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ABSTRACT

The oxidation of platinum at high temperatures (above 800° C) is controlled by boundary-layer diffusion, except at the lowest pressures. The rate of oxidation is determined by the rate of diffusion of oxide through the boundary layer away from the platinum. This is in contrast to the situation in tungsten and molybdenum oxidation, where the rate is controlled largely by the diffusion of oxygen through the boundary layer towards the metal. The difference in mechanism is a consequence of the much lower rate of oxidation of platinum. Evidence is presented that supports this mechanism for the oxidation of platinum.

INTRODUCTION

Some years ago we reported[1] a study of the oxidation of platinum in ordinary oxygen in the temperature region above 800° C, where the oxide is volatile. All the data available up to that time had been obtained with platinum crucibles or plates heated in tube furnaces. The results were widely variant and highly dependent on the flow rate of gas through the furnace; the faster the gas flow rate, the higher the measured oxidation rate. These results indicated to us[2] that reaction equilibrium was being approached in the furnace and that the rate was diffusion limited. To minimize these effects, we employed[1] electrically heated ribbons placed in a cooled bulb.

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[redacted]

We were primarily interested in the low-pressure region, but some experiments were performed at pressures up to 1 atmosphere. We found a peculiar pressure dependency which was explained on the basis that the rate of oxidation was proportional to the pressure at all pressures, but that with increasing pressure an increasing fraction of the volatilizing oxide was back-reflected to the ribbon by the surrounding gas molecules. The oxide molecules are not stable at the temperature of the platinum and are decomposed on impact, the platinum being redeposited on the specimen. Because of the limitations of space, this explanation was offered summarily without detailed support. Recently, Jaffee and associates[3,4] have suggested that the pressure dependency of our data up to 0.5 torr could be explained on the basis of a Langmuir-type adsorption of molecular oxygen followed by dissociation. Since the correct explanation of the effect of pressure on the oxidation rate is a necessary requirement to the development of the basic mechanism of the oxidation reaction, we felt that the back-reflection theory should be presented in more detail. This is the object of the present paper.

RESULTS AND DISCUSSION

A typical set of results showing the pressure dependency of the oxidation reaction is presented in Fig. 1, where we have plotted, on logarithmic scales, the rate of oxidation, R, versus the pressure, p. For comparison some results of Krier and Jaffee[4] and of Raub and Plate[5] are also shown. These data were taken at atmospheric pressure using furnaces. The effect of reaction equilibrium within the furnace is apparent from the much smaller values that these observers obtained: Raub and Plate in O_2 found a rate of 3.1 $\mu g\ cm^{-2}\ hr^{-1}$ compared to our value of 300 $\mu g\ cm^{-2}\ hr^{-1}$, different by a factor of about 100; and Krier and Jaffee in air found a rate of 0.38 $\mu g\ cm^{-2}\ hr^{-1}$ compared to our 66 $\mu g\ cm^{-2}\ hr^{-1}$, a factor of about 175.

Examining the pressure dependency of our data, one sees that at the lowest pressures the rate increases directly with the pressure, as evidenced by the straight line with a slope of 1. This dependency on the first power of the pressure indicates that the rate of oxidation in this low pressure region is determined by the rate of collision of the O_2 molecules with the platinum surface. At higher pressures, the rate falls below the straight-line relation and continues to fall off more and more as the pressure increases. In general, the curve has the form of a Langmuir adsorption isotherm. However, the pressure at which the fall-off from the straight-line relation occurs is dependent on the width of the ribbon: the wider the ribbon, the lower the fall-off pressure. In addition, for pressures above the fall-off pressure, the rate of oxidation also varies with ribbon width: the wider the ribbon, the smaller the rate.

