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The Diffusion of Hydrogen in Pd–Ni Solid Solutions

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An electrochemical permeation method has been used to determine the variation of the diffusivity of hydrogen through annealed and cold rolled Pd–Ni membranes as a function of temperature in the range 279 to 335 K and of Ni composition in the range 0 to 100 at. %. At a given temperature the hydrogen diffusivity decreases with an increase of Ni content in an almost logarithmic fashion, and at the same composition, the D values in the annealed samples are higher than those in the cold rolled samples. The experimental diffusivities have been discussed in terms of the proposed diffusion model with the lattice dilation effects.

1. Introduction

It is of interest to investigate the diffusion behavior of hydrogen in Pd–Ni binary alloy system which has generally been regarded as a complete series of solid solution with no evidence of long-range order [1], because of the fundamental elucidation of interstitial diffusion.

The diffusivity of hydrogen in a palladium alloy has been in general attributed to differences in the lattice parameter and compressibility of the alloys, i. e., an elastic interaction, or to the electronic interaction between hydrogen and the substitutional solute atoms [2–7]. Assuming that elastic interaction predominate, and that the interstitial volume available to hydrogen atoms, i. e., the activation volume of hydrogen for diffusion is kept constant, we may expect that the addition of an alloying element which expands the Pd lattice produces an increase in the diffusivity, whereas addition of an element which contracts the Pd lattice causes a decrease in the diffusivity.

Recently, the lattice dilation effect on the diffusivity of hydrogen in Pd–Ag alloys [5, 6] and in Pd–(Ce, Y, B) alloys [7] as a function of θ_u , the atom fraction of the alloying element has been examined by an electrolytic method. There are initially slight predicted increase in the hydrogen diffusivity, as the alloying contents increase. At least at small values of θ_u , the lattice dilation effect is thought to play a role in the hydrogen migration process.

The diffusion data available in the literature on the Pd–Ni alloys are not abundant. Buchold et al. [3] studied the hydrogen diffusivity in Pd–Ni alloys with Ni contents in the range 0 to 26 at. % and in the temperature range 273 to 323 K by measuring the β -radiation of tritium decay and showed that the iso-electronic Ni as alloying partner does not influence the activation energy for diffusion within the experimental error. Yoshihara–McLellan [8] obtained the similar results of the composition dependence of the activation energy for diffusion of Pd–0 to 41.83 at. % Ni alloys by an electrolytic method.

The present study has been carried out to determine the diffusivity of hydrogen in annealed and cold rolled Pd–Ni alloys containing Ni in the atom fractions up to $\theta_u = 1$ and in the temperature range 279 to 335 K by an electrochemical permeation method, and especially for the fully annealed alloys of Pd-rich and Ni-rich sides to examine the lattice dilation effect on the diffusivity.

2. Experimental

The Pd-Ni alloy samples were received in the form of cold rolled foils of about 50–100 μm in thickness prepared at Tanaka Kikinzoku Kogyo K. K. by arc-melting Pd (99.98 wt. %) and Ni (99.95 wt. %) metals under an argon atmosphere. The analysis of composition of the alloys were also performed by the same company.

The sample foils used here were subjected to the following heat treatments *in vacuo* of about 2×10^{-6} Torr, in addition to (1) as cold rolled; (2) annealed at 773 K for 3.6 ks, and (3) annealed at 1123 K for 7.2 ks (fully annealed). X-ray diffraction line profiles revealed that all the alloy samples had a fcc single phase and showed no evidence of long-range order. In addition, the determination of the lattice parameter of the fully annealed samples (at 1123 K for 7.2 ks) was carried out at room temperature using $\text{CuK}\alpha$ radiation with a Ni filter.

Before carrying out the hydrogen permeation measurement, all the samples were chemically etched with a solution of 2 : 2 : 1 - H_2SO_4 : HNO_3 : H_2O mixture. At least, two new samples were used for each permeation run to avoid the hysteresis effects due to the hydrogen damage and / or the formation of microvoids etc. The electrochemical permeation method used under the galvanostatic charging conditions was similar to that described previously [7, 9, 10]. The anodic compartment of the permeation cell was filled with a 0.1 k mol m^{-3} NaOH and an anodic potential of -350 mV (Ag / AgCl) was applied at the diffusion side using potentiostat. The specimen was cathodically polarized at a constant current density of $i_c = 10 \text{ Am}^{-2}$ in the cathodic compartment which contained a solution of 160 mol m^{-3} $\text{H}_2\text{SO}_4 + 2.5 \times 10^{-3} \text{ kg m}^{-3}$ H_2SeO_3 . The cell was enclosed in a thermostatically controlled air bath that kept the temperature within ± 1 K between 279 and 335 K.

