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Charactization of Point Defects in B2 NiAl

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I.INTRODUCTION

B2 alloys often exist in exist over range of compositions on either side of stoichiometric composition [3]. The structure of B2 type is body centered ordered structure where, say A, atom occupies the body centered position and say B atom, occupies the corner site, as is shown in figure 1.It is the most common ordered structure with a simple cubic Bravais lattice. The B2 structure has two atoms per unit cell and thus can be described as two interpenetrating simple cubic sub lattices.

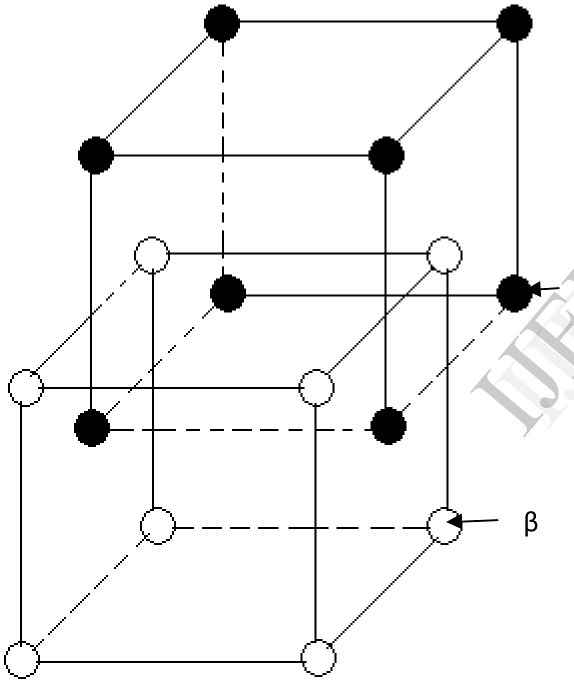


Figure .1.1a: Structure of B2 ordered compound

On the other hand, the disordered structure of the type B2 is shown in figure 2 consisting of two identical lattice points, one at the corner position and the second at the body centered position[1][2].

In contrast with ionic compounds, which normally exist at the stoichiometric composition with limited ranges of homogeneity, most of the B2 intermetallic compounds exist over a wide range of homogeneity[9].

The mechanical properties of B2 compounds are dominated by the presence by the presence constitutional defects, i.e. constitutional vacancies and antisite defects [3].

Defects In B2 Intermetallic Compounds

The homogeneity is retained to high temperatures at even large deviations from the stoichiometric composition, the defect formation in intermetallic compounds is much more complex. Considering a binary inter metallic phase $A_{0.5-x}B_{0.5+x}$, where A atoms occupy the sublattice-1 and the B atoms occupy the sublattice-2 [1][2]. Six mechanisms of defect formation may occur:

1. Substitution of B atoms on the sublattice-1 (called B antisite)
2. Substitution of A atoms on the sublattice-2 (called A antisite)
3. Creation of vacancies on sublattice-1.
4. Creation of vacancies on sublattice-2.
5. Formation of A interstitials.
6. Formation of B interstitials.

The overall amount of the defects is the sum of the numbers of defects caused by finite temperature and by the deviation from the stoichiometric composition[1][2]. The interactions among point defects in inter metallic compounds are generally small; therefore vacancies and antistructure atoms are expected to be more or less independent of each other[7][8].

Thermal defects in an ordered binary alloy of a fixed composition must appear in a balanced manner in order to preserve the stoichiometry of alloy. Thermal disorder in the B2-type intermetallics is often of a triple defect type[39] and the triple defect formed by two Ni vacancies and one antisite Ni atom is considered to be the dominant thermal excitation in NiAl[10][11]. Here the ab initio calculations of the electronic structure and total energy of NiAl intermetallic compounds containing four types of point defects in different combinations and spatial configurations in order to find the defect formation enthalpies and pair defect interaction energies will be studied on the basis of the values the constitutional defects and the statistics of thermal defects.

II.GENERAL FORMALISM

A. *Alloy Configuration*

The general B2 NiAl has been considered having the fixed atomic composition $Ni_{1/2-\delta}Al_{1/2+\delta}$, where δ is the deviation from stoichiometry. The alloy components(Al and Ni atoms) and vacancies, i={Al, Ni, V} occupy N lattice sites on the two sublattice (α={Al, Ni}) of the B2 structure. Each sublattice has

$N_\alpha = 1/2N$ sites occupied by n_{i_α} atoms or vacancies.

