Chapter 6

Short-Range Ordering in bcc Nb-Ti-V-Zr System

6.1 Introduction

Chapter 5 describes the effect of CECs, temperature, and composition on thermodynamic properties. This chapter will focus on the impact of CECs, temperature, and alloy composition on SRO. Results for binary, ternary, and quaternary systems are given in Section 6.2, Section 6.3, and Section 6.4, respectively. Section 6.5 discusses the effect of pure ternary interactions on SRO in the bcc Nb-Ti-V-Zr System.

6.2 Binary systems

All the SRO parameters consistently approach zero values at both ends, indicating pure elements where all the atoms are surrounded by like atoms in Figure 6-1. Increasing the concentration of one component of the lattice of another atom increases the SRO parameter up to equiatomic composition. It decreases afterward, suggesting a change in the host lattice. 1NN SROs are symmetric for all systems except Nb-Zr and V-Zr. The deviation of both these systems is mainly coming from triangle interaction. The V-Zr system has a strong phase separation tendency, whereas the Ti-Zr system has the least.

At higher temperatures, the random behavior of atoms is prominent in alloys. The temperature-dependent evolution of six different SRO parameters for the first nearest-neighbor (1NN) shell for the equiatomic composition is shown in Figure 6-2. In the high-temperature limit, it can be seen clearly from Figure 6-2 that all the SRO parameters tend to zero value corresponding to the presence of an ideal randomly single phase of solid solution with the configuration entropy of mixing $\Delta S_{mix} = -R\sum X_i\, lnX_i$ (R is the gas constant and X_i is mole fraction). In the temperature region lower than 1800 K, it is found that the SRO parameter for the V-Zr pair, α_1^{VZr} becomes the most positive one. This indicates a strong probability of not having Zr atoms around a V atom in the first shell of the considered equiatomic Nb-Ti-V-Zr bcc alloy. The next and strong positive SRO parameter has been predicted for the Nb-Zr pair, and the SRO parameter for the Nb-V pair follows it. In the low-temperature region, there is a strong tendency for segregation with the positive values of α_1^{NbV} , α_1^{NbTi} α_1^{NbZr} α_1^{TiV} and α_1^{VZr} namely for SRO parameters of the pairs between elements of the same groups, IV and V (Widom 2016).

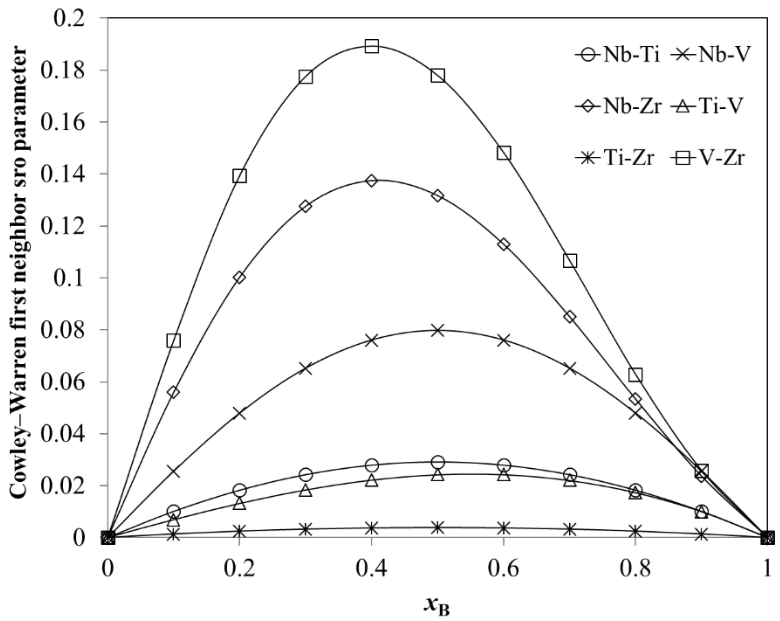


Figure 6-1 Variation of Cowley-Warren 1NN short-range-order parameters in six binaries of Nb-Ti-V-Zr system as a function of composition calculated at (1800 K). The x-axis of this figure shows the composition of the second element in the corresponding binary pair, where elements are arranged alphabetically within each pair.

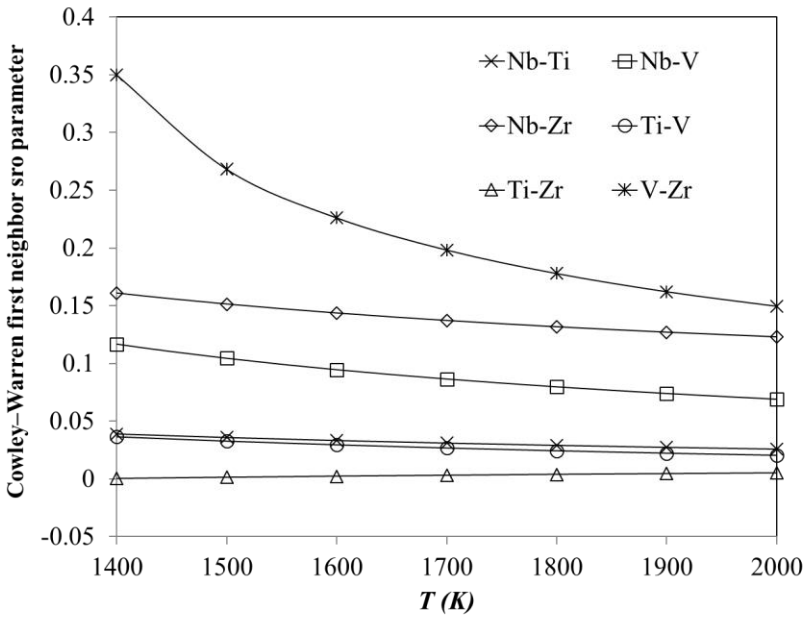


Figure 6-2 Variation of Cowley-Warren 1NN short-range-order parameters in six binaries of Nb-Ti-V-Zr HEAs as a function of temperature.

6.3 Ternary systems

(i) Nb-Ti-V system

Variations of the 1NN SRO parameters of the Nb-Ti-V system as a function of temperature are shown in Figure 6-3. The short-range order in the Nb-Ti-V system decreases and tends to zero with increasing temperature. The 1NN SRO of Nb-Ti, Nb-V, and Ti-V pairs are positive. Figure 6-4(a) shows 1NN SRO of Nb-Ti in the Nb-Ti-V system. The Nb-Ti system is phase-separating, whereas adding V in this system changes the SRO parameter from positive to negative. Consequently, changing the nature of SRO from phase separating to ordering. Figure 6-4(b) shows the 1NN pair SRO of the Nb-V type in the Nb-Ti-V system. The addition of Ti in the Nb-V system does not affect the system and keeps the SRO positive only. In comparison, adding Nb in the Ti-V system increases ordering tendency, as shown in Figure 6-4(c), changing the SRO from positive to negative.

