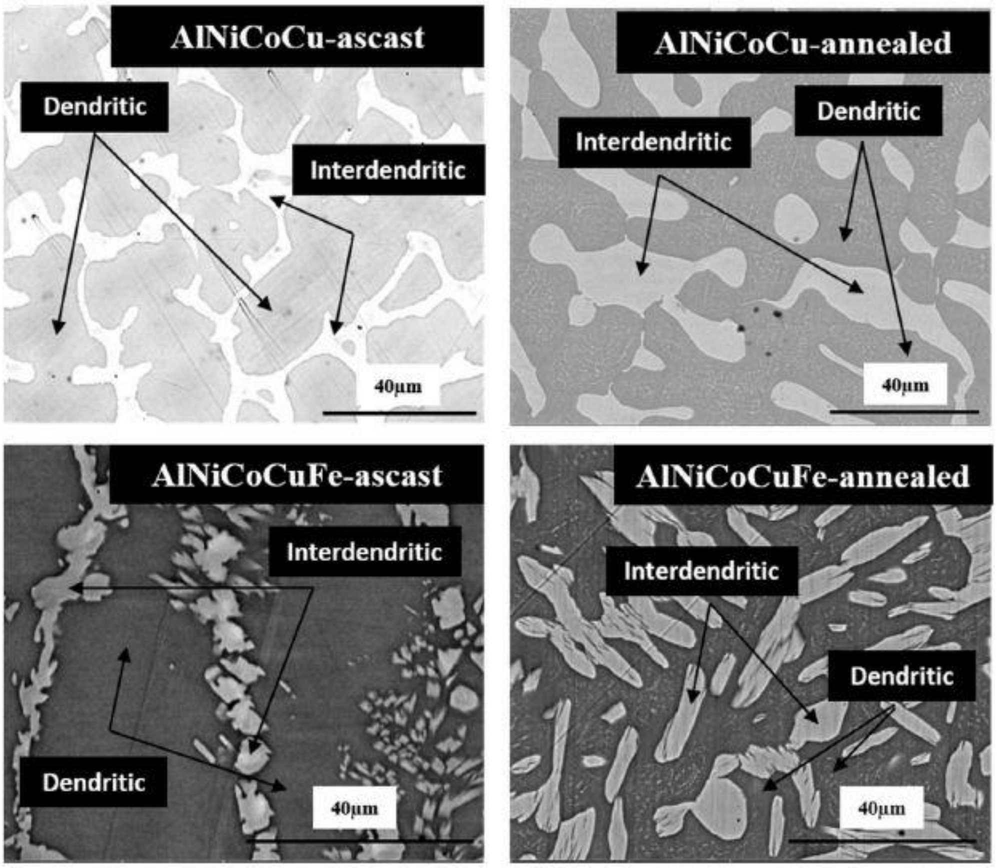

Figure 1.12: Microstructure of as-cast and as-annealed Cu containing alloys showing the dendritic and interdendritic regions [48].

At this stage, particles size distribution will be narrower containing all the constituent elements. The heavy deformation during MA is apparently due to the presence of various defects, i.e. dislocations, vacancies, stacking faults and increased number of grain boundaries. These defects enhance the diffusivity of solute atoms. Further, the refined microstructural feature reduces the diffusivity distance. Diffusion kinetics is also assisted by a slight increase in temperature during milling of the powder [47,49]. This route was originally developed to produce oxide dispersion strengthened (ODS) nickel and iron base superalloys [50]. MA has been successfully applied to synthesize a variety of alloys phases, i.e. solid solutions, intermetallics, ordered compounds, amorphous structures, nanocomposites and quasicrystalline phases. This technique also offers the advantage of extended solid solubility even in immiscible systems. This can be attributed to the enhanced diffusion rates due to the nanosize of the powder component before alloying [51]. Apart from the above-mentioned advantages of MA, this processing route also has the possible problem of powder contamination [52,53]. This problem can be overcome by proper selection of milling media and the use of inert atmosphere during MA [45]. Varalakshmi et al. [54] was the first group to synthesize the nanostructured HEAs [55] by MA. 20 h milled powder showed the formation of single phase BCC structure in equiatomic AlFeTiCrZnCu HEA (Fig.1.13). Vaidya et al. [56] reported a new approach to design HEAs by sequential milling and studied how the phase fraction of evolving phases changes by choice of the initial binary composition. Three different compositions in the binary forms like, B2 (AlNi, AlCo, AlFe), BCC (FeCr) and FCC (CoNi and FeNi) were taken as starting alloys. Other remaining elements of AlCoCrFeNi HEA were added step wise in varying sequence to get the final alloy of AlCoCrFeNi. In all these sequence, final AlCoCrFeNi HEA ended up with the BCC structure except for the FeNi binary composition where the two phase structure of BCC and FCC was reported. The consolidation of the milled powder is challenging and needful for better bulk properties. Sintering plays an important role in densification of these nanostructured materials. Sintering is a process in which bonding of particles takes place by diffusion of atoms. It can be classified as solid state, liquid phase and reactive sintering. Conventional sintering (pressure less) requires more time and leads to considerable grain growth during exposure at high temperature.

