Chapter 1: Introduction

Complex energy landscapes ranging from binaries to ternaries to quaternaries and higher order systems has intrigued the researchers which has led to the development of complex intermetallics, quasicrystals, glasses and high-entropy alloys. The phase diagrams of binary systems are well established for most of the combination of elements and is given in ASM Metal Handbook, however many of the phase diagrams do not explicitly define the phase and the phase field and is often shown by the dotted lines in the composition-temperature plot. For ternaries or quaternaries or higher order systems, phase diagrams are not well established for most of the combinations of elements. As additional components are added in higher order phase diagrams, the volume of data increases enormously adding to the complexity of the phase diagram. A. Lindsay Greer [1] has published an article "Confusion by Design" in Nature journal where he states "*two is a company, three is a crowd to those wishing to analyse fully the thermodynamics and kinetics of alloy transformations*".

This thesis covers the areas of polymorphic transformation in Ni-Mn equi-atomic binary system, microstructural evolution and phase stability of ternary semi-Heusler NiMnSb and vanadium added semi-Heusler NiMnSb multicomponent systems and it also throws light on how the non-equilibrium processing "mechanical alloying" of the same composition as of semi-Heusler NiMnSb and vanadium added semi-Heusler NiMnSbV, has configurationally stabilised the system as a single phase solid solution.

1.1 "Allotropic" and "Polymorphic" transformation

"Allotropic" or "Polymorphic" transformation are the terms which are generally interchangeable and is quite often used as synonymously in the technical literature, however there is a subtle difference between these two terms. The term "allotropy" is coined by Jacob Berzelius in 1840 from the greek word "allotropia" which is a combination of two words "allos" meaning other and "tropos" meaning forms which altogether has a meaning other forms of the same matter. Allotropic transformation can be defined as the transformation of pure elements where a change in the crystal structure is observed either w.r.t temperature or pressure. Pure Iron transforms from body centred

cubic (BCC) structure to face centred cubic (FCC) structure at ~ 910°C and FCC structure of pure iron again changes to BCC structure at ~1400°C, this kind of phase transformations where the crystal structures resulting from the phase transformation are independent of each other are referred as allotropic transformation. The term allotropic transformation should be used with a caution that it should always refer to the pure elements. Polymorphic transformation can be defined as the same phenomenon as it has been defined for the former "allotropic transformation", however it can only be used for compounds. The polymorphic transformation in the present day is a more generalized term which is often used by researchers for the transformation of any given element or compound which bears different crystal structures without change in its physical state of matter.

For the unary (one component) system, α-phase transforming to β-phase (allotropic or polymorphic transformation)

$$dG^{\alpha} = V^{\alpha}dP - S^{\alpha}dT \tag{1}$$

$$dG^{\beta} = V^{\beta}dP - S^{\beta}dT \tag{2}$$

Condition of equilibrium for two phases, $dG^{\alpha} = dG^{\beta}$

$$V^{\alpha}dP - S^{\alpha}dT = V^{\beta}dP - S^{\beta}dT$$

$$\frac{dT}{dP} = \frac{\Delta V^{\alpha\rightarrow\beta}}{\Delta S^{\alpha\rightarrow\beta}} \tag{3}$$

At the transformation temperature,

$$\Delta S_{tr} = \frac{\Delta H^{tr}}{T^{tr}} \tag{4}$$

$$\frac{dT}{dP} = \frac{T^{tr}.\ \Delta V^{\alpha\rightarrow\beta}}{\Delta H^{tr}} \tag{5}$$

where, $\frac{dT}{dP}$ is the slope in the unary phase diagram, T^{tr} is the transformation temperature, $\Delta V^{\alpha\rightarrow\beta}$ is the change in volume between the phases (α and β). ΔH^{tr} is the

enthalpy of transformation at the transformation temperature.

The allotropic or polymorphic transformation can be best understood with the G-T plots.

The condition for the allotropic transformation is given in figure 1(a) which shows that the allotropic or polymorphic transformation happens at T_{tr}, which is below the melting point T_m.

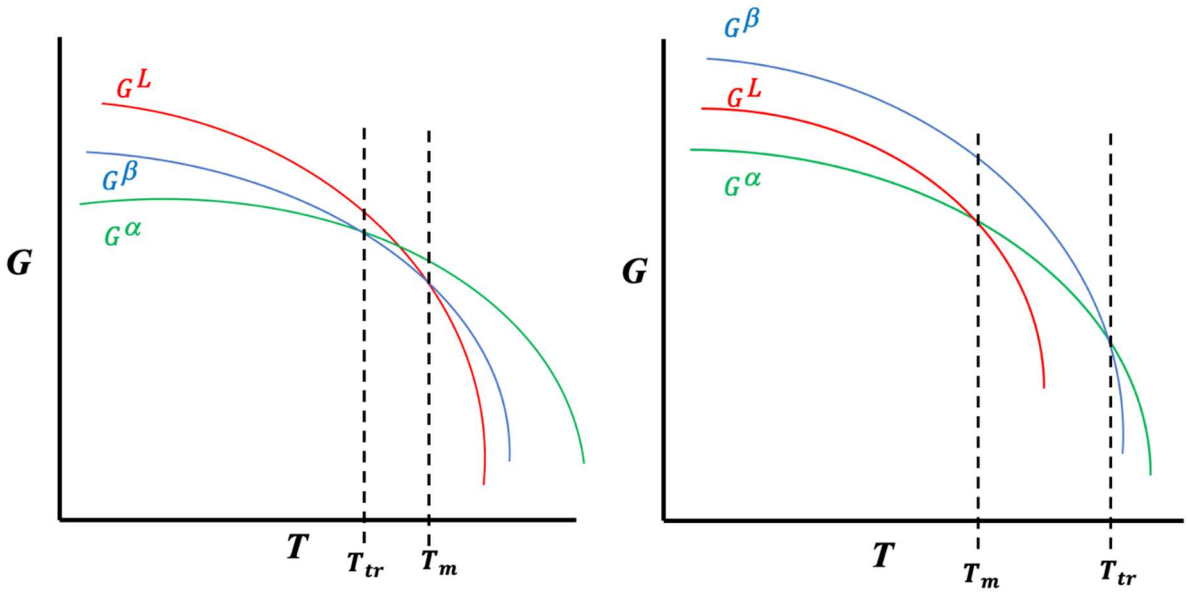

Figure 1.1 Gibbs free energy - Temperature plot at constant pressure (a) showing the condition of allotropism or polymorphism prior to melting (b) showing the condition of melting prior to allotropism or polymorphism [2]

In this plot, the Gibb's free energy curve of β-phase is steeper than α-phase and Liquid phase which results into the intersection of G^α and G^β prior to $G^\alpha$and G^L which necessarily means allotropism or polymorphism. In figure 1(b) which is the condition of melting not allotropism, where melting happens at T_m, which is below the T_{tr}. In this case, the Gibb's free energy curve for Liquid phase is steeper than α-phase and β-phase which results into the intersection of $G^\alpha$and G^L prior to G^α and G^β which necessarily means melting.

Apart from thermodynamics, crystallography has a major role to play in the allotropic or polymorphic phase transformations as it defines the route of transformation. Aschcroft and Mermin [3] has shown the hierarchy of crystallography of phase transformations, which is shown in the figure given below.

