

A STUDY ON THE DIFFUSIVITY OF HYDROGEN IN SOME METAL-ALLOYS AS A VITAL SOURCE OF RENEWABLE ENERGY

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Abstract- The diffusion of hydrogen in metal alloys is a very versatile technique now a day for the storage of hydrogen as a fuel to be used in the transportation sector and considered as a pollution-free alternative sources of energy. In this present study the diffusivity of both ^1H and ^2H isotopes in $\text{Ni}_{0.88}\text{Fe}_{0.12}$ and $\text{Ni}_{0.76}\text{Fe}_{0.24}$ alloys has been studied theoretically on the basis of Born-Von-Karman Formalism. The force constants have been calculated within the frame work of Born-Von-Karman formalism and the pressure dependent diffusion parameters of ^1H and ^2H for both the alloys have been estimated using Green's function technique and Scattering matrix formalism for pressures ranging from normal to 2.5GPa. Arrhenius behavior of both the alloys was observed for the temperature range 500K-1250K. Finally, the activation energy E_a , pre-exponential factor of diffusivity D_0 and diffusion constant D were calculated for both the systems. The variation of the ratio of diffusion co-efficients of ^1H and ^2H for both the alloys with temperature at normal pressure was studied and the ratio was found to maintain almost a constant value of 1.5 for the entire temperature range of study. And the diffusivity of ^1H in both the alloys was found to be greater than that of ^2H . Finally, the results were compared with similar reported works for some other systems and $\text{Ni}_{0.76}\text{Fe}_{0.24}$ was found to be a better medium satisfying all required conditions of suitability for storing hydrogen.

Keywords: Hydrogen diffusion, Metal-Alloy Hydrogen Systems, Diffusion Processes, Different Systems of Hydrogen Storage, Metal-Hydrides.

1. INTRODUCTION

The topic "Hydrogen storage in metals and metallic alloys" is the subject of more intensive theoretical and experimental research for many years, hence a number of measurements of diffusivity have been published [1-4]. The diffusion of interstitial hydrogen in metals is known to depend strongly on the host metal. Host metal properties such as lattice type, electronic structure and elastic moduli are thought to play key roles in determining the diffusion rate of hydrogen isotopes [5]. To present the estimated diffusion parameters for the hydrogen isotopes ^1H and ^2H in binary alloys $\text{Ni}_{0.88}\text{Fe}_{0.12}$ and $\text{Ni}_{0.76}\text{Fe}_{0.24}$ is the ultimate objective of this paper. Here, only the migration process in the classical temperature region $k_B T > h\nu_D$ has been considered. The jump frequency for this transition is given by

$$\Gamma_{(u \rightarrow v)} = \Gamma_0 \exp(-E_a/k_B T) \quad (1)$$

Where, $E_a = [E_{(s,o)} - E_{(u,o)}]$, the activation energy and the pre-exponential factor Γ_0 is an average of the frequency values over the entire spectrum of fluctuation called attempt frequency of jump. When hydrogen isotopes are

pumped into the alloys $\text{Ni}_{0.88}\text{Fe}_{0.12}$ and $\text{Ni}_{0.76}\text{Fe}_{0.24}$ under high pressure, hydrogen migrates through host lattice by thermally activated jumps to neighbouring empty interstitial sites. The Born-von Karman formalism using the average atomic mass and resulting in the average force constants can be used for these alloys to compute the phonon dispersion. When the alloy is loaded with hydrogen, it occupies the octahedral interstitial sites. Calculations of diffusion parameters have been carried out for the octahedral- octahedral (O-O) jump.

2. METHOD OF CALCULATION

Phonon frequency spectrum of the host metal lattice and their corresponding eigen vectors are needed for the estimation of diffusion parameters. The binary alloys $\text{Ni}_{0.88}\text{Fe}_{0.12}$ and $\text{Ni}_{0.76}\text{Fe}_{0.24}$ have the face centred cubic (fcc) structure with lattice constants 3.539Å and 3.553 Å respectively [7]. The Born-von Karman formalism has been employed for the estimation of the force constants by considering the interactions up to six nearest neighbours and hence the dynamical matrix has been constructed. The dynamical matrix has been diagonalised using a set of 122 wave vector points obtained by uniformly dividing the Brillouin zone. When the pressure

