Sorption of Gases on Evaporated Nickel Films. I. Sorption of Oxygen

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Although the sorption of oxygen by evaporated metal films has been studied by various authors[1,2,3,4] there appears some discrepancies in the present view on the sorption mechanism and the structure of evaporated metal films.

The present work was undertaken to understand the behaviour of oxygen adsorbed on the surface more clearly and to examine the applicability of the Cabrera-Mott's theory of oxidation[5] for evaporated metal films.

Experimental

The rate of sorption was measured by a constant-volume method, employing slight modification of the apparatus used by Rideal and Trapnell[3]. A sensitive Pirani gauge and a McLeod gauge were used to measure the pressure ranging from 10^{-6} to 10^{-2} mmHg.

A U-shaped pure nickel filament 0.5 mm. in diameter and 11 cm. long was spot-welded to stem leads and sealed in a vacuum tube. Evacuating the system, the nickel filament was evaporated onto the inner wall of the bulb.

After the bulb was backed for 4 hrs. or longer, the trap was cooled with liquid oxygen and the filament was outgassed at about 1000°C. for half an hr. or longer. Immersing the bulb in melting ice, filament temperature was raised to 1300°C. and maintained at that temperature for a desired period with control of heating current. Since the film thus prepared on the wall of the bulb was unstable, it was kept at 0°C in vacuum for 20 min. before the gas was admitted. Electron diffraction study[6] showed that the films thus prepared consist of fine crystallites with their (110) planes slightly orientating parallel to the base.

The weight of the film was finally determined by weighing the bulb before and after the dissolution of the film.

In measuring the change of electrical resistance of the film in the course of sorption, the test tube described elsewhere[7] was attached to the adsorption apparatus.

Results and Discussions

Although the reaction temperatures were 0°, −78° and −183°C., the sorptions of oxygen were unchanged substantially and found to consist of two stages, i.e., an initial rapid process and a subsequent slow process.

(1) On admitting a known amount of gas to a clean film, a number of increments were consumed at the same very rapid rate and reached an equilibrium pressure of 10^{-6} mmHg. within 5 min.

(2) Subsequent increments were consumed at successively decreasing rate.

A typical example of these uptakes with a film at 0°C. is shown in Fig. 1, where the first fifteen increments are the rapid process, after which the rate of uptake falls with the number of increment.

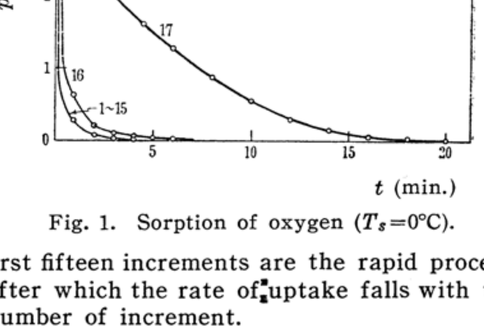

Fig. 1. Sorption of oxygen (T_s=0°C).

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1) O. Beeck, A. E. Smith and A. Wheeler, *Proc. Roy. Soc.*, (A) **177**, 64 (1941); O. Beeck, "Advances in Catalysis" II, Academic Press, New York (1950), p. 151.

2) J. A. Allen and J. W. Mitchel, *Disc. Farad. Soc.*, no. 8, 309 (1550).

3) E. K. Rideal and B. M. W. Trapnell, *Proc. Roy. Soc.*, (A)**205**, 409 (1951).

4) W. Scheuble, *Z. f. Phys.*, **135**, 125 (1953).

5) N. Cabrera and N. F. Mott, *Reports on Progress in Physics*. Vol. XII, 163 (1949).

6) K. Ono and Z. Oda, unpublished.

7) Z. Oda, *Ōyōbutsuri* (*J. Appl. Phys., Japan*), **22**, 142 (1953).

