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## ATOMIC ORDERING BEHAVIOR OF CoTi ALLOY WITH ADDITION OF TRANSITION METALS

The statistical-thermodynamic theory of ordering and electronic theory of ordering in the pseudo-potential approximation was used to study the influence of ternary addition of some transition metals on the atomic ordering behavior of  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys with  $M = \text{Fe, Pt, Re, V, Cr, Mn, Ni, Cu, Zn, Zr, Ag, Hf}$  or  $\text{Au}$  up to a concentration of 1 at.%. The partial ordering energies, order-disorder phase transformation temperatures and partial short range order parameters have been calculated for these alloys. The analysis shows that the impurity elements in  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys can be divided into two main groups on the basis of lattice site occupancy i.e.  $M = \text{V, Cr, Mn, Cu, Zn, Zr, Ag, Hf}$  and  $\text{Au}$  mainly substitute for Co sublattice sites whereas  $M = \text{Fe, Ni, Pt}$  or  $\text{Re}$  mainly substitute for Ti sublattice sites. Further, the order-disorder transformation temperatures were found to either increase or remain nearly unchanged by the addition of ternary impurities in the CoTi alloy depending on the absolute value of the partial ordering energies. Alloys of Ti with  $\text{V, Cr, Mn, Cu, Zn, Zr, Ag, Hf}$  or  $\text{Au}$  in place of Co and alloys of Co with  $\text{Fe, Ni, Pt}$  or  $\text{Re}$  in place of Ti can be predicted for future. The results of the present analysis are in good agreement with the available experimental data on these alloys.

*Keywords:* transformation temperature, order parameter, ternary alloys, ordering energy

### 1. Introduction

B2-type titanium based alloys have attracted enormous attention due to their unique properties like high corrosion resistance and light weight as compared to other metallic alloys. Nevertheless, these properties can be optimized by addition of other elements. Cobalt alloys possess better corrosion resistance and are immensely used in medicine and dentistry since long [1]. Thus, Co-Ti intermetallics are considered the suitable candidates for aforementioned applications.

In ordered state, B2-type alloys generally have excellent corrosion resistance, high melting temperature and phase stability that makes them most appropriate for outstanding biocompatibility and high temperature application. Atomic ordering at equiatomic composition of Co and Ti in CoTi intermetallics are observed. That is why many researchers are trying to investigate the physical properties of these intermetallics that depend on ordering at equiatomic composition of constituent elements. CoTi intermetallic has B2-type ordered structure and has stability upto 1598 K because of the significant ionic contribution to the metallic bonding and charge transfer from Ti to Co due

to which it has shape memory properties and high-temperature ductility [2]. This higher value of melting temperature and elastic modulus has limited their biomedical applications. However, by the addition of third alloying element, their properties can be improved significantly which makes them suitable for biomedical applications [3-7].

In disordered state of CoTi alloy, the Ti and Co atoms occupy the sites of bcc lattice randomly and for each atom, there exists an equal probability of occupation of each atomic site in the lattice. It is probable that a change in symmetry and physical properties of the alloy and basis of the unit cell would ultimately lead to a significant change in electronic structures and physical properties [8]. As the constituent atoms in alloys strongly influence their numerous physical properties so, it is expected that an addition of a third element to the binary CoTi alloy will bring a drastic change in its physical properties, making it useful for several technological applications [9-13].

This paper aims to study the influence of addition of a third element on various ordered parameters such as ordering energy, short range order (SRO) parameter and order-disorder (O-D) phase transition temperature by a combination of statistico-

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thermodynamical theory of atomic ordering with an electronic theory of alloys in pseudo-potential approximation [14-25]. The novelty of this paper with respect to SRO parameter and ordering energy of CoTi alloys, so homogenous solid solution of Ti with some of the added elements or homogenous solid solution of Co with remaining of the added elements can be predicted.

The availability of experimental data serves as a supporting proof for obtained theoretical results.

