

INTRODUCTION AND LITERATURE REVIEW

1.1 Historical preview of alloying

The importance of materials in human life can be understood based on human development along the materials time scale. The accidental and rather the most remarkable invention was arsenical bronze (3000 BC), the first alloy of copper and arsenic [1,2]. Later an intentional alloying of copper and tin was done, which gave birth to the Bronze age (2500 BC) [3]. Due to easy reduction of copper, tin, mercury, lead and iron from their respective ores, the subsequent ages of bronze, iron, and steel can be seen in **Figure 1.1**. Either the availability or the complex reduction process, the development of the material world was slow. But after the industrial revolution in 1750, the pace of material development geared up and many new elements and alloys were developed based on their applications as can be seen in **Figure 1.1**.

Since the accidental discovery of the bronze alloy, humans have prepared alloys by considering only one or two principal alloying elements and by adding other elements in minimal amounts. Due to this, at present, the alloy world is dominated by iron-, aluminium-, copper-, nickel-, titanium- etc. based alloys, which consist of these elements as principal elements. The most widely used alloys of the modern era are steels, which have iron as the primary element while the other elements are added to enhance/optimize properties such as corrosion resistance, fatigue strength, toughness, magnetism etc. needed for specific applications. Thus, the alloying strategy of the humans has been the addition of secondary elements in small amounts to any principal component to enhance the properties of the principal elements. This conventional alloying strategy of adding secondary element to any one or two principal elements to strengthen the properties of the principal components is being practised for millennia.

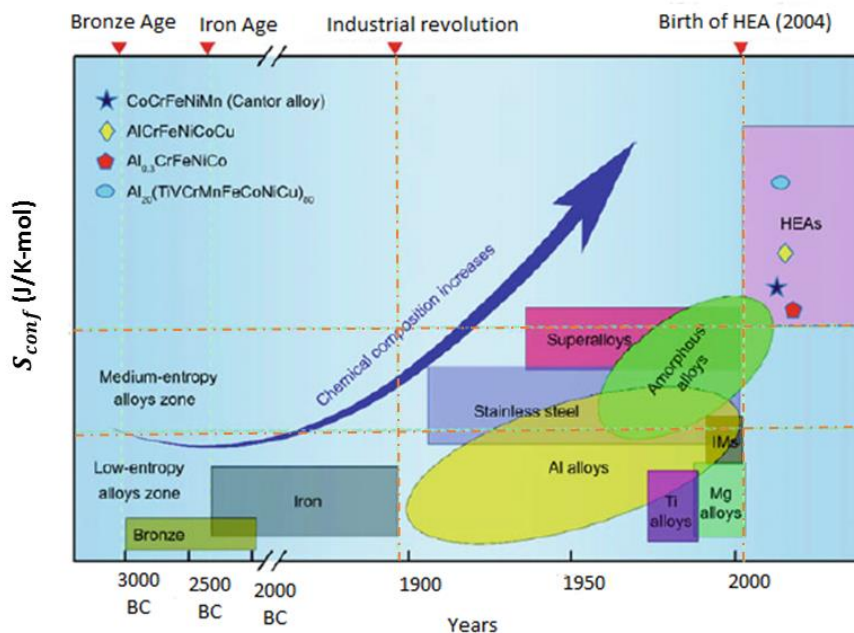


Figure 1.1: Materials development with increasing entropy [4]

Based on the binary and ternary phase diagrams information, development of the multicomponent alloys was not encouraged. Stoichiometric compounds or intermediate phases form in most of the binary phase diagrams. For example, Al-Cu-Zn ternary alloys have approximately 20 intermetallic phases. On analyzing their binary counterparts, we found that Al-Cu, Al-Zn and Cu-Zn forms 13, 0 and 5 intermetallic phases respectively. Such examples indicate that on increasing the number and concentration of elements, one is likely to end up in a large number of intermetallic phases in the system.

The multi-principal alloys have been practised in India for the last 3000 years as reported by archaeological surveys [4,5]. These alloys were composed of elements present in antiquity, i.e., Copper (Cu), Gold (Au), Silver (Ag), Lead (Pb), Tin (Sn), Mercury (Hg), Zinc (Zn) and Iron (Fe) in equimolar or near to equimolar compositions as stated in the *Shilpshastra*. *Panchaloha* (an alloy of five elements containing Cu, Au, Ag, Pb and Zn) and *Ashtadhatu* (an alloy of eight elements containing Cu, Au, Ag, Pb, Zn, Sn, Fe and

Hg) are practised using the lost wax method to prepare idols. Few sculptors in southern India carry out this practice, but they have modified the composition depending on the cost of the elements, i.e. amount of Au and Ag is reduced compared to other elements. Now-a-days, the composition of the *panchaloha* is copper, brass and lead in 29:2:1 ratio [4].

Franz Karl Achard, a German scientist in the late eighteenth century (modern era) was probably the first person to study equimolar multicomponent alloys with five to seven elements as reported by Smith [6]. He prepared over 900 equimolar alloys having 11 different elements. He published a report of basic properties (hardness, density etc.) without any discussion on concepts and results. Approximately after two centuries of the Franz Karl Achard, Brian Cantor [7] started work with one of his undergraduate student in 1981, with a concept of exploring the central region of the multicomponent phase diagram. They prepared the first equiatomic multi-principal element alloy consisting of 20 elements. On analyzing the microstructure and composition of the prepared alloy, they found that an FCC phase formed as primary phase while intermetallic phases formed were dispersed in it. On doing compositional analysis of the primary FCC phase, they found that it contains mainly Cr, Mn, Fe, Co and Ni. Based on the above observation, he prepared CrMnFeCoNi equiatomic alloy having single-phase FCC structure, which was later termed as Cantor alloy. This work was submitted as an undergraduate thesis at Sussex University [8,9]. Similar work was repeated by another undergraduate student under Cantor in 1998 was also recorded as a thesis at Oxford. Finally, Isaac Chang repeated the same work in 2000 and presented his work at the conference in Bangalore. Later it got published in the year 2004 [9].

J. W. Yeh in Taiwan independently started working on equiatomic multicomponent alloy in 1996 with one of his master's student. He has a different concept of choosing the multicomponent alloy in equiatomic composition. His central idea was to use high configurational entropy of mixing in preparing equiatomic or near to equiatomic composition, to reduce the possibility of formation of intermetallics. He was expecting the reduced number of simple phases due to the high entropy of mixing in the multicomponent alloys. He investigated microstructure, hardness and corrosion resistance of the as-cast and annealed alloys. Out of the 40, he published 20 alloy systems in his thesis [3,8,10]. After this work, two more master's students carried out similar work and published their work in their theses [11,12]. Yeh and his group members published four papers in 2004 [13–16]. The term 'High Entropy Alloys' was coined by Yeh et al. [17]. S. Ranganathan in 2003 [2], published an article entitled "Alloyed pleasures – multimetallic cocktails" discussing three new multicomponent fields; bulk metallic glasses by Inoue, gum metals by Saito and HEAs by Yeh. This is the first such publication which talks about the HEAs for the first time and opens a whole new world of unexplored multicomponent alloys [2].

Since the independent effort was made by [17] as high entropy alloy and [9] as a multi principal alloy in 2004, now the alloying strategy of the researchers has changed from conventional to the new design of alloys. Cantor et al. [7] pointed out that the number of alloys studied using traditional approach is relatively small compared to those studied using the new strategy. Conventional alloys are clustered around the corners and edges of the phase diagram, restricting the possible number of alloys compared to the vast space unexplored in the central regions of the phase diagrams.

1.2 Definitions of HEAs

Yeh [17] has coined the name of HEAs and defined them as alloys composed of five or more principal elements in equiatomic or near to equiatomic ratio (**Figure 1.2**). In the same paper, he expanded the definition by saying that the principal element may have concentration lying between 35 at% to 5 at%. Later in 2006, [18], the above description was modified by including minor elements less than 5 at% may be added to alter the properties of base HEAs. This definition is solely based on the composition of the chosen alloy.

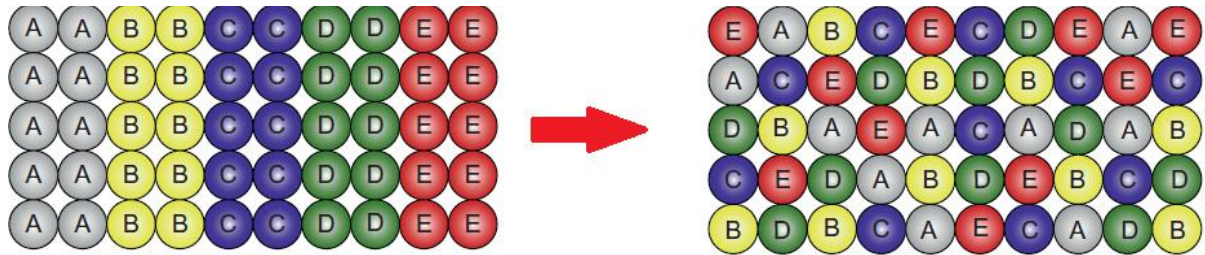


Figure 1.2: Schematic representation of 5 elements mixed to form a quinary random solid solution [19]

Yeh in 2006 [18], came up with a new definition of HEAs based on the magnitude of ideal configurational entropy as represented in **Figure 1.3**, which can be described as follows:

Low entropy alloys: $\Delta S_{conf} \leq 0.69 R$; binary systems.

Medium entropy alloys: $0.70 R \leq \Delta S_{conf} \leq 1.61 R$; ternary and quaternary systems.

High entropy alloys: $\Delta S_{conf} \geq 1.61 R$; Quinary and higher order systems.

The entropy-based definition assumes that the alloys are in a liquid state or high-temperature solid solution state where due to thermal energy different elements occupy random positions within the alloy structures.

