



Natural-convective high-temperature oxidation of iridium  
by Neil Kelly Wahl

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

An investigation of oxidation of iridium wire in naturally-convected oxygen and air was performed in the temperature range of 1675 to 2260°C (1948 to 2533°K) and the pressure range of  $9.8 \times 10^{-8}$  to 1.32 atmospheres ( $7.5 \times 10^{-5}$  to 1000 torr). Two theoretical models were developed, each extending over specific pressure ranges. One model described the surface recession rate at low pressures where metal vaporization predominated the rate. The second model described the surface recession rate at high pressures where it was assumed that diffusion of Ir(g), IrO<sub>2</sub>(g), and IrO<sub>3</sub>(g) through a gaseous boundary layer controlled the rate. A close correlation between the experimental results and theoretical calculations was achieved for oxidation in both oxygen and air.

Empirical equations that describe the temperature dependence of the free energies of formation of IrO<sub>2</sub>(g) and IrO<sub>3</sub>(g) were developed. Results from these equations agree fairly well with results of previous investigators.

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Date May 24, 1974

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## NOMENCLATURE

## Symbols

A	Equivalent weight equal to 192.2 gms of iridium consumed per gm mole of oxide formed divided by the density of the iridium.
$\alpha$	Accommodation coefficient
$\alpha'$	Power used in describing diameter dependencies
$\alpha_v$	Vaporization coefficient
$\beta$	Coefficient of thermal expansion - $(^{\circ}\text{K})^{-1}$
$C_p$	Specific heat at constant pressure of the oxidizing gas - cal/(gm $^{\circ}$ K)
$C_v$	Specific heat at constant volume of the oxidizing gas - cal/(gm $^{\circ}$ K)
D	Diameter of wire - cm
$D_v$	Molecular diffusivity - cm $^2$ /sec
$\Delta F_f^{\circ}$	Standard-state free energy of formation - kcal/mole
$\Delta L$	Percent thermal expansion of the iridium wire
$\Delta T$	Difference between wire temperature and ambient temperature - $^{\circ}\text{K}$
$\epsilon_{12}$	Energy of molecular interaction - ergs
$\epsilon_1/\bar{k}$	Force constant for oxidizing gas - $^{\circ}\text{K}$
$\epsilon_2/\bar{k}$	Force constant for oxide specie - $^{\circ}\text{K}$
g	Gravitational acceleration - cm/sec $^2$
$\gamma$	Specific heat ratio for the oxidizing gas
Gr	Grashof number
h	Convective heat-transfer coefficient - cal/(cm $^2$ sec $^{\circ}$ K)

## Symbols

$I_D$	Collision integral for diffusion
$J$	Flux equal to moles of vapor molecules that leave a surface per unit area and time
$k$	Thermal conductivity of the oxidizing gas - cal/(cm sec °K)
$\bar{k}$	Boltzmann constant - $1.38 \times 10^{-6}$ ergs/°K
$K$	Equilibrium constant
$k_G$	Gas-film mass transfer coefficient for diffusion of oxide specie through the boundary layer - gm mole/(sec cm <sup>2</sup> atm)
$\lambda$	Mean free path of gas molecules - cm
$M$	Molecular weight of the oxidizing gas
$M_i$	Molecular weight of the diffusing oxide specie
$\mu$	Viscosity of the oxidizing gas - gm/(cm sec)
$Nu$	Nusselt number
$P$	Total pressure - atm
$P_{BM}$	Logarithmic mean pressure of nondiffusing oxygen - atm
$P_{eq}$	Equilibrium pressure of the vaporizing specie - atm
$P_i$	Partial pressure of the $i^{\text{th}}$ specie - atm
$P_{O_2}$	Partial pressure of oxygen - atm
$P_M$	Partial pressure of the iridium metal - atm
$Pr$	Prandtl number
$R$	Ideal gas constant - 1.987 cal/(gm mole °K) or 82.06 cm <sup>3</sup> atm/(gm mole °K)
$(r_0)_1$	Collision diameter for collision between oxidizing gas molecules - angstroms