In the canonical ensemble[5] the number of Al atoms $n_{Al} = n_{Al_{Al}} + n_{Al_{Ni}}$ and the number of Ni atoms $n_{Ni} = n_{Ni_{Al}} + n_{Ni_{Ni}}$ as well as the total number of lattice sites may vary. The distribution of alloy components between the sublattices may be described in terms of site concentration $c_{i_\alpha} = n_{i_\alpha} / N_\alpha$. However , since the number of lattice sites is not conserved in the presence of vacancies, it is more convenient to use atomic concentrations defined with respect to the total number of atoms $N_{at} = n_{Ni} + n_{Al}$:

$$x_{i_\alpha} = \frac{n_{i_\alpha}}{N_{at}}$$

(2.1 If necessary, one can easily transform between the atomic concentration and site concentration using the following relation:

$$c_{i_\alpha} = 2x_{i_\alpha} \big/ (1 + x_V)$$

With these definitions one can have six atomic concentrations and three constraints:

$$\sum_i x_{i_{Al}} = \sum_i x_{i_{Ni}},$$

$$x_{Al} = \sum_\alpha x_{Al_\alpha} = \frac{1}{2} + \delta, \qquad (2.2)$$

$$x_{Ni} = \sum_\alpha x_{Ni_\alpha} = \frac{1}{2} - \delta,$$

The problem is to find out four concentrations of point defects: two antisite atoms, d={Ni_{Al}, Al_{Ni}}, and to vacancies d={V_{Ni}, V_{Al}}, as a function of temperature T. according to equation 2.2 only three of the the four defect concentrations are independent:

$$x_{Al_{Ni}} - x_{Ni_{Al}} + \frac{1}{2}(x_{V_{Ni}} - x_{V_{Al}}) = \delta$$

(2.3)

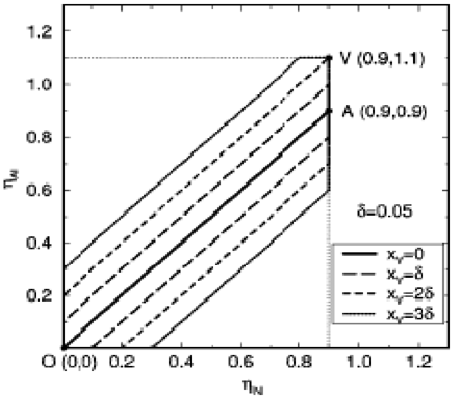


Fig 1.1: three dimensional domain of possible configurations for the binary off-stoichiometric $Ni_{0.45}Al_{0.55}$ alloy.

Points A or V corresponds to the maximally ordered state of the alloy havinganti-site atoms or vacancies. Alternatively, the atomic ordere can be specified by the three independent variables: the net concentration of vacancies and two long-range order (LRO) parameters

$$x_V = x_{V_{Ni}} + x_{V_{Al}},$$

$$\eta_{Ni} = 2(x_{Ni_{Ni}} + x_{Ni_{Al}}), \qquad (2.4)$$

$$\eta_{Al} = 2(x_{Al_{Al}} + x_{Al_{Ni}}).$$

The atomic concentrations of the alloy components can be uniquely expressed through these variables as follows:

$$4x_{Al_{Al}} = 2x_{Al} + \eta_{Al}, \qquad 4x_{Al_{Ni}} = 2x_{Al} - \eta_{Al},$$

$$4x_{Ni_{Al}} = 2x_{Ni} + \eta_{Ni}, \qquad 4x_{Ni_{Ni}} = 2x_{Ni} - \eta_{Ni},$$

$$4x_{V_{Al}} = 2x_V - \eta_{Al} + \eta_{Ni}, \qquad 4x_{Al_{Ni}} = 2x_V + \eta_{Al} - \eta_{Ni}$$

(2.5)

The processes can be expressed in the form of defect reactions:

$$0 \to V_{Ni} + V_{Al},$$

$$V_{Al} \to V_{Ni} + Ni_{Al}, \qquad (2.6)$$

$$V_{Ni} \to V_{Al} + Al_{Ni}$$

B. Wagner-Schottky Model

The equilibrium state of the alloy at temperature T and Pressure *p* is determinedby the minimum of the gibb's free energy. Here the pure fcc Ni and Al have been considered, therefore, the energy of alloy formation is defined as

$$\Delta E = E_{Ni_{1/2-\delta}} Al_{1/2+\delta} - x_{Ni}E_{Ni} - x_{Al}E_{Al}, \qquad (2.7)$$

