The high temperature oxidation of iridium in a forced convection oxygen atmosphere
by Clair Russell Tempero

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Aerospace and Mechanical Engineering
Montana State University
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Abstract:
The oxidation rate of iridium wire in force-convected oxygen was investigated at temperatures in the range of 1600-2200°C, pressures in the range of 3.5-1,000 torr, and oxygen flow rates in the range, of 0.56-148.8 liter/min (STP).

Attempts were made to correlate experimental, results with three derived theoretical, models, resulting in only limited success. Experimental data at 1600 °C, 1905°C, and 2200 °C was then least-squares curve fit to three separate empirical equations. Subsequently all of the experimental data were curve fit to an empirical equation containing a velocity, pressure, diameter, and temperature dependence.

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Date _May 25, 1972_

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IN A FORCED CONVECTION OXYGEN ATMOSPHERE

by

CLAIR RUSSELL TEMPERO

A thesis submitted to the Graduate Faculty in partial
fulfillment of the requirements for the degree

of

MASTER OF SCIENCE

in

Aerospace and Mechanical Engineering

Approved:

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I am especially grateful to Dr. R. T. Wimber, Aerospace and Mechanical Engineering Department, who, in addition to serving as chairman of the thesis committee, made this report possible through his support and guidance.

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ABSTRACT

The oxidation rate of iridium wire in force-convected oxygen was investigated at temperatures in the range of 1600-2200 °C, pressures in the range of 3.5-1,000 torr, and oxygen flow rates in the range of 0.56-148.8 liter/min (STP).

Attempts were made to correlate experimental results with three derived theoretical models, resulting in only limited success. Experimental data at 1600 °C, 1905 °C, and 2200 °C was then least-squares curve fit to three separate empirical equations. Subsequently all of the experimental data were curve fit to an empirical equation containing a velocity, pressure, diameter, and temperature dependence.

Introduction

Iridium is the only metal with a sufficiently high melting point and sufficiently slow oxidation characteristics to be used unprotected in air for any reasonable length of time at temperatures in the range of 2000 °C to 2300 °C. Although iridium is not perceptibly oxidized at room temperature, heating in an oxygen bearing atmosphere to about 600 °C produces a thin oxide film. At temperatures greater than about 1000 °C iridium displays a weight loss which is linear in time as the result of the formation of volatile oxides.

Iridium is presently available commercially as iridium and iridium-rhodium alloy wires, used as heating elements in high-temperature furnaces and as standardized high-temperature thermo-couples. Iridium has fairly good high-temperature strength properties, but is not used as a primary structural material in large applications due to the high cost of iridium metal. Considerable effort has been expended in the development of iridium coatings intended for the protection of less expensive high-temperature structural materials having very poor oxidation resistance, including graphite[1], tungsten[2], and tantalum base alloys[3]. Work to date has demonstrated the potential of iridium in coating form in applications including leading edges of re-entry space craft, components in rocket motors, and nuclear reactors.

Wimber[4] has provided a fairly complete resume of previous

work which is briefly summarized below.

Several workers have investigated the composition of the prod-

ucts of oxidation of iridium and the thermodynamics of the equi-

libria involved. By passing oxygen or oxygen-nitrogen mixtures

over a boat containing iridium metal at atmospheric pressure and

temperature in the range of 1169-1462°C, Cordfunke and Meyer[5]

found IrO_3 to be the main volatile oxide. They also found values

of equilibrium constants that were slightly higher than values

obtained by Alcock and Hooper[6] and also those obtained by Schäfer

and Heitland[7]. Holburn, Henning, and Austin[8] studied iridium foil,

self-resistance heated to 1670°C in slowly flowing oxygen, air,

or nitrogen containing 1.77% oxygen, at atmospheric pressure. They

concluded that IrO_3 was the main gaseous oxide specie formed.

