Preface

High entropy alloy (HEA) has gotten significant acceptance among researchers Since its inception by Yeh and co-workers in 2004 (Yeh et al. 2004). It can achieve the required property by tailoring the number of elements and compositions or types of elements. Among HEAs, refractory high entropy alloy (RHEA) has shown outstanding corrosion resistance and is a potential candidate for creep resistance. Yeh et al. defined the HEA by considering five or more elements in 5 to 35 at%. However, three or four elements of alloys are currently reported in the literature.

To design a single-phase solid solution HEA, some empirical formula has been widely accepted among researchers, such as the entropy must be maximized, the enthalpy must be less than five kJ/mol and higher than -10 kJ/mol, the Ω greater than 1.1, the atomic size difference must be less than 6.6%, and valence electron concentration greater than 8 for fcc and less than 6.87 for bcc, in between these two values both bcc and fcc will co-exist. Some other design criteria adopted recently are insufficient to predict the phases present in an alloy correctly. *Hence, there is a need for thermodynamics-based criteria*.

Thermodynamics-based criteria require thermodynamic databases. Several commercial software packages using CALPHAD-based approaches for materials modeling and design are available, such as Thermo-Calc, FactSage, and Mat-Calc. Thermo-Calc software has recently developed TCHEA6 and MOBHEA2. TCHEA6 consists of critically assessed 301 binary and 192 ternary systems and a few partially ternary systems. Although HEA requires information on four or more elements, no such assessments are included in this database. For example, this database does not describe an important RHEA system NbTiVZr. *So, we need a database where the quaternary system information is available.*

Another issue with currently available commercial software and modeling approaches is related to the modeling of configurational entropy of the solution phases. Using an ideal configurational entropy model in these databases, which overestimates the entropy of mixing in real solutions, often leads to incorrect application of High entropy-based design criteria. Many researchers have indicated this issue. In their experiments with Cantor alloys, Otto et al (2013) have shown that merely the number of elements in HEAs is insufficient. Further, Miracle (Miracle and Senkov 2017) suggested that real solutions are not ideal, and the presence of short-range ordering (SRO) decreases the configurational entropy from ideal estimates. Singh et al. (Singh, Smirnov, and Johnson 2015) studied the electronic origin of SRO in HEA under the framework of concentration waves using the KKR-CPA method. Fernandez-Caballero *et al.*(2017) have used combined CE and first-principles formalism along with Monte Carlo simulations to investigate the evolution of the ten different SRO parameters in the MoNbTaVW and the sub-quaternary systems. This work describes the degree of local deviation from the average on a local scale in terms of chemical occupation. SRO affects several physical properties, such as mechanical (Fisher 1954) (Flinn 1958) (Kang et al. 2014), electrical (Pfeiler 1988), and magnetic properties (Narita and Enokizono 1979). SRO also affects the phase stability and other properties of high entropy alloys (HEA) (Abe 2021)(Sobieraj et al. 2020). There is experimental evidence for SRO for a significant number of alloys, and it looks like it is a common property of concentrated alloys. *Hence, an explicit treatment of SRO in the thermodynamic modeling of the phases is required for reliable descriptions of alloy systems.*

In view of the above, the objectives of this thesis are as follows: (i) the development of a thermodynamic description of the bcc NbTiVZr phase using CE-CVM, and (ii) 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 such as Gibbs energy of mixing, enthalpy of mixing) and their correlations with SRO parameters.

The thermodynamic description of bcc NbTiVZr is done using the computational thermodynamics (CT) approach. The procedure starts with experimentally well-established binary systems and their thermodynamic assessment. This involves determining the binary contribution to excess Gibbs energy through a suitable model. This procedure is then extrapolated to the ternary system with modeling of ternary contribution to excess Gibbs energy and so on. Thermochemical data enhances the reliability of thermodynamic modeling. However, measuring reliable thermochemical data, such as the enthalpy of mixing, is challenging compared to phase equilibrium data. Limited solubility range and sluggish kinetics at low temperatures limit the reliability of these measurements. Hence, the first principles (FP) calculations are used to determine thermochemical data. Density functional theory (DFT), along with techniques such as cluster expansion (J. M. M. Sanchez, Ducastelle, and Gratias 1984) and Special Quasirandom Structures (SQS) (Zunger et al. 1990) (Wei et al. 1990), can be used to calculate thermochemical data. *Chapter 3 gives the results of these calculations.*

Most of the binary phase diagrams are available, and, in principle, thermodynamic descriptions of the phases in terms of Gibbs energy can be obtained by assessments. These systems were reassessed because all the earlier phase diagrams based on phase data and the incorporation of thermochemical data are necessary to draw the phase diagram correctly. The issue of treatment of SRO in the solution phases is addressed in the present work using the Cluster Expansion and Cluster Variation Methods (CE-CVM) model for the bcc solid phase. *Details of assessments of the binary subsystems are given in Chapter 4.* In most cases, experimental data is either unavailable or not satisfactory for higher-order systems. All the available experiments, in this case, will be supplemented with theoretical calculations. Using the CT approach, a consistent thermodynamic description of the bcc NbTiVZr phase was developed.

The role of model parameters (CECs) and macroscopic parameters (such as temperature and compositions) on the entropy of mixing (and other thermodynamic quantities such as Gibbs energy of mixing, enthalpy of mixing) and their correlations with SRO parameters are discussed in *Chapter 5* and *Chapter 6* respectively.