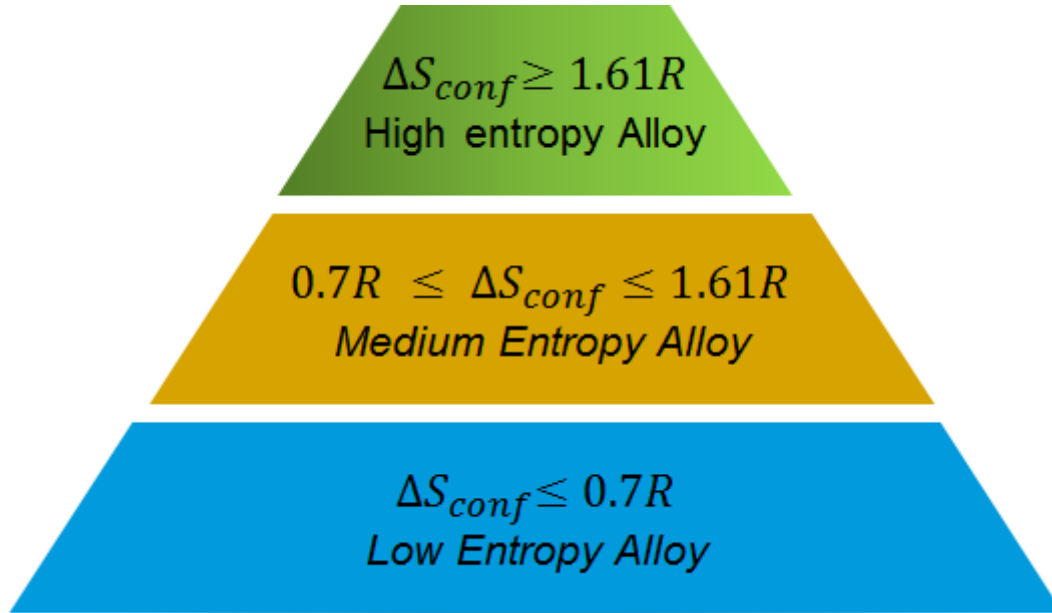


Figure 1.3: Entropy based definition of HEAs

When both the above-mentioned definitions are combined an ambiguity can be seen, i.e. minimum ideal configurational entropy for a quinary alloy is 1.36 R (for an alloy with 35% A, 35% B, 20% C, 5% D and 5% E). Thus, we find that if we design an alloy on a composition-based definition, then it may violate the entropy-based definition, i.e., minimum configurational entropy (1.36 R) is well below the defined limit of high entropy alloy (1.61 R). Due to this ambiguity Miracle et al. [20] suggested a new range for entropy-based definition that alloys having $\Delta S_{conf} \geq 1.5 R$ will be considered as high entropy alloys.

Based on the above definitions, we can conclude that only equiatomic or near to equiatomic compositions for quinary alloy systems may be considered as HEAs. At the

same time, sexenary and higher order multi-principal element alloys can be composition-based. None of the definitions given by Yeh shows any intention of a single solid solution phase but talks about obtaining a simple and reduced number of phases in the final alloy. But nowadays researchers [8,21,22] are motivated for getting single-phase solid solutions to be called as high entropy alloys. There is a logic behind this motivation, that if any secondary phase precipitates from the primary phase, then the individual phases no longer meet the composition based or entropy-based HEA definition. Thus, any multi-principal element alloy system that is a single phase up to a desired temperature (depending on the intended application) can only be termed as HEAs.

1.3. Four core effects of HEAs

Numerous books and reviews available on HEAs have echoed the importance of four core effects. They all pointed out the significant role of these core effects on phase stability and mechanical properties. The four core effects are as follows:

1. High entropy effect
2. Lattice distortion effect
3. Sluggish diffusion effect
4. Cocktail effect

The four core effects were proposed in 2006 by Yeh [23]. The high entropy effect controls the thermodynamics of the prepared alloy, and lattice distortion effects control the mechanical properties. In contrast, the kinetics of the atoms and molecules are controlled by sluggish diffusion effect while the cocktail effect is used to enhance the inherent properties of the constituent elements.

1.3.1. High entropy effect

According to its definition, HEAs propose that increased configurational entropy may favour formation of solid solution phases over competing intermetallic compounds. In the multi-principal element alloys, each atom in the alloy is surrounded by different kinds of constituent atoms, having different types of interactions. This may result in the formation of different kinds of binary, ternary and quaternary compounds, making the microstructure and its analysis very complicated.

According to the atomistic or statistical approach, entropy is defined as the number of ways to distribute the composing atoms over lattice sites. Consider a system composed of 4 lattice sites. For pure system all the lattice sites will be occupied by the same atoms, i.e. there is only one way to distribute A atom over four available sites. Suppose there are 3 A and 1 B atoms. Then the A and B atoms can be distributed in 4 ways. Similarly, for 2 A and 2 B atoms, there are six ways to distribute the atoms over four lattice sites, as shown in **Figure 1.4**. Likewise, the number of ways to distribute 3 B and 1 A and pure B system are 4 and 1 respectively. From the above considerations, it is clear that the number of ways to distribute atoms over lattice sites is maximum for an equal number of atoms (equimolar composition).

The Boltzmann's relation is used to determine the ideal configurational entropy of a binary substitutional (A-B) solution,

$$\Delta S = k \ln \omega \quad (1.1)$$

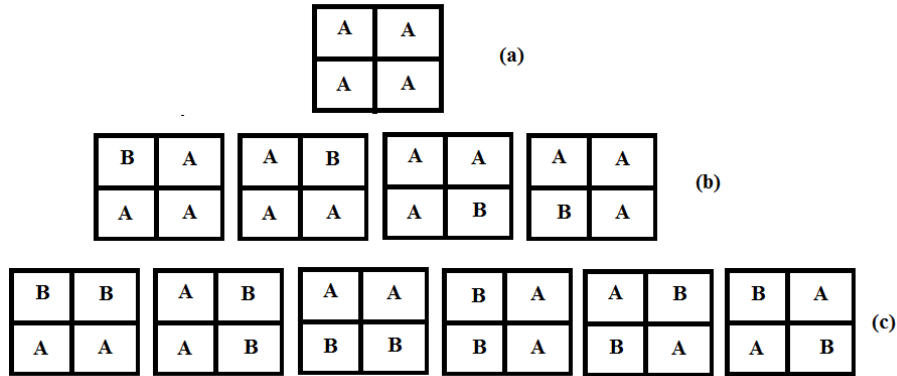


Figure 1.4: Number of ways to distribute A and B atom over 4 lattice sites. (a) pure A (b) 3 A and 1 B atoms (c) 2 A and 2 B atoms.

$$\Delta S = k \ln \frac{N!}{n!(N-n)!} \quad (1.2)$$

where,

ω : no. of ways of distribution of atoms over lattice sites.

N : Number of lattice sites.

n : Number of A atoms.

$(N - n)$: Number of B atoms.

k : Boltzmann's constant = $1.380 \times 10^{-23} \text{ JK}^{-1}$.

On expanding equation (1.2), we get the entropy of mixing as

$$\Delta S = k[\ln N! - \ln(N-n)! - n \ln n!]$$

The Stirling's approximation (namely, $\ln N! = N \ln N - N$ for $N \gg 1$) is used to simplify

the above equation

$$\begin{aligned} \Delta S &= k [N \ln N - N - (N-n) \ln(N-n) + (N-n) - n \ln n + n] \\ &= k [N \ln N - (N-n) \ln(N-n) - n \ln n] \end{aligned}$$

Since the atomic fraction of A is $x_A = \frac{n}{N}$ and that of B is $x_B = \frac{N-n}{N}$,

the above equation can be rewritten as

$$\begin{aligned}\Delta S &= Nk \left[-\frac{(N-n)}{N} \ln \frac{(N-n)}{N} - \frac{n}{N} \ln \frac{n}{N} \right] \\ \Delta S &= -Nk [x_A \ln x_A + x_B \ln x_B]\end{aligned}\quad (1.3)$$

For 1 mole solution of A-B, N is equal to Avogadro's number ($6.023 \times 10^{23} \text{ mol}^{-1}$)

$$\Delta S_m = -R[x_A \ln x_A + x_B \ln x_B] \quad (1.4)$$

For multicomponent alloys having K-components, equation (1.4) can be written as

$$\Delta S_m = -R[x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3 + \dots + x_K \ln x_K]$$

For equiatomic alloys $x_1=x_2=x_3= \dots =x_K=1/K$

$$\Delta S_m = -R\left[\frac{1}{K} \ln \frac{1}{K} + \frac{1}{K} \ln \frac{1}{K} + \frac{1}{K} \ln \frac{1}{K} + \frac{1}{K} \ln \frac{1}{K}\right] \quad (1.5)$$

$$\Delta S_m = R \ln K \quad (1.6)$$

The effectiveness of high entropy effect was overemphasised by Yeh and his colleagues in the initial studies of the HEAs [16–18]. However, recent studies have a conviction that the effect of configurational entropy does not have much influence on the phase stability of HEAs [24–29], as per our discussion in the definition section that those alloys which form single-phase solid solution after annealing will only be considered as high entropy alloys. The number of alloy systems that forms a single-phase solid solution is very limited. Otto et al. [26] have conducted elaborate experiments demonstrating the influence of the configurational entropy on the phase stability. He considered CrMnFeCoNi alloy which is also known as Cantor alloy. He replaced one element in the Cantor alloy by a component of the same crystal structure and nearly similar atomic size

and electronegativity. From his study, Otto et al. concluded that the resulting phase formed after substitution was not stable as a single solid solution phase.

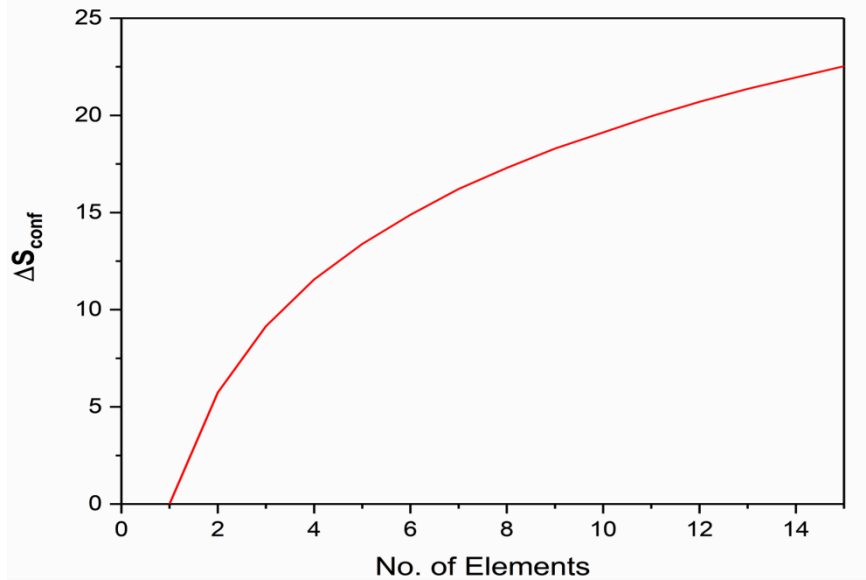


Figure 1.5: Increasing entropy of mixing with an increase in the number of elements.