Norman, et al[9] conducted a series of mass spectrometric

studies of oxidizing iridium by feeding oxygen into an iridium

Knudsen cell heated from 1557 to 1760°C while bombarding the ex-

isting gaseous species with a stream of electrons. The Ir^+, IrO^+,

IrO_2^+ and IrO_3^+ ions were detected. These workers concluded that

IrO_2 and IrO_3 were the main volatile oxides present in their stud-

ies. They also obtained values for the standard-state enthalpy

and entropy changes for the formation of $IrO_2(g)$ of $+48.5 \pm 0.8$

kcal/mole and $+3.9 \pm 2.0$ eu and for $IrO_3(g)$, values of $+5.5 \pm 1.5$

kcal/mole and -13.1 ± 2.5 eu. In an independent study, Margrave[10] considered the formation of Ir_2O_3 from which he concluded that it is a minor species at high temperatures.

There have been a number of kinetic studies of the oxidation of iridium in recent years.

Phillips[11] studied the oxidation of ¼ inch diameter by ½ inch long iridium specimens in air moved only by natural convection in the temperature range of 650-1300 °C. He obtained an activation energy of 9.2 kcal/mole. Krier and Jaffee[12] studied the oxidation of rectangular shaped iridium specimens in slowly moving air in a vertical furnace tube at 1000-1400 °C. They obtained an activation energy of 16 kcal/mole.

Criscione,[13] et al, studied the oxidation of ½ inch diameter iridium rods in oxygen and argon-oxygen mixtures at a total pressure of 710 torr and temperatures of 1150-1900 °C. Rates of recession of the hemispherical end of the rod were measured for a relatively wide range of mass velocities for the gas flow. An activation energy of 23 kcal/mole was obtained.

Kuriakose and Margrave[14] performed experiments on iridium foil (0.002-inch thick) at temperatures of 1010-1301 °C and on iridium wire (0.010-inches diameter) at temperatures of 1198-2217 °C. The specimens were resistance heated in a vertical one-inch pyrex tube in oxygen or oxygen-helium mixtures at one

atmosphere total pressure with downward gas flow parallel to the specimen. They observed an increase in activation energy from 12.5 to 30-33 kcal/mole with increasing gas temperature at a hot-wire oxidation temperature of 1600 °C. In addition to the above activation energies, the various workers have observed values of 1.2, 1.34, and approximately 1.5 for the exponent in the exponential dependency of the oxidation rate on oxygen partial pressure.

Although the above variations in results indicate that the overall process of the oxidation of iridium is quite complex, several meaningful results have been obtained. The volatile oxides $IrO_2(g)$ and $IrO_3(g)$ appear to be the major species formed with $IrO(g)$ and $Ir_2O_3(g)$ being possible minor species, at least under some conditions. Reasonably good values for $\Delta S^°_f$ and $\Delta H^°_f$ for the two major oxides have been determined and are expected to vary little with changes in temperature; allowing values for the equilibrium constants for both major species to be calculated over a reasonable temperature range with a fair degree of accuracy.

None of the above studies has led to a characterization of the oxidation process which would allow taking into account the effects on oxidation rate of varying the temperature, oxygen partial pressure, total pressure, flow rates, specimen size and specimen configuration. For this reason the present study was undertaken in an attempt to determine a theoretical model that

would describe the dependence of the oxidation process of iridium on the above parameters.

Theoretical Models

Under conditions where all oxides formed are volatile, metals in general are considered to oxidize in the following manner:

1. Bulk transport of the oxygen-bearing gas from a source to the general vicinity of the metal being oxidized,

2. Diffusion of oxygen through the gaseous boundary layer adjacent to the surface of the metal,

3. Adsorption of oxygen from the gas phase onto the surface,

4. Reaction on the surface (including possible rearrangement and migration processes),

5. Desorption of the oxide(s) from the surface and

6. Diffusion of the oxide(s) through the gaseous boundary layer with possible further chemical reaction within the boundary layer of one oxide species with a different oxide species and/or oxygen.

The rate at which the reaction process takes place is controlled by one or more of the above steps which are slower than the rest of the steps. Environmental conditions determine which of the above steps controls the reaction process. Thus a change in environmental conditions may result in a change in the step(s)

which control the overall oxidation process.