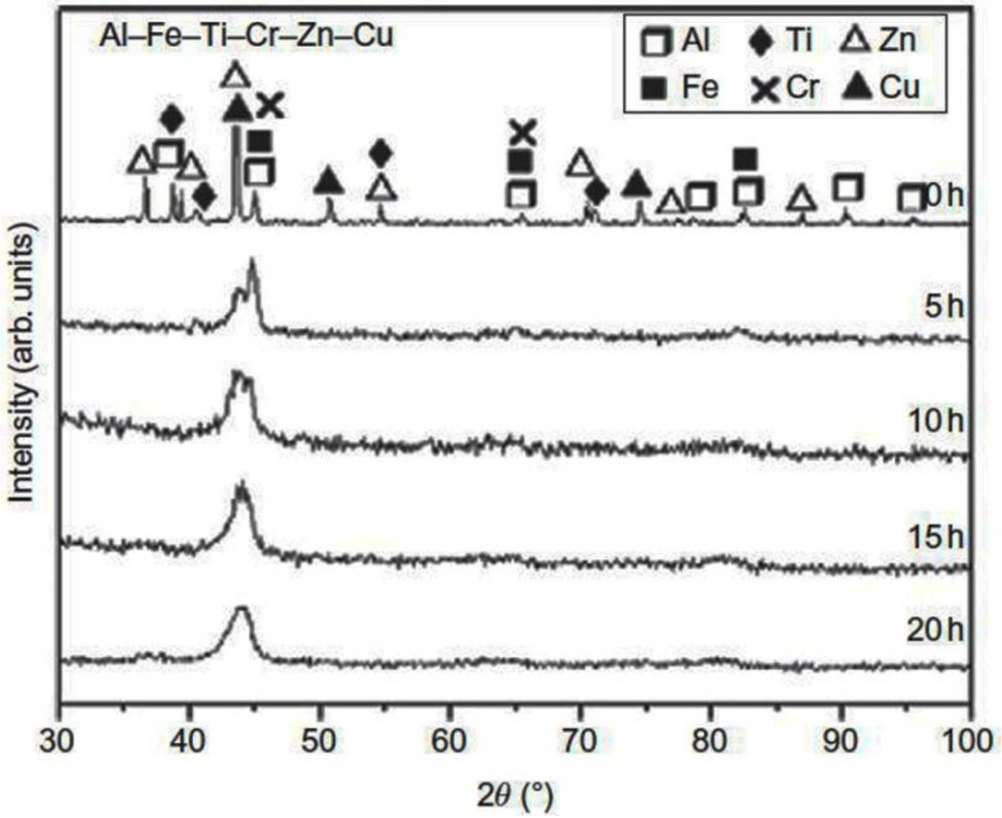

Figure 1.13: XRD patterns of equiatomic AlFeTiCrZnCu HEA synthesized by MA [54].

Spark plasma sintering (SPS) has addressed all the above mentioned issues to some extent and can be used to consolidate the nanocrystalline alloy powder [57–59]. SPS utilizes the high-pulsed current through the alloy powder, which is kept inside the graphite die with the arrangement of simultaneous pressure application. Spark plasma is induced at the particle-particle interfaces in a short duration, causing immediate heating of the powder [60]. This short period of soaking time helps in retaining the nano structured nature in the alloy powder compaction. Praveen et al. [61] have reported the retention of nanocrystallinity in SPSed CoCrFeNi alloy annealed at 700 ºC for 600 h. Wang et al. [62] have found that grain size increases from 10nm to several hundred nanometers during SPS of $CoCr_{2-x}CuFeNi_x$ HEAs. Joo et al. [63] reported that the milled powder of CoCrFeMnNi HEA showed the average grain size of 11nm and after SPS it increased from 0.28μm to 1.87μm at the temperature of 1173 K and 1373 K respectively. So, one should carefully select the sintering temperature and pressure because it affects the nanocrystalline behaviour of the pellet. Apart from the SPS technique, HEA powder can be consolidated by vacuum hot pressing and sintering (VHPs), hot isostatic pressing (HIP) and microwave heating [64–66]. Veronesi et al. [67] studied the effect of Si modifier on microstructure and hardness of microwave heated MnFeNiCu based HEA. Si free HEA showed the microstructures of Fe rich dendritic and Cu rich interdendritic regions and Si added HEA resulted in the formation of an acicular structure with enhanced hardness value.

