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HIGH-TEMPERATURE CORROSION STUDIES

Nickel and Cobalt in Air and Oxygen

By Robert M. Doerr

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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HIGH-TEMPERATURE CORROSION STUDIES

Nickel and Cobalt in Air and Oxygen

by

Robert M. Doerr[1]

ABSTRACT

Isothermal oxidation kinetics were determined for three grades of Ni and for 99.99 percent Co in O_2 and in air from 800° to 1,200° C. The oxidation reactions followed approximately the parabolic rate law. For 99.99 percent Ni in O_2 at 1,200° C, the parabolic rate constant was 2 mg cm^{-2} $hr^{-\frac{1}{2}}$. For 99.99 percent Co in dry air, the constant ranged from 1 mg cm^{-2} $hr^{-\frac{1}{2}}$ at 800° C to 18 mg cm^{-2} $hr^{-\frac{1}{2}}$ at 1,200° C; for 99.99 percent Co in O_2 the constant was 2 mg cm^{-2} $hr^{-\frac{1}{2}}$ at 800° C and 10 mg cm^{-2} $hr^{-\frac{1}{2}}$ at 1,000° C. For 99 percent Ni in dry air, the constant ranged from 0.2 mg cm^{-2} $hr^{-\frac{1}{2}}$ at 800° C to 3 mg cm^{-2} $hr^{-\frac{1}{2}}$ at 1,200° C. By X-ray diffraction measurements, only divalent oxides were found in the scales.

Volumetric and quartz-helix gravimetric methods were used. The volumetric apparatus was designed to permit less stringent restrictions on the corrosion specimens; it was also more convenient to use. The agreement between the weight gain determined gravimetrically and the O_2 consumption determined volumetrically was not good enough for direct comparison of gravimetric and volumetric results.

INTRODUCTION

The studies described in this report were undertaken by the Bureau of Mines in a preliminary phase of research on alloy corrosion at high temperatures. Literature on the oxidation of unalloyed nickel and cobalt was examined to establish a basis for comparison of alloy corrosion results. The oxidation kinetics of nickel and cobalt at elevated temperatures have been studied extensively by a number of investigators. Because of variations in specimen and test conditions, the published data vary considerably. Little of the earlier research extended into the temperature range of 1,200° and above.

[1] Physicist, Rolla Metallurgy Research Center, Bureau of Mines, Rolla, Mo.

Work on manuscript completed August 1962.

Gravimetric methods are widely used in high-temperature corrosion research and would have been adequate for the preliminary tests undertaken; however, such methods are inapplicable to oxidation studies on certain materials. For example, the weight gain of a corroding specimen is not a valid index of the reaction progress if some of the reaction products are significantly vaporized at the test temperature. Moreover, most of the sensitive gravimetric units for corrosion work are restricted to lightweight specimens that are wholly reacted after relatively short periods of oxidation. These limitations are not inherent in volumetric apparatus.

Because of these considerations, the objectives defined for this research were to study the high-temperature oxidation of nickel and of cobalt under the conditions selected for subsequent work on the isothermal oxidation of nickel and cobalt alloys and to develop a volumetric apparatus for determining the corrosion rates of a variety of materials at high temperatures.

According to existing theory, isothermal oxidation reactions follow one or more of four different rate laws (12).[2] When oxidation proceeds at a constant rate, which is clearly the result of the formation of a scale that affords constant protection or of the absence of a protective scale, the linear rate law is said to be followed. In the equation form, $W = k_1 t$, where W is the quantity of reaction product formed, k_1 is the linear rate constant, and t is time.

When the oxidation products form a scale, the protective value of which depends linearly on scale thickness, the parabolic rate law is said to be followed. Pilling and Bedworth (21), recognizing the role of diffusion of a reactant through the solid product in processes which follow the parabolic rate law, and recognizing that the instantaneous rate of reaction depends inversely on the thickness of the reaction product layer, derived the parabolic expression quite simply:

$$\frac{dH}{dt} = k' \frac{1}{H};$$

$$\int HdH = k' \int dt;$$

$$\frac{H^2}{2} = k' t + C.$$

When $t = 0$, $H = 0$; therefore $C = 0$ and $H^2 = 2 k' t$. If the reaction product is of constant density,

$$W = mH,$$

and

$$W^2 = k_p t,$$

[2] Underlined numbers in parentheses refer to items in the list of references at the end of this report. Accompanying figure numbers refer to figures in the items and not to figures in this report.

where

H is the thickness of the oxide layer,

W is the weight of reaction product per unit area,

t is time,

m is the density of the oxide,

k_p is the parabolic rate constant,

k' is $\frac{1}{2} m^{-2} k_p$

and

C is an arbitrary constant of integration.

Mott (18 19) developed a detailed theory of diffusion in oxidation reactions. The cations, electrons, and anion vacancies in the oxide lattice are mobile, but the only diffusing species are the cations and electrons.

Practically, the materials that prove useful in long-term elevated-temperature service are those on which the oxidation products form protective scales. As the scales build up, the reaction rates decline in accordance with the parabolic rate law.

Some materials that oxidize in accordance with other rate laws corrode at decreasing rates, but when these materials are corroded at highly elevated temperatures, rate laws such as the cubic and logarithmic are not found to apply. Some oxidation reactions follow the cubic rate law (19) $W^3 = k_c t$, where W is the quantity of reaction products, k_c is the cubic rate constant, and t is time. For certain conditions, the logarithmic rate law is followed (12): $W = k_e \ln (At + 1)$, where W and t are as before, and k_e and A are constants.

A number of authors have investigated the corrosion of nickel; extensive bibliographies of the literature have been published (4 12 13). Frederick and Cornet (5) and Friebel (6) have investigated the oxidation of nickel at temperatures as high as 1,200° C and above. Frederick and Cornet oxidized nickel at temperatures up to 1,400° C in air but did not follow the progress of the reactions. Friebel, working in the Bureau of Mines, determined the influence of purity on the oxidation rate of nickel; his data, but not his computed results, are included as part of this report.

Preece and Lucas (22) oxidized nickel at temperatures up to 1,075° C and reported no radical change in the corrosion process. They noted that the nickel oxide comprised two layers, a light-green powdery inner layer and a tightly adherent dark-green outer layer. Moore and Lee (16 17) reported that nickel oxidizes at parabolic rates up to 900° C. Gulbransen and Andrew (8 9), basing their observations on a series of 2- to 6-hour runs, confirmed the parabolic oxidation of nickel to 900° C. They reported that the rate departed from the parabolic relation at higher temperatures. Kubaschewski and von Goldbeck (14) showed the considerable, though irregular, effect of metal purity on the oxidation rate of nickel.

