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CALCULATION OF SHORT RANGE ORDERING IN Ni-Ti ALLOYS

Tahir Abbas, R. M. Arif Khalil, A. M. Rana and Mehtab-Ullah
Department of Physics, Bahauddin Zakariya University Multan, Pakistan

Abstract: The concentration dependence of atomic short range order(SRO) was studied in the $Ni_{100-x}Ti_x$(x=2,5,10 ,15,20,25,35,50 at.%) alloys using the frame work of the transition metal model pseudopotential (TMMP). The ordering energies and SRO parameters were calculated for Ni-Ti alloys. It was observed that this model predicted the correct sign of the SRO parameters for Ni-Ti alloys.

Keywords: Ni-Ti alloys, pseudopotential, short range order.

INTRODUCTION

One of the properties of a metallic system is its atomic arrangement. The arrangement of atoms or of vacancies in a crystal is complete at low temperature (long range order (LRO) while the arrangement of atoms may be random at high temperature. When the temperature is lowered, the average crystal lattice may look periodic over sufficiently large distances, but the occupancy of atomic sites varies from one unit cell to the other.

Short range order (SRO) parameters provide information about the arrangement of atoms in the immediate neighborhood of particular atoms of the lattice. Thus the name SRO is given to the case when unlike atoms tends to become near neighbors [Warren 1990]. The degree of SRO-ing or clustering may be defined in terms of a suitable parameter called the Warren-Cowley parameter α_i (WCP) and the value of WCP may be related to the diffraction effects produced. It is defined as follows [Warren 1990].

$$\alpha_i = \left[1 - \frac{P_A^i}{C_A}\right] = \left[1 - \frac{P_B^i}{C_B}\right]$$

Where P_A^i, P_B^i are the conditional probabilities of having B or A as near neighbors in the *i*-th coordination sphere, respectively. The values of Warren-Cowley parameters α_i provide information about the atomic arrangements in the lattice, whether there is a tendency to be like or unlike atoms as near neighbors according to the following:

α_i <0 ; for SRO

α_i >0 ; for clustering or local order

α_i =0 : for randomness

All real solid solutions probably exhibit either short range ordering or clustering to the greater and lesser degree simply because they are composed of unlike atoms with particular forces of attraction or repulsion operating between them. SRO is more common than clustering [Cullity 1978].

Many researchers have shown that SRO, its degree, its type and sign depend upon the concentration, nature and temperature of solid solution and the history of the material [Iveronova and Katsnelson 1973].

X-ray and neutron diffraction techniques have been used frequently to study SRO experimentally mainly due to the reason that they provide a direct measurement of the degree of SRO. The SRO parameters have been determined experimentally for a large number of metallic solid solutions [Abbas 1980, Katsnelson and Iveronova 1980, Saha *et al*. 2002, Saha *et al*. 2003, Sembiringa *et al*. 2003] by diffuse X-rays scattering intensity measurements (DSIM) and in ternary alloys [Bruade *et al.* 1996]. Ikram and Ali [1993] studied SRO in Ni-Al system using electrical resistivity measurements. SRO has also been studied by differential scanning calorimetery (DSC) in mechanically alloyed Hf_{75} $Al_{7.5}$ $Cu_{7.5}$ Ni_{10} and amorphous Zr_{75} $Al_{7.5}$ $Cu_{7.5}$ Ni_{10} alloys by Damonte *et al.* [2000]. Theoretically short range ordering has been investigated by statistical and electronic theories of SRO as well as by pseudo potential theory [Harrison 1966]. Electronic theory of ordering has been applied to calculate the SRO parameters in Ni-Rh and Ni-Ir alloys [Abbas *et al.* 1980]. The pseudopotential theory has been applied successfully for the calculations of many atomic properties and was found useful for studying ordering characteristics of alloy formation, if not for all then at least for a series of groups [Katsnelson *et al*. 1979, Abbas 1986]. Khawaja *et al.* [1977] applied pseudopotential technique in the second order perturbation theory to calculate local ordering energy and SRO parameters to have good agreement with the experimental results on Al- Zn systems.

