Chapter 5

Thermodynamic Calculations of bcc Nb-Ti-V-Zr System

5.1 Introduction

The second aim of this work was 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. This chapter gives details of calculations of enthalpy, entropy, and Gibbs energy of mixing performed for the binary (Section 5.2), ternary (Section 5.3), and quaternary (Section 5.4) systems. The thermodynamic description of the bcc Nb-Ti-V-Zr system obtained in Chapter 4 is used for these calculations.

5.2 Binary Systems

Variation of different thermodynamic parameters (ΔH_{mix}, ΔS_{mix}, and ΔG_{mix}) with the composition at 1800 K is shown in Figure 5-1. The enthalpy of mixing is positive for all the systems. The V-Zr system's enthalpy values are highly positive compared to other binary systems. This is in confirmation with the values of the pair CECs. These values are 22,499.2 J/mol (e2VZr1) and 11,249.6 J/mol (e2VZr2) for the V-Zr system compared to 913.92 J/mol (e2TiZr1) and 456.96 J/mol (e2TiZr2) for the Ti-Zr system. In general, Gibbs energy shows a minimum near equiatomic compositions. The effect of triangle CECs can be seen in the Nb-Zr (e3NbZr2 = -4224 J/mol) and V-Zr systems (e3VZr2 = -5760 J/mol), where the Gibbs energy curves are asymmetric about equiatomic compositions (Figure 5-2). A more positive value of CEC results in a lower Gibbs energy at a given composition.

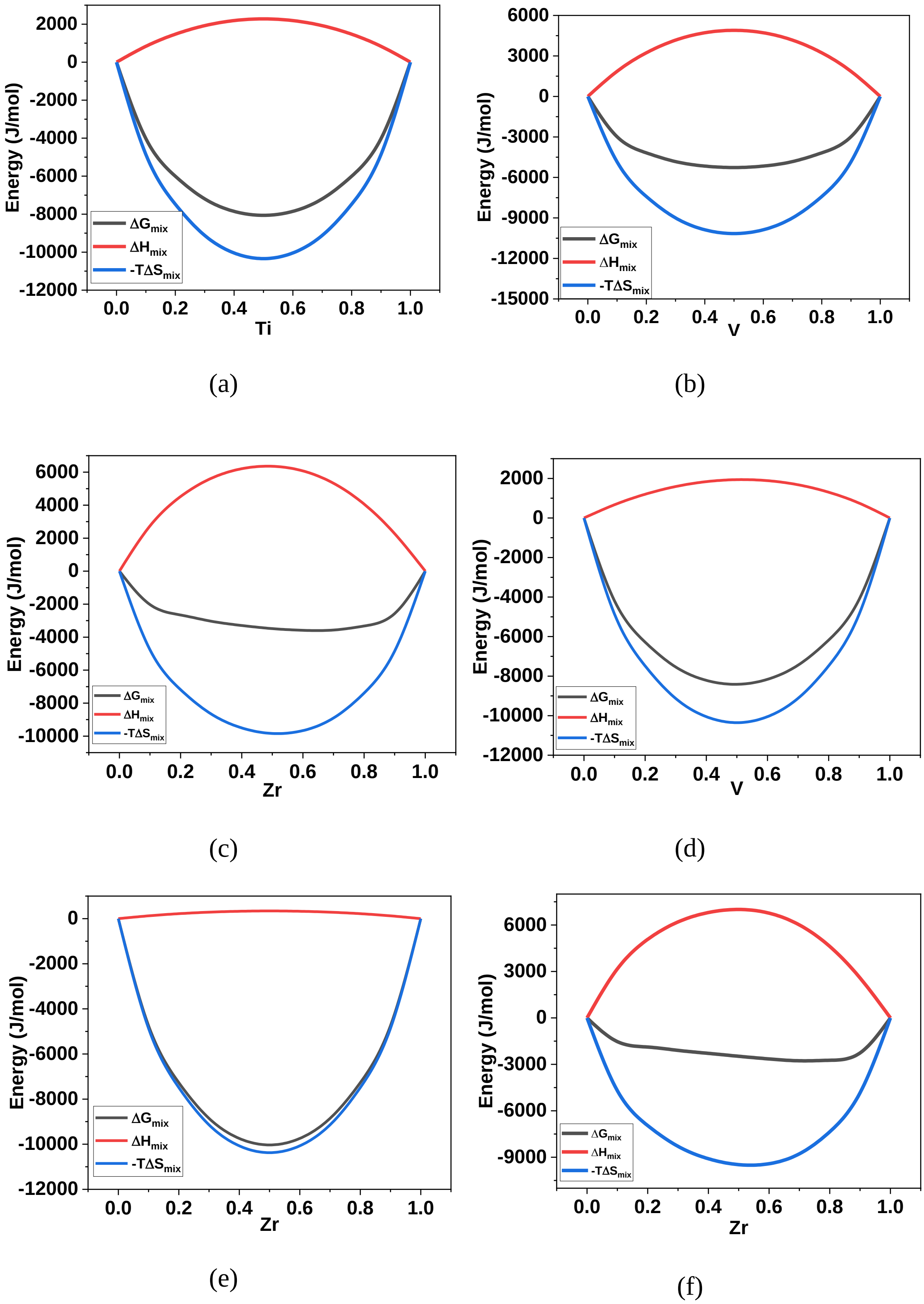


Figure 5-1 Variation of $\Delta H_{mix}, \Delta S_{mix},$ and ΔG_{mix} for (a) Nb-Ti (b) Nb-V (c) Nb-Zr (d) Ti-V (e) Ti-Zr, and (f) V-Zr at a temperature (1800 K) with composition.

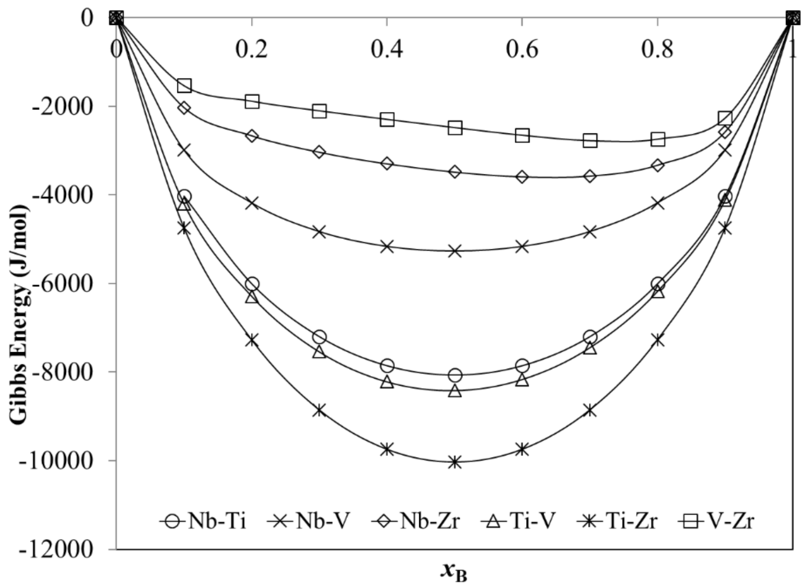


Figure 5-2 Comparision of ΔG_{mix} for (a) Nb-Ti (b) Nb-V (c) Nb-Zr (d) Ti-V (e) Ti-Zr, and (f) V-Zr at 1800 K.

