Hydrogen Permeation through Nickel, Ni-Cr and Ni-Mo Alloys at Elevated Temperatures

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The hydrogen permeation through Ni, austenitic Ni-Cr and Ni-Mo alloys were studied at temperatures from 500 to 1000°C. The measurement of hydrogen permeability was made using a one-piece diffuser in which the membrane was a flat disc. The data of permeability for each metal fitted to a semi-empirical equation, and the activation energy and pre-exponential constant for hydrogen permeation were derived from their temperature coefficient. Moreover, hydrogen diffusivities of these alloys were calculated using the data of permeability and those of solubility. The hydrogen permeability was decreased with an increase in the amount of Cr or Mo in Ni. The addition of Cr to Ni increased the values of activation energy for hydrogen permeation from 13.0 kcal/mol (pure Ni) to 16.5 kcal/mol (Ni-29wt%Cr). The addition of Mo to Ni, on the other hand, decreased the values of pre-exponential constant for hydrogen permeation from 1340 cm³(NTP) mm/cm² hr $p^{1/2}$ (pure Ni) to 560 cm³(NTP) mm/cm² hr $p^{1/2}$ (Ni-15wt%Mo).

1. Introduction

It is desirable that Ni-base heat resisting alloys used for heat exchangers in a high temperature gas cooled reactor (HTGR) for multiple purposes have excellent high temperature mechanical properties and further that the hydrogen permeation be as low as possible[1-3]. Only a few studies, however, have been reported on the hydrogen permeability of Ni-base heat resisting alloys[4-7] at elevated temperatures and the effect of metallurgical factors on the permeation is not so clear.

In this paper, an investigation has been made of hydrogen permeability through austenitic Ni-Cr and Ni-Mo alloys, and metallurgical factors affecting the permeability are discussed.

2. Experimental

2.1 Apparatus

Fig. 1 shows the apparatus employed, which consists of a hydrogen gas purifying system, the permeation assembly and heating furnace, and gas collecting and measuring systems. Hydrogen permeated through a specimen was collected into the measuring tank which
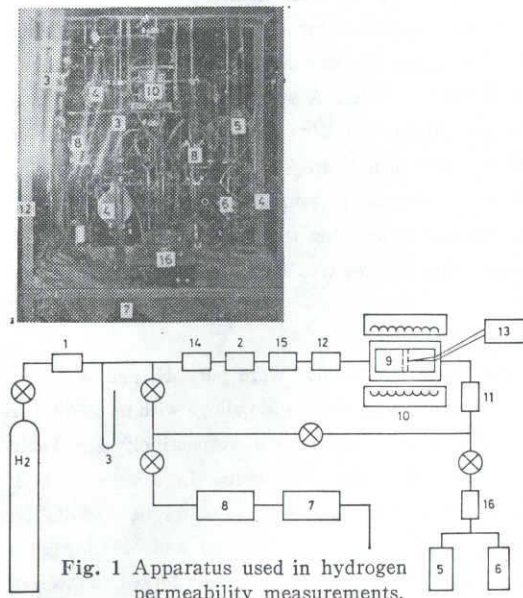

Fig. 1 Apparatus used in hydrogen permeability measurements.

1) Silica gel	2) Molecular sieve (5A, llX)
3) Hg manometer	4) Reserve tank
5) Pirani gauge	6) McLeod gauge
7) Rotary pump	8) Hg diffusion pump
9) Specimen	10) Furnace
11) Liquid N_2 trap	12) Dew point meter
13) A.C. thermo couple	14) Pd black catalyser
15) Zr-sponge getter	16) Toepler pump

Table 1 Chemical composition of metal and alloys. (wt%)

| Alloys	Ni	Cr	Mo	Al
Ni	99. 95	N.D.	N.D.	0. 003
Ni–10Cr	Bal.	9. 97	——	0. 005
Ni–20Cr	Bal.	19. 52	——	0. 003
Ni–29Cr	Bal.	28. 84	——	0. 004
Ni–8Mo	Bal.	N.D.	7. 97	0. 004
Ni–15Mo	Bal.	N.D.	14. 97	0. 003

N.D.; not detected

was kept a vacuum, and permeability was determined by measuring the increase of pressure by a Hg Mc-Leod gauge. As the volume of the measuring system was previously determined and the specimen dimensions were known, the increase of pressure could be converted into permeability in cm^3 (NTP) per unit time. On the outgoing side, the pressure was reduced as far as possible before isolating from the pump. During measurement the pressure never rose to more than 0. 1 mmHg, even at the highest permeability encountered.

