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THE DIFFUSION AND TRAPPING OF HYDROGEN IN COLD WORKED NICKEL

by

Yoshiichi SAKAMOTO and Akira MIURA

(Department of Materials Science and Engineering)

Summary

The hydrogen diffusion and trapping phenomenon in cold worked polycrystalline nickel have been studied in the temperature range of 283 to 333 K by means of an electrochemical permeation technique. The cold working reduces the hydrogen diffusivity and that results in a slight increase in the activation energy for diffusion. While the solubility of hydrogen increases and the mode of absorption changes from the endothermic to exothermic with cold working. The increase in permeability of hydrogen is attributed not to the short-circuit diffusion but to the hydrogen trapping at dislocations and their stress fields, introduced by cold working. There is also slightly enhanced permeability of hydrogen through grain boundaries. The free energy change in the hydrogen trapping reaction was evaluated by assuming that the dislocations and their stress fields around them in cold worked nickels provide the trapping regions for hydrogen atoms. The energy values are comparable to the binding energy of a hydrogen atom with a dislocation in nickel estimated by the Portvin–Le Chatelier effect.

1. Introduction

There have been extensive studies on the permeability, diffusivity and solubility of hydrogen in nickel\(^{12-10}\) and the agreement among investigators is good in the case of well–annealed specimens.\(^9\) This agreement implies that the trapping of hydrogens at extraordinary sites, especially around impurity atoms does not have marked effect on the measured transport properties of hydrogen in nickel. However, the trapping of hydrogen to dislocations in nickel has been indicated experimentally by measurements of hydrogen–induced yielding\(^{11-14}\). Louthan et al.\(^7\) have observed an increase in permeability of hydrogen in cold worked polycrystalline nickel and considered that this increase is attributed to dislocation networks providing short–circuit diffusion paths. An earlier investigation\(^5\) indicated that there is no measurable effect of grain size on the permeability or the diffusivity of hydrogen. Stafford and McLellan\(^9,9\) have shown that the solubility of hydrogen in polycrystalline

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Department of Materials Science and Engineering
nickel does not seem to be strongly affected by the grain size and the Arrhenius plots of the solubility are not linear between 573 to 1673 K, showing a positive deviation at low temperature. The same authors\(^8\),\(^9\) observed that the solubility of hydrogen in single crystal nickel is lower than that in polycrystalline one at lower temperature, but at high temperature the Arrhenius plots of the solubility in single crystal and polycrystal are approximately parallel to each other.

The present investigation has been conducted in attempt to establish the effect of the cold working on the diffusivity and solubility of hydrogen in nickel. The diffusion coefficient and solubility of hydrogen in both cold rolled and annealed nickels were determined in the temperature range of 283 to 333 K by means of an electrochemical permeation technique.

2. Experimental Procedure
The materials used are polycrystalline nickels, received in the form of as cold rolled foils of 30 and 50 μm thickness prepared by the Japan Lamp Industrial Co., and had the following chemical composition. (wt%): Ni=99.45, Cu=0.10, Fe=0.15, Mn=0.20, Si=0.05, S=0.005, Co<0.045. The foil specimens of 25×10^{-3} m square were annealed in vacuum at 773 K for 1h and 1123 K for 2h to obtain different states of lattice strains. Besides, to obtain different grain sizes, the specimens were annealed at 1123, 1173 and 1223 K for a fixed time in vacuum. The grain size was determined by optical microscope after the annealing. Before permeation measurement, the foils were degreased and etched in a 2:2:1 H\(_2\)SO\(_4\)-HNO\(_3\)-H\(_2\)O mixed solution to remove the surface oxides, and the anodic side of the membrane was electroplated with a thin layer (0.2 μm) of Pd to protect the specimens against anodic dissolution. The apparatus used to determine the diffusion coefficient and the solubility of hydrogen is of the electrochemical permeation type and has been described in the previous reports on the determination of diffusivity and solubility of hydrogen in prestrained iron\(^1\),\(^2\) and tempered steels\(^3\),\(^4\).