TABLE I

RAPID SORPTION OF OXYGEN

Evap. time	Evap. amount[1]	Sorpt. temp.	No. of Ni atom	No. of sorbed O atom	Ni/O atomic ratio
min.	mg.	°C.			
30	7.1	0	7.34×10^{19}	4.44×10^{18}	16.5
30	6.7	0	6.91	4.58	15.1
45	8.4	0	8.67	5.34	16.2
15	2.7	0	2.79	2.36	11.8
30	5.3	−183	5.47	2.96	18.5
		0		4.66	11.7
30	6.3	0	6.51	4.56	14.4
30	6.2	−183	6.92	3.32	20.8
		0		5.08	13.6
30	5.3	0	5.47	2.70	20.3
30	4.2	0	4.34	2.20	19.7
30	8.1	0	8.36	4.72	17.7
30	11.2	−78	11.56	4.46	25.9
		0		5.32	21.7
30	11.0	−78	11.36	4.38	25.9
30	8.8	0	9.09	1.50	60.6(2)
30	5.6	−183	5.78	2.78	20.8
30	6.4	−183	6.61	3.70	17.8

1) The average thickness of film is 141Å/mg. using the bulk density of nickel.

2) run 22, which has been pre-sintered at 240°C. for 30 min.

I. Rapid Process

Sorption amount.—The amount of oxygen sorbed in this stage is given with that of nickel deposited in Table I, where allowance is made for the amount adsorbed by nickel filament. It is noticed that the amount sorbed at −78° and −183°C. were 85 and 60% as much as that at 0°C. respectively. Comparing the mean thickness of film and the corresponding atomic ratio of deposited nickel to sorbed oxygen (Ni/O), it is supposed that the oxygen would penetrate into the film as deep as 40 to 60 Å at this initial stage, if the film had a compact structure without any pores or cracks. However, this does not seem to be the case according to the data of Beeck.[1] The atomic ratio (Ni/O) at 0°C. sorption increases with the deposit, i.e., the oxygen sorbing capacity per unit weight of nickel decreases with increase of the deposit in these experimental regions. In run 22, in which the film was pre-sintered at 240°C. for 30 min. before gas admission, this ratio is about 60 and the sorbed amount is about 1/3 of that of the non-heat-treated films. Electron diffraction study[6] has suggested that the nickel film consists of fine crystallites which grow larger with film thickness and heat-treatment.

From these results, it is reasonable to explain the sorption process of oxygen on the basis of granular structure of film. If this is the case, oxygen will penetrate into the grain boundary at the rapid process and further diffuse in the crystallites with oxidation.

Low-temperature-adsorption of nitrogen.—As has been reported previously, the adsorption of nitrogen at −183°C. on the nickel film shows saturation at a pressure of 2×10^{-2} mmHg or higher. Comparing the number of nitrogen melecules sorbed at this saturation region with that of oxygen rapidly sorbed at −183°C. in Table II, the ratio O_2/N_2 is found to be about 6. According to Beeck, one molecule of nitrogen can occupy two surface atoms of nickel. If this relation is applied to the present case, three oxygen molecules will correspond to one surface atom of nickel, so that it is reasonable to expect that even at the temperature of −183°C. oxygen can penetrate into the interior of crystallites to some extent.

TABLE II

SORPTION AMOUNT OF O_2 AND N_2 AT −183°C.

Expt. No.	O_2 sorbed at rapid process moles/10 mg. Ni $\times10^{17}$	N_2 saturation adsorption moles/10 mg. Ni $\times10^{17}$
7	29.05	
9	27.98	
24	24.82	
15		5.20
23		4.06
mean	27.66	4.63

Changes of electrical resistance.—It was also expected that the measurement of electrical resistance of film under sorption could furnish considerable insight into the behaviour of sorbed oxygen. After newly prepared film had been stabilized[8] to some extent, a known amount of gas was admitted and changes of gas pressure and film resistance were recorded

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[8] This stabilization process of evaporated nickel films was discussed in detail in ref. (7).

with time. Data obtained at 0° and −183°C. are shown in Figs. 2 and 3, respectively. It should be noticed that similar changes of resistance are observed with sorption at both temperatures.

