A STUDY OF THE OXIDATION MECHANISM OF NICKEL AROUND THE CURIE POINT

by

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B. S., McPherson College, 1951

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1954

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INTRODUCTION

A study of the oxidation rates of a metal may yield information about the oxide structure, diffusion processes within the oxide, and utilization of the metal or oxygen ions bordering the oxide. For oxides in which the ratio of the volume of a unit cell of the metal oxide to the volume of a unit cell of the metal is less than unity, the oxide formed on the metal is usually a porous, non-protective coating which grows linearly with time (31). If the ratio is greater than unity, the oxide forms a protective coating on the metal, and in most of these cases the oxide growth is limited by a process of diffusion of ions and electrons through the oxide (32, 19, 10, 27). According to Frank and Van der Merwe (Mott (27)) the dividing line between the two oxide types occurs when a metal to oxide volume ratio lies not exactly at unity, but between 0.85 and 1.15. Oxide growths limited by diffusion obey a parabolic relation between the oxide thickness and time. Within an approximate temperature range between 360 and 410°C, the thickness is proportional to the square root of the time of oxidation. There is, in addition, a variation in growth rate with temperature and an anomalous thickness-time relationship if the temperature is near that of transition from the ferromagnetic to paramagnetic state in iron, nickel, and cobalt. Cardwell (6, 7) has shown that an anomalous behavior exists in the thermionic and photoelectric emission of electrons from nickel and iron in the region of the Curie Temperatures. Lustman (21) and Rideal and Wansborough-Jones (31) have each suggested the possibility of an oxide growth dependent to some extent upon the activity of a surface and the ease of electron emission. This leads to the study presented here: a redetermination of the oxidation rates of nickel at temperatures between 300 and 700 degrees Centigrade, and especially in the Curie region of 350 to 360°C.

A number of workers have considered this nickel oxidation problem (30, 8, 34, 24). The majority have observed a parabolic rate for the oxidation of nickel at temperatures between 400 and 1000 degrees Centigrade. Many of the methods used to study oxidation rates were awkward, inaccurate, and limited by doubtful assumptions. More and Lee (24), and Dunn (9) used volumetric methods to follow the rate of oxygen uptake at constant pressure. Others (19) used electrometric methods, recording varied resistance or electronic emmission of the sample. Bardeen, Brattain, and Shockley (2) used a radioactive tracer method to study the oxidation of copper and verified the theoretical approach made by Wagner (35). Wagner based his ideas, to be discussed later in this paper, on a limited gravimetric method in which the sample was alternately oxidized and weighed (34). The most direct and accurate approach to oxidation rate studies is the method used by Gulbransen (15), in which a vacuum microbalance allows continual observation of weight change during the oxidation. The microbalance and apparatus used in this study were constructed by W. G. Wilson after that described by Gulbransen. The sensitivity of the method is sufficient to give reliable data even at the slow oxidation rates which occur below the Curie temperature of nickel.

PRELIMINARY STUDY

Metal oxides may be divided roughly into four classes (33, 27, 3, 4, 31): 1. thick, porous, non-protective films which grow linearly with time; 2. "thick", protective films which obey a parabolic or logarithmic rate law; 3. thin, highly protective films which reach a maximum thickness in a comparatively short time; and 4. rare oxides such as platinum oxide which do not form a film upon the parent metal.

The first type of metal oxides mentioned has a ratio of oxide volume to corresponding metal volume of less than one (33), which indicates a porous, irregular nature of the oxide film. This also explains the linear growth rate when it is considered that the growth of the oxide is limited by the availability of either the oxygen or the metal ions, there being no concentration gradient of either constituent throughout the oxide. Examples of metals which form oxides of this type are lithium, sodium, calcium, barium and others in which the oxide to metal volume ratio varies from 0.57 for lithium to 0.71 for barium (33).

For the second type of oxide films, an oxide to metal volume ratio greater than one causes a protective, essentially non-porous oxide to form. The rate of growth of the oxide is dependent upon a diffusion process through the oxide, provided that there is sufficient oxygen available surrounding the metal (25, 28). Diffusion may take place as the result of the solubility of either (a) metal ions or (b) oxygen ions in the oxide. In these cases the oxide will either possess a concentration gradient of (a) metal ions or (b) vacant metal ion sites extending throughout the oxide from the oxygen interface to the metal interface, respectively (26, 27, 33, 3, 12, 2). Case (a) is exemplified by a "reduction semi-conductor" oxide such as zinc oxide or aluminum oxide and case (b) is applicable to an "oxidation semi-conductor" oxide such as cuprous oxide. Electrons considered in these cases may pass through the oxide layer by thermionic emission, by the motion of positive electron holes (electrons missing from the uppermost filled band), or by the quantum mechanical tunnel effect (26). It is expedient here to cite a review of Wagner's assumptions in dealing with the theory of the formation of Cu_2O

as stated by Bardeen, Brattain, and Shockley (2):

