



High-temperature oxidation of iridium  
by Thomas Leigh George

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE  
in Mechanical Engineering  
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Abstract:

An investigation of the oxidation of iridium wires was conducted in the temperature range of 1965 to 2260 C (2238 to 2533 K). The wires were oxidized in naturally convected CO<sub>2</sub> at pressures ranging from  $1.32 \times 10^{-3}$  to 1.32 atm (1 to 1000 torr). The experimental results were compared to values calculated from a model based on the assumptions that the oxidation rate was controlled by the rate of CO<sub>2</sub> dissociation, the rate of vaporization of IrO<sub>2</sub>(g), IrO<sub>3</sub>(g) and Ir(g) and the rate of the subsequent diffusion of these species through the boundary layer.

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A thesis submitted in partial fulfillment  
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## ABSTRACT.

An investigation of the oxidation of iridium wires was conducted in the temperature range of 1965 to 2260 C (2238 to 2533 K). The wires were oxidized in naturally convected  $\text{CO}_2$  at pressures ranging from  $1.32 \times 10^{-3}$  to 1.32 atm (1 to 1000 torr). The experimental results were compared to values calculated from a model based on the assumptions that the oxidation rate was controlled by the rate of  $\text{CO}_2$  dissociation, the rate of vaporization of  $\text{IrO}_2(\text{g})$ ,  $\text{IrO}_3(\text{g})$  and  $\text{Ir}(\text{g})$  and the rate of the subsequent diffusion of these species through the boundary layer.



## CHAPTER I

### INTRODUCTION

#### Characteristics and Uses of Iridium

Iridium is considered to be the most corrosion resistant metal known when it is compared with all other metals over a broad range of temperature and in a great variety of corrosive environments [1]. These corrosive environments include numerous acids and salt solutions, molten oxides, fused salts and molten metals.

When iridium is heated in oxygen to about 600 C (873 K) a thin oxide film is produced. At temperatures greater than 1000 C (1273 K) the oxidation products are volatile resulting in an oxidation rate which is constant with time. However, this rate is low enough to allow the use of iridium in contact with oxygen at temperatures above 2000 C (2273 K).

Although iridium has reasonably good high-temperature strength properties, its high cost limits its use as a structural material. Iridium wires are used as heating elements in high-temperature furnaces and as high-temperature thermocouples. Other possible applications for iridium include coatings for components in rocket engines and leading edges on re-entry spacecraft. Iridium has also been considered as a protective coating for components in high temperature gas cooled nuclear reactors where CO<sub>2</sub> is used as a coolant. The present study is particularly relevant to this consideration.

### Review of Previous Work

An extensive review of the literature available on the oxidation of iridium has been presented by Wimber [2] and a brief summary of that review is presented here.

Oxidation studies of iridium carried out by Cordfunke and Meyer [3] indicated  $\text{IrO}_3$  as the major oxide species formed and at temperatures above 1110 C (1383 K) the oxides formed were volatile. Similar results were obtained by Schafer and Heitland [4] and by Alcock and Hooper [5]. Cordfunke and Meyer also arrived at equilibrium constants for the oxidation reaction which were slightly higher than those reported by the other investigators.

A mass spectrometric study by Norman, et al [6] indicated the presence of  $\text{Ir}^+$ ,  $\text{IrO}^+$ ,  $\text{IrO}_2^+$ , and  $\text{IrO}_3^+$  ions during the oxidation of iridium at temperatures between 1557 and 1760 C (1830 and 2033 K).  $\text{IrO}_2$  and  $\text{IrO}_3$  were found to be the major oxide species. The presence of  $\text{IrO(g)}$  could not be ruled out, but if it did exist, its partial pressure would be less than 1/50 of the partial pressure of the  $\text{IrO}_2$  at the highest temperature and oxygen pressure ( $10^{-4}$  atm) involved in the study.

The work of Bartlett [7] on the oxidation of platinum at temperatures greater than 800 C (1073 K) is relevant to the present study because of the chemical similarities between platinum and iridium (Ir is a member of the platinum group) such as the formation of volatile

oxides. Bartlett predicted oxidation rates from calculations involving the reversible reaction,  $O_2 + Pt \rightleftharpoons PtO_2$ , which takes place at the solid-gas interface and the subsequent diffusion of the oxide through the gaseous boundary layer which forms as a result of the natural convection of the oxidizing gas.