## Symbols

$(r_0)_2$	Collision diameter for collision between molecules of iridium containing species - angstroms
$r_{12}$	Collision diameter for collision between oxygen molecule and molecule of iridium containing species - angstroms
Ra	Rayleigh number
$\rho$	Density of the oxidizing gas - gm/cm <sup>3</sup>
$\rho_{\text{Ir}, T_k}$	Density of iridium at $T_k$ - gm/cm <sup>3</sup>
$T_f$	Film temperature - °K
$T_k$	Wire temperature - °K
$T_M$	Melting temperature for oxides - °K
$(V_0)_1$	Molal volume of oxidizing gas - cm <sup>3</sup> (gm mole)
$(V_0)_2$	Molal volume of the oxide specie - cm <sup>3</sup> (gm mole)
$\dot{x}$	Surface recession rate - cm/sec
$\dot{x}_s$	Standardized recession rate - cm/sec

## ABSTRACT

An investigation of oxidation of iridium wire in naturally-convected oxygen and air was performed in the temperature range of 1675 to 2260°C (1948 to 2533°K) and the pressure range of  $9.8 \times 10^{-8}$  to 1.32 atmospheres ( $7.5 \times 10^{-5}$  to 1000 torr). Two theoretical models were developed, each extending over specific pressure ranges. One model described the surface recession rate at low pressures where metal vaporization predominated the rate. The second model described the surface recession rate at high pressures where it was assumed that diffusion of Ir(g), IrO<sub>2</sub>(g), and IrO<sub>3</sub>(g) through a gaseous boundary layer controlled the rate. A close correlation between the experimental results and theoretical calculations was achieved for oxidation in both oxygen and air.

Empirical equations that describe the temperature dependence of the free energies of formation of IrO<sub>2</sub>(g) and IrO<sub>3</sub>(g) were developed. Results from these equations agree fairly well with results of previous investigators.

## CHAPTER I

### INTRODUCTION

#### Characteristics and Uses of Iridium

Iridium, the 77<sup>th</sup> element, is a platinum group metal. It is the only elemental metal known to man that possesses a low enough oxidation rate and a high enough melting point, 2454°C (2727°K), that it can be used unprotected in an oxygen containing gas for extended periods of time at temperatures greater than 2000°C. At temperatures greater than 1000°C, iridium forms volatile oxides and a bare surface is left behind. This results in oxidation rates that are linear with time.

When compared to other metals, iridium is one of the most corrosion resistant over a wide range of temperatures and corrosive environments. The corrosive environments included various acids, salt solutions, fused salts, molten metals, and molten metal oxides.

Iridium has been used as heating elements in high temperature furnaces, standardized high-temperature thermocouples, and for protective coatings of less expensive materials such as tungsten and tantalum base alloys. Potential applications for iridium are leading edges of reentry space vehicles, reactor components, and parts in rockets and turbine engines.

Iridium also has limitations. Being a platinum group metal, the cost of iridium could be a factor restricting extensive use. Weight could be another constraint. Iridium is one of the most dense (22.57 gm/cm<sup>3</sup>) elements known to man. The very low emittance of iridium could

restrict its use as leading edges for reentry vehicles. The primary means of heat dissipation from the leading edge is radiation. The low emittance would then restrict the heat dissipation. The emittance of iridium can be enhanced by oxide overcoats and would not present serious problems to the use as a leading edge material.

#### Review of Prior Work

The brief review of past work done on the oxidation of iridium contained in the following resulted in conclusions used as a starting point for the present studies.

Several separate investigators have studied the products of the oxidation of iridium and the thermodynamics involved in the formation of these products. Cordefunke and Meyer (1) studied the oxidation of iridium in the temperature range of 1169 to 1462°C (1442 to 1735°K). They concluded that  $\text{IrO}_3(\text{g})$  was the major specie formed. Their results were confirmed by other workers (2,3).