> (a)-The lattice defects in Cu_2O are vacant sites ordinarily occupied by Cu^+ ions (Shottky defects). These vacant sites have an effective negative charge of one electron.
>
> (b)-Electrical neutrality is maintained by an equivalent number of positive electron holes. These electron holes are responsible for the electrical conductivity of Cu_2O.
>
> (c)-The electron holes and vacant sites are completely dissociated at temperatures of the order of 1000 degrees C.—
>
> (d)-The equilibrium number of vacant sites depends on the pressure of the oxygen gas in contact with the oxide. The concentration in equilibrium with metallic copper is small. During oxidation there is a concentration gradient of vacant Cu^+ sites extending from the oxide-oxygen interface to the metal.
>
> (e)- The oxide is formed at the oxide-oxygen interface, the Cu^+ ions arrive by diffusion through the oxide from the metal.
>
> (f)-The mechanism of diffusion of the Cu^+ ions is by motion of vacant Cu^+ sites from the oxide-oxygen interface to the metal.
>
> (g)-Electrical neutrality is maintained by an equal current of positive electron holes from the oxide-oxygen interface to the metal.

These assumptions by Wagner on the formation of Cu_2O are valid (26, 2) for the case of the oxidation of nickel, and form a basis for the work set forth in this paper. The following theory is reviewed from the work of Mott (25 to 29).

Let n_i and n_e denote the concentration of ions and electrons or of positive holes and vacant lattice points. The consideration here is only for films of thickness less than a critical thickness x_c, the thickness at which the space charges, set up when $n_i \neq n_e$, become important in controlling the diffusion process. Mott (26) has shown that $x_c = \sqrt{kT/4\pi ne^2} \cong 3 \times 10^{-5}$ cm. Let ϕ denote the work required to bring an electron from the metal into the oxide, and W denote the work required to bring a positive ion from the metal to an interstitial position in the oxide. Then for films of thickness less than x_c the following discussion holds true.

For the case where $\phi < W$, it is easier to bring electrons than ions into the oxide from the metal, and so there will be a uniform concentration of electrons in the oxide and a concentration gradient of ions. Let n (x) be the number of ions per unit volume at a distance x from the metal-oxide interface. The ion flux density will then be

$$j = - \frac{\partial n}{\partial x} D_i \qquad \text{——1}$$

where D_i represents the diffusion coefficient of the ions. It may be assumed that n varies only with x, hence this expression may be integrated with limits of $n = 0$ at the oxide-oxygen interface and $n = n_o$ at the metal-oxide interface. n_o is the concentration of the ions in the oxide in equilibrium with the metal and is given by

$$n_o = N e^{-W/kT}$$

where N is the number of interstitial positions per unit volume of the oxide. Thus, when a concentration gradient of ions exists in the oxide,

$$j = n_o D_i / x \quad . \qquad \text{——2}$$

Now the rate of growth of the oxide is

$$\frac{dx}{dt} = j \Omega \qquad \text{——3}$$

where Ω is the volume of oxide per metal ion. On combining equations 2 and 3, it is seen that

$$\frac{dx}{dt} = \frac{n_o \Omega D_i}{x}$$

which integrates to

$$x^2 = K_i t \qquad \text{where } K_i = 2\, n_o \Omega D_i. \qquad \text{——}4$$

Thus, a parabolic law holds for films of thickness less than the critical thickness x_c and where $\phi < W$.

Consider the film of thickness greater than x_c, for which again $\phi < W$. If F is the electric field intensity in the film, the current j_e carried by the electrons is

$$j_e = -D_e \frac{\partial n_e}{\partial x} + F\, n_e v_e$$

and the current carried by the ions

$$j_i = -D_i \frac{\partial n_i}{\partial x} - F\, n_i v_i$$

where v denotes the electron's or ion's mobility. In a steady state these currents are equal and opposite, and the ratio $\frac{D_e}{v_e} = \frac{D_i}{v_i} = \frac{D}{v}$ = a constant. Thus it is seen on eliminating F between the two equations,

$$j \left[\frac{1}{n_e v_e} + \frac{1}{n_i v_i}\right] = -\frac{D}{v} \frac{\partial}{\partial x} \left[\ln(n_e n_i)\right] \text{——}5$$