Wahl [8] describes two models to predict oxidation rates of iridium wires in air and pure oxygen for both forced and natural convection. One model based on the assumption of diffusion control proved reliable for pressures above  $10^{-4}$  atm. The other model predicted oxidation rates at lower pressures assuming vaporization of the oxide species from the metal surface as the rate limiting process. More recently an equation, similar to that used by Bartlett, was formulated to accommodate both models and produced accurate results for the entire pressure range [9]. The major steps in the derivation of this model are presented in Chapter III.

#### Purpose of Present Study

The present study attempts to show that the diffusion/vaporization model described above [9] applies to the rate of oxidation of iridium in  $CO_2$ , given the amount of oxygen produced by the dissociation of the  $CO_2$ .

Several approaches were formulated to predict the available oxygen at the gas-solid interface, none of which proved completely satisfactory.

These included an approach based on the assumption of local equilibrium at the gas-metal interface, an approach assuming kinetic control for the entire dissociation oxidation process, and a model based on kinetic control for the  $\text{CO}_2$  dissociation with the major portion of the reaction products being removed by diffusion through the boundary layer.

## CHAPTER II

### EXPERIMENTAL PROCEDURE

#### Experimental Materials

The 0.508 mm diameter iridium wire used in this study was commercially pure and from a single lot. Mass spectrometer analysis indicated that the wire was better than 99.8% pure with the major impurities being W (800 ppm), Fe (60 ppm) and Cu (35 ppm).

The CO<sub>2</sub> used was typically 99.99% pure with N<sub>2</sub> the major impurity (20 ppm). Prior to entering the oxidation cell, it was dried first in anhydrous calcium sulfate (CaSO<sub>4</sub>) and then in magnesium perchlorate (Mg(ClO<sub>4</sub>)<sub>2</sub>).

#### Apparatus and Procedure

A detailed description of the apparatus and experimental procedure has been given by Wahl [8]. Consequently a more general and brief explanation will be presented here.

A schematic representation of the experimental system is shown in Fig. 1. The iridium wire was mounted between two electrodes in the water-cooled oxidizing cell. The cell was provided with two sight ports covered with rotatable pyrex windows. Through one port an optical pyrometer was focused on the wire and through the opposite window a motor-driven, timer-actuated camera fitted with a telemicroscope was focused on the same point of the wire.

