



High temperature oxidation of iridium
by Steven Wayne Hills

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

An investigation of the oxidation of heated iridium wires was performed in the temperature range of 1675 to 2260°C (1948 to 2533°K). The wires were oxidized in naturally convected oxygen and air in the pressure range of 9.8×10^{-8} to 1.32 atmospheres (7.5×10^{-5} to 1000 torr) and in force-convected oxygen and air at pressure from 0.0046 to 1.32 atmospheres (3.5 to 1000 torr). The experimental results were compared to values calculated by a theoretical equation whose development was based on control of the oxidation by the rates of evaporation of Ir(g), IrO₃(g), and IrO₃(g) and by the rates of the subsequent diffusion of these species through the gaseous boundary layer.

Empirical equations were developed which describe the temperature dependencies of the standard-state free-energies of formation of IrO₂(g) and IrO₃(g). An equation was developed for the Nusselt number for natural-convection heat transfer from the high temperature wires. Also, an earlier equation for the thermal expansion of iridium was revised.

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Steven Wayne Hills

Date

Dec. 9, 1974

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Mechanical Engineering

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December, 1974

ACKNOWLEDGMENTS

Special thanks and appreciation are extended to Dr. R.T. Wimber for his guidance and assistance in the development of this research project. Dr. H.W. Townes, Dr. D.O. Blackletter, and Dr. J.A. Scanlan are also thanked for serving on the thesis committee.

A special word of thanks is also due my wife JoAnne for her effort in typing this thesis.

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ABSTRACT

An investigation of the oxidation of heated iridium wires was performed in the temperature range of 1675 to 2260°C (1948 to 2533°K). The wires were oxidized in naturally convected oxygen and air in the pressure range of 9.8×10^{-8} to 1.32 atmospheres (7.5×10^{-5} to 1000 torr) and in force-convected oxygen and air at pressure from 0.0046 to 1.32 atmospheres (3.5 to 1000 torr). The experimental results were compared to values calculated by a theoretical equation whose development was based on control of the oxidation by the rates of evaporation of Ir(g), IrO₂(g), and IrO₃(g) and by the rates of the subsequent diffusion of these species through the gaseous boundary layer.

Empirical equations were developed which describe the temperature dependencies of the standard-state free-energies of formation of IrO₂(g) and IrO₃(g). An equation was developed for the Nusselt number for natural-convection heat transfer from the high temperature wires. Also, an earlier equation for the thermal expansion of iridium was revised.

CHAPTER I

INTRODUCTION

Characteristics and Uses of Iridium

An oxidation study of iridium is of engineering interest because it is the only elemental metal known to man that has a high enough melting point (2454°C or 2727°K) and a low enough oxidation rate that it can survive for extended periods of time at temperatures greater than 2000°C in an oxygen bearing atmosphere. In fact, iridium is one of the most corrosion resistant metals known when it is compared to other metals as they are subjected to a wide variety of environments at high temperatures. Iridium is quite resistant to corrosive attack by acids, salt solutions, fused salts, molten metals, and molten metal oxides.

A general oxidation characteristic of iridium is that a thin oxide film is formed on the surface when the metal is subjected to temperatures in the range of 600 to 1000°C in the presence of oxygen. However, at temperatures greater than 1000°C volatile oxides are formed and the surface of the metal is left clean and shiny. It is this formation of volatile oxides which causes the oxidation rate to become linear with respect to time at the higher temperatures.

Iridium is presently available in commercial quantities as iridium and iridium-rhodium alloy wires which are used as standardized high temperature thermocouples and filaments in high temperature electric

furnaces. Other uses of iridium as a structural material are limited even though its strength properties at high temperature are quite desirable. The principal drawback of using iridium is the cost. Being a platinum group metal, iridium is very expensive. Another limitation of using iridium as a structural material is the weight factor. At 22.57 gm/cm^3 , iridium is one of the most dense elements known to man. Thus, the most promising use of iridium appears to be in the form of coatings to protect structural materials from rapid oxidation at high temperatures.

