Chapter 1

Introduction

High-entropy alloys (HEAs), or multi-principal element alloys (MPEAs), have been attracting tremendous attention from researchers since their discovery. The ability to screen the large compositional space of the HEAs methodically and efficiently to identify new single-phase solid solution alloy systems is required for further development of HEAs research. Many empirical parameters were designed for this purpose. A brief introduction to HEAs is given in section 1.1. Section 1.2 deals with some important empirical and thermodynamic-based design criteria. Among these approaches, the Calphad method has been widely and successfully employed in alloy development and research for decades. In this approach, thermodynamic properties and phase equilibria in multicomponent systems can be calculated using suitable Gibbs energy models and databases. A brief overview of database development is provided in section 1.3. Details of available commercial thermodynamic software and databases are given in section 1.4. Various Gibbs energy models for the solid solution phases are discussed in section 1.5. Cluster expansion (CE) and cluster variation method (CVM) models are given in Section 1.6. Section 1.7 explains the first principle calculations and its uses. Two sets of input data are used in the CALPHAD type modeling: thermochemical data and phase equilibrium data. Thermochemical data is usually for individual phases and is scarcer than phase equilibrium data, which generally involves more than one phase and is relatively easier to obtain experimentally than thermochemical data. First-principles calculations thus complement experiments ideally by providing much-needed thermochemical data of individual phases. Section. The scope of the present investigation is given in section 1.8.

1.1 High Entropy Alloys

HEAs were first proposed in 2004 by Yeh *et al*. (2004), and since then, they have been the subject of intense research. High entropy alloys (HEAs) belong to a category of metallic materials characterized by the presence of multiple principal elements, usually five or more, distributed in approximately equal atomic proportions. The substantial degree of entropy inherent in these alloys contributes to a diverse range of intriguing and beneficial material properties. They can also exhibit unique mechanical, thermal, and electrical properties that are not found in conventional alloys. High entropy alloys (HEAs) have several unique features that set them apart from traditional alloys, including:

(i) Multi-element composition: HEAs are composed of five or more elements, usually in roughly equal proportions. This composition gives HEAs a high degree of chemical complexity, which can lead to unique and desirable properties.

(ii) High configurational entropy: The large number of elements in HEAs creates many possible configurations of atoms, which leads to high configurational entropy. This high entropy can result in unusual crystal structures and unique mechanical, physical, and chemical properties.

(iii) Superior mechanical properties: HEAs have been found to have superior mechanical properties, such as high strength, ductility, and toughness. These properties can be further improved by appropriate alloy design and processing.

(iv) Improved corrosion and wear resistance: HEAs have been shown to exhibit improved corrosion and wear resistance compared to traditional alloys. This makes them suitable for applications in harsh environments.

(v) Good high-temperature stability: Some HEAs have excellent high-temperature stability, making them ideal for use in high-temperature applications such as gas turbines and nuclear reactors.

Overall, the unique combination of these features makes HEAs an exciting and rapidly growing area of research and development in materials science and engineering.

1.2 Criteria and methods for predicting HEA stability

The Hume-Rothery Rules

Hume-Rothery rules, named after William Hume-Rothery (1969), are perhaps the earliest guide to the formation of solid solution alloys. The Hume-Rothery rules are usually applied to the solubility of a single solute in a single solvent, i.e., to binary alloy systems. The solubility of an element in a host metal depends mainly on four factors: the crystal structure, the atom size, the chemical affinity, and the valence electron concentration. Among them, the atom size plays a crucial role in forming random solid solutions, and the solute solubility falls rapidly for size differences larger than 15%. The other three empirical rules can be specified as the smaller difference between the electronegativities of the constituent elements and the similarity of the valence electron number of the constituent elements, similar crystal structure plays main role in solid solubility. Recently, as a result of the emergence of HEAs, new empirical rules have been proposed to predict solid–solution HEAs. These empirical rules are based on some additional parameters, such as thermodynamic parameters, including mixing entropy, enthalpy, and Ω parameters; the other parameters include valence electron concentration and electron/atom (e/a) ratio. These parameters are briefly discussed in the following sections.

Mixing Entropy (ΔS_{mix})

According to Yeh *et al*. (2004), a multicomponent alloy's mixing Entropy (mainly configuration entropy) gradually rises as the number of components does as well. When the solid solution phase forms more readily, and the Gibbs free energy of the solid solution phase decreases, a high-entropy alloy (HEA) is created. (Particularly at higher temperatures). Eq. 1.1 illustrates the calculation formula for high-entropy alloy mixing entropy.

$$\Delta S_{mix} = -R \sum_{i=1}^{N} x_i ln x_i \qquad 1.1$$

Where N = number of components present in the multicomponent system; x_i = concentration of the i^{th} component (in at. %); and, $R = 8.314$ J/ (mol. K) gas constant. According to the formula for mixing entropy, the alloy system has the highest mixing entropy value if there is a 1:1 atomic ratio between the *N* types of constituents. $\Delta S_{mix} = 1.5\ R$ value is the threshold for distinguishing between high and medium entropy. Past research suggested that a configurational entropy of mixing exceeding $1.5\ R$ is essential for high-entropy alloy synthesis. However, later studies suggested that high-entropy alloys are not created, even if entropy values for some multicomponent alloys are high. While adding more alloying elements will undoubtedly increase the entropy of any solid solution's configuration, this will also improve the likelihood that a stable intermetallic compound phase will form. Ideal configurational entropy often overestimates the entropy of mixing in real solutions. To predict phases in HEA Otto *et al.* (2013) have shown that the number of elements definition is insufficient. The addition of elements is shown in Figure 1-1**,** where the added elements have a similar crystal structure, electronegativity, and atomic diameter. According to the definition of HEA, all these alloys with replaced elements must have single phase solid solution as shown by base alloy/Cantor alloy (CoCrFeMnNi). But Figure 1-1 X-ray diffraction patterns of the six alloys with

equiatomic composition.(Otto et al. 2013) (Scintag DMC-008 diffractometer (Scintag Inc., Cupertino, CA, USA operated at 40 kV) shows that not even a single alloy has a single-phase solid solution; instead, they all show multiple phases. Metallic solid solutions are generally not ideal (Tomilin and Kaloshkin 2015). The temperature change from the alloy's melting point to room temperature changes the short-range order. In the solid phase, a temperature change may lead to chemical partitioning between the product and the parent phase. In all these cases, a difference in entropy is attributed to a change in temperature (Miracle and Senkov 2017).