Under forced convection conditions, the bulk transport of the
oxygen bearing gas (step 1) would not be expected to control the
oxidation rate. Under conditions where the oxygen partial
pressure is a sizable portion of one atmosphere, iridium has a
relatively slow rate of oxidation so that the inward diffusion
of oxygen through the boundary layer (step 2) would not be ex-
pected to control the rate of oxidation. Kinetic studies in
general indicate that an increase in temperature causes a slow
surface reaction rate to speed up so that eventually the slow
step in the overall oxidation process becomes diffusion through
the boundary layer, (i.e. change in rate controlling step from
step 4 to steps 2 or 6 in the above listing). Increasing flow
rate decreases the effective thickness of the boundary layer and
increases the diffusion rates so that a process initially under
diffusion control might change to control by surface reaction
rates. Increasing the pressure increases the rate of surface
reaction in many systems but decreases the gaseous diffusivities
so that a change from surface control to diffusion control is
possible.

By noting that any one of the above steps could be expected
to control the oxidation process and by considering $IrO_2(g)$ and
$IrO_3(g)$ as being the principle oxides, Wimber was able to derive

a theoretical surface recession rate equation that would be
expected to be applicable at all temperatures where all of the
oxides formed are volatile. His complete derivation of this
equation, from which the final equation is listed below, can be
found in his first annual report on the high-temperature oxida-
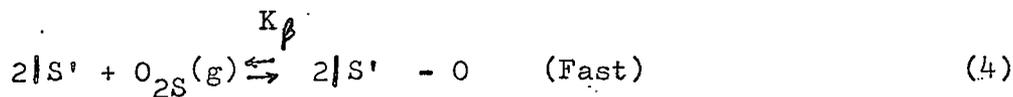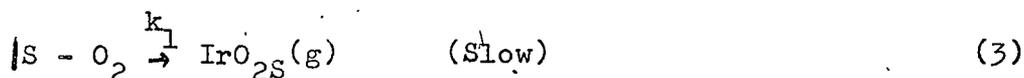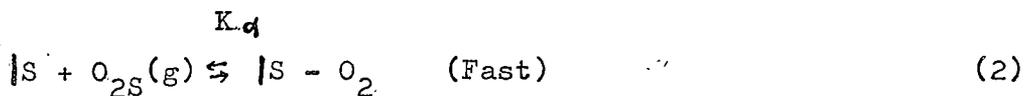tion of iridium.[15]

$$
X = \frac{\left[M_1' \, k_{G1} + M_2' \, k_{G2} K_3 P_{O_2}^{1/2} \right] \left[\dfrac{M_1' K_1 P_{O_2}}{(2 \pi M_1 RT)^{1/2}} + \dfrac{M_2' \, K_2 P_{O_2}^{3/2}}{(2 \pi M_2 RT)^{1/2}} \right]}{\rho \left[\dfrac{M_1'}{(2 M_1 RT)^{1/2}} + \dfrac{M_2' K_3 P_{O_2}^{1/2}}{(2 M_2 RT)^{1/2}} + M_1' \, k_{G1} + M_2' \, k_{G2} K_3 P_{O_2}^{1/2} \right]}
\tag{I}
$$

where M_1' and M_2' are effective equivalent weights having a value
of 192.2 grams iridium consumed per gram mole of IrO_2 or IrO_3
formed. M_1 and M_2 are the molecular weights of IrO_2 (g) and
IrO_3(g) respectively, k_{G1} and k_{G2} are mass transfer coefficients
corresponding to the diffusion of gaseous IrO_2 and IrO_3 through
the boundary layer, and ρ is the density of iridium metal at the
oxidation temperature. K_1 is the equilibrium constant for the
overall reaction of gaseous oxygen with iridium metal to form
IrO_2, K_2 is the equilibrium constant for the overall reaction of
gaseous oxygen with iridium metal to produce gaseous IrO_3, K_3 is

the equilibrium constant for the overall gas-phase reaction of IrO_2 and oxygen to form IrO_3, P_{O_2} is the oxygen partial pressure, R is the ideal gas law constant, and T is the absolute temperature.

The above equation was subsequently modified and two new theoretical models introduced.[16] in the hope of obtaining a theoretical correlation that would compare with experimentally obtained data. Two different rate equations were obtained for each of the three models by making two different assumptions: (1) the gaseous oxides once formed at the inner surface of the boundary were assumed to enter into a gas phase equilibrium reaction or alternately (2) the gaseous oxides were assumed to form completely independently of each other and diffuse through the boundary layer without reaction.