A change of parabolic oxidation rate during the course of oxidation runs has been reported. Harrison and Darrah (15)[3] oxidized unalloyed nickel in air at about 900° C and found different parabolic oxidation rates that fell within the following three time periods: 0 to 26 hours, 26 to 66 hours, and over 66 hours. The different oxidation rates, evident on the oxidation-time curve, were attributed to fissuring of the oxide.

Sartell and Li (23) oxidized high-purity nickel at 994° to 1,115° C for time periods to 140 hours. They fitted their data for each test temperature to two successive parabolic curves that intersect at about 12 hours and stated that the data of Gulbransen and Andrew (9) can be fitted to two such intersecting parabolic curves.

The oxidation of cobalt has been investigated by a number of workers. Johns and Baldwin (11) studied the high-temperature oxidation of cobalt in air up to 1,100° C by before-and-after weighings. They reported that the reaction rates followed the Pilling and Bedworth parabolic rate law. Gulbransen and Andrew (7) investigated the oxidation of cobalt of 99 percent purity at temperatures up to 700° C. They listed a number of factors to which the commonly observed high initial oxidation rates of various materials can be attributed. These factors include: (a) The influence of the decrease in surface roughness as the reaction proceeds, (b) the influence of the solution of oxygen in the metal, and (c) the influence of the concentration of impurities in the oxide during the early stages of the reaction.

Carter and Richardson (3) evaluated the oxidation of cobalt at temperatures from 1,000° to 1,350° C. The parabolic oxidation rates determined were functions of the 0.29th power of oxygen pressure. Previously, the same authors (2) reported that cobalt oxidizes by cobalt ion diffusion; they showed that completely oxidized cobalt specimens exhibited porous centers, and that the rate of diffusion of cobalt in cobaltous oxide depends on oxygen pressure.

Bridges, Baur, and Fassell (1) oxidized cobalt at 800° to 1,200° C; they determined that the oxidation rate is a function of the 0.29th power of oxygen pressure, which is in agreement with Carter and Richardson (3).

ACKNOWLEDGMENTS

In preparing this report the author was assisted by Virgil R. Friebel, formerly a Bureau of Mines fellowship student, and Harold A. Koelling, formerly a metallurgist at Rolla Metallurgy Research Center.

EQUIPMENT AND PROCEDURE

Gravimetric

Apparatus

The gravimetric apparatus is shown in block diagram in figure 1. The quartz-helix microbalance has a sensitivity of 10 centimeters per gram. The

[3] This research was reported by a staff writer for Metals Progress.

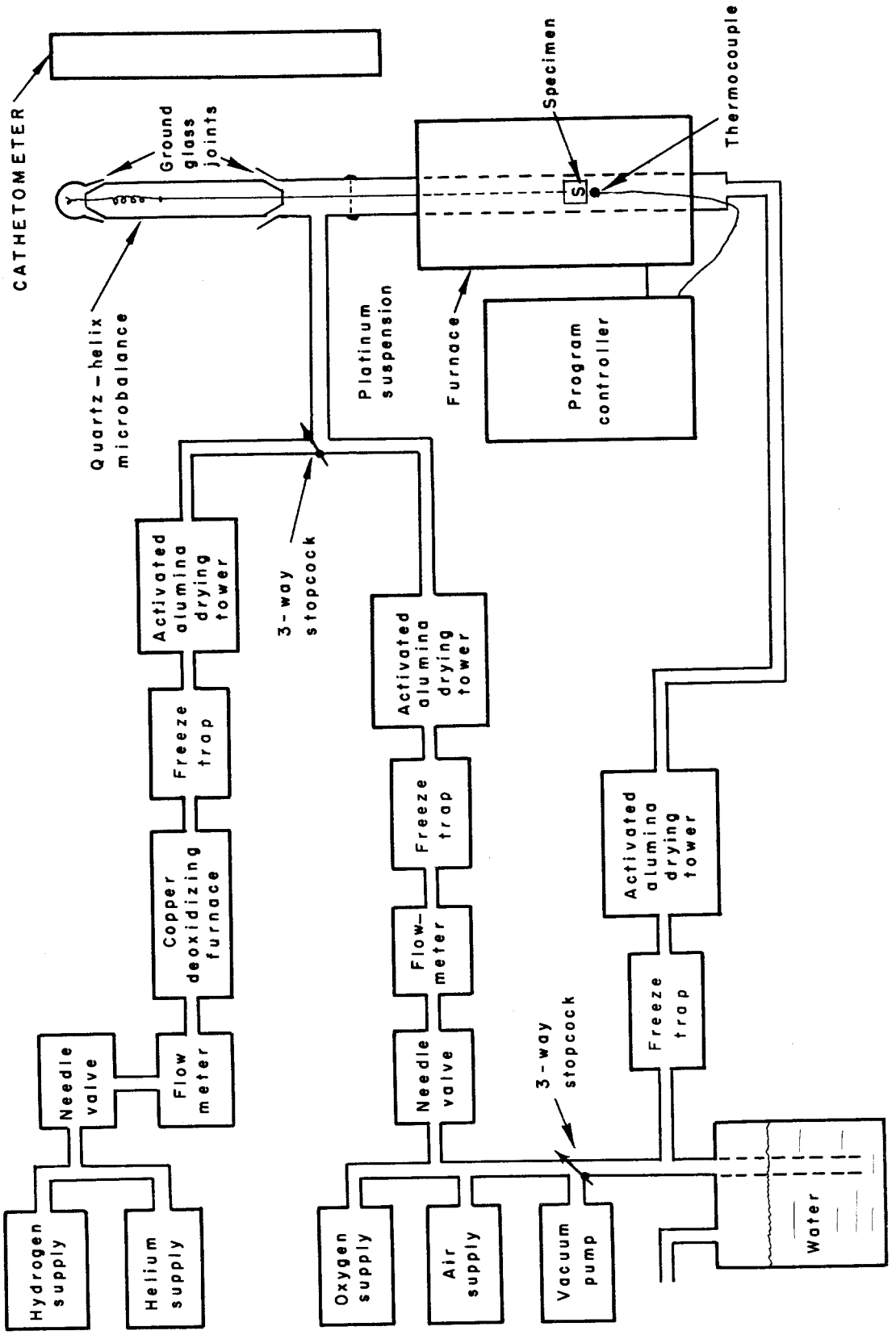

FIGURE 1. - Gravimetric Oxidation Apparatus.

cathetometer has a vernier divided for reading to 0.005 centimeter. Thus the system sensitivity, when the specimen has 5 square centimeters of surface area, is 0.1 milligram per square centimeter. The microbalance is equipped with a reference rod so that readings can be related to zero during the course of a run. No correction is made for the small effect of specimen buoyancy, as appreciable bouyancy changes occur only at the initiation of a run when the specimen-weight change is too rapid to be determined.