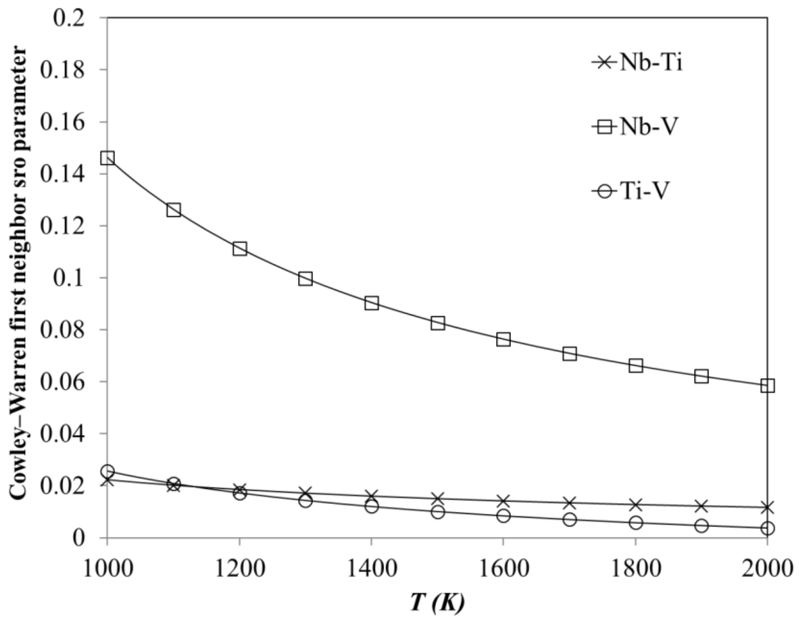
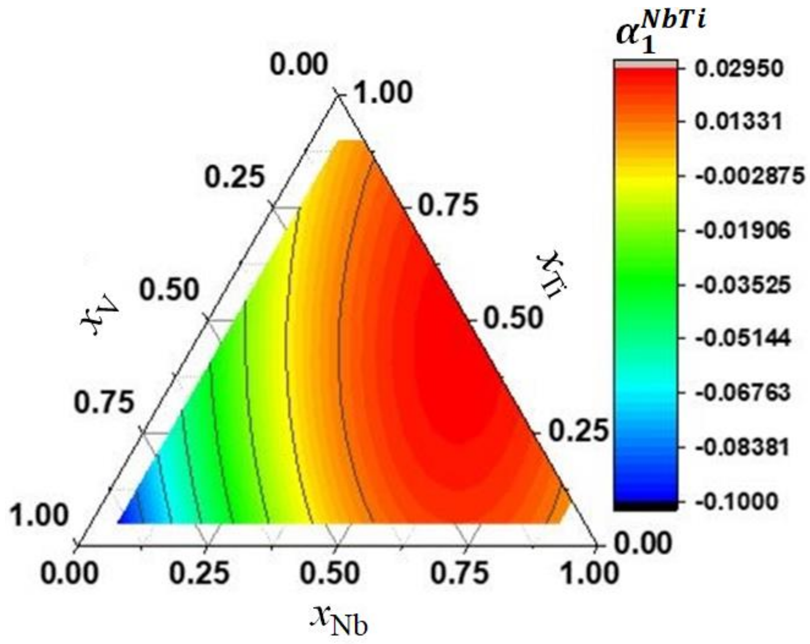
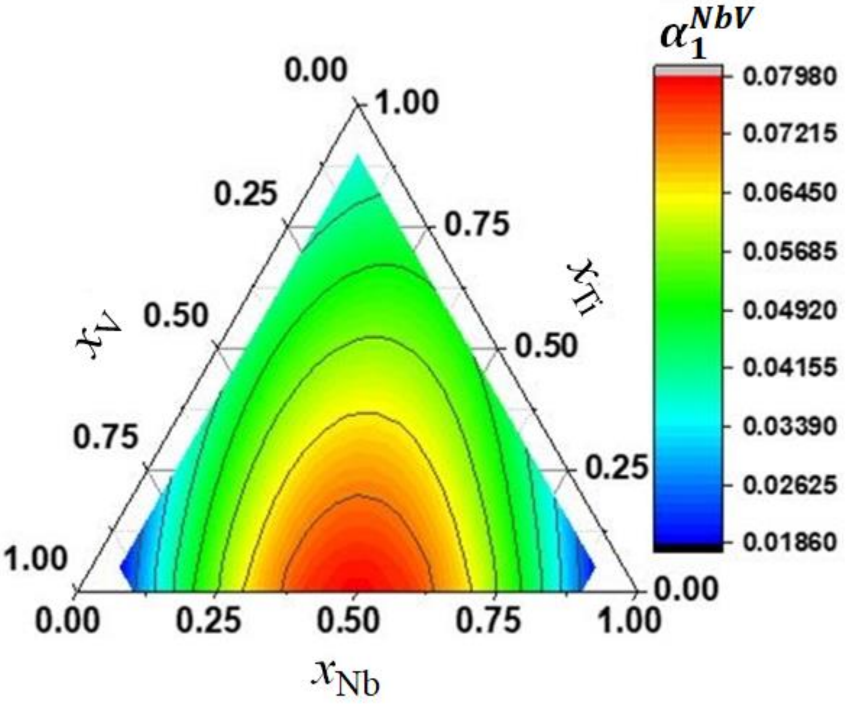


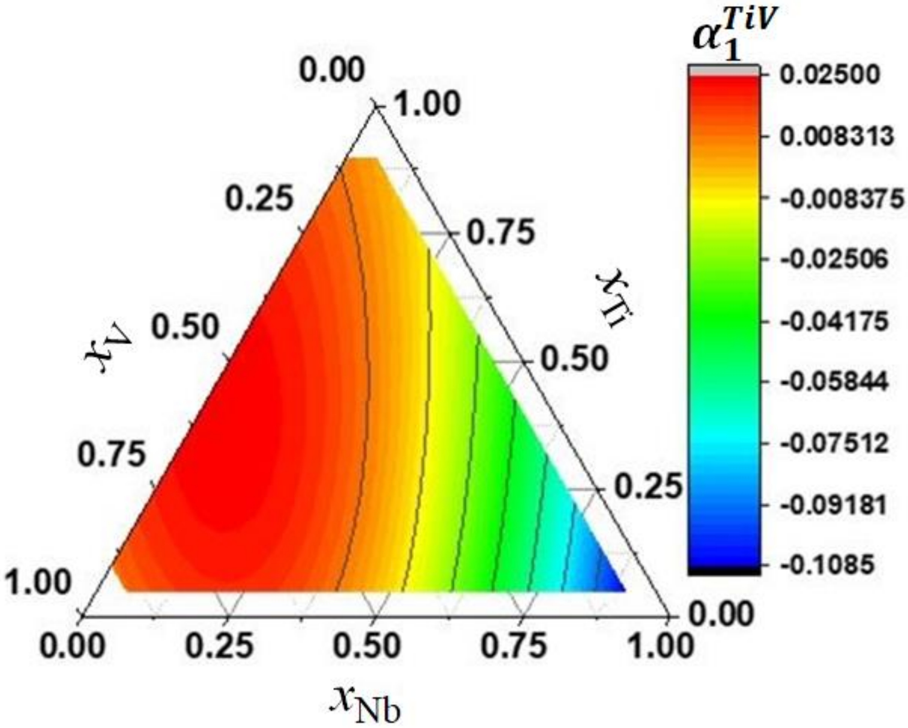
Figure 6-3 Variation of Cowley-Warren 1NN SRO parameter of the Nb-Ti-V system as a function of temperature.