## 2. Theory of ternary alloys

This work is based on the statistical atomic ordering theory which was established on quasi-chemical approximations and stands applicable to the processes of atomic ordering in substitutional ternary alloys having two kinds of sites [11,12]. If number of one kind of sites are equal to that of the other and each one is merely surrounded by sites of other kind and taking the correlation effects besides nearest neighbour interactions into account, the configurational amount of free energy for such alloys is expressed as [14]:

$$F = - \sum_{X',Y'} N_{X'Y'}^{12} V_{X'Y'} - k_B T \left\{ N \left( \ln \frac{N}{2} - 1 \right) - \sum_{X'} \left[ N_{X'}^{(1)} \left( \ln N_{X'}^{(1)} - 1 \right) + N_{X'}^{(2)} \left( \ln N_{X'}^{(2)} - 1 \right) \right] + \sum_{X',Y'} \left[ N^{(0)} \left( \ln N_{X'Y'}^{(0)} - 1 \right) - N_{X'Y'}^{(12)} \left( \ln N_{X'Y'}^{(12)} - 1 \right) \right] \right\} \quad (1)$$

where  $N_{X'Y'}^{12}$  is the number of  $X'Y'$  atomic pairs (here atom  $X'$  is sited at the first kind of site and  $Y'$  on the second one),  $V_{X'Y'}$  is the interaction potential of  $X'Y'$ ,  $k_B$  is the Boltzmann's constant,  $T$  is the absolute temperature,  $N$  is the total number of lattice sites, and

$$N_{X'Y'}^0 = 2Z \frac{N_{X'}^{(1)} N_{Y'}^{(2)}}{N} \quad (X', Y' = A, B, C)$$

Where  $Z$  is the coordination number,  $N_{X'}^{(1)}$  and  $N_{Y'}^{(2)}$  are the number of  $X'$  and  $Y'$  atoms on the first and second kind of sites, respectively. The minimum free energy condition regarding  $N_{X'}^{(1)}$ ,  $N_{Y'}^{(2)}$  and  $N_{X'Y'}^{12}$  variables in Eq. (1) accomplishes the equilibrium numbers of  $A, B$  and  $C$  atoms at the two kind of sites along with the number of  $X'Y'$  pairs,  $N_{X'Y'}^{12}$ . These quantities are related to each other by the following conditions:

$$\left. \begin{aligned} N_A^{(1)} + N_B^{(1)} + N_C^{(1)} &= N_A^{(2)} + N_B^{(2)} + N_C^{(2)} \\ N_{X'}^{(1)} + N_{X'}^{(2)} &= N_{X'}, N_{X'A}^{12} + N_{X'B}^{12} + N_{X'C}^{12} = ZN_{X'}^{(1)} \\ N_{AX'}^{12} + N_{BX'}^{12} + N_{CX'}^{12} &= ZN_{X'}^{(2)} \end{aligned} \right\} \quad (2)$$

$$X' = A, B, C$$

The correlation parameter,  $\varepsilon_{X'Y'}$  for  $X'Y'$  pair of a disordered ternary  $A-B-C$  alloy, in an equilibrium state can be determined by solving a set of following non-linear equations [11,12]:

$$\left. \begin{aligned} X^2 + EXY + FXZ &= c_A \\ EXY + Y^2 + DYZ &= c_B \\ FXZ + DYZ + Z^2 &= c_C \end{aligned} \right\} \quad (3)$$

Where

$$\begin{aligned} E &= \exp\left(\frac{W_{AB}}{2k_B T}\right), \quad F = \exp\left(\frac{W_{AC}}{2k_B T}\right) \\ D &= \exp\left(\frac{W_{BC}}{2k_B T}\right), \quad X = \exp\left(\frac{2N_{AA}}{ZN}\right)^{\frac{1}{2}} \\ Y &= \exp\left(\frac{2N_{BB}}{ZN}\right)^{\frac{1}{2}}, \quad Z = \exp\left(\frac{2N_{CC}}{ZN}\right)^{\frac{1}{2}} \end{aligned} \quad (4)$$