The diffusivity was determined from the build-up transient of the permeation curve by using the linear relation of $\log(t^{1/2}J_i)$ vs. $1/t$ which is the first term ($n=0$) approximation of eq. (1),

$$J_i = \frac{2\sqrt{DC_0F}}{\sqrt{\pi t}} \sum_{n=0}^{\infty} \exp\left[-\frac{(2n+1)^2L^2}{4Dt}\right], \quad (1)$$

where D = the diffusivity of hydrogen, C_0 = the concentration of hydrogen beneath the cathodic surface, L = the thickness of the specimen, F = Faraday's constant and t = the permeation time.

3. Results and Discussion

The lattice parameters a_0 for the fully annealed Pd-Ni alloys are given in Fig. 1, together with earlier data [11, 12]. The a_0 values obtained in this study are in agreement with the previous results [11, 12], and they decrease with an increase of Ni content, i. e., the Ni addition effects a negative dilation of the Pd-lattice, and the Pd addition produces a positive dilation of the Ni-lattice.

In all cases of the annealed and as cold rolled samples the hydrogen diffusivity D measured in the temperature range 279 to 335 K obeyed an Arrhenius relationship. Values of the frequency factor of diffusion D_0 and the activation energy ΔH_D for diffusion were determined by a least-squares fit and they are summarized in Table 1.

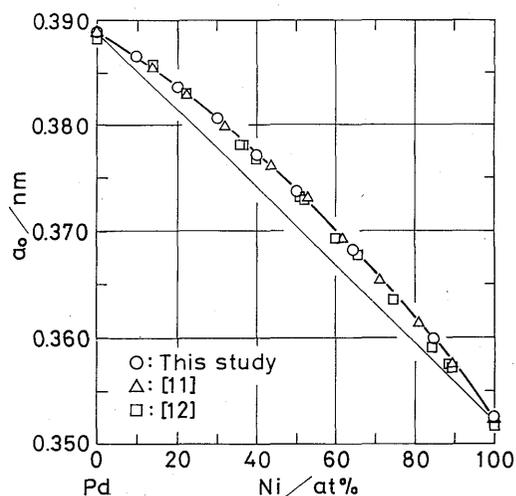


Fig. 1 Lattice parameters of fully annealed Pd-Ni alloys at 298 ± 1 K.
 ○ : this study, △ : data from ref. 11,
 □ : data from ref. 12.

Table 1 Temperature dependence of hydrogen diffusivity, $D = D_0 \exp[-\Delta H_D(\text{Jmol}^{-1}) / RT](\text{m}^2\text{s}^{-1})$ and lattice parameter, a_0 for various Pd-Ni alloys. Temperature range = 279–335 K, $i_c = 10 \text{ Am}^{-2}$.

	as cold rolled		773 K, 3.6 ks annealed		1123 K, 7.2 ks annealed		Lattice parameter, a_0 $\pm 0.0001 \text{ nm}$
	$D_0 / \text{m}^2\text{s}^{-1}$	$\Delta H_D / \text{Jmol}^{-1}$	$D_0 / \text{m}^2\text{s}^{-1}$	$\Delta H_D / \text{Jmol}^{-1}$	$D_0 / \text{m}^2\text{s}^{-1}$	$\Delta H_D / \text{Jmol}^{-1}$	
Pd	8.07×10^{-8}	22180 ± 960	1.01×10^{-7}	21760 ± 1090	1.05×10^{-7}	21420 ± 1210	0.3890
9.6 at% Ni	7.64×10^{-8}	23970 ± 1000	8.67×10^{-8}	22550 ± 1000	8.68×10^{-8}	22130 ± 1260	0.3866
20.0 at% Ni	4.94×10^{-8}	24690 ± 920	6.67×10^{-8}	23180 ± 1510	6.32×10^{-8}	22890 ± 1050	0.3836
30.1 at% Ni	3.29×10^{-8}	25060 ± 1050	4.74×10^{-8}	23680 ± 1170	4.60×10^{-8}	23430 ± 1210	0.3807
40.0 at% Ni	2.82×10^{-8}	25820 ± 920	2.86×10^{-8}	23810 ± 920	2.80×10^{-8}	23510 ± 960	0.3771
50.0 at% Ni	2.75×10^{-8}	26820 ± 1090	1.74×10^{-8}	24020 ± 1260	1.65×10^{-8}	23720 ± 960	0.3737
64.3 at% Ni	2.76×10^{-8}	28450 ± 1380	9.51×10^{-9}	24560 ± 1130	7.98×10^{-9}	24020 ± 1210	0.3682
84.8 at% Ni	1.42×10^{-7}	36530 ± 1590	1.79×10^{-8}	29370 ± 1510	1.82×10^{-8}	29080 ± 1300	0.3599
Ni	3.03×10^{-6}	47990 ± 1050	5.43×10^{-7}	40960 ± 920	7.05×10^{-7}	40880 ± 840	0.3525