Figure 5-3, Figure 5-4, and Figure 5-5 represent the variation of (ΔH_{mix}, ΔS_{mix}, and ΔG_{mix}) of binary sub-systems of Nb-Ti-V-Zr systems with the temperature at equiatomic composition. The stability of the bcc phase increases with temperature in all these systems. The variation of enthalpy of mixing with temperature is significant. All systems' enthalpy of mixing increases with an increase in temperature. The entropy part of the Gibbs energy of these systems decreases with an increase in temperature. Ti-Zr is the most stable in all temperature ranges, whereas V-Zr is the least stable. These trends can be collaborated with pair CECs of these systems.

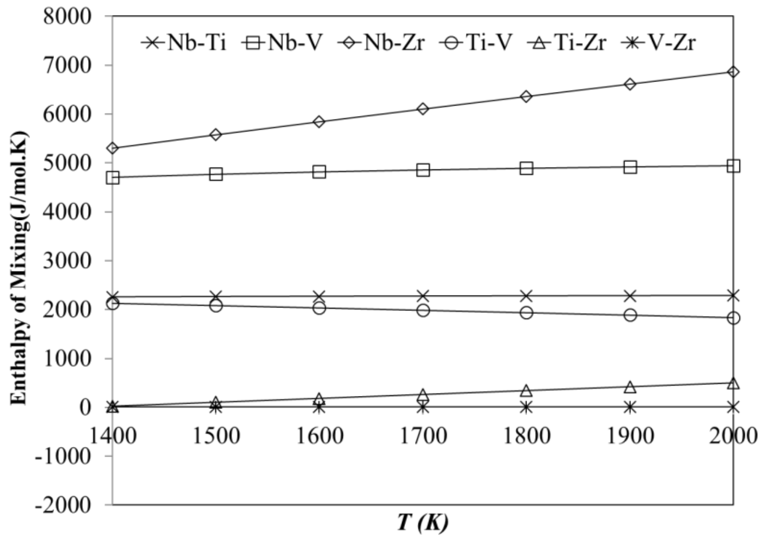


Figure 5-3 Variation of enthalpy of mixing of different systems bcc phases with temperature.

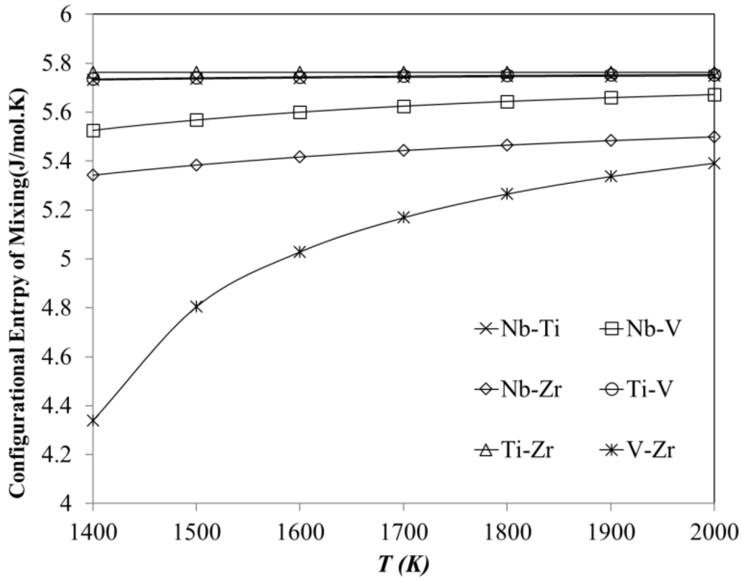


Figure 5-4 Variation of entropy of mixing of different systems bcc phases with temperature.

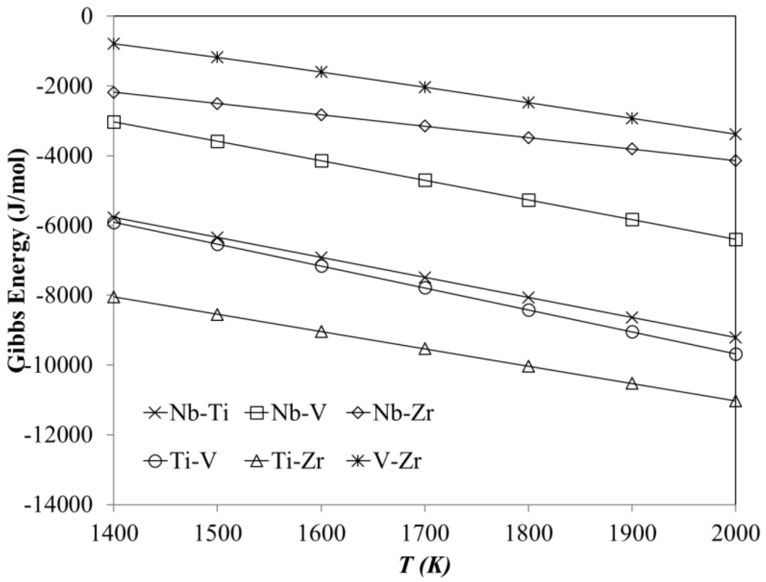
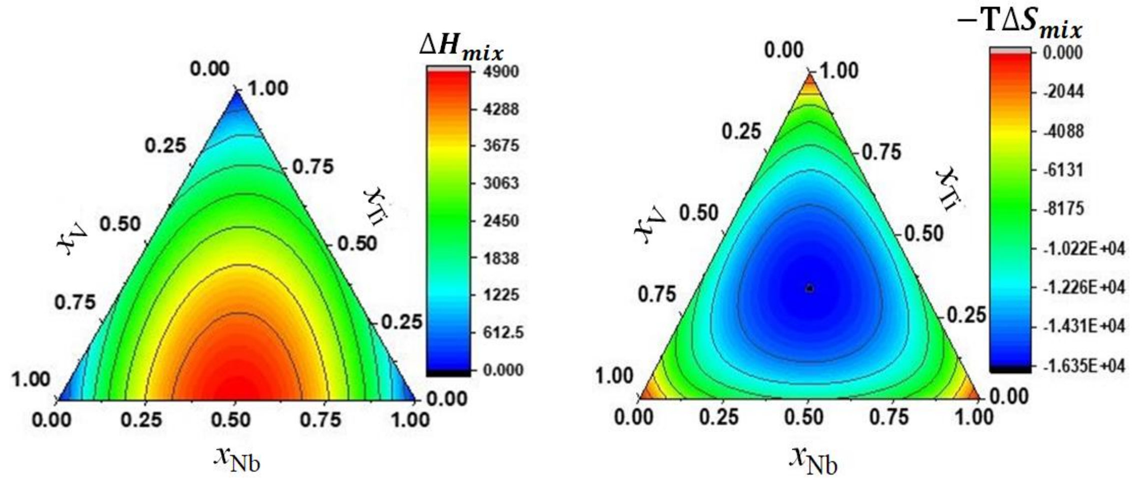


Figure 5-5 Variation of Gibbs of mixing different systems bcc phases with temperature.