The stopcocks, ground joints, and butyl rubber connections are sealed with silicone high-vacuum grease.

Oxidation Kinetics Measurements

The specimen selected for a given run is heated in an atmosphere of dried hydrogen in the test furnace at a rate of about 100° C per hour to the test temperature and is held at temperature for not less than one-half hour. The system is then evacuated, and the air or oxygen is admitted. The progress of the reaction is followed semicontinuously, that is, observations are made at intervals short enough to provide effectively continuous information on the progress of the reaction. Readings are taken more frequently during the early part of a run, when the reaction is most rapid. The data for each observation consist of the cathetometer reading corresponding to the microbalance indication and of the time elapsed from the initiation of oxidation.

When oxidation is conducted in air, a slight flow of air is used to offset both thermal diffusion and oxygen consumption. Thus a constant partial pressure of oxygen is maintained throughout the reaction chamber.

Specimen Preparation

Three grades of nickel and one grade of cobalt were used in the studies. The cobalt and two of the grades of nickel were prepared by powder metallurgy (powder met.) techniques. The specimens were foil rectangles cold-rolled to a thickness of about 0.03 centimeter and cut to about 1.2 centimeters in width and 2 centimeters in length. The broad faces were dry-abraded through 4/0 emery paper; the edges were wet-ground for squareness. All readied specimens were both cleaned and stored in ethanol. Immediately before they were used, they were dried in an airflow sufficient to minimize drying marks and film formation.

The analyses of the materials used as specimens are shown in table 1. The gases used in this research were: Hydrogen, electrolytic, analyzed as 99.8 percent hydrogen; oxygen, commercial, analyzed as 99.5 percent oxygen; and helium, USBM Grade A, analyzed as 99.995 percent helium.

TABLE 1. - Analyses in percent of specimen materials[1]

Element	Material and source[2]			
	Ni, 99 percent (electrolytic)	Ni, 99.8 percent (powder met.) National Lead Co.	Ni, 99.99 percent (powder met.) International Nickel Co.	Co, 99.99+ percent (powder met.) Johnson-Matthey
Ni	Basis	Basis	Basis	None
Co	0.55	0.11	0.002	Basis
Fe	.04	.007	.006	0.0005
Cu	.006	Trace	None	<.0001
Mn	.1	.0005	None	None
Si	.01	Trace	None	.0002
Al	Trace	Trace	None	None
Ca	Trace	.004	None	.0002
S	.001	<.001	.001	-

[1] The analyses were performed at the Bureau of Mines.
[2] The use of company names is to identify the source and does not imply endorsement by the Bureau of Mines.

Volumetric

Apparatus

The volumetric apparatus (fig. 2) used for most of the runs on nickel is Friebel's (6) modification of Jenkins' (10) apparatus. A later modification, shown in block diagram in figure 3, was used for the runs on cobalt and the remainder of those on nickel.

The apparatus consists essentially of a small reaction chamber connected through a horizontal precision-bore tube to a large reservoir. The reaction side of the system is separated from the reservoir side by a drop of mercury that serves as a movable indicator and gastight plug in the precision-bore tube. The withdrawal of 5 milliliters of gas from the 19-liter reservoir does not significantly affect the system pressure. The temperature of the reservoir and of the precision-bore tube is held constant within 0.1° C at approximately 35° C. The volume of the reaction chamber is about 75 milliliters. The overall design is such that the displacement of the indicator is in very nearly linear proportion to the volume of gas consumed in the reaction.

To permit both long runs and high sensitivity, the equipment was designed to allow sequential traverses of the indicator through the precision-bore tube. A needle valve is used to add just enough oxygen to the reaction side of the system to restore the system to the initial pressure and the indicator to its initial position.

The precision-bore tube has a cross-sectional area of 0.0792± 0.0003 square centimeter. The density of oxygen at standard pressure and temperature is 1.429×10^{-3} gram per cubic centimeter. When the oxygen is at standard pressure (1 atmosphere) and temperature (0° C) and the specimen area is 3 square centimeters, the sensitivity of the volumetric apparatus is 2.65×10^4 $cm/(g/cm^2)$, that is, 2.65×10^4 centimeters of indicator movement per gram of