Senkov [27,28] and Troparevesky [29] have independently concluded that the likelihood of intermetallic formation increases with an increase in the number of elements. The work of Cantor et al. [9] also supports the above conclusions, that chances of formation of intermetallic phases increase with the increase in the number of elements. From the above reports, it can be quickly concluded that only the configurational entropy cannot stabilize single solid solution phase in multi-principal alloys. Other factors dominate over and above configurational entropy to stabilize as a single phase.

1.3.2 Lattice distortion effect

It is well known that introduction of bigger/smaller atoms compared to solvent atoms in conventional alloys displace the neighbouring solvent atoms from their ideal positions, thus changing the lattice parameter of the traditional alloys. This kind of localized lattice distortion interacts elastically with the moving dislocation, resulting in

the solid solution strengthening [30], number of studies on HEAs report the significant impact of lattice distortion on the strength of prepared alloy [16,31,32]. Generation of lattice distortion is not only due to size mismatch but also due to the differences in the crystal structure and bonding preference among the alloying elements [33]. Thus, the gross lattice distortion in a HEA would be more severe compared to conventional alloys. Researchers have proposed that decreased XRD peak intensity indicates lattice straining due to increased diffuse scattering [16,31,33,34].

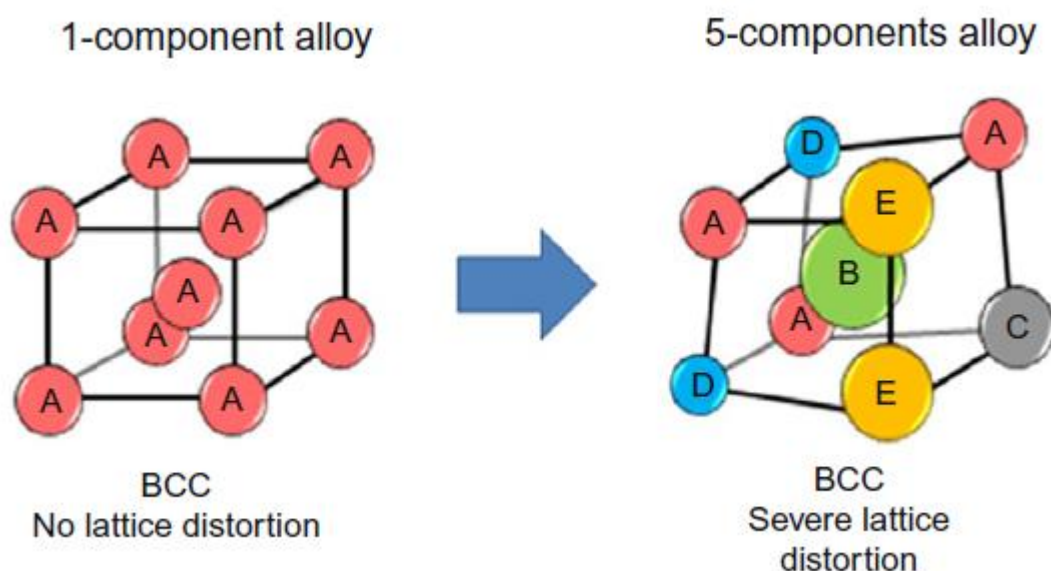


Figure 1.6: Schematic diagram showing severe lattice distortion in a BCC cell containing 5- components.[3]

The atomic size difference is not the only cause of lattice distortion, but the differences in bonding and crystal structure of neighbouring elements also induce strain. High degree of lattice distortion destabilizes random solid solution and results in a multiphase system. A large number of HEAs add Al to the multi-principal transition alloys, to decrease the density of alloy. Size of the Al atom is quite big compared to that of most of the transition elements. Thus if Al is mixed with the transition metals, results

in the formation of intermetallic and the probability of solid solution formation decreases drastically [35–38]. Whatever be the reason behind strain induction, it results in decomposition of the solid solution phase to a mixture of phases, i.e., stability of a single phase alloy decreases.

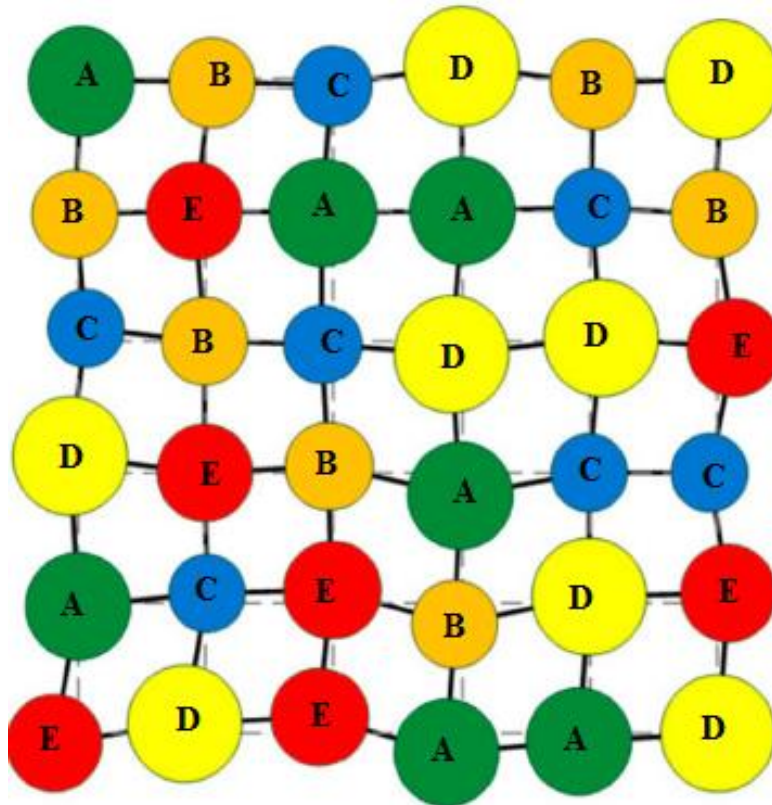


Figure 1.7: A 2-D representation of atom distribution and lattice distortion due to the varying size of constituent elements. [3]

1.3.3. Sluggish diffusion

Phase transformation in multiprincipal alloys requires cooperative movement of several elements. Yeh and other researchers [23,33,39,40] explain that the reason behind the sluggish diffusion is potential energies of lattice sites for diffusing elements. From an example, it can easily be understood. Consider a pure component or dilute solid solution. In both cases, an atom is possibly surrounded by similar atom. If an atom diffuses through

such surrounding, then the interaction of the diffusing atom with the surrounding atoms will be uniform, i.e. potential energy will be uniform. Now consider HEA, in this, different types of atoms surround an atom. An atom of one element has varying interaction energy with other atoms, present in the surrounding based on the bonding preference. If an atom diffuses through such an environment, the diffusing atom will have varying potential energies. The preferable binding sites act as deep traps for diffusing species, slowing the rate of diffusion, as can be seen from **Figure 1.8**. Sluggish diffusion results in the modification of mechanical properties due to fine precipitation particles in the microstructures, increased recrystallization temperature and slower grain growth rate.

Tsai et al. [40] have examined the diffusion rate of constituent elements in an equiatomic CrMnFeCoNi high entropy alloy. The sequence of elements in the decreasing order of diffusion in the chosen system was Mn, Cr, Fe, Co and Ni. They also pointed out that the degree of sluggish diffusion increases with an increase in the number of components.

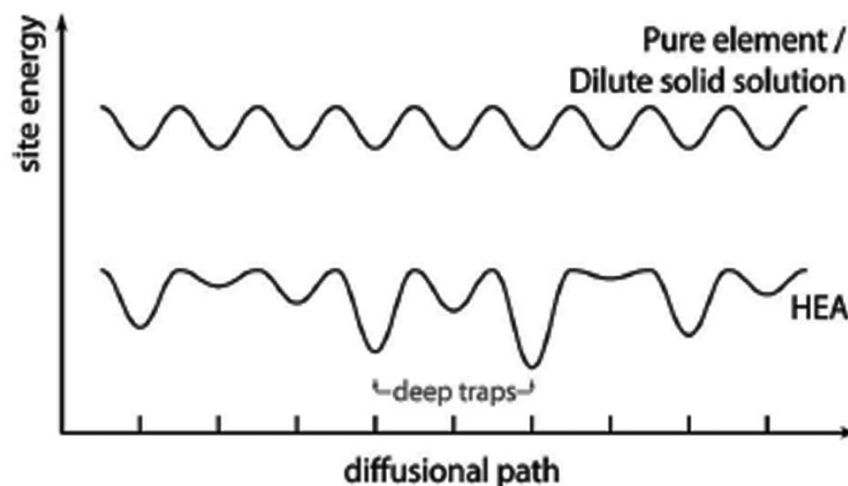


Figure 1.8: Fluctuation of lattice potential energy for diffusion path of atom compared to pure elements. [34]

1.3.4. Cocktail effect

Ranganathan coined this term in the article “Alloyed pleasures: multimetallic cocktails” [2]. He emphasizes on unique behaviour of bulk metallic glasses, super-elastic and superplastic metals and HEAs. The cocktail effect has been used to highlight the synergistic effect due to the addition of multiple elements to achieve extraordinary properties that cannot be explained by conventional rule of mixtures.