Deposition route for synthesizing the HEAs have significant contribution in the HEAs literature. This route basically covers the various deposition techniques involving vapour and liquid state. Vapour state deposition technique involves magnetron sputtering and plasma nitriding [68, 69]. Magnetron sputtering is a widely used coating technique for HEAs. This technique produces a thin layer of HEA on the substrates such as mild steel & Al alloys in order to improvise the oxidation, corrosion and wear resistance [70]. The liquid state of deposition involves various cladding techniques such as gas tungsten arc welding (GTAW) and laser cladding by melting and casting of the coating material onto a substrate [5].

In recent years, a new processing route is used to fabricate HEAs, i.e. additive manufacturing (AM), that is known to produce complex near-net-shaped dimensions of materials which are difficult to process by conventional manufacturing. AM is also known as 3D printing, or rapid prototype involves the sequential melting of powder layers followed by rapid solidification. Based on their melting and deposition procedures, AM is classified into three methods i.e. direct laser fabrication (DLF), selective electron beam melting (SEBM) and selective laser melting (SLM) [71]. DLF technique involves the fusion of premelted powder on the deposited surface layer. Fused powder is carried by an inert gas into a laser beam for melting. Through this technique, the highest buildup rates can be used with no restriction on build size. In SLM, laser energy is used to melt the layer of the powder after which a new layer is added [72]. This technique is the most versatile AM process because it can fabricate the wide range of materials and their composites along with the amorphous materials. The SEBM method applies the electron beam energy in place of laser for melting, which can produce better build rates with the compromised surface finish. Brif et al. [73] used the CoCrFeNi HEA powder for SLM of AM and reported that the alloy is stable as a single phase FCC structure with increase in strength and reduction in ductility (from 50 % - 32 % elongation) as compared to its as-cast counterpart. Li et al. [74] have studied the processability, and their emphasis on microstructure evolution and mechanical properties of selective laser melted CoCrFeMnNi HEA powder. Increase in sample density was observed with an increase in laser energy and then it decreased with high laser energy.

1.7 Solid solution formation in HEAs

In quest of formation of HEAs, various compositions have been tried which are expected to results in simple solid solution structures. In some cases, these were taken in equiatomic as well as in non-equiatomic composition [75]. The effect of configurational entropy is more in case of equiatomic alloys compared to non-equiatomic compositions. So the possibility of formation of solid solution phases is more in equiatomic composition compared to non-equiatomic [76]. This difference could be minimized by the proper selection of non-equiatomic composition. On the other hand, non-equiatomic compositions have the flexibility to understand the microstructure and properties evolution by varying the elemental composition [77–79].

1.7.1 Major observed phases in HEAs

HEAs are known to form simple solid solution phases of BCC, FCC, HCP or mixture of BCC and FCC structures. The formation of these simplified phases is attributed to their high configurational entropy, which reduces the free energy of solid solutions. Yeh et al. [12] have emphasized that the solid solution phases at high temperature may undergo phase transformations, such as spinodal decomposition (SD), ordering or precipitation during cooing because the importance of high mixing entropy reduces in stabilizing the solid solution as temperature decreases. Formation of these phases have been discussed briefly in the following sections.

1.7.2 HEAs with BCC structure

HEAs with BCC structure are reported to possess better mechanical properties, i.e. high strength than FCC phase. It has been observed that the crystallization of the BCC phase in HEAs is governed by the binary constituent elements rather than individual elements. These binary pairs are crystallized in the BCC lattice. This can be understood in a more elaborate way by considering most studied AlCoCrFeNi HEA, which has been processed by various techniques [80,81]. This alloy has been found to stabilize the BCC/B2 phase irrespective of the processing techniques. Interestingly, it could be noted that except Cr and Fe, none of the other constituent element has the BCC structure. Qiao et al. [82] have reported that the lattice parameter of AlCoCrFeNi HEA (0.289 nm) is very close to Cr (0.288 nm) and AlNi (BCC based B2 structure). The presence of the superlattice reflection confirmed the presence of ordered B2 type phase rather than Cr.

This was also supported by the phase diagram of Cr and Al in which Cr will remain segregated from the liquid mixture upto 1350 ºC. Formation of the B2 phase was also confirmed by Al-Ni phase diagram, which indicates that at equiatomic composition solid AlNi will form at 1638ºC. It has been found that the Al-Ni binary pair has the largest negative enthalpy of formation compared to other binary pairs in AlCoCrFeNi HEA.