is increased from normal to 2.5 GPa, the lattice gets compressed. By using the procured values of the elastic constants and the following equation

$$\frac{1}{K} = -\frac{1}{V} \left(\frac{dV}{dP} \right) \quad (2)$$

new lattice constants values and hence force constant parameters using Born Mayer potential are calculated.. When the alloy is loaded with hydrogen, it occupies the octahedral position. With the interstitial atom in the $(000) a_o$ position, there are six nearest neighbour

metal atoms at $\left(\frac{1}{2} 00\right) a_o$, $\left(\frac{1}{2} \bar{0} 0\right) a_o$, $\left(0 \frac{1}{2} 0\right) a_o$,

$\left(0 \frac{1}{2} \bar{0}\right) a_o$, $\left(00 \frac{1}{2}\right) a_o$, and $\left(00 \bar{\frac{1}{2}}\right) a_o$ positions, with a_o

as the lattice constant. Thus the defect space consists of seven atoms. The displacement of six metal atoms in the defect space has been calculated using the relation

$$u_i = \left\{ I + g \left(\delta l + a \gamma a^T \right) \left[I - g \left(\delta l + a \gamma a^T \right)^{-1} \right] \right\} u_{oi} \quad (3)$$

here the Green's function matrix [12] g and the change in the dynamical matrix δl are of the order (18×18) and the metal hydrogen interaction matrix a is of order (18×3) , g and δl matrix are symmetric. The matrix u_{oi} of order (18×1) represents the displacement of the six host crystal atoms in the normal lattice. The displacement of the interstitial hydrogen atom is

$$\xi = -\gamma a^T u_i \quad (4)$$

The interstitial Green's function matrix γ of order (3×3) is determined from the equation

$$\gamma \left(\omega^2 \right) = \left[m_i \{ \omega_j^2(q) - \omega_i^2 \} \right]^{-1} I \quad (5)$$

where m_i is the mass of the interstitial atom and ω_i is the vibrational frequency of the interstitial in the otherwise frozen lattice. As three degenerate modes are associated with the vibration of the interstitial atom, the matrix γ is

$$\text{of the form } \begin{pmatrix} \gamma & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \gamma \end{pmatrix}$$

The force constant parameters representing metal hydrogen interaction in the matrix elements are calculated using the potential form discussed by Machlin [6],

$$\phi = \left[\frac{-\alpha}{r^4} + \frac{\beta}{r^8} \right] \quad (6)$$

Parameters α & β are fitted using localized mode [10] as given below $\omega_{1H} = 1.001335 \times 10^{14} \text{ rad s}^{-1}$ and $\omega_{2H} = 7.08151 \times 10^{13} \text{ rad s}^{-1}$. When hydrogen tries to jump from an octahedral interstitial position to other, two atoms at

the positions $\left(\frac{1}{2} 00\right) a_o$ and $\left(00 \frac{1}{2}\right) a_o$ will obstruct the jumping atom.

So the reaction coordinates become of the form

$$\bar{\chi} = \left(\bar{\epsilon}_d - \frac{1}{2} \sum_{j=1}^2 u_j \right) \hat{\chi} \quad (7)$$

where ϵ_d is the displacement of the diffusing atom and u_j is the displacement of the neighbour along the jump path with $j=1, 2, 3, \dots$

The jump rate has been calculated in terms of the reaction coordinates using equation

$$\Gamma = \left[\frac{\sum_{q,j} \omega^2(q,j) |\chi(q,j)|^2}{\sum_{q,j} |\chi(q,j)|^2} \right]^{\frac{1}{2}} \exp \left[-\frac{\chi_c^2}{\sum_{q,j} |\chi(q,j)|^2} \right]$$

Arrhenius behaviour is observed for the temperature range 500K-1250K for various pressures ranging from normal to 2.5 Pa. The diffusion parameters E_a and D_o have been calculated from the above measurements.

Finally, using the calculated values of force constant parameters, pre-exponential factor of diffusion D_o and activation energy E_a at various temperatures and pressures the values of diffusion co-efficient D were calculated through the procedure as mentioned above for both the alloys of study.