and

$$\begin{aligned} N_{AB}^{12} &= \frac{ZN}{2} EXY, \quad N_{AC}^{12} = \frac{ZN}{2} FXZ, \\ N_{BC}^{12} &= \frac{ZN}{2} DYZ \end{aligned} \quad (5)$$

where  $W_{AB}$ ,  $W_{AC}$  and  $W_{BC}$  are the partial ordering energies of  $AB$ ,  $AC$  and  $BC$  atomic pair in ternary alloy, respectively and  $c_A$ ,  $c_B$  and  $c_C$  are the respective concentrations of  $A$ ,  $B$  and  $C$  atoms. So, the correlation parameter  $\varepsilon_{X'Y'}$  is expressed as:

$$\varepsilon_{X'Y'} = \left[ \frac{2N_{X'Y'}}{NZ} \right] - c_{X'} c_{Y'} \quad (6)$$

The SRO parameter,  $\alpha_{X'Y'}(R_i)$  is related to the correlation parameter,  $\varepsilon_{X'Y'}(R_i)$  as under [14]:

$$\varepsilon_{X'Y'}(R_i) = -c_{X'} c_{Y'} \alpha_{X'Y'}(R_i) \quad (7)$$

Where  $R_i$  is the radius of  $i^{\text{th}}$  coordination sphere.

It is clear from Eqs. (3)-(7) that in order to calculate the correlation parameter,  $\varepsilon_{X'Y'}(R_i)$  and SRO parameter,  $\alpha_{X'Y'}(R_i)$ , the partial ordering energy,  $W_{X'Y'}(R_i)$  is a prerequisite. In alloys, the partial ordering energy,  $W_{X'Y'}(R_i)$  can be calculated by employing electronic theory of ordering under pseudo-potential approximation [14]:

$$W_{X'Y'}(R_i) = \frac{\bar{\Omega}_0}{\pi^2} \int_0^\infty F_{X'Y'}(q) \frac{\sin qR_i}{qR_i} q^2 dq \quad (8)$$

$$\begin{aligned} F_{X'Y'}(q) &= -\frac{\bar{\Omega}_0}{8\pi} \left| \omega_{X'}^0(q) - \omega_{Y'}^0(q) \right|^2 q^2 \frac{\varepsilon(q) - 1}{\varepsilon^*(q)} + \\ &+ \frac{2\pi}{\bar{\Omega}_0 q^2} \left| Z_{X'}^* - Z_{Y'}^* \right|^2 \exp\left(-\frac{q^2}{4\eta}\right) \end{aligned} \quad (9)$$

where  $\bar{\Omega}_0$  is the average volume of atoms,  $\varepsilon(q)$  is a dielectric function in Hartree approximation,  $\varepsilon^*(q)$  is a modified dielectric function (taking into account the exchange and correlation effects),  $\omega_{X'}^0(q)$  and  $\omega_{Y'}^0(q)$  are the respective unscreened pseudo-potential form factors of  $X'$  and  $Y'$  atoms,  $Z_{X'}^*$  and  $Z_{Y'}^*$  are the respective valences of  $X'$  and  $Y'$  atoms and  $\eta$  is the Ewald's parameter whose value is taken as  $\eta = 0.1$  [14].

The O-D transformation temperature,  $T_o$  and long range order (LRO) parameter, for a binary alloy with a B2-type superstructure at high temperatures are estimated by a method of mean field approximation in the static concentration waves [16]:

$$\ln \left[ \frac{\left( c_B + \frac{1}{2}S \right) \left( c_A + \frac{1}{2}S \right)}{\left( c_B - \frac{1}{2}S \right) \left( c_A - \frac{1}{2}S \right)} \right] = \frac{1}{k_B T} SW(\vec{K}_o) \quad (10)$$

and

$$T_o = -\frac{c_A c_B}{k_B} W(\vec{K}_o) \quad (11)$$

where  $W(\vec{K}_o)$  is the ordering energy for the shortest wave vector,  $\vec{K}_o = 2\pi(\vec{a}_1^* + \vec{a}_2^* + \vec{a}_3^*)$ ,  $\vec{K}_o$  and  $\vec{a}_n^*$  are the lattice vectors in reciprocal space. For a B2-type superstructure,  $W(K_o)$  is related to  $W(R_i)$  by:

$$W(R_i) = 8W(R_1) - 6W(R_2) - 12W(R_3) + 24W(R_4) - 8W(R_5) + \dots \dots \dots \quad (12)$$

Thus, it is obvious that in order to calculate the temperature  $T_o$ , the values of ordering energy for first five coordination spheres are prerequisite.