Inpurity O_2 in H_2 gas (99. 99%) was removed by Pd-black catalyzer, then humidity was removed by silica gel and molecular sieves (5A and 11X), further small amounts of residual O_2 and N_2 were removed by Zr-sponge getter. A specimen was degassed in a vacuum higher than 10^{-5} mmHg for at least 5 hr at 1000°C, and then hydrogen gas was introduced. The temperature was measured by an alumel-chromel thermo couple touching the specimen directly and the temperature control was made by a thermo regulator within $\pm$ 1°C.

2. 2 Materials

The materials studied were pure Ni and a series of austenitic Ni-Cr and Ni-Mo alloys with up to 29%Cr and 15%Mo alloying element, respectively (see Table 1). The materials were melted in a vacuum high frequency furnace, by using electrolytic low-Co Ni (99. 98%), electrolytic Cr (99. 5%) and Mo chip (99. 9 %), cast in 6 cmϕ ingots, and then forged to the size of 3 cmϕ bars by hot rolling. The specimens were accurately machined in a lethe. The surface roughness was less than 0. 5 μm. A cross section of the membrane assembly is shown in Fig. 2. Specimen holders made from 18-8 stainless steel (SUS 27) were welded to a specimen by an electron beam at both sides.
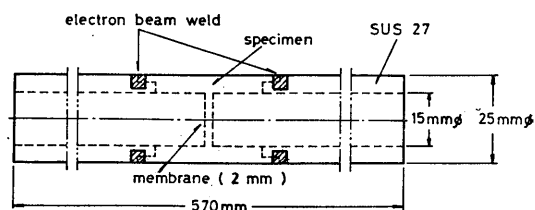
Fig. 2 Diagram of hydrogen permeability test specimen.

Since there are no welds in the vicinity of the membrane, there can be no possibility of diffusion of the holder materials into the membrane. The specimen were rinsed in petroleum benzine and trichloroethylene to remove the anti-corrosion oil before each set of measurements.

3. Results and Discussion

The permeation of a diatomic H_2 gas through a metallic membrane essentially involves the following consecutive steps[8];

(a) Transfer of the molecule from the gas phase to the surface (van der Waals adsorption).

(b) Dissociation of the molecule to single atoms on the surface (chemisorption).

(c) Transfer of an atom from the surface to the bulk of the metal (dissolution of gas in the metal).

(d) Diffusion of gas atoms through the membrane under the concentration gradient established.

(e) Transfer of atoms from the solution at the low pressure side to the vacuum surface.

(f) Recombination of atoms to form molecules on the low pressure surface.

(g) Desorption of gas from the low pressure surface. It is noted that steps (e) to (g) are simply a reversal of (c) to (a), respectively. In principle, any one of

the above seven steps might be sufficiently slow to become rate controlling. In general, the diffusion step (d) becomes the rate controlling step in the hydrogen permeation through metal at elevated temperature, if the surface is clean and the surface reaction is sufficiently fast.

Hydrogen flux, J, is expressed for one dimensional flow by Fick's first law,

$$J = -D \cdot dC/dX \cdots\cdots (1).$$

D is the diffusion coefficient, characteristic of the gas metal system and the temperature, and dC/dX is the concentration gradient along the X-coordinate, which is normal to the surface of the membrane. For plane sheet diffusion it may be shown that the steady-state concentration gradient is a constant, independent of X. The gradient is then simply

$$dC/dX = (C_2 - C_1)/d \cdots\cdots (2)$$

in which C_1 and C_2 are the hydrogen concentration at the inlet and outlet surfaces, respectively, and d is the membrane thickness (Fig. 3). Then, J is simplified as below,

$$J = -D(C_2 - C_1)/d \cdots\cdots (3).$$

Between the hydrogen concentration C and the hydrogen solubility S, the next relationship is fulfilled by Sievert's law,

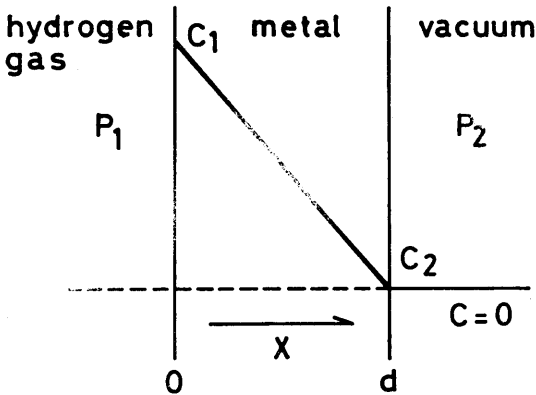**Fig. 3** Steady-state distribution of hydrogen atom in a plane sheet membrane.