Table 1-1 Five alloys with equiatomic composition with different elements. The base alloy is Cantor alloy.

Base alloy	CoCrFeMnNi				
Elements Replaced	Ni	Cr	Co	Fe	Cr
Alloy	CoCrFeMnCu	CoMoFeMnNi	TiCrFeMnNi	CoCrVMnCu	CoVFeMnNi

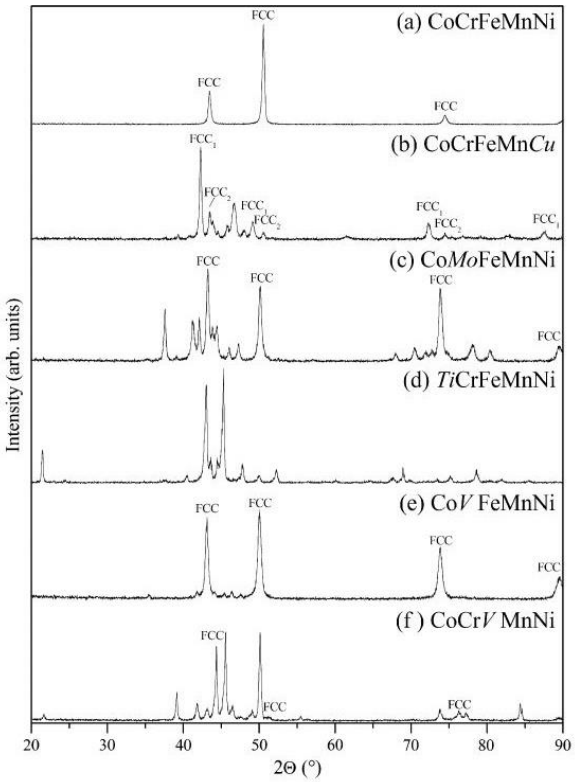

Figure 1-1 X-ray diffraction patterns of the six alloys with equiatomic composition.(Otto et al. 2013)

George *et al.* stated many alloys with elements lower than five possess single-phase solid solutions (George, Raabe, and Ritchie 2019). These alloys are, for sure, enthalpy stabilized rather than entropy stabilized. So, determining the phase stability based on entropy criteria is not wise. Instead, one should consider the enthalpy and entropy while predicting the phase stability of HEAs. The Gibbs energy (Gibbs and Willard 1903; J. W. Gibbs 1873) of a phase, which accounts for both enthalpy and entropy contributions, determines the stability of that phase. The equal-atomic composition reflects the state with the highest entropy of mixing, albeit not necessarily the lowest Gibbs energy, for a multicomponent solid solution phase. A system's equilibrium state results from stability competition between the system's phases. In addition to increasing the entropy of mixing

solid solution phases, increasing the number of critical components can also create other undesirable phases.

Mixing Enthalpy (ΔH_{mix})

The stability of phase is governed by thermodynamics, specifically Gibbs energy, if kinetic considerations are ignored. The formula for Gibbs energy is shown in Eq. 1.2.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad 1.2$$

The mixing enthalpy (ΔH_{mix}), in addition to the mixing entropy (ΔS_{mix}) is one of the parameters that need to be considered. Consequently, Zhang *et al*. (2008) introduced the (ΔH_{mix}) parameter, and its formula is shown in Eq. 1.3

$$\Delta H_{mix} = \sum_{i=1, i\neq j}^{N} 4\Delta H_{AB}^{mix}\, x_i x_j \quad 1.3$$

Where x_i *and* x_j are the mole fractions of two elements (*A*-*B*) and mixing enthalpy of a two-component alloy, ΔH_{AB}^{mix}, is a quantity that denotes the chemical affinity between components. It is computed using the Miedema model.

The Delta (δ) parameter

Zhang *et al*.(2008) proposed the Delta (δ) parameter to jointly envisage the phases that the multicomponent alloy goes through, the mixing Entropy (ΔS_{mix}) and enthalpy (ΔH_{mix}) are combined with the delta (δ) parameter. The Delta (δ) parameter's formula is displayed in Eq. 1.4

$$\delta = \sqrt{\sum_{i=1}^{N} x_i(1 - r_i/\bar{r})^2} \quad 1.4$$

Where N = number of elements x_i is the atomic percentage of i element and r_i is the atomic diameter of the i^{th} component. $\bar{r}$ is the molar average atomic radius, $\bar{r} = \sum_{j=1}^{N} x_j r_j$.

Computational thermodynamics approach

According to thermodynamics, an alloy's equilibrium state and developed microstructure result from stability competition among all the phases in a system. In recent years, a phenomenological approach, or the CALPHAD approach (Kaufman and Bernstein 1970) has been widely used for the study of phase equilibria of multicomponent systems. This approach converts separately measured phase equilibrium data and thermodynamic properties to a unique thermodynamic description of the system. The term "thermodynamic database" or "database" is usually used for a multicomponent system instead of "thermodynamic description." The ultimate goal of the CALPHAD approach is to use the developed thermodynamic database to predict phase equilibria and thermodynamic properties of a multicomponent system that are usually not experimentally available. Once the database has been developed, it can be used to predict this system's phase diagrams and thermodynamic properties. Therefore, CALPHAD can be regarded as the most direct approach to designing HEAs.

CALPHAD has been one of the major success stories in materials development over the last quarter century (Spencer 2008). This approach is increasingly being applied in the design and development of HEAs. Zhang et al. (2012) used this approach to develop Al-Co-Cr-Fe-Ni HEAs. A thermodynamic database for the Al-Co-Cr-Fe-Ni was developed, and phase diagrams of this system were calculated. Zhang et al. (2014) have discussed using the CALPHAD approach in aiding the development of high entropy alloys. Similarly, The HfNbTaTiVZr alloy was designed by inspecting the experimental binary and ternary phase diagrams and using the CALPHAD method (M. C. Gao et al. 2016). Senkov et al. (2015) established a fundamentally new combinatorial approach to rapidly screen many candidate structural metal alloys using the CALPHAD.