(a)



(b)



(c)

Figure 6-4 (a)Variation of SRO parameter of (a) Nb-Ti, (b) Nb-V, and (c) Ti-V 1NN pairs the Nb-Ti-V system as a function of composition at a temperature of 1800 K.

(ii) Nb-Ti-Zr system

Variations of the 1NN pair SRO parameters of the Nb-Ti-Zr system as a function of temperature and compositions are shown in Figure 6-5 and Figure 6-6, respectively. The short-range order in the Nb-Ti-Zr system decreases and tends to zero with increasing temperature. The Nb-Ti and Nb-Zr type 1NN is positive, whereas the Ti-Zr are negative. Figure 6-6(a) shows 1NN pair of Nb-Ti type in the Nb-Ti-Zr system. The Nb-Ti system is phase-separating, whereas adding Zr in this system changes the nature of the Nb-Ti type 1NN SRO parameter from positive to negative. Figure 6-6(b) shows the 1NN pair of Nb-Zr type in the Nb-Ti-Zr system. The addition of Ti in the Nb-Zr system keeps the system unchanged. Whereas the addition of Nb in the Ti-Zr system, pushes the system for ordering with negative values of SRO as shown in Figure 6-6(c). Shi et al. (2022) also reported strong tendency for Nb-Nb clustering and a moderate tendency for Zr-Ti clustering in this system.

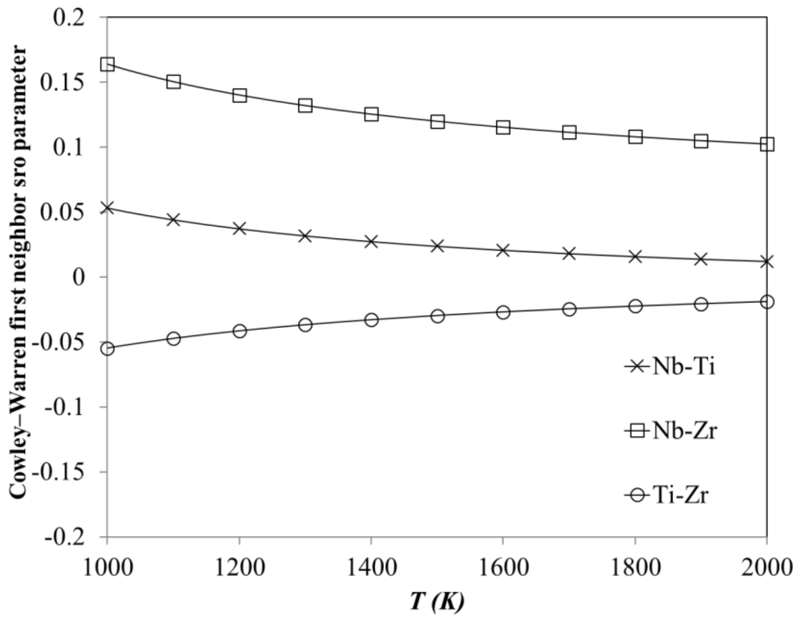
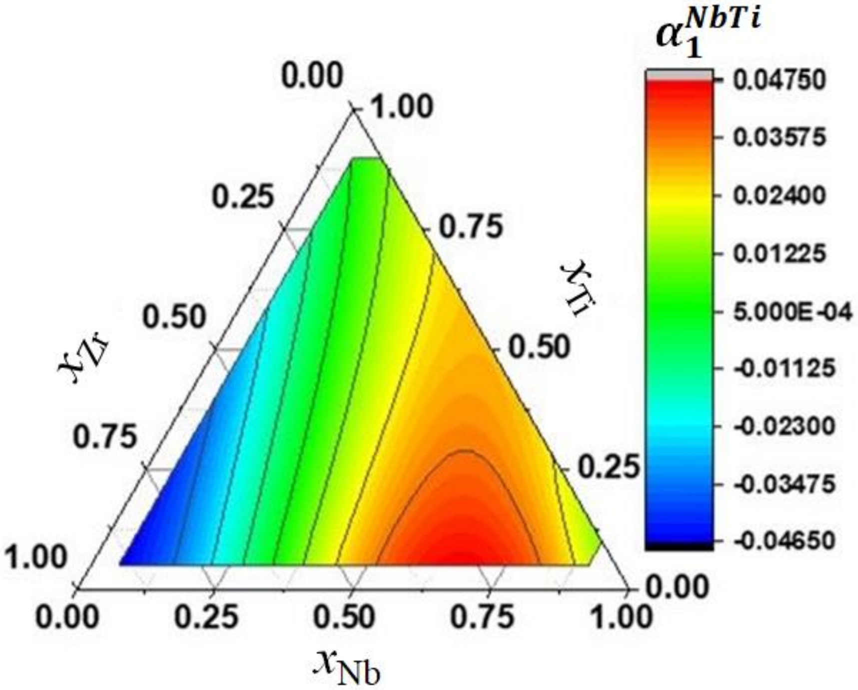
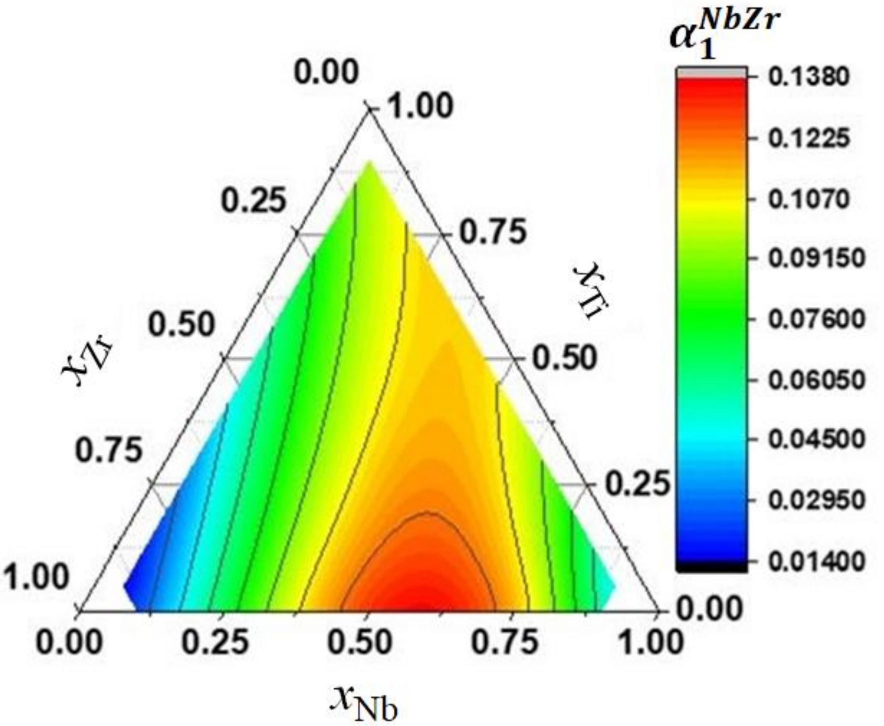