This chart shows that the phase transformations are not random events, any phase transformation has to go through a series of events which is governed by this chart. In this chart, it has been explained that cubic system which has the highest symmetry in all the crystal systems with four 3-fold symmetries can either transform to tetragonal system with one 4-fold

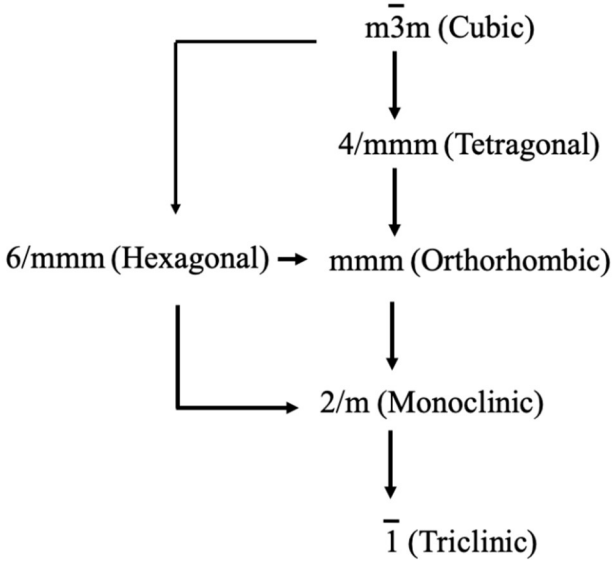

Figure1.2 The hierarchy of symmetries and the phase transformation route among the seven crystal systems [3]

symmetry or trigonal system with one 3-fold symmetry, hexagonal system with one 6-fold symmetry can transform to orthorhombic system with three independent 2-fold symmetry which can also be obtained from the tetragonal system. The orthorhombic system can transform to monoclinic system with one 2-fold symmetry and this can again transform to the lowest symmetry of all the crystal system i.e triclinic with a centre of inversion. All the crystal system has its own highest symmetry class known as holohedral class which has the maximum number of order in that particular crystal system and it is essentially seven as there are only seven crystal systems. All these holohedral class contains centre of inversion and is therefore a subset of Laue groups.

It is an interesting phenomenon to discuss the transformation on the basis of the symmetry of crystallographic point groups. From this part, it can be understood that how important the symmetry of any crystal system is to understand the phase transformation with reference to the crystal system we can once again understand the difference between allotropic and polymorphic transformation, if the transformation happens

within the same crystal system for example cubic I to Cubic F, or tetragonal P to tetragonal I, then it can be inferred as allotropic transformation. If the transformation happens within the different crystal system and the product crystal can be derived from the parent crystal by simple lattice translations for example cubic to tetragonal or tetragonal to orthorhombic, then it can be inferred as polymorphic transformation.

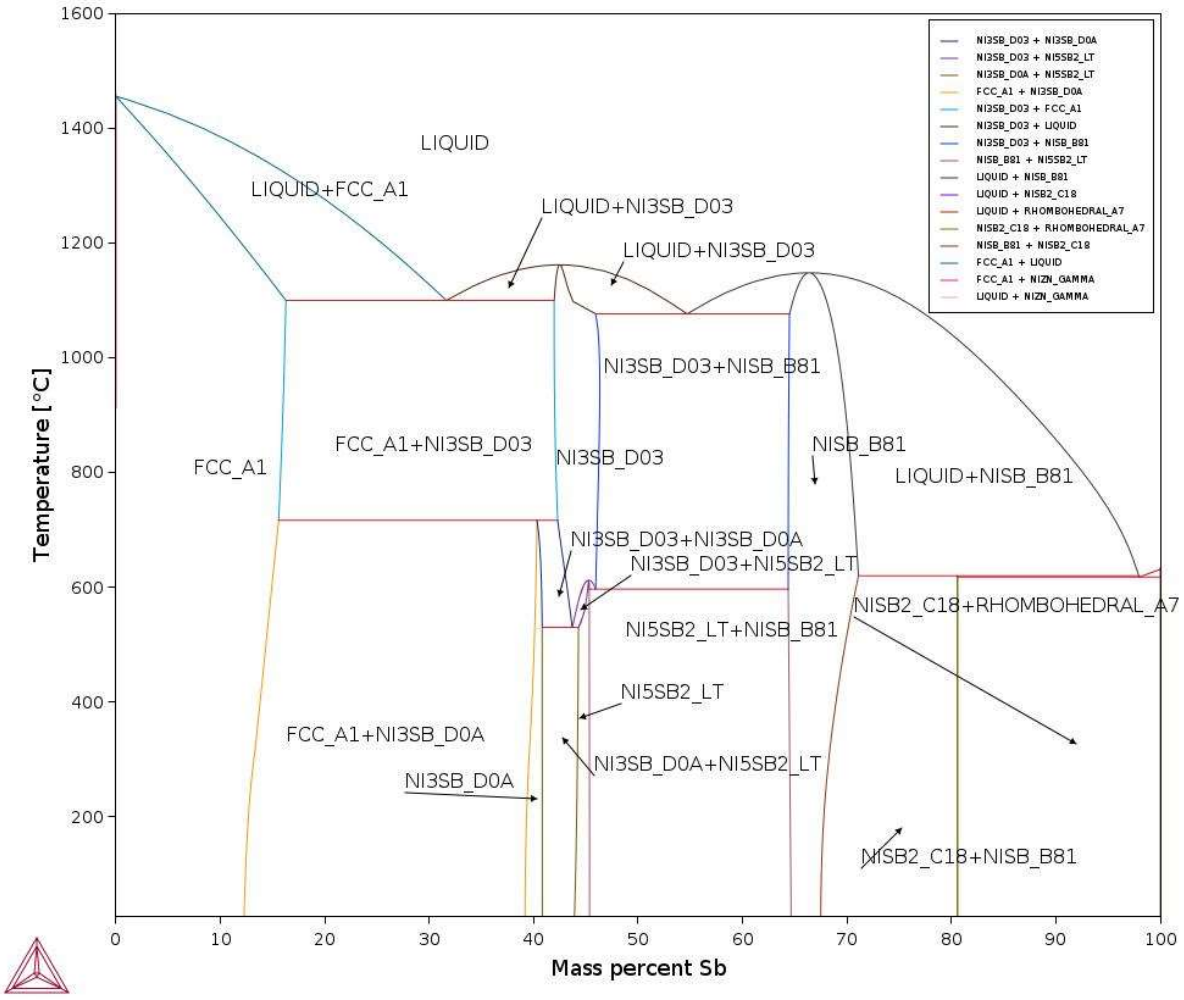

Figure 1.3 Equilibrium Phase diagram of Ni-Sb [4]

It is better to understand this kind of phase transformations with respect to phase diagrams of Ni-Sb, Mn-Sb and Ni-Mn as these phase diagrams have all the necessary features which are discussed in the above mentioned section.

In this Ni-Sb phase diagram, there are solid solubility of Sb in Ni but almost no solid solution in Ni in Sb, however there are many intermetallics in the phase diagram, which mostly includes Ni_3Sb with an orthorhombic crytsal structure, Ni_7Sb_3 with monoclinic

crystal structure, Ni_5Sb_2 with tetragonal structure, NiSb with hexagonal crystal structure and the line intermetallic compound $NiSb_2$ with an orthorhombic crystal structure. At near (~) 30 atomic percent Sb, Ni_7Sb_3 with tetragonal structure transforming to Ni_5Sb_2 monoclinic structure is an example of polymorphic transformation. Even if the exact crystallographic determination of both theses phases is not evaluated but the classification can be done purely on the basis of change in the crystal system. In this phase diagram, any allotropic transformations could not be encountered as the pure elements Ni and Sb does not show any kind of change in the crystal structure with respect to temperature at the ambient pressure.