It may be assumed that $v_e \gg v_i$. For an oxide which is an insulator in the absence of dissolved metal or oxygen, and for which $x \gg x_c$, it may also be assumed that $n_i(x) = n_e(x) = n(x)$ throughout the film except for the boundary zone, which is neglected. Equation 5 then becomes

$$j = -2\, D_i \frac{\partial n}{\partial x}$$

which upon integration gives

$$jx = 2 D_i \left[n(0)-n(x)\right]$$

and the oxidation rate, from equation 3, is

$$\frac{dx}{dt} = A/x \qquad \text{where } A = 2 D_i \Omega \left[n(0)-n(x)\right] .$$

So it is seen that the parabolic rate law is also satisfied by films where $\phi < W$ and where thickness is greater than x_c.

The third classification of films mentioned (thin films which are highly protective) has an oxide to metal volume ratio greater than one and reaches a maximum thickness in a relatively short time. This is the case for which $\phi > W$ with temperatures below a critical temperature equal to $W/39k$, such that a high contact potential exists between the metal and oxygen molecules adsorbed on the oxide surface. In all cases where $\phi > W$ there are more ions in solid solution in the oxide than electrons. For very thin films (< 20 A°) sufficient electrons are supplied by the tunnel effect so that the oxide growth is again controlled by the very high rate of diffusion of ions which was described above. As the oxide thickens its rate of growth will become restricted by the availability of the electrons supplied by the tunnel effect. For temperatures below the critical temperature, $[W/39k,]$ the film grows rapidly at the rate of

$$\frac{dx}{dt} = K e^{-x/x_0} \qquad \text{where } K \text{ and } x_0 \text{ are constants,}$$

or

$$x = x_0 \ln(Kt/x_0 + \text{const}).$$

This logarithmic oxide growth continues to the limiting thickness

$$x_L = V a' q/(W-39kT)$$

where V is the strong contact potential set up between the metal and an adsorbed layer of oxygen, q is a constant, and a' is the distance from the electron at rest to the top of the barrier separating the metal and an interstitial position within the oxide. x_L varies from 20 to 100 Angstroms for the metal oxides under discussion where $\phi > W$ and temperatures are less than the critical temperature $W/39k$. For higher temperatures there is no limiting thickness. The initial rapid growth rate goes over to the previously discussed parabolic rate. The thin, highly protective oxide formation discussed here is displayed by aluminum at room temperature and by copper, iron, barium and other metals at the temperature of liquid air.

The remaining classification of oxides includes those formed by rare oxidation phenomena such as that displayed in the oxidation of platinum. Rideal and Wansbrough-Jones (31) conducted an investigation of the oxidation of platinum and observed rather unusual data, as it was thought for some time that platinum did not oxidize. Platinum samples were weighed before and after being heated to 1500 to 1900° K in the presence of oxygen. It was found that the sample lost weight, and that an oxide, PtO_2, collected on the walls of the system surrounding the sample. The platinum evaporates and then reacts with oxygen. It is beyond the scope of this paper to present here the mechanism of formation of this type of oxide.

It is known that nickel in the region between 300 and 900° C obeys the parabolic law of oxide growth considered second in the above discussion (36 35, 33), and that the basic assumptions used in the theory of oxide formation for copper also apply to the oxidation mechanism of nickel.

In order to obtain a value of the activation energy for electron and ion diffusion through nickel oxide, equation 4 will be recalled: $x^2 = 2\, n_o \Omega D_i t$ where n_o is the concentration of metal ions in the oxide in equilibrium with the metal and is given by $n_o = N e^{-W/kT}$. N is the number of interstitial positions per unit volume. D_i is equal to $b\, e^{-U/kT}$ (9, 12) where U is the activation energy and b is a constant. Then the oxidation rate constant

$$K_i = 2\, n_o \Omega D_i = 2\, N \Omega\, b e^{-(W+U)/kT}.$$

Gulbransen (14), using $x^2 = Kt$ where $K = 2\, n_o \Omega D_e$ from Mott (25), and $D_e = \lambda^2 K_e$, $K_e = \frac{kT}{h} (e^{-\Delta F_e / RT})$ from Eyring (12), evolved a parabolic rate law constant applicable to the data obtained in this study. In the preceding equations λ is the distance between successive interatomic sites, ΔF_e refers to the standard free energy of the activation process which transfers one Faraday of electrons from the metal to the conduction band in the oxide, k is Boltzmann's constant, and h is Planck's constant. Since, by definition, $\Delta F = \Delta H - T \Delta S$ where ΔS refers to the entropy of activation and ΔH to the enthalpy of activation, then $D_e = \lambda^2 \frac{kT}{h} e^{(\Delta S_e/R)} e^{-(\Delta H_e/R)}$. Now $n_o = N e^{-\Delta F_i / RT}$ where ΔF_i refers to the free energy necessary to bring a positive ion from the metal lattice to an interstitial position in the oxide. If the assumption $N \Omega = 1$ is made, then