When a minor concentration of a ternary impurity is introduced to a binary B2-type ordered alloy, a change in O-D phase transformation temperature  $\Delta T = T_{oc} - T_o$  is expressed as [13]:

$$\frac{\Delta T}{T_o} \approx 49c_C \left[ 1 - \frac{49}{48 \cosh^2 \left( \frac{W_{AC} - W_{BC}}{4k_B T_o} \right)} \right] \quad (13)$$

In binary alloys, a normalized temperature change,  $\frac{\Delta T}{T_o}$  merely reflects a parameter that defines the effect of alloying on the O-D phase transformation temperature. Eq. (13) shows that  $\left( \frac{\Delta T}{T_o} \right) \%$  is also a function of the partial ordering energy,  $W(R_i)$ .

### 3. Results and discussion

The physical properties of CoTi alloys are strongly influenced by the addition of numerous impurities of ternary metals [16-21]. In an ordered B2-type lattice, the atomic configuration of the ternary alloying element on nano-scale is merely responsible for any change in the physical properties. Thus, a study of the ordering energies as well as structural parameters becomes vital to determine the factors governing such changes.

Firstly, it is a prerequisite to check the validity of this theory on binary alloys and subsequently, a study of influence of ternary impurity on structural properties and ordering energy with respect to the atomic ordering of CoTi based ternary alloys can be carried out using FORTRAN language.

Fig. 1 shows a plot of ordering energy versus radial distance for a CoTi binary alloy. For this alloy, the coordination radii ( $R_i$ ) were found from the lattice constants taken from Ref. 22. The ordering energy dependence on the radial distance tends to be semi-oscillatory having a sign changing character as generally observed for alloys. Commonly, three factors are responsible for such a dependence of ordering energy i.e. (1) the alloy composition (2) the electronic concentration (e/a) (3) the radial distance [23]. Table 1 shows the calculated values of ordering energy and the experimental values of  $T_o$ .

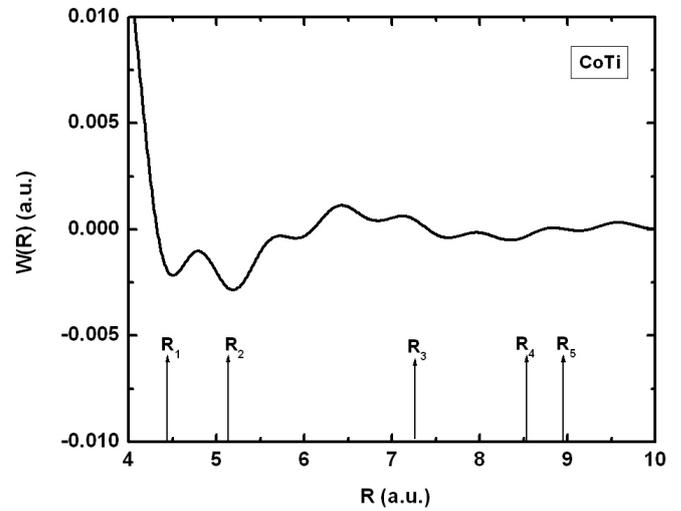


Fig. 1. The dependence of ordering energy on radial distance for CoTi alloy (1 a.u. of energy = 27.2 eV and 1 a.u. of length = 0.529 Å)

For CoTi binary alloys, the calculations of O-D phase transformation temperature are in good agreement with the corresponding experimental values. Subsequently, a similar analysis is carried out to estimate the effects of ternary additives of transition metals on the characteristics of atomic ordering in  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  ternary alloys.