Table 1.1:Different stable phases with their respective composition range along with the crystallographic information in Ni-Sb equilibrium phase diagram [4]

Phase	Composition, wt % Sb	Pearson Symbol	Space Group
Ni	0 to 17	cF4	$Fm\bar{3}m$
$Ni_{15}Sb$	12.2	Unknown	Unknown
Ni_3Sb	39.2 to 41	oP8	Pmmm
Ni_5Sb_2	41.1 to 45.6	mC28	Unknown
Ni_7Sb_3	45	t**	Unknown
NiSb	61.0 to 69.2	hP4	$P6_3/mmc$
$NiSb_2$	80.2 to 80.5	oP6	Pnnm
Sb	100	hR2	$R\bar{3}m$

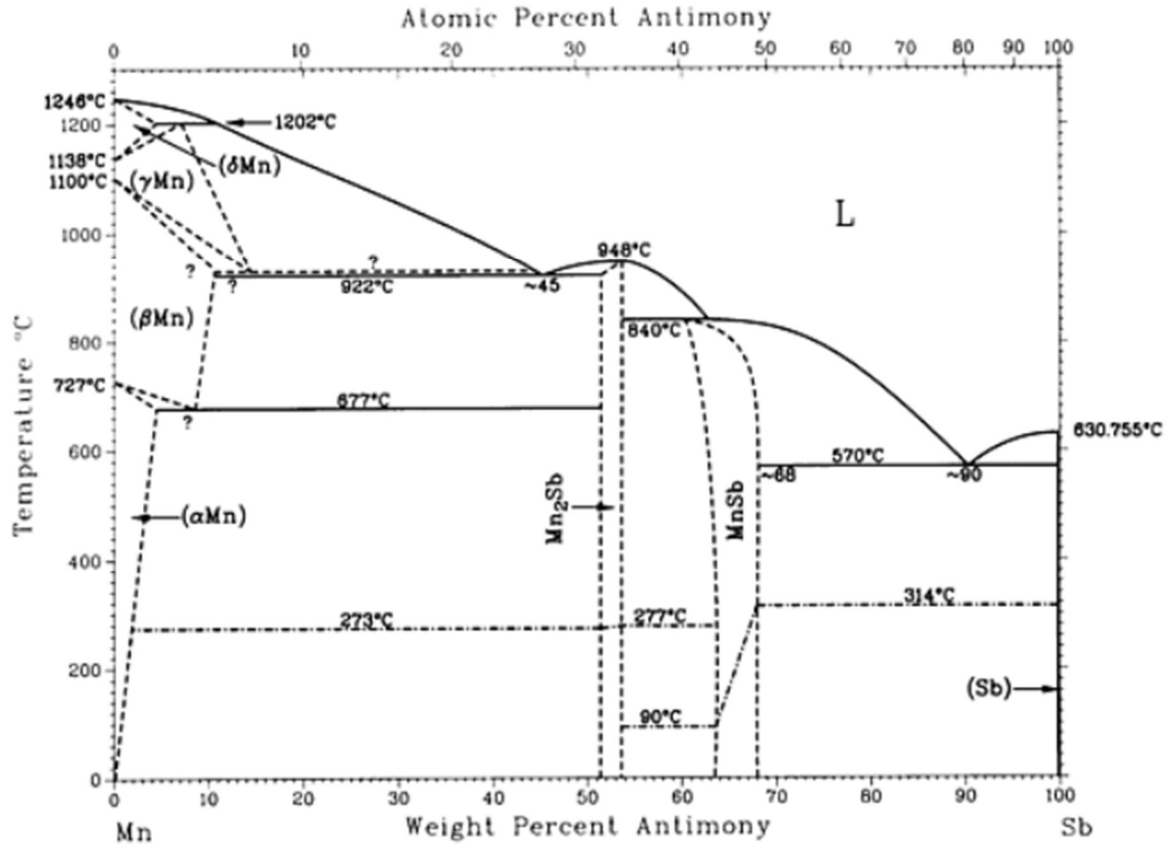

Figure 1.4 Equilibrium Phase Diagram of Mn-Sb [5]

In this phase diagram of Mn-Sb, we see allotropic transformations in pure Mn, as α-Mn which is a gamma brass type structure changes to primitive cubic structure at ~ 727°C which remains to be stable up to ~ 1100°C and then transforms to face centred cubic structure, which remains stable up to 1138°C and then transforms to δ-Mn which is body centred cubic structure. This whole series of phase transformation of manganese with respect to temperature is an example of an allotropic transformation. There is solid solution of Sb in Mn rich side but the boundary is not well defined and hence drawn in dotted lines only. There are stable intermetallics Mn_2Sb and MnSb in this phase diagram, which does not change into any other crystal structure with respect to temperature. The solid solubility of Mn in Sb is almost nil. In this phase diagram, the polymorphic transformation could not be encountered which is unlike of Ni-Sb phase diagram. A careful examination of the phase diagram upto ~ 33 atomic percent Sb resembles after famous Fe-C equilibrium diagram as almost all the features are there including peritectic

reaction, eutectic reaction and eutectoid reaction, however the temperatures of those reactions are not identical with the Fe-C equilibrium diagram.

Table 1.2 Different stable phases with their respective composition range along with the crystallographic information in Ni-Sb equilibrium phase diagram [5]

Phase	Comosition, wt % Sb	Pearson Symbol	Space Group
δ-Mn	0	cI2	$Fm\bar{3}m$
γ-Mn	0	cF4	$Im\bar{3}m$
β-Mn	0	cP20	$P4_132$
α-Mn	0	cI58	$I\bar{4}3m$
Mn_2Sb	~52.5	tP6	P4/nmm
MnSb	~61.0 to ~68	hP4	$P6_3/mmc$
Sb	100	hR2	$R\bar{3}m$

In this phase diagram of Ni-Mn system, there are many intermetallics which are forming within narrow range of composition and the boundaries of the composition range is also not well defined. This is an interesting phase diagram, as it shows an extended solid solubility over the entire range of composition when Mn is in its FCC structural allotrope. The γ (Ni,Mn) has a wide composition-temperature space in Ni-rich side, whereas it is narrow in the Mn-rich side, which can be attributed to different allotropic forms of Mn which has been discussed in the previous phase diagram. Apart from the allotropes of Mn, the polymorphic transformation is also observed at the equi-atomic proportion where, η which is primitive cubic structure transforming to η' which is tetragonal structure and η' transforming to η'' which is an unknown structure. This whole series of transformation can be seen as polymorphic transformation.