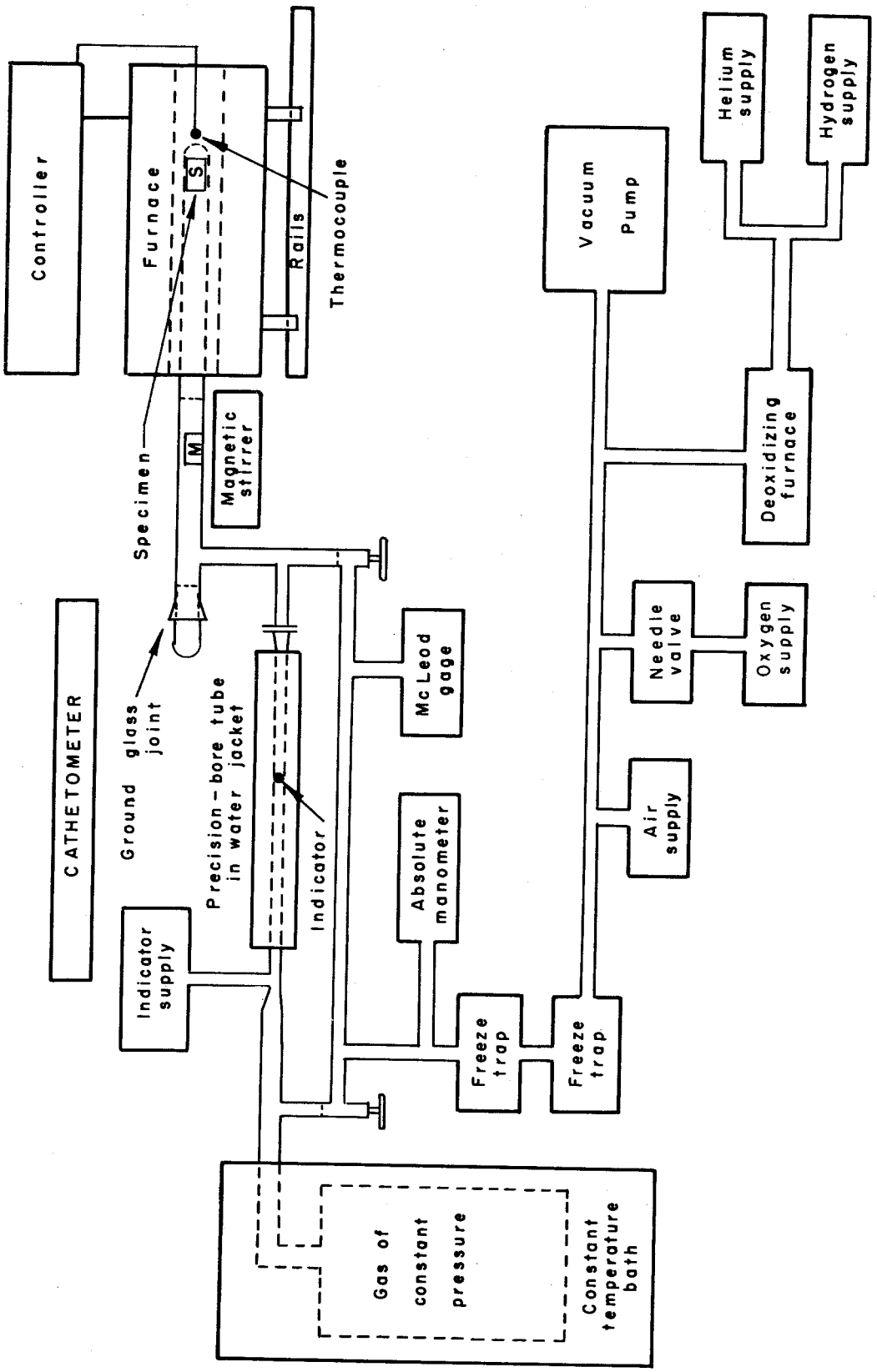

FIGURE 2. - Volumetric Oxidation Apparatus.

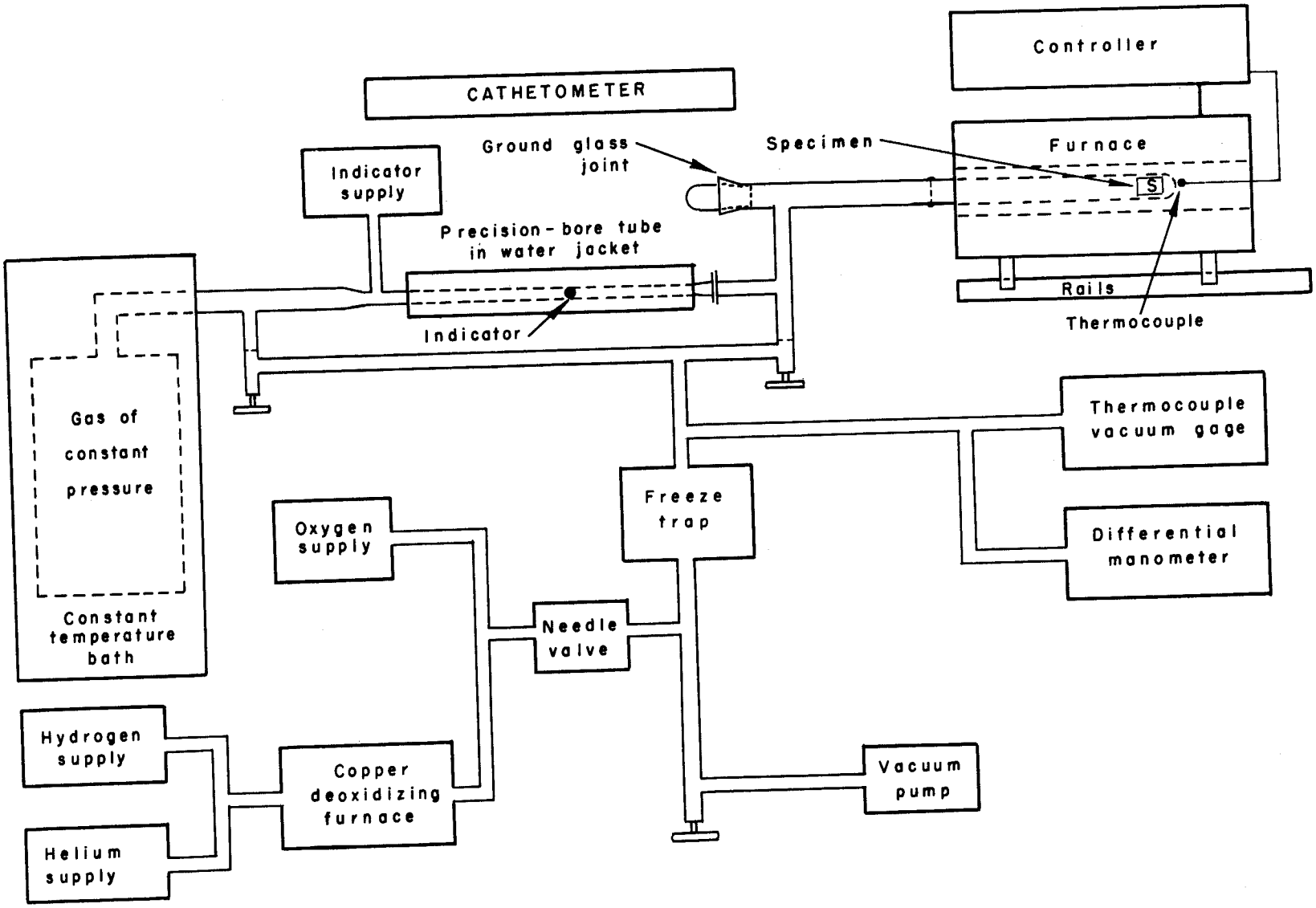

FIGURE 3. - Modified Volumetric Oxidation Apparatus.

oxygen per square centimeter of specimen surface. The cathetometer is read to the nearest 0.01 centimeter, that is, to the nearest 3.77×10^{-7} gram per square centimeter. Because the sensitivity of the apparatus depends on oxygen pressure and specimen area, this sensitivity value is indicative rather than fixed.