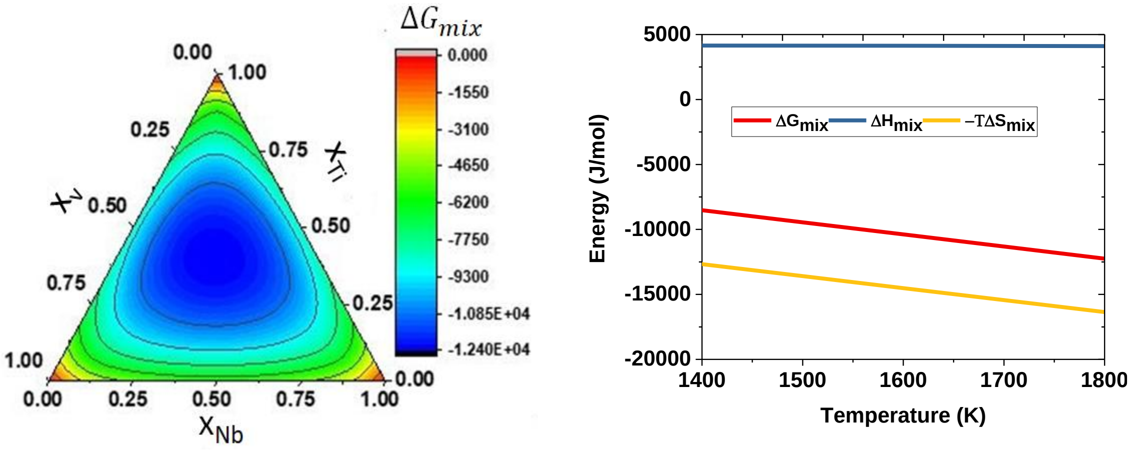
5.3 Ternary systems

(i) Nb-Ti-V system

Figure 5-6 shows Gibbs energy, enthalpy, and entropy of mixing plots of the Nb-Ti-V system at 1800K. The contour lines in these plots show the iso-energy lines of the system. The adjacent column indicates the color coding of the energies. Figure 5-6(a) shows the enthalpy of mixing of the Nb-Ti-V system. The contour plot is asymmetric. The maximum value of mixing is more concentrated towards the Nb-V side. Adding Ti in Nb-V decreases the mixing enthalpy. The maximum value of enthalpy (4830.793 J/mol) is at composition (0.5, 0.05, 0.45). The addition of element Nb in Ti-V and V in Nb-Ti increases the enthalpy of mixing of the system. Comparing the enthalpy value from binary equiatomic composition to ternary equiatomic composition, the enthalpy value has an increasing trend except for Nb-V. The CECs values of the binary system reported in Table 4-10, the value of CECs of Nb-V is maximum, whereas the other two (Nb-Ti and Ti-V) have lesser value than Nb-V. The higher value of CEC of Nb-V is responsible for the shift of enthalpy value to the Nb-V side. A similar trend is observed in this system's cluster expansion and SQS results. Figure 5-6(b) shows the mixing entropy of the Nb-Ti-V system. The contour plot is symmetric. The mixing entropy is maximum at equiatomic composition with an energy value of -16342.8 J/mol.K. The entropy of mixing increases from binary equiatomic to ternary equiatomic composition. This effect can be attributed to increasing the number of components and the corresponding increase in the configurational entropy of the system. The Gibbs energy plot is almost symmetric about its composition axis, as shown in Figure 5-6(c). But the minimum Gibbs energy composition is different from the equiatomic composition. At the equiatomic composition, the Gibbs energy value is -12300.00 J/mol. However, a lower Gibbs energy value is -12387.00 J/mol is observed at composition (0.3, 0.4, 0.3). Figure 5-6(d) shows the variation of $\Delta H_{mix}, \Delta S_{mix},$ and ΔG_{mix} with temperature. The mixing enthalpy of mixing value increases with increasing temperature, and the entropy part of Gibbs energy decreases with an increase in temperature. Consequently, the Gibbs energy decreases with temperature increases.



(a) (b)

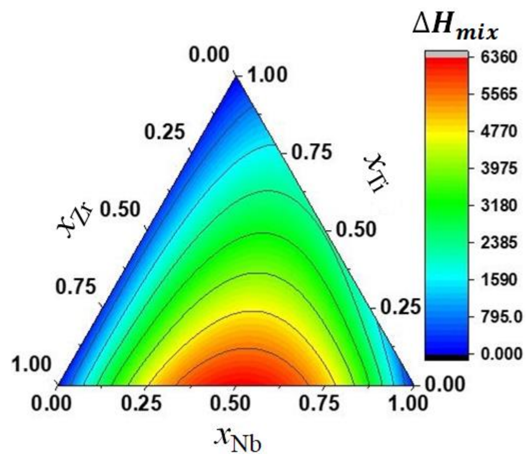


(c) (d)

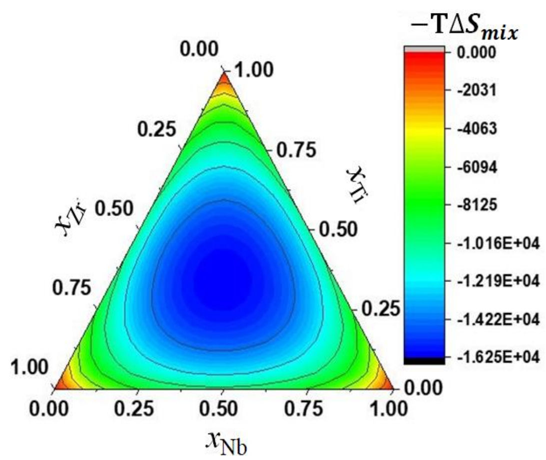
Figure 5-6 Shows the mixing energies (a) enthalpy, (b) entropy, (c) Gibbs energy of the Nb-Ti-V system at 1800 K. The contour plots with heat map show variations of energies with composition. (d) Variation of thermodynamic parameter with temperature.