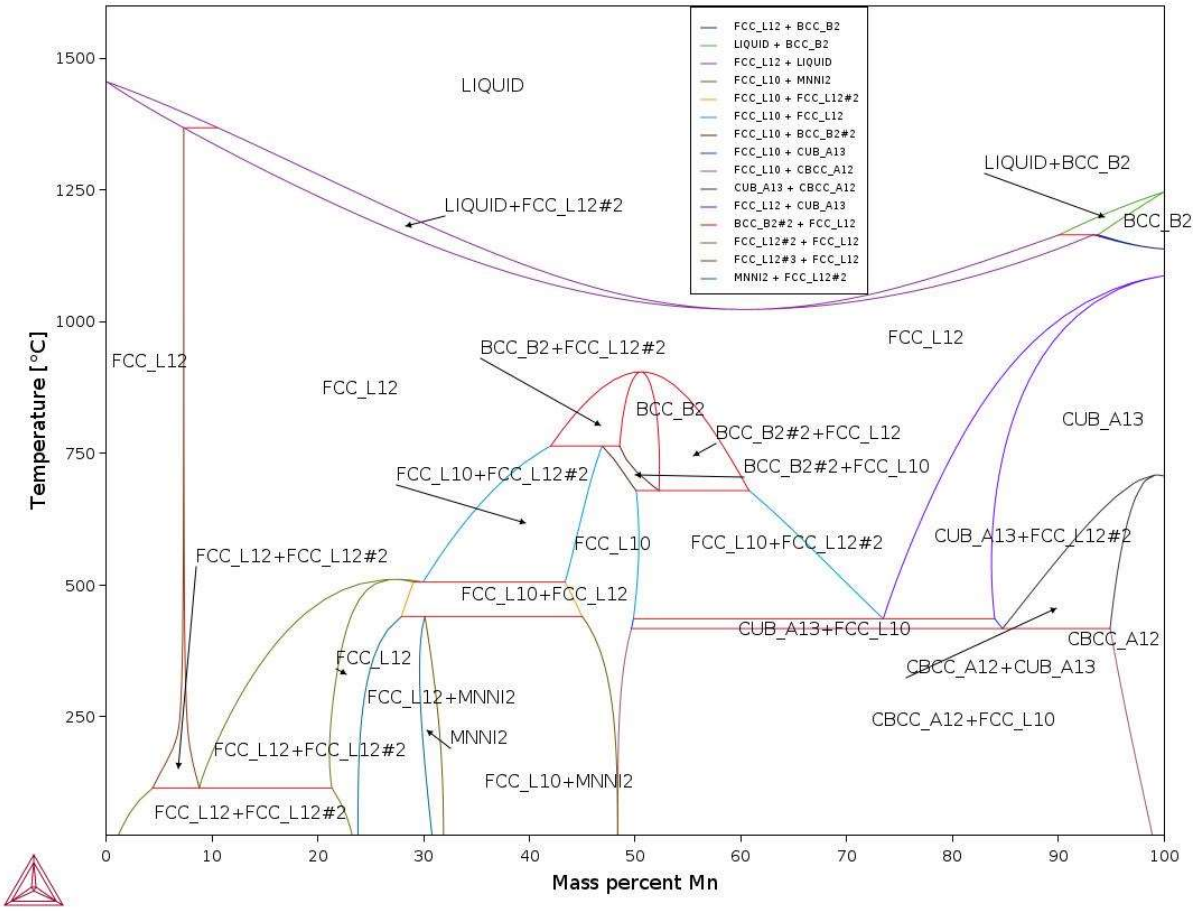

Figure 1.5 Equilibrium Phase Diagram of Ni-Mn [4]

Table 1.3: Different stable phases with their respective composition range along with the crystallographic information in Ni-Sb equilibrium phase diagram [4]

Phase	Composition, wt %Ni	Pearson Symbol	Space Group
δ-Mn	0 to 6	cI2	$Im\bar{3}m$
γ-(Mn,Ni)	0 to 100	cF4	$Fm\bar{3}m$
β-Mn	0 to 19	cP20	$P4_132$
α-Mn	0 to 10	cI58	$I\bar{4}3m$

φ	26	Unknown	Unknown
ε	34 to 38	Unknown	Unknown
η	47 to 54	cP2	$Pm\bar{3}m$
η'	49 to 57.1	tP4	P4/mmm
ζ	66 to 70	Unknown	Unknown
γ'	72 to 86	cP4	$Pm\bar{3}m$

1.2 Quasi-chemical theory for the formation of solid solution or intermetallic

E.A Guggenheim [6] proposed a quasi-chemical theory for the formation of solid solution and intermetallic compound in 1935 which can be presented here in a nutshell as

A-A + B-B = A-B

$\Omega = N Z \nu$,

where, Ω is the interaction parameter coefficient,

N is the Avogadro's number,

Z is the number of nearest neighbours relative to A and B,

ν is the interaction energy which can be computed as $\left|v_{AB} - \frac{1}{2}(v_{AA} + v_{BB})\right|$

v_{AB} is the interaction energy of the compound AB, whereas v_{AA} and v_{BB} are the self-interaction energies of A and B respectively.

Condition for the formation of solid solution, where $|v_{AB}| = |v_{AA}| = |v_{BB}|$ and Ω becomes 0 for which an ideal solid solution is defined.

Condition for the formation of an intermetallic compound $|v_{AB}| \gg |v_{AA}|\ and\ |v_{BB}|$and Ω becomes high in magnitude for which different intermetallics can be formed based on the stoichiometry.

1.3 Miedema's model

Miedema's model [7] is originally proposed for the binary systems to calculate the enthalpy of formation of solid solution for a particular composition. The enthalpy term in this model comprises of three factors which are chemical enthalpy, elastic enthalpy and structural enthalpy.

$$\Delta H^{\text{solid solution}} = \Delta H^{C} + \Delta H^{e} + \Delta H^{S}$$

$$\Delta H^{C} = X_A X_B \left[X_A \Delta H^{sol}_{B \text{ in } A} + X_A \Delta H^{sol}_{A \text{ in } B} \right]$$

X_A and X_B are the mole fractions of A and B respectively, ΔH^{sol} is the enthalpy of formation at infinite dilution.

$$\Delta H^{e} = X_A X_B [X_A \Delta H^{e}_{B \text{ in } A} + X_A \Delta H^{e}_{A \text{ in } B}]$$

The elastic enthalpy term is based on the relative difference in the atomic sizes and is related to the strain energy of the lattice

$$\Delta H^{e}_{i \text{ in } j} = \frac{2\mu_j (V_i - V_j)^2}{V_j (3 + 4\mu_j K_i)}$$

This term was proposed by Simozar and Alonso [25], μ_j is the shear modulus of the solvent, V_i and V_j are the molar volumes of i and j respectively, K_i is the compressibility of the solute.

The structural enthalpy term which mostly depends on the crystal structure of the elements, is almost negligible in the equation and hence it is neglected.

Just like the former case is presented for the solid solution formation, an equation can also be developed for the formation of an amorphous phase. The enthalpy for the formation of an amorphous phase majorly comes from the ΔH^{C}, whereas the ΔH^{e} term is neglected as there is no periodicity of the atoms in the material.

$$\Delta H^{am} = \Delta H^{C} + 3.5(X_A T_A^m + X_B T_B^m)$$

where, T_A^m and T_B^m are the melting points of pure A and pure B respectively.

For a given composition in the binary system, if $\Delta H^{solid\ solution} < \Delta H^{am}$, favors the formation of solid solution, and if $\Delta H^{am} < \Delta H^{solid\ solution}$ favors the formation of an amorphous phase.

1.4 Intermetallics

An intermetallic or an intermetallic compound or an intermetallic phase can be defined as the combination of elements of metals and metals, or metals and non-metals which is not necessarily needs to be strictly stoichiometric. The nature of bonding in these compounds should be majorly "metallic" in nature, however partial "covalent" or "ionic" character could be observed as well. The crystal structure of the resulting compound formed by these elements are often different from its parent crystal structures of the elements.

Classification of intermetallics

1. Stoichiometric intermetallic compounds.
2. Non-stoichiometric intermetallic compounds.
3. Electron Compounds / Hume-Rothery compounds.
4. Frank-Kasper phases / Size Factor compounds.
5. Heusler Alloys

1.4.1 Stoichiometric intermetallic compounds

These are the compounds which are strictly fixed by their stoichiometric ratio. The stoichiometry gets fixed because the self-interaction parameter "omega" gets a highly negative value for that particular fixed composition and we get a line compound in the phase diagram and are classified as strictly stoichiometric compound.