Mass spectrometric studies by Norman et al (4) resulted in their conclusion that  $\text{IrO}_2(\text{g})$  and  $\text{IrO}_3(\text{g})$  were the major species of oxidation. The presence of  $\text{IrO}(\text{g})$  could not be ruled out completely. If  $\text{IrO}(\text{g})$  was present, its partial pressure was estimated to be less than 2 percent of the partial pressure of  $\text{IrO}_2(\text{g})$  at the highest temperature investigated. The work of Norman et al involved feeding oxygen at  $10^{-4}$  atm into an iridium Knudsen cell heated to 1557 - 1760°C (1830 - 2033°K). Standard-state enthalpies and entropies of formation for  $\text{IrO}_2(\text{g})$  were reported as 48.5

$\pm 0.8$  kcal/mole and  $3.9 \pm 2.0$  eu respectively. The standard-state enthalpies and entropies of formation for  $\text{IrO}_3(\text{g})$  were reported as  $5.5 \pm 1.5$  kcal/mole and  $-13.1 \pm 2.5$  eu respectively.

Studies performed by Olivei (5) resulted in the conclusions that  $\text{IrO}_2(\text{g})$  and  $\text{IrO}_3(\text{g})$  were the major species formed. This work was done over the pressure range of  $10^{-8}$  to  $10^{-10}$  atm and over the temperature range of 880 to 1780°C (1153 - 2053°K). Mass spectrometric studies in the temperature range of 627 to 2227°C (900 - 2500°K) yielded standard-state enthalpy and entropy of formation for  $\text{IrO}_3(\text{g})$  of 6.0 kcal/mole and -9.5 eu respectively.

Wimber and Kraus (6) concluded that  $\text{Ir}(\text{g})$  was an important specie at high temperatures and that  $\text{IrO}(\text{g})$  contributed very little to the overall recession rate.

Based upon the conclusions of these investigators, the iridium containing species that significantly contributed to the oxidation rate were thought to be  $\text{Ir}(\text{g})$ ,  $\text{IrO}_2(\text{g})$ , and  $\text{IrO}_3(\text{g})$ .

## CHAPTER II

### EXPERIMENTAL EQUIPMENT AND PROCEDURES

#### Experimental Materials

Commercially pure iridium wire was purchased in three lots. Results of mass spectrometric and emission spectrographic analyses along with an indication of the sources and wire diameters are given in Table 1. The major impurity in Lots 1 and 2 was tungsten at 0.6 percent and 0.071 percent respectively. The major impurities in Lot 3 were tungsten (0.02%) and barium (0.02%). The analyses did not include all known elements, but the iridium content was estimated to be 99.3, 99.9, and 99.9 percent in Lots 1, 2, and 3 respectively.

The oxygen used in the present studies was USP grade. Nitrogen and argon were the major impurities and were assumed to be inert to iridium. The oxygen content was typically 99.7 percent.

The air used in the present studies was atmospheric and was assumed to have an oxygen content of 21 percent (based upon a volume percent).

#### Experimental Apparatus and Procedure

The equipment used in the present study is shown schematically in Figure 1. An iridium wire specimen 5.6 cm long was mounted horizontally between two electrodes in a cell. The cell, which had water-cooled copper walls, had the internal dimensions of 2.5 x 7.6 x 8.9 cm. The cell was provided with two sight ports containing rotatable optical-quality pyrex windows. Through one window, a timer-actuated camera fitted with a



