

# Iridium Losses During Oxidation

## REACTIONS AT HIGH TEMPERATURES IN LOW-PRESSURE OXYGEN ATMOSPHERES

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*Iridium reacts with oxygen at high temperatures forming volatile oxides, the evaporation of which considerably increases the iridium losses in oxygen-containing atmospheres, when compared with high-vacuum conditions. This paper describes investigations carried out to determine the metal losses from polycrystalline iridium discs, by means of a magnetic suspension balance, at low pressures and high temperatures. The results are presented and discussed, and a strong temperature and pressure dependence is noted.*

At high temperatures the platinum metals and alloys are increasingly used as thermo-couple pairings and as a crucible material for liquid glasses and oxides, that is for the growth of single crystals. In both fields iridium metal and iridium alloys have considerable advantages due to their high melting points and good physical and mechanical properties. They also show good chemical stability even in oxidising atmospheres. At low temperatures thin protective oxide films are formed but at temperatures above about 1100°C the oxides decompose and the metal surfaces remain bare. However, volatile oxides are formed and increase the metal losses when compared with the evaporation of the pure metal in high vacuum. In that temperature range the oxidation rates in air of the various platinum metals show differences up to about six orders of magnitude (1,2). Platinum and rhodium have the lowest metal losses, followed by iridium and ruthenium, while osmium has the highest losses. The high-temperature oxidation of iridium metal has only rarely been studied (2 to 7). In a recently published paper by Wimber et al, systematic investigations extended over a wider pressure and temperature range,  $10^{-2}$  to  $1.3 \times 10^5$  pascals of oxygen and 1675 to

2260°C, have now been reported (7).

In the present study the metal losses of polycrystalline iridium in an oxygen atmosphere have been determined gravimetrically at high temperatures of 1500 to 2100°C and low pressures of 0.1 to 100 pascals of oxygen.

### Experimental

The experiments were performed under a flow of 99.99 volume per cent oxygen in a high vacuum apparatus, shown schematically in Figure 1. The pressures were adjusted by a needle valve and were measured by an ionisation gauge, and the temperature of the inductively heated specimen was measured by an optical micropyrometer.

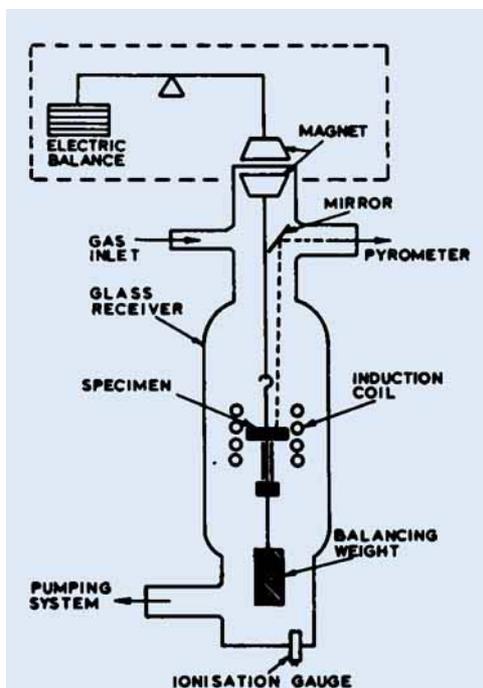
The weight change of the iridium discs was determined by a suspension balance having an accuracy of  $1 \mu\text{N}$ . The oxidation anneals were interrupted for weighing because the electromagnetic forces did not allow continuous weighing during the induction heating. The oxidation periods were chosen in a manner which gave reliable readings of the weight changes.

Polycrystalline iridium discs 10 mm diameter and 1 mm thick were employed as specimens, and before the experiments they were cleaned and then recrystallised and

degassed by a vacuum heat treatment at 1800°C for 15 minutes. When the same sample was used for different runs it was vacuum annealed, at 1800°C for 10 minutes, before each series, to give defined starting conditions. An analysis of the impurities found in the samples is given in the Table.