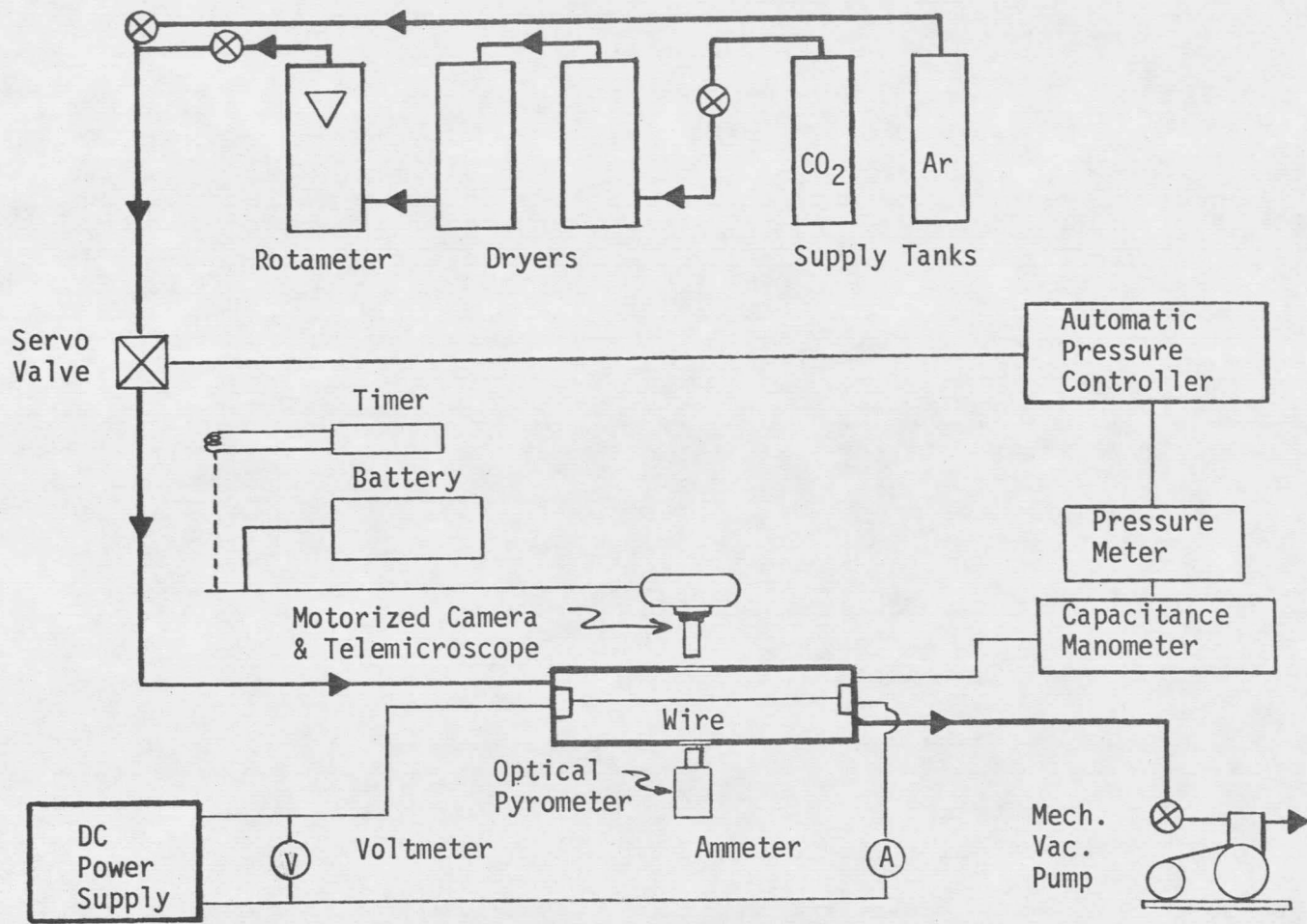


Figure 1: Schematic Representation of Oxidation Apparatus.

The pyrometer was calibrated to compensate for readings taken through the pyrex window as described by Wahl [8]. This calibration was checked periodically throughout the course of the experiments. The wire was maintained at the desired temperature by self-resistance heating. Pressure was held constant at a selected value by use of a servo-controlled valve, coupled with a capacitance monometer. To insure an atmosphere of  $\text{CO}_2$  essentially free from oxidation products, a small, constant flow of  $\text{CO}_2$  was maintained by continuously operating a vacuum pump connected to the system.