The original model above is characterized by the following equilibrium reaction equations:

$$|S + O_{2S}(g) \overset{K_\alpha}{\rightleftharpoons} |S - O_2 \quad \text{(Fast)} \tag{2}$$

$$|S - O_2 \overset{k_1}{\rightarrow} IrO_{2S}(g) \quad \text{(Slow)} \tag{3}$$

$$2|S' + O_{2S}(g) \overset{K_\beta}{\rightleftharpoons} 2|S' - O \quad \text{(Fast)} \tag{4}$$

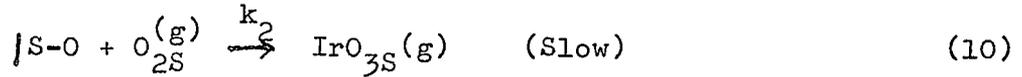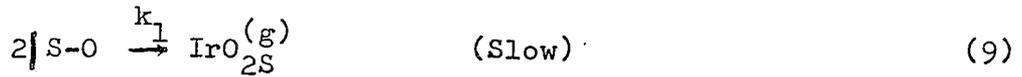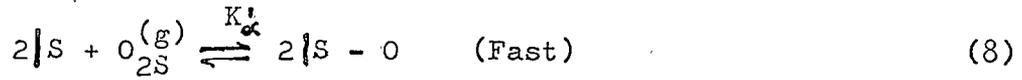$$|S' - O + |S - O_2 \xrightarrow{k_2} IrO_{3S}(g) \quad (Slow) \quad (5)$$

where the $\underline{S}$ in the subscripts for the gaseous species denotes a location immediately adjacent to the surface of the iridium metal and the $|S$ and $|S'$ denote surface reaction sites on the iridium metal. Assuming equilibrium reaction between the gaseous IrO_2, IrO_3, and O_2 at the inner surface of the boundary layer followed by diffusion led to the following equation:

$$\overset{\circ}{X} = \frac{A(k_{G1} + k_{G2}K_3P_{O_2}^{1/2})(k_{1b}K_1P_{O_2} + k_{2b}K_2P_{O_2}^{3/2})}{(k_{1b} + k_{2b}K_3P_{O_2}^{1/2} + k_{G1} + k_{G2}K_3P_{O_2}^{1/2})} \quad (6)$$

where $\underline{A}$ is an effective equivlent weight equal to 192.2 grams of iridium consumed per gram mole of IrO_2 or IrO_3 formed divided by the density of iridium at the reaction temperature, and k_{1b} and k_{2b} are specific reaction rate constants for the reverse reactions in Equations 3 and 4. If it is assumed that the two oxides form and diffuse independently, the following equation results:

$$\overset{\circ}{X} = A\left[\frac{k_{G1}k_{1b}K_1P_{O_2}}{(k_{G1} + k_{1b})} + \frac{k_{G2}k_{2b}K_2P_{O_2}^{3/2}}{(k_{G2} + k_{2b})}\right] \quad (7)$$

A second model was developed which is described by the following equations:

$$2|S + O_{2S}^{(g)} \underset{\rightleftharpoons}{\overset{K'_{\alpha}}{}} 2|S - O \qquad \text{(Fast)} \tag{8}$$

$$2|S-O \overset{k_1}{\rightarrow} IrO_{2S}^{(g)} \qquad \text{(Slow)} \tag{9}$$

$$|S-O + O_{2S}^{(g)} \overset{k_2}{\longrightarrow} IrO_{3S}(g) \qquad \text{(Slow)} \tag{10}$$

From this second model the following rate equation was obtained by assuming an equilibrium reaction between gaseous IrO_2, IrO_3, and O_2 at the inner surface of the boundary layer followed by diffusion:

$$\overset{.}{X} = \frac{A(k_{G1} + k_{G2}K_3 P_{O_2}^{1/2}) \left[\dfrac{k_{1f} P_{O_2}}{(1 + WP_{O_2}^{1/2})^2} + \dfrac{k_{2f} P_{O_2}^{3/2}}{(1 + WP_{O_2}^{1/2})} \right]}{\left[k_{G1} + k_{G2}K_3 P_{O_2}^{1/2} + \dfrac{k_{1f}}{K_1 (1 + WP_{O_2}^{1/2})^2} + \dfrac{k_{2f} K_3 P_{O_2}^{1/2}}{(1 + WP_{O_2}^{1/2}) K_2} \right]} \tag{11}$$