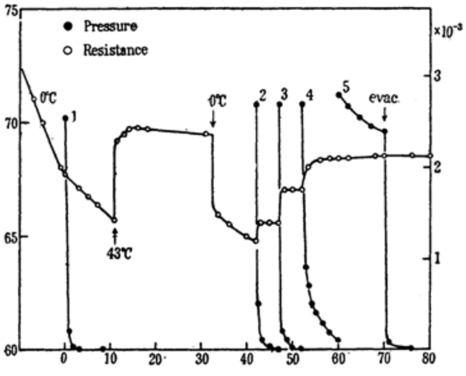

Fig. 2. Changes of electrical resistance with sorption (T_s=0°C)

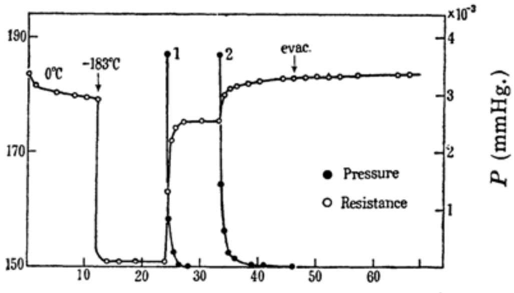

Fig. 3. Changes of electrical resistance with sorption (T_s=−183°C)

On the other hand, adsorption of nitrogen and carbon monoxide which is considered to be chemisorbed on the surface gives rise to the increase of resistance within 1% and tend to restore its original value with desorption in the case of the former. Hence, the larger irreversible changes in resistance caused by oxygen uptake appear to account for the fact that oxidation proceeds even at −183°C. in the rapid process.

Estimation of thickness of oxide layer.—It is now possible to estimate the thickness of oxide layer formed in the rapid process at 0°C. from the data shown in Table I and electron diffraction patterns. The values calculated on suitable assumptions[9] are 5 Å and 4.5 A for thicker and thinner films, respectively. These values correspond to approximately 2 layers[10] of nickel atom. However, owing to the variety in size and mutual contact in actual films the effective surface of crystallite is supposed to be reduced and the oxide layer may correspondingly become thicker than ca. 10 Å.

II. Slow Process in Room-Temperature-Sorption

Pressure and temperature dependency of sorption rate.—Reducing the pressure stepwisely on the way of slow sorption, the rate of uptake also falls with pressure. Evaluating the rate of uptake $r_s\left(=-\frac{dp}{dt}\right)$ for each pressure range and plotting log r_s against log p, a straight line is obtained for each run. From the slope of these lines, the rate is well expressed as a function of pressure by the equation

$$-\frac{dp}{dt}=kp^{1/2}, \tag{1}$$

where k is a constant. Integration of Eq. (1) gives

$$p^{1/2}=\text{const.}-kt/2, \tag{2}$$

which represents a linear relation between $\sqrt{p}$ and t. In fact, as shown in Fig. 4, the data give a good agreement with Eq. (2) except for those in an early stage. Since the above rate versus pressure relationship inplies the sorption sites to be kept constant in course of one increment, it is naturally anticipated that deviations from linearity are observed at the early stage where the decrease

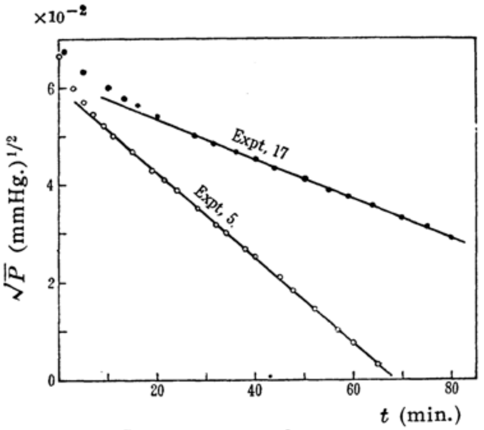

Fig. 4. Square root of pressure versus time (T_s=0°C)