The two compartments of the permeation cell were separated by the foil specimens. A 100 mol/m\(^3\) NaOH solution at a certain temperature, deoxygenated by hydrogen gas in a separate cell, was admitted into the anodic compartment. The potential of the anodic side of the specimen was maintained by means of a potentiostat at -480 mV with respect to the saturated calomel reference electrode. When both temperature and background current in the anodic circuit attained steady state values, a 160 mol/m\(^3\)H\(_2\)SO\(_4\) solution containing 2.5g/m\(^3\)H\(_2\)SeO\(_3\) was let into the cathodic compartment and the current density of 300 A/m\(^2\) was imposed on the cathodic side and the corresponding permeation transient was recorded. The diffusion coefficient and solubility of hydrogen were calculated from the build up transient utilizing the following approximate solution:

\[
\log(t^{1/2} \cdot J_t) = \log \frac{2 \cdot C \cdot F \cdot D^{1/2}}{\pi^{1/2}} - \frac{L \cdot \log e + \frac{1}{4 \cdot D}}{t}
\]

where \(J_t\) is the permeation current, \(t\) the permeation time, \(D\) the diffusion coefficient, \(F\) Faraday's constant, \(C\) the solubility and \(L\) the thickness of the specimen. On plotting \(\log(t^{1/2} \cdot J_t)\) vs. \(1/t\), a straight line is obtained at large value of \(1/t\) and the slope leads to the determination of diffusion coefficient. From the intercept of this line on the ordinate, the value of solubility can readily be obtained.

Furthermore, in order to investigate the
effect of microstrains on hydrogen diffusion, the lattice strains were determined by X-ray diffraction technique.

3. Results

3-1. Hydrogen permeation transient

The permeation current vs. time curves at various temperatures for as cold rolled specimens and specimens annealed at 1123 K for 2 h are shown in Fig. 1. The non-steady state permeation rate through nickel foils increases with temperature, and at the same temperature the time up to the beginning of hydrogen permeation through as cold rolled specimens are longer than that in the annealed one. This fact shows that the presence of lattice imperfections, such as dislocations, faults and subgrain boundaries etc., affects the solubility and/or the diffusivity of hydrogen.

3-2. Effect of grain size

The results measured at 309 K on the diffusion coefficient and solubility of hydrogen with different grain sizes are presented in Fig. 2. The diffusivity seems to be independent of the grain size. Contrarily the solubility slightly decreases with increasing grain size and it is described by the following equation in the range of grain size of 17 to 48 μm.

\[ C = 8.19 \times 10^2 \exp \left( -3.10 \pm 1.62 \right) \times 10^{-3} L \] (mol/m³)

where \( L \) is the average grain size in μm.

This result substantially accords with that of Stafford and McLellan, who have shown that the solubility of hydrogen in nickel single crystal is lower than that in polycrystalline nickel, containing low energy sites in grain boundaries.

Since the permeability \( P \) is the product of \( D \) and \( C \), at least at lower temperatures,

*1 The permeability values in this study do not correspond to the permeability at a pressure of square root of 1 atm of \( H_2 \) on one side (cathodic side) and vacuum on the other side under the unit length of specimen. This is the value of the electrochemical situation, corresponding to the overpotential for hydrogen evolution reaction under \( i_\text{c} = 300 \text{ A/m}^2 \).
there is enhanced permeability of hydrogen through grain boundaries in nickel. The implication of these results is that the short-circuit diffusion at grain boundaries does not predominantly occur but the grain boundaries act as an enhanced hydrogen trapping site and hence an increase in solubility and a corresponding increase in permeability occur.

3-3. Effect of cold working

The diffusion coefficients between 283 and 333 K for three specimens, 1) as cold rolled, 2) 773 K, 1 h annealed and 3) 1123 K, 2 h annealed, are plotted against the reciprocal of the absolute temperature in Fig. 3. The as cold rolled specimen has the lowest values. With the progress of annealing, the diffusivity increases. The value of lattice microstrains obtained by analyzing half-value breadth of X-ray diffraction line profiles was $\varepsilon = 2.4 \times 10^{-3}$ for the as cold rolled specimen and $\varepsilon = 1.2 \times 10^{-3}$ for the 773 K, 1 h annealed specimen.