(ii) Nb-Ti-Zr system

The enthalpy of mixing of the Nb-Ti-Zr system is shown in Figure 5-7 (a). The contour plot is asymmetric. The minimum value of mixing is more concentrated towards the Nb-Zr side. At composition (0.5, 0.05, 0.45), the maximum value of enthalpy is 6032.143 J/mol, and at the composition (0.5, 0.1, 0.4), the enthalpy value is 5688.92175 J/mol. Increasing the concentration of Ti in the Nb-Zr system decreases the mixing enthalpy. A similar result is obtained by SQS and CE calculation in Chapter 3. This result can be confirmed by the CE result of the system, where the empty cluster shows a positive value. Zhang et al.(2023) have reported the mixing enthalpy value using Miedema Model for equiatomic composition, which agrees with the present result. Figure 5-7(b) shows the mixing entropy of the Nb-Ti-Zr system. The contour plot is symmetric, and the mixing entropy is maximum at equiatomic composition with an energy value of -16283.6 J/mol. The entropy value of ternary equiatomic composition is lower than binary suggesting increase in configurational entropy with addition of elements. The Gibbs energy plot is almost symmetric about its composition axis, as shown in Figure 5-7 (c). Increasing the concentration of each element in proportion decreases Gibbs's energy. But the minimum Gibbs energy composition is different from the equiatomic composition. At the equiatomic composition, the Gibbs energy value is -12454.4 J/mol. The lowest Gibbs energy composition is (0.2, 0.45, 0.35) with energy -12718.8 J/mol. Consequently, the non-equiatomic composition becomes the most stable structure in the bcc phase due to the enthalpy effect. The addition of Ti in the Nb-Zr system decreases the Gibbs energy. The value of Gibbs energy is almost similar to that reported by (Senkov et al. 2018; Xu et al. 2020). The symmetricity in the Gibbs energy plot is present at higher concentrations of Nb and Ti. The binary CECs values of Ti-Zr and Nb-Zr are temperature dependent (-2928 + 2.1334*T), (7401.6 + 6.6432*T) whereas for the system Nb-Ti and 6240 is independent of temperature. Figure 5-7(d) shows variation of $\Delta H_{mix}, \Delta S_{mix},$ and ΔG_{mix} with temperature. The mixing enthalpy of mixing value increases with increasing temperature, the entropy part of Gibbs energy decreases with increase in temperature consequently the Gibbs energy decreases with increases in temperature.



(a)



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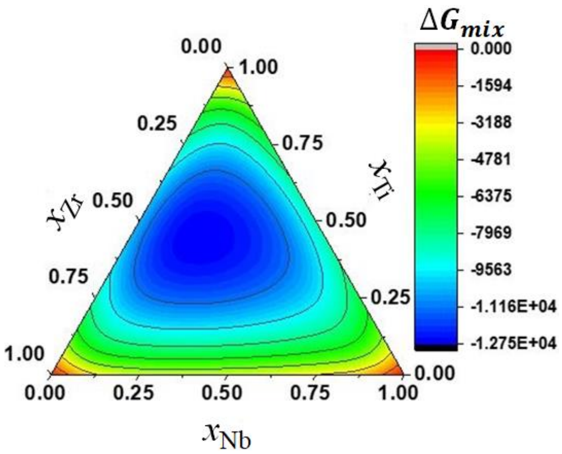

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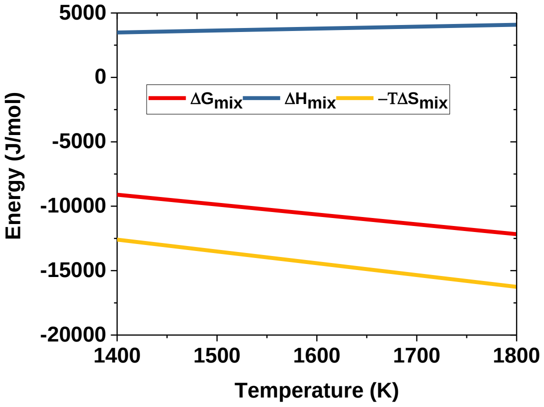


(d)

Figure 5-7 Shows the mixing energies ((a) enthalpy, (b) entropy, (c) Gibbs energy) of the Nb-Ti-Zr system at 1800 K. The contour plots with heat map show variations of energies with composition. (d) variation of thermodynamic properties with temperature.

(iii) Nb-V-Zr system

Figure 5-8(a) shows the mixing enthalpy contour plot of the Nb-V-Zr system. The composition contour plot is asymmetric. The mixing value of enthalpy is more concentrated towards the V-Zr end. The addition of Nb in V-Zr decreases the mixing enthalpy value. The pair CECs of all these ternary systems are negative. The V-Zr has the highest pair CECs value compared to Nb-V and Nb-Zr. Because of the highest CECs, the enthalpy values are higher, close to the V-Zr end. The maximum value of enthalpy is at composition (0.3. 0.35, 0.35). The value of energy at this composition is 8610.982 J/mol. From the equiatomic composition of binaries subsystems, ΔH_{mix} at the ternary equiatomic composition has higher values, suggesting the increase in phase separating nature of the Nb-V-Zr system. The models CE and SQS provide similar results for the Nb-V-Zr system. Figure 5-8(b) shows the mixing entropy of the Nb-V-Zr system. The contour plot is symmetric. The mixing entropy is maximum at equiatomic composition with an energy value of -15999.7 J/mol. Even though the enthalpy part is asymmetric in the Nb-V-Zr system, the resulting Gibbs energy is also asymmetric and more inclined towards the Nb-V side. The lowest Gibbs energy value is -7522.31 J/mol at the composition (0.4, 0.35, 0.25). The entropy part, in this case, dominates the enthalpy part.

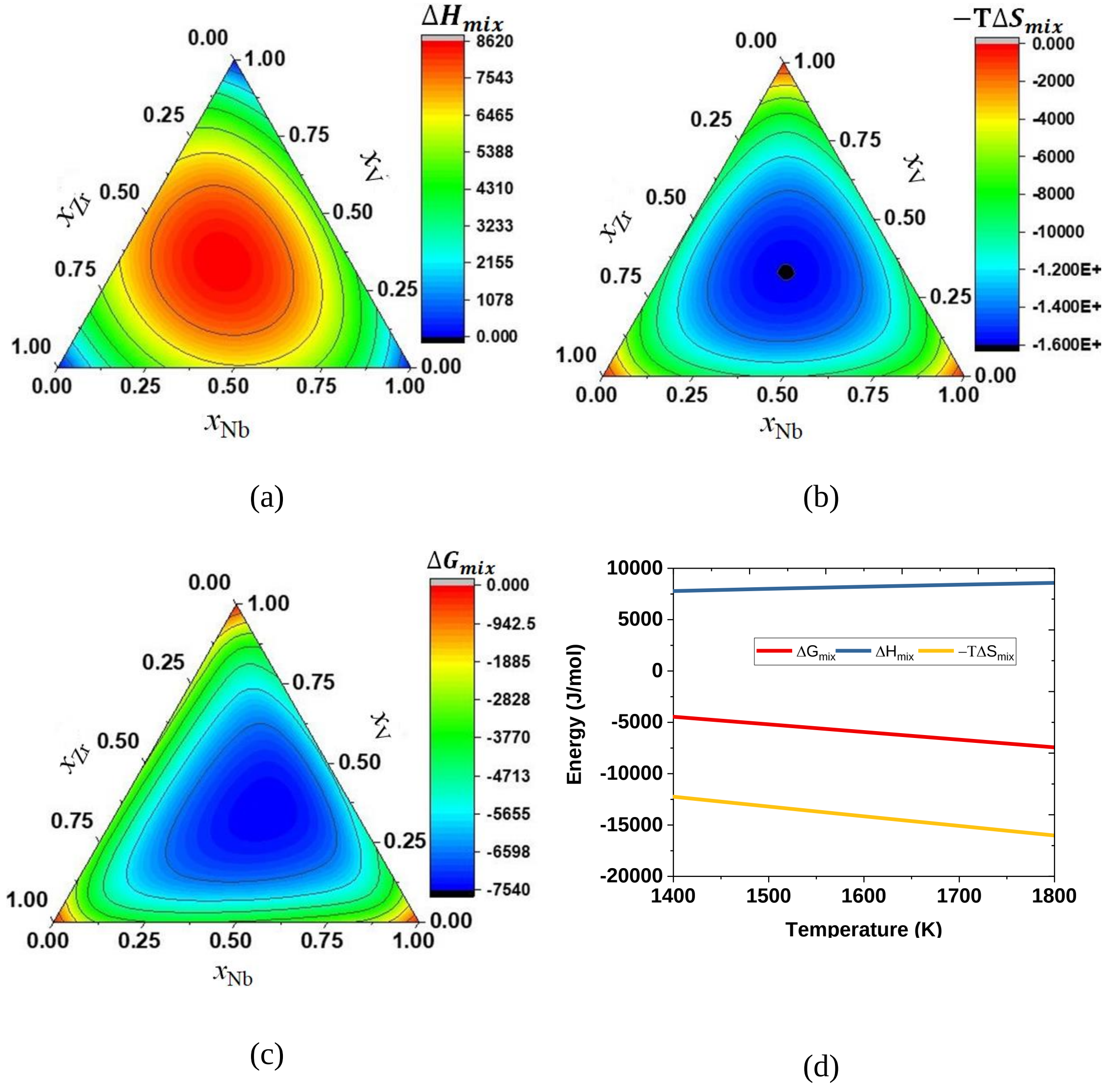
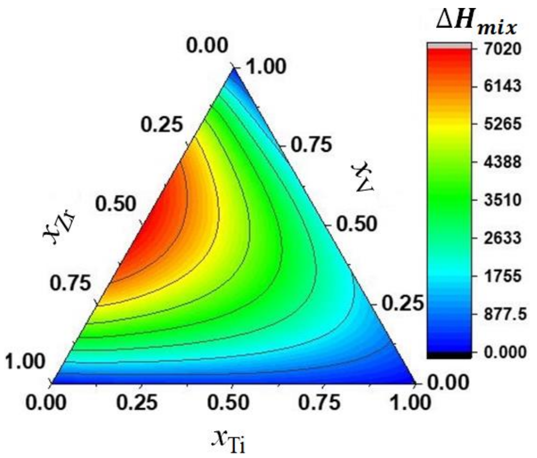