The fact of stabilizing the single-phase BCC structure is more dependent on the binary pairing compared to individual elements could be better understood by considering the example of AlCoCuNiTiZn HEA. None of the constituent element has the BCC structure at room temperature, but alloy form a single phase structure by different processing route [83]. In AlCoCuNiTiZn HEA, Al has the FCC structure, which has the strong affinity to form the binary compounds with AlFe, AlNi, AlCo and AlTi, which crystallizes in BCC lattice due to the formation of the d-p orbital. Wang et al. [84] have mentioned that the concentration of Al plays an important role in promoting the BCC lattice. If the concentration of Al is less the 11 at%, then it promotes the FCC; otherwise, it stabilizes the BCC structure. On the other hand, individual elements consisting of BCC structure also promotes the BCC phase formation. Predictions of phase type in HEAs are done by qualitative manner form constituent elements similar to H-R rules. Generalize prediction is not possible because it is comprehensive, simply due to presence of multi elements.

1.7.3 HEAs with FCC structure

As discussed in the previous section, the formation of the phases in HEAs is more dependent on the binary constituents rather than individual elements. In the case of FCC phase formation, binary constituents crystallize in the FCC structure. For instance, when Al is replaced by Cu in the AlCoCrFeNi HEA, an FCC phase is formed [85]. In CoCrCuFeNi HEA, the binary constituents of CoNi, CoFe, CuNi, CuCo and FeNi all have the FCC structure and stabilizes the FCC phase. Zhang et al. [86] reported the formation of a single phase FCC structure in CoCrFeMoNi HEA by MA. Dwivedi et al. [85] have observed that the CrNbTiVZn HEA formed an FCC phase without having no FCC elements. FCC based HEAs are the good candidate for the high-temperature applications due to the slower diffusion kinetics owing to their close pack structure.

1.7.4 HEAs with HCP structure

Reports on the formation of the single phase HCP structure in the HEAs are very limited. In most of the cases, the crystallization of the HCP structure is accompanied by other phases. Li et al. [88] have reported the formation of HCP phase along with the quasicrystalline phase in as-cast $Mg_x(AlCuMnZn)_{100-x}$(x=20,33,43,45.6,50) alloys [89]. Miracle et al. [14] have reported that the HCP phase occurs only in 7 alloys, which are coming from three different alloy families, i.e. light metal, 4f transition metal, and other CCAs. It has been found that there are no common elements in these alloys family. No single phase HEA has been synthesized with a HCP structure through MA [45].

Along with the single-phase HEAs, there are numerous reports that are available on more than two phases. It has been found that most of the multiphase HEAs are processed through equilibrium processing route. Non-equilibrium processing route, i.e. MA, is more likely to form single phase HEAs due to extended solid solubility. Numerous reports on HEAs have suggested that the formation of the simple random solid solution phases cannot be only governed by the configuration entropy in cases where the atomic size difference between the atoms are large or when there is a strong attraction between certain elements. In such cases, various intermediate phases such as B2, $L1_2$, sigma (σ) phase and Laves phases have been reported in the literature more frequently [5,90-92]. Mohanty et al. [80] have processed the AlCoCrFeNi HEA by MA and reported the evolution of FCC and BCC phase. The sintered alloy showed the phase separated microstructure consisting of Al-Ni rich $L1_2$ phase, tetragonal Cr-Fe-Co based σ phase along with FCC solid solution phase. Yadav et al. [91] have reported the formation of a single Laves intermetallic phase in equiatomic TiZrVCrNi HEA by conventional melting and melt spinning technique. Formation of micron size Laves phase of C14 type in as-cast alloy and nanocrystalline Laves phase in melt-spun alloy was observed.

1.7.5 Amorphous HEAs

After the discovery of HEAs, attempts have been made to prepare glasses and amorphous alloys with high configurational entropy. This was done by replacing the elements of similar nature to glass forming alloys [93]. Ge et al. [94] reported the formation of the amorphous phase in AlCuNiTiZr HEAs based on $Cu_{60}Zr_{40}$ binary glass composition fabricated by MA. Milling for longer hours has also shown the formation of amorphous phases in HEAs [31,95]. Solid solution phases in AlCoCrCuFeMoNiTi HEA showed the formation of an amorphous structure on extending the milling hours [96,97]. The heat-treatment of the amorphous HEAs leads to the formation of simple solid solution phase or complex phases. It has been reported that the AlBCoFeNiSi and AgAlBFeNiSi HEAs show better phase stability than AlBFeNiSi and AlBCuFeNiSi HEAs on annealing [98].

