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RESEARCH ON SURFACE PROPERTIES OF
Ni AND Ni-Se COATED Ni FILMS

(Part 1)

By

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The change of the work function of an evaporated Ni film due to the adsorption of H_2, to the treatment with Se, or to the Se treatment and the adsorption of H_2 or $H_2 +$ NH_3, has been measured quantitatively by means of the retarding potential method used in the study of thermoionic emission. The increase in work function of the Ni film was 0.1 eV when it adsorbed H_2, or $0.6 \sim 0.8$ eV when it was coated with NiSe; that of the NiSe-coated Ni film was $-0.1 \sim -0.2$ eV when it adsobred H_2.

Introduction

Horiuti[1], in his theory of the hydrogen electrode process and catalysis, has inferred that the intermediate state of hydrogen adsorbed on the surface of a hydrogen electrode or a metal catalyst is either $H_2^+(a)$ or $H(a)$ depending upon the magnitude of the work function of the electrode or the catalyst. Bosworth[2], on the other hand, has experimentally found that the work function of Ni was increased by 1.40 eV when it adsorbed O_2 because of the electronegativity of oxygen. In view of this consideration or observation, several workers in this Institute[3,4] have investigated on Ni catalysts coated with electronegative elements like sulphur or selenium, and suggested that the hydrogen intermediate on these coated catalysts is a H_2^+ ion.

In this research we have investigated on the change in work function of an evaporated Ni film due to the adsorption of H_2, to the treatment with Se, or to the treatment with Se and the adsorption of H_2. The change in work function of a NiSe-coated Ni film due to the

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1) J. Horiuti, this Journal 3, 52 (1954), and previous papers quoted there.
2) R. C. L. Bosworth, Trans. Faraday Soc. 35, 397 (1939).
3) T. Kwan et al., Shokubai (Catalyst), No. 1, pp. 5, 18, 28 and 99 (1946); No. 3, pp. 6 and 14 (1948), in Japanese.
4) A. Matsuda, Shokubai (Catalyst), No. 3, p. 1 (1948), in Japanese.

mixed adsorption of H_2 and NH_3 was also examined in connection with KANENO and ENOMOTO's experiment[5] on the temperature variation of the exchange rate between heavy ammonia and hydrogen on a NiSe-coated Ni catalyst, in which they found an abrupt change of the rate at 35°C.

I. Apparatus and Procedure

A. Measuring Cell (C).

In Fig. 1, a coiled pure tungsten wire (E) of 10.6 cm length and 0.15 mm diameter was mounted at the center of a hard glass cell of 3 cm radius, and served for an electron emitter. Ni film (N) of about 5000 Å thickness to serve for the electron collector was evaporated in
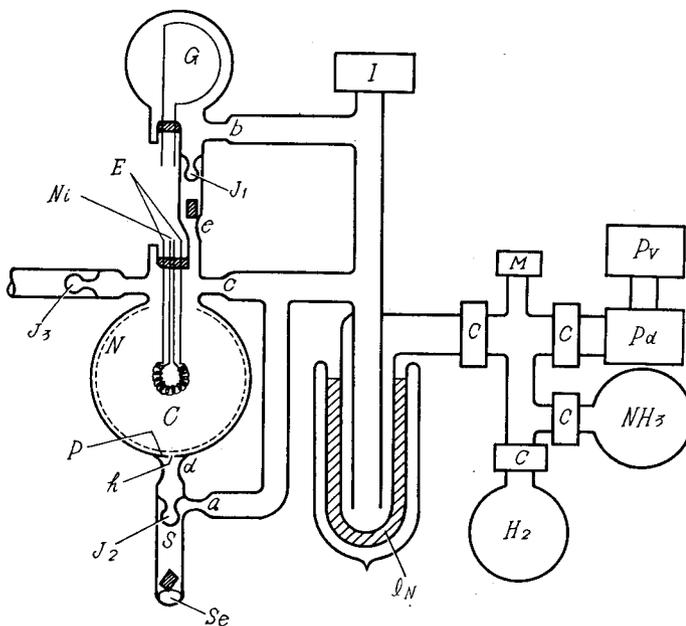

Fig. 1.