$$K = 2 \frac{kT}{h} \lambda^2 e^{(\Delta S_e + \Delta S_i)/R} \; e^{-(\Delta H_e + \Delta H_i)/RT}.$$

Since ΔH differs from U by a very small factor, $P \Delta V$, for a nearly constant pressure reaction with negligible volume change,

$$K = 2 \frac{kT}{h} \lambda^2 e^{-\Delta S/R} \; e^{-U/RT} \quad . \qquad \text{——6.}$$

This equation will be used in calculating the activation energy U.

APPARATUS

The oxidation system used in this study was constructed by W. G. Wilson and is described in his theses—"An Introductory Study of the Oxidation Mechanism of Nickel" (36). Some modifications of the system were made. The substitution of a large flexible sylphon bellows for a rigid copper tube greatly eased the takedown process, removed some stress from glass parts of the system, and reduced the vibration carried to the balance from the pumps. Black wax joints between brass fittings and glass were replaced by soldering the brass directly to the glass with Cerroseal solder. At the outset the delicate balance was damaged several times, which necessitated shutting down operations each time until the balance could be repaired and recalibrated. To remedy this two spare balances were made and calibrated, so that damaging of the balance in the system merely required that one remove it and substitute another. The damaged balance could then be repaired at leisure. This saved considerable time, gave assurance to the operator and reduced the breakage. The sensitivities of the microbalances used varied from 0.0127 to 0.0119 mm per microgram.

PROCEDURE

The nickel used in this study was obtained from the International Nickel Company in thicknesses of 15 to 18 and 2 to 3 thousandths of an inch. The impurities in the special electrolytic nickel were Co-0.043 percent, Fe-0.002 percent, Cu-0.005 percent, and Pb-0.0008 percent. It was found (36) that annealing the sample for one hour at 900° C was sufficient to dispel any preferred orientation of the crystals due to the rolling or processing of the nickel sheets. Three sample sizes were used. A sample of 15 thousandths of an inch nickel with an apparent surface area of about 4.4 cm^2 and a weight of near 0.7 grams was used for the oxidation runs at temperatures of 575° C and above. Another run at 575° C was made with a sample of 27 cm^2 apparent surface area, and a thickness of three thousandths of an inch in order to compare true surface areas. At temperatures below 575° C samples two thousandths of an inch thick and of about 50 cm^2 apparent area were used. After properly preparing its surface, the sample was suspended from the balance in the system, counterbalanced by trimming the counterweight, and annealed for an hour at a temperature of 900° C in a vacuum of at least 5×10^{-5} mm Hg. The temperature was then lowered and stabilized at the specified point for the run. The pumps were then shut off and pure, dry oxygen admitted into the system by heating potassium chlorate until a pressure of 10 cm of Hg was reached. A scale reading was taken with a travelling microscope of the microbalance beam position before and after the annealing process, and as soon as a deflection was noticed after the admission of oxygen. Periodic readings of the position of the balance were taken throughout the remainder of the run until either the balance went off scale beyond the viewing window or the rate of oxidation became so slow as to give no further essential data.

To find the value of the oxidation rate constant K, the square of the weight increase per unit area $(\rho x)^2$ was plotted against the oxidation time and K calculated from the slope of the curve. It must be remembered, however, that the balance gives readings in mass, and to find the true thickness x, the true area must be known as well as the density of the oxide ρ. The true area A is equal to the apparent area A_{ap} times the surface roughness factor $r = A/A_{ap}$. Thus the value of K will contain the parameter $1/r$. Values of ln K are then plotted against $1/T$. The slope of the loci of these points is seen to be a constant $-T-U/R$ from equation 6 above. It was found that neglecting the $-T$ term in the expression for the slope produces an error of less than 5 percent. Thus the value of the activation energy U may be calculated, provided again that the surface roughness factor is known.