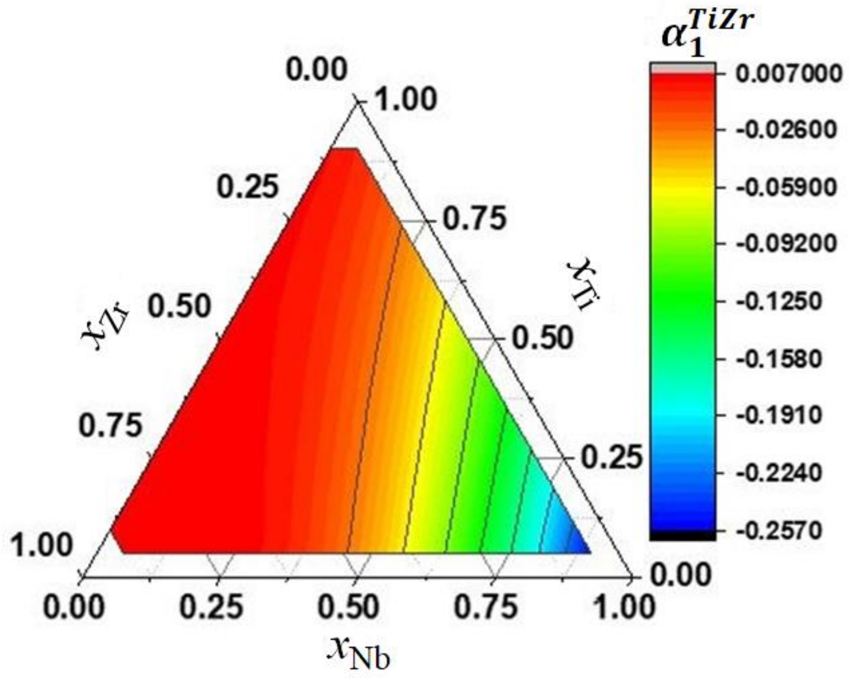
Figure 6-5 Variation of Cowley-Warren 1NN SRO parameter of the Nb-Ti-Zr system as a function of temperature.


α_1^{NbTi}
0.04750
0.03575
0.02400
0.01225
5.000E-04
-0.01125
-0.02300
-0.03475
-0.04650
x_{Zr}
x_{Ti}
x_{Nb}
0.00
0.25
0.50
0.75
1.00

(a)


α_1^{NbZr}
0.1380
0.1225
0.1070
0.09150
0.07600
0.06050
0.04500
0.02950
0.01400
x_{Zr}
x_{Ti}
x_{Nb}
0.00
0.25
0.50
0.75
1.00

(b)



(c)

Figure 6-6 (a) Variation of SRO parameter of (a) Nb-Ti, (b)Nb-Zr, and (c)Ti-Zr 1NN pairs in the Nb-Ti-Zr system as a function of composition at a temperature of 1800 K.

(iii) Nb-V-Zr system

Variation of INN SRO parameters of the Nb-V-Zr system as function of temperature are shown in Figure 6-7.s The SRO in the Nb-V-Zr system decresase with increase in temperature. The 1NN SRO of V-Zr in the Nb-V-Zr system follows the same trend as Nb-Zr. Figure 6-8(a) shows 1NN pair SRO of Nb-V type in the Nb-V-Zr system. The Nb-V system is phase-separating, whereas adding Zr in this system changes the SRO parameter from positive to negative. Consequently, changing the nature of SRO from phase separating to ordering. Figure 6-8(b) shows the Nb-Zr pair INN SRO in the Nb-V-Zr system. Adding V in the Nb-Zr system also changes the SRO parameter from positive to negative with a high concentration of V. In the V-Zr system, a strong phase separation tendency appears, and the addition of Nb does not affect this pair SRO in Nb-V-Zr system as shown in Figure 6-8(c), but at a high concentration of Nb, the SRO changes from positive to negative.