The activation energies for diffusion were determined by regression analysis and the results are described as follows: As cold rolled specimen:

$$D = 3.03 \times 10^{-6} \exp\left[\frac{-47900 \pm 1000}{RT}\right] \text{ (m}^2 \text{/s)}$$

773 K, 1 h annealed specimen:

$$D = 5.43 \times 10^{-7} \exp\left[\frac{-40900 \pm 900}{RT}\right] \text{ (m}^2 \text{/s)}$$

1123 K, 2 h annealed specimen:

$$D = 7.05 \times 10^{-7} \exp\left[\frac{-40800 \pm 800}{RT}\right] \text{ (m}^2 \text{/s)}$$

Although the activation energy for diffusion is almost the same for the 1123 K, 2 h and the 773 K, 1 h annealed specimens, it is slightly larger for the as cold rolled specimen. The Arrhenius equation for diffusion in the 1123 K, 2 h annealed specimen is in good agreement with Robertson's "best" fit value of $D = 6.44 \times 10^{-7} \exp(-40200/RT)$ (m$^2$/s) in the temperature range of 273 to 1669K. Furthermore, this diffusivity datum is in good accord with data measured for nickel single crystals in the range of 673 to 1173 K reported by Katz et al., $D = 7.04 \times 10^{-7} \exp(-39400/RT)$ (m$^2$/s) and Eichenauer et al.'s data, $D = 6.73 \times 10^{-7} \exp(-39600/RT)$ (m$^2$/s) in the range of 623 to 923 K. Considering these data obtained from specimens of various purities ranging from 99.983 to 99.999 % Ni, it is interesting that the effect of impurities on diffusivity is not remarkable.

The solubility values obtained at a constant current density of 300 A/m$^2$ are plotted against the reciprocal of the absolute temperature in Fig. 4. It can be seen that the cold working not only increases the solubility of hydrogen but also changes the mode of absorption from the endothermic to exothermic. This observation is similar to that for the solubility of hydrogen in prestrained $\alpha$-iron found in the previous experiment. The results of
The diffusion and trapping of hydrogen in cold worked nickel

The solubility are described as follows:

- As cold rolled specimen,
  \[ C = 4.85 \times 10^4 \exp \left( \frac{13800 \pm 3000}{RT} \right) \text{ (mol/m}^3 \right) \]
  \[ 773 \text{ K, 1 h annealed specimen ;} \]
  \[ C = 1.38 \times 10^4 \exp \left( \frac{-6400 \pm 3400}{RT} \right) \text{ (mol/m}^3 \right) \]

- As 1123 K, 2 h annealed specimen;
  \[ C = 1.36 \times 10^5 \exp \left( \frac{-13700 \pm 1500}{RT} \right) \text{ (mol/m}^3 \right) \]

The heat of solution of hydrogen in the 1123 K, 2 h annealed specimen is slightly smaller than Louthan et al.'s value, 15.8 kJ/mol in the temperature range of 300 to 550 K, but the value is in agreement with Robertson's "best" fit value, 12.5 kJ/mol within the experimental errors.

It is apparent that the decrease in the heat of solution is dependent upon the amount of the trap sites, such as dislocations introduced by cold working.

As both diffusivity (D) and solubility (C) depend upon the temperature through the Arrhenius type relation, permeability (P) will also have an Arrhenius type temperature dependence in the form, \( P = P_0 \exp \left( -\frac{\Delta H_p}{RT} \right) \), where \( P_0 = D_0 \cdot C_0 \) and \( \Delta H_p = \Delta H_D + \Delta H_C \). \( D_0 \) and \( C_0 \) are pre-exponential constants. \( \Delta H_D \) and \( \Delta H_C \) are the activation energy for diffusion and the heat of solution, respectively. The permeabilities of hydrogen through the three specimens are described as follows:

- As cold rolled specimen:
  \[ P = 1.47 \times 10^{-5} \exp \left( \frac{-34100 \pm 3200}{RT} \right) \text{ (mol/m-s)} \]

- 773 K, 1h annealed specimen:
  \[ P = 7.49 \times 10^{-3} \exp \left( \frac{-47300 \pm 3500}{RT} \right) \text{ (mol/m-s)} \]