1.8 Thermal stability

Thermal stability of the multicomponent alloys is one of the alluring fields for the research community. This property of the alloys is the key for them to be qualified for higher temperature application. The nanostructure nature of the alloy at a higher temperature is a positive attribute to good mechanical properties as well [99,100]. In this regard, HEAs are getting more attention and emerging as a new area of physical metallurgy [101]. Alloys formed by non-equilibrium processing route, i.e. M.A showed the formation of metastable phases at room temperature. Their metastable phases may change and forma new structure when subjected to heat treatments. For the MAed HEAs, the main aspect of thermal stability is to retain the fine microstructure, slower grain growth and controlled phase formation. Table 1.2 lists the phase stability of the various HEAs processed by MA. Varalakshmi et al. [54] have reported the high thermal stability in AlCoCuNiTiZn HEA by retaining the BCC structure upto 800ºC for 1h. Praveen et al. [61] have observed the sluggish grain growth behaviour in CoCrFeNi alloy at 900ºC for 25 days. Christofidou et al. [102] have reported the stability of phases in CrFeCoNi and $CrMn_xFeCoNi$ HEA upon thermal exposure at 500,700 and 900ºC for 1000h. Formation of $M_{23}C_6$ like carbide was observed in the solid solution of FCC phase, however, when the concentration of Mn increases from 11.11 to 20 at%, the alloy showed the formation of sigma phase at 1000 h heat treatment. On the other side, equilibrium processing routes, i.e. melting/casting, formed the equilibrium structure, and most of them retained their structures during thermal treatment. Evolutions of new secondary phases have also been reported in the literature. Table 1.3 lists some of the AlCoCrFeNi based HEAs processed by melting route and their microstructural stability during heat-treatments. These phases were broadly dependent upon alloy composition, processing conditions, initial phases and heat-treatment conditions.

Table 1.2: Phase stability of equiatomic high-entropy alloys (HEAs) formed by MA and subsequent consolidation/ heat-treatment.

Alloy	**Processing route**	**Phases**	**Phases after consolidation/ heat treatment**	**References**
AlFeTiCrZnCu	MA	BCC	Sintered-800 °C for 1h -BCC	[54]
CuNiCoZnAlTi	MA	BCC	Annealed -800°C for 1h- BCC HP 800°C- Major BCC and two minor FCC	[83]
CoCrFeNiCuAl	MA	BCC	Annealed-600& 1000°C for 1h- BCC &FCC respectively	[103]
CoCrFeNiAlTi	MA	BCC+FCC	Annealed- 600&1000°C for 1h- two BCC SPSed- 800°C-orderd BCC , BCC&FCC	[104]
AlCrCuFeNiZn	MA	BCC	Hot pressed-850 °C for 2 h- BCC,FCC 1&FCC 2	[105]
CoCrFeNiMnAl	MA	BCC	SPS-800 °C- BCC&FCC	[106]
AlCoCrFeNi	MA	FCC+BCC	SPS- Ni-Al rich $L1_2$& Co-Cr-Fe rich σ	[80]
AlCoCrCuNiFeZn	MA	BCC	Hot pressed- 850°C for 2h- BCC	[107]
AlCoCrFeNi	MA	BCC	Annealed -500°C for 1h- Stable BCC &900°C- FCC SPSed- 900°C- FCC+BCC	[108]

CoCrFeMnNi	MA	FCC	SPSed-900&1000ºC-FCC	[63]
(1) AlCoCrCuFe (2) NiCoCrCuFe	MA	(1) BCC (major) and FCC (minor) (2) FCC (major) and BCC(minor)	Both SPSed-900ºC Ordered BCC (B2 phase),Cu rich FCC, sigma phase (σ) Two FCC and sigma phase (σ)	[109]
CoCrFeNi	MA	Major FCC &minor BCC	SPSed- 900ºC FCC & secondary phases-Cr_7C_3&Cr2O3 Annealed-sintered sample at 900ºC for 600 h- no change in phase	[61]
(1) CoCrFeNi (2)CoCrFeMnNi	MA	(1)FCC& tungsten carbide (WC) (2)FCC&WC	SPSed-900ºC FCC&Cr_7C_3 FCC&Cr_7C_3 Annealed- MAed powder for 96 h FCC&Cr_7C_3 (2)FCC&Cr_7C_3	[110]
CoCrFeMnNi	MA	FCC&BCC	SPSed-800ºC FCC	[111]
WMoNbZrV	MA	BCC	HT-700ºC-BCC	[94]
MoNbTaW	MA	BCC	HT-1200ºC-BCC	[112]
NbTaTiV	MA	BCC	SPSed-1700ºC-BCC	[113]

Table 1.3: Brief summary of microstructural stability in AlCoCrFeNi based HEAs processed by melting / casting route.