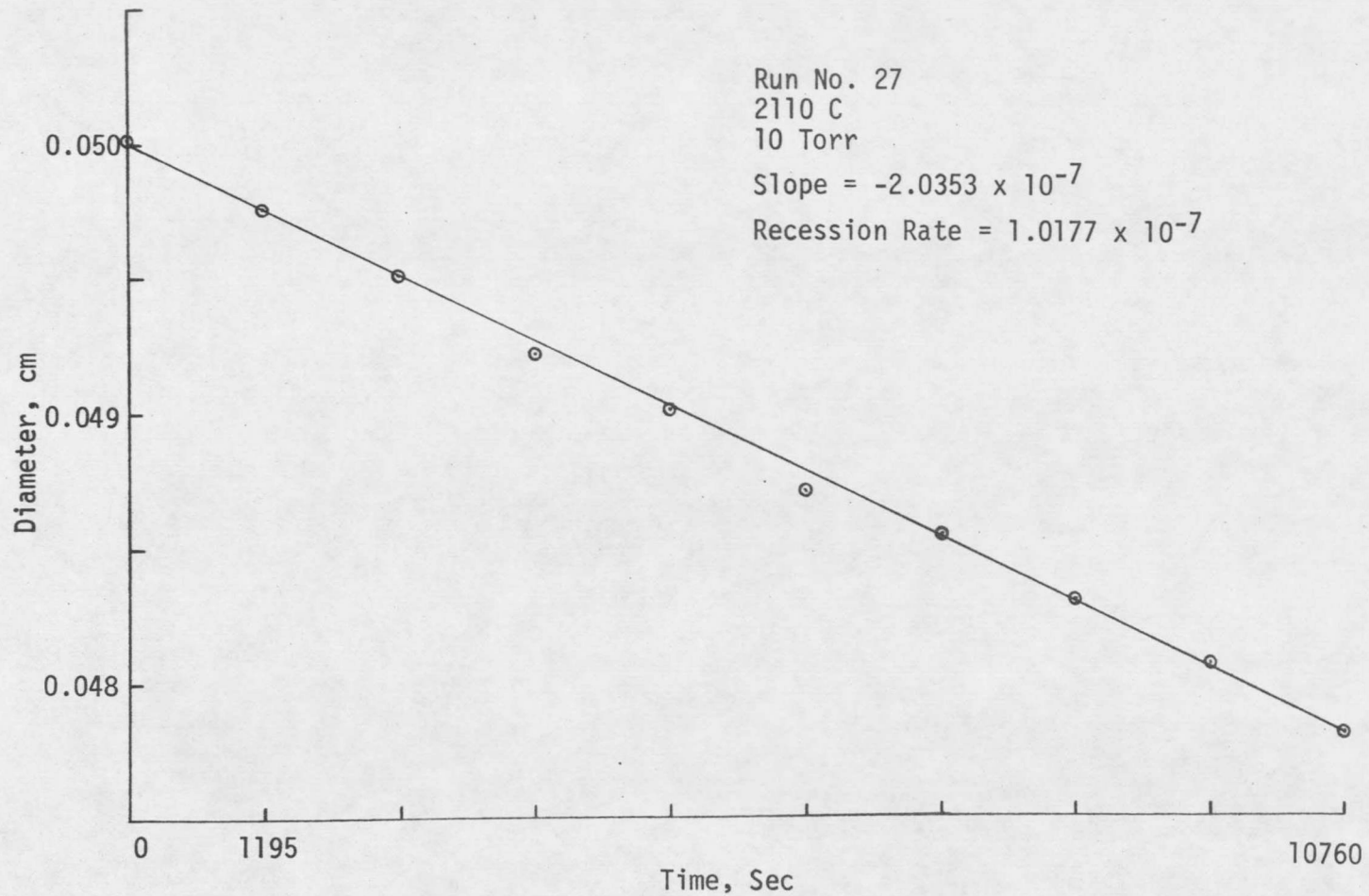
At the beginning of an experimental run a length of iridium wire was cleaned in acetone and mounted between the electrodes in the oxidation cell. The wire was then annealed in an argon atmosphere at 1.05 atm (800 torr) and 2200 C (2437 K) for 30 minutes to prevent excessive recrystallization and grain growth from occurring during oxidation measurements. The argon was then pumped out; the cell was then leak-tested and filled with  $\text{CO}_2$  to the desired pressure. The servo mechanism was activated and allowed to establish a steady flow. The wire was brought to temperature by adjusting the current from the power supply. The camera-timer system was started and a series of ten exposures was taken of the wire.

The time interval between exposures was set so that approximately 0.025 mm would be removed from the wire diameter during the course of the run. The wire temperature was monitored with the optical pyrometer

and kept constant by current adjustments. On longer runs (up to 48 hours) the system was shut off for periods of time. This procedure was not believed to influence the experimental results because the time required to bring the wire back to temperature was negligible compared to the total elapsed time. Upon completion of the run an exposure was made of a drill rod of known diameter at the same focal length as the wire. This served as a standard for determining the wire diameters. The wire images were measured using a modified cathetometer in which a foil with a 0.05 mm slit was incorporated in the telemicroscope. Using a high-intensity back light on the film and a light meter attached to the eyepiece of the telemicroscope, the image width could be obtained, and converted to a wire diameter using the relationship between the image width of the drill rod and the known drill rod diameter. The repeatability of a single measurement was typically  $\pm 0.05$  to 0.1 percent. Hills [10] reported that in using this procedure a correction in the diameter measurements must be made due to the appearance of a fringe zone at the edges of the wire image. The thickness of this fringe zone was determined to be a function of the wire temperature and is included in the final calculations for this study.