This can be well understood from the work of Senkov [41]. They prepared a quaternary equiatomic alloy (MoNbTaW) and a quinary equiatomic alloy (MoNbTaVW). Both these should possess a melting point around 2600 °C, but the melting point was significantly greater than 2600 °C. To obtain an appropriate combination of magnetic, electrical and mechanical properties, Zhang [42] designed CoNiFe(AlSi)_{0.8} HEA. He chose ferromagnetic elements Fe, Co and Ni in an equiatomic composition to obtain ductile FCC phase. On adding two non-magnetic elements (Al and Si) to the above combination result in high magnetization and low coercivity.

1.4. Phase formation rules in binary systems

A binary alloy made by mixing two pure elements A and B can form either crystalline solid solution or one or more intermetallic phases or non-crystalline solid solution. The formation of these phases is dependent on various chemical and physical conditions that help the atoms to arrange themselves in the most thermodynamically stable phases. In this section, we will look at some of the basic conditions required for the formation of one of the above phases.

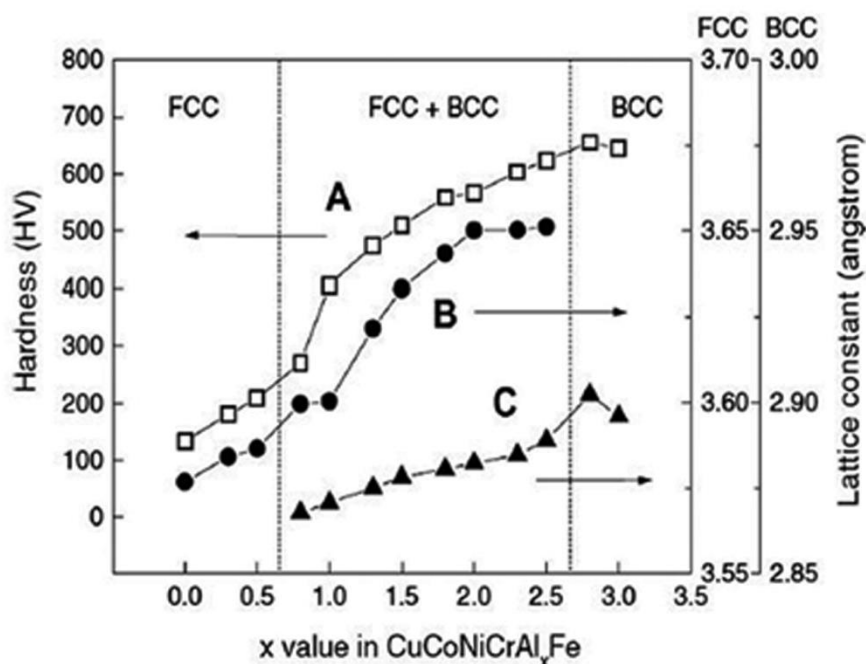


Figure 1.9: Hardness and lattice constants of a $\text{CuCoNiCrAl}_x\text{Fe}$ alloy system with different x values: (A) hardness of the $\text{CuCoNiCrAl}_x\text{Fe}$ alloys (B) Lattice constants of an FCC phase (C) lattice constant of a BCC phase. [24]

1.4.1. Hume-Rothery rules

The solid solubility of binary alloys is usually predicted by the Hume-Rothery rules, based on the various factors, namely (i) crystal structure, (ii) atomic size, (iii) the valence electrons, and (iv) electronegativity. However, the Hume-Rothery rules cannot be used directly for multi-component systems without appropriate modification. The behaviour of an element concerning other elements in the alloy systems can also be understood based on the enthalpy of mixing for binary subsystems. A large negative deviation in the enthalpy of mixing from ideal behaviour (i.e., $\Delta H_{mix} = 0$) favours the formation of intermetallic compounds, whereas positive enthalpy of mixing will favour clustering and segregation of phases. It is observed that formation of the disordered solid solution takes place at moderate values of enthalpy of mixing. It is intuitively clear that the solubility of one component into another depends on substitutional solid solution

forming criteria, which in turn is related to enthalpy of mixing as well as configurational entropy. High entropy in the multi-principal elemental compositions overcomes the effect of positive enthalpy of mixing and favours the formation of disordered solid solutions.

Hume-Rothery studied a number of binary alloy systems which led him to propose simple rules on the extent of solute element that might dissolve in the solvent element to form extended substitutional solid solutions. These are known as Hume-Rothery rules and are as follows:

1. **Size mismatch:** For a solute atom to have good solubility in the solvent, the solute and solvent atoms must have very small size difference, preferably below 15%. A large solute atom induces compressive stress while small atom will induce tensile stress around the solute atom. Due to these stresses, the solid solution becomes unstable, resulting in limited solubility.
2. **Electronegativity difference:** The solubility of solute atoms in the solvent increases, if both elements have very small electronegativity difference (preferably near to zero). The electronegativity difference between the two elements can be computed from the Pauling's electronegativity numbers. If the difference is large, then the formation of the intermetallic compound is favourable.
3. **Crystal structure:** For appreciable solid solubility, the crystal structure of solute and solvent elements must be the same.
4. **Valency:** The solute and solvent atoms should preferably have the same valency to achieve maximum solubility. Solute atoms having greater valency dissolve to a greater extent compared to solute with lower valency with respect to solvent atoms.

1.4.2. Ideal solid solutions

An ideal solution is one that closely follows the Hume-Rothery rules for a substitutional solid solution. This means that the A and B atoms have same atomic size, electronegativity, crystal structure and valency. In other words, we can say that A and B are chemically and physically identical. Thus, the interaction energies between A-A, B-B and A-B atoms are equal. In such a condition, the enthalpy of mixing of the ideal solution is zero. As the interaction energy between the A and B atoms are independent of the types of atoms involved, these two atoms are distributed in a truly random fashion on the lattice sites. The Gibbs energy of mixing for an ideal binary solution is given by

$$G_m^{id} = \Delta H_m - T\Delta S_m = 0 - T\Delta S_m = RT[x_A \ln x_A + x_B \ln x_B] \quad (1.7)$$

1.4.3. Real solutions

Real solutions do not often follow Hume-Rothery rules and deviate from the ideal solid solutions. They deviate either in a negative direction or in a positive direction. To understand the effect of deviation, one has to understand the interaction among the atoms. Consider a binary solution of A and B. Then there can be three types of interactions among them, i.e. A-A, B-B and A-B. The total enthalpy of solution (due to interaction between nearest neighbour pair) can be represented as

$$H = n_{AA}V_{AA} + n_{BB}V_{BB} + n_{AB}V_{AB} \quad (1.8)$$

where n_{AA} , n_{BB} and n_{AB} are the number of bonds and V_{AA} , V_{BB} and V_{AB} represent bond energies of type A-A, B-B and A-B respectively. Conventionally, attractive forces are represented by negative values for these bond energies, while repulsive forces are represented by positive values of bond energies. In a homogeneous solution having a random distribution of atoms on the atomic sites, probability of finding A (B) atom at any

atomic site is $x_A(x_B)$. Likelihood of finding A-A pairs (B-B pairs) is $x_A^2(x_B^2)$ while that of A-B is $2x_Ax_B$. If the coordination number of the solid solution is Z and the total number of atomic sites available is N, then the total number of bonds forming in the structure will be $\frac{1}{2}ZN$. Thus,

$$n_{AA} = \frac{ZN}{2} \times \text{the probability of A-A bond formation} = \frac{ZN}{2} x_A^2.$$

Similarly, $n_{BB} = \frac{ZN}{2} x_B^2 = \frac{ZN}{2} (1-x_A)^2$ and $n_{AB} = \frac{ZN}{2} \times 2x_Ax_B = ZNx_A(1-x_A)$

The total enthalpy of the homogeneous solution is given by

$$H = \frac{ZN}{2} V_{AA} x_A^2 + \frac{ZN}{2} V_{BB} (1-x_A)^2 + ZN V_{AB} x_A (1-x_A) \quad (1.9)$$

Enthalpies of pure A ($x_A = 1$) and pure B ($x_A = 0$) can be calculated from the above equation and are given by $H_A = \frac{ZN}{2} V_{AA}$ and $H_B = \frac{ZN}{2} V_{BB}$.

Enthalpy of mixing $\Delta H_m = \text{Total enthalpy} - (\text{weighted sum of enthalpies of pure A and B})$

$$\begin{aligned} \Delta H_m &= H - x_A H_A - (1-x_A) H_B \\ &= ZN V_{AB} x_A (1-x_A) - \frac{ZN}{2} V_{AA} x_A^2 - \frac{ZN}{2} V_{BB} (1-x_A)^2 \\ \Delta H_m &= Z N x_A (1-x_A) \left[V_{AB} - \frac{V_{AA} + V_{BB}}{2} \right] \end{aligned} \quad (1.10)$$

The value of $ZN x_A (1-x_A)$ is always positive. Thus, the value of $\left[V_{AB} - \frac{1}{2}(V_{AA} + V_{BB}) \right]$ will decide the sign of enthalpy or direction of deviation of real solution from an ideal solution. If $V_{AB} > \frac{1}{2}(V_{AA} + V_{BB})$, then the enthalpy of mixing will be positive, indicating that similar atoms (A-A and B-B) will attract more strongly compared to dissimilar

atoms. This results in A rich and B rich phases at low temperature. As the temperature is increased, the entropy effect helps in more association of A-B bond. If $V_{AB} < \frac{1}{2}(V_{AA} + V_{BB})$, then the enthalpy of mixing will be negative, indicating that dissimilar atoms (A-B) attract more strongly than similar atoms (A-A or B-B). Thus, the solution has ordering tendency. More is the magnitude of negative ΔH_m , more will be the tendency of ordering.

1.4.4. Ordered compounds

For enthalpy of mixing being negative, there is a tendency of formation of greater number of unlike bonds. Suppose the probability of finding unlike atoms (y_{AB}) in the neighbourhood is greater than the probability of like bonds in random solid solution. In that case, such a substitutional solid solution is said to have ordering tendency. Two types of (chemical) ordering have been detected in the substitutional solid solution, short-range order and long-range order.

Table 1.1: Summary of various substitutional solid solution phases based on departures of enthalpy of mixing value from ideality.