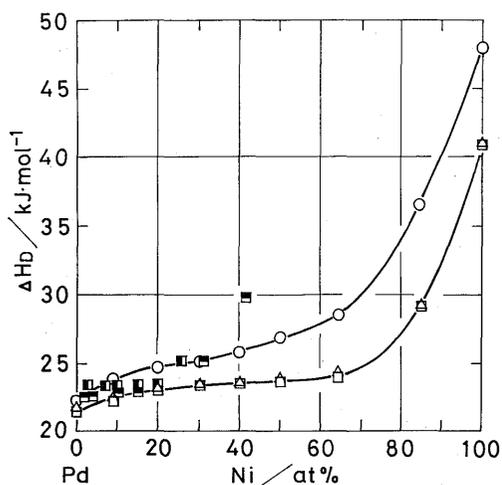


Fig. 2 Activation energy for diffusion of hydrogen vs. Ni content in Pd-Ni alloys.
 ○ : as cold rolled, △ : annealed at 773 K for 3.6 ks, □ : annealed at 1123 K for 7.2 ks, ■ : data from ref. 3, ▣ : data from ref. 8.

Figure 2 shows the plots of ΔH_D vs. Ni content, together with earlier data [3, 8]. There is no remarkable difference in the activation energy for diffusion between the samples annealed at 773 K for 3.6 ks and at 1123 K for 7.2 ks, but the energy values for the as cold rolled samples are larger than those for the annealed samples over the alloy compositions. This is attributed to the hydrogen trapping effect at the lattice defects such as dislocations introduced by cold rolling.

The activation energy for diffusion in fully annealed samples increases slowly from 21.42 kJmol^{-1} for pure Pd up to about 60 at. % Ni and rises steeply at higher Ni contents, reaching a value of 40.88 kJmol^{-1} for pure Ni. Below about 20 at. % Ni, the energy values obtained in this work are a little smaller than those of earlier works [3, 8]. The activation energy

for diffusion in the annealed specimens with small addition of nickel is in qualitative agreement with the theory of diffusion in fcc palladium alloys proposed by Buchold et al. [3], i. e. the isoelectronic solute element is appeared to have virtually no effect on the activation energy.

Figure 3 shows the plot of the hydrogen diffusivity vs. Ni content at 298 K. The diffusivity in the annealed Pd-Ni alloys decreases in an almost logarithmic fashion, with an increase of Ni content, i. e., with decreasing the lattice parameters of the alloys. At the same composition, the D values in the annealed samples are higher than those in the cold rolled samples. The reduction in diffusivity for the cold rolled samples can be explained in terms of hydrogen trapping process involving the lattice imperfections.

