Diffusion Coefficients of Hydrogen in Ni-Cu and Ni-Co Alloys*

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The diffusion of hydrogen in nickel and copper, and in fcc nickel-copper and nickel-cobalt alloys has been investigated over the temperature range from 260 to 1000 K by a technique of electrochemical permeation and a technique of gas phase permeation. The temperature dependence of the diffusion coefficient of hydrogen (D) in nickel and copper is described as follows: In nickel, $D(\text{m}^2/\text{s}) = 9.2 \times 10^{-7} \exp(-41.4(\text{kJ/mol})/RT)$, and in copper, $D(\text{m}^2/\text{s}) = 9.0 \times 10^{-7} \exp(-43.5(\text{kJ/mol})/RT)$. Arrhenius plots of D in Ni-Cu and Ni-Co alloys can also be represented by straight lines. The activation energy for diffusion of hydrogen changes with the concentration of alloying element. It has a maximum at 70 at% Cu in Ni-Cu alloys and increases with increasing concentration of Co in Ni-Co alloys.

The solubility of hydrogen (S) in nickel, copper, Ni-Cu alloys and Ni-Co alloys has been measured by a gas phase permeation method at temperatures between 560 and 1000 K. The temperature dependence of S in nickel and copper is given by $S(\text{mol H}_2/(\text{mol Ni Pa}^{1/2})) = 2.2 \times 10^{-6} \exp(-10.8(\text{kJ/mol})/RT)$ in nickel and $S(\text{mol H}_2/(\text{mol Cu Pa}^{1/2})) = 1.4 \times 10^{-5} \exp(-37.6(\text{kJ/mol})/RT)$ in copper. Arrhenius plots of S in Ni-Cu and Ni-Co alloys can also be represented by straight lines. The solution enthalpy of hydrogen has a minimum at 30 at% Cu alloys and increases with increasing concentration of Co in Ni-Co alloys.

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I. Introduction

In many pure metals and alloys, the temperature dependence of the diffusion coefficients of hydrogen obeys Arrhenius equations over a wide temperature range. However, in some pure metals and alloys Arrhenius plots of the diffusion coefficients cannot be represented by straight lines. This is caused by (i) lattice transformation⁽¹⁾ and magnetic transformation⁽²⁾, i.e., the change in the activation energy of hydrogen diffusion and (ii) the effect of impurities (alloying elements)⁽³⁾⁻⁽⁵⁾ and lattice imperfections⁽⁶⁾⁽⁷⁾, i.e., the existence of several kinds of the activation energy of hydrogen diffusion.

The effect of alloying elements on the hydrogen diffusivity has been experimentally

investigated particularly in iron-base alloys⁽¹⁾⁽⁵⁾⁽⁸⁾⁻⁽¹²⁾, and it is known that the hydrogen atoms dissolved in iron alloys are trapped by substitutional elements such as nickel, chromium and cobalt, and the trapping of hydrogen causes a slowing down of the diffusion.

The dependence of the hydrogen diffusivity upon temperature and composition of alloys has been derived by using the model in which the potential energy of hydrogen at the neighboring interstitial sites around an atom of alloying elements is different from that at normal interstitial sites⁽⁵⁾⁽¹³⁾⁽¹⁴⁾. However, only a few investigators have theoretically discussed the measured diffusion coefficient of hydrogen in alloys on the basis of the interaction of hydrogen and alloying elements because of few experimental data on the diffusion coefficient of hydrogen in alloys⁽⁵⁾.

In order to know the process of diffusion of hydrogen in alloys, the measurement of the diffusion coefficient of hydrogen should be carried out in substitutional type alloys having

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various compositions over a wide temperature range.

The binary systems of nickel with copper and cobalt have wide solid solution regions: The Ni-Cu system is a complete solid solution system and nickel has high solubility for cobalt. Furthermore, the Ni-Cu alloys and nickel-rich Ni-Co alloys do not transform at temperatures between 260 and 1300 K. Therefore, the Ni-Cu and Ni-Co alloys are suitable for investigation of the effect of alloying elements on the temperature dependence of the hydrogen diffusivity.