Potential applications for iridium coatings are nuclear reactor components, assemblies in rocket and gas turbine engines, leading edges of re-entry spacecraft, and other applications where oxygen exposed surfaces are subjected to high temperature. The very low emittance of iridium could restrict its use on spacecraft where the ambient pressure is slight and the primary means of heat dissipation is by radiation.

Review of Previous Work

Wimber [1] has made a thorough review of the information available from other experimenters' work. A brief summary of that review is presented here.

The composition of the oxides of iridium and the kinetics of the chemical reactions involved have been investigated by several

independent researchers. Cordefunke and Meyer [2] passed oxygen bearing gas over iridium metal in the temperature range of 1169 to 1462°C (1442 to 1735°K). They concluded that $\text{IrO}_3(\text{g})$ was the major compound formed. Cordfunke and Meyer also obtained values of the equilibrium constants that were slightly higher than those noted by Alcock and Hooper [3] and Schafer and Heitland [4]. Holburn, Henning, and Austin [5] studied heated iridium foil exposed to oxygen in gases flowing slowly past the foil. They also concluded that $\text{IrO}_3(\text{g})$ was the main oxide formed.

Mass spectrometric studies made by Norman et al [6] caused them to conclude that both $\text{IrO}_2(\text{g})$ and $\text{IrO}_3(\text{g})$ were formed in appreciable quantities when iridium was oxidized. They also noted that the presence of $\text{IrO}(\text{g})$ could not be ruled out but its partial pressure was estimated to be less than 2 percent of the partial pressure of $\text{IrO}_2(\text{g})$. In this same study the values for the standard-state enthalpies of formation for $\text{IrO}_2(\text{g})$ and $\text{IrO}_3(\text{g})$ were reported as 48.5 ± 0.8 kcal/mole and 5.5 ± 1.5 kcal/mole, respectively.

Olivei [7] also concluded from his studies that $\text{IrO}_2(\text{g})$ and $\text{IrO}_3(\text{g})$ were the major oxide species formed. He performed mass spectrometric studies in the range of 627 to 2227°C (900 to 2500°K) which yielded a standard-state enthalpy of formation for $\text{IrO}_3(\text{g})$ of 6.0 kcal/mole.

On the basis of this preliminary work recent studies have been made at Montana State University of the surface recession rate of hot oxidizing iridium wires. Wimber and Kraus [8] concluded that Ir(g) was also an important species at high temperature and that IrO(g) contributed very little to the overall recession rate. In this study a theoretical model was derived to predict the surface recession rate of iridium wires in the temperature range of 1675 to 2260°C (1948 to 2533°K) as they were oxidized in pure oxygen at pressures ranging from 1.32×10^{-3} to 1.32 atmospheres (1 to 1000 torr). Wahl [9] extended the experimental data to lower pressures in oxygen (7.5×10^{-6} torr) and also oxidized the wires in air. This study showed that two theoretical models were needed to describe the recession rates; one was used at low pressures and one was used at high pressures.

On the basis of information gathered by these investigators it was proposed that a theoretical model can be developed which will predict the surface recession rate of oxidizing iridium wires over the temperature range of 1675 to 2260°C (1948 to 2533°K) and throughout the pressure range of 9.8×10^{-8} to 1.32 atmospheres (7.5×10^{-5} to 1000 torr) in oxygen or air. Furthermore, it is expected that this model will be valid for wires in both naturally convected and force convected regions.

CHAPTER II

THEORETICAL CONSIDERATIONS

Oxidation Characteristics of Solid Materials

A study of the general corrosion of a material leads to a study of the specific chemical reactions which can occur under the imposed conditions. A consideration of the equilibrium constants of these reactions reveals the most thermodynamically stable point toward which the reactants will tend to move.

From an engineering view point, the most applicable facet of corrosion is a determination of the rate at which it takes place. To find the rate of corrosion the rates of the steps involved in the reaction mechanism must be found or, if one step of the mechanism is much slower than the others, the rate of this "rate controlling step" must be determined.