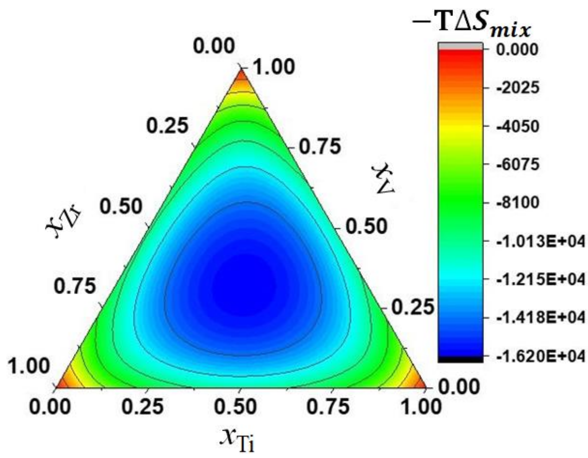
Figure 5-8 Shows the mixing energies (a) enthalpy, (b) entropy, and (c) Gibbs energy of the Nb-V-Zr system at 1800 K. The contour plots with heat map show variations of energies with composition. (d) variation of thermodynamic properties with temperature.

(iv) Ti-V-Zr system

Figure 5-9(a) shows the enthalpy of the mixing plot for the Ti-V-Zr system. The contour plot is asymmetric and concentrated toward the V-Zr end. The addition of Ti decreases the mixing enthalpy value. The maximum value of enthalpy is at the composition (0.05, 0.5. 0.45) with an energy value of 6625.73 J/mol. The present work observes a similar trend from CE and SQS calculations for the enthalpy of mixing. Figure 5-9(b) shows the mixing entropy of the Ti-V-Zr system. The contour plot is symmetric to the composition axis. The mixing entropy is maximum at equiatomic composition with an energy value of -16338.1 J/mol. Because of the increase in the number of elements in the system (from binary to ternary) the configurational entropy increses from binary equiatomic composition to ternary equiatomic composition. Figure 5-9(c) is a mixing Gibbs energy plot of the Ti-V-Zr system. The Gibbs energy plot is almost asymmetric. The minimum Gibbs energy composition is (0.45, 0.2, 0.35) with an energy value of -12575.1 J/mol. The asymmetricity in the enthalpy plot can be explained using the CECs of this binary system. The V-Zr has a maximum value of CEC at 1800 K with a value of 22499.2 J/mol, whereas Ti-Zr and Ti-V have lower values (-2543 and 5286.4). Such a huge difference in CECs is the main reason for asymmetricity in the system.



(a)



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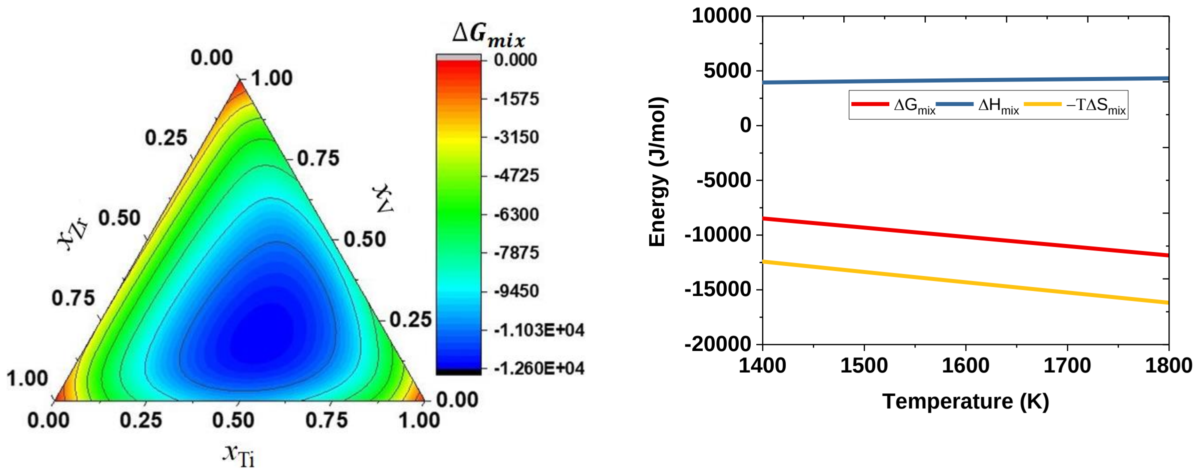


(c) (d)

Figure 5-9 Shows the mixing energies ((a) enthalpy, (b) entropy, (c) Gibbs energy) of the Ti-V-Zr system at 1800 K. The contour plots with heat map show variations of energies with composition. (d) variation of thermodynamic properties with temperature

5.4 Quaternary System

The Gibbs energy mixing plot in the composition space of Nb-Ti-V-Zr is shown in Figure 5-10(a). A comprehensive explanation of the composition mapping technique for quaternary alloys, as illustrated in Figure 5-10 and subsequent figures, can be found in Appendix D. The distribution of energy with varying compositions is marked by different color coding. The various color-coded energy is shown in the adjacent column. The center of the square pattern presents the equiatomic composition. The iso-energy lines are asymmetric towards the V-Zr side, whereas others are symmetric with composition. The value of the equiatomic composition is -13624.9 J/mol. The lowest energy composition in the Nb-Ti-V-Zr composition space is (0.24, 0.36, 0.24, 0.16) with an energy value of -14490.3 J/mol. Figure 5-10(b) shows the enthalpy of mixing of the Nb-Ti-V-Zr system. The contour plot is asymmetric. The maximum value of mixing is more concentrated towards the V-Zr side.