Many investigators have studied the diffusion coefficient of hydrogen in nickel: Belyakov and Ionov⁽²⁾ have reported a small step in the diffusion coefficient at the Curie point of nickel, but the Arrhenius plot of the diffusion coefficient measured in the wide temperature range from room temperature to 1300 K can be approximately represented by a straight line. The consistency of the data is good⁽¹⁵⁾. In contrast to a large amount of work on the diffusion coefficient of hydrogen in nickel, only a few investigators have reported data for the diffusion coefficient in copper and cobalt, and in Ni-Cu and Ni-Co alloys⁽¹⁵⁾.

In the present work, the diffusion coefficient of hydrogen in nickel and copper, and in fcc Ni-Cu and Ni-Co alloys were investigated by a technique of electrochemical permeation between 260 and 340 K and by a technique of gas phase permeation between 560 and 1000 K. In addition, the change in the potential energy of hydrogen was discussed as a function of composition of the alloys from measurements of the solubility and permeability of hydrogen between 600 and 1000 K by a gas phase permeation method.

II. Experimental Procedure

1. Specimen

The material used were nickel and copper, and Ni-Cu and Ni-Co alloys. These specimens were prepared by induction melting of commercially pure nickel, copper and cobalt in vacuum. The thickness of specimens used for electrochemical permeation and gas phase

permeation experiments is 19–56 μm and 0.1–0.4 mm, respectively. Copper specimens were annealed at 873 K for 28.8 ks, and nickel and Ni-Cu and Ni-Co alloys at 973 K for 28.8 ks. A thin layer of palladium was electrodeposited on the anodic surface of the specimens used for electrochemical permeation experiments.

2. Experimental procedure

The diffusion coefficient of hydrogen between 260 and 340 K was measured by an electrochemical permeation method⁽¹⁶⁾: Hydrogen was produced electrolytically at a constant current density on one side of a specimen (which is called the cathodic surface) by the use of a galvanostatic circuit, while on the other side of the specimen (which is called the anodic surface) the hydrogen was potentiostatically ionized. The potential of the anodic surface of the specimen was maintained at 0 V vs. Ag-AgCl by a potentiostat. The potentiostatic current, which was proportional to the rate of hydrogen permeation, was recorded. The cathodic electrolyte was a 0.5 kmol/m³ H₂SO₄ aqueous solution containing 5 g/m³ As₂O₃ (at 273–340 K) and a CH₃OH (69.8 vol%)+H₂O (27.8 vol%)+H₂SO₄ (2.4 vol%)+NaAsO₂ (10 g/m³) solution (at 260–273 K), and the anodic electrolyte was a 0.2 kmol/m³ NaOH aqueous solution (at 273–340 K) and a 0.2 kmol/m³ KOH alcoholic solution containing a small amount of H₂O (at 260–273 K).

The observed permeation curves of hydrogen, i.e., the time dependence of the potentiostatic current density (the hydrogen permeation rate), were analyzed using a transient method to obtain values of the diffusion coefficient of hydrogen D : In the case where the concentration of dissolved hydrogen at the cathodic surface increases to a constant value C_H immediately after cathodic polarization and that at the anodic surface is maintained at zero, the following equation is derived for short charging times⁽¹⁷⁾:

$$\log(J\sqrt{t}) = \log \frac{2C_H\sqrt{D}}{\sqrt{\pi}} - \frac{L^2 \log e}{4D} \cdot \frac{1}{t}, \quad (1)$$

where J is the permeation rate of hydrogen, t charging time, and L specimen thickness. The permeation curves in short charging times is ar-

ranged in the relation between $\log(J\sqrt{t})$ and $1/t$, and then the diffusion coefficient of hydrogen D is calculated from a slope of the curve.

The diffusion coefficient D , solubility $S^\dagger$ and permeability $P^{\dagger\dagger}$ of hydrogen were measured by a gas phase permeation method between 560 and 1000 K: The permeation rate of hydrogen in a specimen under nonstationary and stationary conditions was measured, i.e., the time dependence of permeation after a sudden rise of the pressure of hydrogen gas. The permeability P is the stationary rate of permeation of hydrogen through a specimen and the product of the diffusion coefficient D and solubility S . The diffusion coefficient D can be deduced from the relaxation time to the new stationary state by using so-called time-lag method⁽¹⁸⁾:

$$D = L^2/6\tau, \quad (2)$$

where τ is the relaxation time, i.e., so-called lag-time.

The solubility S is determined from the diffusion coefficient D and permeability P .