Sensitivity to Temperature Variations

Because the reservoir is much larger than the reaction chamber, the system pressure is almost proportional to the reservoir temperature. A temperature change in the reservoir causes a pressure change that is transmitted to the reaction side by indicator displacement; the volume of the reaction side varies inversely with such a pressure change. Symbolically,

$$\frac{P}{P + P'} = \frac{T}{T + T'}$$

and

$$\frac{v + v'}{v} = \frac{P}{P + P'}.$$

Solving for v',

$$v' = \frac{-vT'}{T + T'}$$

or when T' is small,

$$v' \approx \frac{-vT'}{T}.$$

Although this change in the reaction chamber volume is partially offset by the thermal expansion of the reservoir glassware, which is approximately $3LVT'$, this glassware expansion is negligible.

The indicator displacement is proportional to the change in the volume on the reaction chamber side; that is,

$$D = -v' = \frac{-vT'}{T}.$$

In the foregoing expressions,

P is the initial pressure,

T is the initial temperature,

v is the initial volume of the reaction chamber side,

V is the initial volume of the reservoir side,

D is the indicator displacement multiplied by the cross-sectional area of the precision-bore tube,

L is the linear coefficient of expansion of the glass,

and

the primed quantities are the changes in these values.

For the system in use, $L = 3.25 \times 10^{-6}$ per ° K for the glass employed, $V = 1.9 \times 10^{4}$ milliliters, $T' = 0.1°$ K, $v = 75$ milliliters, $T = 308°$ K, and 1 centimeter of indicator displacement represents a volume of 0.0792 milliliter. Therefore, a change of 0.1° K in reservoir temperature results in an indicator displacement of 0.3 centimeter.

Because approximately 25 milliliters of the reaction chamber volume is in the hot zone, a temperature change of 2° K in the hot zone would cause an indicator displacement of 0.4 to 0.6 centimeter, depending on the operating temperature.

Static tests with the system hot disclosed no indicator motion; this indicates an absence of significant low-frequency temperature cycling. High-frequency cycling is precluded by thermal sluggishness. Moreover, the data curves disclose little or no cycling. Thus, the system is considered free of spurious indicator motion.

Oxidation Kinetics Measurements

The reaction chamber, containing the specimen, is repeatedly flushed with helium and evacuated; the valve to the system is then closed. The preheated furnace is drawn around the evacuated reaction tube, which, with the contained specimen, is maintained at operating temperature for about 2.5 hours for degassing before oxidation is begun. Although time is counted from the initiation of oxidation, the indicator, a drop of mercury, is injected into the precision-bore tube only when gas-pressure equilibrium is approximated throughout the system. The progress of the reaction is followed semicontinuously by cathetometer readings of indicator position. Most of the specimens were oxidized for about 3 hours.

Specimen Preparation

The stock materials (table 1) were cold-rolled to a thickness of about 0.03 centimeter. Specimens about 0.8 centimeter wide and 2 centimeters long were cut from the rolled material and were dry-abraded through 4/0 emery paper. After they were cleaned in acetone and annealed in dry hydrogen for 20 minutes at 770° C, they were stored in a desiccator until required for testing.

Gravimetric and Volumetric Data Analysis

Because diffusion of a reactant through the oxide layer was expected to control the rate of oxidation of nickel and cobalt at high temperatures, the data were plotted as total oxidation product formed against square root of

time. This procedure served both to test the parabolic rate hypothesis (which was also tested by log-log plots of the data for the early runs) and to evaluate the parabolic rate constants. Several times the data had to be fitted to two successive parabolic relationships. The linear portion of the plot was selected visually and was evaluated by the method of least squares. When two approximately linear portions were found, the one for the later part of the run was used. The rate constant was determined separately for each of several replications, and these constants were averaged; the limits shown in table 2 represent the 95-percent confidence intervals based on the sample standard deviations (not the population standard deviations) (20) of the rates.

X-Ray Diffraction Measurements

The scales on selected specimens were analyzed in situ by standard X-ray diffractometer studies after the specimens had cooled to room temperature. The radiation used was from a nickel target at 50 kilovolts; the current was 8 milliamperes. The beam and detector slit widths were 3° and 0.2°, respectively. The goniometer scanning rate was 2° per minute (2θ = 2° per minute), and the recorder chart speed was selected for a sensitivity of 0.1 inch per degree.

RESULTS AND DISCUSSION OF RESULTS

The results of the corrosion experiments are shown in table 2. For either of the metals tested, the rate of oxidation depends primarily on temperature. The data indicate a tendency for the corrosion rate to be greater for specimens of higher impurity, in agreement with Kubaschewski and von Goldbeck (14).

The parabolic rate constants for the oxidation in air of 99 percent nickel (electrolytic) ranged from 0.198 to 2.94 mg cm^{-2} $hr^{-\frac{1}{2}}$ (milligrams of oxygen consumed per square centimeter of specimen surface per square root of hours) for temperatures from 800° to 1,200° C. The constants for 99.99 percent nickel (powder met.) ranged from 1.95 to 3.8 mg cm^{-2} $hr^{-\frac{1}{2}}$ for temperatures of 1,200° and 1,300° C in oxygen. The constants for 99.99 percent cobalt (powder met.) ranged from 1.190 to 18.5 mg cm^{-2} $hr^{-\frac{1}{2}}$ for temperatures from 800° to 1,200° C in air. The indicated rate constants for the same material corroded in oxygen ranged from 1.76 to 9.5 mg cm^{-2} $hr^{-\frac{1}{2}}$ for 800° and 1,000° C, but the differences may be partly attributable to the use of the volumetric apparatus for the experiments with oxygen and the gravimetric for those with air.

The reactions followed approximately the parabolic rate law. In most instances, however, the reaction rate during an initial period of oxidation exceeded that indicated by the parabolic relationship. (For cobalt oxidized at 1,200° C, and for a few experiments on nickel, no such period of rapid oxidation was observed.) For certain material-atmosphere-temperature combinations investigated, a distinct break in the parabolic rate became apparent. After this break, a parabolic rate of lesser magnitude was resumed. For example, in fitting the data for 99 percent nickel (electrolytic) oxidized in air at 800° C for over 100 hours, the break was located at 1.4 ± 0.3 root hours for four runs. As any run progressed, small, continuous deviations from the parabolic rate law were found, in agreement with Gulbransen and Andrew (8). These deviations were greater in magnitude than can be accounted for by the diminishing metal surface area.