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[9] The following assumptions are made: (1) all crystallites composing a film are spheres of uniform size and their surfaces are entirely available for sorption. (2) Oxide layer has a composition of 1:1 atomic ratio and extends from surface to interior concentrically in each crystallite. From Table I O/Ni is given to be 1/20 for thicker films. Hence, atomic ratio of reacted metal to total one is given by

$$\frac{4/3\pi\{r_0^3-(r_0-r_1)^3\}}{4/3\pi r_0^3}=\frac{1}{20}$$

where r_0 and r_1 are the radius of original crystallite and the thickness of reacted layer, respectively. We set r_0=250 Å the magnitude roughly estimated from electron diffraction patterns. For thinner films, one may set O/Ni=1/12 and r_0=150 Å.

[10] Estimated from distance between (110) planes (2.48 Å).

of sites is appreciable. Eq. (2) suggests that the dissociation of adsorbed molecules must take place faster than the migration of atoms, and so the dissociation is not a rate-determining step.

To obtain the activation energy E from the measured sorption rate itself, sorption rates were measured with a single film by changing the bulb temperature stepwise without changing the other surface characters, and k was obtained from a stepwise $\sqrt{p}$ versus t plot. Temperature-dependency of the rate constant k in Eq. (2) is then given by

$$k = k_0 \exp(-E/RT),$$

Hence, by plotting log k against $1/T$ for each experiment, an activation energy of 12.6 ±1 kcal/mol. is obtained as a mean of three experiments.

Recovery of bare metallic surfaces.—The rapid sorption can be observed again by the film which has taken up sufficient gas to show no more rapid uptake, if it is kept in high vacuum at higher temperature than of sorption, but if the film is allowed to be evacuated at 0°C. one finds no such rapid sorption to recover. A few examples are shown in Fig. 5. The cause is considered to be a recovery of bare metallic surfaces due to either the desorption of gas already sorbed or diffusion of metal ions through oxide layers or both. Since there is found no further liberation of gases in the closed system by raising the temperature, this recovery may be attributed to the latter mechanism.

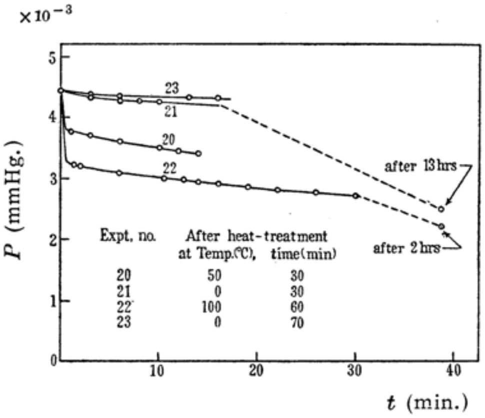

Fig. 5. Effects of heat-treatment on sorption in slow process ($T_s = 0°C$)

From the above results, the most probable rate-determining step in this slow process is concluded to be the migration of metal ions to the oxygen atoms adsorbed on the oxide surface.

III. Slow Process in Low-Temperature-Sorption

Pressure dependency of sorption rate.—From the sorption rate versus pressure relationship obtained by the same method as described above, the rate of sorption at this temperature is expressed approximately by

$$-\frac{dp}{dt} = k'p, \tag{3}$$

where k' is a constant. That is, the linear rate law can be applied to the present case.