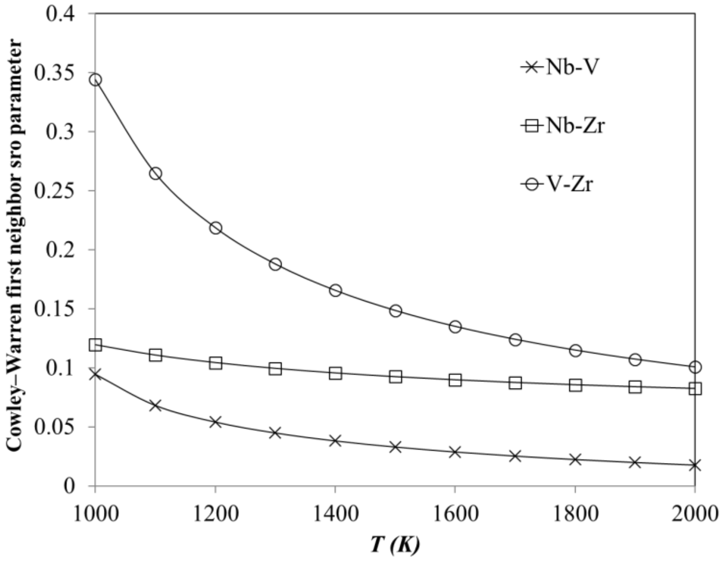
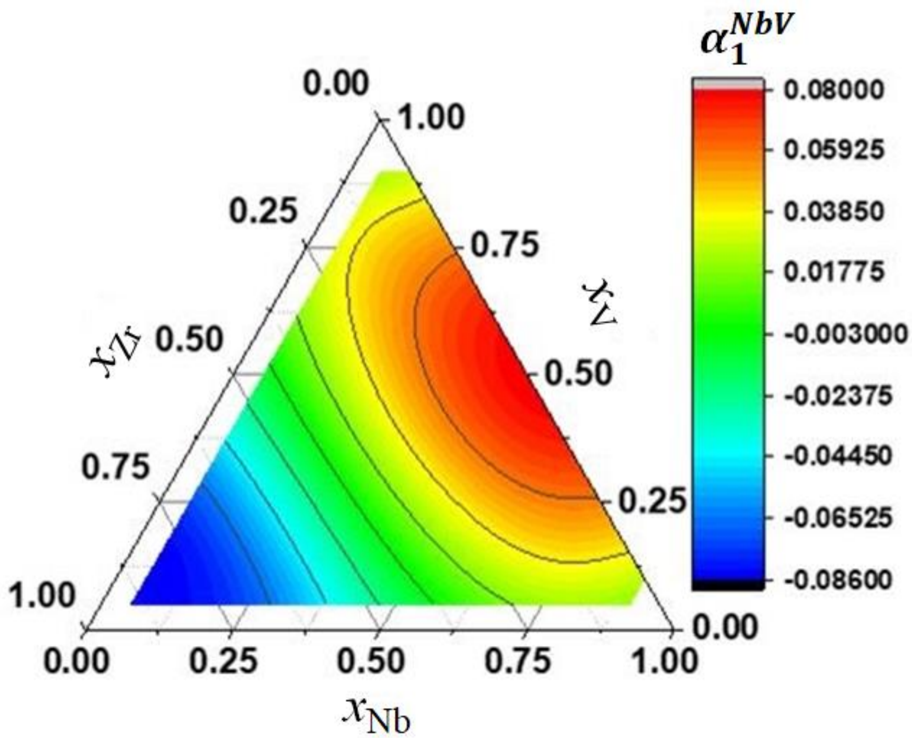
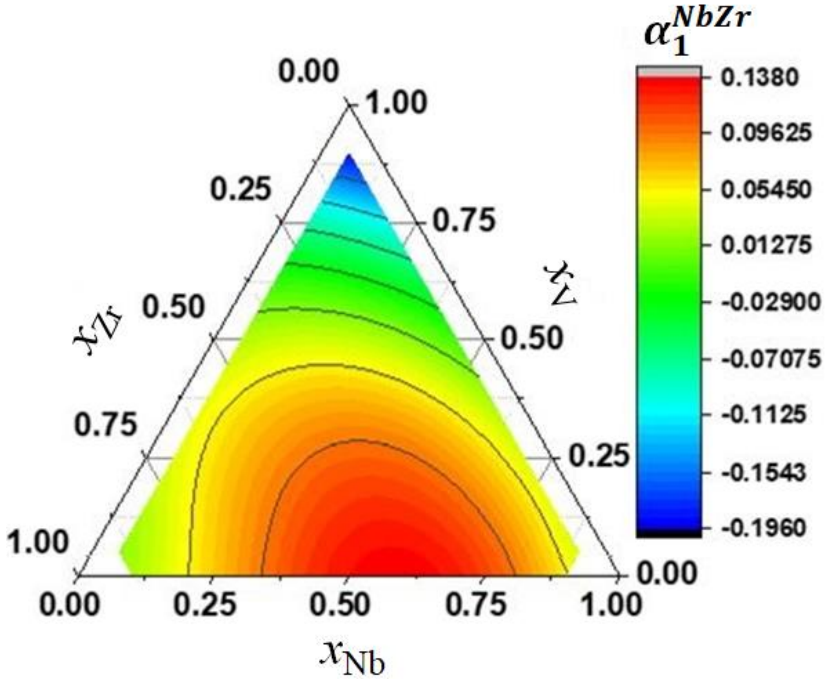


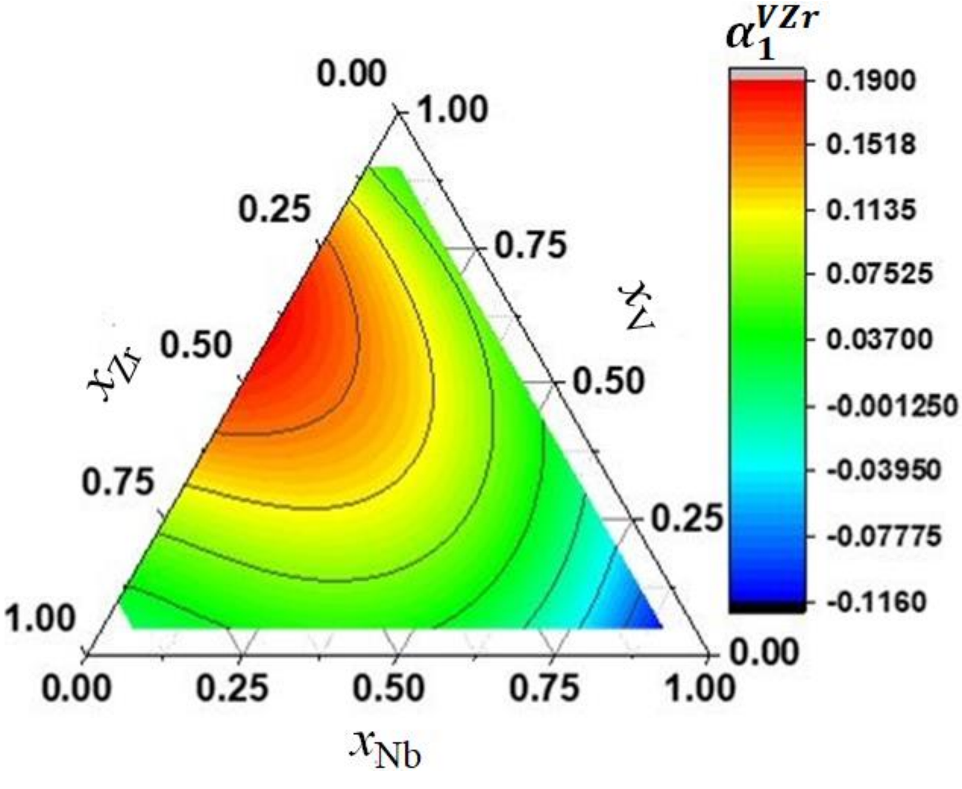
Figure 6-7 Variation of Cowley-Warren 1NN SRO parameter of the Nb-V-Zr system as a function of temperature.



(a)



(b)



(c)

Figure 6-8 Variation of SRO parameter of (a)Nb-V(b) Nb-Zr and (c) V-Zr 1NN pairs the Nb-V-Zr system as a function of composition at a temperature of 1800 K.

(iv) Ti-V-Zr system

The 1NN SRO in the Ti-V-Zr system, as shown in Figure 6-9, decreases and tends to zero with increasing temperature. The Ti-V and V-Zr 1NN SRO are positive, whereas the Ti-Zr is negative. Figure 6-10(a) shows 1NN SRO of Ti-V in the Ti-V-Zr system. The Ti-V system is phase-separating, whereas adding Zr in Ti-V-Zr system this type (Ti-V) of SRO changes from positive to negative. Consequently, changing the nature of SRO from phase separating to ordering. Figure 6-10(b) shows the 1NN SRO of Ti-Zr in the Ti-V-Zr system. Increasing concentration of V in the Ti-V-Zr system the Ti-Zr type 1NN SRO remains unchanged. V-Zr type 1NN SRO in Ti-V-Zr system remains unchanged with the addition of Ti, and only the magnitude of SRO is changing, as shown in Figure 6-10(c).