In order to develop the standard procedure used in sample preparation, and in order to determine the effects of varied sample preparations on oxidation rates, eleven runs were made at a temperature of 700° C, each with a different preparation of the sample. Each sample was the small size ($A_{ap} = 4.4\ cm^2$) previously described. The samples were variously rough ground with aluminum oxide cloth to remove old oxide, polished with rouge cloth, and etched in nitric acid (Table I). By varying the strength of the acid, the time of the etch, the amount of polishing, and the roughness of the grinding the following interesting effects were noticed.

The most significant change in oxidation rate was observed when the polishing of the sample was omitted. It was found that polishing the sample before etching effectively doubled the oxidation rate. Varying the time of etch by a factor of twenty, other procedures remaining the same, caused a change in oxidation rate of less than five percent, which is not considered to be significant. Likewise a variation in the normality of the acid from 7.6 to 1.9 caused no significant change in the oxidation rate. As the acid strength was varied from 1.9 N all the way to zero erratic variations of the oxidation rates occurred. This variation was probably due to a slight difference in the polishing as well as to the acid strength changes, since the oxidation rates did not change in proportion to the etch as was expected. If the polishing is omitted altogether from preparation techniques the oxidation rate is duplicated, even with variations in the roughness and in the amount of the grinding.

Table I. Results of varied sample preparation

Run no.	Grind in strokes of #240 grit, except where otherwise noted	Polish in strokes of rouge paper	Etch time in min.	Acid normality	Comparative oxidation rate in µgm/min.
1	50	50	60	7.6	21
2	50	50	15	7.6	40
3	50	50	3	7.6	27
4	50	50	5	7.6	23
5	50	50	5	1.9	23
6	50	50	10	0.2	14
7	50	50	10	0.05	33
8	50	50	none	none	28
9	10	none	60	7.6	10
10	4,#180 grit	none	30	7.6	12

Thus, it was concluded that the grinding and the etching have very little overall effect upon the rate of oxidation, but that polishing makes for a considerable change. This may be explained by the fact that polishing causes an amorphous layer called a Beilby layer to form on the surface for possibly as deep as 400 Angstroms (1). The Beilby layer is more active and thus more subject to corrosion, so the etching causes a greater true surface area for the sample that has been polished.

Electron diffraction experiments to prove the existence of a Beilby layer on samples that had been polished before etching were inconclusive, and further work is planned in this direction.

The standard preparation technique decided upon was that in which the sample was ground with #240 aluminum oxide cloth ten firm strokes on each side and etched in 7.6 N nitric acid for one hour. This produced a specific surface area most easily reproduced.

RESULTS

The graphs of oxidation rates of the nickel samples used were generally parabolic in form, as seen in Plates I and II, although deviations from the parabolic rate law may be noticed for temperatures above 500° C where the oxide growth rate is somewhat linear. In Plates I and II it is noticed that curves representing different oxidation runs cross over one another. This is due to the fact that all of the runs were normalized to fit most systematically on one graph, thus giving different values of ordinate and abscissa for each curve. For each curve in Plate II, slopes were taken at two or three points. From these slopes values of the rate constant K were calculated by means of equation 4. The natural logarithms of the values of K were plotted as function of 1/T °K on Plate III. A straight line drawn through the loci of these points has a slope which gives a value of the activation energy, by the use of equation 6. It seems, from Plate III that there are two values of the activation energy: 52,600 cal/mole ± 3 percent for temperatures between 450 and 700° C, and 25,300 cal/mole ± 20 percent for temperatures below 450° C. When more data are taken it may be found that there is another lower activation energy throughout the Curie temperature region, since there seems to be a general horizontal flattening of the point loci in the 350 to 360° C range.

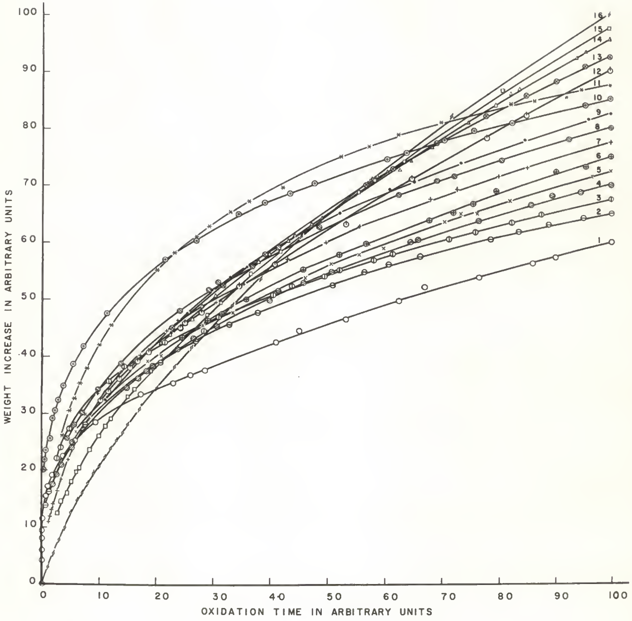
The points on Plate III are spread vertically much more than would be expected from the highly accurate apparatus used. This spread will be diminished