Ideal solution ($\Delta H_{mix} = 0$)	Negative departure ($\Delta H_{mix} < 0$)	Positive departure ($\Delta H_{mix} > 0$)
A and B atoms identical	A and B atoms different	A and B atoms different
$V_{AA} = V_{AB} = V_{BB}$	$V_{AB} < \frac{1}{2}(V_{AA} + V_{BB})$	$V_{AB} > \frac{1}{2}(V_{AA} + V_{BB})$
$y_{AB} = y_{AB}^{rand} = x_A \cdot x_B$	$y_{AB} > x_A \cdot x_B$	$y_{AB} < x_A \cdot x_B$
No preferential occupation of atoms i.e., random occupation of atoms on the atomic sites.	A atom is preferentially surrounded by B atoms and vice versa.	A and B atoms get surrounded more by like atoms.
Disordered solid solution	Preferential occupation of A and B atoms on certain sets of sites forming sublattices, say, α and β sites extending over 100 or more atomic distances. Such an arrangement of	Clustering tendency, leading to the occurrence of miscibility gap in phase diagrams.

	atoms is termed as long range ordering.	
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It must be noted that any departure from random distribution of atoms on atomic sites, confined to 5-10 atomic distances in the structure is known as (chemical) short range ordering (SRO). Even though the short-range ordering tendency decreases with the increasing temperature, it is always present in materials systems. If the negative deviation from the ideal solution is large, then solution at low temperature shows more probability of non-randomness over large atomic distance. This is known as a long-range order (LRO). In the long-range order, crystal can be divided into sublattices such that each sublattice is preferentially occupied by one type of atoms.

1.4.5. Amorphous alloys

Amorphous alloys are non-crystalline solids. Metallic glasses and bulk metallic glasses are a subset of this class. The structure of amorphous alloys is similar to a solidified liquid state. The tendency of formation of amorphous alloys increases with the increasing atomic size mismatch and electronegativity difference. Due to the large variation in these two parameters, the crystalline solid becomes unstable and takes a non-crystalline structure for the stability [43].

1.5. Phase prediction rules in high entropy alloys

The HEAs are multi-principal element alloys that form random solid solutions, partially ordered solid solutions, intermediate phases or a mixture of these. In a few cases, they form bulk metallic glasses. In the case of HEAs, single random solid solution is the desired phase. Phase prediction in HEAs is important in view of various applications which demand specific phases for specific properties. The most common solid solutions

formed in HEAs are BCC, FCC or mixture of BCC and FCC [36]. The HCP phase is limited to a very small class of alloys. The HEAs containing FCC phases possess good ductility due to the presence of a greater number of slip planes compared to BCC. But the strength of the BCC phase is relatively low [44], whereas HEAs having FCC phases possess high strength but relatively low ductility [41].

In the quest for predicting phases that may form in the HEAs, a number of empirical and parametric approaches have been developed by the researchers. The phase predicting rules are mostly based on enthalpy of mixing, size mismatch, crystal structure, valence electrons and melting temperature of elements.

1.5.1. Parametric approaches to predict phases

The enthalpy of mixing (ΔH_m) of the HEAs is calculated using Miedema's model [45,46]. Miedema's model is applicable only for binary systems. First, the chosen HEA is divided into all the binary subsystems. It may be pointed out that experimental data for ΔH_{mix}^{ij} are rarely available for many binary alloys. Therefore, ΔH_{mix}^{ij} is estimated for binary solutions using the semi-empirical Miedema model considering electron density changes at the boundary of dissimilar atoms and the work function of pure metals [46].

Formation enthalpy using Miedema model has been calculated for binary system as

$$\Delta H_{mix}^{ij} = \frac{V_i^{2/3}}{(n_{ws}^{-1/3})_{avg}} \{-P (\Delta\phi)^2 + Q(\Delta n_{ws}^{1/3})^2\} \quad (1.11)$$

where,

$$(n_{ws}^{-1/3})_{avg} = \frac{1}{2} \left(\frac{1}{(n_{ws}^i)^{1/3} + (n_{ws}^j)^{1/3}} \right) \quad (1.12)$$

Now these ΔH_{mix}^{ij} are extrapolated using the regular solution model to calculate the enthalpy of chosen HEA (ΔH_m) as shown below.

$$\Delta H_m = \sum_{i=1, i < j}^n \Omega_{ij} x_i x_j \quad (1.13)$$

where $\Omega_{ij} = 4\Delta H_{mix}^{ij}$ is an interaction parameter between A and B elements of the regular solution model, x_i the atomic fraction of the i^{th} component, ΔH_{mix}^{ij} is the mixing enthalpy for the binary equiatomic alloy, which is determined using Miedema's model.

The ideal configurational entropy of mixing of N-elements can be expressed as follows

$$\Delta S_{mix} = -R \sum_{i=1}^N x_i \ln x_i \quad (1.14)$$

where x_i is the atomic fraction of i^{th} element, R the Gas constant.

Atomic size mismatch is calculated using the relation proposed by Zhang et al. [47]. The parameter δ arising from the atomic size difference is also used to establish a relationship with solid solubility for multicomponent systems, which is defined as

$$\delta = 100 \sqrt{\sum_{i=1}^n x_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \quad (1.15)$$

where r_i is the atomic radius of the i^{th} element of molar concentration and \bar{r} is a weighted

average of r_i , which is given by $\bar{r} = \sum_{i=1}^n x_i r_i$.

Valence electron concentration (VEC) is defined as the total number of electrons (including d electrons) present in the valence band. The VEC is chosen in preference to e/a defined by Hume-Rothery due to the fact that e/a values vary for transition elements in a different environment. The VEC of multicomponent alloy system is defined as the weighted average of VEC values of each constituent element. For an N component system, the VEC is given [36] by

$$VEC = \sum_{i=1}^N x_i (VEC)_i \quad (1.16)$$

A thermodynamical parameter Ω introduced by Yang and Zhang [48] is also used as a criterion to check the feasibility of solid solution formation. This parameter is defined as the ratio of the entropy of mixing times the average melting temperature of the elements and the magnitude of the enthalpy of mixing as shown below

$$\Omega = \frac{T_m \Delta S_m}{|\Delta H_m|} \quad (1.17)$$

This dimensionless parameter consists of a ratio of terms used in the calculation of the Gibbs energy ($\Delta G_m = \Delta H_m - T\Delta S_m$). Basically, this parameter measures the competition between enthalpy and entropy terms. T_m is calculated by the rule of mixture applied to the melting temperatures of the constituent elements.

Prediction of formation of solid solution in high entropy alloys was first studied by Zhang et al. [47]. They calculated the values of ΔH_m , ΔS_m and δ in order to determine solid solution forming criterion for the previously studied HEAs. Zhang's criterion for the formation of a solid solution in HEAs is $-20 \leq \Delta H_m \leq 5 \text{ kJ.mol}^{-1}$; $12 \leq \Delta S_m \leq 17.5 \text{ J.mol}^{-1}\text{K}^{-1}$; $\delta \leq 6.4\%$. For the formation of a disordered solid solution, the criterion is more constrained: $-15 \leq \Delta H_m \leq 5 \text{ kJ.mol}^{-1}$ and $\delta \leq 4.6\%$. Later Zhang came up with another thermodynamic parameter (Ω) based on Gibbs energy function. We all know that Gibbs energy function is defined as $\Delta G_m = \Delta H_m - T\Delta S_m$, if the entropy term in the Ω is higher than the absolute value of enthalpy then the ratio will be > 1 and the chances of solid solution formation can increase. If enthalpy dominates over entropy then $\Omega < 1$ and formation of intermetallics or multiphase alloy is probable.

In 2011, Guo et al. [36] found that the valence electron concentration (VEC), number of total electrons including d-orbital electrons in the valence band act as a critical parameter in predicting the type of phases that will form. These are primarily used to distinguish whether a BCC phase will form or FCC or mixture of two.

$$VEC < 6.87 \text{ BCC phase}$$

$$VEC > 8 \text{ FCC phase}$$

$$6.87 \leq VEC \leq 8 \text{ BCC + FCC phase}$$

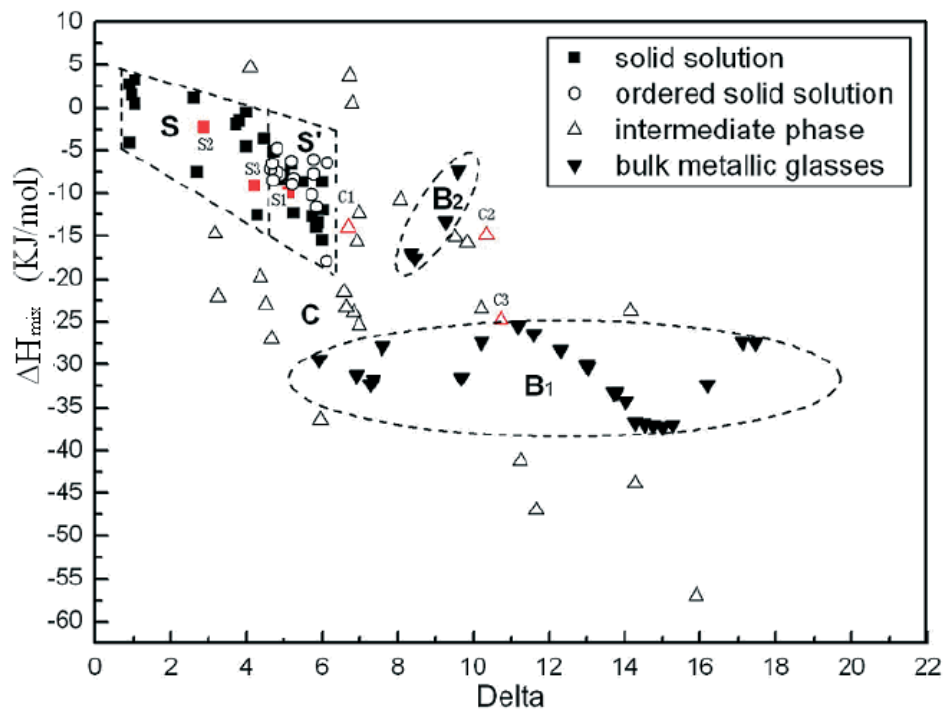


Figure 1.10: Phase selection plot based on the enthalpy of mixing and atomic size mismatch (delta). [39]

However, this parameter does not say that it will form single-phase BCC or FCC. It may form a single-phase or mixture of similar phases based on the criteria given for VEC. In the same year, Guo and Liu. [37] pointed out that based on $\Delta H_m, \Delta S_m$ and δ one can mark the range for the formation of solid solution and bulk metallic glasses. For

the formation of solid solution, the criterion is $-22 \leq \Delta H_m \leq 7 \text{ kJ.mol}^{-1}$; $\delta \leq 8.5\%$; $11 \leq \Delta S_m \leq 19.5 \text{ J.mol}^{-1}\text{K}^{-1}$. For the formation of bulk metallic glass: $-49 \leq \Delta H_m \leq -5 \text{ kJ.mol}^{-1}$; $\delta \geq 9\%$; $7 \leq \Delta S_m \leq 16 \text{ J.mol}^{-1}\text{K}^{-1}$. They concluded that δ plays a critical role in the formation of amorphous phase while enthalpy overlaps in both solid solution and bulk metallic glass formation range. Later in 2013, Guo et al. [35] pictorially represented the data on a 2D map having ΔH_m as ordinate and δ as abscissa. From this representation, they redefined the range for the solid solution and bulk metallic formation: $-11.6 \leq \Delta H_m \leq 3.2 \text{ kJ.mol}^{-1}$; $\delta \leq 6.6\%$ for SS and $\Delta H_m < 12.2 \text{ kJ.mol}^{-1}$ and $\delta > 6.4\%$ BMGs.