$$C = S/\overline{p} \cdots\cdots (4),$$

where p is hydrogen pressure. Then,

$$J = -D \cdot S(/\overline{p_2} - /\overline{p_1})/d \cdots\cdots (5)$$

is obtained. When p_2 is maintained at nearly zero pressure,

$$J = D \cdot S/\overline{p_1}/d \cdots\cdots (6).$$

In this report, flux J is the permeability at 1 atmospheric pressure and 1 mm membrane thickness, consequently the permeability is expressed as follow,

$$P = D \cdot S \cdots\cdots (7).$$

For example, the hydrogen permeability through Ni at 700°C, measured in this experiment, was 1.7 cm³(NTP) mm/cm² hr $p^{1/2}$. This value was nearly equal to 1.1 cm³(NTP) mm/cm² hr $p^{1/2}$ calculated from equation (7), by adopting 0.58 cm³/cm³ [5] and 5.1 cm²/sec [10] as the solubility S and the diffusion coefficient D of hydrogen in Ni at 700°C, respectively. The relation of P=D·S is relatively fulfilled to the steadystate hydrogen permeation in which the diffusion step is determinative. Next, both D and S depend upon temperature through Arrhenius type relations of the form

$$D = D_0 \exp(-E_D/RT) \cdots\cdots (8)$$
$$S = S_0 \exp(-E_S/RT) \cdots\cdots (9)$$

where D_0 and S_0 are pre-exponential constants and E_D and E_S are the activation energy for diffusion and that for solution, respectively. Thus P will also have an Arrhenius type temperature dependence of the form

$$P = P_0 \exp(-E_P/RT) \cdots\cdots (10)$$

where

$$P_0 = D_0 \cdot S_0 \cdots\cdots (11)$$

and

$$E_P = E_D + E_S \cdots\cdots (12).$$

In all of these equations, R is the gas constant and T the absolute temperature.

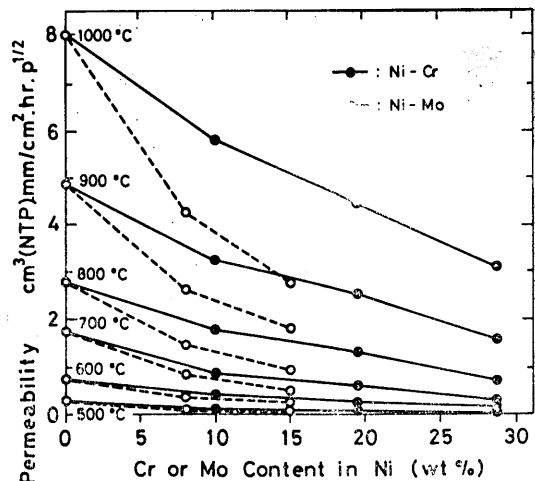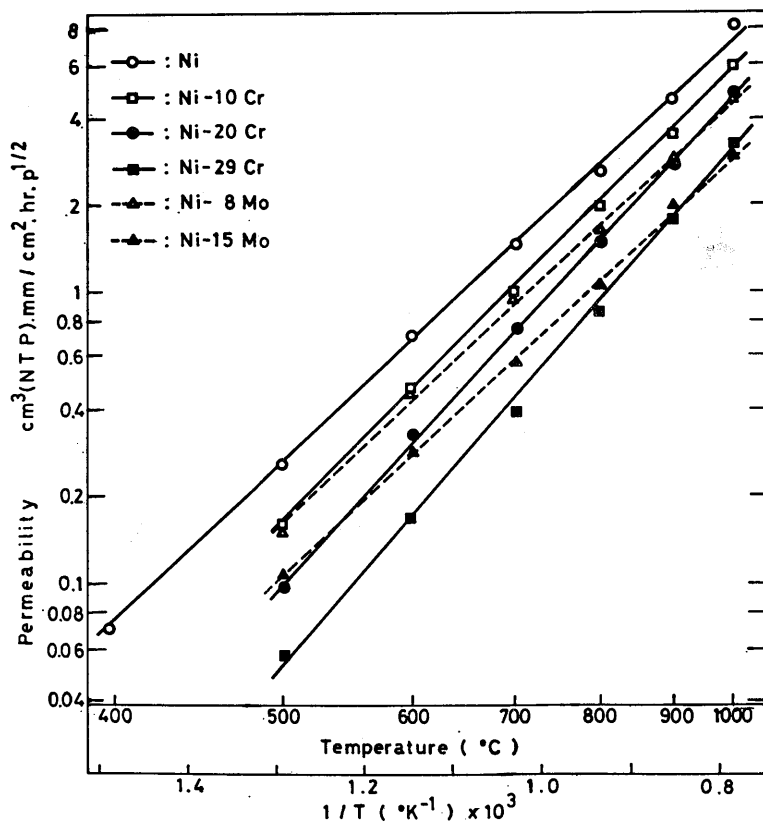Fig. 4 shows the results of hydrogen permeability, together with data for pure Ni, in the form of perme-

Fig. 4 Hydrogen permeability isotherms for Ni-Cr and Ni-Mo alloys.