EXPLANATION OF PLATE I

A plot of the weight increase as a function of the oxidation time in units explained below:

Curve number	Temperature in degrees Centigrade	one unit of ordinate equals:	one unit of abscissa equals:
(1)	320	0.0645 $\frac{\mu gm}{cm^2}$	1.063 hr.
(2)	360	0.1543	0.797
(3)	363.5	0.1506	0.842
(4)	366	0.1978	0.992
(5)	370	0.1455	0.9508
(6)	374.5	0.1273	1.090
(7)	380	0.2014	0.749
(8)	390	0.1437	0.701
(9)	399.5	0.1830	0.814
(10)	425	0.2820	0.655
(11)	450	0.2375	0.800
(12)	500	0.1521	0.266
(13)	575 (large area)	0.7940	0.392
(14)	575 (small area)	4.40	1.25
(15)	650	3.70	0.0717
(16)	700	3.21	0.94 min.

PLATE I

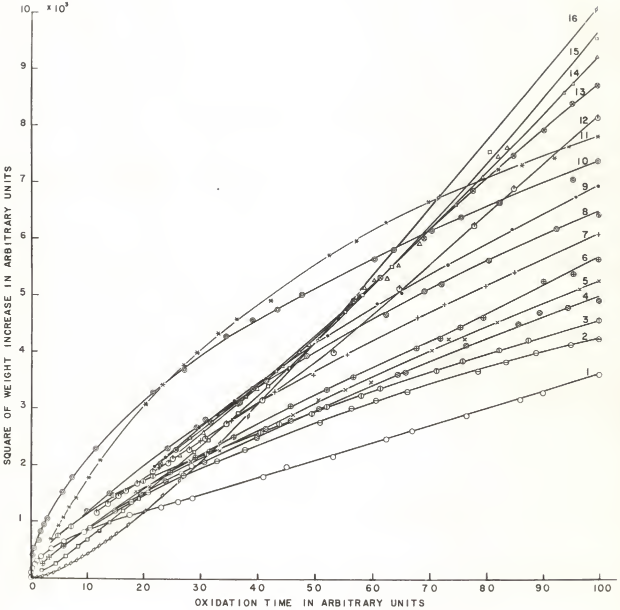

WEIGHT INCREASE IN ARBITRARY UNITS
OXIDATION TIME IN ARBITRARY UNITS
0
10
20
30
40
50
60
70
80
90
100
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

EXPLANATION OF PLATE II

A plot of the square of the weight increase as a function of the oxidation time in units explained below:

Curve number	Temperature in degrees Centigrade	one unit of ordinate equals:	one unit of abscissa equals:
(1)	320	0.00415 $\frac{\mu gm^2}{cm^4}$	1.063 hr.
(2)	360	0.0238	0.797
(3)	363.5	0.0227	0.842
(4)	366	0.0390	0.992
(5)	370	0.0211	0.9508
(6)	374.5	0.0162	1.090
(7)	380	0.0405	0.749
(8)	390	0.0206	0.701
(9)	399.5	0.0334	0.814
(10)	425	0.0793	0.655
(11)	450	0.0563	0.800
(12)	500	0.0232	0.266
(13)	575 (large area)	0.629	0.392
(14)	575 (small area)	19.36	1.250
(15)	650	13.69	0.0717
(16)	700	10.304	0.940 min.