3. RESULTS AND DISCUSSIONS

The phonon frequency spectrum of the host metal lattice and their corresponding eigen vectors are essential for the estimation of diffusion parameters. Using scattering matrix formalism, phonon frequencies and eigen vectors are calculated for a set of 122 wave vector points by uniformly dividing the Brillouin zone.

When a defect atom is introduced in an alloy, it occupies the interstitial position in the host crystal lattice. This atom can jump from one interstitial site to a neighbouring vacant one and they can diffuse this way over large distance through the alloy. The jump frequencies for O-O jump of hydrogen in $\text{Ni}_{0.88}\text{Fe}_{0.12}$ and $\text{Ni}_{0.76}\text{Fe}_{0.24}$ alloys have been calculated for the temperature range 500K-1250K. Using Green's function technique and scattering matrix formalism, the parameters χ^2 and $\omega^2 \chi^2$ which are involved in the calculation of jump frequency have been calculated. The values of χ^2 and $\omega^2 \chi^2$ increase with pressure up to 1GPa. With rising pressure more than

1GPa, the values of χ^2 and $\omega^2 \chi^2$ start decreasing. Hence the force constant parameters also change with changing pressure. This observation indicates that the lattice dimensions get to be changed under high pressure, hence the related parameters like reaction coordinates, jump frequencies vary with pressure.

With the localised mode contribution to the reaction co-ordinates, the jump frequency for the O-O jump in the temperature range 500 K – 1250 K in steps of 250 K have

been estimated. The same calculations have been carried out for the different pressures from normal to 2.5 GPa. The parameters χ^2 and $\omega^2\chi^2$ of both the host crystal and localised mode contribution for the alloys $\text{Ni}_{0.88}\text{Fe}_{0.12}$ and $\text{Ni}_{0.76}\text{Fe}_{0.24}$ were calculated for the respective temperatures and pressures. The diffusion parameters such as pre-exponential factor D_0 , activation energy E_a and diffusion co-efficient D are evaluated from the calculated jump frequency values for various pressures for both ^1H and ^2H interstice in $\text{Ni}_{0.88}\text{Fe}_{0.12}$ and $\text{Ni}_{0.76}\text{Fe}_{0.24}$ alloys for the above mentioned temperature range. The diffusion constants for both ^1H and ^2H in $\text{Ni}_{0.88}\text{Fe}_{0.12}$ alloy are increased with pressure at the beginning and then they decreased up to 2.0GPa and again increased at 2.5GPa. But the diffusion constants for both ^1H and ^2H in $\text{Ni}_{0.76}\text{Fe}_{0.24}$ alloy are increased with pressure in the beginning and then they decreased. The diffusion data for the given temperature range are displayed graphically for both the alloys in Fig.1 and Fig.2 respectively. The diffusion co-efficient of ^1H and ^2H are found to obey the Arrhenius relation over the complete temperature range of study.

Variation of the ratio $\frac{D_{1H}}{D_{2H}}$ with temperature at normal

pressure is shown in Fig.3 and Fig.4 respectively. The ratio between the diffusion co-efficients of ^1H and ^2H in these two alloys at various pressures are found to be almost a constant of around 1.5. The variation of diffusion parameters with pressure for hydrogen isotopes at temperature 750 K is plotted in Fig.5 and Fig.6 respectively for the above alloys. The values of D_0 , E_a and D are compared with some existing experimental results for other systems, which are compiled in Table.1 This table shows that the values of the diffusion parameters vary with the various experimental techniques used even for a single system. The present results are almost of the same order. But the diffusivity of hydrogen is found to be greater in both the alloys of study than that in case of pure Nickel [13] as shown in Fig.7.