C : Measuring Cell J_1, J_2 and J_3 : Breakable joints
E : Electron Emitter l_N : Liquid N_2
N : Electron Collector   I : Ionization Gauge (Alpert type)
P : Pt Plate   c : Vacuum Tap
S : Se Container   M : Manometer
G : Getter Tube   Pd : Diffusion pump
a, b, c, d and e : Constrictions   Pv : Rotary pump

5) Y. KANEKO and S. ENOMOTO, Shokubai (Catalyst), No. 6, pp. 8 and 36 (1950); No. 7, p. 98 (1951), in Japanese.

vacuo onto the inner wall of the cell from a Ni wire (spectroscopically pure grade, previously treated in a hydrogen furnace) of 4 cm length and 0.25 mm diameter, the cell wall being kept at room temperature. Analytically pure Se powder (Kahlbaum) was sealed in a glass tube (S) at the bottom of the cell. A breakable joint (J_2) prevented the effusion of Se vapour into the cell. (P) was a thin Pt plate of 0.05 mm thickness having a pinhole (h) of 9.32×10^{-3} cm^2 area.

B. Vacuum System.

The vacuum system is shown in Fig. 1. In our experiment the cell was outgassed to about 10^{-7} mmHg pressure, and after flushing a barium getter in the side tube (G) by the Joule heat and sealing off the constrictions (a) and (b), Ni was evaporated onto the cell wall, while the emitter (E) was flashed at 2500°K for 30 seconds. The flashing of the emitter (E) to clean up its surface was indispensable for each measurement.

C. NiSe Coating.

In order to coat the Ni film with Se, (S) was immersed in a thermostat bath of liquid paraffin, and by breaking (J_2) Se vapour was allowed to effuse into the cell (C) through the pinhole (h). The temperature of (S) was kept at 470°K, the vapour pressure of Se being about 1.2×10^{-3} mmHg at this temperature. The number of Se molecules effusing through (h) is given by

$$1.59 \times 10^{19} \, pT^{-\frac{1}{2}} \text{ molecules per second,}$$

in which p and T are the pressure and absolute temperature of the Se vapour respectively, and a Se molecule is assumed to consist of six atoms. Since these Se molecules were to be deposited uniformly on the Ni film according to LAMBERT's cosine law, the thickness of the deposited Se in our experiment could be estimated geometrically. By the heat treatment at 200°C, the deposited Se reacted with Ni to form β-NiSe crystallites, and the surface of the Ni film was covered with a NiSe layer[*], a monomolecular layer of Se yielding a ten-molecular layer of β-NiSe.

D. Purification of Gases.

Electrolytically prepared hydrogen was purified by passing it through an electrically heated Pd tube and stored in a flask containing

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[*] MATSUI has studied the structure of this Se-treated Ni film with X-ray diffraction, electron diffraction and electron microscopy, and confirmed the formation of a layer of β-NiSe crystallites. T. MATSUI and K. AZUMA, "Catalyst", No. 10, p. 14 (1954), in Japanese.

Pt-black powder. Industrial ammonia, introduced into the vacuum system through traps of caustic potash and soda lime, was stored in a reservoir after several distillations.

E. Circuit.

The measuring circuit was similar to that used by Sano[6]; i. e., by heating the emitter pulsatively and observing the emission current only during cessations of the pulses, one could avoid the disturbances of electrostatic and magnetic fields due to the heating current[*]. In our experiment, the heating current was 1.300 ± 0.002 Amp and the temperature of the emitter (E) was kept at $1650 \pm 10°$K. No photoelectric emission from the collector (N) was observed in any measurement.