Using this same model with the assumption that the gaseous IrO_2 and IrO_3 form independently and diffuse through the boundary layer without reacting resulted in the following equation:

$$\overset{'}{X} = \cfrac{A. k_{G1} P_{O_2} k_{1f}}{(1 + WP_{O_2}{}^{\frac{1}{2}})^2 \left[k_{G1} + k_{1f}/K_1 (1 + WP_{O_2}{}^{\frac{1}{2}})^2 \right]} +$$

$$\cfrac{A k_{G2} P_{O_2}{}^{3/2} k_{2f}}{(1 + WP_{O_2}{}^{\frac{1}{2}}) \left[k_{G2} + k_{2f}/K_2 (1 + WP_{O_2}{}^{\frac{1}{2}}) \right]} \tag{12}$$

In the above two rate equations, k_{1f} and k_{2f} are specific reaction rate constants for the forward reactions in Equations 9 and 10, and W is the product of a proposed equilibrium constant and the ratio of two activity coefficients.

A third model was characterized by the following equations.

$$Ir_S + O_{2S} \underset{k_{1b}}{\overset{k_{1f}}{\rightleftharpoons}} IrO_{2S}{}^{(g)} \tag{13}$$

$$Ir_S + 3/2\ O_{2S} \underset{k_{2b}}{\overset{k_{2f}}{\rightleftharpoons}} IrO_{3S}{}^{(g)} \tag{14}$$

This model, derived assuming an overall-reaction approach without specification of the intermediate adsorption, surface reaction, and desorption processes led to the following equation by assuming an equilibrium reaction between gaseous IrO_2, IrO_3, and O_2 at the inner surface of the boundary layer followed by diffusion:

$$\dot{X} = \frac{A(k_{G1} + k_{G2}K_3 P_{O_2}^{1/2})\ (k_{1f}P_{O_2} + k_{2f}P_{O_2}^{3/2})}{(k_{G1} + k_{G2}K_3 P_{O_2}^{1/2} + k_{1f}/K_1 + k_{2f}K_3 P_{O_2}^{1/2}/K_2)} \qquad (15)$$

Assuming independent formation and diffusion of the gaseous IrO_2 and IrO_3 yielded the following equation:

$$\dot{X} = \frac{Ak_{G1}k_{1f}P_{O_2}}{k_{G1} + k_{1f}/K_1} + \frac{Ak_{G2}k_{2f}P_{O_2}^{3/2}}{k_{G2} + k_{2f}/K_2} \qquad (16)$$

Experimental data used in evaluating the validity of the above models was obtained using iridium wire specimens and equipment as described in the following sections. The equipment was designed to have a well characterized velocity profile, capability to operate at reduced pressure, and the capacity to permit a large variation in gas flows, as well as a means of varying specimen temperature. By varying these parameters, it was hoped that the actual processes that control the oxidation of iridium could be determined.

Specimen Analysis

All oxidation studies were conducted using commercially pure iridium wire, initially 0.635 mm (25 mils) in diameter. This wire was purchased from Engelhard Industries, Carteret, New

Jersey. Results of a spectrographic analysis of the wire,

performed at the Matthey Bishop Co., Malvern, Pennsylvania, as

well as the results of a vacuum fusion analysis for oxygen,

hydrogen, and nitrogen, performed at the Magnflux Testing

Laboratories, Los Angeles, California, are contained in Table I.

The total measured impurity content of the iridium wire was

0.028%. The iridium content was estimated to exceed 99.95%

although the analysis did not include all known elements.