III. Experimental Results and Discussion

1. Measurement of diffusion coefficient of hydrogen

The electrochemical permeation curves usually change in various ways depending the experimental conditions such as cathodic current density (i_c), specimen thickness (L) and composition of electrolyte⁽¹⁶⁾. It is necessary to obtain the intrinsic values of the diffusion coefficient that the apparent values of the diffusion coefficient obtained from the analysis of the measured permeation curves based on eq.

[†] hydrogen solubility; the concentration of dissolved hydrogen in equilibrium with the hydrogen gas of pressure of 1 Pa.

^{††} hydrogen permeability; the permeation rate of hydrogen per unit time, sec, per unit surface area, m^2 , through the 1 m thick specimen of which one side of surface is in contact with the hydrogen gas of pressure of 1 Pa and the other side is under a vacuum condition.

Fig. 1 The effect of specimen thickness on the measured diffusion coefficient of hydrogen in nickel at 313 K.

(1) are independent of these experimental conditions. Therefore, the permeation curves were measured as a function of i_c , L and composition of electrolyte.

As an example, the measurement of the diffusion coefficient of hydrogen in nickel is considered: The hydrogen permeation experiment was done for nickel specimens of various thicknesses. The apparent values of D were independent of the thickness L , as shown in Fig. 1. The dependence of the apparent diffusion coefficient on cathodic current density i_c is shown in Fig. 2. The apparent values of D are independent of i_c . In order to study the effect of composition of electrolyte on D , the permea-

Fig. 2 The effect of cathodic current density i_c on the measured diffusion coefficient of hydrogen in nickel at 313 K.

tion curves were measured at 273 K by using the two pairs of electrolyte described above. The experimental result shows that the difference in electrolyte has little influence on the value of D at 273 K. Because the values of D obtained are independent of L , i_c and composition of electrolyte, the method of analysis of permeation curves based on eq. (1) is considered to be a method appropriate for determining the intrinsic value of D .

In order to determine the intrinsic value of D from a gas phase permeation experiment by using eq. (2), it is required to check that the measured relaxation time, from which D is deduced, is proportional to the square of the specimen thickness and independent of the pressure of hydrogen gas p_{H_2} in the hydrogen input chamber. Therefore, the hydrogen permeations were measured as a function of p_{H_2} and L .

As an example, the measurement of the diffusion coefficient of hydrogen in nickel is considered: The apparent values of D were independent of L (0.1–0.4 mm) and p_{H_2} (2.2×10^4 – 6.7×10^4 Pa). These experimental results indicate that the rate of hydrogen entry into specimens is very fast compared with that of bulk diffusion and the intrinsic values of D can be obtained by the experimental procedure described above.

The procedure similar to that for nickel was employed in determination of the diffusion coefficient of hydrogen in copper and Ni–Cu and Ni–Co alloys, and the intrinsic diffusion data were obtained.

2. Diffusion coefficient of hydrogen in nickel and copper

As shown in Fig. 3, the temperature dependence of D in nickel and copper is given regardless of the temperature range of the measurement and the experimental method by the following Arrhenius equations:

$$\begin{aligned} \text{Ni: } D \text{ (m}^2\text{/s)} &= 9.2 \times 10^{-7} \\ &\times \exp(-41.4 \text{ (kJ/mol)/RT}) \\ &\quad \text{(at 260–980 K).} \end{aligned} \quad (3)$$

$$\begin{aligned} \text{Cu: } D \text{ (m}^2\text{/s)} &= 9.0 \times 10^{-7} \\ &\times \exp(-43.5 \text{ (kJ/mol)/RT}) \end{aligned}$$

Fig. 3 Arrhenius plot of the diffusion coefficient of hydrogen in nickel, copper and Ni–Cu alloys.

$$\text{(at 320–930 K).} \quad (4)$$

Tables 1 and 2 give some previous data on the activation energy Q_D and preexponential factor D_0 for diffusion of hydrogen in nickel and copper, respectively. The values of Q_D and D_0 obtained in this study, i.e., eqs. (3) and (4), are in good agreement with those reported in the literature.

3. Diffusion coefficient of hydrogen in Ni–Cu and Ni–Co alloys

The temperature dependence of D in Ni–Cu and Ni–Co alloys is shown in Figs. 3 and 4, respectively. The Arrhenius plots of D can be represented by straight lines. The value of D has a minimum at 70 at% Cu in Ni–Cu alloys, and it decreases by alloying nickel with cobalt.