II. Results and Analysis of Experiments

The results of the measurements of the emission current *I versus* applied potential *V* characteristics are given in the following Table and Fig. 2.
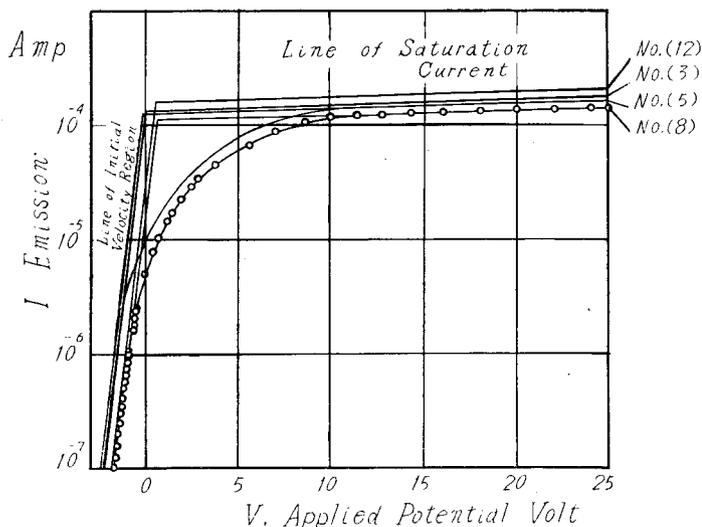

Fig. 2.

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[*] During the application of pulses the potential drop across a non-inductive resistance which was in series with the emitter, was applied negatively to the collector, so that the thermoionic current during the pulse was perfectly retarded and the effect of the heating current could be avoided.

6) S. Sano, "Denki-Tsushin-Gakkai Zasshi", April (1941), in Japanese.

TABLE   Results of Measurements

Measurement No.	Surface Condition	Emission Current I at 25 Volts (in 10^{-4} Amp)	(c. p. d.)$_{\varphi_e=\text{const.}}$ (in Volt)	(c.p.d.)$_{A=\text{const.}}$ (in Volt)
(1)	Ni	1.44	− 0.08	− 0.08
(2)	Ni	1.44	0	0
(3)	Ni+H₂	1.79	− 0.15	− 0.12
(4)	Ni	1.79	− 0.12	− 0.09
(5)	Ni	1.63	− 0.02	0
(6)	NiSe	1.63	− 0.61	− 0.59
(7)	NiSe	1.44	− 0.81	− 0.81
(8)	NiSe	1.44	− 0.70	− 0.70
(9)	NiSe	1.29	−0.71	− 0.73
(10)	NiSe+H₂	2.00	−0.62	− 0.57
(11)	NiSe+H₂+NH₃	1.81	− 0.54	− 0.51
(12)	NiSe+H₂+NH₃	2.09	− 0.64	− 0.59

Accuracy of $\varepsilon\varphi_e$ was ± 0.015 eV.

Theoretically the emission currents in the retarding and accelerating potential regions are

$$I = I_S \cdot \exp\left\{\varepsilon(V + V_{\text{c.p.d.}})/kT\right\} \qquad \text{for } V + V_{\text{c.p.d.}} \leqq 0 \qquad (1)$$

and

$$I = I_S \cdot \exp\, \alpha E^{\frac{1}{2}} \qquad \text{for } V \gg V_{\text{c.p.d.}}, \qquad (2)$$

where V is the applied potential, $V_{\text{c.p.d.}}$ the contact potential difference of the collector referred to the emitter, E the electric field on the emitter surface, and α, ε, k and T are the slope of SHOTTKY's line, the elementary charge, the BOLTZMANN constant and absolute temperature respectively. I_S is the saturation current expressed by the well-known expression

$$I_S = AT^2 \cdot \exp\left(-\varepsilon\varphi_e/kT\right) \qquad (3)$$

where A is the DUSHMAN constant, $\varepsilon\varphi_e$ the work function of the emitter.