Table 1. Analysis\* of Iridium Wire

Impurity	Lot #1 †	Lot #2 ‡	Lot #3 ‡
Pt	19	<0.5	<30
Rh	20	38.0	<50
Pd	10	11.5	<10
Ru	166	1.5	<50
Au	<1	<0.5	10
Ag	50	<0.5	<10
Pb	<5	<0.5	<30
Sn	5	<0.5	<10
Zn	<10	0.41	<300
Fe	170	64	30
Cu	96	17	<10
Si	43	6.1	10
Mg	41	1.1	<10
Ca	78	0.61	<50
Al	14	35	<10
Ni	10	1.1	<10
Cr	31	0.84	<10
Mn	10	0.69	<10
Sb	<10	<0.5	<500
B	<50	0.0032	<10
Co	10	1.8	<10
As	<10	0.066	<300
Bi	<1	<0.5	<10
Cd	<5	<0.5	<300
W	6000	710	200
N	50	0.24	-
H	4	-	-
O	70	8.3	-
Ta	-	46	<500
In	-	0.26	<10
Zr	-	1.1	<10
Ga	-	0.20	<10
V	-	0.096	<10
Ti	-	0.49	<10
K	-	0.67	-
Cl	-	0.59	-
S	-	0.57	-

Table 1 (continued)

Impurity	Lot #1 +	Lot #2 †	Lot #3 †
P	-	0.81	-
Na	-	2.2	-
F	-	0.27	-
C	-	15.0	-
Li	-	0.00072	-
Ba	-	0.5	200

\* Impurity contents expressed in parts per million.

+ 25 mil diameter wire drawn by Englehard Industries, Carteret, New Jersey.

† 20 mil diameter wire drawn by Johnson, Matthey & Co., London, England.