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Table 2   Pre-exponential constant and activation energy for the hydrogen permeation, solution and diffusion in Ni, Ni-Cr and Ni-Mo alloys.

Metal and Alloys	$P=P_0\exp(-E_P/RT)$		$S=S_0\exp(-E_S/RT)$ **		$D=D_0\exp(-E_D/RT)$	
	P_0	E_P	S_0	E_S	D_0	E_D
	$\dfrac{cm^3\,(NTP)\,mm/}{cm^2\cdot hr\cdot p^{1/2}}$	kcal/mol	$\dfrac{cm^3\,(NTP)\,/}{100gr\ metal}$	kcal/mol	$(cm^2/sec)\times10^{-3}$	kcal/mol
Ni	1340^{+610}_{-500}	13.0 ± 0.5	$32.9^{+2.2}_{-2.0}$	3.09 ± 0.08	$12.7^{+8.5}_{-5.1}$	9.9 ± 0.6
Ni–10Cr	1610^{+360}_{-320}	14.6 ± 0.3	$28.6^{+1.1}_{-1.0}$	3.22 ± 0.08	$17.8^{+4.3}_{-3.8}$	11.4 ± 0.4
Ni–20Cr	1900^{+470}_{-410}	15.4 ± 0.3	$36.8^{+3.8}_{-3.4}$	3.89 ± 0.21	$16.6^{+5.9}_{-4.4}$	11.5 ± 0.5
Ni–29Cr	1680^{+600}_{-480}	16.5 ± 0.4	$34.1^{+4.7}_{-4.0}$	3.56 ± 0.27	$16.3^{+8.0}_{-5.3}$	12.9 ± 0.7
Ni–8Mo	860^{+530}_{-370}	13.7 ± 0.5	$24.6^{+2.5}_{-2.2}$	2.76 ± 0.20	$10.5^{+8.3}_{-4.5}$	10.9 ± 0.7
Ni–15Mo	560^{+180}_{-160}	13.7 ± 0.4	$20.7^{+3.0}_{-2.7}$	2.85 ± 0.30	$7.9^{+6.6}_{-3.6}$	10.9 ± 0.7
Ni*	868 ± 36	13.04 ± 0.05	33.4 ± 1.2	2.98 ± 0.06	6.44 ± 0.35	9.61 ± 0.06

* by W.M. Robertson[10]   **by K. Masui et al.[11]

Fig. 5   Hydrogen permeability in solid Ni, Ni-Cr and Ni-Mo alloys as a function of temperature.

ability isotherms. The permeability was monotonically decreased with an increase in the amount of Cr and Mo in Ni. **Fig. 5** shows the results plotted as a conventional Arrhenius type temperature relation. The parameter P_0 and E_P derived from each plot, with the 90 percent confidence intervals for each, is presented in **Table 2**. Student's t distribution was used for all statistical calculations. The present datum on the permeability of pure Ni is in relatively close agreement with that of W.M. Robertson [11], yielding the results $P_0 = 868 \pm 36$ cm³(NTP) mm/cm² hr $P^{1/2}$ and $E_P = 13.04 \pm 0.05$ kcal/mol for pure Ni. There appears to have been no previous studies made on austenitic Ni-Cr and Ni-Mo alloys. Recently the author had reported the hydrogen solubility in these binary alloys [12]. Those data are also cited in **Table 2**. As shown in equation (7), permeation data alone are of limited value; of more fundamental interest in various problems is the diffusion coefficient. Combining the above mentioned values P and S using equations (9), (10), (11) and (12), we can calculate D. The results obtained are also presented in **Table 2**. The result of hydrogen diffusivity in pure Ni is in good accord with that of W.M. Robertson [11], who gave $D = 6.44 \times 10^{-3}$ cm²/sec exp$(-9.61 \pm 0.06$ kcal/mol$)$/RT. **Fig. 6** re-