Ex –Mg_2Ni, $MgNi_2$ in Mg-Ni system, Mg_2Pb in Mg-Pb system, AlSb in Al-Sb system, Au_2Pb in Au-Pb system.

1.4.2 Non-stoichiometric intermetallic compounds

These are the compounds in which the composition may vary over a range. They are not fixed by the law of definite proportion. As they vary over a range of composition, they are always associated with the defects. In the phase diagram, these compounds exist over some narrow range of composition and hence are not line compounds.

Ex- Ni_3Al, AlNi, Al_3Ni in Al-Ni system, Ti_3Al, Al_3Ti, AlTi in Al-Ti system, Cu_3Au, Au_3Cu, AuCu in Au-Cu system.

1.4.3 Electron compounds / Hume-Rothery compounds

Electron compounds or "Hume-Rothery compounds" are the ones which forms at a particular electron/atom ratio. The forte of these types of phases is that its crystal structure stabilisation does not depend on its composition rather it is completely dependent on the valence electron concentration (VEC).

Table 1.4: Classification of electron compounds on basis of their electron-atom ratio

Composition	Number of valence electron	Number of atoms	VEC
β-phase			
CuZn	1+2	2	3:2 =21/14
Cu_3Al	3+3	4	6:4=21/14
γ-phase			
Cu_5Zn_8	5+16	13	21/13
Cu_9Al_4	9+12	13	21/13

ε-phase			
$CuZn_3$	1+6	4	7:4 =21/12
Au_5Al_3	5+9	8	14:8 =21/12

1.4.4 Frank-Kasper phases / Size Factor compounds

It is a class of intermetallic compounds, which are formed at a particular radius ratio of the constituent atoms. Frank Kasper were the first one to introduce this concept and hence it is also referred to as Frank-Kasper Compounds [8]. This class of intermetallic compounds is one of the largest group of intermetallic compounds where typical crystallographic structures are dealt within its sub-classification.

1.4.4.1 A-15 compounds

A15 Compounds are found with the stoichiometry AB_3, where A is a metalloid and B is mostly a transition metal. These compounds have a Pearson symbol cP8, and there are two coordination environments i.e CN12 and CN14. Complex interpenetration of different coordination environment leads to the formation of this structural class. Many of these compounds are generally superconducting in nature.

Ex- Cr_3Si, V_3Sb, Nb_3Sn

1.4.4.2 Laves phase

Laves phases are a subclass of Frank-Kasper phases which forms at 1:2 stoichiometric ratio. These kinds of phases were first discovered by the scientist Fritz Laves [9] and the characterization were purely based on the arrangement of atoms. These phases are categorised into the three classes which are i) cubic $MgCu_2$ (C15) ii) hexagonal $MgZn_2$ (C14) iii) hexagonal $MgNi_2$ (C36).

1.4.4.3 σ, μ, χ, P, and R phases

The sigma (σ) phase forms without a definite stoichiometric ratio of the constituent elements. However, electronic contribution is an important factor to stabilise

this phase with c/a ratio ~ 0.5. The properties of this class of intermetallic compounds are strongly dependent of the constituent elements, their stoichiometric ratio and other crystallographic attributes.

The μ phase generally crystallises in a hexagonal unit cell (c/a =5.4), with its prototype W_6Fe_7. The χ phase crystallises in a complex cubic (α-Mn type / γ-brass type) form with its prototypes $Fe_{62}Cr_{19}Mo_{19}$, $Fe_{59}Ti_{20}Cr_{20}$, $Fe_{50}V_{25}Si_{25}$ etc. It has cubic space group with 58 atoms per unit cell. The P-phase crystallises in an orthorhombic crystal structure with its prototype $Ni_{40}(Cr,Mo)_{60}$. It has a primitive orthorhombic cell with 56 atoms per unit cell. The R-phase crystallises in Rhombohedral form with its prototype $Ti_{18}Mn_{82}$, $Fe_{60}Mo_{40}$, etc. It contains 53 atoms per unit cell.

1.4.5 Heusler alloys

This class of alloy was first discovered by Freidrich Heusler [10] in 1903 which has the composition Cu_2AlMn and is unique in the sense that the compound is ferromagnetic in nature, however none of its constituent element is magnetic by itself. This class of material is considered as an excellent material for its functional properties [11–14]. The classification of Heusler alloys can be made which are purely based on the crystal structure, where the underlying lattice of all the sub classifications are same but there is a difference in the occupancy of atoms in their relative positions. There are four different class of Heusler alloys [15]

i) Full Heusler alloy which has the stoichiometry A_2BC with Pearson symbol cF16, where A atoms occupy the fundamental FCC positions along with the octahedral positions, B atoms and C atoms occupy the alternate tetrahedral void positions respectively.
ii) Semi-Heusler alloy which has the stoichiometry ABC with Pearson symbol cF12, where A atoms occupy the fundamental FCC positions, whereas B and C occupy the alternate tetrahedral void positions.
iii) Inverse Heusler alloy which has the stoichiometry A_2BC with Pearson symbol cF16, where A atoms occupy the fundamental FCC positions and half of the tetrahedral void positions. B atoms and C atoms occupy the

octahedral void positions and remaining half of tetrahedral void positions respectively.

iv) Quaternary Heusler alloy which has the stoichiometry ABCD with Pearson symbol cF16, where A atoms occupy fundamental FCC positions, B atoms occupy the octahedral void positions, C and D atoms occupy the alternate tetrahedral void positions.

1.5 High-entropy alloys

The term "high-entropy alloy" is coined by J.W.Yeh [16] and Prof. Brian Cantor [17] independently for forming a single phase solid solution by the addition of five or more elements in equi-atomic proportion leading to the maximum "configurational" entropy. "Entropy" itself is an extensive property (size dependent) which includes vibrational, electronic, magnetic, configurational entropies etc. [18] According to the classical definition, $S_{conf} = -R \Sigma X_i \ln X_i$. Combination of different elements in the equi-atomic proportion which takes up the S_{conf} to 1.63R or more. In this situation, the alloy should be termed as "HEAs". But as this term has already been contested by Walter Steurer [19], out of 118 elements in the periodic table, if combinations are made in the group of five, there would be **17,49,63,438** independent ways which is quite a large number. Even if we omit the gases, noble gases and some non-metals out from the periodic table to represent only the alloy systems and not the oxides ones, even then the combination comes out to be **7,52,87,520** which is still not a small number, and adding the variables of composition and temperature for the construction of phase diagrams would need quantum computers to predict the phase fields in the phase diagram. These large numbers of alloys cannot be cast and studied simultaneously because it's not feasible in terms of resources and time available to us. Out of such large spectra of alloys only a few have been studied so far, and the attempt has been made to mostly look for the alloys which form single-phase solid solution (SPSS). The general composition of studied HEAs is mainly the transition elements of the fourth row of the periodic table (3-d transition elements) and it does not prove that all the compositions of this sort would end up in forming SPSS. Among them, there are only few alloys which forms SPSS which follow the Hume-Rothery rules [20] (extending the idea to multicomponent systems). The configurational entropy alone cannot be held responsible for the formation of SPSS. It can be understood in this way that in binary alloys also we have

seen that there are isomorphous regions in the many of the phase diagrams and the reason given is not even closely related to the concept of “configurational entropy” rather it has been attributed to the empirical rules made by Sir Hume-Rothery.