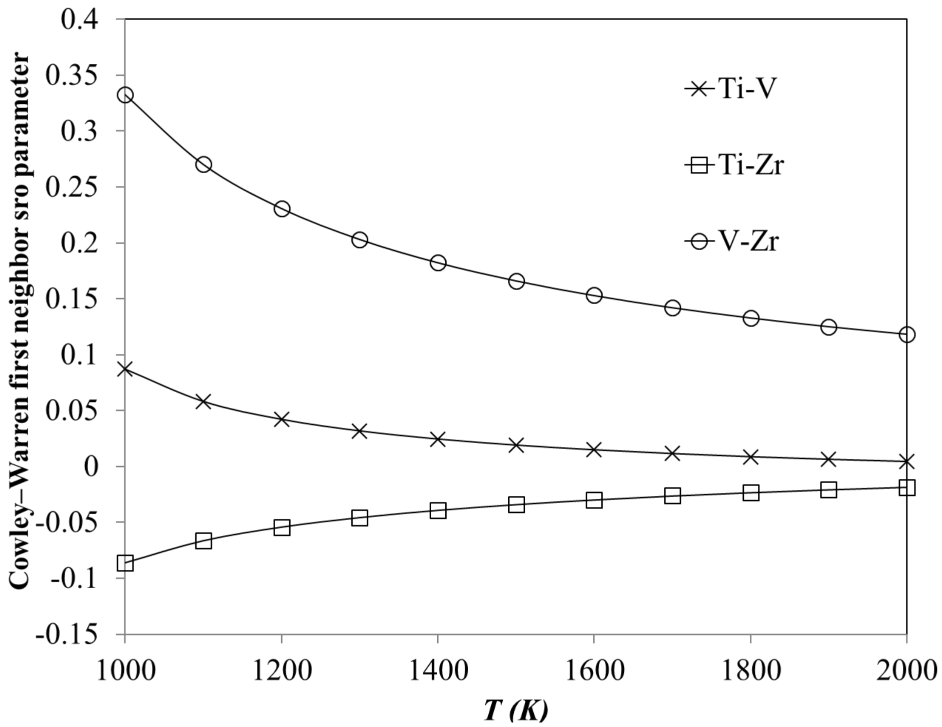
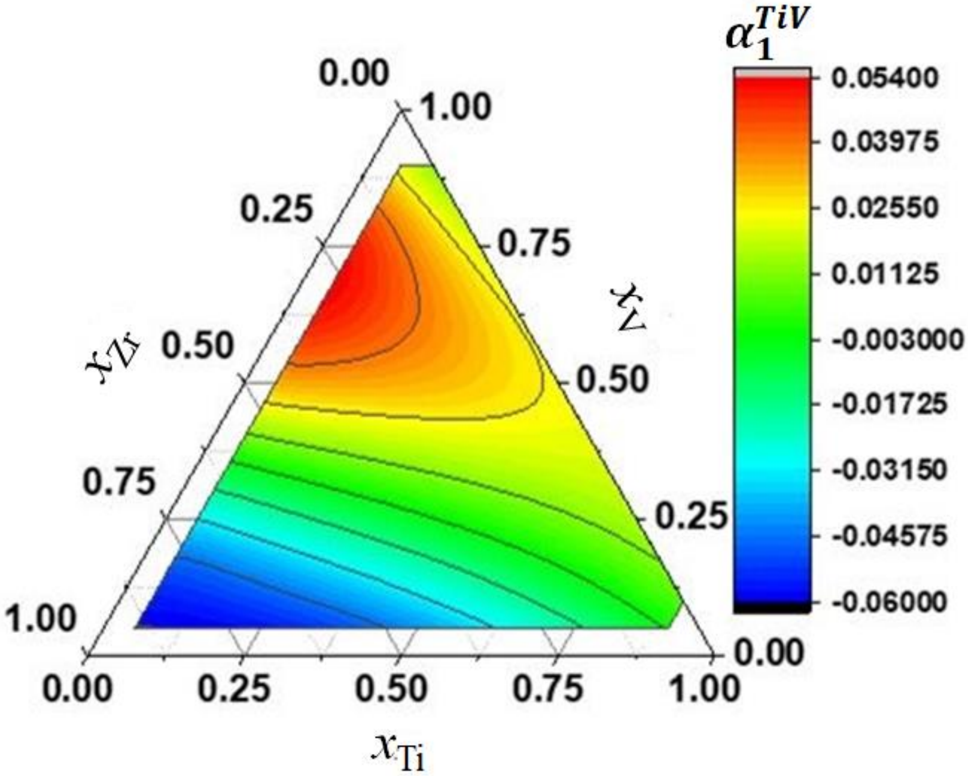
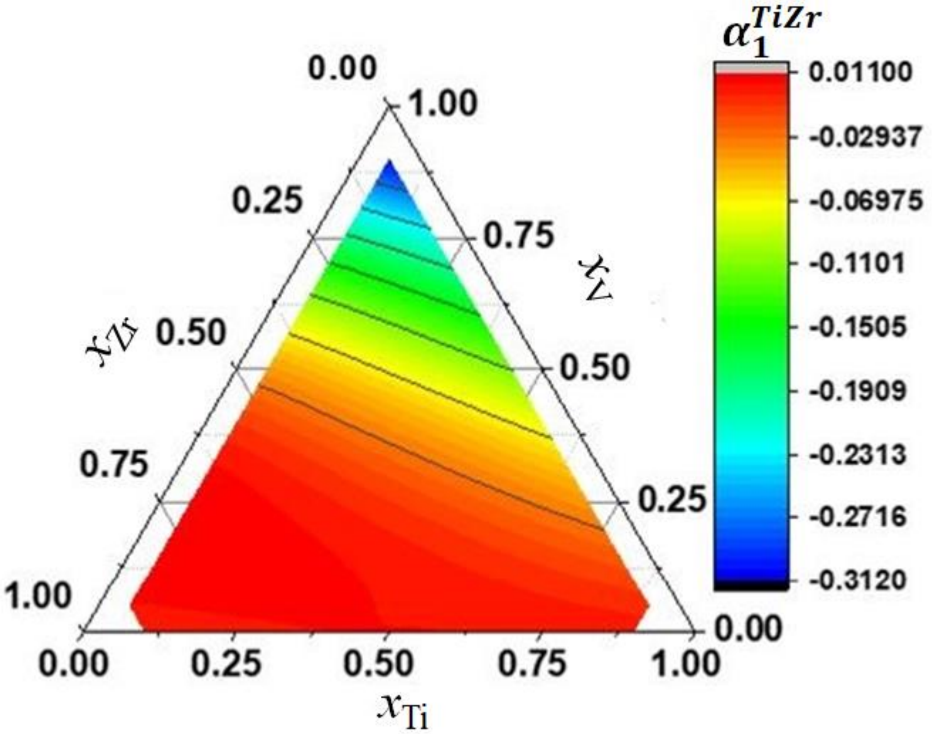