Oxygen Analysis

The oxygen used in the present study was commercial USP grade,

typically of 99.7% purity with nitrogen and argon as the primary

impurities along with traces of water vapor.
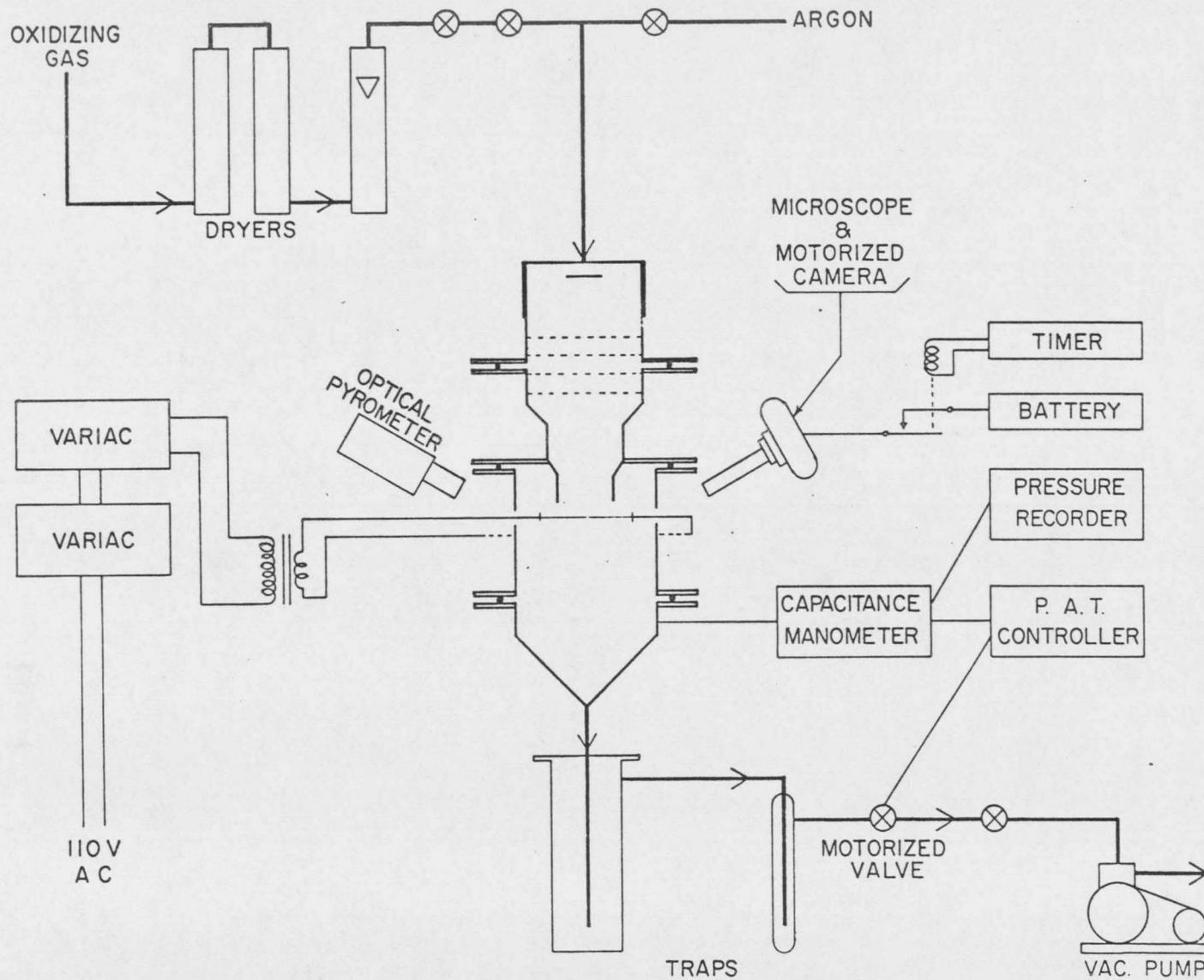
Experimental Equipment

The equipment used allowed placement of an iridium wire in a

vertical position, perpendicular to a horizontal oxygen stream

free of turbulence with a reasonable length of wire exposed to

constant velocity conditions. A heating current was then passed

through the wire to obtain the high temperatures used in the

oxidation studies.