Raghavan et al. [49] have predicted the phase formation based on the CALPHAD approach. They have assumed that the stable phase is one, that solidifies first when cooled from the liquid state having the highest driving force. From this result, they calculated the ratio of $\Delta S_{config} / \Delta S_{fusion}$. Solid solution forms if equiatomic multicomponent alloys have ratio >1 , while for non-equiatomic alloys this ratio should be >1.2 . They also pointed out that the BCC phase is predicted more accurately using this method compared to the FCC phase.

Otto et al. [26] studied various quinary alloys by substituting different $3d$ and $4d$ transition elements. From this study, they concluded that it is the elements having attractive and repulsive nature that decide the formation of solid solution or intermetallics. They also pointed out that atomic size mismatch plays a critical role in the formation of SS and BMGs.

Singh et al. [50] developed a new parameter called Λ ($\Lambda = \Delta S_m / \delta^2$) to predict whether the alloy will form a single-phase disordered solid solution (DSS) or a mixture of

phases. They pointed out that increased configurational entropy favours the formation of DSS, but the increasing δ reduces the probability. For the formation of single-phase DSS $\Lambda > 0.96$ while for the formation of a mixture of compounds $\Lambda < 0.24$. If the value lies between these limits, then a mixture of solid solution and compounds forms.

Ye et al. [51] developed a geometric model based on the root mean square (RMS) value of residual strain around an atom in multicomponent HEAs. According to Hume-Rothery, atomic size difference in an alloy induces internal strain in the lattice, due to which lattice destabilize and phase transformation takes place. Ye et al. plotted the RMS strain developed around the atoms within the lattice versus elastic energy of various HEAs, as shown in **Figure 1.11**. From this plot, they concluded that RMS residual strain $\geq 10\%$ induces amorphization in the multicomponent alloys. They also found that the transformation of DSS to multiphase structure occurs at 5% RMS residual strain.

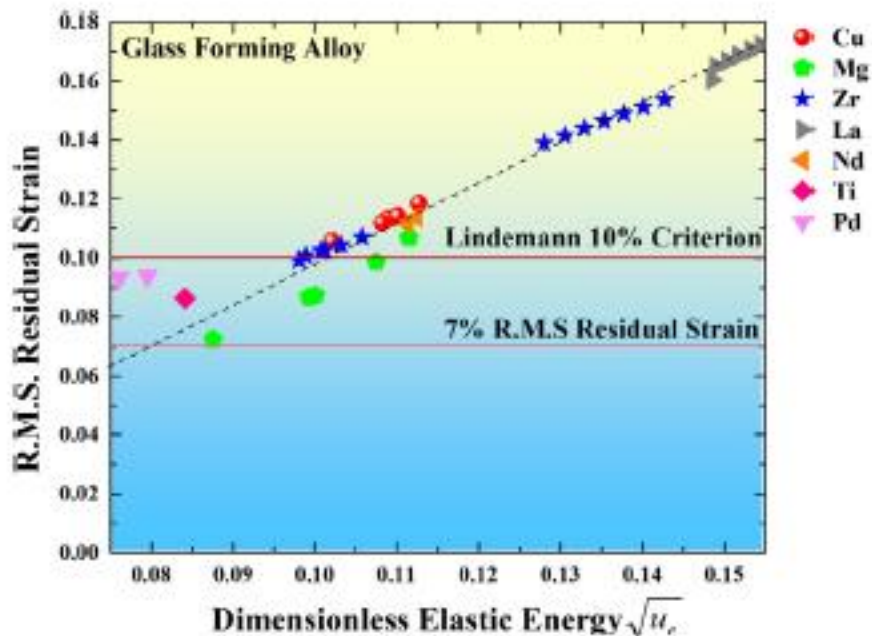


Figure 1.11: The RMS residual strain versus the dimensionless elastic energy for the typical glass-forming alloys, including Cu-, Mg-, Zr-, La-, Nd-, Ti- and Pd-based bulk metallic glasses.[3]

Troparveski et al. [29] proposed a criterion based on calculating the enthalpy values of binary subsystems using Density Functional Theory and then predicting the combination of elements that are favourable in forming a single-phase solid solution. They proposed ten most probable 5-, 6- and 7-component HEAs which will form a single-phase solid solution. Sheikh et al. [52] proposed that the solid solubility limit of BCC and FCC based HEAs containing 3d and 4d elements can be predicted, by calculating the average energy of d-orbital (Md). They have examined various previously studied HEAs prepared by casting route. They have included HEAs forming single-phase solid solution (BCC and FCC) and a mixture of solid solution. From their study, they concluded that FCC based HEAs containing 3d transition elements show a critical value of Md (0.97), below which single phase FCC phase is formed. However, FCC HEAs containing 4d elements are not showing any such critical value of Md. The critical value of Md for BCC HEAs containing 3d and 4d elements are 0.92 and 0.86 respectively, below which these alloys will form single-phase solid solution.

King et al. [53] studied 4-, 5-, 6-component systems from 73 metallic elements of the periodic table. They introduced a new parameter ϕ ($= -\frac{\Delta G_{SS}}{|\Delta G_{max}|}$). ΔG_{SS} is Gibbs energy for DSS whereas ΔG_{max} is the minimum and maximum Gibbs energy for the intermetallic formation and segregated binary system, respectively. On plotting ϕ versus δ and ΔH a clear boundary between solid solution and multiphase HEAs can be seen, as shown in **Figure 1.12**. for the formation of solid solution the $\phi \geq 1$ while for multiphase alloys $\phi < 1$. They are sure of the prediction capability, as out of 185 experimentally reported system 177 were predicted correctly. Senkov and Miracle. [54] developed a new thermodynamic parameter to predict the formation of intermetallics and solid solution at a

given temperature. Previously reported 45 HEAs were considered for the following analysis. On the basis of this, they were able to predict the formation of a solid solution.

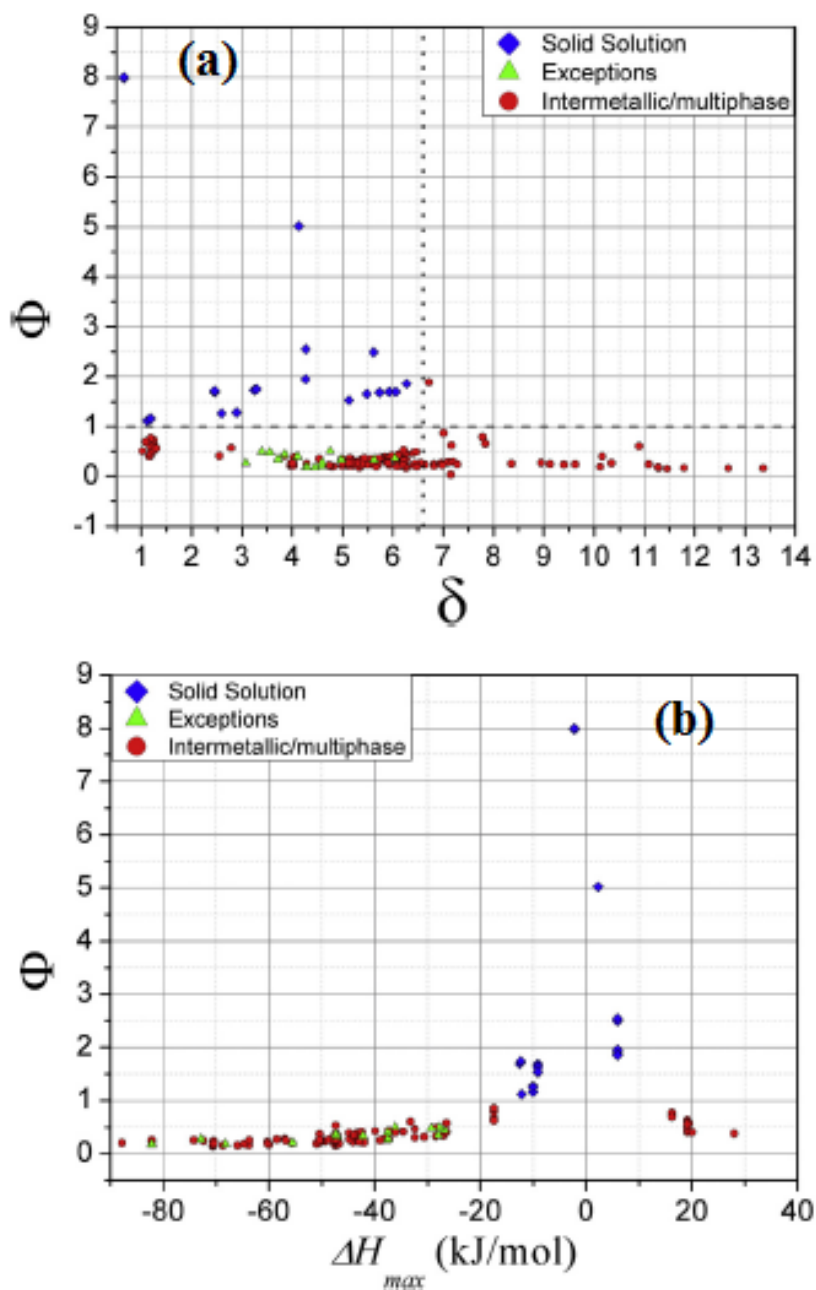


Figure 1.12: Experimentally determined 185 HEAs are plotted on (a) Φ vs δ and (b) Φ vs ΔH_{mix} forms solid solution with exception of 16 HEAs [55].