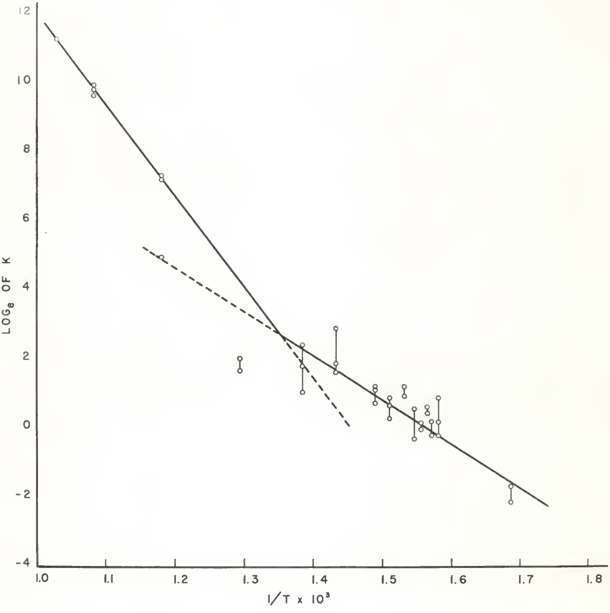
PLATE II


× 10³
10
9
8
7
6
5
4
3
2
1
0
SQUARE OF WEIGHT INCREASE IN ARBITRARY UNITS
0
10
20
30
40
50
60
70
80
90
100
OXIDATION TIME IN ARBITRARY UNITS
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

EXPLANATION OF PLATE III

A plot of $\log_e$ of K as a function of the reciprocal of the absolute temperature. (Discontinuous straight lines are schematic).

PLATE III



considerably when values of the surface roughness factor are found. A large, unaccounted-for surface roughness factor would give a high value for the activation energy. Variations of the surface roughness factor between different samples would cause considerable change in the rate constant for different temperature oxidation runs.

Mott and Cabrera (27) have suggested a change in the rate constant with oxide thickness. This may have been due to a surface area which changes as the oxide grows, or to different surface roughness factors for samples at different temperatures. If the surface roughness factor or the oxide thickness were known, the slopes of the curves in Plate II could be taken at values of equal oxide thickness. This would avoid any dispersion of K values caused by a variation in surface area with oxide film thickness.

Wilson (36) observed an anomalous oxidation rate for the first hour of oxide film formation at 450° C, and attributed this to a possible shift in the lattice structure of the oxide. This seemed to occur when the film reached a thickness at which new formations of oxide were free from the influence of the metal lattice structure. However, these results have not been duplicated in this study, nor were they verified by electron diffraction. Therefore, it is assumed here that the nickel oxide forms its own, essentially unstrained, lattice structure throughout, and not that of nickel for a region of narrow thickness adjacent to the surface of the metal.

Published values of the activation energy of nickel vary from 21,710 to 38,400 calories per mole. Wilson (36) obtained a value of 30,400 calories per mole using the same apparatus as that used in this study. The value of 52,600 calories per mole is high, but it is expected that this value will be revised to a lower value when the surface roughness factor is introduced, since the value of K used in Plate III will be reduced by a factor of $1/r^2$. The value of 25,300 calories per mole is quite reasonable for temperatures below 450° C.

CONCLUSIONS

The data obtained in this study seem to give evidence of a change in the activation energy of nickel around 450° C, and a possible shift to a lower value of activation energy in the region around the Curie temperature. The results cited here will be modified by the use of the surface roughness factor to give values of the activation energy over a wide range of temperature. This leads to a consideration of the oxide thickness as it varies with time instead of the variation of the weight gained with time. No literature has been found in which a study of the oxidation rates of metals has been considered using average oxide film thicknesses obtained from a knowledge of the true surface area of the sample. The problem of surface preparation has a significant place in the consistent production of samples with equal surface roughness. The surface preparation technique was well standardized. Different sample areas have been oxidized at the same temperature. It remains to establish the true surface area of the sample or the thickness of the oxide film in order to determine more accurately the activation energies and the variation of oxide thickness with time.

FUTURE STUDIES

In an effort to determine the true surface area of the sample and bouyancy and convection effects on the balance three adsorption isotherm runs were made. Following Gregg (13) the monolayer capacity X_m of an adsorbent is proportional to the specific surface S (cm^2/gm) as follows:

$$S = \frac{X_m}{M} N A_m$$

where M is the molecular weight of the adsorbate, A_m its molecular cross sectional area, and N is Avagadro's number. Depending upon the type of adsorption curve obtained, X_m may be found by several different methods. The Langmuir adsorption isotherm equation $x = X_m B P/(1+BP)$ and the equation of Bangham and Fakhoury $P = C x/(X_m-x) \exp. x/(X_m-x)$ were used, plotting data in such a way as to find X_m from the adsorbed weight x at various pressures P (10, 13). The symbols B and C are constants in the above equations.