Figure 1 is a schematic representation of the experimental

equipment. The oxygen stream was passed through a two-stage

pressure regulator followed by two driers (in series) containing

TABLE I, ANALYSIS OF THE IRIDIUM WIRE

(Amounts of Impurity Elements Expressed in P.PM)

P.t	15	Sb	<10	Fe.	87	Sn	<1
Pd	5	As	<10	Pb	<1	Ti	6
Rh	54	Bi	<1	Mg	5	Zn	<10
Ru	25	B	5	Mn	1	Ca	7
Os	<3	Cd	<1	Mo	1	O	30
Au	3	Cr	<1	Ni	3	H	1
Ag	<1	Co	<1	Si	7	N	15
Al	9	Cu	2	Te	<10		

Figure 1   SCHEMATIC DRAWING OF EXPERIMENTAL EQUIPMENT

calcium sulfate hemihydrate and anhydrous magnesium perchlorate

respectively. From the driers the gas passed to a rotometer;

three different rotometers were used to allow oxygen flows from

0.5 liters/min (.025 CFM) to 150 liters/min (6.7 CFM). After

passing from the rotometer, a multi-turn micrometer needle valve

was used to regulate the gaseous flow prior to its passing

through a second valve providing rapid on-off type action. The

oxygen then entered the apparatus through a horizontal injector

mounted on the end of the oxidation chamber.

The injector consisted of a circular tube provided with a

baffle and a series of stainless-steel screens provided to

eliminate turbulence introduced into the gas stream as it ini-

tially entered the apparatus. The series of stainless-steel

screens consisted of one 20-mesh screen, two 40-mesh screens, and

one final 100-mesh screen. The final portion of the injector was

necked down and connected to a one-inch by 7/8-in-ID copper tube

terminating approximately one-eighth inch from the oxidizing

wire at its center.

Hot-wire-anemometry work was conducted[17] with the injector in

place to determine velocity profiles under varying flow and

pressure conditioned. The velocity was found to be constant in a

0.25 to 0.6 inch-diameter region for the flow conditions studied.

The turbulence level was found to be equal to or less than one

percent throughout the range of flow rates investigated. The above anemometry work also provided a means of determining the relationship between center-line velocity and gas flow.

After passing over the oxidizing wire the gas stream passed through a water cooled condenser trap followed by a liquid-nitrogen or a dry-ice-acetone-cooled trap, all of which were designed to remove a major portion of the volatile iridium oxides from the gas stream. The dry ice trap was used at pressures over 200 torr due to the tendency of the oxygen stream to liquify, caused by a higher boiling point for oxygen at this pressure than for liquid nitrogen at atmospheric pressure. Following the two traps, the gas stream passed through a motorized diaphragm valve used to provide continuous pressure control of the system. The gas then passed on through a manually operated one-inch bellows-type vacuum valve and left the system through a 425 liters per minute (15 CFM) capacity vacuum pump.

The heating current of 15 to 35 amps in the wire was obtained by passing AC line current through two variacs connected in series, followed by a 20:1 stepdown transformer. The current was regulated by pre-setting one variac for maximum sensitivity and then using the other variac to make necessary adjustments of the wire current to maintain the experimental wire temperature. The wire temperature was monitored by sighting on the wire with a

8630 series Leeds and Northup optical pyrometer provided with a 3.8-cm focal-length lens.

Continuous measurement of the pressure within the oxidation chamber was provided by a Baratron model 77M-XRP capacitance manometer. The above unit was also used to provide a control signal for a Leeds and Northup Electromax PAT-type controller which regulated the motorized diaphragm valve through a Model 10218 Barber-Colman type MP drive unit. The output signal from the capacitance manometer was continuously recorded during oxidation experiments using a Leeds and Northup Speedomax-H recorder. Also incorporated in the equipment, although not shown in Figure 1, was a second vacuum pump (of 25 liter/min, 0.9 CFM capacity) used to provide a static reference vacuum for the capacitance manometer.

The wire oxidation took place in a rectangular water-cooled chamber having dimensions of 1X3X3½ inches. Each 3X3½ inch side was fitted with a sight port having a rotatable window. Through one window of Shadowgraph grade pyrex the above mentioned optical pyrometer was sighted onto the wire. The second window, also of Shadowgraph grade pyrex, allowed viewing the specimen through a M101A Gaertner microscope and Beseler Super D single-lens-reflex 35-mm motor-driven camera, used to obtain film images of the wire at 20X magnification. The exposure and film advancing process

for the camera was cyclically actuated by a Lafayette model
51013T timer. The films thus provided a timed sequence of photo-
graphs of wire diameters from which oxidation rates could be
determined. The electrical current used to heat the wire speci-
men was passed through the walls of the chamber using water-
cooled copper-alloy terminals which were electrically insulated
from the walls of the oxidation chamber by means of teflon gas-
kets. One end of the wire specimen (2 3/16 inches in length) was
clamped in the top terminal and the other end passed into a
mercury pool contained in the second terminal; allowing for ther-
mal expansion of the wire without deflection.