To study all the composition space w.r.t temperature of ternary, quaternary and quinary alloys is very cumbersome exercise and to validate it with the experiments is again a mammoth task. Therefore, with the help of CALPHAD [21,22] and by the use of throughput calculations [23] very few of such problems have been handled so far and that too within a very narrow composition regime. Since from the inception of high-entropy alloys, each and every one of us are trying to understand that how the entropy term and that too configurational one is important in stabilising the system and in the process [24], we have mostly ignored the “enthalpy” term. Most of the high-entropy alloys which have been studied so far are at the room temperature and hence therefore configurational entropy term alone cannot dominate as at the lower temperature, frequency of atomic vibration steeply goes down therefore the “TS” term can be equally compared with “H” term which have been completely ignored in the aspect of inventing the term “high-entropy”. The high-entropy term can only be valid if the atoms of the constituent elements in the lattice could freely exchange their positions and it is possible only at the temperatures close to the melting points of the respective alloys. The configurational entropy term would count for this condition and when multiplied with the temperature would dominate the term “H-TS”, therefore if the alloy gets solidified from the melt at a very high cooling rate so that the microstructure can be retained, then high-entropy term can be given to the alloy, otherwise if the cooling rate is slow and the microstructure develops according to equilibrium conditions and it would be very difficult to establish this term.

When the researchers tried to blend the elements in equal atomic proportions, in most of the alloys they were not getting the single phase so they have coined a new term multi principal elemental alloys “MPEAs” or complex concentrated alloys “CCAs” [25] which is quite a reasonable term to be used for this class of alloys. The term “MPEAs or CCAs” is a more “generalized term” where the elements of any choice can be added and melted and can have any microstructural features, but the “HEAs” is a “specialized term” and should be given to only those alloy composition configurations, where it would form a SPSS with a homogeneous microstructure. According to the standard

definition in terms of configurational entropy, MEAs (Medium entropy alloys) are defined when configurational entropy falls in the range from 1.09 R to 1.63R. Medium entropy alloys have shown exceptional mechanical properties in B2 ordered refractory $Al_{15}Nb_{40}Ti_{40}V_5$ alloy, where grain boundary strengthening in the alloy is found to be almost 3 times the regular refractory HEA[26]. The grain boundary strengthening is also reported Liu et al.[27] in VCoNi medium entropy alloy, the strengthening is mainly attributed to the high lattice friction stress. VNbTa bcc medium entropy alloy has also shown excellent cryogenic strength and ductility, attributing the properties to mechanical twins, cross-slip of dislocations and their interaction[28]. NiCoCr medium entropy alloy doped with Nb has also shown good ductility with yield strength, this combined strength is due to strengthening from nano precipitates, high-density stacking faults and nano twins[29].

The scientists who were involved with the work on glasses or bulk metallic glasses or quasicrystals gained traction [30] with this new realm of materials (HEAs) as this class deals with multicomponent system. Many of the research scientists are even trying to compare the CCAs or MPEAs or HEAs with BMGs (Bulk metallic glasses). BMGs concept is not in total different contrast with this one, as one of the essential criteria for the formation of glass is based on the **confusion principle** as proposed by Greer for the multicomponent alloys [1], where he quotes "*The most confusing elements will be those that differ most from each other in size*", he has made this statement when the so called "high-entropy" term was not even discovered. There are reports of different MPEAs forming SPSS (HEA) which are mostly based on 3-d transition elements and when their lattice parameters were calculated, it has been found that they are approximately close to the transition elements only [31,32]. The HEAs are purely crystalline phases and at times form quasicrystalline phase when rapidly solidified [33], and very rarely it also forms glasses if the composition chosen is closely related to the glass forming composition of alloys [34]. Miedema's model, which was originally proposed for the binary system for the prediction of enthalpy of formation for solid solution can be extended to ternary components. The Miedema's model has been extended to ternary system by Gallego et al. [35]. However, the equation includes only the binary combinations of enthalpies and the major contributing term "self-interaction coefficient" which should have been in the equation is missing. To calculate the ternary

self-interaction coefficients of different combination of elements is an exorbitant task to perform, that's why the thermodynamic database for the ternary and higher order systems are very less available in the literature. Can we use this model for the prediction of multicomponent SPSS or not? Extending the concept to multi-composition space would require large number of variables which must be invoked into the equation (eg. ternary, quaternary or quinary interaction coefficients) and the experimental thermodynamic database for multi-component systems are not available. The major drawback of extending the Miedema's model to multi-component system is that there is very limited thermodynamic database available to us so far.

The digression of strictly equi-atomic proportion to non-equiatomic proportion in the search of SPSS has been the trend of research as it is supposed to give exotic functional and mechanical properties [36]. There are evidences of stabilisation of alloys as a single phase concentrated solid solution suitable for high-temperature strength, oxidation resistance, corrosion resistance and can be seen as a potential candidate for fission reactors [37]. The quest for the search of SPSS alloy is based on the properties, which should not change with respect to either temperature or pressure. If one has to look for the properties which should withstand high temperature, then the alloy should not be amenable to any kind of phase transformation at the higher temperature else it will lead to deterioration of the properties, similarly, if an alloy has to be used for high-pressure application, then also the alloy should not exhibit to any kind of phase transformation at high pressure.

There are four "core" effects of high-entropy alloys. We have already discussed much about the **"high-entropy"** effect and have already contested for it and have found that this parameter is not so effective in forming SPSS at the room temperature. The second core effect is **"severe lattice distortion"**. Is it really possible to distort the lattice severely by adding elements of nearly the same kind (talking of most of the HEAs which has formed SPSS)? If the system has formed the SPSS, then it simply can't distort the lattice severely [38]. Severe lattice distortion can be best understood with the help of high-energy ball milling, where we serendipitously increase the Gibb's free energy of the system (by imparting the balls to the powders) and there only the lattice is severely distorted and if continued for a very long time depending upon the ball size and frequency of the vibration of balls, it will ultimately lead to not only distort the lattice

severely rather it might end up in having no lattice at all which is basically known as "glass" [39]. The next effect which is discussed in the literature focuses on **"sluggish diffusion"** effect, which says that the diffusion rates of elements in the high-entropy alloys would be relatively slower than the conventional dilute solid solution. In high entropy alloys, the solute elements are mostly substitutional and hence the diffusion rates steeply go down. The slower diffusion rates would result in slowing down the kinetics of phase transformation. This effect is said to be dependent on the composition elements, if the elements are too different from each other in terms of atomic radii, then the diffusion plays a major role in deciding the sluggishness [40], this point can be discussed and thought of in terms of atomic position of elements in the periodic table and it can be mostly understood by basic knowledge of high school chemistry. The HEAs found so far are mostly based on the 3-d transition elements and they fall in the same period of the periodic table and there is not much difference in terms of atomic radii, so diffusion has to be sluggish, however if the elements are blended, which are having different atomic radii and their relative positions in the periodic table are also different with negative enthalpy of mixing then the possibility of forming intermetallics becomes prompt. This parameter does plays a vital role for forming SPSS. The last core effect of high entropy alloy is **"cocktail"** effect, this term was coined by Prof S Ranganathan [41] and is considered to be the most important point for the discussion because it says that possibilities of outcome (in terms of microstructure and crystal structure) is depending upon the material chemistry and thermodynamics of phase equilibria. This is the only criteria which cannot be contested in any terms and would like to deal with it.

1.6 Alloy design strategies

The emphasis of designing an alloy should be related to the desired properties which we aim for. Designing an alloy is mostly composition and crystal structure driven and therefore we should have a scrupulous understanding of the phase diagrams and crystallography involved for that particular composition of any alloy. The design parameter from the very early days of metallurgy focuses on the strength and ductility and correlating it with the grain size of the material has been an active area of research in the recent past.