In order to conduct isothermal adsorption runs with the system discussed herein some modification and adjustment were necessary. A fused silica tube containing solid calcium grains was constructed for the purification of the inert gas (argon) used in the runs as the adsorbate. The gas was purified by passing it through the calcium filter, which was kept at a temperature of 700 to 730 degrees Centigrade. Purified argon was stored in a large, clean glass bottle at a pressure of about two atmospheres. The balance was hung with a sample and counterweight of equal size and with similar surface preparations. The sample in these cases was at a temperature of 900, 903, and 100° C for the three runs made. The counterweight was at room temperature. Sample and counterweight were outgassed with a high voltage spark at a pressure of less than 5×10^{-5}mm Hg before heating the sample. With the temperature at the constant values mentioned, the adsorbate was introduced to various pressures between one millimeter and one atmosphere, and a balance reading (x) was obtained at each pressure (P). It was thought that there would be no adsorption at the high temperature of the sample, so that the isotherm curve would represent the adsorption on the counterweight, less, of course, the corrections for bouyancy and convection current effects. However, the sample gained weight, causing the adsorption curves to double back upon themselves and making them most difficult to interpret in terms of the true amount of gas adsorbed. Perhaps this was caused by some impurity in the system, allowing the sample to oxidize at the high temperature. Future studies are planned in which the temperatures compared are room temperature and that of liquid air instead of 900° C and room temperature. This should eliminate the difficulties in the attempt described, and should give an effective means of calculating the surface roughness of the samples used.

A method of determining the thickness of the oxide directly might be to use the color of the oxide, calculating the thickness by using the interference theory of thin films (8, 11). An unusual color of straw yellow was noticed for the nickel oxide layer on the sample used for the 320° oxidation run. Colors of blue, green, and red-violet resulted at other temperatures. An effort was made to account for these oxide colors by the method mentioned (8, 11, 16, 20, 32). The same principle might be used in a study of interference fringes from the reflection of X-rays at grazing incidence to determine the thickness of the oxide film. Still, the surface roughness factor remains unknown, and its calculation is the basis for much possible future study.

The true surface area of the sample, which may be from 4 to 75 times as great as the apparent surface area (10), does not stay constant throughout the growth of an oxide film. As far as is known, there is no literature available in which the problem of a dynamic surface area is discussed, and it presents quite a challenge as this problem remains a factor in every tarnishing reaction.

ACKNOWLEDGMENTS

The author gratefully acknowledges the clear guidance and sincere counsel given by Dr. R. D. Dragsdorf of the Department of Physics. Appreciation is also extended to W. G. Wilson, of Inyokern, California, who initiated this study and designed and built the apparatus used, and to the National Research Corporation, New York, for their financial support.

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A STUDY OF THE OXIDATION MECHANISM OF NICKEL AROUND THE CURIE POINT

by

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B. S., McPherson College, 1951

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1954

A study of the oxidation rates of a metal may yield information about the oxide structure, diffusion processes within the oxide, and utilization of the metal or oxygen ions bordering the oxide. Nickel is generally found to obey a parabolic rate law of oxidation in which the square of the thickness of the oxide is proportional to the time of oxidation. Deviations from this law have been reported by previous investigators at very high temperatures and at temperatures below 400° C.

The present theories for formation of oxides were presented. It was found that four general classifications of oxides each required a different theoretical approach in order to account for the oxidation rate. The type of oxide which nickel exhibits suggests a rate controlled by a diffusion mechanism in which nickel ions migrate from the nickel-oxide to the oxide-oxygen interface.

To study the oxidation of nickel a quartz beam vacuum microbalance of high sensitivity was used. The apparatus was constructed by Mr. W. G. Wilson, and modified for the study presented here. The oxidation rate could be accurately recorded by observing the weight gain of a nickel sample suspended from the microbalance in a controlled atmosphere of oxygen.

Side studies included in this problem were measurements pertaining to the true surface area of the sample in an attempt to determine the actual thickness of the oxide from the weight gained. Uniform sample preparation was a problem, and some eleven oxidation runs were made to determine the best preparation technique.

Results obtained from sixteen oxidation runs used in the oxidation rate study showed rates of oxidation that were almost linear for temperatures above 500° C, and parabolic oxidation rates in the region from 370 to 410° C.

Two values of the activation energy of nickel were apparent from the data taken. For temperatures between 450 and 700° C a value of 52,600 calories per mole, ± 3 percent, was obtained. At temperatures below 450° C a value of 25,300 calories per mole, ± 20 percent, was apparent. There appears to be another lower activation energy for temperatures throughout the Curie region of 350 to 360° C.

These values of the activation energy are subject to modification when the values of the true surface areas or the thicknesses of the oxide films are found. The values were obtained under the assumption that the apparent area of the sample was equal to the true area, and so they contain a parameter which depends upon the surface roughness factor. Future studies will include an x-ray reflection analysis of the thickness of the oxide film, and an effort to account for the variation of the true surface area with oxide growth.