1.3 Development of the Thermodynamic database

Traditionally, phase diagrams and databases have been determined purely by experimentation, which is often laborious, expensive, and practically impossible for phase diagrams of multicomponent systems over wide ranges of compositions and temperatures. Complementary to this traditional approach is to do theoretical calculations, which in many ways can minimize the overall effort required. The foremost advantage of this approach is the following: Based on appropriate thermodynamic descriptions of the phases present in the alloy system, the information from lower-order systems can be used to determine a preliminary phase diagram of the multicomponent system of interest. This predicted diagram can be used to identify regimes of composition and temperature from where critical information can be obtained with minimum experimental effort. A final assessment can then be performed to fine-tune the interaction parameters pertaining to the multicomponent system to optimize the entire data set, including the newly observed data, after which the phase diagram can be calculated. In this way, a complete thermodynamic description of the higher-order systems can be obtained with minimum experimental effort. These techniques are referred to as computational thermodynamics (CT) (Kattner 1997). The fact that only binary, ternary, and, in rare cases, quaternary compounds are observed in nature leads to the conclusion that interactions beyond quaternary ones are insignificant. Hence, phase diagrams of quinary and higher-order systems can be computed in a straight forward manner based on reliable thermodynamic descriptions of the respective component subsystems. At present, a number of phase diagrams and thermodynamic data optimization packages, and corresponding databases are available, making the calculation of complex binary and multicomponent phase diagrams possible.

A significant development in the calculation of phase equilibria was the development of a method to treat order/disorder phenomena and SRO by Kikuchi (1951). This method later came to be known as the cluster variation method (CVM). This method chooses a group of nearby atomic sites in the crystal as the basic cluster. The CVM then develops an analytical, though approximate, expression for configurational entropy of mixing, considering correlations only within the chosen basic cluster representing the particular CVM cluster approximation. Usually, CVM is used in conjunction with the cluster expansion (CE) method (Sanchez et al., 1984), which gives configurational enthalpy (energy) of the system as a bilinear sum of energy parameters, which in this context, are known as cluster expansion coefficients (CEC) or effective cluster interactions (ECI) and configuration variables called correlation functions. These energy parameters give a description of the configurational thermodynamics of the system under consideration.

The CECs are preferably obtained independently using heats of formation of alloys (Connolly and Williams 1983) which may be obtained from experimental measurements or calculated from quantum mechanical first-principles methods. However, the thermodynamic values obtained from first principles calculations are, at present, not accurate enough to make correct quantitative predictions of multicomponent phase diagrams. Thus, for the near future, experimental data in binaries and ternaries will always be needed.

Phase Diagrams and Thermochemical Data

The reliability of CALPHAD thermodynamic modeling depends on the quantity and quality of data used to evaluate thermodynamic model parameters. Thermodynamic modeling for most binary systems of industrial importance has been achieved quite reliably thanks to the great amount of experimental data which have been accumulated over the centuries. Two sets of input data are used in the CALPHAD modeling:

thermochemical data and phase equilibrium data. Thermochemical data is usually for individual phases and is scarcer than phase equilibrium data, which generally involves more than one phase and is relatively easier to obtain experimentally than thermochemical data. First-principles calculations thus complement experiments ideally by providing much-needed thermochemical data of individual phases (Liu 2009).

1.4 Thermodynamic Software and Database packages

Commercial Softwares

Several commercial software packages are available that use CALPHAD-based approaches for materials modeling and design. Here are some examples:

(i) Thermo-Calc (Andersson et al. 2002): Thermo-Calc is a software package that uses CALPHAD-based methods to calculate the thermodynamic properties of multi-component systems. It is widely used in materials science and engineering research and has modules for calculating phase diagrams, diffusion coefficients, and other thermodynamic and kinetic properties.

(ii) Pandat (Cao et al. 2009): Pandat is another commercial software package for thermodynamic modeling that uses CALPHAD-based methods. It can be used for a wide range of applications, including phase diagram calculation, diffusion modeling, and precipitation modeling.

(iii) FactSage (Bale et al. 2016): FactSage is a comprehensive software package for thermodynamic modeling and simulation based on the CALPHAD approach. It includes a large thermodynamic database, as well as tools for calculating phase diagrams, thermodynamic properties, and other materials properties.

(iv) MatCalc: MatCalc is a commercial software package for materials modeling and simulation that uses a combination of CALPHAD-based methods and ab initio

calculations. It can be used for a range of applications, including phase diagram calculation, diffusion modeling, and microstructure evolution.

These are just a few examples of commercial software packages that use CALPHAD-based methods for materials modeling and design. Several open-source software packages are available that use CALPHAD-based approaches for materials modeling and design. Here are some examples:

(v) Open Calphad (Sundman et al. 2015)***:*** OpenCalphad is an open-source software package for thermodynamic modeling and simulation based on the CALPHAD approach. It includes a database of thermodynamic properties for a wide range of materials and tools for calculating phase diagrams, thermodynamic properties, and other materials properties.

(vi) Pycalphad (Otis and Liu 2017)(Kozeschnik 2021)***:*** PyCalphad is a Python-based open-source software package for thermodynamic modeling and simulation using the CALPHAD approach. It includes a database of thermodynamic properties for a range of materials and tools for calculating phase diagrams, thermodynamic properties, and other materials properties.

Most commercial software comes with its own thermodynamic databases optimized for one principal element, such as steel or aluminum databases. Hence a very limited number of databases are available that are suitable for HEAs. Another issue with these databases is the Gibbs energy model being used for modeling solid solution phases. Most of them utilize Compound energy formalism (Hillert 2001) or its variation. These models do not account for the short-range order (SRO) and often overestimate the configuration entropy of mixing.

Databases for HEAs

(i) TCHEA 6: Thermo – Calc software recently developed TCHEA 6 and MOBHEA2. TCHEA2 consists of critically assessed 301 binary and 192 ternary systems and a few partially ternary systems.

(ii) PanHEA: Pandat has a HEA database named as PanHEA database. This database has significant elements such as Ti, V, Zr, Ni, Si, Sn, and Mg, Mn, Mo, Fe, Hf, Li, Cr, Cu, Fe, Ag, Al, Co. The number of components considered in this database is 19, and the phase is 565. This database also lacks a quaternary database of the NbTiVZr system.