But now, in our experiment, on account of the non-uniformity of the emitter surface, Eq. (1) of the I *vs.* V relation for $V + V_{\text{c.p.d.}} \leqq 0$ should be replaced by

$$I = I_n \cdot \exp\left\{\varepsilon\beta(V + V_{\text{c.p.d.}})/kT\right\}, \qquad (4)$$

or $$\log I = \log I_n + \frac{\varepsilon\beta}{kT}\,(V + V_{\text{c.p.d.}})\cdot\log\,e, \qquad\qquad (4')$$

where β is a factor due to the surface non-uniformity and was found to be 0.48 in this experiment.

For the accelerating potential region we used such an approximation that Eq. (2) was substituted by the tangent lines to the observed $\log I$ *vs.* V curves at the applied potential of 25 Volts. These lines as well as the tangent lines at $I=10^{-7}$ Amp were parallel to each other as shown in Fig. 2. We shall call, for the time being, the former lines "lines of saturation current", and also call the latter lines "lines of the initial velocity region". Then I_n of Eq. (4) is determined by the intersect of the line of initial velocity region with the line of saturation current at $V=V_n$ for the observation No. (n).

From Eq. (4'), we obtain the relation

$$V_n + V_{n,\ \text{c.p.d.}} = 0 \qquad\qquad (5)$$

when $I=I_n$ for the observation No. (n), then we get the following relation between the measurements No. (l) and No. (m)

$$V_l + V_{l,\ \text{c.p.d.}} = V_m + V_{m,\ \text{c.p.d.}}\ ,$$

or $$V_{l,\ \text{c.p.d.}} - V_{m,\ \text{c.p.d.}} = -(V_l - V_m)\,. \qquad\qquad (6).$$

Since $V_{l,\ \text{c.p.d.}} = \varphi_{e,l} - \varphi_{c,l}$ and $V_{m,\ \text{c.p.d.}} = \varphi_{e,m} - \varphi_{c,m}$,
where $\varepsilon\varphi_c$ represents the work function of the collector,

$$\varphi_{c,l} - \varphi_{c,m} = (V_l - V_m) + (\varphi_{e,l} - \varphi_{e,m})\,. \qquad\qquad (7).$$

In Eq. (7), $\varphi_{c,l} - \varphi_{c,m}$ is the contact potential difference, (c.p.d.), of the collector of No. (m) referred to that of No. (l).

The disagreement of the lines of saturation current shown in Fig. 2 is due to the fluctuation of the work function of the emitter and/or the DUSHMAN constant. If we assume $\varphi_{e,l} = \varphi_{e,m}$, then $(\text{c.p.d.})_{\varphi_e=\text{const.}} = (\varphi_{c,l} - \varphi_{c,m})_{\varphi_e=\text{const.}} = V_l - V_m$. When $\varphi_{e,l} \neq \varphi_{e,m}$, on the other hand, the difference of $\varphi_{e,l}$ and $\varphi_{e,m}$ can be determined from Eq. (3) with an assumption that $A_l = A_m$, and $(\text{c.p.d.})_{A=\text{const.}} = (\varphi_{c,l} - \varphi_{c,m})_{A=\text{const.}}$ is obtained. In the Table, $(\text{c.p.d.})_{\varphi_e=\text{const.}}$ and $(\text{c.p.d})_{A=\text{const.}}$ are shown referred to the collector of the measurement No. (2).

In the following will be explained the procedure of the sequence of measurements in the Table. The measurement No. (1) was made immediately after the deposition of evaporated Ni, and No. (2) 10 hours