These observations of the affect of filament width on the rate of oxidation cannot possibly be explained by an adsorption mechanism. However, all the facts can be explained by the back-reflection theory. At low pressures the mean-free-path of the volatilizing oxide molecules in the surrounding gas is large compared to the width of the ribbon, and all the oxide escapes and is condensed on the cooled bulb. The width of the ribbon has no influence on the rate of oxidation. The oxidation is reaction-rate controlled, and depends on the first power of the pressure. As the pressure increases, the mean-free-path decreases and the oxide molecules suffer collisions at distances closer and closer to the ribbon. The chance of being back-reflected to the ribbon increases, and any oxide molecule that is back-reflected is decomposed on the hot ribbon; the platinum is redeposited on the platinum surface. The oxidation is diffusion limited. The pressure at which the oxidation starts to deviate from reaction-control should depend in some manner on the relative values of the mean-free-path

of the oxide molecule and the width (or diameter) of the filament: the larger the filament, the lower the fall-off pressure should be. Furthermore, for any given pressure, the wider the filament, the lower the rate of oxidation.

The phenomenon is very similar to that occurring when a metal evaporates in an inert gas. This problem was studied some years ago by Fonda[6] who investigated the effect of pressure of N_2-A mixtures on the rate of evaporation of tungsten wires. Similar to us, Fonda found that the diameter of the filament had a noteowrthy effect on the rate of evaporation: the larger the diameter, the smaller the rate of evaporation.

It is possible to compare the diffusion phenomenon occurring in the oxidation of platinum with that occurring in the evaporation of tungsten by considering a quantity called the escape probability, P_e. The escape probability is defined as the chance that any chemical particle evaporating from the surface of the filament will escape from the filament. It may also be considered as the fraction of particles evaporating that escapes. For our data the escape probability at any pressure is the ratio of the measured rate of oxidation to the true rate obtained by extrapolating from the straightline region to the given pressure. For a tungsten atom evaporating in an inert gas the escape probability at any pressure can be calculated from Fonda's data; it is the ratio of the rate of evaporation at the given pressure to the rate of evaporation in vacuum.

The comparison of the data is shown in Fig. 2(a) where we have plotted, for our ribbons and for Fonda's wire, the escape probability versus the log of the pressure. While Fonda reports data only for the higher pressures, his results appear similar to ours. For our oxidation data the escape probability is one in the reaction-controlled region and these data do not appear in this figure.

However, this type of plot points out very nicely the effect of ribbon width on the rate of oxidation in the higher pressure regions. The escape probability starts falling-off from one at some pressure which is a function of the width of the ribbon. This effect is shown by the different intercepts on the abscissa for the different width ribbons. Examination of the fall-off pressure of the different ribbons indicates that the fall-off occurs at the pressure where the mean-free-path of the oxygen, L, equals the width of the ribbon. This fact is shown in Table I by the data for ribbons with three different widths. The equality of the ribbon width and L is probably fortuitous, but the constancy of the ratio of the width to L for the different width ribbons definitely establishes a direct relationship between the two.

For pressures above the fall-off pressure, P_e decreases rapidly through a region in which it is inversely proportional to the log of the pressure. If one remembers that the rate of oxidation at any given pressure is directly proportional to P_e, one sees what a marked effect ribbon width has; the wider ribbons have much smaller rates of oxidation. At still higher pressures, P_e decreases less rapidly, reaching rather small values at atmospheric pressure.

To show better the behavior in the high pressure region, one can plot the log P_e versus log p as done in Fig. 2(b). Here the similarity of Fonda's results and ours is quite evident. We have extended Fonda's data back to the pressure at which L is equal to the diameter of his wire. In the region of viscous flow, above 100 torr, the data for the different width ribbons and for Fonda's wire lie on parallel straight lines. The value of the slope indicates that for both phenomena P_e is proportional to $p^{-3/4}$. Even in this high pressure region there is still a marked effect of filament diameter on the rate of oxidation at any given pressure.

The effect of filament diameter can be illustrated most clearly from a cross-plot of these data, as shown in Fig. 3, where we have plotted P_e for various pressures against the width or diameter of the filament. One can see that the rate of oxidation falls very rapidly at first with increasing diameter and then decreases more and more slowly. This is especially true at the higher pressures. At 750 torr P_e appears to be leveling off at a minimum value, as one might expect, probably about 0.0015. This means that for any reasonably sized platinum specimen, 99.85 percent of the platinum oxidized is reflected back to the specimen, and explains in part the stability of platinum ware at high temperatures under atmospheric air.