Although HEA requires information on four or more elements, no such assessments are included in any databases. For example, the Thermo – Calc database does not describe an important RHEA system NbTiVZr. We need a database capable of dealing with the quaternary system.

1.5 Thermodynamic Models

For the calculation of phase equilibria in a multicomponent system, it is necessary to minimize the total Gibbs energy, G, of all the phases that take part in the equilibrium

$$G = \sum_{i=1}^{p} n_i G_m^i \tag{1.5}$$

where $n_i$and G_m^i are the number of moles and Gibbs energy of phase i.

The general form of the Gibbs energy of a phase $\emptyset$ is expressed as (Lukas, Fries, and Sundman 2007)

$$G_m^{\emptyset} = {}^{srf}G_m^{\emptyset} + {}^{phys}G_m^{\emptyset} - T \cdot {}^{cnf}S_m^{\emptyset} + {}^{E}G_m^{\emptyset} \tag{1.6}$$

where pre-superscript "*srf*" represents "surface of reference" and contains Gibbs energy of an unreacted mixture of the constituents and ${}^{phys}G_m^{\emptyset}$ represents physical contributions such as magnetic transition. Configurational entropy is denoted by ${}^{cnf}S_m^{\emptyset}$ and ${}^{E}G_m^{\emptyset}$ is the excess Gibbs energy due to non-ideal interactions between the components. The reference term is given in terms of the molar Gibbs energies $G_A^{\varphi,0}$ and $G_B^{\varphi,0}$ of the components A and B, respectively

$$ {}^{srf}G_m^{\emptyset} = G_{ref}^{\varphi} = x_A^{\varphi} G_A^{\varphi,0} + x_B^{\varphi} G_B^{\varphi,0} \qquad 1.7$$

Here x_A^{φ} and x_B^{φ} represent the mole fractions of components A and B, respectively. The mixing term can be expressed as a sum of the ideal G_{mi}^{φ} and excess G_{me}^{φ} contributions.

$$ G_m^{\varphi} = G_{mi}^{\varphi} + G_{me}^{\varphi} \qquad 1.8$$

The ideal Gibbs energy of mixing is given by

$$ G_{mi}^{\varphi} = RT(x_A^{\varphi}\, ln\, x_A^{\varphi} + x_B^{\varphi}\, ln\, x_B^{\varphi}) \qquad 1.9$$

Gibbs energy of pure components

The temperature dependence of the Gibbs energy of a pure component *i*, $G_i^{\varphi,0}$ described by a power series in temperature (Dinsdale 1991)

$$ G_i^{\varphi,0}(T) - H_i^{\mathrm{SER}} = a_0 + a_1 T + a_2 T\, ln(T) + a_3 T^2 + a_4 T^{-1} + \qquad 1.10$$

$$ a_5 T^3 + \ldots, .., T_1 < T < T_2$$

where H_i^{SER} represents the enthalpy of the component *i* in its reference state, usually the stable state at 298.15K and 1 bar. This representation has been accepted internationally as a standard. Such a power series is valid only for a limited range of temperature, usually well above the Debye temperature and here delimited by T_1 and T_2. The data for each phase are stored in the form of Gibbs energies relative to the H_i^{SER} in the internationally accepted SGTE database. Additional terms are added to the above expression to account for pressure dependence or magnetic contributions, if required. The pressure dependence

for condensed phases is expressed in the form of the Murnaghan Eq. (Murnaghan 1944). Lu *et al.* (2005) have proposed a new model for representing pressure-dependent contributions to the Gibbs energy. This model has the advantage of including composition-dependent parameters and can be extended to higher pressure ranges in comparison to the Murnaghan model. At normal pressures, the pressure dependence of the Gibbs energy is negligible and shall be ignored. Similarly, the magnetic contribution can be added to the Gibbs energy using the model proposed by Hillert and Jarl (1978). However, we shall confine attention to non−magnetic systems.

Gibbs energy of stoichiometric phases

The Gibbs energy of stoichiometric phases is given by

$$G^{\varphi} = G^{\varphi}_{ref} + G^{\varphi}_{m} = G^{\varphi}_{ref} + G^{\varphi}_{me} = x^0_A G^{\varphi,0}_A + x^0_B G^{\varphi,0}_B + \Delta G^f \qquad 1.11$$

where x^0_A and x^0_B are mole fractions of elements *A* and *B* in the stoichiometric compound, and ΔG^f is the Gibbs energy of formation. The ideal Gibbs energy of mixing vanishes in this case.

Gibbs energy of solutions

Solution models in common use can be divided into two broad categories based on the treatment of SRO. In the first group of models, the excess Gibbs energy of mixing is expressed as a polynomial in the compositions. These models are empirical and do not explicitly account for SRO. The most commonly used models in this group in order of increasing complexity are those for stoichiometric or ordered phases which do not disorder before melting, regular solution models and their extensions for disordered phases, and Gorsky−Bragg−Williams type or sublattice models for ordered phases exhibiting an order−disorder transformation. In the second group of models, the expression for the excess Gibbs energy of mixing is based on statistical mechanics and

accounts for SRO. The latter involves unknown internal variables that describe the SRO and can be found by finding the state of internal equilibrium through a minimization of the Gibbs energy with respect to these microscopic state variables. This group of models is typified by the quasi−chemical model, the cluster site approximation (CSA) method, and the CVM. An alternative approach based on statistical mechanics which accounts for SRO is Monte−Carlo (MC) simulation (Binder and Heermann 2010). However, MC simulations do not provide Gibbs energy directly. Efforts are being made to devise suitable algorithms to solve this problem (van de Walle and Asta 2002). These methods are explained briefly in the following sections.