Fig. 2 shows the partial ordering energies  $W_{\text{Co-M}}(R_1)$  and  $W_{\text{Ti-M}}(R_1)$  for  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  ternary alloys as a function of radial distance, where M = Cu and Re as example. An arrow in the figure indicates the radius of the first coordination sphere. A dilute nature of  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys yields an approximately matching coordination radii with those for the binary CoTi alloy. This has happened due to a very small change in lattice constants upon additions of ternary elements.

TABLE 1

The calculated ordering energies  $W(R_i)$  for the first five coordination spheres and the O-D transformation temperatures  $T_o$ , in Kelvin (K) for the binary CoTi alloy

Alloy	$W(R_1)$ (a.u.)	$W(R_2)$ (a.u.)	$W(R_3)$ (a.u.)	$W(R_4)$ (a.u.)	$W(R_5)$ (a.u.)	$T_o(\text{Cal.})$ (K)	$T_o(\text{Exptl.})$ (K) [23]
CoTi	$-2.09 \times 10^{-3}$	$-2.82 \times 10^{-3}$	$3.65 \times 10^{-4}$	$-2.70 \times 10^{-4}$	$3.05 \times 10^{-5}$	861	873

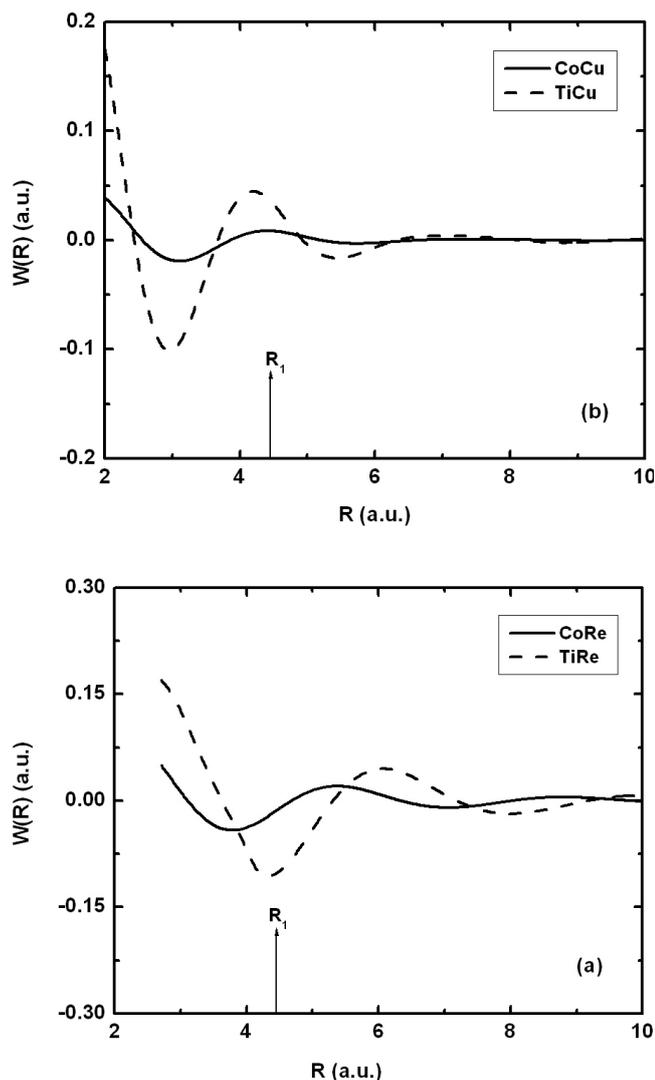


Fig. 2. The dependence of ordering energy on radial distance for  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  ternary alloys. The ordering energies are shown for (a) Co-Re and Ti-Re (b) Co-Cu and Ti-Cu atomic pairs

The dependence of ordering energy on radial distance in  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  ternary alloys has exhibited a semi-oscillatory behavior and a sign-changing character analogous to binary CoTi alloys. For different pairs of atoms, a difference in magnitudes of ordering energies has also been observed.