1.6. Miedema's model: A semi-empirical approach

Due to the scarcity of experimental thermodynamic data (enthalpy of alloy formation), Miedema and Niessen. [45] formulated an empirical approach to determine the sign of heat of formation from the known binary phase diagram. Two parameters that are needed for the calculation of heat of formation are n_{ws} and ϕ^* . Former being the electron density at Wigner-Seitz boundary while the latter is the chemical potential of electronic charge. They were able to separate all the binary alloys with positive and negative heats of formation calculated from the defined model. The magnitude of the heat of formation of the binary alloys measured experimentally was fixed in such a manner that Miedema et al. were able to predict the values for those binary alloys, whose experimental values were not available.

Miedema's method is basically used for binary systems only. For a multicomponent system, we will divide the system into its component binary subsystems. The heat of formation for each of the binary subsystem is calculated using Miedema's model. The heat of formation of the multicomponent system will be calculated by extrapolating the values of binary subsystems using the regular solution model. As stated above, this model is good for predicting the sign of enthalpy rather than the magnitude of enthalpy. Due to error in the magnitude of enthalpy for binary systems, the extrapolated value also will have error. But being quick and handy, this method is extensively used in the prediction of phases. Most of the rules defined for the prediction of phases in HEAs use enthalpy calculated by using Miedema's model.

1.7. Density functional theory: A theoretical approach

In the new materials design strategies, researchers are looking for a tool which can precisely predict the final product properties [55]. Quantum mechanics serve as an

important tool to understand the effect of interaction between atoms and molecules on the mesoscopic and microscopic behaviour of materials. The behaviour of electrons and ions in a solid or in a molecule can be known by solving the Schrödinger equation [55]. Density functional theory is based on solving the Schrödinger equation by using Hohenberg-Kohn theorem [56]. The theorem states that the total energy of the many-electron system in an external potential is a unique function of electron density. This functional is minimum at the ground state of the system. Minimization of functional helps in determining the formation enthalpy of disordered solid solution and partially alloyed solution. From this, one can also derive the mechanical and magnetic properties of the prepared alloy.

Initially, the formation enthalpy of the ordered compound was calculated using DFT. Later with the development of codes that can generate cell having randomly arranged atoms, enthalpy of mixing for the disordered solid solution was also evaluated. However, the simulation of the multicomponent system using the *ab-initio* method necessitates high computational power and computational time for obtaining meaningful results.

Ma et al. [57] have employed EMTO-CPA to examine the entropic contribution to the phase stability of CoCrFeMnNi HEA for disordered BCC, FCC and HCP structure. He explained that due to lattice vibration energy FCC phase was stable over HCP phase at high temperature. Kormann et al. [58] used mean field approach to estimate Curie temperature of large range of CoFeNi based HEAs. Huang et al. [59] used Monte Carlo simulation to investigate the Curie temperature of $\text{Al}_x\text{CoCrFeNi}$. The effect of crystal structure on Curie temperature was examined and reported by Sun et al. [60] for $\text{Al}_x\text{CoCrFeMnNi}$ HEA. Niu et al. [61] examined the energy and magnetic property of

FCC CoCrFeNi HEA using ab-initio methods. The short range ordering (SRO) present in the systems is estimated using ab-initio Monte Carlo methods and are reported in the works of Tamm et al.[62], Feng et al. [63] and Niu et al. [64]. The impact of the atomic vibrations at finite temperatures is studied using ab-initio molecular dynamics and reported in Widom et al. [65–67].

1.8. CALPHAD: Phase diagram approach

Graphical representation of the stable phases of the alloy system, as a function of pressure, temperature and concentration of composing component are defined as a phase diagram. Generally, phase diagrams of binary systems are represented at constant pressure, whereas for ternary it is expressed at constant pressure and temperature. But for higher component systems this representation becomes difficult. A preliminary phase diagram can be predicted for the multicomponent system from the extrapolation of assessed constituent binary and ternary subsystems. These assessed binary and ternary subsystem can be easily accessed from the commercially available databases, i.e. PANDAT, Thermo-Calc, MTDATA etc.

The CALPHAD (Calculation of Phase Diagrams) method offers a relatively less empirical and more scientific approach for the design of HEAs with a moderate computational burden. Existing thermodynamic databases available for unary, binary and few ternary systems can be used for predicting the possible phases based on thermodynamic models and reasonably sound theoretical approach. However, the databases developed for the single principal element-based approach of alloy design can be used in order to ascertain the phase constituents in a multi-principal element alloy with reasonable accuracy. Thus the extrapolation of existing classical thermodynamic databases to quinary and higher systems remains to be explored in much more depth [68].

Zhang et al. [69] used binary phase diagrams to understand the mutual solubility of the components in the Cantor alloy. The CALPHAD technique with dedicated databases have very good predictive ability to estimate the phases present, volume fraction of phases and transformation temperature of phases [70]. The phase stability of 130,000 equimolar alloys based on the 45 elements were investigated by Miracle et al. [20] and Senkov et al. [27,28] by using CALPHAD and some well-established rules for structural strength. Gao and Alman. [71] have investigated phase stability of sixteen multicomponent alloys having single phase BCC structure using CALPHAD approach. They have also applied this strategy to propose single phase FCC and HCP structures [8,72].

1.9. Processing routes of high entropy alloys

A variety of processing routes are adapted to prepare high entropy alloys, such as casting (liquid mixing), mechanical alloying (MA) (solid mixing), and thin film deposition (gas mixing) [24] as shown in **Figure 1.13**. Many scientific studies have reported the synthesis route for their chosen HEAs is using liquid state mixing of the elements (melting route). Most commonly melting route used for the synthesis of the alloys are arc melting (AM). The advantages of the arc melting technique are its low power and time consumption and getting low porosity in the final product. The major drawback of this technique is the difficulty in handling low melting temperature elements (<600 °C) due to the high temperature of arc. Thus, this method is suitable for the synthesis of high-temperature refractory HEAs. Low melting temperature elements if any, in the alloy can be synthesized using Induction melting (IM). In vacuum arc melting method, pure elements are placed in the water-cooled copper crucible. Then the chamber is closed and evacuated, followed by filling of pure argon in the evacuated chamber. After

the initiation of the arc, pure titanium block is melted first to ensure the absorption of the remaining oxygen in the chamber, if any. The prepared button sample is flipped for 4-5 times and remelted to ensure homogeneity of the elements within the final alloy.

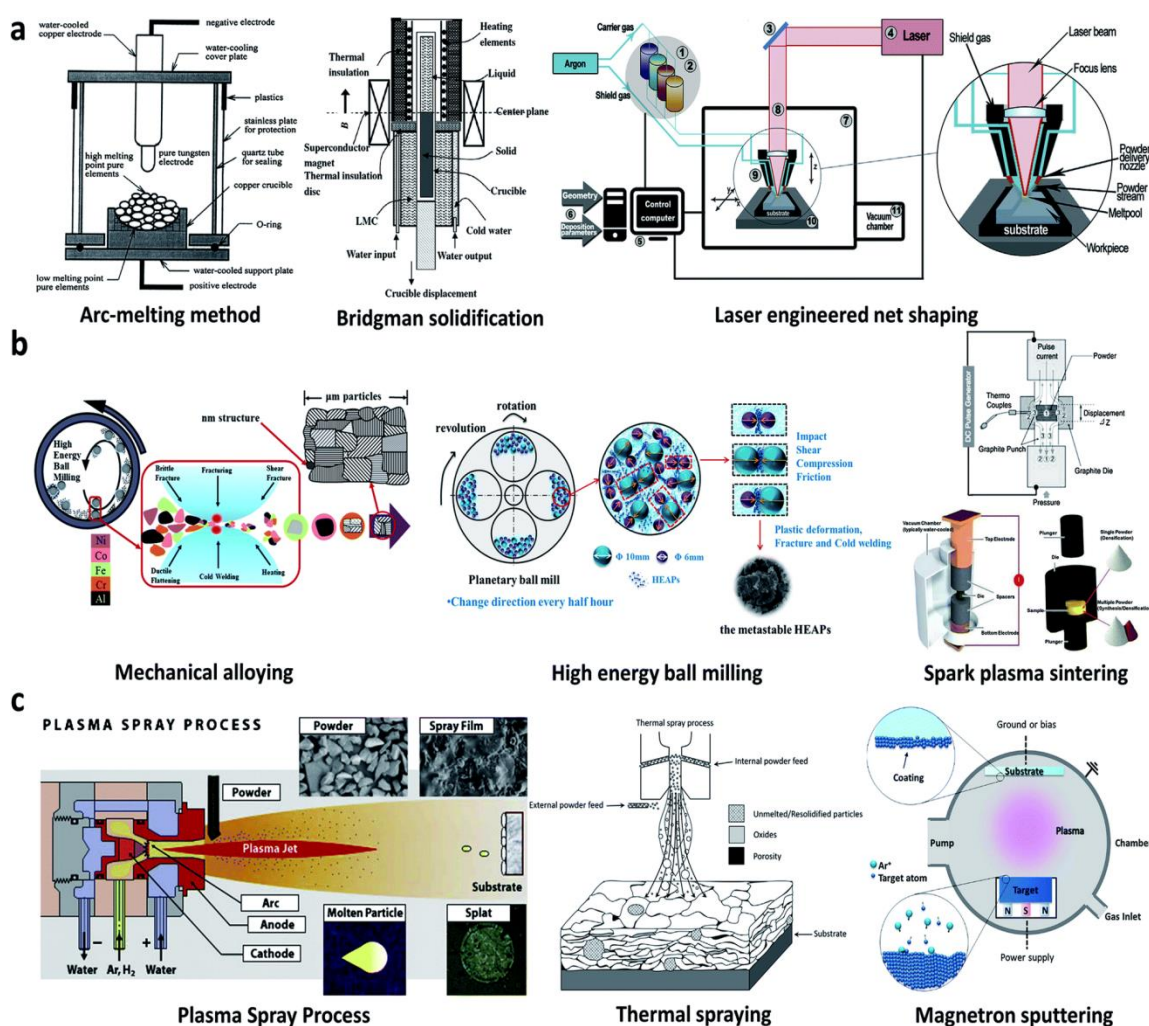


Figure 1.13: Traditional synthesis methods for HEAs. (a) Liquid-state synthesis, including arc-melting method[74] Bridgman solidification,[75] and laserengineered net shaping.(LENS)[76] (b) Solid-state synthesis, including mechanical alloying,[77] high-energy ball milling,[73] and spark plasma sintering.[74] (c) Gas-state synthesis, including plasma spray process, thermal spraying,[75] and magnetron sputtering.