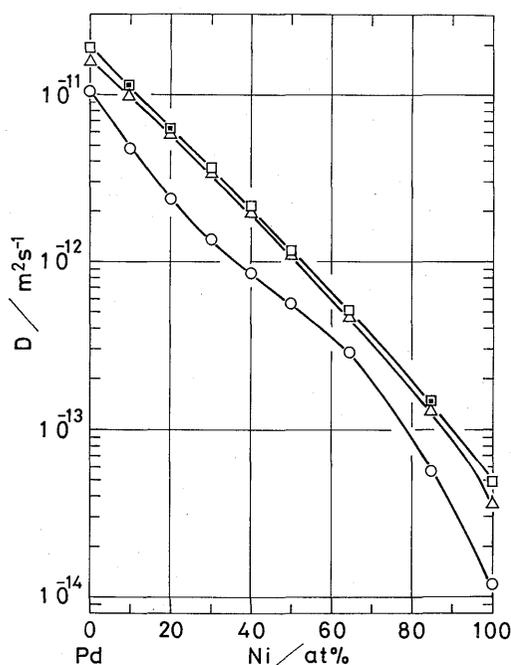


Fig. 3 Diffusion coefficient of hydrogen at 298 K vs. Ni content in Pd-Ni alloys.
 ○ : as cold rolled, △ : annealed at 773 K for 3.6 ks, □ : annealed at 1123 K for 7.2 ks,
 ■ : calculated value.

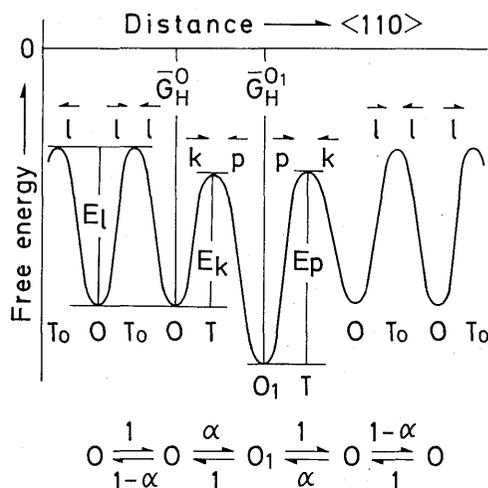


Fig. 4 A model of hydrogen diffusion for an fcc substitutional disordered alloy.

Now, the results found for the fully annealed samples (at 1123 K for 7.2 ks) of Pd-rich and Ni-rich sides will be discussed in terms of a diffusion model of hydrogen in a random substitutional solid solution along the $\langle 110 \rangle$ direction in an fcc lattice proposed recently [7, 13]. It was assumed for simplicity that hydrogen atoms occupy octahedral sites only, although the previous report [13] has taken into account the diffusion paths through the two types of O (octahedral) and T (tetrahedral) interstitial sites. Furthermore, in general, two possible migration paths along the $\langle 110 \rangle$ direction in the fcc lattice structure are considered, but we consider here only one of the model paths, because the model for the other path [13] has too many unknown jump parameters to enable a comparison to be made with the experimental data.

Figure 4 shows the model path used here for the disordered alloys. The influence of lattice defects such as vacancies and dislocations on the diffusion is not considered here.

The O_1 -site is the 1st nearest neighbor octahedral site around a solute atom, i.e., it is surrounded by one solute and five Pd atoms. Other O-sites are unaffected by solute atoms. The sum of the site fractions, f_O for O and f_{O_1} for O_1 , is unity. There are two types of saddle points for jumps. T_0 actually consists of two tetrahedral sites, each of which is surrounded by four Pd atoms. T similarly consists of two tetrahedral sites; one similar to that for T_0 and the other surrounded by one solute and three Pd atoms.

\bar{G}_H^O and $\bar{G}_H^{O_1}$ are the migration free energies for hydrogen atoms at O and O_1 -sites, respectively. The energy zero is taken as that of atoms at rest in vacuum so that the energies are numerically negative. The hydrogen jump rates l , k and p , the diffusivities D_l , D_k and D_p , and the corresponding activation energies E_l , E_k and E_p for diffusion refer to those for the jumping processes of $O \leftrightarrow O$, $O \rightarrow O_1$ and $O \leftarrow O_1$, respectively. α is the jump fraction for an atom at an O-site to jump to an O_1 -site with the jump rate k and $1 - \alpha$ the jump fraction for an atom at an O-site to jump to an adjacent O-site with the rate l . Since the jump path with the jump rate k is the same as that with the jump rate

p , the relation of $\alpha f_0 = f_{01}$ holds. From the geometry of the jump path, we can specify each jump fraction with the value of f_{01} . That is,

$$\alpha = f_{01} / (1 - f_{01}), \quad 1 - \alpha = (1 - 2f_{01}) / (1 - f_{01}). \tag{2}$$

Furthermore, the site fraction of the neighboring sites around a solute atom can be given by

$$f_{01} = Z_{01} \theta_u / \beta_0, \tag{3}$$

where Z_{01} is the number of neighbouring octahedral sites around a solute atom along the $\langle 110 \rangle$ direction (i. e., $Z_{01} = 2$), and β_0 has the usual meaning ($\beta_0 = 1$). Thus, we can obtain $f_{01} = 2 \theta_u$ and the effective range of θ_u for this model is limited to $0 < \theta_u < 1/4$, because $0 < f_{01} < 1/2$.