The main aim of this investigation was to study the short range ordering (SRO) in Ni-Ti alloys using the pseudopotential approach by applying second order perturbation theory. The SRO parameters were calculated using the dielectric screening function $\varepsilon(q)$ in the Hartree approximation [Hartree *et al*. 1941], and energy exchange and correlation correction parameters $f(q)$ by applying two different approaches as proposed by Kleinman [1967, 68] and Singwi *et al.* [1968, 70].

CALCULATION OF ORDERING ENERGY AND WARREN-COWLEY SRO PARAMETERS

Total energy-wave number characteristics F(q), and the ordering energy $V(R_i)$ along with dielectric screening function $\varepsilon(q)$ and energy exchange and correlation correction parameter $f(q)$ are the main factors in the calculation of SRO parameters [Iveronova and Katsnelson 1973].

In the second order perturbation theory, the band structure contribution to the structure and configuration dependent part of the total energy may be written as [Khawaja *et al.* 1977]:

$$E_{bs} = \frac{\Omega_o}{8\pi} \sum_q^{/} q^2 F^{/}(q) \qquad (1)$$

Where $\Omega_o = \Omega/N$ is the volume per atom, N is the number of atoms in crystal of volume Ω, $F^{/}(q)$ the energy–wave number characteristics which in the local pseudopotential approximation may be expressed as [Harrisson 1966]:

$$F^{/}(q) = \left|W^O(q)\right|^2 \frac{1-\varepsilon(q)}{\varepsilon^*(q)} \qquad (2)$$

where $W^0\ (q)$ is the local approximation of total unscreened pseudo-potential form factor. $\varepsilon(q)$ is the static dielectric constant in the Hartree approximation and is given by:

$$\varepsilon(q) = 1 + [1 - f(q)](\frac{4\pi z e^2}{\Omega_o q^2})\chi(\frac{q}{2K_F}) \qquad (3)$$

where $\chi(q)$ is the perturbation characteristic given by:

$$\chi(q) = \frac{3E_F}{2}[\frac{1}{2} + \frac{4K_F^2 - q^2}{8K_F q}\ln\left|\frac{2K_F + q}{2K_F - q}\right|] \qquad (4)$$

where $E_F = \frac{\hbar^2 K^2{}_F}{2m}$ is the Fermi energy and $K_F = (\frac{3\pi^2 Z}{\Omega})^{1/3}$ is the Fermi wavevector.

The relations for exchange and correlation effects $f(q)$ as proposed by and Kleinman [1967, 1968] and Singwi *et.al.* [1968, 1970] are as follows:

$$\text{Kleinman: } f(q) = \frac{1}{4}\left[\frac{q^2}{q^2 + K^2{}_F + K_S^2} + \frac{q^2}{q^2 + K^2{}_S}\right],\ K_S = \frac{2K_F}{\pi}(a.u.) \qquad (5)$$

$$Singwi\ et.al.:\ f(q) = A\left[1 - \exp[-B(\frac{q}{K_F})^2]\right]$$

$$A = 0.8994 \qquad (6)$$

$$B = 0.3401$$

$\varepsilon^*(q)$ is the modified dielectric constant which accounts for the exchange and correlation effects in the interacting electron gas. Using the SRO-dependent part, the band structure energy may be written as:

$$E_{bs}^{SRO} = \frac{\Omega_O}{8\pi}\frac{c(1-c)}{N}\sum_q\sum_R q^2\alpha(R)e^{iqR}\ \left|\Delta W^O(q)\right|^2\frac{1-\varepsilon(q)}{\varepsilon^*(q)} \qquad (7)$$