- 1123 K, 2h annealed specimen:
  \[ P = 9.59 \times 10^{-2} \exp \left( \frac{-54500 \pm 1700}{RT} \right) \text{ (mol/m-s)} \]

The activation energy of permeation in the 1123 K, 2 h annealed specimen is in good agreement with Robertson's "best" fit value of 54.55 kJ/mol in the temperature range of 297 to 1333 K. Furthermore, this energy datum is in accord with data measured for nickel single crystals in the range of 473 to 693 K by Ebisuzaki et al., 55.06 kJ/mol and Louthan et al.'s data, 55.30 kJ/mol in the range of 300 to 550 K.

It can be seen that cold working decreases the activation energy of permeation, and resulting in increase of the permeability of hydrogen through nickel. Therefore, under the steady state permeation, hydrogen is more easily permeable through cold worked specimen than the annealed one. For the similar reasons of grain boundary effect, this increase is attributed to not so much the short-circuit diffusion as the hydrogen trapping at the lattice imperfections, such as dislocations, faults, lattice vacancies and/or sub-grain boundaries etc., introduced by cold working, because the cold working reduces the diffusivity and that results in a slight
increase in the activation energy for diffusion.

4. Discussion

It would seem that the major source of the more increased solubility of hydrogen in cold worked nickel than the annealed one is dislocation-enhanced solubility for the reasons arose from the direct observation of a high dislocation density by electron transmission microscopy\(^2\) and from the measurement of the large values of lattice microstrains by X-ray line broadening. On the other side, in view of the theoretical considerations, Bockris et al\(^9\) have shown that the concentration of hydrogen in a cylindrical volume around an edge dislocation increases the solubility of hydrogen in iron at a dislocation density of \(1 \times 10^{15} \text{m}^{-2}\) by about 76 times, by using the stress field of a dislocation based on the elasticity theory and the concept that the chemical potential of a mobile interstitial solute must be equalized throughout at equilibrium\(^2\).

In this discussion, in order to consider quantitatively the trapping of hydrogen in the cold worked specimen and to evaluate the free energy change of the hydrogen trapping reaction, the following simple assumptions are used.\(^2\) 1) The dislocations and their surrounding stress fields can act as trapping sites for diffusing hydrogen atoms. 2) The partial equilibrium of hydrogen between such traps and normal lattice sites exists during the permeation of hydrogen through the specimen. Such situation can be expressed by the following equilibrium constant \(K_1\),

\[
K_1 = \frac{C_{\text{H,tr}} \cdot C_0}{C_{\text{H,L}} \cdot C_{\text{tr}}}
\]

where \(C_{\text{H,L}}\) is the concentration of H atoms in the normal lattice sites, which is assumed to be the octahedral site. \(C_{\text{tr}}\), the concentration of the unfilled traps. \(C_{\text{H,tr}}\), the concentration of the trapped H atoms and \(C_0\) is that of normal lattice sites occupying no H atoms. The total concentration of normal octahedral lattice sites \((C_L)\) available to interstitial occupancy in well annealed specimen can be calculated to \(C_L = 1.52 \times 10^5 \text{mol/m}^3\) \((n_L = 9.15 \times 10^{28} \text{m}^{-3})\).

In order to obtain a reasonable equilibrium constant of trapping reaction, we assumed that the value of \(C_{\text{H,L}}\) is the same as that in the annealed specimen at 1123 K, for 2 h, containing no lattice defects introduced by cold working. However, for the cold worked specimen, the hydrogen concentration in the normal lattice site is corrected to \(C_{\text{H,L}} = C_{\text{H,L}}(C_L - C_{\text{tr}})/C_L\) by assuming that the trap site is the "deformed octahedral one" around the dislocation, where \(C_{\text{tr}}\) is the concentration of total traps. Because the dislocation density \(\rho_{\text{ws}}\) evaluated from the formula by Williamson & Smallman\(^2\) was \(1.5 \times 10^{15} \text{m}^{-2}\), \(3.7 \times 10^{14} \text{m}^{-2}\) for the as cold rolled and 773 K, 1h annealed specimen respectively, the value of \(C_{\text{tr}}\) could be estimated to be \(7.11 \times 10^4 \text{mol/m}^3\) \((n_{\text{tr}} = 4.28 \times 10^{28} \text{m}^{-3})\), \(1.77 \times 10^4 \text{mol/m}^3\) \((n_{\text{tr}} = 1.07 \times 10^{28} \text{m}^{-3})\) respectively by taking that the average radius of the limiting circle of the stress field around dislocation is \(r_f^* = 1 \times 10^{-8} \text{m}\) and neglecting the radius of the