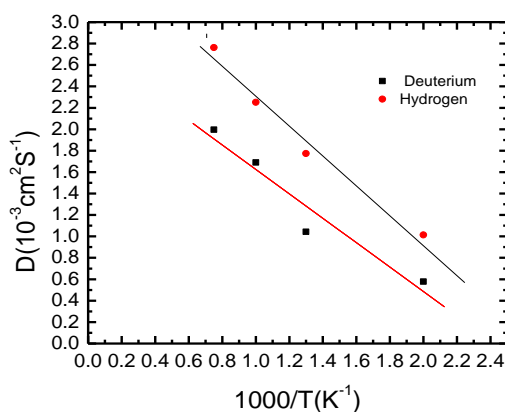


Fig.1: Arrhenius plot for ^1H and ^2H diffusion in $\text{Ni}_{0.88}\text{Fe}_{0.12}$ alloy at normal pressure

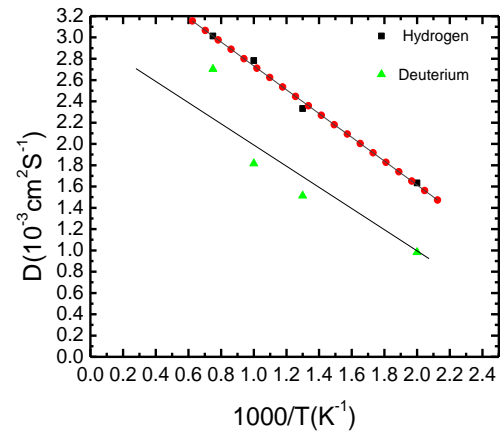


Fig.2: Arrhenius plot for ^1H and ^2H diffusion in $\text{Ni}_{0.76}\text{Fe}_{0.24}$ alloy at normal pressure

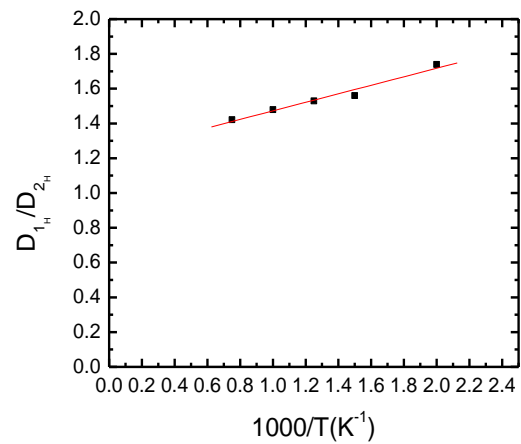


Fig.3: Variation of diffusivity ratio D_{1H}/D_{2H} with temperature in $\text{Ni}_{0.88}\text{Fe}_{0.12}$ alloy at normal pressure

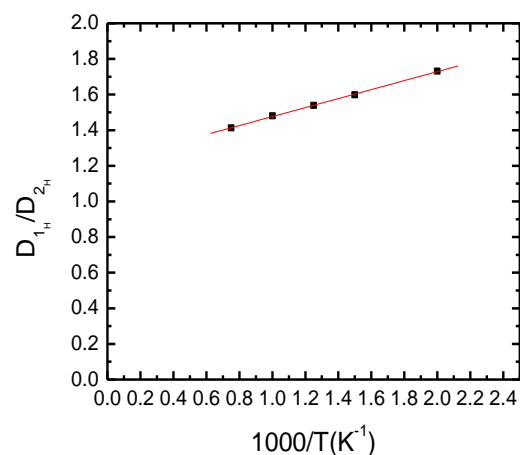


Fig.4: Variation of diffusivity ratio D_{1H}/D_{2H} with temperature in $\text{Ni}_{0.76}\text{Fe}_{0.24}$ alloy at normal pressure

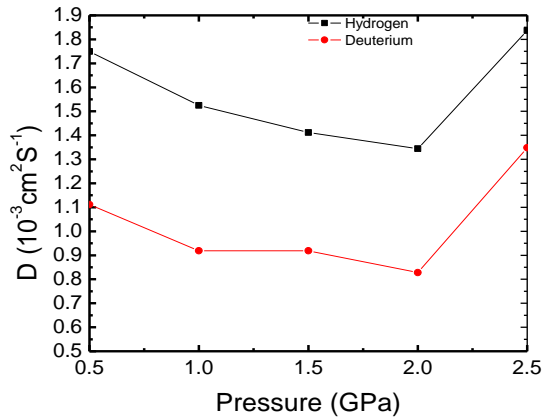


Fig.5: Diffusivity of ^1H and ^2H in $\text{Ni}_{0.88}\text{Fe}_{0.12}$ alloy as a function of pressure at 750K