Similarly, the SRO dependent part of the electrostatic energy contribution to the total energy of the crystal may be given in the form:

$$E_{es}^{SRO} = \frac{c(1-c)}{N} \sum_{q} \sum_{R} \frac{(Z_A - Z_B)^2}{2} \frac{4\pi}{\Omega_O q^2} e^{(-q^2/4\eta)} \alpha(R)\ e^{iqR} \qquad (8)$$

where Z_A, Z_B are valancies of the component atoms *A* and *B* of the A-B alloy and η is the Ewald parameter. Combining Eqs. (7) and (8) an expression can be obtained for the total energy of the crystal:

$$E^{SRO} = E_{bs}^{SRO} + E_{es}^{SRO} = \frac{c(1-c)}{N} \sum_{q} \sum_{\{R\}} \alpha(R)\ e^{iqR} F(q) \qquad (9)$$

where *F(q)* is an additive energy-wave number characteristics depending upon the band structure and electrostatic energy:

$$F(q) = \frac{\Omega_O}{8\pi} \sum_{q} q^2 \left|\Delta W^O(q)\right|^2 \frac{1-\varepsilon(q)}{\varepsilon^*(q)} + 2\pi \frac{(Z_A - Z_B)^2}{\Omega_O q^2} e^{(-q^2/4\eta)} \qquad (10)$$

Changing the summation in Eq. (5) to integration and averaging over all lattice sites q and R, one gets:

$$E^{SRO} = c(1-c) \sum_{\{R_i\}} \alpha(R_i)\ e^{iqR} V(R_i) \qquad (11)$$

where

$$V(R_i) = \frac{\Omega_0}{\pi^2} \int dq q^2 F(q) \frac{\sin(qR_i)}{qR_i} \qquad (12)$$

V(R$_i$) is the local ordering energy and co-ordination number of the *i*-th co-ordination sphere of radius R_i [Hail and Philhours 1965].

Using the expression for entropy [Hashimoto and Iwasaki 1992], SRO parameter can be expressed as:

$$\frac{\alpha_1}{(1-\alpha_1)^2} = c(1-c)\left[e^{-\frac{V(R_i)}{K_B T}} - 1 \right] \qquad (13)$$

where K_B is the Boltzmann Constant.

RESULTS AND DISCUSSION

We have investigated the concentration dependence of SRO in Ni-Ti alloys using the TMMP. These alloys were selected for present investigation due to the reason that they are alloys of transition metals and they form solid solutions over the composition ranges selected. The alloy compositions selected were Ni_{100-x} Ti_x (x=2,5,10,15,20,25,35,35,50 at.%). The Ni-Ti alloys form fcc solid solutions for first three compositions selected and for other compositions upto 35 at.%, a mixture of solid solution and intermetallic compounds and a single phase compound for 50 at.% as clear from phase diagram [Brandes and Brook 1992]. The lattice constants for three alloy compositions of this alloy were calculated using the Vegard's rule and are given in Table 1. It can be seen that lattice constant "a "decreases with increase of Ti concentration in Ni-Ti alloys. This may be attributed to the size difference between Ni (a =3.52Å) and Ti (a = 2.95Å) atoms. The radii for the three co-ordination spheres of the selected alloy compositions in Ni-Ti are calculated and are given in the same Table 1.

Table 1: Radii of co-ordination spheres.

Alloy Composition	$R_1 = \frac{a}{\sqrt{2}}$ (Å)	$R_2 = a$ (Å)	$R_3 = \sqrt{2}\, a$ (Å)
Ni-02 at. %Ti	2.4809	3.5086	4.9619
Ni-05 at. %Ti	2.4688	3.4915	4.9377
Ni-10 at. %Ti	2.4487	3.4630	4.8974
Ni-15 at. %Ti	2.4285	3.4345	4.8571
Ni-20at. %Ti	2.4084	3.4060	4.8168
Ni-25 at. %Ti	2.3882	3.3775	4.7760
Ni-35 at. %Ti	2.3479	3.3205	4.6958
Ni-50 at. %Ti	2.2874	3.2350	4.5749

For calculations, a computer program was written in MATLAB7. The model parameters of the TMMP for Ni and Ti used as input are given in Table 2. These values were taken from Animalu [1973].

Table 2: Parameters of the model pseudopotential used for the calculation of the ordering energy from Animalu [1973].