When a large number of such migration paths are randomly distributed in the x -direction, a fiducial plane between the x and $(x+a)$ planes ($a =$ unit jump distance) intersects any part of the fluxes across the plane. Therefore, by summing the parts of the fluxes in one lattice plane, we can calculate the total flux corresponding to the situation of the migration path illustrated in Fig. 4. The diffusivity expression in this model is given by eq. (4) by assuming a system of low occupation probability on individual sites, and that the local equilibrium exists between the sites.

$$D = \frac{(1 - 4\theta_u)D_j^0 \exp\left[-\frac{E_j}{RT}\right] + 2\theta_u(D_k^0 + D_p^0) \exp\left[-\frac{E_k}{RT}\right]}{1 - 2\theta_u \left\{ 1 - \exp\left[-\frac{\Delta\bar{G}_H^{01,0}}{RT}\right] \right\}}, \tag{4}$$

Where D_j^0 , D_k^0 and D_p^0 are the jump frequency factors corresponding to the D values. $\Delta\bar{G}_H^{01,0}$ is the difference in depth of the potential well between the sites. As θ_u changes, the specific volume of the substitutional lattice in general changes, and then the solute atoms would change the local interatomic potential experienced by hydrogen atom as a consequence of the dilation. Now, by taking account of the lattice dilation effect [5-7], and assuming that $\Delta\bar{S}_H^{xs,01,0} = \bar{S}_H^{xs,01} - \bar{S}_H^{xs,0} = 0$, where \bar{S}_H^{xs} is the partial non-configurational entropy of hydrogen atoms, it is easy to show that the value of $\Delta\bar{G}_H^{01,0}$ is expressed in the form,

$$\Delta\bar{G}_H^{01,0} = E_k - E_p = \Delta\epsilon + \frac{\Delta V \theta_u B V^*}{V_s}, \tag{5}$$

where $\Delta\epsilon = \epsilon_{H-u} - \epsilon_{H-v}$, the difference between the H-u and H-v nearest neighbor binding energies. The 2nd term is the migration energy ($\Delta\bar{G}_H^{dil}$) of the hydrogen atoms concomitant to the lattice dilation [5-7]. Then, the activation volume of hydrogen V^* for diffusion is $V^* = (\Delta\bar{G}_H^{dil} / \Delta p)_T$, where Δp is the pressure applied to return the molar volume of the binary Pd-u (solute) alloy to that of Pd, i. e., V_v^0 . The V^* is assumed not to depend on the pressure. For an elastically isotropic solid, Δp can be given in terms of the bulk modulus B at a given temperature. The V_s is the molar volume of the Pd-u binary solid solution,

$$V_s = V / (n_v + n_u) = \theta_u \bar{V}_u + (1 - \theta_u) \bar{V}_v \simeq \Delta V \theta_u + V_v^0, \tag{6}$$

where n 's is number of moles, \bar{V} 's the partial molar volume, $\bar{V}_u \simeq V_u^0 + \Delta V$ and $\bar{V}_v \simeq V_v^0$

The quantity ΔV is obtained from lattice parameter measurements, and is defined by

$$\Delta V = \left[\frac{\partial V_s}{\partial \theta_u} \right]_P = \frac{3}{4} N_0 a_{Pd}^2 \left[\frac{\partial a_0}{\partial \theta_u} \right]_P, \tag{7}$$

where N_0 is Avogadro's number, a_{Pd} the lattice parameter of Pd, a_0 the lattice parameters of the solid solutions. Of course, if $\theta_u = 0$, then $\Delta\bar{G}_H^{01,0} = 0$ and equation (4) reduces to Arrhenius relation. In the case of $\Delta\bar{G}_H^{01,0} > 0$, the interstitial site feels totally an "anti-trapping" effect, and in

the opposite case, the site feels a trapping effect.