Adding Nb or Ti in V-Zr decreases the mixing enthalpy and makes it suitable for forming a single-phase solid solution. The addition of Ti in the V-Zr system decreases the Gibbs energy same is true for Nb addition in V-Zr. The enthalpy values of the system reduce when tending toward equiatomic composition. At composition (0.06, 0.04, 0.36, 0.54), the maximum value of enthalpy is 9689.28 J/mol. The mixing enthalpy reported by Feng (2019) contradicts the present reported value, whereas the Senkov (2018) value agrees with the present value. Figure 5-10(c) shows the mixing entropy of the Nb-Ti-V-Zr system. The contour plot is symmetric about the composition axis except for the V-Zr side. The mixing entropy is maximum at equiatomic composition with energy value -20343.2 J/mol.K.

Beyond the equiatomic composition, the entropy is symmetric except on the V-Zr side. The interaction between V-Zr in this system in the bcc phase results in the highest mixing enthalpy. Figure 5-10(d) explains the variation of thermodynamic quantities with temperature. With increasing temperature, the enthalpy value reaches higher positive values, whereas the entropy and Gibbs energy reach more negative values, and the system tends toward the random solid solution. The CECs of binary systems produce a combined effect on the overall phase stability of the system. The 1NN value of V-Zr is maximum, which reflects in the mixing enthalpy plot of the quaternary system. The nature of the higher-order system can be predicted by looking at the optimized CECs of the binary system. Figure 5-10(d) depicts the variation of thermodynamic parameters with temperature. With increasing temperature, all the parameters tend towards random behavior as the CECs are diminishing at higher temperatures.

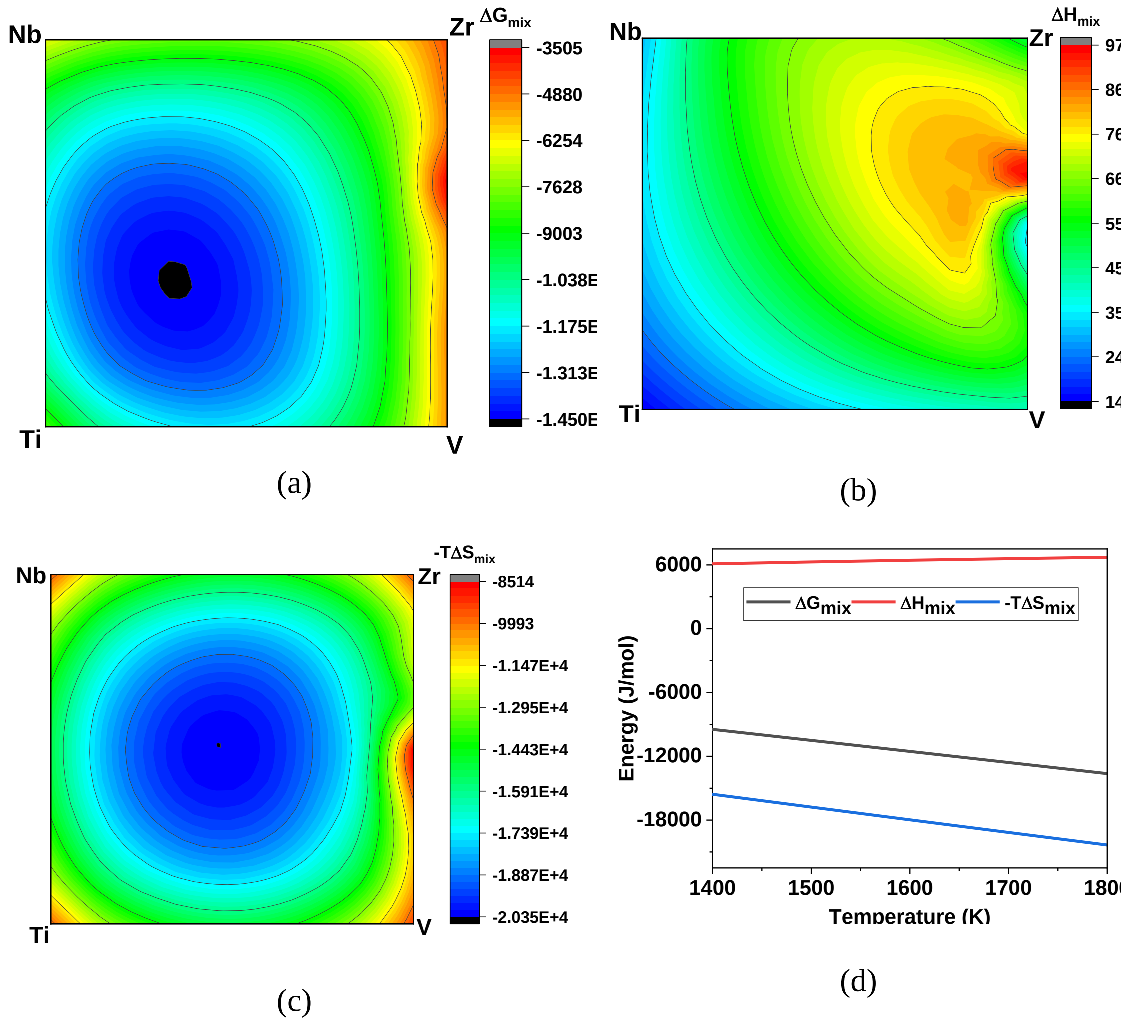


Figure 5-10 Shows the mixing energies ((a) Gibbs energy, (b) enthalpy, (c) entropy) of the Nb-Ti-V-Zr system at 1800 K. The contour plots with heat map show variations of energies with composition.

Figure 5-11 explains the variation of Gibbs energy with decreasing temperature. Figure (a) represents the Gibbs energy of random solid solution, Figure (b) represents the Gibbs energy of mixing at 1800 K, Figure (c) represents the Gibbs energy of mixing at 1600 K, and Figure (d) at 1500 K The random entropy of mixing Figure 5-11(a) provides the energetically most favorable composition as equiatomic composition. The effect of SRO can be ascertained as the composition shifts from equiatomic composition to non-equiatomic composition at lower temperatures.