1.6.1 Strength-ductility trade-off dilemma

The strength and ductility trade-off dilemma in the alloys is a fascinating subject in the field of mechanical metallurgy. This dilemma is seen in many alloy systems including steels, Al-Si alloys, recently discovered high-entropy alloys, etc. The alloy processing techniques such as rapid solidification, mechanical alloying which are non-equilibrium processes have led to the development of alloys which shows this dilemma. However, their phase stability has been a subject of discussion. Therefore, the practice is to attain a composition which if processed through non-equilibrium solidification processing route should end up in having near stable or stable phase. Dang et al. [42] have reported the trade-off dilemma in rapidly solidified Al-Si alloys followed by PHT (Post Heat Treatment) and the increase in strength has been attributed to nanoscale Si particles in the alpha-Al and the ductility trade-off is attributed to nanoscale Al particles embedded in the eutectic silicon (brittle). Wei et al. [43] have shown that how purposefully twins were introduced in the high manganese steel by the torsion. The microstructures were recorded as a function of radial distance and there was hierarchical twinning (primary, secondary and tertiary) and the density of twins in the grain was also observed to increase against the radial direction. The dissociation of a perfect Burger's vector to partial dislocations and gliding of these partial dislocations on the plane of shear and conjugate twinning plane is considered to be one of the prime causes of retaining ductility without losing the yield strength. Huang et al. [44] have observed the similar behaviour in Co based multicomponent alloys, through the TRIP (transformation induced plasticity), where the FCC phase transforms to martensite during deformation. They have attributed it to Σ3 twin boundaries, stacking faults and interaction of precipitates with the defects giving rise to increase in the ductility. Fu et al. [45] and Li et al. [46] have reported that the CrFeCoNiMnCu HEA showed extraordinary mechanical properties, which are processed by laser shock peening. It introduces the gradient in the microstructure along the depth of the sample. When followed by deep cryogenic treatment, which induces primary and secondary nanotwins along with dense dislocation walls, that helps the alloy to increase the yield strength along with the increase in ductility. Tu et al. [47] have reported that CuAlMn alloy, which is one of the promising candidate for the shape memory alloy, can be modified by the addition of Fe to the base alloy which leads to refinement of grains by the precipitation of

intermetallics. By the subsequent heat treatments (base alloy and its modified form) mainly by step quenching within a very narrow temperature range results in the formation of two phase microstructure (α-phase delineated along the grain boundaries of primary β-phase, where α is FCC and β is BCC). The step quenched alloy (modified) with larger volume fraction of α-phase and with some other intermetallics have shown greater yield strength without losing its ductility.

1.6.2 Inverse Hall-Petch relationship

After the advent of nanotechnology and understanding about the nanostructures, a phenomenon known as "Inverse Hall-Petch" relationship has been discovered. There is a decrease in strength with refinement in the grain size (after reaching a threshold). Chokshi et al. [48] were the first one to report this dilemma which was made on oxygen free high conductivity copper and palladium. They consolidated nanopowders from inert gas method and have observed the hardness values with respect to grain size. They attributed this trade-off dilemma to the diffusional creep mechanism, where the vacancy migration towards the grain boundary led to the decrease in the hardness value. Carlton and Ferreira [49] have tried to assess the problem using different models proposed by different researchers and have established a good reasoning behind the phenomenon. The different models proposed were dislocation based models [50–54], where the authors claimed the propagation of dislocations was the primary cause of strengthening the material and decreasing the length scales of grains would not be able hold up the propagation of dislocations within the grain and therefore the yield strength decreased with further refinement in the grain size. Another model [55] was based on the diffusion and coble creep, where a relationship between the yield strength of the material with respect to grain size was compared to the equicohesive temperature (where the grain and grain boundary have equal strength). The model tried to establish that the yield strength of the material increased with decreasing grain size. However, beyond a threshold limit (length scale of grains ~ 10-30 nm), the yield strength started decreasing with decreasing grain size. In addition to it, the model stated that shearing of grain boundary was the dominant mechanism for the deformation at low grain sizes and this model was designed by taking the grain and grain boundary as two different phases.

1.6.3 Structure-Property correlations

The structure-property correlation can be diversified in the following two sections i) crystal structure-property correlation ii) microstructure-property correlation. The crystal structure –property correlation is evident in case of pure metals. Pure metals having identical structure and having same nature of chemical bonding behaves in a similar fashion. The mechanisms of deformation in pure metals of identical crystal structure remains to be the same [56]. The functional properties such as electrical conductivity or thermal conductivity are also driven by the crystallography and chemistry of metals. The microstructure-property correlation is of utmost importance in binary, ternary or higher order systems as it governs the mechanical properties. The morphology of precipitates, the orientation of the second phase with the matrix, planar defects arising from deformation, nature of interfaces (coherent, semi-coherent or incoherent) plays crucial role in determining the mechanical behaviour of materials. The mechanism of growth, "nucleation and growth" and "spinodal decomposition" in different alloy systems defines the functional properties such as magnetic properties in solids [57]. In general, functional properties attain its maximum when the microstructure consists of single phase, or the microstructure has two phases with very similar crystal structures and with coherent interfaces. Loken et al. [58] have reported that Mg based alloys after ECAP (Equal Channel Angular Pressing) and HEBM (High Energy Ball Milling) has a better absorption and desorption rates of hydrogen as the defects produced by these severe plastic deformation techniques provides better hydrogen diffusion routes and this is quite effective if HEBM is followed by ECAP. Xialon Li et al. [59] have shown that modified Cantor alloy with the addition of Al and V to the alloy composition changes the microstructure of the alloy to the larger extent. However, without Al addition the whole microstructure consists of either CCP structure or BCC structure along with the ordered intermetallic compound (B2) coherently embedded with the BCC matrix. Golumbsfique et al. [60] have done the rapid solidification of Al-late transition metal alloys by spray forming method. They have found that the volume fraction of precipitates which takes up almost 75% of the microstructure with the major fraction being Al_3Y with sharp edges, Al_9Co_2 as the second major phase of near spherical shape and $Al_{16}Co_3Y$ precipitates which are elongated and least in the volume fraction among all the precipitates, leads to the increase in the mechanical properties of the alloy. Mishra

et al. [61] have reported that in Full Heusler alloy (Cu_2AlMn) after the addition of Ga for the substitution of Al upto x=0.28, retains the single phase microstructure ($L2_1$ or cF16). It gives rise to higher degree of crystallinity as the peaks from the reflecting planes becomes more intense. Further addition of Ga to the alloy splits the microstructure into two phases, of which one is hexagonal and the other is complex cubic (gamma brass) which deteriorates the magnetic property of the alloy.

1.6.4 Grain boundary engineering

The grain boundary engineering is a process by which the mechanical properties of a material can be enhanced by altering the grain boundaries in any given alloy. The concept of CSL (coincidence site lattice) is essential and key to the fundamentals of grain boundary engineering. The aged Ni base alloy, showed a good resistance to deformation at higher temperature as compared to its annealed counterpart [62] as reported by Liu et al. The presence of low Σ CSL boundaries inhibits primary recrystallisation and becomes barrier to the grain boundary migration. The formation of multiple twinning is the underlying fundamental of GBE in this alloy system. Mao et al. [63] have reported that the mechanical properties of nickel based superalloys can be improved by grain boundary engineering. The alloy when cold rolled, followed by heat treatment at higher temperature for less period of time, it introduces low Σ CSL boundaries. Volume fraction of $Ni_3(Al,Ti,Nb)$ (needle shaped morphology) precipitates increases with ageing time. Introduction of the CSL boundaries along with the increase in the volume fraction of precipitates is believed to be the operating mechanism for the increase in ductility of the alloy. The enhancement in the thermoelectric properties of semi-Heusler alloy TiNiSn is observed by Zhang et al. [64] The increase in the performance (figure of merit) can be attributed to the refinement of the microstructure by passing pulverised powder through sieving. The GBE is applied to the sulphur induced polycrystalline nickel to increase the fracture toughness of the alloy [65] as shown by Kobayashi et al. The doping of sulphur causes a homogeneous fine grained microstructure with major fraction of low Σ CSL boundaries resulting into higher fracture toughness of the alloy.