The Newton's method has been employed to solve the non-linear equations (Eqs. 3) and thus the partial SRO parameter  $\alpha_{XY}(R_i)$  values corresponding to a temperature of 1073 K are found with an accuracy of  $1 \times 10^{-16}$  [24]. Table 3 shows the summarized results of such calculations.

It is concluded from the data given in Table 2 and 3 that in CoTi alloy, the two major factors are responsible in determining the atomic arrangement of the ternary alloying element over the sublattices of Co and Ti. These two factors are to be the magnitude and the sign of the partial ordering energy. An analysis of such tabulated values indicates that for  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys, where  $M = \text{V, Cr, Mn, Cu, Zn, Zr, Ag, Hf}$  or  $\text{Au}$ , the partial SRO parameter for Co-M pairs has a positive sign ( $\alpha_{\text{Co-M}}(R_1) > 0$ ) and for Ti-M pairs has a negative sign ( $\alpha_{\text{Ti-M}}(R_1) < 0$ ). This in-

TABLE 2

Partial ordering energies of  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys, for  $x = 0.01$  at the first coordination sphere. Ordering energy for CoTi pair,  $W_{\text{CoTi}}(R_1) = 1.594 \times 10^{-3}$  a.u.

Elements	Ordering energies (a.u.)	
	$W_{\text{Ti-M}}$	$W_{\text{Co-M}}$
Fe	$2.40 \times 10^{-4}$	$7.25 \times 10^{-4}$
Pt	$-3.16 \times 10^{-2}$	$-2.30 \times 10^{-3}$
Re	$-1.02 \times 10^{-1}$	$-1.30 \times 10^{-2}$
V	$-5.47 \times 10^{-4}$	$-1.26 \times 10^{-2}$
Cr	$1.70 \times 10^{-1}$	$-5.87 \times 10^{-2}$
Mn	$6.94 \times 10^{-3}$	$9.81 \times 10^{-4}$
Ni	$1.27 \times 10^{-3}$	$-1.00 \times 10^{-6}$
Cu	$3.44 \times 10^{-2}$	$8.38 \times 10^{-3}$
Zn	$5.25 \times 10^{-3}$	$-1.22 \times 10^{-3}$
Zr	$4.01 \times 10^{-2}$	$1.17 \times 10^{-2}$
Ag	$6.21 \times 10^{-2}$	$1.86 \times 10^{-2}$
Hf	$2.20 \times 10^{-2}$	$5.23 \times 10^{-3}$
Au	$4.26 \times 10^{-2}$	$1.18 \times 10^{-2}$

TABLE 3

Partial SRO parameters  $\alpha_{XY}(R_i)$  for  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys, for  $x = 0.01$  at  $T = 1073$  K

Elements	Partial SRO parameters					
	$\alpha_{\text{CoTi}}$	Exptl.	$\alpha_{\text{Ti-M}}$	Exptl.	$\alpha_{\text{Co-M}}$	Exptl.
Fe	-0.117	-	0.036	-	-0.036	-0.040 [29]
Pt	-0.117	-	0.974	-	-0.894	-
Re	-0.117	-	1.000	-	-0.501	-
V	-0.117	-	-0.688	-	0.709	-
Cr	-0.117	-	-1.000	-	1.000	-
Mn	-0.117	-	-0.417	-	0.406	-
Ni	-0.117	-	0.093	0.074 [28]	-0.063	-0.060 [29]
Cu	-0.117	-	-0.976	-	0.956	-
Zn	-0.117	-	-0.447	-	0.437	-
Zr	-0.117	-	-0.989	-	0.969	-
Ag	-0.117	-	-1.000	-	0.997	-
Hf	-0.117	-	-0.858	-	0.840	-
Au	-0.117	-	-0.998	-	0.978	-

icates that  $M = \text{V, Cr, Mn, Cu, Zn, Zr, Ag, Hf}$  or  $\text{Au}$  atoms are surrounded by Ti atoms and these are selectively substituted for Co sublattice sites in CoTi superstructure.