It is well known that the enthalpy of formation and lattice parameters[10][11] of NiAl are essentially a linear functions of alloy composition. The Wagner-Schottky Model rests on two assumptions:

1. The enthalpy of alloy formation depends linearly on the defect concentrations,

$$\Delta H = \Delta H_{NiAl} + \sum_d H_d x_d \qquad (2.8)$$

2. Only the mean-field configurational entropy is taken in to account

$$S = (1 + x_V)\ln\left(\frac{1 + x_V}{2}\right) - \sum_\alpha \sum_i x_{i_\alpha} \ln x_{i_\alpha}, \qquad (2.9)$$

Where i={Al, Ni, V} and α={Al, Ni}. The parameters of the Wagner-Schottky Model are the defect formation enthalpies

$$H_d = \frac{\partial \Delta H}{\partial x_d}$$

(2.10)

Where E_d is the defect formation energy and Ω_d is the defect formation volume which may be obtained from the results of *ab initio* calculations performed at T=0 , *p=0*:

$$E_d = \frac{\partial \Delta E}{\partial x_d}, \ \Omega_d = \frac{\partial \Delta \Omega}{\partial x_d}$$

(2.12)

The minimization of the Gibbs free energy in configurational space (x_{V}, η_{Ni}, η_{Al}) in the Wagner-Schottky Model leads to the following equations for equilibrium defect concentrations:

$$\frac{4 x_{V_{Al}} x_{V_{Ni}}}{(1+x_V)^2} = \exp[-H_D / T], \quad (2.13a)$$

$$\frac{x_{Ni_{Al}} x_{V_{Ni}}}{x_{Ni_{Ni}} x_{V_{Al}}} = \exp[-H_{JN} / T],$$

(2.13b)

$$\frac{x_{Al_{Ni}} x_{V_{Al}}}{x_{Al_{Al}} x_{V_{Ni}}} = \exp[-H_{JA} / T]$$

2.13c)

Here H_D, H_{JA} and H_{JN} are the enthalpies of the defect reactions (2.6) which are connected with the formation enthalpies of four point defects by the following equations:

$$\begin{aligned} H_D &= H_{V_{Al}} + H_{V_{Ni}}, \\ H_{JN} &= H_{Ni_{Al}} + H_{V_{Ni}} - H_{V_{Al}}, \qquad (2.14) \\ H_{JA} &= H_{Al_{Ni}} + H_{V_{Al}} - H_{V_{Ni}}. \end{aligned}$$

Expressed in terms of site concentrations, the set of equations (2.13) take the usual form of mass action law for the quasichemical reactions (2.6).

Thermal Defects

The various thermal defects have been discussed here. In addition to the the constitutional defects the thermal defects at finite temperature also added to the point defect concentration. Since the alloy composition is fixed they can appear only in the

2. Off- stoichiometric Alloys

The presenceof the constitutional defects in the maximally ordered atate of an off-stoichiometric

In practice it is common to lineraize the dependence of the defect formation enthalpy at *p*=0

$$H_d = E_d + p\Omega_d \qquad (2.11)$$

$$x^t_{Al_{Ni}} - x^t_{Ni_{Al}} + \frac{1}{2}\left(x^t_{V_{Ni}} - x^t_{V_{Al}}\right) = 0$$

(2.15)

compositionconserving combination of single point defects obeying the condition:

It follows from the above equation that none of the point defects can be alone thermal defects. The simple composition conserving defects are discussed here:

1. General case:

There are four composition conserving defects consisting of two types of point defects[13](64) which can be either thermally generated in the maximally ordered alloy of any composition including the defect free stoichiometric alloy. The defect reactions are as follows:

Exchange antisite defect (*X*),

$$0 \rightarrow Ni_{Al} + Al_{Ni} : \ x_X = x^t_{Ni_{Al}} = x^t_{Al_{Ni}} \qquad (2.16)$$

Divacancy or Schottky defect (D):

$$0 \rightarrow V_{Al} + V_{Ni} \ : \ \ x_D = x^t_{V_{Al}} = x^t_{V_{Ni}} \qquad (2.17)$$