later. Then hydrogen of 4.2 cmHg was introduced into the measuring cell (C) through a liquid nitrogen trap, and after standing for 3 hours the hydrogen was pumped out. At the final stage of outgassing, (C) was heated for several minutes at 100~120°C, then the measurement No. (3) was made. No. (4) was measured after leaving the cell at 300°C for half an hour. Then the constriction (c) was sealed off, the joint (J₁) was broken, and after heating the cell at 300°C for several minutes, No. (5) was carried out. The joint (J₂) was opened and Se was effused into the cell through (J₂) from the Se-container (S) until Se deposited on the Ni film (N) forms a seven-molecular layer. After heating the Se-coated Ni at 200~250°C for 10 minutes, No. (6) was carried out. After further deposition of Se to form an about 60-molecular layer and heat-treatment at 200~250°C for 10 minutes, No. (7) was carried out. Sealing off the constriction (d) to take away the Se-container (S), No. (8) was carried out after heat-treatment at 200~250°C for half an hour. After sealing off the constriction (e) and connecting (C) with the vacuum line through (J₃) again, No. (9) was carried out. Then hydrogen of 2.6 cmHg was introduced into (C) and after the same process as in the case of No. (3), the results of No. (10) were obtained. Then the Dewar vessel of liquid nitrogen was removed from the trap, NH₃ of 1.5 cmHg was introduced into the cell (C), and after standing for 2 hours, (C) was immersed in a thermostat bath of 42°C. After evacuating (C) quickly and immersing the trap in liquid nitrogen again, the measurement No. (11) was made[*]. Finally, descending the temperature of the bath to 16°C, No. (12) was carried out.

III. Discussion

Since our experiment has been carried out at the residual pressure of about 10^{-7} mmHg, it was perhaps impossible to get an clean Ni surface without contamination. Considering the experimental conditions, we preferred the surface of No. (2) or No. (5) to that of No. (1) or No. (4) as a "bare" Ni surface. From the results of No. (1) to No. (5), we can conclude that hydrogen is adsorbed on the Ni film with slightly negative charge[7),8)] at 60°C.

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[*] The measurements No. (1) to (10) were carried out at room temperature without a thermostat, and under these circumstances the temperature of the wall of the cell (C) was maintained at about 60°C by radient heat from the filament (E).

7) J. C. P. MIGNOLET, Discussions of Faraday Soc. No. 8, 105 (1950).

8) I. OGAWA, et al., "Ōyo Buturi" **22**, 101 (1952), in Japanese.

The increment of the work function of the NiSe-coated Ni was about 0.2 eV when the thickness of the NiSe layer was increased from 70- to 500-molecular. We can understand this result qualitatively by the barrier theory[9] for the interface between a *p*-type semicondctor and a metal[*].

The smaller value of the work function of No. (8) than that of No. (7) may be explained by the decrease of the acceptor levels by the reaction of excess Se with Ni due to the heat treatment. Anyway, by coating Ni with NiSe its work function increased by 0.7 eV. Adding this value to that of Ni, i. e. 4.62 eV by WAHLIN's experiment[10], we obtain 5.3 eV for the work function of NiSe.

Since the work function of the NiSe-coated Ni film decreased by about 0.1 eV when hydrogen was adsorbed, it is inferred that hydrogen molecules are adsorbed with positive charge. The work function of the NiSe-coated Ni film adsorbing H_2 and NH_3 was larger at lower temperature 16°C than at higher temperature 42°C. However, the determination of the changes in work function due to the adsorption of such a polar molecule as NH_3 by means of the thermoionic emission method is not conclusive. Further studies on the changes in work function of a NiSe-coated Ni film by the adsorptions of H_2 and NH_3 by means of KELVIN's method[11] will be reported in part II.

9) H. C. TORREY and C. A. WHITMER, "Crystal Rectifiers" (1948).
*) Since NiSe is a *p*-type semiconductor whose work function is larger than that of Ni and the NiSe layer is very thin, its acceptor levels are almost filled up and a negative space charge layer is formed in the NiSe layer when it is brought into contact with Ni. On account of this negative space charge layer, the work function of NiSe-coated Ni becomes larger as the NiSe layer grows thicker, until the thickness reaches several hundred Angstroms and the formation of the space charge layer is completed.
10) H. B. WAHLIN, Phys. Rev. **61**, 509 (1942).
11) H. PALEVSKY, R. K. SWANK and R. GRENCHIK, Rev. Sci. Instr. **18**, 298 (1947).