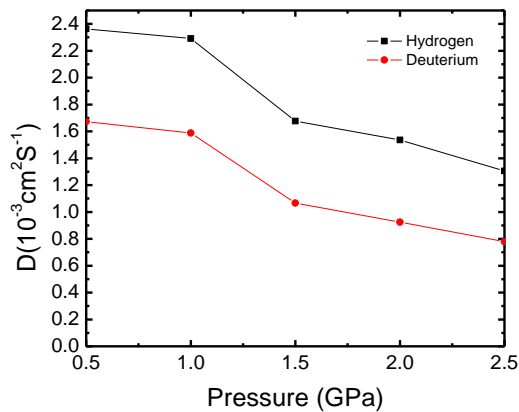


Fig.6: Diffusivity of ^1H and ^2H in $\text{Ni}_{0.76}\text{Fe}_{0.24}$ alloy as a function of pressure at 750K

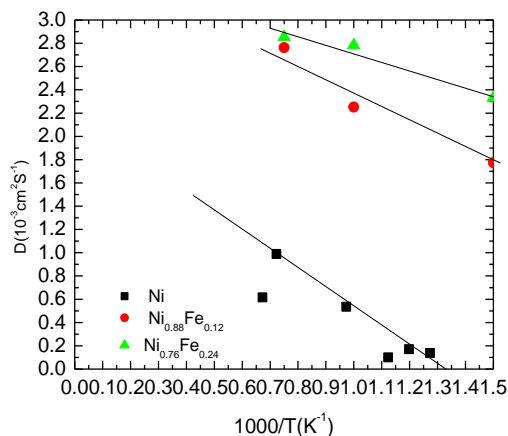


Fig.7: Variation of diffusivity of ^1H with temperature in $\text{Ni}_{0.88}\text{Fe}_{0.12}$, $\text{Ni}_{0.76}\text{Fe}_{0.24}$ and pure Ni

4. CONCLUSION

The values of activation energy for ^1H and ^2H in both the alloys $\text{Ni}_{0.88}\text{Fe}_{0.12}$ and $\text{Ni}_{0.76}\text{Fe}_{0.24}$ have been calculated using the reaction co-ordinate technique. The results obtained show that the activation energy values for ^1H and ^2H in $\text{Ni}_{0.88}\text{Fe}_{0.12}$ are greater than those obtained in case of the alloy $\text{Ni}_{0.76}\text{Fe}_{0.24}$. The same effect has also been observed for most of the pressure values in the range from normal to 2.5GPa. The diffusion parameters for both the systems of study are presented in Table-2 along with the reported results of other selected metals and alloys. The activation energy and diffusivity of ^1H and ^2H for some other alloys at 500K temperature and normal pressure are compiled in Table-3 for comparison. From the above results it is noted that the activation energy for ^1H and ^2H diffusion are decreasing with an increase in Fe content in the alloys. It may be due to the increase in interstitial space because with increasing Fe content the lattice dimension gets extended. Moreover, the diffusion parameter results indicate that pressure does not influence much on the interstitial diffusion of hydrogen isotopes in $\text{Ni}_{0.88}\text{Fe}_{0.12}$ and $\text{Ni}_{0.76}\text{Fe}_{0.24}$ alloys. Higher diffusivity and less influence of pressure on the diffusion of ^1H and ^2H in $\text{Ni}_{0.76}\text{Fe}_{0.24}$ alloy conclude that $\text{Ni}_{0.76}\text{Fe}_{0.24}$ system is comparatively better medium for hydrogen storage among other systems of study including pure Nickel. This result can be verified by the experimentalists for these alloys of study with hydrogen as interstice.