The diffusion of hydrogen atoms in an alloy, which occupy different interstitial sites, occurs under different energy conditions, because the potential energy of hydrogen changes with the interaction energy between hydrogen and metal atoms, and the configuration of metal

Table 1 Activation energy Q_D and D_0 values for diffusion of hydrogen in nickel.

D_0 (m ² /s)	Q_D (J/mol)	Temp. (K)	Source	Ref.
6.73×10^{-7}	39600	660–890	Eichenauer <i>et al.</i>	(20)
7.04×10^{-7}	39400	673–1273	Katz <i>et al.</i>	(21)
6.44×10^{-7}	40200	273–1669	Robertson	(22)

Table 2 Activation energy Q_D and D_0 values for diffusion of hydrogen in copper.

D_0 (m ² /s)	Q_D (J/mol)	Temp. (K)	Source	Ref.
1.15×10^{-6}	40800	700–910	Eichenauer <i>et al.</i>	(20)
1.13×10^{-6}	38800	720–1200	Katz <i>et al.</i>	(21)
3.69×10^{-7}	36800	292–339	Sakamoto & Takao	(23)

atoms which surround a hydrogen atom. Therefore, in general, it is estimated that the Arrhenius plots of D in alloys are not expressed by straight lines. Nevertheless, the linear dependence of $\log D$ on $1/T$ for Ni-Cu and Ni-Co alloys was observed in this study. This discrepancy must be discussed considering the accuracy of measurement and experimental procedure. When the interaction energies of the three pairs of hydrogen—metal atoms (Ni, Cu and Co) are nearly equal, the deviations from straight lines are small and noticeable only over a very wide range of measuring temperatures: It is probable that this deviation cannot be detected in the present work because of insufficient accuracy of measurement or an inadequate range of measuring temperatures.

The diffusion coefficient measured by the permeation methods is the mean value for long range diffusion of many hydrogen atoms and is not the value for individual jumps of a hydrogen atom between neighboring interstitial sites. Therefore, it is probable that only a part of the potential energies of hydrogen determine the activation energy for diffusion of hydrogen in alloys which is obtained experimentally from permeation experiments: One can imagine that hydrogen atoms diffuse through only the most energetically favorable path and then the

Fig. 4 Arrhenius plot of the diffusion coefficient of hydrogen in nickel and Ni-Co alloys.

measured activation energy becomes seemingly single. These speculations can be given for the interpretation of the linear dependence of $\log D$ on $1/T$ for Ni-Cu and Ni-Co alloys, but the complete explanation is not given.

4. Solubility and permeability of hydrogen in Ni-Cu and Ni-Co alloys

The solubility S and permeability P of hydrogen cannot be easily measured by an electrochemical permeation method⁽¹⁹⁾, but they can be obtained without difficulty by a gas phase permeation method. Figures 5 and 6 show the values of S and P , respectively, measured by a technique of gas phase permeation for nickel, copper and Ni-Cu alloys. Arrhenius plots of S and P in these specimens can be given by straight lines. The temperature dependence of S and P in Ni-Co alloys is shown in Figs. 7 and 8, respectively. In Ni-Co alloys also, the values of S and P obey Arrhenius relationships.

The temperature dependence of S is expressed by an Arrhenius equation: $S = S_0 \exp(-Q_S/RT)$, where S_0 is a preexponential factor

Fig. 5 Arrhenius plot of the solubility of hydrogen in nickel, copper and Ni-Cu alloys.

Fig. 7 Arrhenius plot of the solubility of hydrogen in nickel and Ni-Co alloys.

Fig. 6 Arrhenius plot of the permeability of hydrogen in nickel, copper and Ni-Cu alloys.

and Q_S is the solution enthalpy of hydrogen. Table 3 gives some previous data on S_0 and Q_S for nickel and copper. The values of S_0 and Q_S obtained in this study agree approximately with those reported in the literature.