Triple Ni r Simply triple defect (TN):

$$0 \rightarrow 2V_{Ni} + Ni_{Al} \ : \ \ x_{TN} = \frac{1}{2} x^t_{V_{Ni}} = x^t_{Ni_{Al}} \ (2.18)$$

Triple Al Defect (TA):

$$0 \rightarrow 2V_{Al} + Al_{Ni} \ : \ \ x_{TA} = \frac{1}{2} x^t_{V_{Al}} = x^t_{Al_{Ni}} \qquad (2.19)$$

The formation enthalpies of a composition conserving defect H_{CD} for the exchange, triple Ni and triple Al defects is given by:

$$\begin{aligned} H_X &= H_{Ni_{Al}} + H_{Al_{Ni}} = H_{JN} + H_{JA}, \\ H_{TN} &= H_{Ni_{Al}} + 2H_{V_{Ni}} = H_{JN} + H_D, \qquad (2.20) \\ H_{TA} &= H_{Al_{Ni}} + H_{V_{Al}} = H_{JA} + H_D, \end{aligned}$$

The formation energy of the composition-conserving defect is then the sum of the formation energies of the constituent.

alloy gives an additional possibility to satisfy the equation (2.15) The process of the formation of such defect may be considered as a transition from stable state to a unstable branch, and hence called interbranch defect. The defect reactions and the Interbranch Ni Defect (IN):

$$Ni_{Al} \rightarrow 2V_{Al}: \quad x_{IN} = -x^{t}_{Ni_{Al}} = \frac{1}{2} x^{t}_{V_{Al}} \quad (2.21)$$

Interbranch Al Defect (IA):

$$2V_{Ni} \rightarrow Al_{Ni}: \quad x_{IA} = -x^{t}_{V_{Ni}} = \frac{1}{2} x^{t}_{Al_{Ni}} \quad (2.22)$$

The formation enthalpies are given by:

$$\begin{aligned} H_{IN} &= 2H_{V_{Al}} - H_{Ni_{Al}} = H_D - H_{JN}, \\ H_{IA} &= H_{Al_{Ni}} - 2H_{V_{Ni}} = H_{JA} - H_D. \end{aligned} \quad (2.23)$$

They characterize the relative stability of the antisite and vacancy branches in the Ni-rich and Al-rich NiAl, respectively. Since the antisite and vacancy branches in Al-rich *B*2 transition metal aluminides are competitive in energy, the interbranch Al defect may become the lowest-energy thermal defect in this compositional region

Thermal Defect Concentration

In this section the thermal defect concentration equations will be given which were derived using mass action law. Here the triple defect is considered as dominant thermal defectin stichiometric NiAl. The defect concentration in the maximally ordered are:

$$x^{c}_{Ni_{Al}} = \begin{cases} -\delta, & \delta < 0 \\ 0, & \delta > 0 \end{cases}, \quad x^{c}_{V_{Ni}} = \begin{cases} 0, & \delta < 0 \\ 2\delta, & \delta > 0 \end{cases}$$

(2.24)

For nearly stoichiometric alloy(NiAl), the equilibrium concentration of triple defcts in the stoichiometric is given by:

$$x_{TN} \approx 2^{-5/3} \exp[-H_{TN} / 3T].$$

(2.25)

$$\left.\frac{dx_{TN}}{d\delta}\right|_{\delta=0} = \begin{cases} 1/3, & \delta<0, \\ \text{-}2/3, & \delta > 0. \end{cases} \quad (2.26)$$

For concentrated Ni-rich NiAl the estimate of the concentration of thermal triple defects is given by:

$$x_{TN} \approx 2^{-5/2} (-\delta)^{-1/2} \exp[-H_{TN} / 2T] \quad (2.27)$$

Whereas for Al-rich NiAl, concentrations of thermal point defects are as follows

$$x_{TN} \approx 2^{-5} \frac{1+2\delta}{\delta^2} \exp[-H_{TN} / T]$$

And $$x_{IA} \approx 2^{3} \frac{\delta^2}{1+2\delta} \exp[-H_{IA} / T] \quad (2.28)$$

Depending on the assumption whether interbranch Al defect dominates or interbranch Ni defect dominates.. if the formation enthalpy of an interbranch Al defect is sufficiently small, one can expect a competition between triple and interbranch Al defects in the Al-rich NiAl.