Metal	A_O	A_1	A_2	R_M	Ω	Z	$\lvert R_C \rvert$	α_{eff}	E_C	η
Ni	0.990	1.050	0.980	2.200	73.6	2.000	1.304	0.063	0.093	0.0150546
Ti	2.300	2.500	2.100	2.0000	119.0	4.000	1.285	0.037	0.090	0.0075343

The ordering energy for three co-ordination spheres are calculated by using Eq. (12) [Hail and Philhours 1965] and values are given in Table 3. It is seen that the ordering energies for all the concentrations have positive sign on the first co-ordination sphere which indicates the presence of short-range ordering. The sign of the ordering energy on the second and third co-ordination spheres is negative and has small absolute value in Ni-Ti alloys. It can be said that the ordering energy has a semi-oscillatory character.

SRO parameters were calculated using Eq. (13) [Hashimoto and Iwasaki 1992] at room temperature (300K). It was observed that value of SRO parameters become more negative with increase of Ti contents in the alloy up to 15 at. %. This increase of Ti in the alloy leads to an increase in degree of SRO for first co-ordination sphere. It was also observed that value of SRO parameters become more positive with increase of Ti contents in alloy for first coordination sphere. The theoretically calculated values of SRO and clustering parameters in these alloys are given in Table 4. It is seen that the TMMP gives the correct sign of the SRO and clustering parameters for Ni-Ti alloys as given by Warren [1990].

Table 3: Ordering energies for Ni-Ti alloys calculated taking into account exchange and correlation correction parameter *f(q).*

	Kleinman [1967, 68]		
Concentration	V(R_1) (a.u)	V(R_2) (a.u)	V(R_3) (a.u)
Ni-02at. % Ti	0.0013	-0.0019	-0.0011
Ni-05at. % Ti	0.0028	-0.0047	-0.0025
Ni-10at. % Ti	0.0044	-0.0087	-0.0041
Ni-15at. % Ti	0.0048	-0.0119	-0.0047
Ni-20at. % Ti	0.0043	-0.0141	-0.0042
Ni-25at. % Ti	0.0029	-0.0154	-0.0028
Ni-35at. % Ti	-0.0019	-0.0152	0.0019
Ni-50at. % Ti	-0.0113	-0.0091	0.0108
	Singwi *et al*. [1968, 70]		
Ni-02at. % Ti	0.0013	-0.0019	-0.0011
Ni-05at. % Ti	0.0028	-0.0047	-0.0025
Ni-10at. % Ti	0.0044	-0.0087	-0.0041
Ni-15at. % Ti	0.0048	-0.0119	-0.0047
Ni-20at. % Ti	0.0043	-0.0141	-0.0042
Ni-25at. % Ti	0.0029	-0.0154	-0.0028
Ni-35at. % Ti	-0.0019	-0.0152	0.0019
Ni-50at. % Ti	-0.0113	-0.0091	0.0108

Table 4: Warren-Cowley SRO parameters α_i for Ni-Ti alloys.

Concentration	α_1	α_2	α_3
		Kleinman [1967, 68]	
Ni-02at. % Ti	-0.0009	0.0013	0.0008
Ni-05at. % Ti	-0.0021	0.0031	0.0017
Ni-10at. % Ti	-0.0032	0.0058	0.0028
Ni-15at. % Ti	-0.0035	0.0079	0.0032
Ni-20at. % Ti	-0.0031	0.0095	0.0029
Ni-25at. % Ti	-0.0021	0.0104	0.0020
Ni-35at. % Ti	0.0014	0.0103	-0.0014
Ni-50at. % Ti	0.0078	0.0063	-0.0079
		Singwi *et al*. [1968, 70]	
Ni-02at. % Ti	-0.0009	0.0013	0.0008
Ni-05at. % Ti	-0.0021	0.0031	0.0017
Ni-10at. % Ti	-0.0032	0.0058	0.0028
Ni-15at. % Ti	-0.0035	0.0079	0.0032
Ni-20at. % Ti	-0.0031	0.0095	0.0029
Ni-25at. % Ti	-0.0021	0.0104	0.0020
Ni-35at. % Ti	0.0014	0.0103	-0.0014
Ni-50at. % Ti	0.0078	0.0063	-0.0079

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