Alloy	**Processing route**	**Heat-treatment condition-Microstructure**	**References**
AlCoCrFeNi	Arc melting	As cast-BCC	[114]
$Al_{0.3}CoCrFeNi$	Induction melting	As-cast -FCC + spherical nano-precipitate of $L1_2$ ordered structure Ageing at 700& 900°C for 72 h-FCC +B2	[115]
$Al_xCoCrFeNi$ $(0 \leq x \leq 2)$	Arc melting	As-cast (heat-treatment-1100°C -24 h) - FCC, FCC+BCC,BCC	[116]
$Al_xCoCrFeNi$ (x= 0-2.0)	Arc melting	As-cast -BCC-FCC	[117]
$Al_{0.7}CoCrFe_2Ni$	Suction casting	As-cast -B2+BCC+FCC	[118]
AlCoCrFeNi	Arc melting	As-cast - BCC+B2 Heat-treatments at 650°C-BCC+B2, 975°C-B2+FCC+σ,1200°C-BCC+B2+FCC	[119]
$Fe_{36}Mn_{21}Cr_{18}Ni_{15}Al_{10}$	Arc melting	As-cast -Dual phase BCC1+BCC2 Annealing 1200°C for 24 h- No Change in structure	[120]
$Fe_{34}Cr_{34}Ni_{14}Al_{14}Co_4$	Arc melting	As-cast - Dual phase B2+BCC	[121]
AlCoCrFeNi	Arc melting	As-cast - Dual phase B2+BCC,Annealed- 850°Cfor3 h-B2+BCC&FCC+σ	[90]
$Al_{0.7}NiCoFe_{1.5}Cr_{1.5}$	Suction casting	As-cast - B2+BCC matrix Annealed- 673-1273K followed by water quenching- Dual phase upto 773K-BCC+B2+FCC	[122]
AlCoCrFeNi	Induction melting	As-cast - BCC matrix of Al-Ni rich (dendrites) +precipitates Fe-Cr rich (interdendritic)	[81]

1.9 Properties of HEAs

The vast ranges of composition design flexibility of HEAs have an immense scope to manipulate the properties. Many of their properties are attributed to the core effects of HEAs, which were discussed previously. This section deals with the various properties of HEAs as follows-

1.9.1 Mechanical behaviour of HEAs

Major accomplishments for mechanical properties have been established, especially in the 3d transition elements by controlling the composition and microstructure of the HEAs. The better mechanical properties of MAed HEAs are governed by different strengthening mechanism compared to the HEAs produced by melting/ casting route. In the melting /casting route, HEAs show their strength primarily derived from solid solution and precipitation strengthening. $Al_xCoCrCuFeNi$ HEA is the widely studied alloy system in the literature [20,123]. The variation of hardness from 133 HV to 655 HV by varying the Al concentration(x=0-3) has been shown in Fig. 1.14 [124]**.** The high value of hardness is attributed to lattice distortion effect as Al is the largest atom among the constituent elements. In addition, Al has a strong affinity to form the binary compounds with other elements, which strengthen the solid solution. In the same line, increasing the concentration of Al, favours the formation of the BCC/B2 phases, which are stronger than the FCC phase. Fig.1.14 also showed the variation of crack length with the transformation of phase from FCC to BCC. Increase in length was observed for the BCC phase, which indicates in increase in hardness.