---

*2 The value of \(r_f^*\) can be roughly estimated by \(r_f^* = 1/\pi \rho_{\text{ws}}\), after which the effective value of \(r_f^*\) used must satisfy the following two conditions: 1) \(\sqrt{n_{\text{H,tr}} x a_0^3 x 10^{-20}/4\pi \rho_{\text{ws}}} < r_f^* < r_L\), where \(n_{\text{H,tr}}\) is the number of trapped H atoms \((\text{m}^{-2})\), \(a_0\) lattice constant (Å), \(\rho_{\text{ws}}\) is dislocation density \((\text{m}^{-2})\) and 2) \(r_f^*\) must be the same value for both the as cold rolled specimen and 773K, 1h annealed one. Thus, in this study we used approximately \(r_f^* = 1 \times 10^{-8} \text{m}\).
dislocation core, \( r_0 = b \) in comparison with \( r_i^* \). The concentration of unoccupied lattice site is expressed by \( C'_0 = C_L - C'_{H,L} - C_{tr} \). The total concentration of hydrogen (\( C_H \)) is \( C_H = C'_{H,L} + C_{H,tr} \) and the concentration of un-filled traps leads to \( C_{tr} = C_{tr} - C_{H,tr} \). Therefore, the equation [2] can be rewritten by the following equation.

\[
K'_1 = \left[ \frac{[C_{H1} - C_{H1,L} \cdot (C_L - C_{tr}) / C_L]}{[C_{H1,L} \cdot (C_L - C_{tr}) / C_L]} \right] \cdot \left[ \frac{C_L - C_{H1,L}}{C_{H1,L} - C_{H1,L}} \right] \cdot \left[ \frac{C_{H1} - C_{H1,L}}{C_L - C_{tr}} \right] \cdot \left[ \frac{C_L - C_{tr}}{C_{tr}} \right] \quad [3]
\]

The free energy change of the hydrogen trapping reaction, \( \Delta G = -RT \ln K'_1 \) was calculated and the results are given in Table 1. The free energy changes of hydrogen trapping reaction increase with an increase in temperature and at the same temperature, the values of the as cold rolled specimen are smaller than that of the 773K, 1h annealed one. These energy values, in magnitude can be comparable to the maximum binding energy of hydrogen atom and dislocation in nickel of about 7700 J/mol\(^{112}\)(0.08 ev) estimated by assuming that the atmospheres become condensed when the Lower Critical Temperature of the Portevin-Le Chatelier phenomenon is approached and are also approximately equal to the binding energy of hydrogen to dislocations of 13500 J/mol\(^{110}\) (0.14 eV) obtained by the difference between the activation energies for the Upper and Lower Critical Temperatures. While the values of

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5. Conclusions

1) The diffusivity in polycrystalline nickel does not depend upon the grain size, while the solubility decreases with increasing grain size and there is slightly enhanced permeability of hydrogen through grain boundaries in nickel.

2) The cold working result in a lower value of diffusivity, resulting in a slight increase in the activation energy for diffusion and that brings not only an increase in the solubility of hydrogen but also a change in the mode of absorption from the endothermic to exothermic. The increase of permeability can be attributed not to the short-circuit diffusion but to the hydrogen trapping at dislocations and their surrounding stress fields produced by cold working.

3) The free energy change of hydrogen trapping reaction in cold rolled nickel was evaluated and the energy values, in magnitude are comparable to the average hydrogen-dislocation binding energy estimated by Portevin-Le Chatelier effect.

References

5) W. M. Robertson, Z. Metallk., 64, 436 (1973).