Fig. 7 Relationships between Cr or Mo content in Ni and the activation energy for hydrogen diffusion E_D (a), and the pre-exponential constant D_0 (b). The values of E_D and D_0 were calculated with the data of hydrogen permeability and those of hydrogen solubility.
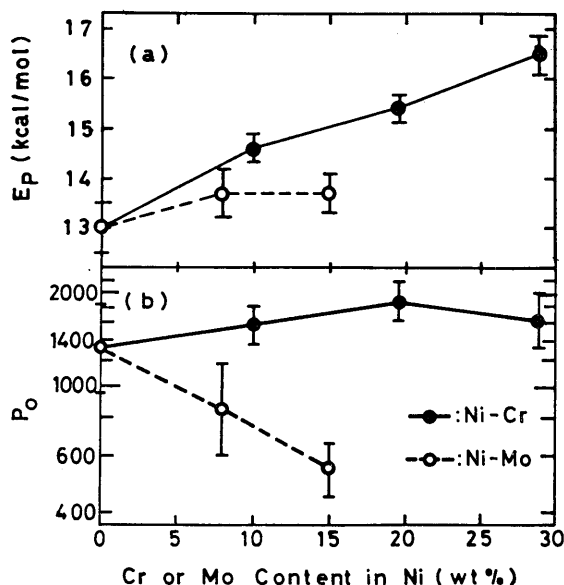

Fig. 6 Relationships between Cr or Mo content in Ni and the activation energy for hydrogen permeation E_P (a), and the pre-exponential constant P_0 (b).
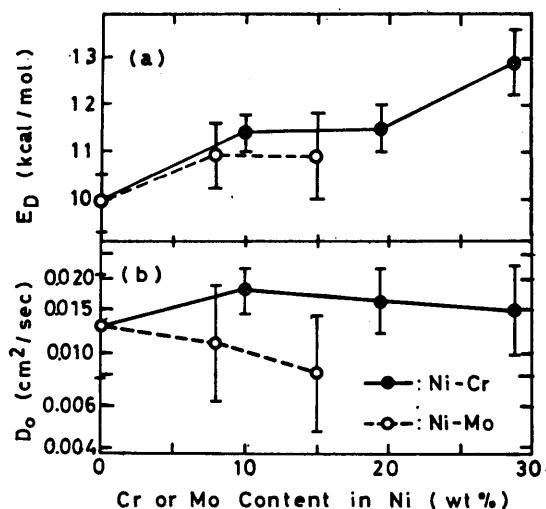
presents the relation between Cr or Mo content in Ni and the activation energy E_P and the pre-exponential constant P_0 for hydrogen permeation. With increasing Cr content in Ni, the activation energy for hydrogen permeation increases. On the other hand, it can be seen that the activation energy for hydrogen permeation is independent of Mo content in Ni. **Fig. 7** represents the relationships between Cr or Mo content in Ni and the activation energy E_D and the pre-exponential constant D_0 for hydrogen diffusion, calculated with the data of permeability and those of solubility. The activation energy of hydrogen diffusion increases with increasing Cr content in Ni. It is shown that the hydrogen permeability in these alloys is appreciably smaller than that for pure Ni. In the Ni-Cr alloys, this is due mainly to the reduced diffusivity of hydrogen in the alloy which can in turn be traced to the enhanced activation energy of diffusion $(12.9 \pm 0.7$ kcal/mol$)$ in Ni–29 wt%Cr alloy compared with 9.9 ± 0.6 kcal/mol for the activation energy of diffusion in pure Ni. In the Ni-Mo alloys, on the other hand, this is due mainly to the reduced solubility of hydrogen which can be traced to the lower pre-exponential constant of solution $(20.7 \pm 3.0$ cm³/100 gr metal$)$ in Ni-15wt%Mo alloy compared with 32.9 ± 2.2 cm³/100 gr

metal for the pre-exponential constant of hydrogen solution in pure Ni.

4. Summary

The permeation of hydrogen was measured in pure Ni, austenitic Ni-Cr and Ni-Mo alloys. Measurements were made of the functions of temperature changes in a range from 500 to 1000°C. The hydrogen permeability measured in pure Ni was in agreement with accepted published values. This agreement was taken to be proof of the suitability of the experimental procedure. The addition of Cr or Mo to Ni lowers the hydrogen permeability. In the concentration range investigated, Mo exerts the larger influence than Cr. In the Ni-Cr alloys, the permeation-retarding effect is due mainly to the reduced diffusivity of hydrogen in the alloys. On the other hand, this is due mainly to the reduced solubility of hydrogen in the Ni-Mo alloys.

Acknowledgement

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