In the case of a solid oxidizing in a fluid where all of the oxides formed are volatile, the corrosion rate is expected to be controlled by one or more of the following steps of oxidation:

- 1) Diffusion of the oxygen through the fluid and through the boundary layer next to the surface.
- 2) Adsorption of the oxygen onto the surface.
- 3) Reaction of the oxygen with the solid material on the surface.

- 4) Desorption of the oxide from the surface.
- 5) Diffusion of the oxide through the boundary layer away from the material.

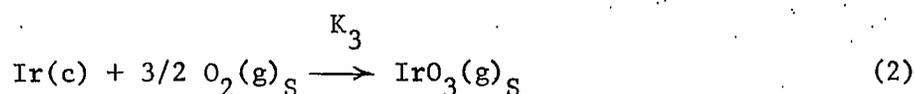
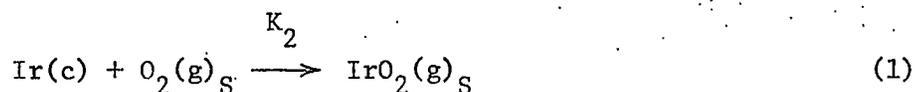
Theoretical Model for the Oxidation of Iridium

Wimber [10] previously derived a model which takes into account the formation of Ir(g) , IrO(g) , $\text{IrO}_2(\text{g})$, and $\text{IrO}_3(\text{g})$ and their partial pressures at the inner surface of the boundary layer. This model assumes that the oxidation rate is controlled by the rate of diffusion of these gaseous species through the boundary layer. Kraus [11] showed that this model did predict the surface recession rates of the iridium wires quite effectively at pressures in the range of 1.32×10^{-3} to 1.32 atmospheres (1 to 1000 torr). Wahl [9] concluded that this model did not predict the experimentally determined rates at low pressures. It was found that another model was needed for pressures of approximately 10^{-4} atmospheres and below. At these low pressures there is essentially no boundary layer present, and a theoretical model was developed by assuming that the rate controlling step is the surface reactions and/or the desorption of the oxide species from the surface.

With this information in mind, it appears that a theoretical model could be developed from which an equation for the oxidation rate could be written which has a pressure dependency such that at the higher

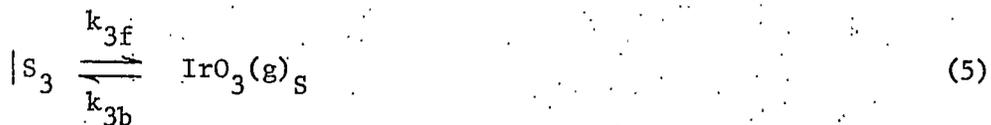
pressure range the diffusion of the oxide species would predominate and at the lower pressure range the vaporization of the oxide species would predominate.

From the information presented in Chapter I it is assumed that the major oxide species of iridium formed are Ir(g), IrO₂(g), and IrO₃(g). Following this assumption, equilibrium conditions at the gas-metal interface can be represented by the following reactions:



where the subscript S denotes conditions at the solid boundary.

Equations (1), (2), and (3) are overall reactions for the process. When the oxygen is adsorbed onto the metal surface it comes in contact with an iridium atom and creates a site for a potential reaction and, following the reaction, a potential desorption or evaporation site of the oxide species. Thus, assuming equilibrium between the oxygen and the metal surface, the following reaction equations can be written:



where $|S_2$, $|S_3$, and $|S_M$ are the entities at the sites where the respective vapor species may form and the subscript S denotes a location at the inner surface of the boundary layer. Referring to the reaction represented by Eq. (4), the contribution of the formation of $\text{IrO}_2(g)$ to the overall oxidation rate may be expressed as

$$X_{S2} = A(k_{2f}C_{S2} - k_{2b}P_{2S}). \quad (7)$$

In Eq. (7) the subscripts 2 refer to quantities pertaining to $\text{IrO}_2(g)$ and X is a surface recession rate with units of length per time. Also, P_{2S} is the partial pressure of $\text{IrO}_2(g)$ at the inner surface of the boundary layer, C_{S2} is the concentration of the $|S_2$ entity, A is an equivalent weight (having the units of mass of iridium consumed per mole of oxide species formed) divided by the density of iridium, and k_{2f} and k_{2b} are the specific reaction rate constants for the reaction of Eq. (4) in the forward and reverse directions, respectively.