Binary disordered solid and liquid solution phases are treated as having a random distribution of atoms of the two elements in regular−solution type models most frequently used in CALPHAD. The excess Gibbs energy is modeled by using Redlich–Kister (RK) polynomial expansion (Redlich and Kister 1948) as follows

$$G_{me}^{\varphi} = x_A^{\varphi} x_B^{\varphi} \left[L_0^{\varphi}(T) + L_1^{\varphi}(T)\left(x_A^{\varphi} - x_B^{\varphi}\right) + L_2^{\varphi}(T)\left(x_A^{\varphi} - x_B^{\varphi}\right)^2 + \ldots \right] \qquad 1.12$$

With

$$L_k^{\varphi} = L_{k0}^{\varphi} + L_{k1}^{\varphi} T \qquad 1.13$$

where $L_k^{\varphi}(T)$ is the k^{th} interaction parameter, can be further divided into L_{k0}^{φ} and L_{k1}^{φ} are of temperature-independent and temperature dependent respectively.

Ordered binary solution phases are most frequently treated by the Compound Energy Formalism using sublattices (Hillert & Staffansson, 1970; Sundman & Ågren, 1981; Andersson et al., 1986). Each crystallographically distinct site in the structure is assigned a separate sublattice in this formalism. As a simple example, the sites in the B2 (CsCl) structure constitute two sublattices corresponding to the corner and body-center sites

which are predominantly occupied by A and B atoms, respectively. In this simple case, the Gibbs energy can be expressed in terms of its constituents as

$$G_{ref}^{\varphi} = y_A^{'} y_A^{''} G_{A:A}^{\varphi,0} + y_A^{'} y_B^{''} G_{A:B}^{\varphi,0} + y_B^{'} y_A^{''} G_{B:A}^{\varphi,0} + y_B^{'} y_B^{''} G_{B:B}^{\varphi,0} \quad 1.14$$

$$G_{mi}^{\varphi} = RT\left[y_A^{'} ln(y_A^{'}) + y_B^{'} ln(y_B^{'}) + y_A^{''} ln(y_A^{''}) + y_B^{''} ln(y_B^{''})\right] \quad 1.15$$

$$G_{me}^{\varphi} = y_A^{'} y_B^{'} (y_A^{''} L_{A,B:A} + y_B^{''} L_{A,B:B}) + y_A^{''} y_B^{''} (y_A^{'} L_{A:A,B} + y_B^{'} L_{B:A,B}) + y_A^{'} y_B^{'} y_A^{''} y_B^{''} L_{A,B:A,B} \quad 1.16$$

Here the primes refer to the two sublattices, $y_A^{'}$, $y_B^{'}$, $y_A^{''}$ and $y_B^{''}$ are the constituent fractions and the L_k represents interaction parameters restricted to five in the above expression. The constituent fraction $y_A^{'}$ equals the fraction of component A on the sublattice represented by a single prime with similar definitions for the other constituent fractions. In the notation for $G^{\varphi,0}$ and L, the colon in the subscript is used to distinguish components in different sublattices, and the comma indicates the interacting components on the same sublattice. The parameters $G_{A:B}^{\varphi,0}$, $G_{B:A}^{\varphi,0}$, $G_{A:A}^{\varphi,0}$ and $G_{B:B}^{\varphi,0}$ respectively represent the Gibbs energies of formation of the compounds AB, BA, pure A with the same structure as the compound, and pure B with the same structure as the compound.

Models for treating SROs in solutions

SROs represent the strong fluctuation of the local atomic environment in HEAs, and their effects on deformation mechanisms may vary in different types of HEAs. SROs can appreciably affect the slip barrier of dislocations in solid solutions. First, a dislocation motion would destroy the order and produce an interface of positive energy, and extra stress is thus necessary to move the dislocation forward accordingly (Fisher 1954). As a result, SROs can contribute a portion of the strength due to the break of the chemical order. Chemical complexity in HEAs stimulates the formation of SROs and thus elevates the energy barrier dominating the effective frictional resistance to dislocation movement

(Q. Ding, Fu, et al. 2019) (Saroukhani and Warner 2017). Compared with traditional alloy, dislocation motion in HEA lattices usually overcomes a larger energy barrier, which enhances the strengthening effect of SROs. In other words, any approach that can further increase the SRO degree can effectively strengthen HEAs, as demonstrated in the FCC FeCoNiCrPd (Q. Ding, Zhang, et al. 2019) and BCC NbMoTaW (Körmann, Ruban, and Sluiter 2017) HEAs. Preliminary results suggest that SROs in BCC HEAs mainly affect the dislocation behavior, e.g., increasing dislocation core energy, pinning dislocations, and promoting their cross-slip and multiplication (Lei et al. 2018) (Yin et al. 2019). The cluster Variation Method, which is one of the most sophisticated models for treating SRO, will be considered in the next section.

1.6 Cluster Expansion−Cluster Variation Methods (CE–CVM)

Configurational variables

Consider a disordered crystalline system with N crystallographically equivalent atomic sites. In a binary ($A-B$) alloy, in the absence of vacancies, A atoms occupy $x_A N = (1-x_B)$ N of these N sites, while the remaining $x_B N$ sites are occupied by B atoms.

A site operator σ_i is assigned to each site i in the crystal such that the operator takes the value τ_K when an atom of type K (A or B here) occupies the site. The τ_K are arbitrary numbers which serve as atomic labels. The N−dimensional vector $\sigma_N = \{\sigma_1, \sigma_2, \ldots \sigma_N\}$ specifies the configuration of the crystal completely.

Site occupation operators are defined as binary variables (Clapp and Moss 1966) through $p_i^A = 1$ ($p_i^B = 1$) if an A (B) atom occupies site i (i = 1 to N) and $p_i^A = 0$ ($p_i^B = 0$) otherwise. As vacancies are not considered,

$$p_i^A + p_i^B = 1 \qquad 1.17$$

It follows that the averages of these operators over all sites in disordered structures are the respective mole fractions.

$$\langle p_i^A \rangle = x_A = 1 - x_B \text{ and } \langle p_i^B \rangle = x_B \quad 1.18$$

$$\langle p_i^A \rangle = x_A = 1 - x_B \text{ and } \langle p_i^B \rangle = x_B \quad 1.19$$

The site operators σ_i can be related to the occupation operators through

$$\sigma_i = \tau_A \, p_i^A + \tau_B \, p_i^B \quad 1.20$$

where τ_A and τ_B ($\neq \tau_A$) serve as atomic labels. The matrix representation of Eq. (1.20) and (1.22) is

$$\begin{bmatrix} 1 \\ \sigma_i \end{bmatrix} = \begin{bmatrix} 1 & 1 \\ \tau_A & \tau_B \end{bmatrix} \begin{bmatrix} p_i^A \\ p_i^B \end{bmatrix} \quad 1.21$$