The remaining ternary additions of  $M = \text{Pt, Fe, Ni}$  or  $\text{Re}$  atoms in  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys show that the  $\alpha_{XY}(R_1)$  have a positive sign for Ti-M atomic pairs and negative sign for Co-M pairs. This shows that the atoms of these third elements are mainly substituted for Ti sublattice sites in CoTi alloys besides being surrounded by Co atoms. A magnitudes comparison of the  $\alpha_{XY}(R_1)$  indicates that the probability of substitution of Pt atoms for Ti sublattice sites are higher than that of Fe atoms. However, Re atoms are absolutely substituted for Ti atoms and are preferentially surrounded by Co atoms. As, the exact magnitude of  $\alpha_{XY}(R_1)$  for Cr is 1.0 so, Cr atoms are absolutely substituted for Co atoms and preferentially surrounded by Ti atoms. In literature,

the availability of experimental data on the SRO parameter of  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys stands limited and the data available regarding the sign of the SRO parameter for  $\text{Co}_{0.5}(\text{Ti}, \text{Fe})$  and  $\text{Co}_{0.5}(\text{Ti}, \text{Ni})$  alloys are in good agreement with the contemporary calculations [25,26].

An addition of the ternary element causes a change in the O-D transformation temperature which can be seen by the calculation of a normalized change in O-D phase transformation temperature. The values of this parameter are calculated and given below.

Table 4 shows the summarized values calculated for the normalized temperature change for  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys. It is observed that the ternary additive in the binary CoTi alloy either increases or maintains the O-D transformation temperature. This variation in the O-D transformation temperature is thus assumed to be due to its dependence on the ordering energy.

TABLE 4

The normalized temperature change  $(\Delta T/T_0)\%$  calculated for  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys, at various impurity levels  $x$ . ( $T_0 = 873$  K for CoTi alloy [27])

Elements	$(\Delta T/T_0)\%$		
	$x = 0.0025(0.25\%)$	$x = 0.005(0.5\%)$	$x = 0.01(1\%)$
Fe	-0.116	-0.231	-0.462
Pt	6.000	12.00	24.004
Re	6.120	12.24	24.499
V	3.822	7.653	15.364
Cr	6.125	1.225	24.500
Mn	1.385	2.769	5.542
Ni	-0.046	-0.092	-0.183
Cu	5.904	11.810	23.609
Zn	1.603	3.207	6.414
Zr	5.981	11.945	23.917
Ag	6.120	12.238	24.461
Hf	5.027	10.053	20.108
Au	6.102	12.186	24.121

Table 2 shows that on the basis of absolute values of partial ordering energy, the ternary additives in the CoTi alloys can be categorized into two groups  $W_{\text{Co-M}}(R_1)$  and  $W_{\text{Ti-M}}(R_1)$ :

- 1) The absolute values of partial ordering energies  $W_{\text{Co-M}}(R_1)$  and  $W_{\text{Ti-M}}(R_1)$  are either very close to or greater than  $W_{\text{CoTi}}(R_1)$  for any ternary addition of Pt, Re, Cr, Cu, Zr, Ag, Hf or Au. These ternary additions cause a large increase in  $T_{oc}$  value. It is observed that a rapid increase in  $T_{oc}$  is caused by an increase in the concentration of the ternary additive.
- 2) The absolute values of the partial ordering energies  $W_{\text{Co-M}}(R_1)$  and  $W_{\text{Ti-M}}(R_1)$  are either very close to or less than  $W_{\text{CoTi}}(R_1)$  for any ternary addition of Fe, V, Mn, Ni or Zn. The ternary additions of these elements cause a lesser increase in the value of  $T_{oc}$  as compared to that of elements of the first group. These ternary elements belong to a group which largely substitutes for Co sublattice sites excluding Fe. Additionally, an increase in  $T_{oc}$  has a same ratio as that of the ternary additives.