A relationship between k_{2f} and k_{2b} which is valid under nonequilibrium conditions may be obtained by considering two different reactions proceeding under equilibrium conditions. The expression involving the equilibrium constant for the overall reaction represented by Eq. (1) is

$$P_2 = K_2 P_{O_2} \quad (8)$$

where P_2 is the partial pressure of $IrO_2(g)$ for an oxygen partial pressure of P_{O_2} and K_2 is the equilibrium constant for the reaction of Eq. (1). Here it should be noted that $P_2 > P_{2S}$. However, at equilibrium conditions no net corrosion is taking place and $P_2 = P_{2S}$. Also the forward reaction rate equals the backward reaction rate at equilibrium. Therefore

$$k_{2f} C_{S2} = k_{2b} P_{2S} = k_{2b} P_2 \quad (9)$$

Substituting Eq. (8) into Eq. (9) gives

$$k_{2f} C_{S2} = k_{2b} K_2 P_{O_2} \quad (10)$$

or
$$k_{2b} = k_{2f} C_{S2} / (K_2 P_{O_2}) \quad (11)$$

Substitution of Eq. (11) into Eq. (7) gives

$$X_{S2} = A k_{2f} C_{S2} [1 - P_{2S} / (K_2 P_{O_2})]. \quad (12)$$

The vaporization flux can be calculated by the Knudsen modification of the Hertz-Langmuir equation [12]. The flux in moles of vapor molecules that leave the surface per unit area per time is given by

$$J = \alpha_v P_{eq} (2\pi M R T_k)^{-1/2} \quad (13)$$

where α_v is the vaporization coefficient, P_{eq} is the equilibrium partial pressure of the species, M is the molecular weight of the species, R is the ideal gas constant, and T_k is the absolute temperature of the solid. If only the forward reaction process of Eq. (4) is considered (i.e. evaporation process into a perfect vacuum) the forward rate is equal to the evaporation or $k_{2f} C_{S2} = J_2$ where

$$J_2 = P_2 (2\pi M_2 R T_k)^{-1/2} = K_2 P_{O_2} (2\pi M_2 R T_k)^{-1/2} \quad (14)$$

when α_v is assigned a value of unity.

Thus,

$$k_{2f} C_{S2} = K_2 P_{O_2} (2\pi M_2 R T_k)^{-1/2}. \quad (15)$$

Substitution of Eq. (15) into Eq. (12) yields

$$X_{S2} = AK_2 P_{O_2} (2\pi M_2 RT/k)^{-1/2} [1 - P_{2S}/(K_2 P_{O_2})] \quad (16)$$

The flux of a given species through the boundary layer is equal to the product of its mass-transfer coefficient and the difference in its partial pressure on the two sides of the boundary layer [13]. Since the gas in the experimental apparatus (see Chapter III) is being continuously circulated through the oxidation region while the oxide species are being continuously removed it is logical to assume that the partial pressure of each of the oxide species in the free stream approaching the wire is negligible with respect to its partial pressure at the inner surface of the boundary layer. Thus, the diffusion flux of the species is equal to the product of its mass-transfer coefficient and its partial pressure at the inner surface of the boundary layer. Therefore, the surface recession rate of the metal due to the diffusion of $IrO_2(g)$ can be expressed by

$$X_{D2} = A k_{G2} P_{2S} \quad (17)$$

where k_{G2} is the mass-transfer coefficient of $IrO_2(g)$.

It will be assumed that there are negligible rates of net reactions between the oxide species and other species in the boundary

layer. This allows equating \dot{X}_{D2} to \dot{X}_{S2} . Then Eqs. (16) and (17) can be solved for P_{2S} and \dot{X}_{S2} . The resultant expression for the surface recession rate is

$$\dot{X}_{D2} = \dot{X}_{S2} = \dot{X}_2 = \frac{Ak_{G2} K_2 P_{O_2} (2\pi M_2 RT_k)^{-1/2}}{k_{G2} + (2\pi M_2 RT_k)^{-1/2}} \quad (18)$$

where \dot{X}_2 is just a simpler notation for the surface recession rate component dependent on the evaporation and diffusion of $\text{IrO}_2(\text{g})$.