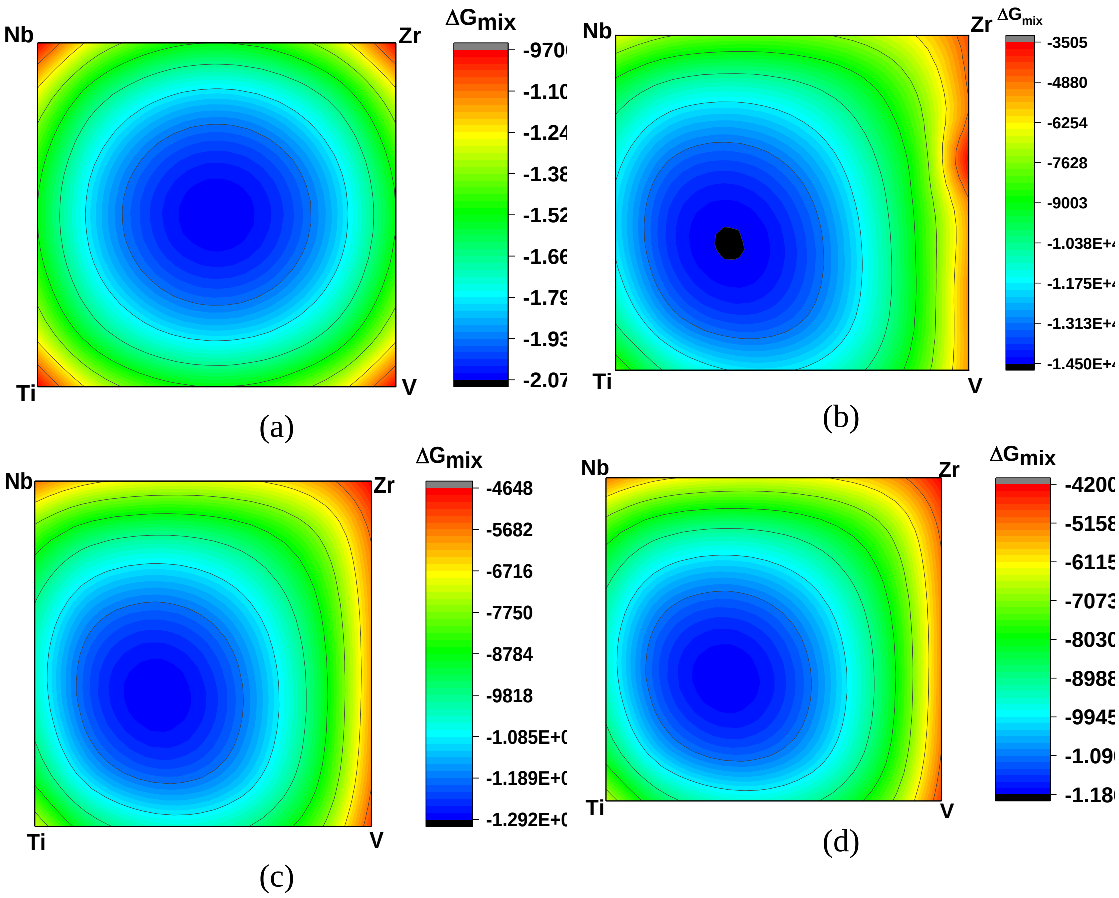


Figure 5-11 Variation of Gibbs energy with temperature as in (a) random (b) 1800K and (c) 1600 K (d) 1500 K.

Figure 5-12 explains the lowest Gibbs energy composition variation at a given temperature. Point A, B, and C corresponds to the different temperature. Point A represents the high-temperature region with the negligible presence of SRO in a solid solution. Point B represents 1800 K, and point C represents 900 K temperature. The composition of point A is (0.25, 0.25, 0.25, 0.25), point B is (0.24, 0.36, 0.24, 0.16), and point C is (0.28, 0.42, 0.18, 0.12). The decrease in temperature increases the effect of SRO on the stability of the composition. The shift in composition from the V-Zr end to Nb-Ti can be observed from this result. At lower temperature, the CECs of Nb-Ti is more predominant than V-Zr CECs.

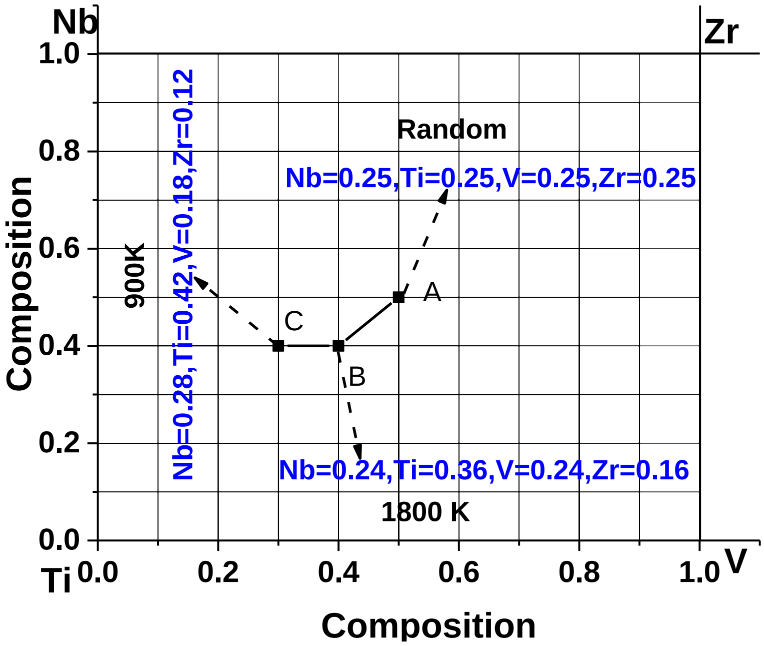


Figure 5-12 Variation of energetically most favored composition at a given temperature

5.5 Effect of temperature on entropy

To examine the role of temperature on entropy, the variation of entropy with temperature in binary, ternary, and quaternary systems is plotted in Figure 5-13. The effect of SRO on entropy is also established. Figure 5-13(a) describes the deviation of actual entropy from the ideal configuration entropy. It is highly likely that when the ideal configurational entropy model is used to calculate the entropy of high entropy alloys, entropy is overestimated by almost 16% at lower temperatures. Figure 5-13(b) explains the same behavior with binary sub-systems, where the percentage deviation is maximum in the case of the V-Zr system and least in the Ti-Zr system. Figure 5-13(c) explains the percentage deviation from ideal entropy for the ternary system, where Nb-V-Zr and Ti-V-Zr show maximum deviation of 7% and 6% at lower temperatures. In contrast, the system Nb-Ti-V and Nb-Ti-Zr is less affected. Figure 5-13(d) compares all the systems, where the binary Nb-V system has a maximum deviation from ideal entropy.