It is possible to develop this theory along more quantitative lines in the region of viscous flow. Fonda explained his results on the basis of Langmuir's thin-film theory of heat conduction[7], and our results yield equally well to the same treatment. In short, one assumes that the filament is surrounded by a stationary, cylindrical film of gas through which the heat is carried purely by conduction. The thickness of the film is determined by the heat transfer and can be calculated from the heat loss of the filament. The oxide molecules, due to their small partial pressure, do not contribute significantly to the heat loss. The filament is assumed to be oxidizing at a rate proportional to the partial pressure of oxygen. The volatile oxide molecules must diffuse through the stationary film of gas. Once a molecule reaches the outer boundary of the film, it is carried away in the convection current and escapes from the filament. The other molecules are back-reflected to the filament and the platinum redeposited.

For simplicity we will set up the diffusion problem in cylindrical coordinates even though we have used ribbons rather then wires. This is reasonable because the diameter of the film for convective conditions is large compared to the width

of the ribbons. Let us consider unit length of filament oxidizing at a given temperature. Then the grams of oxide per unit time, M, diffusing through every imaginary cylinder of radius r concentric with the axis of the filament is given by

$$M = -2\pi r D \frac{dN}{dr} \tag{1}$$

where N is the concentration of oxide in the gas phase in gms/cc, and D is the diffusion coefficient for PtO_2 molecules in stagnant oxygen.

If we assume the diffusion coefficient is constant or may be represented by an average value, we may integrate the expression across the boundaries of the film and obtain

$$M \ln \frac{b}{a} = 2\pi D N_a \tag{2}$$

where a is the diameter of the filament, b is the diameter of the film, and N_a is the concentration of oxide at the surface of the wire. The concentration at the outer boundary of the film was taken as zero.

Equation (2) can be transformed by making use of three relations. First from the kinetic theory of gases, D varies inversely with the pressure of the surrounding gas. Second, our measured rate of oxidation, R, is in terms of grams of oxide per unit time per unit area of wire surface, so $R = M/2\pi a$. Third, N_a is directly proportional to the true rate of formation of oxide, R_{extrap}. Making these substitutions into Eq. (2) and remembering that $P_e = R/R_{extrap}$ for any given temperature, we obtain the expression

$$P_e p a \ln \frac{b}{a} = \text{constant} \tag{3}$$

This expression contains four variables. We know a and p from the experimental conditions. We can calculate P_e from the measured oxidation rates,

and b can be calculated from the experimentally determined heat loss in the manner described by Langmuir[7]. We have calculated the value of the constant in the above expression for our results in the pressure region above 100 torr. The values of the different variables and of the constant are presented in Table II. It should be pointed out that even the temperature of the platinum was changed in these results. Actually, we find that P_e changes little with the platinum temperature.

The constancy of the expression over the wide range of variables is sufficient to allow credence being given to the theory and to the assumptions on which it was based. Therefore, we may conclude that in the oxidation of platinum above 800° C, the true rate of oxidation is proportional to the first power of the oxygen pressure at all pressures, but that above a certain pressure the rate is limited by diffusion of the oxide out through a boundary layer. The oxidation limited by oxide diffusion is in contrast to the situation encountered with tungsten and molybdenum where the rate of oxidation is limited by diffusion of oxygen toward the metal. The difference arises from the fact that tungsten and molybdenum oxidize from 10^3 to 10^4 times more rapidly than platinum.

It should be emphasized that the values for the escape probability presented above are characteristic of conditions of convective flow. Under conditions of higher flow or more turbulent flow, conditions encountered in high speed flight, the escape probability and hence the rate of oxidation of platinum could increase by one or two orders of magnitude.

REFERENCES

1. G. C. Fryburg and H. M. Murphy, Trans. AIME 212, No. 5, 660 (1958).

2. G. C. Fryburg and H. M. Petrus, J. Electrochem. Soc. 108, 496 (1961).

3. R. W. Douglass, C. A. Krier, and R. I. Jaffee, Summary Report from Battelle Memorial Institute to U.S. Office of Naval Research under Contract No. Nonr-2547(00), NR 039-067 (1961).