## Results

The weight change of the iridium specimens as a function of oxidation time is shown in Figure 2. It can be seen that the linear weight loss strongly increases with increasing pressure, at a constant temperature of 2000°C; and with increasing temperature, at a pressure of 1 pascal. From these curves the volatilisation rates and recession rates, respectively, of iridium have been calculated. In Figure 3 these rates are plotted versus  $1/\text{temperature}$ . Each line in Figure 2 is represented by one point in Figure 3. The curves show a continuous increase with rising temperature and at lower pressures approach the straight line plot of the evaporation of the pure metal in vacuum. The temperature dependence of the oxidation



*Fig. 1 Schematic diagram of the high vacuum apparatus, made from Duran glass, used for determining the metal losses*

Impurities in the Iridium Disc Specimens	
Element	Weight, ppm
Platinum	520
Rhodium	280
Palladium	220
Ruthenium	25
Iron	60
Nickel	20
Copper	20
Magnesium	10
Boron	10
Silver	6
Gold	5
Chrome	<5

process lies in the range of 125 kJ/mol. Figure 3 shows that a marked increase of the iridium losses exists when it is annealed in oxygen atmospheres, which extends upwards to several orders of magnitudes, especially in the lower temperature range. In the upper temperature range the increase of the iridium losses by the oxygen atmosphere is less pronounced.

Figure 4 shows the iridium weight loss plotted against the oxygen pressure. The pressure dependence follows the relation  $v \propto p^{0.3}$  between 1 and 100 pascals and at temperatures between 1500 and 2000°C. At lower pressures and at temperatures greater than 2000°C the recession rate becomes pressure independent, because here the pure iridium metal evaporation predominates. Between 1500 and 1900°C and at lower pressures the rate is proportional to the

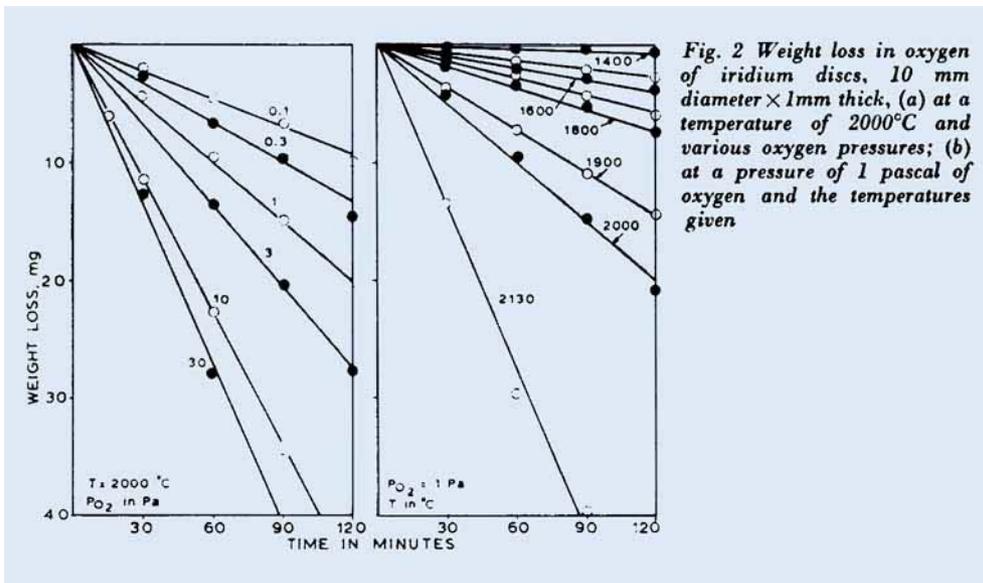


Fig. 2 Weight loss in oxygen of iridium discs, 10 mm diameter  $\times$  1 mm thick, (a) at a temperature of 2000°C and various oxygen pressures; (b) at a pressure of 1 pascal of oxygen and the temperatures given

pressure. In Figure 4 the pure metal evaporation rate at 1900 and 2000°C is plotted additionally at the ordinate.