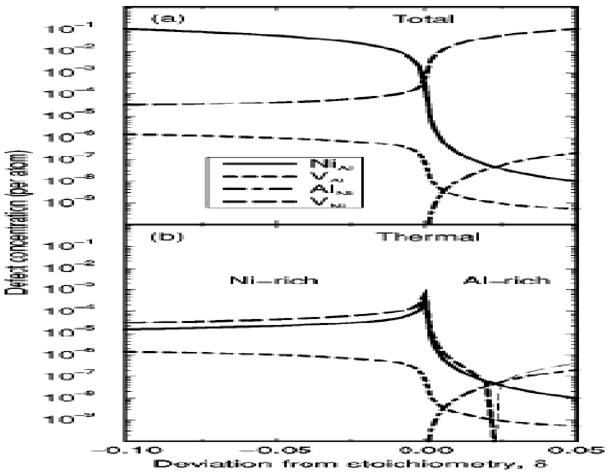
The effective formation enthalpy of the composition conserving defect can be derived from the equations 2.25- 2.28. and is given by and is based on Arrhenius formula:

$$(\partial v / \partial x)_K \rangle 0$$

$$H^{eff}_{CD} = -\left.\frac{d \ \ln x^{t}_{CD}}{dT^{-1}}\right|_{p=const} \quad (2.29)$$

The formation enthalpies of single point defect found for the nearly stoichiometric and off-stoichiometric alloys expressed through the formation enthalpies of composition-conserving defects.

Defect	$\delta<0$	$\delta=0$	$\delta>0$
Ni_{Al}	0	$H_{TN}/3$	H_{TN}
V_{Al}	$H_{IN}/2$	$H_D-H_{TN}/3$	H_D
Al_{Ni}	H_X	$H_X-H_{TN}/3$	H_{IA}
V_{Ni}	$H_{TN}/2$	$H_{TN}/3$	0



The method of calculation used here is the a 54-site cubic supercells to simulate isolated defects, and 108 site supercells to evaluate defect interactions.

III.RESULTS

The thermal defects can be interpreted as composition conserving defects. The calculated equilibrium atomic concentrations of defects, x_d , in NiAl at 1300K and zero external pressure is shown here in the figure 1.4(a) as a function of deviation from stoichiometry.

Here it has been seen that thermal defects are mainly vacancies on the Ni sublattice and antisite Ni atoms, which are the constituents of triple defect. On the Al-rich side, the concentration of thermal antisite Ni atoms quickly becomes very small with increasing off-stoichiometry. But antisite Al atoms appear in a relatively large amount.

In summary, the calculations here show that the onset of defect interactions at low temperatures does not affect the staistics of the constitutional defects in NiAl but leads to a defect ordering which is consistent with experimental observations. At 1300 K the equilibriumconcentration of Ni vacancies in Al-rich NiAl alloys with more than 52.3 at.% Al decreases with temperature. It has been shown in our previous work84 and independently by Meyer and Fa¨hnle22 that this kind of thermal behavior can be associated only with the interbranch Al defect, in which two constitutional Ni vacancies are replaced by one antisite Al atom.

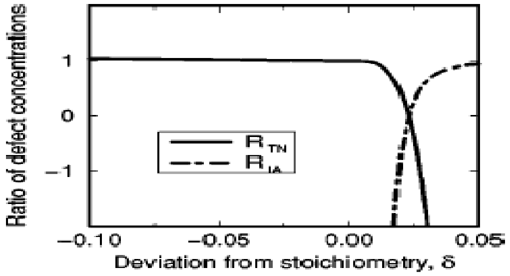


Fig: 1.5 Ratios of the thermal defect concentrations at 1300 K

In fig.1.5 the calculated ratios between thermal defect concentrations have been shown

$$R_{TN} = \frac{x^t_{V_{Ni}}}{2x^t_{Ni_{Al}}}, \qquad R_{IA} = -\frac{x^t_{V_{Ni}}}{2x^t_{Al_{Ni}}}. \qquad (2.30)$$

The ratio R_{TN} should be close to one if the dominant thermal excitations are of triple defect type, while R_{IA} should be close to one if the dominant thermal excitations arethe interbranch Al defects. Thus we find that the thermal excitations in NiAl at 1300K are mainly of triple defect type for deviation >0.023.