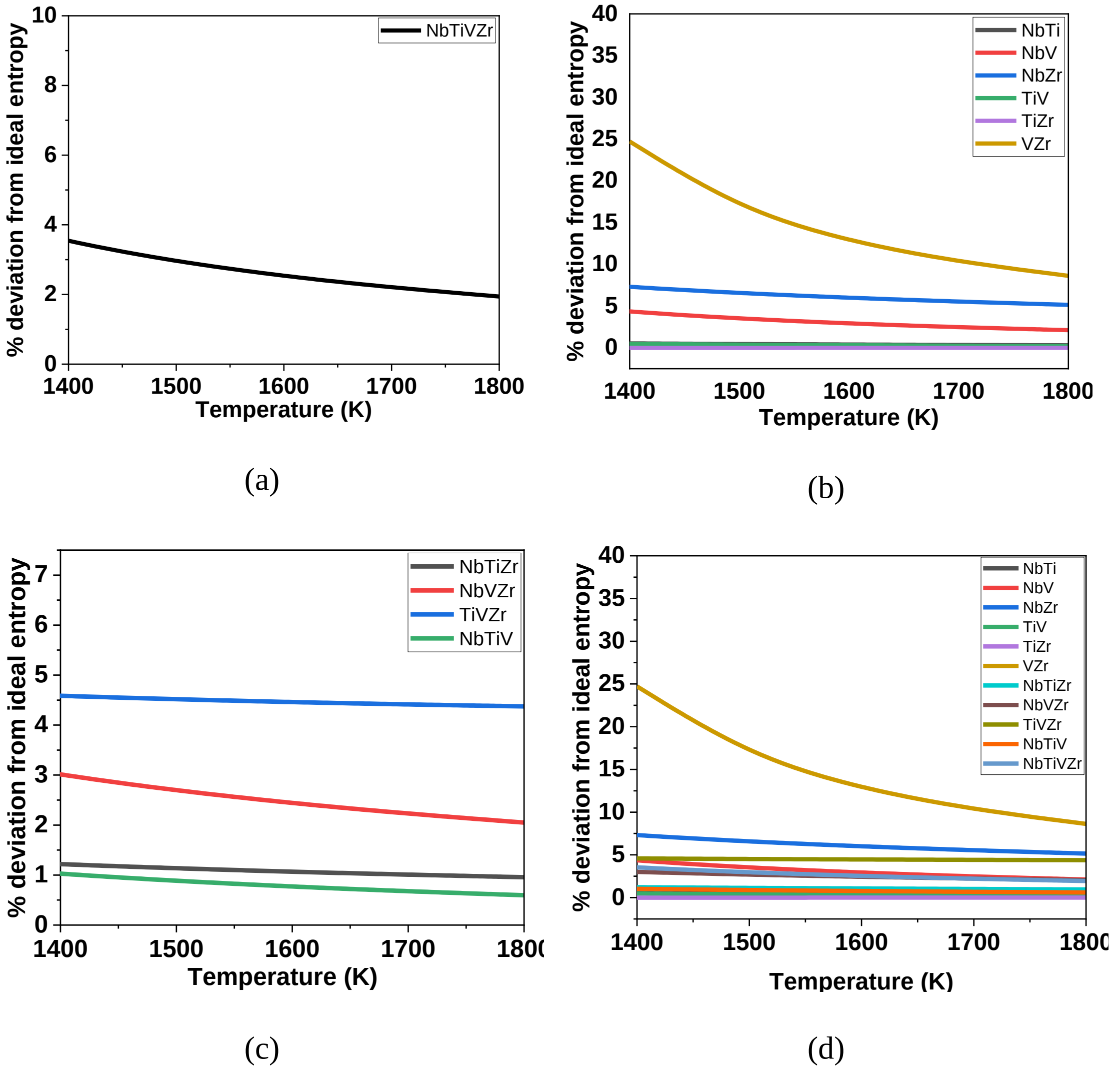
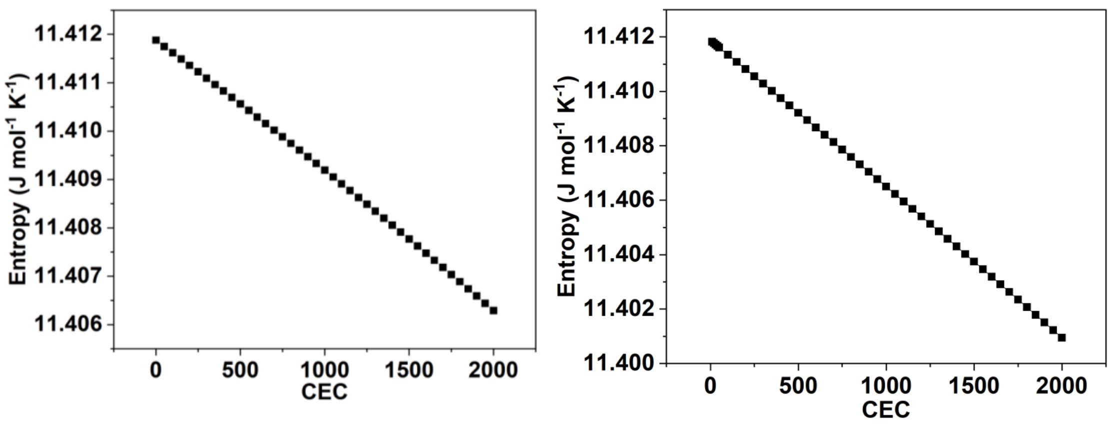


Figure 5-13 deviations of entropy from ideal entropy shown in (a) Nb-Ti-V-Zr, (b) binary systems, (c) ternary systems (d) all systems.

5.6 Effect of pure ternary CECs on thermodynamic quantities

In the above calculation, the pure ternary interactions were considered zero since the CE of all four ternary subsystems, and the quaternary system only resulted in CEC of pair clusters. When quality experimental thermochemical and phase diagram data are available, it may also be possible to include pure ternary and quaternary CECs. Meanwhile, it will be interesting to see the effects of these CECs on the various thermodynamic quantities. The pair CECs of V-Zr have the highest value. So systems accompanying V-Zr are used here for further study. This parametric study uses pure ternary CEC corresponding to Ti-V-Zr and Nb-V-Zr systems. In these calculations, ternary CECs ($e3TiVZr1, e3NbVZr1$) was varied from 0 to 2000, assuming ($e3TiVZr1 = e3TiVZr2 = e3TiVZr3, e3NbVZr1 = e3NbVZr2 = e3NbVZr2$). As shown in Figure 5-14, with increasing CECs values, the entropy values are decreasing for both (a) Ti-V-Zr and (b) Nb-V-Zr. This indicates that with increasing values of CECs, the entropy of mixing moves away from that random value, and its value decreases.



(a) (b)

Figure 5-14 (a) Variation of entropy with increasing pure ternary Ti-V-Zr interaction (b) Variation of entropy with increasing pure ternary Nb-V-Zr interaction.

5.7 Conclusions

The effect of CECs, temperature, and alloy compositions on the various thermodynamic quantities in the binary, ternary subsystems of bcc Nb-Ti-V-Zr, and quaternary bcc Nb-Ti-V-Zr system were studied. In all the systems, the Gibbs energy of mixing decreases with increasing temperature. On the other hand, the enthalpy of mixing and the entropy of mixing increases with temperatures. While going from equiatomic binary to equiatomic ternary/quaternary compositions, the entropy of mixing and Gibbs energy of mixing increases. This indicates an overall tendency to increase phase stability with an increase in the number of components. However, the enthalpy of mixing shows an averaging effect of the corresponding binary systems and results in an asymmetry in the composition space. The entropy of mixing is symmetrical about the alloy compositions, especially at high temperatures. Although entropy of mixing dominates in Gibbs energy of mixing, asymmetry in the Gibbs energy of mixing may be observed due to contributions from the enthalpy of the mixing part. Hence, the most stable HEA alloy may not necessarily be found at the equiatomic compositions. Values of CECs or model parameters determine the overall stability and composition of the most stable state of a HEA.