TABLE 2. - Parabolic rate constants, derived

Material	Atmosphere[1]	Pressure, atmosphere	Temperature, ° C	Apparatus	Interval,[2] hour	Number of tests[3]	Mean parabolic rate constant[4] (mg cm^{-2} $hr^{-\frac{1}{2}}$)
Nickel, 99 percent (electrolytic).....	Air	0.96	800	Gravimetric	1.8 - 100	4	0.198 ± 0.058
Do.....	..do..	.96	1,000	....do.....	.1 - 19	4	1.102 ± .027
Do.....	..do..	.84	1,200	Volumetric	.7 - 2.2	3	2.94 ± .38
Do[5]	Oxygen	.50	1,200	....do.....	.5 - 1.6	4	2.518 ± .027
Nickel, 99.8 percent (powder met.).....	Air	.96	1,200	Gravimetric	.1 - 40	7	2.05 ± .25
Do.....	Oxygen	.64	1,200	Volumetric	.3 4.2	3	2.56 ± .47
Nickel, 99.99 percent (powder met.).....	Air	.96	1,200	Gravimetric	.75 - 30	3	2.44 ± .80
Do.....	Oxygen	.96	1,200	....do.....	.1 - 14	5	2.79 ± .34
Do.....	..do..	.73	1,200	Volumetric	.5 - 3	3	1.95 ± .19
Do.....	..do..	.83	1,300	....do.....	.55 - 3	3	3.8 ± 1.4
Cobalt, 99.99 percent (powder met.).....	Oxygen	.94	800	....do.....	.7 - 1.5	3	1.76 ± .29
Do.....	..do..	.94	1,000	....do.....	.6 - 1.5	3	9.5 ± 1.3
Do.....	Air	.96	800	Gravimetric	.5 - 32	4	1.190 ± .086
Do.....	..do..	.96	1,000	....do.....	.5 - 5.5	3	6.41 ± .63
Do.....	..do..	.96	1,200	....do.....	.05 - .6	4	18.5 ± 1.7

[1] Dried by passing through a freeze trap charged with acetone and solid carbon dioxide.
[2] The parabolic rate constants were computed from data for the intervals shown.
[3] "Sample size" in statistical computations.
[4] Averaged for the parabolic portions of the replications; limits are shown for 95-percent confidence interval. The values are for rate of oxygen consumption.
[5] Analysis approximately as shown in table 1 except manganese content is less than 0.01 percent.

Many factors other than diffusion of reactants through an oxide layer of uniform thickness influence the oxidation rate of a metallic specimen. Therefore, the precise mathematical view expressed by the parabolic equation serves only as a first approximation when applied to experimental data. The apparent breaks in the parabolic oxidation rate, as mentioned above and as reported in the literature (15 23), may be attributed to efforts to fit experimental data too rigorously to the parabolic equation.

Figure 4 depicts graphically the oxidation in air of 99.99+ percent cobalt (powder met.) at 1,200° C as a function of the square root of time. Because the specimen was thin and the reaction was rapid, the specimen was wholly oxidized.

Figure 5 depicts graphically the progress of the oxidation in oxygen of 99.99 percent nickel (powder met.) at 1,200° C as a function of time.

In each of these two graphs is a line segment the slope of which was computed by the method of least squares. The data used in the computations are those for the time intervals delimited by projecting the line segments on the horizontal axes.

The variety of test materials and methods generally precludes the valid determination of the constants in the Arrhenius equation when it is applied to the data of this research. However, the dependence of the parabolic oxidation rates on temperature was evaluated for the limited volumetric data for 99.99 percent nickel (powder met.) by means of Arrhenius plots. The data for the early and late parts of the runs were plotted separately, after the manner of Sartell and Li (23). Within the limits of accuracy of the data, the plots were parallel, and the average slope indicated an activation energy of approximately 66 kilocalories per mole. Sartell and Li reported activation energy of approximately 67 kilocalories per mole for high-purity nickel.

The results obtained with the gravimetric and volumetric apparatus were compared to determine which yielded the more consistent information. The coefficient of variation was calculated for each of the parabolic rate constants shown in table 2; the coefficients for each apparatus were averaged and the two means were compared. The t-test indicated no significant difference in data variability.

In the gravimetric apparatus, to position each specimen properly in the furnace, the length of the fine-wire suspension must be related to the weight of the specimen; thus, a new suspension is required for each run and can be prepared only after the specimen is readied. The fragile balance is partially exposed while each specimen is installed. In contrast, the volumetric apparatus requires no special adjustments and is arranged so that no fragile member is exposed.

At room temperature, the outer surface of the oxide on the nickel specimens oxidized at 1,200° C was matte and dark green. Fracturing the coating disclosed a relatively thick, black layer over a light-green inner layer of