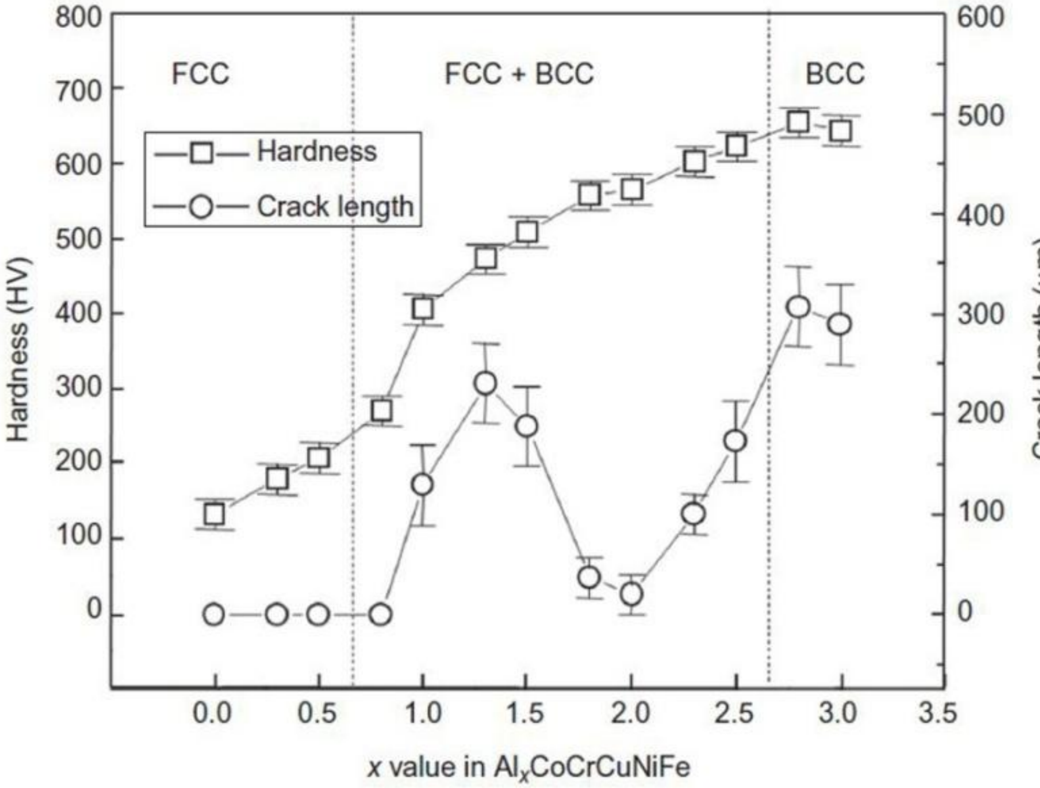

Figure 1.14: Variation of hardness (HV) and crack length around the indent by varying the Al concentration in the $Al_xCoCrCuNiFe$ alloy system [124].

The hardness of most of the HEAs is affected by their crystal structure and phases present in the alloy. The typical range of hardness values for the different phases is given in Table 1.4. Senkov et al. [125] have found the small effects caused by Al addition such as AlNbTaTiVZr and AlNbTaTiZr HEAs, whose hardness range from 30 - 81 HV, respectively. Similar effects were observed for compressive properties. For instance, the effect of Al addition on yield strength (σ_{yc}) is very large in AlCoFeNiSi HEA with the variable range of 2073 MPa [126]. On the other hand, in some cases, the effect is less for examples in AlNbTaTiVZr system whose variation range is 70 MPa. In summary, the effect of Al addition on mechanical behaviour can affect the HEAs in three ways, i.e., influencing phase transformation, introducing solid solution strengthening and modifying the phase structure [127].

Table1.4: Typical range of hardness values in HEAs based on their phase evolution [22]

Type	**Phases**	**Hardness (HV)**
BCC and derivatives	BCC, B2, Heusler	300-700
FCC and derivatives	FCC, $L1_2$, $L1_0$	100-300
Intermetallic phases	σ, Laves, η	650-1300
Valence compounds	Carbides, borides, silicides	1000-4000

Wu et al. [128] have designed the equiatomic binary, ternary, quaternary and non-equiatomic quinary alloys from the elements of Co, Cr, Fe, Mn and Ni and studied the temperature dependent mechanical properties of all alloys. It has been found that all the binary, ternary, quaternary and non-equiatomic quinary alloys have similar properties as the CoCrFeMnNi HEA as long as Cr is included. However, removing the Cr content decreases the strength relative to CoCrFeMnNi. Formation of the σ phase was observed when the concentration of the Cr concentration is above 26 at%, which increases the strength. Zongyang et al. [127] have reviewed the elemental effect on mechanical properties of HEAs. It has been observed that the Fe and Ni in most of the cases have shown the negative effect on the strength of the HEAs, while elements like Mo, V and Si have the positive effect on the strength. Zhou et al. [129] have investigated the mechanical properties of $AlCoCrFeNiTi_x$(x=0, 0.5, 1, 1.5) HEA at room temperature. An alloy of Ti_{05}exhibits the high values of yield and fracture strength with a slight decrease in ductility, i.e. 2.26GPa, 3.14GPa and 23.3% respectively. The better properties are attributed to the solid solution strengthening mechanism because of the Ti atoms. Having the larger atomic radius, Ti distorted the lattice significantly and increased the solid solution strengthening of the alloy. Munitz et al. [119] have studied the effect of heat treatment on mechanical properties for AlCoCrFeNi HEA. They have reported the microhardness of the dendrite core (DC) regions remains almost constant (4.5 GPa) after heat-treatment in the range of 850-1100ºC. The hardness value increases (up to 5.4 GPa) after heat-treatment at 1200º C at inter dendritic regions and it was attributed to the precipitation of the new nano-sized particles. In the same line, the variation of compressive yield stress (σ_y) was observed with the heat-treatment temperatures. As-cast alloy showed the yield stress (σ_y) of 1380 MPa, which increases upto 1690 MPa after heat treatment at 975ºC; this resulted due to the formation of the σ phase which are brittle in nature. Fu et al. [130] reported the high value of strength (2988 MPa) and hardness (~ 704 HV) of $Co_{20}Ni_{20}Fe_{20}Al_{20}Ti_{20}$ HEA produced by MA and SPS. These high values of mechanical properties are due to the formation of the B2 phase and the presence of Al_3Ti particles in FCC matrix. Chuang et al. [131] studied the wear behaviour of $Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti$ HEA. They have compared the wear resistance of HEA to two conventional wear resistant steels. The HEA is found to have the wear resistance of at least 2 times higher than the conventional steels with similar hardness. Yadav et al. [132] have investigated the wear resistance and friction coefficients of mechanically alloyed AlCrFeMnV and CuCrFeTiZn HEAs on the addition of Bi and Pb as soft dispersoids. In both the cases, wear resistance was increased by ~20% with significant decrease in friction coefficient.