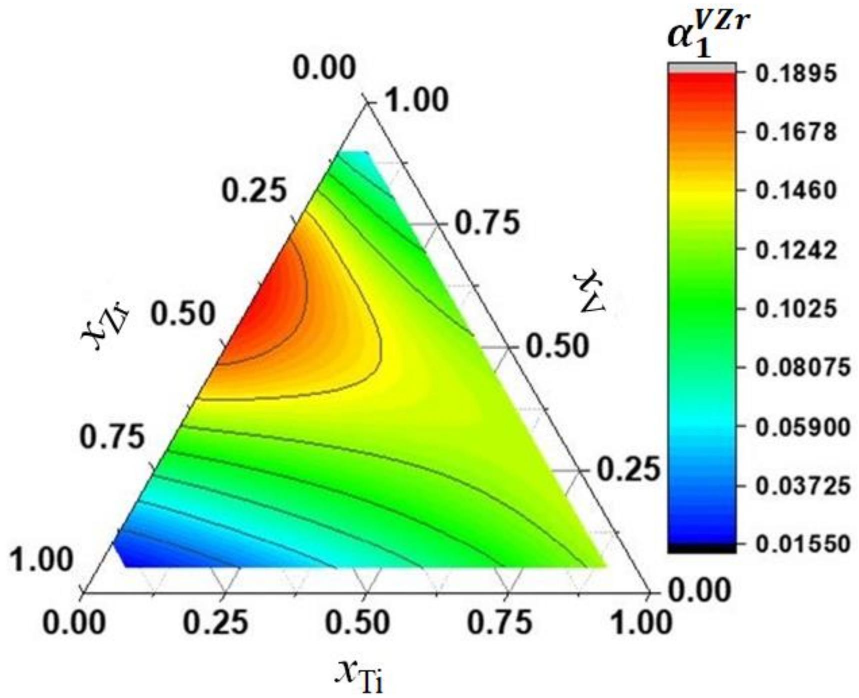
Figure 6-9 Variation of Cowley-Warren 1NN SRO parameter of the Ti-V-Zr system as a function of temperature.


α_1^{TiV}
0.05400
0.03975
0.02550
0.01125
-0.003000
-0.01725
-0.03150
-0.04575
-0.06000
0.00
0.25
0.50
0.75
1.00
x_{Zr}
x_V
x_{Ti}

(a)


α_1^{TiZr}
0.01100
-0.02937
-0.06975
-0.1101
-0.1505
-0.1909
-0.2313
-0.2716
-0.3120
0.00
0.25
0.50
0.75
1.00
x_{Zr}
x_V
x_{Ti}

(b)



(c)

Figure 6-10 Variation of SRO parameter of (a) Ti-V, (b)Ti-Zr, and (c) V-Zr 1NN pairs the Ti-V-Zr system as a function of composition at a temperature of 1800 K.

6.4 Quaternary system

The short-range order in the Nb-Ti-V-Zr system decreases and tends to zero with increasing temperature, as shown in Figure 6-11. The Ti-Zr type 1NN SRO is negative, whereas the Ti-V, Nb-V, and V-Zr are positive. The 1NN SRO of the Nb-Ti and Nb-Zr type show positive values, but both show decreasing trends at a lower temperature. These variation can be explained based on CECs associated with each type of 1NN SRO. The CEC of V-Zr highest among them, and its temperature coefficient is also affecting in the variation of SRO. A similar trend is followed for the rest of the pair SRO in this system. Figure 6-12(a) shows the 1NN Nb-Ti SRO in Nb-Ti-V-Zr quaternary system. The effect of addition of V in Nb-Ti type 1NN SRO. It changes from positive to negative. Zr addition also produces a similar result. This result is consistent with the result obtained from the ternary system. Figure 6-12(b) shows the Nb-Zr SRO in the quaternary system.

Adding Ti, the Nb-Zr type 1NN SRO remains unchanged, whereas adding V converts it to a negative 1NN SRO. Figure 6-12(c) shows the 1NN SRO of Ti-Zr in the Nb-Ti-V-Zr system. The addition of Nb does not affect the Ti-Zr 1NN SRO, but Vanadium converts the positive 1NN SRO of Ti-Zr into a negative. Figure 6-12(d) shows the 1NN SRO of Nb-V in Nb-Ti-V-Zr composition space. Adding Ti further increases the positive value of Nb-V 1NN SRO, and adding Zr reduces it to a negative. Figure 6-12(e) shows the 1NN SRO of the Ti-V system in the Nb-Ti-V-Zr system. The addition of these elements (Nb and Zr) in most of the area of composition space has very little effect. Figure 6-12(f) shows the 1NN SRO of V-Zr in Nb-Ti-V-Zr in the full composition range. Adding Nb and Ti converts the phase separating the V-Zr system into an ordering system. All these results are consistent with the ternary system 1NN SRO.

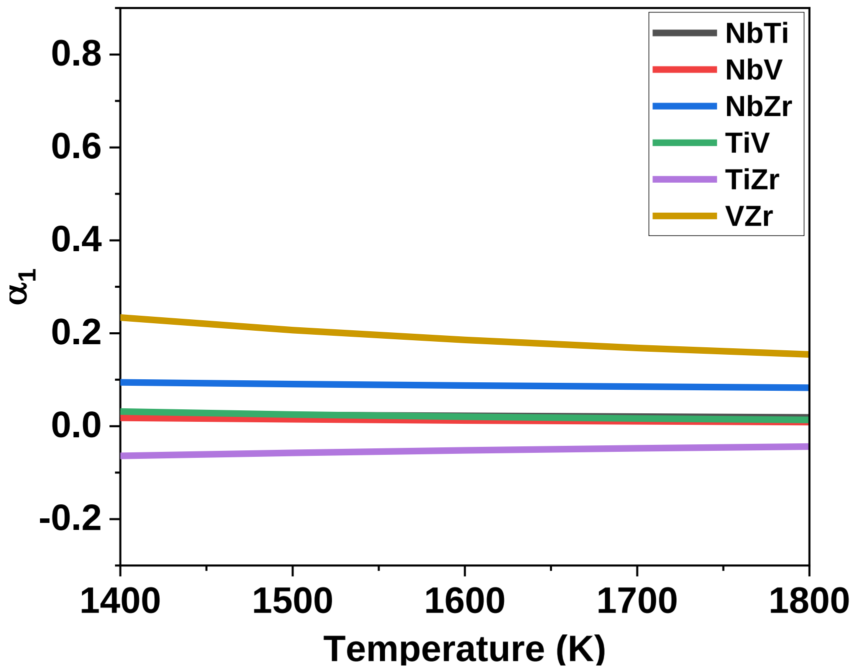


Figure 6-11 Variation of Cowley-Warren 1NN SRO parameter of the Nb-Ti-V-Zr system as a function of temperature.