Therefore, the site occupation operators are given by

$$\begin{bmatrix} p_i^A \\ p_i^B \end{bmatrix} = \frac{1}{(\tau_B - \tau_A)} \begin{bmatrix} \tau_B & -1 \\ -\tau_A & 1 \end{bmatrix} \begin{bmatrix} 1 \\ \sigma_i \end{bmatrix} \quad 1.22$$

Point approximation: The point correlation function $\langle \sigma_i \rangle$ is given by

$$\langle \sigma_i \rangle = \tau_A \langle p_i^A \rangle + \tau_B \langle p_i^B \rangle \quad 1.23$$

and from Eq. (1.21), this becomes

$$\langle \sigma_i \rangle = \tau_A + x_B(\tau_B - \tau_A) \quad 1.24$$

The pair of values(τ_A, τ_B) are referred to as basis (Inden 2001). The choice of (–1, 1) results in orthogonal basis vectors for the configurational space. This basis is used in all the calculations reported in this investigation.

The averages of the site occupation operators can now be expressed in terms of the point correlation function as

$$\langle p_i^A \rangle = x_A = \frac{1}{2}(1 - \langle \sigma_i \rangle) \quad 1.25$$

$$\langle p_i^B \rangle = x_B = \frac{1}{2}(1 + \langle \sigma_i \rangle)$$

Pair Approximation: A pair−occupation operator p_{ij}^{KL} can be defined as a binary variable that takes the value 1 if an atom of type *K* occupies site *i* and simultaneously an atom of type *L* occupies site *j*, otherwise it takes the value 0. From the binary nature of these operators, it readily follows that

$$p_{ij}^{KL} = p_i^K . p_j^L \quad 1.26$$

In the case of binary disordered alloys, there are four pair−occupation operators, namely, p_{ij}^{AA}, p_{ij}^{AB}, $p_{ij}^{BA}$and p_{ij}^{BB}. The averages of these operators over all the crystallographically equivalent pairs of sites in the structure give the corresponding pair probabilities or pair variables ρ_{ij}^{LM} Thus,

$$\rho_{ij}^{KL} = \langle p_{ij}^{KL} \rangle = \langle p_i^K . p_j^L \rangle \quad 1.27$$

The pair probabilities can be expressed in terms of averages of site operators and their products by using Eq. (1.24) and are given by

$$\rho_{ij}^{AA} = \frac{1}{4}\left[1 - 2\langle \sigma_i \rangle + \langle \sigma_i \sigma_j \rangle\right] \quad 1.28$$

$$\rho_{ij}^{AB} = \rho_{ij}^{BA} = \frac{1}{4}\left[1 - \langle \sigma_i \sigma_j \rangle\right]$$

$$\rho_{ij}^{BB} = \frac{1}{4}\left[1 + 2\langle \sigma_i \rangle + \langle \sigma_i \sigma_j \rangle\right]$$

The average of the product of site operators σ_i and σ_j over all pairs of sites (i, j), namely, $\langle \sigma_i \sigma_j \rangle$ is known as the pair correlation function. While the cluster probabilities must remain within the limits

$$0 \leq \rho_{ij}^{KL} \leq 1 \quad 1.29$$

they also sum to unity

$$\rho_{ij}^{AA} + 2\rho_{ij}^{AB} + \rho_{ij}^{BB} = 1 \quad (1.30)$$

Further, they are related to the mole fractions through the so−called geometric reduction relations

$$\rho_{ij}^{AA} + \rho_{ij}^{AB} = x_A = 1 - x_B \quad (1.31)$$

$$\rho_{ij}^{AB} + \rho_{ij}^{BB} = x_B$$

The pair probabilities are automatically functions only of point and pair correlation functions, of which the former is related to composition. Thus, the correlation functions form a natural set of independent variables, and working in terms of these is advantageous.

For binary systems, all the (higher) cluster probabilities can be expressed as linear combinations of a set of independent correlation functions where the set consists of one correlation function, each corresponding to each of the symmetry−wise distinct subclusters contained in the cluster under consideration and indexed by the subscript *j*. The following notation for correlation functions will be used in the remaining part of this thesis.

$$u_j = \left\langle \prod_{i=1}^{r_j} \sigma_i \right\rangle \quad (1.32)$$

Here r_j is the number of sites in the j^{th} cluster.

Cluster expansion method

Any function of configuration, such as the configurational enthalpy H_c for a binary phase can be expressed as a bilinear sum of the products of the correlation functions and their respective cluster expansion coefficients (CECs). The function H_c can be expressed as (J. M. Sanchez 2010; J. M. M. Sanchez, Ducastelle, and Gratias 1984) Eq. (1.33)

$$H_c = \sum_{j=1}^{r_N} C_j \, m_j \, u_j \qquad 1.33$$

Here, the subscript *j* is an index that serves to identify each distinct cluster type, r_N is the number of all distinct cluster types, C_j are the CECs and m_j, the multiplicities corresponding to the respective correlation functions u_j. The multiplicities m_j are defined as the number of symmetry−equivalent clusters of type *j* per site present in the structure. In principle, the summation extends from the empty cluster containing no sites to the cluster containing all *N* atomic sites in the system. In practice, the CECs are expected to be negligible beyond a reasonably small neighborhood. This dictates the choice of a basic cluster or a set of basic clusters such that all interactions are confined within the basic clusters. The summation in Eq. (1.33) is terminated in a corresponding manner. The number of distinct types of symmetry−equivalent subclusters (including basic clusters) will be denoted by α. The multiplicity of the invariant "empty" cluster is unity as also its correlation function. It may be pointed out that a change in the basis used for the definition of correlation functions also changes the corresponding CECs. However, all physically measurable quantities, such as enthalpy, are left invariant. Such changes are necessary, for example, for finding relations among the CECs of a ternary system and those of the binary sub−systems. Transformations of the CECs consequent to a change of basis have been given by Sarma & Lele (2005).