1.7 High-energy ball milling

High-energy ball milling is an unconventional, non-equilibrium process in which a planetary ball mill is used with several balls in it moving at a very high speed (~200 rpm) to synthesize metastable phases, metastable intermetallics, quasicrystals or amorphous phase. This process was invented by John S Benjamin at the Paul D. Mercia Research Laboratory in 1966 [66]. There are many milestones which this process has achieved so far which mainly includes the extension of solid solubility limits, refinement of grains to nanocrystalline range, formation of novel intermetallic phases and quasicrystals, etc. In this process, there are two generic terms which are generally used i) Mechanical milling ii) Mechanical alloying [67]. The fundamental difference between these two terms is that former does not involve material transfer in the process, whereas later involves material transfer in the process. Mechanical milling does not involve material transfer during the process, however it is very useful process for the observation of disordering in any intermetallic, it has also been reported that after long hours of milling it sometimes end up in forming an amorphous phase. Mechanical alloying involves material transfer in the process and results into the formation of metastable phases. Credits of mechanical milling/alloying is discussed in detail in the following sections.

1.7.1 Extension of solid solubility

The events of mechanical alloying consist of collision of planetary balls at a very high speed and the powders trapped between the balls experiences severe plastic deformation. This results in increased dislocations or defects, which helps in increasing diffusion of elements. In turn, results in increasing the solid solubility limit in a given system. Schwarz et al. [68] were the first ones to show the formation of amorphous phase by mechanical alloying in Ni-Ti system. They have also shown that after high-energy ball milling, the solid solubility limit of Ti in Ni which is ~ 8 atomic percent may increase to ~ 28 atomic percent. The Co-Mo and Cr-Mo phase diagrams show almost no solubility of each other at the room temperature. However, when mechanically alloyed, these alloys have shown extended solubility of 4.3 at% of Mo in Cu, and also forms the amorphous phase in almost equi-atomic Cr-Mo system [69]. Similar observation in Cu-Nb system has also been made by Lei et al. [70], where the solid

solubility of Nb in Cu is less than 0.1 atomic percent at the room temperature. However, the solid solubility limit may be extended to 6 atomic percent by high-energy ball milling. The surface and elastic strain energy is considered to be the main driving force for the extension of solid solubility. The presence of defects in the alloy in the form vacancies [71], dislocations and increased area of grain boundaries [72], can be attributed to the increased solubility limit of the alloy.

1.7.2 Refinement of grain size to nanoscale range

This non-equilibrium processing technique "high-energy ball milling" if applied to alloys, it refines its grains to a very large extent. The alloyed powders when premixed for the mechanical alloying inside the vial and given a rotation at a very high angular speed, the particles would get trapped between balls and because of cold welding (high-pressure welding at the ambient temperature), agglomeration takes place, which results in coalescence of the different particles [73]. Further milling creates cracks in the coalesced particle and it disintegrates again into fragments of finer and finer particles of very smaller length scales (~nm) with increased dislocation density. After long hours of continued alloying, system finally reaches to a steady state condition or configuration, where refinement of the grain or particle size comes to saturation which occurs when rate of fragmentation of particles becomes equal to rate of cold welding. The grain refinement process of tungsten powders under the high-energy ball milling process is reported by Liang et al. [74] and Wu et al. [75], where a minimum grain size of ~ 5 nm was obtained.

1.7.3 Formation of intermetallic, metastable phases and quasicrystal

Formation of metastable phases during mechanical alloying is observed quite often as there are many local minima exist along with global minima in the Gibbs free energy landscape. As it is a non-equilibrium processing technique, a metastable phase has a certain chance of getting trapped in one of the local minima, which would be crystallographically related phase transformation with respect to the parent phase. Zhu et al. [76] reported the formation of Fe_3Al when solidified through the melting route. With the addition of Ti, it behaves differently when processed through mechanical alloying followed by HIP (Hot-impression pressing). The mechanically alloyed powders followed by HIP showed a higher yield strength due to the distribution of Ti powders

along the boundaries of the refined grains that hinders the dislocation movement while deformation. However, a paradox is observed in the as cast Fe_3Al alloy with the Ti addition as it shows positive yield strength with temperature compared to the negative slope of yield strength with temperature for the mechanically alloyed and compacted powders. The paradox is attributed to the grain boundary sliding becoming prominent in the former case. Alam et al. [77] reported the formation of Al_2Cu intermetallic compounds by mechanical alloying starting from pure Cu and Al powders taken at the ratio 1:2 volume fraction. It also reported that all the fraction of mechanically alloyed powders has not transformed into Al_2Cu, however with the increased milling duration, the volume fraction of Al_2Cu in the mechanical alloyed powder is increased. Karati et al. [78] synthesized a single phase microstructure with improved thermoelectric properties starting from the combination of two semi Heusler alloys of TiCoSb and TiNiSn. An interesting observation is made by Nakhl et al. [79], in the mechanical alloying and milling process of Y and Ni in equi-atomic proportion. The study shows the formation of new metastable "YNi" compound in both the cases which is different from as-cast stable YNi intermetallic compound. A high pressure metastable Mg_2Sn intermetallic compound has been synthesized by mechanical alloying which initially forms as stable cubic Mg_2Sn which on continued milling transforms to hexagonal Mg_2Sn as a metstable phase modification [80]. The formation of quasicrystals which lies between the crystallinity and amorphization has also been reported by many authors [81–84]. The formation of quasicrystalline phases which is generally observed through rapid solidification, vapour deposition (sputtering) or ion beam technique where these processes can attain a very high cooling rate. The same result has also been obtained by the mechanical alloying because of the interdiffusion of elements which happens at a very high deformation rate.

1.8 Motivation and Objectives

The motivation behind this research is to advance the understanding of complex binary to multicomponent alloys. This includes understanding how variations in alloy composition and processing routes impact phase stability, which is crucial for optimizing material properties in various applications. This knowledge is essential for innovating new materials with tailored properties suited for technological advancements in diverse fields**.** The primary objective of the present work is to understand the polymorphic transformation in concentrated equi-atomic Ni-Mn alloy, microstructural evolution and thermal stability in semi-Heusler NiMnSb and V added NiMnSb alloys and to study the effect of configurational entropy in stabilizing the single phase solid solution of NiMnSb and NiMnSbV mechanically alloyed powders by high-energy ball milling. The broad objectives are mentioned as follows:

- Synthesis of as-solidified NiMn, semi-Heusler NiMnSb and V added NiMnSb alloys by vacuum induction melting and mechanically alloyed powders of NiMnSb and NiMnSbV by high energy ball milling.

- Phase evolution in as-solidifed NiMn, semi-Heusler NiMnSb and V added NiMnSb alloys and mechanically alloyed powders of NiMnSb and NiMnSbV.

- Thermal stability of as-solidified semi-Heusler NiMnSb and V added semi-Heusler NiMnSb alloy.

- The role of configurational entropy in stabilizing the mechanically alloyed powders of NiMnSb and NiMnSbV as a single phase solid solution by non-equilibrium processing.

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