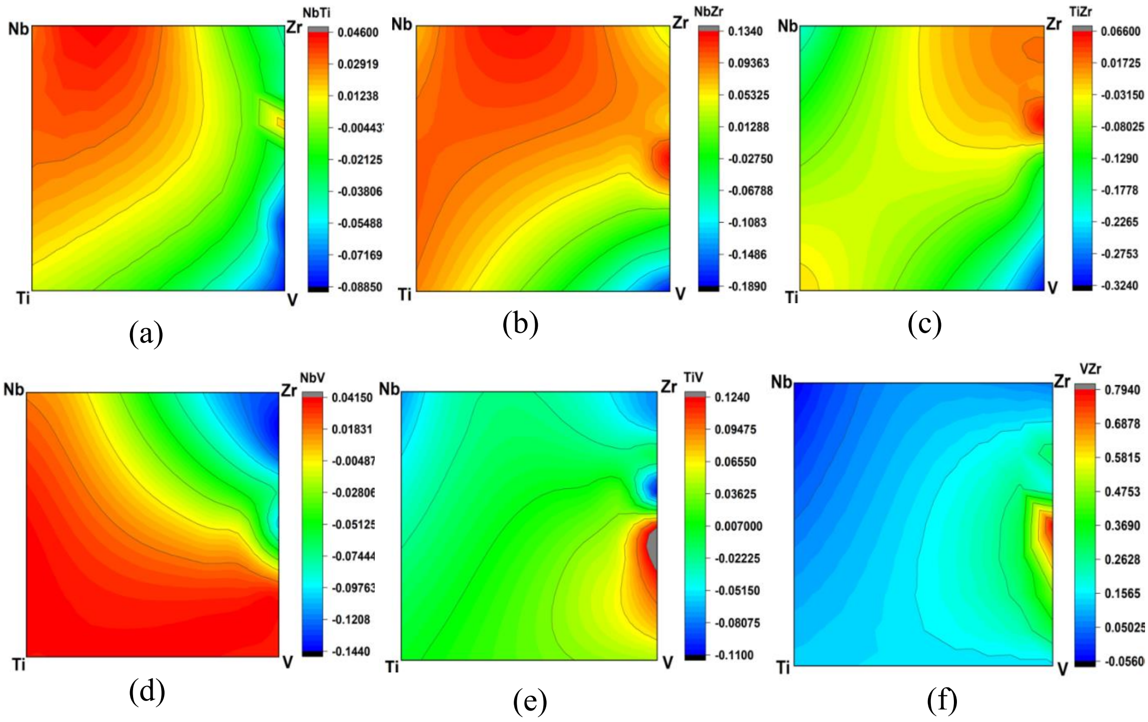


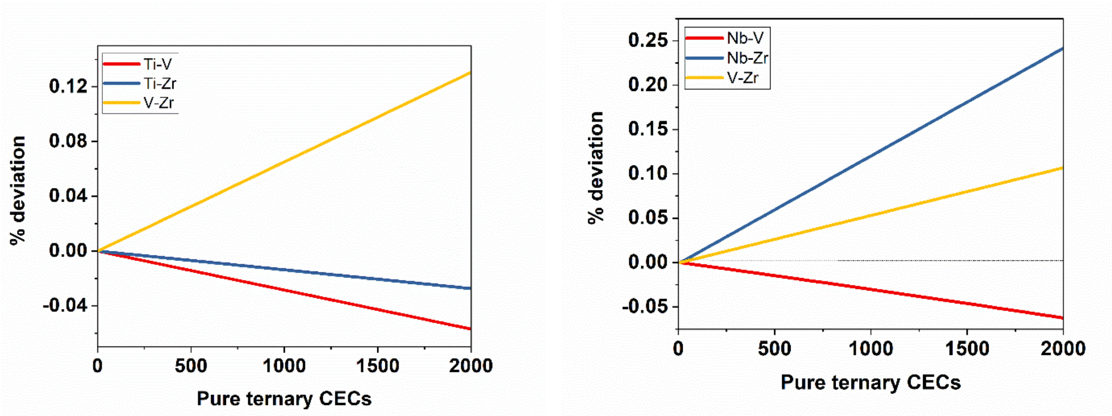
Figure 6-12 Variation of Cowley-Warren 1NN SRO parameter of the Nb-Ti-V-Zr system as a function of composition. Figure (a) Nb-Ti (b) Nb-Zr (c) Ti-Zr (d) Nb-V (e) Ti-V and (f) V-Zr.

6.5 Effect of pure ternary CEC on SROs

To understand the effect of pure ternary CECs (such as $e3TiVZr1, e3TiVZr2$, $e3TiVZr3$) on the INN pair SRO, these CECs were systematic varied in the Ti-V-Zr and Nb-V-Zr system. Figure 6-13 (a) and (b) show the percentage deviation in Eq. 6.1 given below

$$\frac{\alpha(e3PRT)-\alpha(e3PRT=0)}{\alpha(e3PRT=0)} \qquad 6.1$$

Where $\alpha(e3PRT)$ is the value of SRO at the corresponding value of $e3PRT$, and $\alpha(e3PRT=0)$ is the SRO when $e3PRT=0$. For these calculations, we assumed $e3TiVZr1 = e3TiVZr2 = e3TiVZr3 = eTiVZr$ for the Ti-V-Zr system. A similar CEC set is taken for the Nb-V-Zr system as well. With increasing $eTiVZr$, an increase in the INN V-Zr pair SRO value and a decrease in the Ti-V and Ti-Zr pair SRO values may be observed. The overall effect of the V-Zr pair is more than Ti-V and Ti-Zr pair SROs. Hence decrease in the entropy of mixing is observed. On the other hand, With increasing $eNbVZr$, an increase in the Nb-Zr and V-Zr pair SROs and a decrease in the Nb-V pair SRO may be seen.



(a) (b)

Figure 6-13 Variation of 1NN pair SROs with pure ternary CECs of type (a) $eTiVZr$ and (b) $eNbVZr$ in the bcc Nb-Ti-V-Zr system.

6.6 Conclusions

The effect of CECs, temperature, and alloy compositions on short-range ordering in the binary, ternary subsystems, and quaternary bcc Nb-Ti-V-Zr system were studied. As expected, in all the systems, SRO values become more random with increasing temperature. All binary INN pair SROs are a phase-separating nature on all the compositions with a higher tendency around the equiatomic composition. Generally, values of a particular type of SRO decrease from binary to ternary or quaternary compositions. This indicates a reduction in phase separating tendency from binary to ternary or quaternary alloys.