The mixing contribution to configurational enthalpy can be obtained as follows.

$$H_{mc} = H_c - x_A \, H_c^A - x_B \, H_c^B \qquad 1.34$$

where H_c^A and H_c^B are the values of enthalpy of pure components and may be expanded using Eq. (1.33) as follows

$$H_c^A = \sum_{j=1}^{\alpha} C_j \, m_j \, u_j^A \text{ and } H_c^B = \sum_{j=1}^{\alpha} C_j \, m_j \, u_j^B \qquad 1.35$$

where u_j^A and u_j^B are values of the correlation functions for pure *A* and pure *B* and are given by $(-1)^{r_j}$ and $(+1)^{r_j}$, respectively, where r_j is the number of sites in the (sub)cluster corresponding to the particular correlation function. Thus,

$$H_{mc} = \sum_{j=1}^{\alpha} C_j \, m_j \, u_j^{mix} \tag{1.36}$$

where $u_j^{mix} = u_j - x_A u_j^A - x_A u_j^B$. It may be noted that the terms corresponding to empty and point clusters vanish in the expression for H_{mc}.

Cluster variation method

The expression for the configurational entropy of mixing per mole is given by (Kikuchi, 1951)

$$S_{mc} = -R \sum_{j=1}^{\alpha} m_j \gamma_j \sum_{\sigma_j} \rho_j(\sigma_j) \ln \sigma_j \tag{1.37}$$

where $\rho_j(\sigma_j)$ represents a cluster variable for j cluster corresponding to the configuration denoted by σ_j. Here the γ_j represents the overlap correction coefficients and are referred to as Kikuchi−Barker (*K–B*) coefficients. By definition, $\gamma_\alpha = 1$. It may be noted that the above expression corresponds to the total configurational entropy of mixing and not just the excess entropy of mixing. The *K–B* coefficients can be expressed in the general form of recursive Eq.s as given below

$$m_i = \sum_{j=0}^{\alpha-i} m_{\alpha-j} n_{\alpha-j}^i \gamma_{\alpha-j} \quad 1 \le i \le \alpha \tag{1.38}$$

The entropy expression can be obtained alternatively by Möbius inversion, as shown by Morita (Morita 1957) and explicitly by An (1988).

The configurational contributions to the Gibbs energy of mixing are thus given by

$$G_{mc} = H_c + RT \sum_{j=1}^{\alpha} m_j \gamma_j \sum_{\sigma_j} \rho_j(\sigma_j) \ln \sigma_j \tag{1.39}$$

In the above expression, the cluster variables $\rho_j(\sigma_j)$ can be expressed as functions of correlation functions, i.e., $\rho_j(\sigma_j) = \rho_j(\sigma_j)(u_k)$. The calculation of K–B coefficients and the CVM entropy formula is illustrated with reference to the (irregular) tetrahedron approximation of CVM for the bcc structure. The cluster and sub-clusters are depicted in Figure 1-2, while the corresponding multiplicities and K–B coefficients are given in Table 1-2.

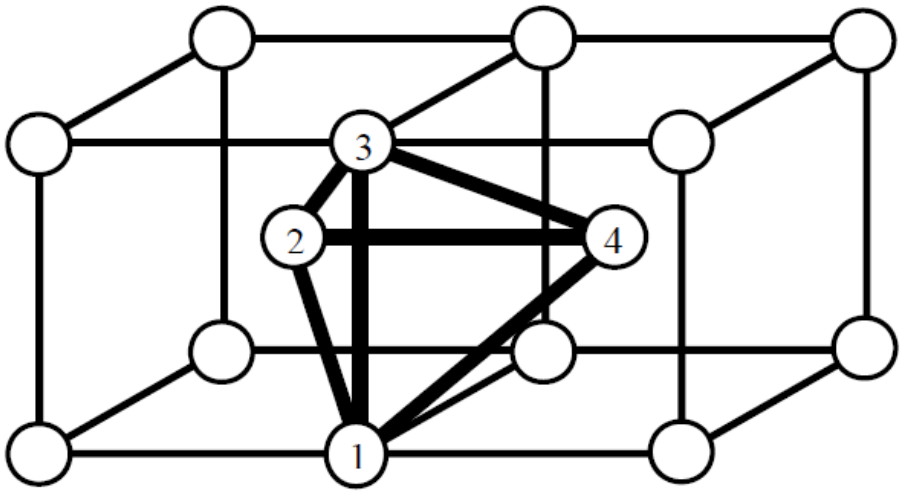

Figure 1-2 Clusters and sub−clusters used in tetrahedron approximation for bcc structure: point (1), I−n pair (1−2), II−n pair (1−3), triangle (1−2−3) and tetrahedron (1−2−3−4)

Table 1-2 List of clusters, multiplicities, number (n_i^j) of sub−clusters j contained in cluster i and K−B coefficients used in tetrahedron approximation for bcc structure (Sarma et al. 2012)

Cluster Number (i)	Cluster Type	m_i	Sub−clusters					γ_i
			n_i^5	n_i^4	n_i^3	n_i^2	n_i^1	
5	Tetrahedron (1234)	6	1	4	2	4	4	1

4	Triangle (123)	12	0	1	1	2	3	−1
3	II−n pair (13)	3	0	0	1	0	2	1
2	I−n pair (12)	4	0	0	0	1	2	1
1	Point (1)	1	0	0	0	0	1	−1

For tetrahedron approximation ($\alpha = 5$), Eq. 1.38 may be expanded as,

$$m_5 = m_5 n_5^5 \gamma_5 \qquad 1.40$$

$$m_4 = m_5 n_5^5 \gamma_5 + m_4 n_4^5 \gamma_4$$

$$m_3 = m_5 n_5^3 \gamma_5 + m_4 n_4^3 \gamma_4 + m_3 n_3^3 \gamma_3$$

$$m_2 = m_5 n_5^2 \gamma_5 + m_4 n_4^2 \gamma_4 + m_3 n_3^2 \gamma_3 + m_2 n_2^2 \gamma_2$$

$$m_1 = m_5 n_5^1 \gamma_5 + m_4 n_4^1 \gamma_4 + m_3 n_3^1 \gamma_3 + m_2 n_2^1 \gamma_2 + m_1 n_1^1 \gamma_1$$

Solving these Eqs, *K–B* coefficients may be obtained as given in Table 1-2.