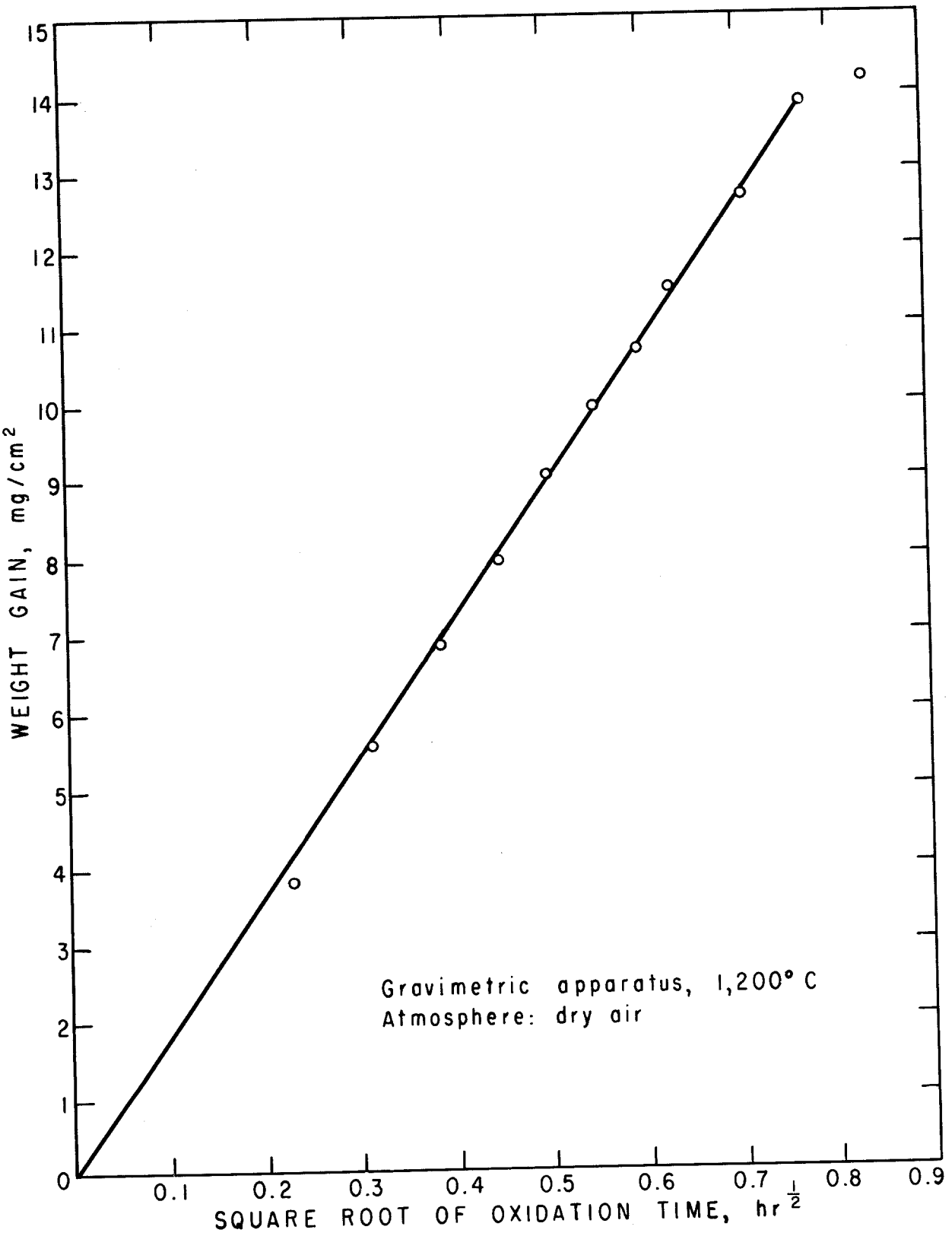

FIGURE 4. - Oxidation of 99.99+ Percent Cobalt (Powder Met.) as a Function of Time.

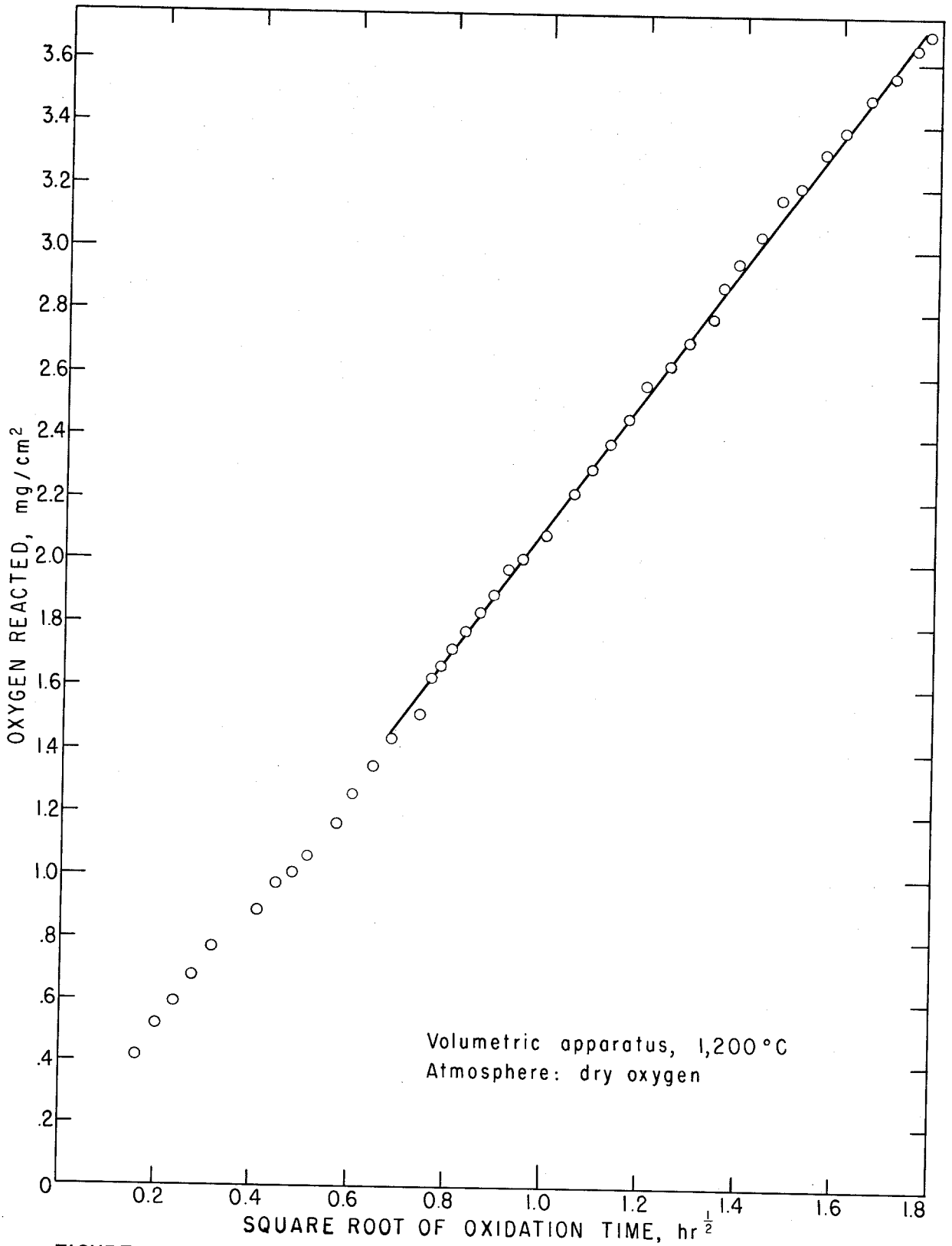

FIGURE 5. - Oxidation of 99.99 Percent Nickel (Powder Met.) as a Function of Time.