Analogous mathematical treatment of the formation and diffusion of the $\text{IrO}_3(\text{g})$ and $\text{Ir}(\text{g})$ species results in similar expressions for \dot{X}_3 and \dot{X}_M where the subscript 3 refers to the quantity pertaining to $\text{IrO}_3(\text{g})$ and the subscript M refers to the quantity pertaining to $\text{Ir}(\text{g})$. If it is now assumed that the total surface recession rate of the metal is the sum of the recession rates for each independent oxide species, then

$$\dot{X} = \dot{X}_2 + \dot{X}_3 + \dot{X}_M \quad (19)$$

or

$$\begin{aligned}
 \dot{X} = A \left[\frac{k_{G2} K_2 P_{O_2} (2\pi M_2 RT_k)^{-1/2}}{k_{G2} + (2\pi M_2 RT_k)^{-1/2}} + \frac{k_{G3} K_3 P_{O_2}^{3/2} (2\pi M_3 RT_k)^{-1/2}}{k_{G2} + (2\pi M_3 RT_k)^{-1/2}} \right. \\
 \left. + \frac{k_{GM} P_M (2\pi M_M RT_k)^{-1/2}}{k_{GM} + (2\pi M_M RT_k)^{-1/2}} \right] \quad (20)
 \end{aligned}$$

where k_{G3} , K_3 , and M_3 are respectively, the mass transfer coefficient, equilibrium constant, and molecular weight of $IrO_3(g)$ and k_{GM} , P_M , and M_M are respectively, the mass transfer coefficient, partial pressure, and atomic weight of $Ir(g)$.

Equation (20), which predicts surface recession rates, was considered to be a complete description of the oxidation/evaporation of iridium wires. The validity of this theoretical development was tested by correlating the surface recession rates which were calculated by Eq. (20) with experimentally determined surface recession rates.

CHAPTER III

EXPERIMENTAL PROCEDURES FOR NATURAL-CONVECTION REGIME

Experimental Materials

The iridium wire used in this study was commercially pure and was purchased in four separate lots which have been labeled Lot 1, Lot 2, Lot 3, and Lot 4. A previous study by Kraus [11] utilized Lots 1 and 2 and the study by Wahl [9] incorporated wire from Lots 1, 2, and 3. The major impurities in the wire of the first three lots have been tabulated [9] and Lot 1 was estimated to be 99.3 percent pure while Lots 2 and 3 were estimated to be 99.9 percent pure. Lot 4 is of similar composition and is estimated to be 99.9 percent pure also. It has been shown [8, 9, 11] that no perceptible differences exist between the oxidation rates of Lots 1, 2, and 3. Thus, Lot 4 is expected to react similarly.