Now, we will compare the above model, i. e., eq. (4), with the experimental data of Pd-rich alloys containing 9.6 at. % Ni and 20.0 at. % Ni, and of Ni-rich alloy with 15.2 at. % Pd. In computer fitting with the observed data, we assumed that the value of $D_i^0 \exp[-E_i / RT]$ in eq. (4) for the Pd-rich and Ni-rich alloys is equal to the experimental data of pure Pd and pure Ni, respectively and that for simplicity E_k is equal to E_l . Thus, by taking $\Delta \bar{G}_H^{01,0}$ and $(D_k^0 + D_p^0)$ as parameters to be determined to get the best fit, the sum of $(D_{\text{obs}} - D_{\text{cal}})^2$ at the solute concentrations and $T = 298$ K was calculated until a minimum was obtained. In this process a wide range of $\Delta \bar{G}_H^{01,0}$ and $(D_k^0 + D_p^0)$ was tried. In particular, we had $\Delta \bar{G}_H^{01,0}$ stepped by 0.1 kJmol^{-1} . The best fit values of $\Delta \bar{G}_H^{01,0}$ and $(D_k^0 + D_p^0)$ are given in Table 2.

It can be seen that the 1st nearest neighbor octahedral sites around Ni atoms in the Pd-rich alloys have an "trapping" effect, and conversely the sites around Pd atoms in the Ni-rich alloy have an "anti-trapping" effect. However the thermodynamic data of hydrogen solution in the alloys do not shed too much light on the situation, because the partial enthalpy of a dissolved hydrogen ΔH_H^0 at infinite dilution increases with increasing Ni content in the Pd-rich alloys [14].

The comparison of the experimental data with calculated values of diffusivity D at 298 K is given in Fig. 3. The closed symbols are the calculated values. Despite the degree of simplification involved, the present model provides a good description of the experimental data.

Now, if the solute atoms are assumed to be identical to Pd atoms and do not act as either trapping or anti-trapping effects for hydrogen atoms, but they only change the local interatomic potential experienced by an isolated hydrogen atom as a consequence of the lattice dilation, i. e., $\Delta \epsilon = 0$, then we can estimate the activation volume V^* from eq. (5), using the bulk modulus of Pd and its variation with the solutes and the lattice parameters of the alloys.

In the calculation, we assumed the bulk modulus does change in a linear manner for the alloys as written in the form $B = B_0 - \delta \theta_u$, by taking the bulk modulus for pure metals [15] as limits, where B_0 is the bulk modulus of Pd [15].

The estimated activation volume V^* are given in Table 2. The V^* values for the Pd-rich alloys are $V^* = (0.3 \sim 0.7) \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, and the value for the Ni-rich alloy is $V^* = 0.9 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. These values are comparable to $V^* = 0.43 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ for Pd-Ag alloys deduced by McLellan-Ishikawa [5, 6], and also to $V^* = (0.43 \sim 1.09) \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ for Pd-(Ce, Y, B) alloys estimated by our previous study [7]. However, as the actual trapping effects are completely neglected in the calculation, the estimates are not necessarily well-established.

4. Conclusions

The diffusivity of hydrogen in annealed and cold rolled Pd-Ni alloys has been measured in the composition range 0 to 100 at. % Ni and in the temperature range 279 to 335 K. In each alloy composition, the hydrogen diffusivity obeyed the classical Arrhenius relation within the temperature range of measurements. As the Ni-concentration increases, the D value decreases. The cold rolling decreases the diffusivity, and that results in an increase in the activation energy for diffusion. This decrease in

Table 2. Calculated values of $\Delta \bar{G}_H^{01,0}$, $(D_k^0 + D_p^0)$ and V^* for Pd-rich and Ni-rich side alloys.

Samples	$\Delta \bar{G}_H^{01,0}$ [kJmol ⁻¹]	$(D_k^0 + D_p^0) \times 10^6$ [m ² s ⁻¹]	$V^* \times 10^6$ [m ³ mol ⁻¹]
Pd-9.8 at. % Ni	-2.5	0.1	0.66
Pd-20.0 at. % Ni			0.31
Ni-15.2 at. % Pd	10.4	4.0	0.93

diffusivity is due to the trapping at the lattice defects; i. e. , dislocations produced by cold rolling.

The diffusivity data found for the fully annealed Pd-rich and Ni-rich alloys are consistent with the proposed diffusion model for solid solution, and the change in diffusivity is explained in terms of the lattice dilation effect.

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