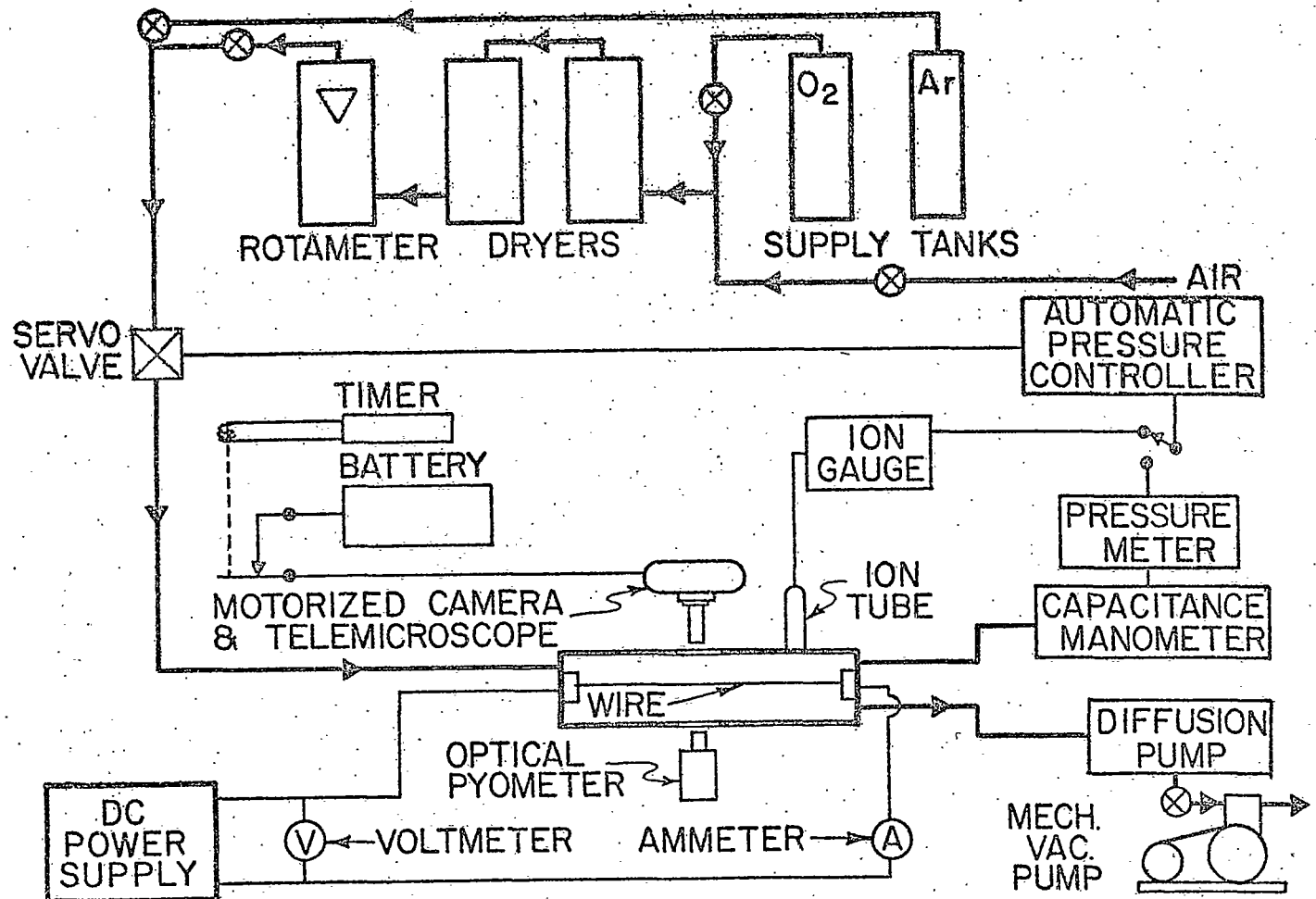


Figure 1. Schematic of Experimental Apparatus

telemicroscope, was used to record the wire diameter at 20x magnification. Through the other window, a Leeds and Northrup 8636-C optical pyrometer equipped with a 38-mm focal length lens was used to determine the brightness temperature of the wire. Errors in temperature measurement would have been caused by condensation of oxides on the windows, but were eliminated by rotating the window to a clean section only when a temperature measurement was being made. The window on the camera side was rotated to a clean section immediately before a picture was taken and immediately after the picture, returned to the original position. The windows were cleaned and polished between runs.

The oxidation cell was mounted on top of a vertical cylinder 10 cm in diameter and 20 cm long. Oxidizing gas was introduced into the cylinder at a point 10 cm below the cell. Through one pressure tap, located 5 cm above and rotated  $90^\circ$  from the gas inlet, an ion tube was used to measure low pressures. Through a second pressure tap, located 5 cm below and rotated  $90^\circ$  from the gas inlet, a capacitive manometer was used to measure high pressures.

Immediately below the cylinder was mounted a water-cooled optically-dense baffle. A Varian/NRC Model M-4 (800 liter/sec) diffusion pump was mounted below the baffle. The baffle prevented a direct line of sight of the pump oil from the pump into the oxidation cell. By means of a hose and tubing, the outlet of the diffusion pump was connected to the inlet of a mechanical pump.

Pressures in the system that were less than  $1.32 \times 10^{-4}$  atm (0.10 torr) were measured with a Westinghouse ion tube (part number WL 7903) and Granville-Phillips Ionization Gauge Controller (series 224) system. Pressures in the system that were greater than or equal to  $1.32 \times 10^{-4}$  atm (0.10 torr) were measured with a MKS Capacitance Manometer 77H-1000 and a MKS Baratron TM Type 77 Pressure Meter. A signal from the measuring instrument was used as an input signal for a Granville-Phillips Automatic Pressure Controller (APC) No. 0-00-216006. The APC operated a servo-driven valve and thus regulated the flow of the oxidizing gas into the system. Before entering the system, the oxidizing gas passed through two driers (the first contained calcium sulfate hemihydrate and the second contained anhydrous magnesium perchlorate) and then through a Matheson No. 74 rotameter.

Current from a Hewlett Packard D.C. Power Supply 6200B was used to self-resistance heat the iridium wire specimen. The voltage across the cell was measured with a Honeywell Digitest Multimeter Model 333R. Current through the wire was measured with a General Electric D.C. Ammeter with a capacity of 50 amperes. The thermal expansion of the wire was accommodated by a cantilever spring arrangement on one of the electrodes. The wire was prestressed to an amount such that when the wire was at the oxidation temperature it was at near zero stress.