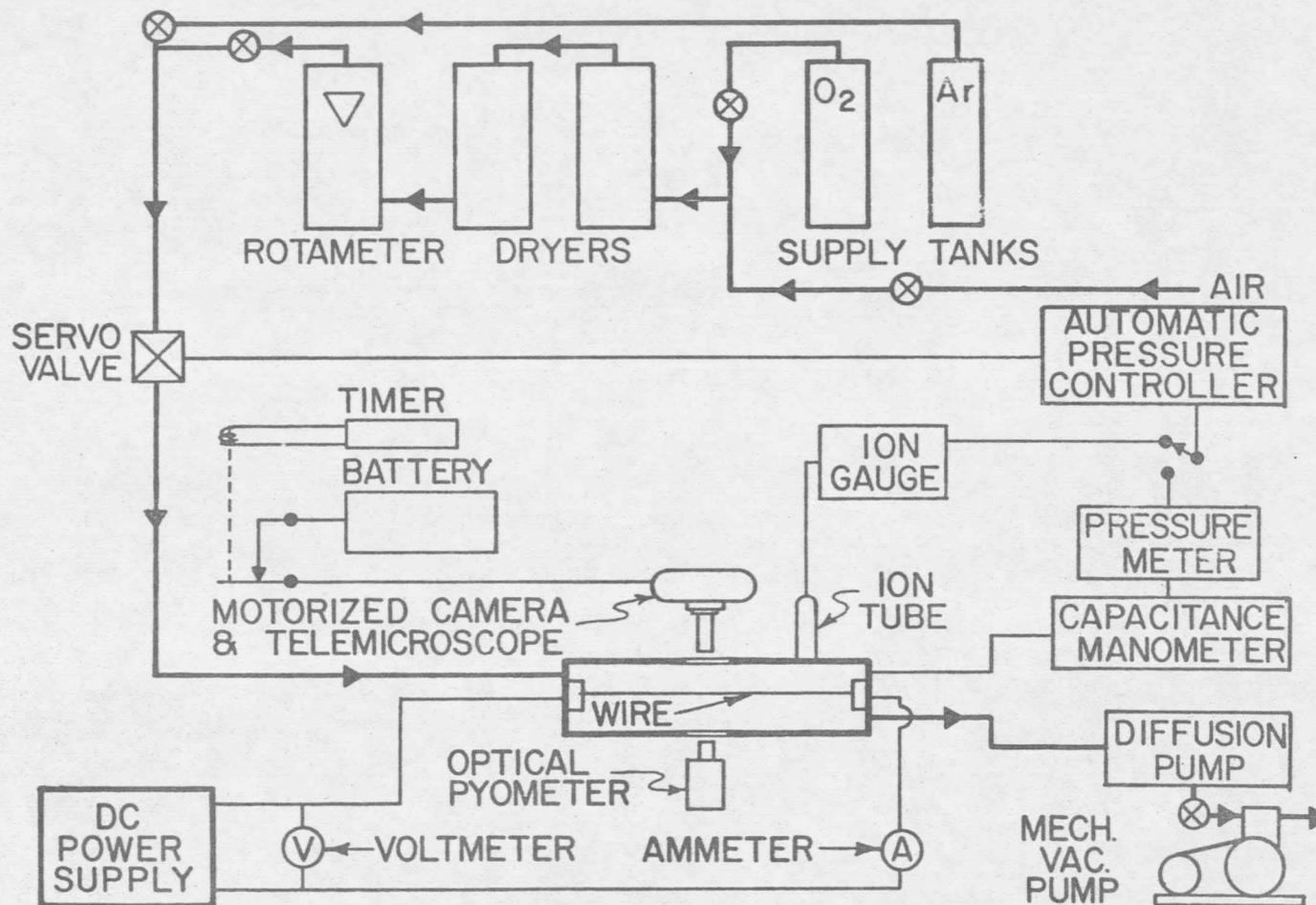
The oxygen used was USP grade and was typically 99.7 percent pure. Nitrogen and argon were the primary impurities and were both expected to be inert to iridium. Both the oxygen and the air were dried before they entered the oxidation chamber so water vapor was not expected to be a contributing part of the oxidation atmosphere.

Apparatus and Procedure

The equipment that was used to experimentally determine oxidation rates of iridium was the same apparatus described in detail by Wahl [9].

A schematic representation of the system is shown in Fig. 1. It basically consists of a water cooled oxidation cell in which the iridium wire is suspended horizontally between two water cooled electrodes. The cell was provided with two sight ports containing rotatable pyrex windows. Through one port an optical pyrometer was sighted on the wire and a timer-actuated, motor-driven camera fitted with a telemicroscope was focused on the same point of the wire through the other window. The optical pyrometer was calibrated [9] to read the true wire temperature through the optical quality pyrex windows. Rotation of the windows (to a clean section) just prior to taking a temperature measurement insured reading the true temperature of the wire since the part of the window which was exposed to the oxidation atmosphere would collect iridium oxide condensate.