Desorption and recovery of bare metallic surfaces.—When the temperature is raised to 0°C., rapid sorption occurs again after instantaneous desorption. However, this desorbed amount is far smaller for the case where the system is previously evacuated to 10^{-6} mmHg at $-183°C$. (1.55×10^{-3} mmHg$-$l.). than for the case without evacuation (5.55×10^{-3} mmHg$-$l.). As shown in Fig. 6, if the sorption is stopped for half an hr. by evacuating the gas (Curve 13), the supplementary admission of gas (Curve 14) is attended with a more rapid uptake than that of curve 13 which has not been kept in high vacuum. In addition, when the bulb temperature is raised to 0°C. in high vacuum (point c) and allowed to stand for 25 min., subsequent admissions (Curves 15 and 16) at $-183°C$. are consumed at a rate as rapid as by the initial fresh film. These facts suggest that there occurs such a weak sorption at $-183°C$. that sorbed gas can be easily liberated even by low temperature evacuation. Therefore, the recovery of bare metallic surfaces observed in this figure is considered to be due to both the desorption and the enhancement of metal ion diffusion through oxide layers by raising the temperature.

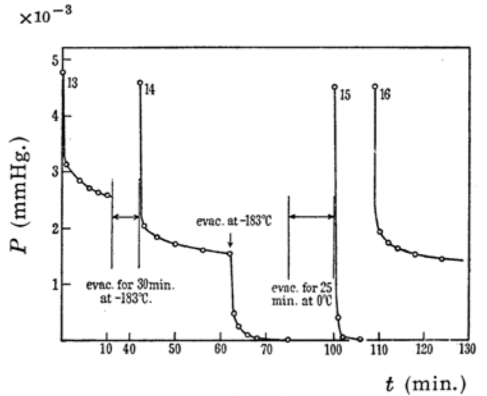

Fig. 6.
Effects of evacuation and temperature raising on sorption rate ($T_s = -183°C$)

Consequently, it is reasonable to consider that in the slow process of low-temperature-sorption, molecular adsorption takes place on the surface of oxide layers which have already formed at the rapid process, and then these adsorbed molecules slowly dissociate to form oxide layers. The rate-determining step in this process may thus refer to either the adsorption of molecules or the dissociation of adsorbed molecules on the oxide surfaces.

IV. Considerations on the Basis of the Cabrera-Mott's Theory of Oxidation

As noticed above, oxygen can be taken up very rapidly with an almost constant rate in the initial stage of oxidation, but the rate falls abruptly after the oxide layer thickens to ca. 10 Å. Following the Cabrera-Mott's theory, the rate of formation of such a very thin oxide layer is given by

$$dx/dt = A \exp.(X_1/X - W/kT), \qquad (4)$$

where $X_1 = naV/kT$, a is the width of potential barrier between metal and oxide, V is the contact potential difference between metal and adsorbed layer, W is the energy required for a metal ion to migrate from a metal point to a vacant lattice point of oxide, A is a constant related only to the state of metal surface and the size of oxide, and k and T have the usual meanings.

If the oxide layer is very thin, i.e., $X \ll X_1$, the term X_1/X related to the strength of electrical field caused by shift of electron from metal to oxide is comparable to the term W/kT and so the apparent energy of activation becomes smaller. Therefore, in this stage the sorption which gives rise to the formation of vacant cation sites on the oxide surface is very much accelerated. While the rate of sorption is very rapid and appears to be almost independent of temperature, the amount rapidly sorbed is found to decrease as the temperature becomes lower. This is also explained by Eq. (4) as due to the fact that on account of predominance of W/kT to X_1/X with increasing X, the rapid process goes over into a slow one at smaller value of X with lowering the temperature.

In the slow process at room temperatures, the apparent energy of activation E is given by 12.6 kcal/mol. (0.57eV.), which must be represented from Eq. (4) by the following relation,

$$W - naV/X = E. \qquad (5)$$

Although the value of W for nickel has not been known, Cabrera and Mott have given 1.8 and 1.1 eV. for aluminum and copper, respectively. In the present case, also, the value of W is expected to be of the order of 1 eV. Hence, it is found that the field-dependent term naV/X has a large influence on the migration of metal ions even in the slow process.

Summary

While the sorptions of oxygen on the evaporated nickel films are very fast at the early stage and become slow at the later independently of the temperature, oxygen is supposed to invade the interior even at the early stage of sorption. On the other hand, at the later stage the rate-determining step of low-temperature-sorption is different from that of room-temperature-sorption.

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