An analysis of this work establishes three points:

- 1) Depending upon the absolute value of partial ordering energy of different pair of atoms, the O-D transformation temperature either increases or remains constant on the addition of a ternary impurity of transition metals to a binary CoTi alloy.
- 2) The nature and type of a ternary additive has a substantial influence on the O-D transformation temperature.
- 3) A major increase in the O-D transformation temperature is observed for a ternary addition corresponding to a larger magnitude of partial SRO parameter.

#### 4. Conclusions

A quantitative and qualitative analysis of the ternary addition of a transition metal such as Fe, Pt, Re, V, Cr, Mn, Ni, Cu, Zn, Zr, Ag, Hf or Au up to a concentration of 1 at.% to  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys has been carried out by employing the statistical-thermodynamic theory of ordering along with the electronic theory of ordering in the pseudo-potential approximations. The partial ordering energy  $W_{XY}(R_1)$ , SRO parameters  $\alpha_{XY}(R_1)$  and O-D transformation temperature  $T_{oc}$  have been calculated.

The analysis can be concluded as:

The impurity additives in  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys can be categorized into two main groups based on the occupancy of lattice sites:

- i) The partial SRO parameters for Co-M pair with  $M = \text{V, Cr, Mn, Cu, Zn, Zr, Ag, Hf}$  and Au in  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys are positive ( $\alpha_{\text{Co-M}}(R_1) > 0$ ) indicating that these elements mainly substitute Co sublattice sites and are preferentially surrounded by Ti atoms.
- ii) The ( $\alpha_{\text{Ti-M}}(R_1) > 0$ ) for  $M = \text{Fe, Pt, Ni}$  or Re in  $\text{Co}_{0.5}(\text{Ti}_{1-x}\text{M}_x)_{0.5}$  alloys which indicates that these elements have mainly substituted Ti sublattice sites and are preferentially surrounded by Co atoms.

Depending on the absolute value of the partial ordering energy of different atomic pair, the O-D transformation temperatures either increase or remain constant on the addition of a ternary impurity in CoTi alloys. In this regard, these ternary impurities can be categorized into two main groups:

- i) For  $M = \text{Pt, Re, Cr, Cu, Zr, Ag, Hf}$  or Au, the absolute values of partial ordering energies of  $W_{\text{Co-M}}(R_1)$  and  $W_{\text{Ti-M}}(R_1)$  are either very close to or greater than  $W_{\text{CoTi}}(R_1)$  and an increase in  $T_{oc}$  is rapid and large and has almost the same ratio as that of the impurity additives.
- ii) For  $M = \text{Fe, V, Mn, Ni}$  or Zn, the absolute values of partial ordering energies of  $W_{\text{Co-M}}(R_1)$  and  $W_{\text{Ti-M}}(R_1)$  are either very close to or less than  $W_{\text{CoTi}}(R_1)$  and an increase in  $T_{oc}$  is slow and has almost the same ratio as that of the impurity additives.

A slow increase in  $T_{oc}$  on adding the impurity  $M = \text{Fe, V, Mn, Ni}$  or Zn that belongs to a group which mainly substitutes for Co sublattice sites excluding Fe.

The results of the contemporary analysis on these alloys are in good agreement with the available experimental data in literatures.

In this work, SRO parameter, ordering energy and order-disorder transformation temperature are calculated theoretically. The partial SRO parameters for Co-M pair with  $M = V, Cr, Mn, Cu, Zn, Zr, Ag, Hf$  and Au in  $Co_{0.5}(Ti_{1-x}M_x)_{0.5}$  alloys are positive and for  $M = Fe, Pt, Ni$  or Re are negative. The significance with respect to SRO parameter is that in CoTi alloys, Co can be replaced with any of the V, Cr, Mn, Cu, Zn, Zr, Ag, Hf or Au atoms, so homogenous solid solution of Ti with any of above elements can be predicted. Similarly, in CoTi alloys, Ti can be replaced with any of the Fe, Pt, Ni or Re atoms, so homogenous solid solution of Co with any of the above four elements can be predicted.

Same type of predictions can be taken into account for ordering energies and order-disorder transformation temperatures.

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