The pressure in the cell was measured by a capacitance manometer for pressures greater than 1.32×10^{-4} atm (0.10 torr) and by a high pressure ion gauge for pressures less than 1.32×10^{-4} atm (0.10 torr). Either one of these systems could be used to signal an automatic pressure controller which controlled a servo-valve regulating the flow of gas into the system. With the system being vacuum pumped continuously, a constant flow of gas insured that the atmosphere in the cell did not contain a high percentage of oxide species. A more detailed description of this apparatus is given by Wahl [9].



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Figure 1: Schematic Representation of Natural-Convection Oxidation Apparatus

Prior to mounting a section of wire in the oxidation cell the wire was thoroughly cleaned in acetone to remove any surface deposits. After the wire was mounted between the electrodes it was annealed for 30 minutes at 2260°C (2533°K) in an argon atmosphere. The annealing eliminated any further recrystallization or grain growth occurring after the oxidation run started. After the argon was removed and the pressure of the flowing gas was stabilized at the preselected value the wire was brought to the desired temperature by self resistance heating caused by passing an electric current through it. As the temperature of the wire was monitored through the optical pyrometer a series of 10 film images of the hot wire was obtained. The time interval between the images was selected so that approximately 0.025 mm (1 mil) was removed from the diameter of the wire during each run.

On each film an exposure was made of a drill rod of known diameter at the same focal length as the oxidizing wire. After the film was developed and dried this image provided a reference of known diameter on the film. The film images of the wire were measured by a modified cathetometer in which a foil with a 0.05 mm (2 mil) slit was incorporated in the telemicroscope. By means of a high intensity light behind the film and a light meter on the eyepiece of the cathetometer the diameter of the film images could be determined and converted to an actual wire diameter by a conversion factor obtained from the image of the known diameter rod. The repeatability of a

single measurement was typically ± 0.05 to 0.1 percent. However, it was found that a minor correction must be made for the variation of the width of the fringe zone located at the edge of the film image (as viewed at 40x magnification through the cathetometer) with change in the wire temperature. This correction factor was determined by heating a wire in argon to the same temperatures used in the oxidation runs and taking photographs in the same manner as was done in the oxidation experiments. After this wire was cooled it was taken from the cell and measured directly by the cathetometer. Correction of this diameter for thermal expansion at the various temperature levels then allowed the comparison of the wire diameters as measured from the film by the previously mentioned procedure to the actual wire diameters.

The improved method of temperature measurement [9] was applied to a previous study of the thermal expansion of iridium [14] and new coefficients in the equation for the expansion of iridium were derived. "Percent expansion" is defined as 100 times the increase in length at T_c ($^{\circ}\text{C}$) divided by the length at 0°C . The new equation is

$$\begin{aligned} \text{Percent Expansion} = & 6.646 \times 10^{-4} T_c - 2.69 \times 10^{-8} T_c^2 \\ & + 1.533 \times 10^{-10} T_c^3 - 3.506 \times 10^{-14} T_c^4. \quad (21) \end{aligned}$$

For the temperature range of 440 to 2220°C (713 to 2493°K) the maximum disparity between Eq. (21) and the experimental data was 2.63 percent of the experimentally determined percent expansion.

CHAPTER IV

RESULTS AND DISCUSSION OF NATURAL-CONVECTION OXIDATION

Experimental Data

After the actual diameter of the wire had been determined from the film measurements the diameter of the wire at each exposure was plotted versus the time elapsed from the first exposure of the run. Fig. 2 shows a typical plot which resulted from this procedure. As was noted earlier, the oxidation of iridium at these elevated temperatures is linear with respect to time since the oxides are all volatile and no protective coating is formed on the surface. The slope of this line is the negative of the rate of decrease of the diameter of the wire. Therefore the surface recession rate of the metal can be found by multiplying the slope of the line by minus one half. Since the calculations for finding the theoretical rate involve the wire diameter, an average diameter for each run was taken as the average of the ten diameters read from each film. Tables (6) and (7) in Appendix A give the experimental conditions and the experimentally determined oxidation rates for the oxidation of iridium in pure oxygen and air. As is noted, most of these data were gathered by Kraus [11] and Wahl [9] but their diameter measurements were modified because of the film image fringe effect discussed earlier. The calculated values on these tables were calculated by Eq. (20).