1.9.2 Physical behaviour

HEAs have been reported to have interesting physical properties. Ma et al. [133] have observed the ferromagnetic properties in the $AlCoCrFeNb_xNi$ (x=0, 0.1, 0.25, 0.5, and 0.75) HEA because their permeability (χ) lies in the range of 0.02-0.003, while $Ti_xCoCrCuFeNi$ and TiCoCrCuFeNi alloys exhibit superparamagnetic properties due to the formation of nano-particles in the alloys. Zhang et al. [103] have studied the annealing effect on the structure and properties evolution of CoCrFeNiCuAl HEA. HEA showed better soft magnetic properties in as-cast and annealed state. The values of saturated magnetization (M_s), remanence ratio (M_r/M_s), and coercivity (H_c) of the as-cast and as annealed alloys are estimated as 38.18 emu/g, 5.98 %, 45 Oe and 16.08 emu/g, 3.01%, 15 Oe respectively. These values are quite comparable to the soft ferrite and can be used as soft magnetic materials. The reduction in the saturation magnetization (M_s) of the as-annealed alloy resulted from the coarsening of the grains and phase transformation.

1.10 Prospective applications of HEAs

Form the HEAs literature it could be understood that the suitable alloy selection and proper processing might lead to the outstanding properties for intended applications. The scientific curiosity on HEAs has convinced the researchers that these alloys have the potential to replace the conventional alloys in difficult and stringent operating conditions by providing superior performance with increased service [18]. Some of the application of HEAs in the demanding field of the current state as follows-

1. High-temperature strength, oxidation resistance, hot corrosion, and creep resistance for engine materials.
2. Enhanced room and elevated-temperature strength and toughness, wear resistance and good impact strength with low friction for tool materials.
3. Marine structures require improved corrosion resistance and erosion in sea water.
4. Light transport materials demands improved specific strength, toughness, fatigue strength, creep resistance and good formability.
5. Materials with lower density, higher strength and good resilience, i.e., for golf club head materials.

6. Constant thermal coefficient of resistivity and thermally stable magnetization for electric and magnetic materials.

1.11 Motivation

Development of the new materials for technological applications is always an exciting field for the materials community. In this connection, HEAs, a new and expanding field of materials science, are getting more attention due to their expected capabilities to meet the technological promises. Due to the design flexibility of these alloys, several compositions have been developed by different processing routes:- melting and casting, solid-state processing, deposition techniques etc. Out of these, melting/casting is a widely used technique to produce HEAs. Application of solid-state processing technique, i.e. MA to produce HEAs with homogeneous microstructure is being widely employed. In fact MA is a well established solid state, non-equilibrium, top-down approach to produce nanocrystalline materials. However, the underlying behaviour pertaining to the atomic scale processes are not understood well.

Nano-structured materials are reported to posses the attractive properties, which makes them the potential candidate for ambient temperature applications. However, these materials are prone to change their structures in the presence of external stimuli such as temperature and pressure. To this end, HEAs have been demonstrated to be interesting materials. Even though there has been a considerable effort made to develop these alloys, a unified picture is still illusive. In addition to that, the phases and microstructural evolution over temperature-time space are the important aspects to be understood as this would eventually play an important role in the application of these alloys. Thus the present work is being carried out to study the phase and microstructural evolution with their stability in both equiatomic and non-equiatomic compositions of HEAs.

1.12 Objectives

The objectives of the thesis are as follows:

- To synthesize nanocrystalline AlCoCrFeNi, AlCoCrFeNiMn & AlCoCrFeNiTi HEAs by mechanical alloying (MA).
- To study the effect of individual elements during phase evolution and determination of the structure of the alloy.
- To investigate the thermal stability of the milled powder.
- To understand the consolidation behaviour of the milled powder with microstructure and phase evolution.
- To investigate the phase, microstructure, thermal stability and mechanical properties of non-equiatomic $Fe_{40}Cr_{25}Ni_{15}Al_{15}Co_5$ HEA processed by induction melting.