The expression of Gibbs energy of mixing for the binary system is given in Eq. 1.36 and 1.39. Gibbs energy needs to be minimized after substituting CVs in terms of CFs, with respect to correlation functions, to obtain an equilibrium configuration.

1.7 First-principles approaches to disordered alloys

The "first-principles calculations" is a technique for calculating various physical properties of a substance, including its energy, using only the atomic number and crystal structure information. Specifically, the total energy of the electron system is expressed in Eq.1.41 by the adiabatic approximation, in which the motion of the nucleus is assumed to be sufficiently less than that of the electron to be negligible. Furthermore, the electron density functional theory (DFT) treats electrons as electron density:

$$E_{total}^{elec}[\rho] = T[\rho] + \int V_{ion}(r)\rho(r)\,dr + \frac{e^2}{2}\int\int \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' + E_{xc}[\rho] \qquad 1.41$$

where ρ is the electron density and $E_{total}^{elec}[\rho]$ is the energy for the electron density distribution. On the right side of the Eq.(1.41), the first term $T[\rho]$ is the electron's kinetic energy; the second term $V_{ion}(r)$ is the electrostatic potential from the nucleus acting on the electrons at the coordinate *r*; and the third term is the classical electrostatic potential between electrons. The fourth term $E_{xc}[\rho]$ is the exchange correlation energy that includes all the remaining manybody interactions, because calculating the exact form of the exchange-correlation energy analytically is challenging, the local density approximation and the generalized gradient approximation are used in the actual calculations.

The total energy acquired from first-principles calculations can be used to calculate the enthalpy of formation of the compound to be introduced into the CALPHAD method. Eq. 1.42 expresses the enthalpy of the formation of a binary compound $A_nB_m\left(H_{A_nB_m}\right)$:

$$H_{A_nB_m} = E_{A_nB_m} - (nE_A + mE_B) \qquad 1.42$$

Here, $E_\emptyset$ is the total energy per composition formula of the structure ϕ determined from the first-principles calculation. That is, $E_{A_nB_m}$ is the total energy of the binary compound A_nB_m, where E_A and E_B are the total energies of the simple substance for elements A and B, respectively, before the reaction.

At present, there are three main approaches to calculate energies of disordered solution phases: the coherent potential approximation (CPA)) (Sigli et al. 1986), the cluster expansion (CE) (Wolverton & Zunger 1995), and the special quasirandom structures (SQS)) (Wei et al. 1990) (Zunger et al. 1990) approach. The coherent potential approximation treats random alloys by considering the average occupations of lattice sites in solving the Kohn–Sham equation. Since a mean-field approach is employed, the

dependence of properties on the local environments surrounding an atom is not treated explicitly in CPA. These effects are considered in the CE and SQS approaches.

The two codes which incorporate DFT are used in this work:

(i) VASP (Kresse and Joubert 1999; Kresse and Hafner 1993; Kresse 1996; Paier et al. 2005): VASP (Vienna Ab initio Simulation Package) is a widely used commercial software package for performing ab initio quantum mechanical calculations of the electronic structure of materials. It is based on density-functional theory and is designed to simulate the properties of molecules, solids, surfaces, and interfaces. It uses a plane-wave basis set and pseudopotentials to calculate the energy of electronic structure of materials.

(ii) Quantum-Espresso(Paolo Giannozzi et al. 2020, 2009) : Quantum ESPRESSO (short for "opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization") is an open-source software package for electronic structure calculations and materials modeling based on quantum mechanics. Quantum ESPRESSO is designed to perform first-principles calculations of the electronic structure of materials using density-functional theory, plane-wave basis sets, and pseudopotentials.

SQS

Special Quasi Random Structures (SQS) (Zunger et al. 1990) are a type of structure used in computational materials science to model disordered materials. They are created by randomly arranging atoms or molecules in a crystal lattice while ensuring that certain constraints, such as the local coordination environment, are preserved. The resulting structure is then called a special quasi-random structure. SQS are designed to accurately capture the disorder in a material while preserving the underlying symmetry of the crystal

lattice. This makes them particularly useful for modeling alloys and other disordered materials where the exact atomic arrangement is unknown or difficult to measure experimentally. SQS are often used in conjunction with density functional theory (DFT) calculations to study the properties of materials. The SQS's for fcc-based alloys and bcc alloys have been generated by Wei et al. (1990) and Jiang et al. (2004), respectively. A new algorithm to generate Special Quasirandom Structures (SQS) is proposed by van de Walle et al. (2013). The method is based on a Monte Carlo simulated annealing loop with an objective function that seeks to perfectly match the maximum number of correlation functions. The method has been implemented in the "mcsqs" code of the Alloy Theoretic Automated Toolkit (ATAT).

1.8 Scope of the present investigation

As mentioned earlier, the computational thermodynamics approach remains successful in developing various materials and is being used for the design of HEA. In the available commercial software and databases, two issues were pointed out (i) lack of databases for the HEAs and (ii) lack of accounting SRO in modeling HEA phases. We will use the CE-CVM approach for modeling SRO in this work. Hence the first objective of this work is to develop a thermodynamic description of the bcc NbTiVZr system using CE-CVM. To develop this database, we will obtain model parameters (CECs) for the binary systems directly from the thermodynamic assessment since experimental phase diagram data are available for most of the binary systems. Since thermochemical data is unavailable for these systems, thermochemical data will be calculated based on first-principle calculations. For the ternary and quaternary systems where the thermodynamic assessment was not feasible, we will use cluster expansion to obtain CECs related to ternary and quaternary interactions.

Once such a database is available, it is possible to understand the role of model parameters (CECs) and macroscopic parameters (such as temperature and compositions) on the thermodynamic properties of these alloys. One advantage of the CE-CVM approach is the availability of SRO parameters. Hence, the second aim of this work is to analyze the role of model parameters (CECs) and macroscopic parameters (such as temperature and compositions) on the entropy of mixing (and other thermodynamic quantities Gibbs energy of mixing, enthalpy of mixing) and their correlations with SRO parameters. This should give valuable insight into the further development of HEAs.