The activation energies for diffusion Q_D and permeation Q_P , and the solution enthalpy Q_S can be calculated from the slope of the straight lines given in Figs. 3–8. The values of Q_D , Q_P and Q_S are shown in Fig. 9. These values may not be determined by all of the potential energies of hydrogen. However, it is useful for theoretical investigation on the process of hydrogen diffusion in alloys to study the dependence of Q_D , Q_P and Q_S on the composition of an alloy. Therefore, assuming that Q_S , Q_P and Q_D correspond to the potential energy at an interstitial site, the potential energy at a saddle point between neighboring interstitial sites, and the difference between these potential energies, respectively, it is concluded that both potential energies at an interstitial site and at a saddle point have minima at 30 at% Cu in Ni-Cu alloys and increase with increas-

Fig. 8 Arrhenius plot of the permeability of hydrogen in nickel and Ni-Co alloys.

Fig. 9 Q_s , Q_p and Q_0 observed in nickel and copper, and Ni-Cu and Ni-Co alloys.

ing concentration of Co in Ni-Co alloys.

Several models for the solution of hydrogen in transition metals were discussed earlier⁽²⁴⁾⁽²⁶⁾. Each of the models considered is based upon solution of hydrogen as a proton and an electron. Three possible changes in the electronic structure of the metal solvent have been postulated by various investigators; (1) the number of effective free electrons per atom in the solvent, (2) the number of vacant sites in the d-band of the solvent, and (3) the density

of states at the Fermi surface of the solvent. An attempt was made to correlate the hydrogen solubility measured in this work with these models, but a clear conclusion was not obtained.

IV. Conclusion

The diffusion coefficient of hydrogen in nickel and copper, and in fcc Ni-Cu and Ni-Co alloys was measured by an electrochemical

Table 3 Comparison of Q_s and S_0 observed in this study with those found in literature for nickel and copper.

Metal	S_0 (mol H ₂ /mol Metal · Pa ^{1/2})	Q_s (J/mol)	Temp. (K)	Source	Ref.
Ni	2.43×10^{-6}	12100	660-890	Eichenauer <i>et al.</i>	(20)
	3.99×10^{-6}	15600	1007-1494	Jones & Pehlke	(24)
	2.78×10^{-6}	12500	358-1726	Robertson	(22)
	7.28×10^{-6}	15800	300-550	Louthan <i>et al.</i>	(25)
	2.18×10^{-6}	10800	620-980	Hagi	this work
Cu	3.20×10^{-5}	37900	700-910	Eichenauer <i>et al.</i>	(20)
	5.09×10^{-6}	38200	1007-1343	Jones & Pehlke	(24)
	1.40×10^{-5}	37600	730-930	Hagi	this work

permeation method between 260 and 340 K, and the diffusion coefficient, solubility and permeability of hydrogen in these specimens were measured by a gas phase permeation method. The results are summarized as follows:

(1) The temperature dependence of the diffusion coefficient D and solubility S of hydrogen in nickel is expressed by

$$D \text{ (m}^2\text{/s)} = 9.2 \times 10^{-7} \times \exp(-41.4(\text{kJ/mol})/RT) \quad (\text{at } 260\text{--}980 \text{ K}),$$

and

$$S \text{ (mol H}_2\text{/(mol Ni Pa}^{1/2}\text{))} = 2.2 \times 10^{-6} \times \exp(-10.8(\text{kJ/mol})/RT) \quad (\text{at } 620\text{--}980 \text{ K}).$$

The temperature dependence of D and S in copper is given by

$$D \text{ (m}^2\text{/s)} = 9.0 \times 10^{-7} \times \exp(-43.5(\text{kJ/mol})/RT) \quad (\text{at } 320\text{--}930 \text{ K}),$$

and

$$S \text{ (mol H}_2\text{/(mol Cu Pa}^{1/2}\text{))} = 1.4 \times 10^{-5} \times \exp(-37.6(\text{kJ/mol})/RT) \quad (\text{at } 730\text{--}930 \text{ K}).$$

(2) Arrhenius plots of the diffusion coefficient of hydrogen between 260 and 1000 K, and the solubility and permeability of hydrogen between 560 and 1000 K in Ni-(0–100 at%)Cu and Ni-(0–50 at%)Co alloys can be represented by straight lines.

(3) The activation energy for diffusion of hydrogen changes with the concentration of alloying element. It has a maximum at 70 at% Cu in Ni–Cu alloys, and increases with increasing concentration of Co in Ni–Co alloys. The solution enthalpy of hydrogen has a minimum at 30 at% Cu in Ni–Cu alloys and increases with increasing concentration of Co in Ni–Co alloys.

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