Prior to making a run, the wire was cleansed in acetone, mounted between the electrodes, and given an anneal for thirty minutes at  $2260^{\circ}\text{C}$  ( $2533^{\circ}\text{K}$ ) in an argon atmosphere. The purpose of the anneal was to elim-

inate recrystallization and grain growth during oxidation and to attain an electrical resistivity nearly constant with time. This anneal was given only to each new section of wire. After the anneal, the system was evacuated and then backfilled with the desired oxidizing gas. The system was again evacuated, leakchecked, and refilled with the oxidizing gas to the desired pressure level. Once the pressure stabilized, the iridium wire specimen was brought up to the oxidation temperature by slowly increasing the current through the wire. Once the temperature had stabilized, a series of ten film exposures were made at a predetermined time interval. The time interval was selected such that approximately 0.0254 mm (1 mil) was removed from the diameter of the wire during the total time of the run. The film was then removed, developed, and allowed to dry for a minimum of 2 hours before the images of the wire were measured. The images were measured by an instrument that consisted of a modified cathetometer, high intensity light source, and a Gossen Luna-Pro Exposure Meter. The telemicroscope of the cathetometer was modified to include a 0.05 mm (2 mil) slit at the reticle plane. Each frame was measured at three locations (the two ends and the center of the image). The average diameter was converted to an actual diameter by using a conversion factor. The conversion factor was obtained from the measurement of an image of a reference rod of 0.0655 cm (25.8 mil) in diameter. The repeatability of a single diameter measurement was  $\pm 0.05$  to 0.1 percent. Asymmetry of the wire was determined by Wimber and Kraus (6) to always be less than 1.2 percent.

## CHAPTER III

### TRUE WIRE TEMPERATURE DETERMINATIONS

A thermocouple technique used by Halvorson and Wimber (7) to determine the relationship between measured pyrometer temperature and true wire temperature was modified based upon the work of McLaren et al (8). The technique used in the present studies consisted of fusion welding each of the leads of an Ir-Ir4ORh thermocouple to an iridium wire specimen which was mounted between the electrodes of the cell. The specimen was self-resistance heated by an AC power supply. An R-C filtering circuit was used to block the AC voltage from the digital millivoltmeter which was used to measure the thermocouple emf. The thermocouple output was taken as an indication of the true wire temperature at the point where the Ir4ORh lead of the thermocouple was attached to the specimen. This point is also the location where the specimen temperature was measured with an optical pyrometer.

Table 2 contains a summary of the pyrometer temperatures measured through a window and the corresponding true wire temperature for wire heated in oxygen or air.

Table 2. Results of True Wire  
Temperature Determinations

Pyrometer Temperature*, °C (K)	True Wire Temperature, °C (K)
1500 (1773)	1675 (1948)
1615 (1888)	1820 (2093)
1730 (1903)	1965 (2238)
1850 (2123)	2110 (2383)
1965 (2238)	2260 (2533)

\* Measured through a 3/16 inch thick shadow-graph-grade, optical-quality pyrex window.



## CHAPTER IV

### EXPERIMENTAL RESULTS

Figure 2 consists of a plot of the diameter measurements versus time for a typical run. The surface recession rate is calculated by dividing the slope of the straight line by minus two. Figure 3 contains the measured surface recession rates at temperatures in the range of 1675 to 2260 °C (1948 to 2533°K) and over the pressure range of  $9.8 \times 10^{-8}$  to 1.32 atmospheres ( $7.5 \times 10^{-5}$  to 1000 torr) for oxidation in oxygen. For sake of clarity not all the results are shown. Figure 4 contains the measured surface recession rates in the temperature range of 1675 to 2260 °C (1948 to 2533°K) and over the pressure range of  $9.8 \times 10^{-8}$  to 0.66 atmospheres ( $7.5 \times 10^{-5}$  to 500 torr) for oxidation in air.

Table 10 in the appendix contains a summary of experimental conditions and recession rates for work done in oxygen by Kraus (9) and the present investigator. Table 11 in the appendix contains a summary of these same parameters for work done in air by this investigator.

Analysis of either the Figures 3 and 4 or the Tables 10 and 11 in the appendix revealed no apparent difference in the oxidation behavior of the various lots of wire.



































