Typical results of film measurements for a single run are plotted in Fig. 2 where the slope of the line divided by negative two gives the recession rate in cm/sec.





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Figure 2: Typical Rate Plot for an Oxidation Experiment.

CHAPTER III  
THEORETICAL MODEL

Modeling Oxidation Rates

The term oxidation is used to define the reaction between a metal and oxygen in the absence of water or aqueous phase. The oxidation of most metals is characterized by the build-up of an oxide film on the surface; in many cases (e.g., Al and Cr oxidation) the film acts as a protective coating, while in others (e.g., Fe oxidation) the film is nonprotective. Over a certain temperature range some metals including tungsten, molybdenum, and iridium form oxide species which are volatile. The oxidation of these metals is characterized by a linear rate law.

From an engineering viewpoint, a factor of major interest in the oxidation process is the rate at which it occurs. In formulating a model describing the oxidation process, each step must be considered as potentially rate limiting. Once the limiting step or steps are determined and described quantitatively the rate can be predicted. For the specific case of iridium oxidation in naturally convected  $\text{CO}_2$ , a reasonable sequence of events based on earlier work is as follows [2]:

- 1) Oxygen production from  $\text{CO}_2$ .
- 2) Adsorption of the free oxygen onto the metal surface.
- 3) Reaction of the oxygen with the solid material on the surface.
- 4) Desorption of the oxide specie or species from the metal surface.

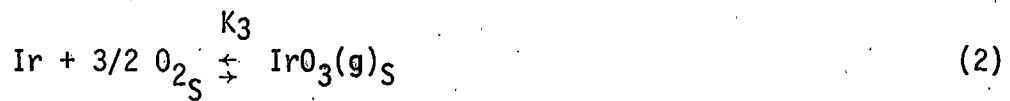
- 5) Diffusion of the oxides through the boundary layer away from the metal surface.

#### Theoretical Model for the Rate of Oxidation of Iridium

Wimber, et al [9] formulated a model for the rate of iridium oxidation assuming the vaporization of  $\text{IrO}_2(\text{g})$ ,  $\text{IrO}_3(\text{g})$  and  $\text{Ir}(\text{g})$  and their subsequent diffusion through the gaseous boundary layer surrounding the material as the controlling step. The model correlated well with experimentally measured recession rates of iridium wires in naturally convected air and oxygen and in forced convection air and oxygen.

As mentioned previously, the model is a synthesis of two separate models, one which held for the higher pressures assuming diffusion of the oxides through the boundary layer as the controlling step, and the other, for the lower pressures, assuming vaporization of the oxide species as the controlling step. The basis for each model and the manner in which they are combined into a single equation are summarized below.

Both models assume each of the oxidation reactions is at equilibrium. Over the temperature and pressure range considered the dominant reactions can be written:



where the subscript S denotes conditions at the solid boundary, and  $K_2$  and  $K_3$  are equilibrium constants for each reaction.

The oxidation rate is expressed in terms of the recession rate of the surface of the iridium wire. To avoid duplication, the recession rate due to the formation of only one of the oxide species,  $\text{IrO}_2$ , will be derived. The derivations for the recession rates due to the formation of  $\text{IrO}_3$  and  $\text{Ir}(\text{g})$  are essentially the same.

Equation (1) represents the overall reaction and can be broken down into the process whereby oxygen is adsorbed onto the surface, creating a potential site for the oxidation reaction, and the vaporization of the  $\text{IrO}_2$  molecule. Assuming equilibrium between the oxygen and the metal surface, the following reaction equation can be written:



where  $|\text{S}_2$  represents the entity at the sites where the vapor specie may form. The net recession rate due to the formation and vaporization of  $\text{IrO}_2$  may be expressed as:

$$\dot{X}_{\text{S}_2} = A(k_{2f} C_{\text{S}_2} - k_{2b} P_{2\text{S}}) \quad (5)$$















































