Determination of the sequence of wire diameters on the film
was obtained using a clamping frame to hold the film between two
glass windows and a Gaertner cathetometer fitted with a Gossen
Luna-Pro light meter and microscope attachment. An aluminum-
foil diaphragm having a 0.002 inch wide slit was placed at the
reticle plane of the microscope mounted in the cathetometer.
This light meter and slitted foil diaphragm arrangement allowed
the diameter of the wire to be determined within about $\pm$ 0.1%.

Experimental Procedure:

Oxidation experiments were done on wire specimens initially
25 mils (0.635 mm) in diameter cut into 2-3/16 inch lengths and

having a flat area ground near one end for a reference as to wire

orientation. The wire was first placed in the oxidation chamber

and annealed for ½ hour at 2200 °C in an argon atmosphere to

relieve any stresses. The wire was then mounted in a rotational

fixture outside of the oxidation chamber along with a drill stem

of known diameter. A picture of the drill stem was then taken

along with pictures of the wire at an orientation of $0°$, $45°$,

$90°$, and $135°$ to the orientation when in the oxidation chamber.

All pictures were taken at a location on the wire even with the

end of the drill stem which corresponded to the approximate

center of the wire. The wire was then mounted in the oxidation

chamber and the chamber closed to the atmosphere.

After sealing the chamber, it was pumped down, checked for

air leaks and back-filled with argon. The chamber was again

evacuated and an oxygen stream introduced into the oxidation

chamber. Alternate adjustments were then made between the needle

valve on the rotometer and the valve on the vacuum pump to get

the correct flow and the approximate pressure in the system.

Once the approximate pressure had been obtained the controller

unit and motorized valve were used to make final adjustments of

the pressure.

Following the above procedure to establish the correct flow

and pressure conditions, the wire was brought up to temperature

by applying a voltage through one of the variacs while observing the wire through the pyrometer. The camera was subsequently actuated to take pictures at predetermined intervals. Characteristically from 0.5 to 1.0 mil was removed from the wire for any given oxidation run which consisted of 10 exposures and ran from five minutes to one hour, depending on values of pressure, temperature and oxygen flow. Plus-X Pan film was used with the camera set at from 1/60 to 1/250 second exposure time.

Following the run, the wire was again removed from the chamber and the sequence of rotational pictures again taken of the wire at the same location as before the oxidation run. After concluding the oxidation run the film was developed and allowed to dry for about two hours to minimize shrinkage during the film reading process. The above mentioned cathetometer was then used to read the film; reading each exposure in the middle and on both edges so that an average value of the diameter on each exposure could be obtained. From the readings taken with the wire in the rotational fixture, the rate of axidation of the wire at 45°, 90°, and 135° could be compared with the oxidation rate of the wire in the same direction as the oxygen flow stream. The sequence of values of diameter obtained for the oxidizing wire were plotted versus time, and a straight line was fitted to the points. From this graph an oxidation rate was determined.

Experimental Results

Initial oxidation studies were conducted using an infrared pyrometer to regulate wire temperature in the range of 1600-2200 °C. In August, 1971, it was discovered that the pyrometer output had been drifting by as much as 200 °C even though the instrument appeared to be functioning properly. This excessive drift rendered all of the previously taken data invalid so that data had to be re-taken using an optical pyrometer. The experimental data that was subsequently compiled is listed in Table II. The data is arranged in the order of increasing temperature with the data at each temperature arranged according to increasing pressure.

The parameters effecting the oxidation rate of the iridium wire specimens were: oxygen pressure in the oxidation chamber surrounding the wire, mass flow rate of oxygen over the wire, surface temperature of the oxidizing wire, and wire diameter. In order to find the effect of each of these parameters on the oxidation characteristics of the test specimens, several different series of runs were conducted in which one of the parameters was varied while holding the other parameter essentially constant. This was done for wire diameter while holding oxygen flow, pressure, and temperature constant (Runs 14-18). Pressure dependency