### Discussion

From the gravimetric determination of the iridium losses in the present work no

direct conclusion can be drawn on the mechanism of the reaction between oxygen and iridium. The weight change gives the iridium losses due to the pure iridium metal evaporation together with the iridium component of the volatilising iridium oxides. The oxygen component is not determined because in the steady state between the oxygen sorption from the gas phase and the evaporation of the volatile oxides this part is continuously compensated.

By mass spectrometric investigations (9) the oxides  $\text{IrO}_2(\text{g})$  and  $\text{IrO}_3(\text{g})$  have been detected by the Knudsen cell technique and partial pressures in the range of 10 pascals within the cell. The oxide evaporation from a free iridium surface in the non-equilibrium kinetically controlled process has not been investigated up to now as it has been done in similarly reacting systems, for example molybdenum (10), tungsten (11) and rhenium (12). In analogy to the rhenium system the reactions between oxygen and iridium at high temperatures and low pressures resulting in the steady states between oxygen sorption and oxide evaporation can be described by a kinetic model based on the following assumptions (12). The chemisorbed

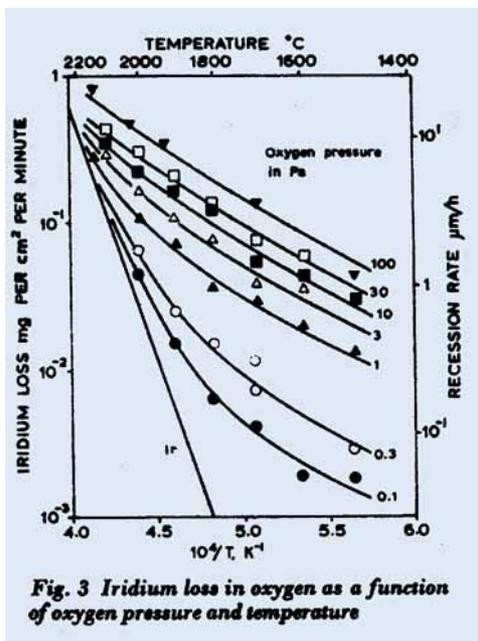
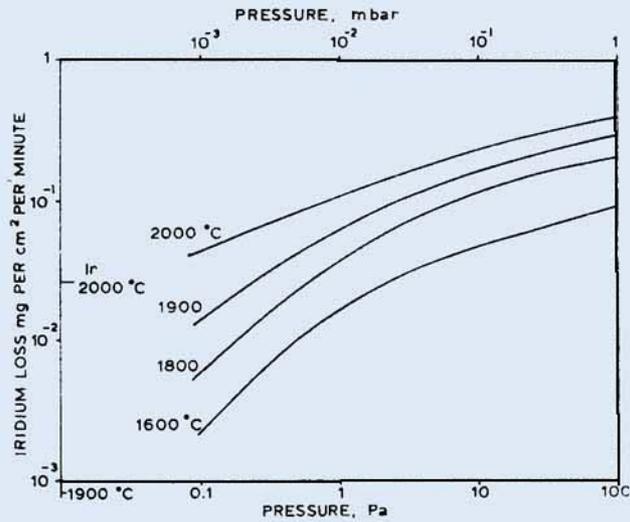


Fig. 3 Iridium loss in oxygen as a function of oxygen pressure and temperature

**Fig. 4 Iridium weight loss as a function of oxygen pressure**



oxygen atoms can desorb as O atoms, as O<sub>2</sub> molecules, and as oxide molecules (predominantly IrO<sub>2</sub> and IrO<sub>3</sub>). All reactions take place in the adsorption layer and the oxygen atoms are mobile on the surface at the experimental temperatures. The total iridium loss  $v_{Ir}$  can be described by the relation:

$$v_{Ir} = k_{IrO_2} \theta_O^2 + k_{IrO_3} \theta_O^3 + k_{Ir}$$

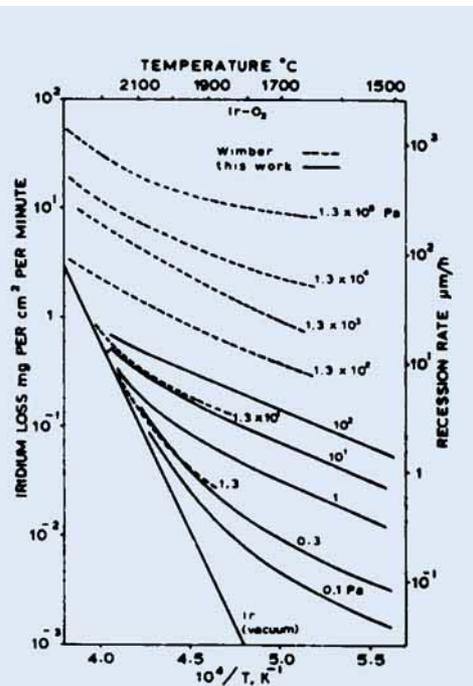
Where  $k_{IrO_2}$ ,  $k_{IrO_3}$  and  $k_{Ir}$  are temperature dependent rate constants of the volatilisation of IrO<sub>2</sub>, IrO<sub>3</sub> and Ir, respectively, and  $\theta_O$  is the oxygen coverage (5, 12, 13). The oxygen is balanced by the absorption and desorption reactions, equalising their rates:

$$2k_{O_2} p_{O_2} = 2k_{IrO_2} \theta_O^2 + 3k_{IrO_3} \theta_O^3$$

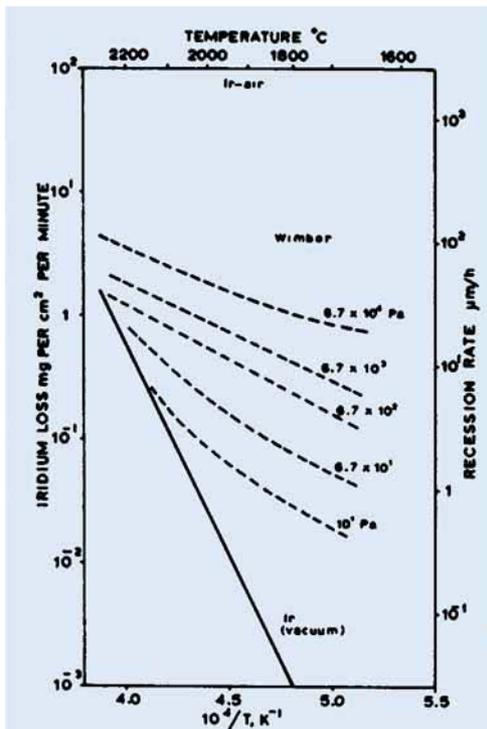
In the low-pressure range under consideration the kinetics of all processes are surface-controlled and neither true equilibrium states between gas phase and adsorption layer are established nor mass transfer in the gas phase or through a gaseous boundary layer near the surface have to be regarded, as in the case of high-pressure oxidation (7, 8).

The results of the present gravimetric investigation are compared in Figure 5 with those of Wimber et al (7), obtained by

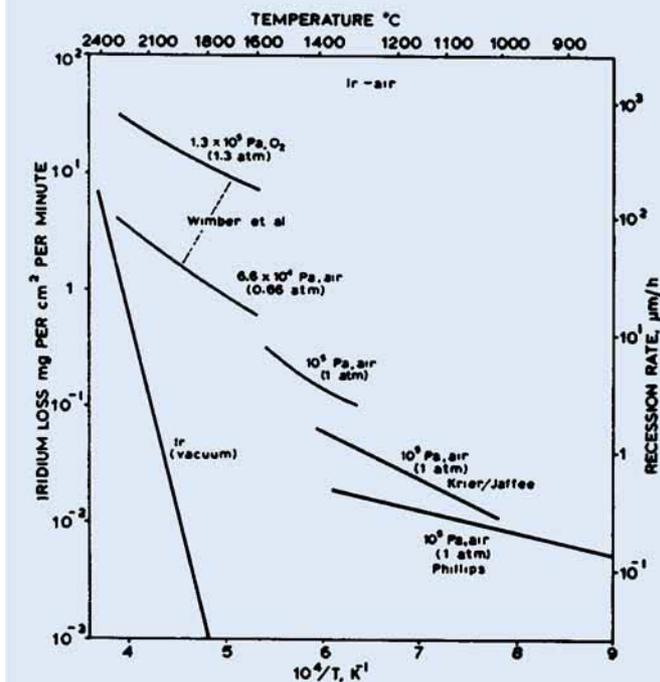
photographically measuring the reduction of the wire diameter during the oxidation anneal. Both studies cover pressure range