The detailed analysis of the microstructure of samples prepared by vacuum arc melting has shown some segregation in dendritic and inter-dendritic regions

[16,24,31,76–78]. The problem of segregation can be avoided by the use of MA [79]. Therefore, its use for the synthesis of HEAs has increased in recent years. Murty *et al.* [80] were the first to prepare the nanostructured solid solution of HEAs by MA. Through MA, almost any kind of material can be produced at room temperature [81]. The extended solid solubility of alloying elements plays a vital role during the synthesis of alloyed powders [79]. Due to this extended solid solubility, simple crystal structures are expected for a similar composition compared to casting route. Further, the MA route used to synthesize HEAs facilitates the formation of nanocrystalline phases [3]. In the MA, pure elemental powders are put in the vials with some hardened ball (Ball to powder ratio (BPR) of 10, 15, or 20). The most commonly used mill for this purpose is the planetary ball mill. In this mill, vertical vials are attached to a disc known as the sun wheel. The direction of rotation of vials is reverse of the rotation of the sun wheel, showing a planetary kind of motion. Milling for few hours results in homogeneous nanostructured powder of the HEA.

In the case of gas state mixing of the elements, a magnetron sputtering (MS) method is the most commonly used technique for the synthesis of the alloys. The prepared HEA is coated over a substrate as a thin film to improve the corrosion-resistant, wear-resistant and oxidation-resistant of the substrate. In the MS method thin film of the HEA is deposited over substrate metal/alloy through the unique magnetic field. The substrate and the target (HEA) are placed in an evacuated chamber later filled with Ar gas. The substrate material is connected to the anode while the HEA to be deposited is connected to the cathode. Under the effect of the magnetic field, Ar is ionized and hit the HEA, which in turn releases HEA particles to coat the substrate.

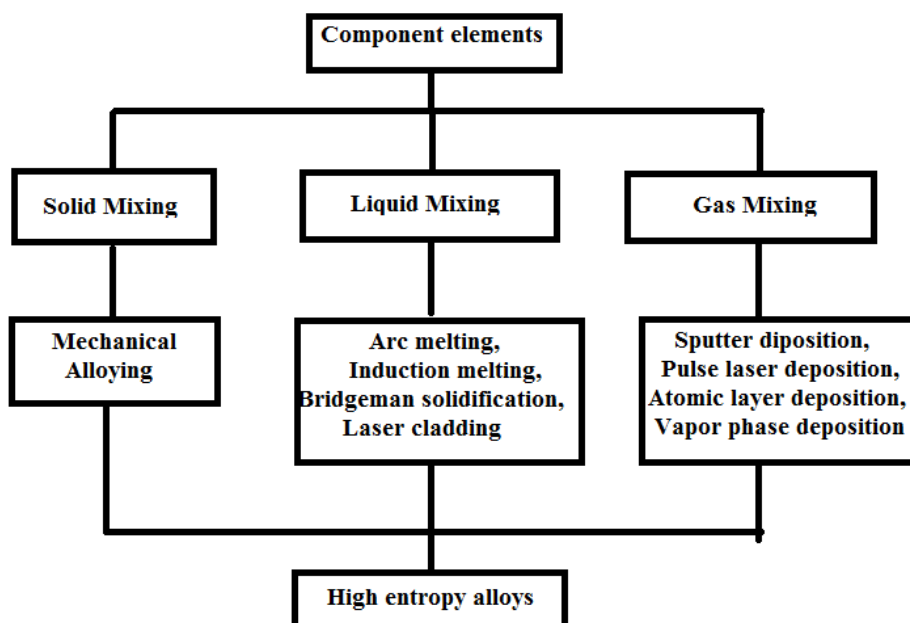


Figure 1.14: Processing routes of high entropy alloys

1.10 Prospective applications of HEAs

The properties of the materials can be characterized broadly into two types i.e. structural properties and functional properties. The literature on the HEAs guide us that the alloy selection and proper processing of the alloy leads 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 life.

1.10.1 Structural properties

The most widely studied alloy is the equiatomic CoCrFeMnNi (Cantor) alloy showing low yield strength but high strain hardening ability at room temperature [82]. Cast and homogenized HfNbTaTiZr RHEA shows high strength in the range of 800-

1000MPa and compressive ductility up to 50% over a wide temperature range from room temperature to 1273 K [28]. Cantor alloy shows exceptional fracture toughness (250 MPa), even better than the best austenitic steels reported in literature till date and retains it at cryogenic temperature due to operation of twinning [83]. NbMoTaW and VNbMoTaW refractory high entropy alloys exhibited a single-phase BCC structure and showed exceptional strength (~400 MPa) at 1600 °C. The hardness of HEAs can rise from ~150HV [84] to ~1200 HV [85], depending on the synthesis method and composition

1.10.2 Functional properties

The DyErGdHoTb alloy has HCP structure and a small magnetic hysteresis. It possesses high refrigerant capacity (a figure of merit parameter for magneto-electric effect) [86]. HEAs like CoCrFeMnNi, Al_xCoCrFeMn and CoCrFeNiPd showed higher resistivity than that of 316 and 304 stainless steels [87]. HfNbTiVZr shows excellent hydrogen absorption which is superior to all the constituent elements indicating that the distorted lattice in HEAs aids in hydrogen absorption at both octahedral and tetrahedral voids [88]. A nanoporous structure of AlCoCrFeNi was fabricated by dissolving Al-Ni rich phase and retaining Cr-Fe rich phase, which shows high capacitance of 700 Fcm⁻¹ and durability of 3000 cycles. [89]. The thermoelectric property of Al_xCoCrFeNi (0 ≤ x ≤ 3) was reported to be 1 μVK⁻¹ for x = 0 and 23 μVK⁻¹ for x = 3 [90].

1.11. Motivation

The motivation of the present investigation came from the intent of exploring the unexplored central region of the multidimensional phase diagrams. We have used the compositional definition of the high entropy alloys for choosing the alloy systems. Thus our aim is to explore the vast region and obtain a disordered solid solution along with a

small amount of other phases, which helps in the improvement of the properties in various ways.

Most of the studies on CrFeCoNiCu alloy systems are carried out on as-cast samples [91], showing single-phase FCC structure. Praveen *et al.* [24] and Thangaraju *et al.* [91] have studied this system by mechanical alloying route followed by sintering. Praveen *et al.* have reported the presence of the σ phase after sintering the alloy. However, Thangaraju *et al.* [91] have not reported any σ phase formation after sintering. Due to these conflicting results on phase stability, it is important to reassess the thermal stability and evolution of the σ phase in the CrFeCoNiCu system. Thus the phase stability of CrFeCoNiCu HEA is studied by experimental (synthesized by mechanical alloying) and theoretical methods to fix the conflict.

A low-density MgAlMnFeCu HEA was synthesized for applications where low density with high strength is needed. The MA technique is used in this case, as the positive enthalpy of mixing between individual elements (based on the Miedema model), may results in segregation or clustering in as-cast samples. The effect of Mg addition on phase evolution in this HEA has been studied carefully through XRD and TEM. A detailed investigation has been carried out to explore the phase evolution after SPS of MgAlMnFeCu HEA. The effect of Mg addition on solid solution formation has been discussed based on thermodynamical calculations, i.e., parametric approach and CALPHAD methods.

The synthesis and phase stability study of two new refractory high entropy alloys using theoretical and experimental methods. As TiVZrMoW alloy has not been studied so far, the aim of the present work is to add W and study its effect on the evolution of phases and thermal stability. W being a high melting point element, is expected to enhance the

thermal stability of the previously studied TiVZrMo quaternary alloy. The second new refractory HEAs selected is TiVZrYHf, in which we have investigated the phase stability of the HCP phase by adding vanadium to previously studied TiZrHfY HEA. TiZrYHf alloy forms single-phase HCP along with a small amount of undissolved Y. A theoretical and experimental investigation of TiVYZrHf RHEA is carried out in the present study to understand the phase evolution and stability. It may be interesting to study the effect of V addition on the TiYZrHf HEA as the likelihood of Laves phase formation increases since the C15 type of Laves phase is very stable in Hf-V and Zr-V binary systems.

1.12. Objectives

Based on the motivation as mentioned above, the following objectives of the present work have been formulated:

1. To synthesize equiatomic CrFeCoNiCu and low-density MgAlMnFeCu HEAs by mechanical alloying.
2. To synthesize equiatomic refractory TiVZrMoW and TiVZrYHf HEAs using vacuum arc melting.
3. To study phase stability and microstructural evolution of equiatomic HEAs (during mechanical alloying).
4. To study phase transformation and stability of the phases after consolidation of mechanically alloyed powder of low-density MgAlMnFeCu HEA.
5. To understand the thermal stability of phases and microstructural evolution of all the synthesized alloys in time-temperature domain.
6. To estimate the phase stability of all the alloys by parametric approach.

7. To understand the theoretical basis of phase stability by Calphad and Density functional theory (DFT).