Table 1: Experimental values of diffusion parameters for other systems

| <u>Metal compound</u> | <u>Diffusing element</u> | <u>Temperature range in Kelvin</u> | <u>Pre-exponential factor D_0 in $10^{-3} \text{ cm}^2 \text{ s}^{-1}$</u> | <u>Activation energy E_a in meV</u> | <u>Diffusing coefficient D in $10^{-3} \text{ cm}^2 \text{ s}^{-1}$</u> | <u>Reference</u> |
|-----------------------|--------------------------|------------------------------------|--|--|---|------------------|
| Ni0.1at %Fe | ^1H | 240-360 | - | 304.0777 | 0.157 | [8] |
| Ni0.1at %Fe | ^1H | 240-360 | - | 355.1720 | 0.804 | [8] |
| Ni | ^1H | 600 | 5.2 | 99.49375 | - | [9] |
| Ni | ^1H | 600 | 5.22 | 99.07929 | - | [10] |
| Ni | ^1H | 600 | 6.7 | 98.45736 | - | [11] |
| Ni | ^1H | 620-1600 | 5.5 | 4.456490 | - | [12] |
| Ni | ^1H | 385-620 | 5.4 | 4.560130 | - | [12] |
| Ni | ^1H | 220-330 | 1.5 | 4.560130 | - | [12] |
| Ni | ^2H | 220-1273 | 3.4 | 4.145573 | - | [12] |
| Ni | ^1H | 490-690 | 6.7 | 98.14645 | - | [10] |
| Ni | ^1H | 490-690 | 4.2 | 87.05704 | - | [10] |
| Ni | ^2H | 490-690 | 4.8 | 95.34818 | - | [10] |
| Ni | ^2H | 490-690 | 4.6 | 92.65356 | - | [10] |
| Ni | ^1H | 673.2 | - | - | 6.15 | [13] |
| Ni | ^1H | 723 | - | - | 9.89 | [13] |

Table-2 Diffusivity data of some selected systems

| <u>System</u> | <u>Structure</u> | <u>Element</u> | <u>D_0 in $10^{-3} \text{ cm}^2 \text{ s}^{-1}$</u> | <u>$E_a$ in meV</u> | <u>$D_0^{^1\text{H}} / D_0^{^2\text{H}}$</u> <u>%</u> | <u>$E_{a, ^1\text{H}} \sim E_{a, ^2\text{H}}$</u> <u>%</u> | <u>Reference</u> |
|---------------------------------------|------------------|----------------|---|--------------------------------|---|--|------------------|
| Ni _{0.88} Fe _{0.12} | FCC | ^1H | 5.86602 | 81.58209 | 1.26491 | 15 | Present |
| | | ^2H | 4.63750 | 94.13318 | | | Work |
| Ni _{0.76} Fe _{0.24} | FCC | ^1H | 5.56820 | 69.03100 | 1.22140 | 18 | Present |
| | | ^2H | 4.55885 | 81.58209 | | | Work |
| Fe _{0.5} Ti _{0.5} | CsCl | ^2H | 0.82000 | 512.0000 | 1.23171 | 03 | [15] |
| Fe _{0.75} Al _{0.25} | BCC | ^1H | 2.87200 | 132.0000 | - | | [14] |

Table-3 Hydrogen diffusivity data of some alloys Normal pressure

| System | $E_{a,1H}$ in meV | D_{1H} in cm^2s^{-1} | $E_{a,2H}$ in meV | D_{2H} in cm^2s^{-1} | Reference |
|---------------------------------------|-------------------|--|-------------------|--|--------------|
| Ni _{0.88} Fe _{0.12} | 81.58209 | 0.88523×10^{-3} | 94.13318 | 0.523177×10^{-3} | Present work |
| Ni _{0.76} Fe _{0.24} | 69.03100 | 1.12404×10^{-3} | 81.58209 | 0.697975×10^{-3} | Present work |
| Cr-Fe | 371.03600 | 3.71230×10^{-3} | - | - | [16] |
| Fe _{0.5} Ti _{0.5} | 496.00000 | 1.01090×10^{-3} | 512.00000 | 5.66140×10^{-9} | [15] |
| Fe _{0.5} Ti _{0.5} | 503.30000 | 8.98970×10^{-3} | - | - | [14] |

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7. NOMENCLATURES

| Symbol | Meaning | Unit |
|------------|------------------------------|----------------------------|
| Γ | Jump frequency of transition | rads^{-1} |
| Γ_0 | Attempt frequency of jump | rads^{-1} |
| D | Diffusion constant | cm^2s^{-1} |
| D_0 | Pre-exponential factor of D | cm^2s^{-1} |
| E_a | Activation Energy | meV |
| ω | Vibrational frequency | rads^{-1} |
| K | Bulk Modulus | dynecm^{-2} |
| χ | Reaction coordinate | cm |
| V | Volume | cm^3 |
| P | Pressure | Pa or dynecm^{-2} |