**Fig. 5 Iridium loss during oxidation in oxygen atmospheres**



**Fig. 6 Iridium loss during oxidation in air at reduced pressure**



**Fig. 7 Iridium losses during oxidation in air, at pressures of the order of atmospheric pressure, according to various sources. Below 2000°C the losses are several orders of magnitude higher than for pure evaporation in vacuum**

from about 0.1 pascal up to atmospheric pressure, and temperatures from 1500 to 2260°C. In the overlapping pressure and temperature range the agreement is good. Again it is evident that at low pressures the weight losses become pressure independent at high temperatures, when the weight losses are predominantly caused by the pure iridium metal evaporation, for example at 2260, 2110 and 2000°C with oxygen pressures less than 2, less than 0.2 and less than 0.01 pascals, respectively.

Further oxidation studies at very low pressures, in the range  $1.3 \times 10^{-5}$  to  $1.3 \times 10^{-3}$  pascals, are reported by Olivei (5), where the fraction of incident molecules pumped by an iridium surface is determined as a function of pressure and temperature. Assuming an

average composition of the volatile oxides of  $\text{IrO}_{2.5}$  the weight loss can be estimated from these values but the results obtained seem to be too high by about two orders of magnitude.

The theoretical treatment of the oxidation process at higher pressures is rather difficult (6 to 8) since in addition to the chemical surface reactions, eventually occurring equilibrium reactions, the mass transfer in the gas phase and natural or forced convection have to be taken into consideration. Specifically, the influence of the convection fluxes cannot be definitely determined due to geometrical parameters like shape and size of the sample and of the receiver. A theoretical treatment of iridium oxidation based on the diffusion of the evaporating species through the gaseous boundary layer is given by Wimber et al (6, 7). The strong influence of the sample dimensions is shown, for example, by Fryburg (8) studying the oxidation of platinum wires 0.29 to 2.2 mm diameter. Further difficulties may arise in an inert gas/oxygen mixture like air, where the inert gas pressure reduces the evaporation rate (14, 15).

Finally, in Figures 6 and 7 the results of oxidation studies in air are compiled. Figure 6 shows the weight loss of iridium during oxidation at reduced pressures, 10 to  $6.7 \times 10^4$  pascals, reported by Wimber et al (7). Compared with oxygen the iridium losses lie half an order to one order of magnitude lower. Figure 7 gives the iridium losses during the oxidation in the range of atmospheric pressure. A relatively fair agreement is obtained over the large temperature range (800 to 2260°C) taking into consideration the difficulties of measuring the very low weight losses at low temperatures, and the factors influencing the oxidation rate, which were mentioned above. In particular at temperatures below 2000°C the iridium losses are enlarged by several orders of magnitude when compared with pure evaporation in vacuum.

*Muhammed I. Ismail has been on leave of absence from the University of Alexandria, Faculty of Engineering, Alexandria, Egypt.*

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## A Review of Fuel Cell Development

As the industrial countries of the world continue to search for satisfactory alternatives to their present sources of energy a timely review of twenty-five years of fuel cell development has been published (*J. Electrochem. Soc.*, 1978, 125, (3), 77C-91C).

Well supported by a bibliography listing 33 major titles on fuel cells and related subjects, and with 187 references from international literature, the review by K. V. Kordešch—formerly with the Union Carbide Corporation, and now at the Technical University of Graz, Austria—covers a third cycle of interest in fuel cells, which is considered to start after the second world war. During this period numerous systems have of course been investigated and in many of them the properties of the platinum group metals have been utilised with advantage.

In the future, if the technology of fuel cells is better supported by basic scientific studies of the principles involved, further improvements in efficiency could result.