At low temperatures, triple defcts dominate for the stoichiometric and Ni-rich compositions, whereas interbranch defects decome dominant for the Al-rich compositions. Fig 2.7 shows that the region in which triple dfect dominateexpands towards Al-rich compositions with increasing temperature.

The cross-over concentration δ_B can be estimated and given as:

$$\delta_B \approx \frac{1}{4}\exp[(H_{IA} - H_{TN})/4T] \quad (2.31)$$

Thus for Al-rich alloy the equilibrium vacancy concentration decreases only up to a certain temperature, below which the interbranch Al defects dominate over the triple defect, while above that temperature the vacancy concentration starts to increase because the triple defect become dominant for this alloy composition.

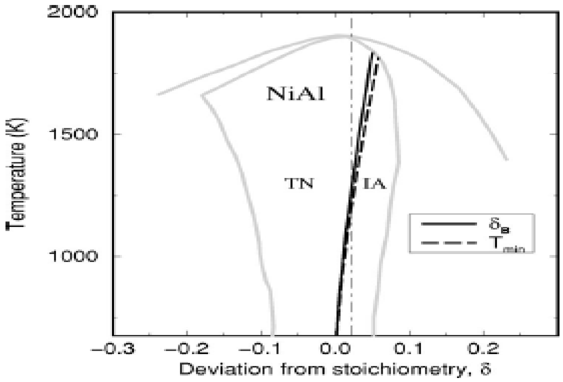


Fig 1.6: Boundary between two regions of NiAl in which triple defect(TN) or interbranch Al defects (IA) dominate respectively(solid line).

It has been found that the ground state of off-stoichiometric NiAl alloy is formed by antisite Ni atoms on the Al sublattice in Ni-rich NiAl and by vacancies on the Ni sublatticein Al-rich NiAl. According to the the calculated defect interactions, the constitutional defects of the same kind must form ordered structures in the ground state, in which they tend to avoid each other at the shortest possible distance on their sublattice.

The dominant thermal defects are shown to be triple defects in Ni-rich and stoichiometric NiAl and interbranch Al defects in Al-rich NiAl. Since an interbranch Al defect annihilates two constitutional vacancies and creates only one antisite Al atom, the equilibrium amount of vacancies as well as the total number of point defects must *decrease* with temperature in Al-rich NiAl at low temperatures. The calculated defect interactions indicate that all three constituents of a triple defect may exist individually in NiAl without forming a bound complex. In contrast, a strong attractive interaction was found for the following defect pairs in NiAl: Ni on the Al sublattice and Al on the Ni sublattice, and vacancy on the Al sublattice and Al on the Ni sublattice. Although the defect interactions are shown to have only minor effects on the equilibrium defect concentrations, they may be of importance for understanding the kinetic processes and metastable defect arrangements in NiAl.

REFRENCES

[1]. James K Wessel and Sikka Vinod, “*The Handbook of advanced marterials”,* John Wiley & sons, 2004.
[2]. Wolfgang pfeiler, “*AlloyPhysics”, 200*
[3]. I.Baker, *Material Science & Engineering A*192/193, pp1-13, 1995
[4]. Chaturvedi D.K, Allnatt A.R, *Philosophical Magazine A*, 69, 821, 1994.
[5]. Belova I.V, Murch. G.E, *Philosophical Magazine,* 151, 46, 2002.
[6]. Gosain K. L, Chaturvedi D.K., Belova I.V. & Murch G.E., *Defect & Diffusion forum, Trans Tec publication,* pp 247-248, 2005, 2006.
[7]. Flynn C.P., *Point Defects and Diffusion (Oxford: Clarendon),* 1972.
[8]. De Groot SR & Mazur P, *Non Equilibrium Thermodynamics (*Amsterdam: North Holland), 1962.
[9]. C.R.Kao, Sungtae Kim, Y.A.Chang, *Material Science & Engineering A* 192/193, pp 965-979, 1995.
[10]. Noebe, R.D., Bowman, R.R., and Nathal, M.V., *Int. Mater. Rev. 38,* 193, 1993
[11]. Bardley.A.J., Taylor.A., *Proc.R.Soc.London,* Ser A 173, 232, 1939.
[12]. G.v. Hevesy and W. Seith-Freiburg, *Diffusion in metallen, Z. Electrochem 3*7 , 528-31, 1931
[13]. A. Fick, *Uber diffusion, Progg.* Ann. 94 (1855) 59.