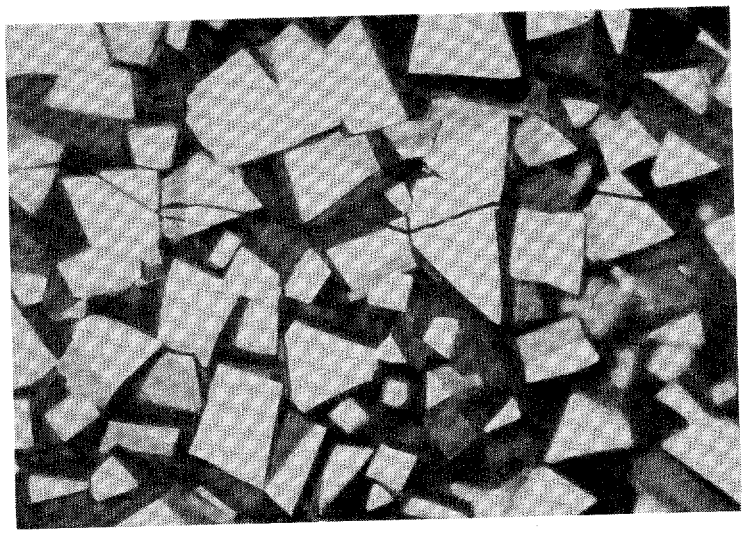

FIGURE 6. - Nickel, 99.99 Percent (Powder Met.), Oxidized at 1,300° C for 224 Minutes in Dry Oxygen. As oxidized (X 500).

somewhat powdery appearance. The outer surface of the oxide on the cobalt specimens was dark and lustrous. When fractured, the cobalt oxide appeared free of an inner layer of contrasting color; the fractured faces had a black semimetallic appearance.

The surfaces of the oxidized specimens exhibit varied appearances. Figure 6 shows the surface of a specimen of nickel (powder met.) oxidized for 224 minutes in dry oxygen at 1,300° C. Figure 7 shows the surface of a specimen of the same material oxidized for 1,920 minutes in dry air at 1,200° C. The reaction of both specimens follows the parabolic rate law. In the former specimen, a crack, probably formed in handling, traverses 7 grains within the field of view. This indicates strong adhesion of the grains to each other and to the underlying metal.

X-ray diffraction analysis (table 3) showed the presence of only one oxide of nickel, nickelous oxide. However, lines for nickel were detected in the lattice for specimens oxidized at temperatures lower than 1,200° C. No nitride was found in the corrosion product of nickel oxidized in air at 1,200° C.

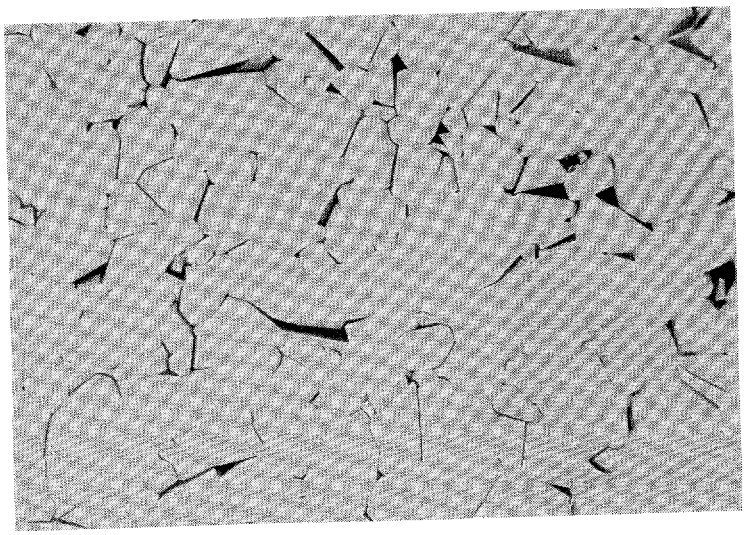

FIGURE 7. - Nickel, 99.99 Percent (Powder Met.), Oxidized at 1,200° C for 1,920 Minutes in Dry Air. As oxidized (X 250).

The corrosion product formed on cobalt was cobaltous oxide. No nitrides were found in the scale on cobalt oxidized in air at 1,000° C.

At low temperatures, the oxidation of cobalt is complicated by the transition from the hexagonal close-packed to the face-centered cubic structure and by the presence of several oxides (7). However, at the temperatures used for this work, both nickel and cobalt and their oxides, nickelous oxide and cobaltous oxide, have the face-centered cubic structure.

TABLE 3. - X-ray diffraction analyses of oxidized specimens[1]

Specimen	Material	Temperature of corrosion,	Atmosphere	Lines identified	Lattice parameter A_o[2] A
Co-8	Cobalt, 99.99+ percent (powder met.)	800	Oxygen	[3] CoO	4.265 ± 0.005
Co-1	.....do.....	1,000	do.	[3] CoO	4.265 ± .005
Co-15	.....do.....	1,200	do.	CoO	4.255 ± .005
D-45	.....do.....	1,000	Air	CoO	4.265 ± .005
F-10	Nickel, 99 percent (electrolytic)..	800	Oxygen	NiO	4.175 ± .005
				Ni	3.525 ± .005
F-33	Nickel, 99.99 percent (powder met.)	1,100	do.	NiO	4.175 ± .005
				Ni	3.525 ± .005
D-82	.....do.....	1,200	do.	NiO	4.180 ± .005
D-44	Nickel, 99.8 percent (powder met.).	1,200	Air	NiO	4.175 ± .005

[1] Unfiltered nickel radiation, 50 kv.
[2] Structures identified as face-centered cubic.
[3] Slight evidence of hexagonal cobalt also detected.

The limited agreement between the gravimetric and volumetric results is not understood. However, as has been noted, specimen pretreatment was different for the two test procedures. In addition, specimens used in the gravimetric apparatus are suspended from a platinum hook; those used in the volumetric apparatus rest on a silica carrier. The presence of a small partial pressure of mercury vapor from the indicator in the volumetric apparatus is not considered significant.

The need for close attention to details throughout the determination of corrosion rates is reemphasized by the differences in the results from the two methods used.

CONCLUSIONS

Oxygen reacted with the grades of nickel studied at 1,200° C at rates from 1.95 ± 0.19 to 2.94 ± 0.38 mg cm^{-2} $hr^{-\frac{1}{2}}$. Cobalt specimens oxidized at rates about eight times as great as those for nickel of comparable purity.

Diffusion of oxygen ions, or of metal ions and electrons, in the oxide layer is indicated as the principal agent governing oxidation rate; the data approximate parabolic rate relationships. Deviations from the parabolic relationship, however, indicate the influence of factors other than diffusion through a uniform, growing film. These factors probably include the phenomena mentioned by Gulbransen and Andrew (7). Sartell and Li (23, fig. 7) clearly demonstrate that the influence of surface roughness is not limited to the early stages of oxidation.

For the temperature range shown in this report, the only oxides in the scales are divalent.

The volumetric apparatus proved effective. Data reproducibility with the volumetric apparatus was not significantly better than with the gravimetric. The volumetric was more convenient to use.

Because the agreement between the gravimetric and volumetric results is limited, volumetric data should be compared with volumetric data and gravimetric data with gravimetric data, for evaluating the corrosion of alloys.

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