4. C. A. Krier and R. I. Jaffee, J. Less-Common Metals 5, 411 (1963).

5. E. Raub and W. Plate, Z. Metallk. 48, 529 (1957).

6. G. R. Fonda, Phys. Rev. 31, 260 (1928).

7. I. Langmuir, Phys. Rev. 34, 401 (1912).

8. S. Dushman, Scientific Foundations of Vacuum Technique. John Wiley and Sons, Inc., 1949.

TABLE I. - COMPARISON OF RIBBON WIDTH WITH MEAN-FREE-PATH OF OXYGEN, L, AT FALL-OFF PRESSURE

Ribbon width, cm	Fall-off pressure, torr	L at fall-off pressure[a], cm	Ratio of ribbon width to L at fall-off pressure
0.0287	0.19	0.0284	1.01
.119	.046	.117	1.02
.22	.023	.235	.94

[a]Values of L calculated from values given in ref. 8.

TABLE II. - CORRELATION OF ESCAPE PROBABILITIES WITH THIN-FILM DIFFUSION THEORY

Filament width, a, cm	Temperature, °C	Pressure of oxygen, p, torr	Film diameter, b, cm	Escape probability, P_e	$ap\ P_e \log b/a$ $\times 10^2$
0.0287	1060	750	0.55	0.0061	16.8
		750	.55	.0059	16.3
		730	.55	.0061	16.3
		157	1.7	.022	17.5
		100	2.15	.024	12.8
.0287	1200	740	.55	.0060	16.3
		445	.81	.0094	17.4
		157	1.70	.020	16.2
.119	1100	745	.85	.0022	16.6
		407	1.25	.0036	17.7
		136	2.71	.0068	15.0
.22	1100	750	1.05	.0018	20.2
		750	1.05	.0017	19.0
		750	1.05	.0019	21.2
		153	2.9	.0055	20.5
		153	2.9	.0058	21.5

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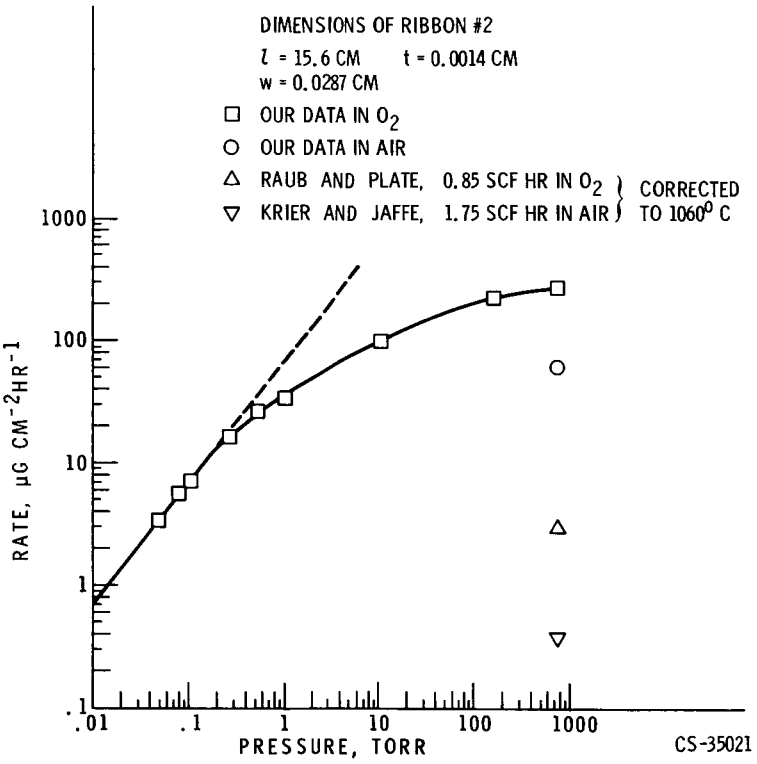

Fig. 1. - Rate of oxidation of platinum ribbon number 2 at 1060° C under various pressures of gas.

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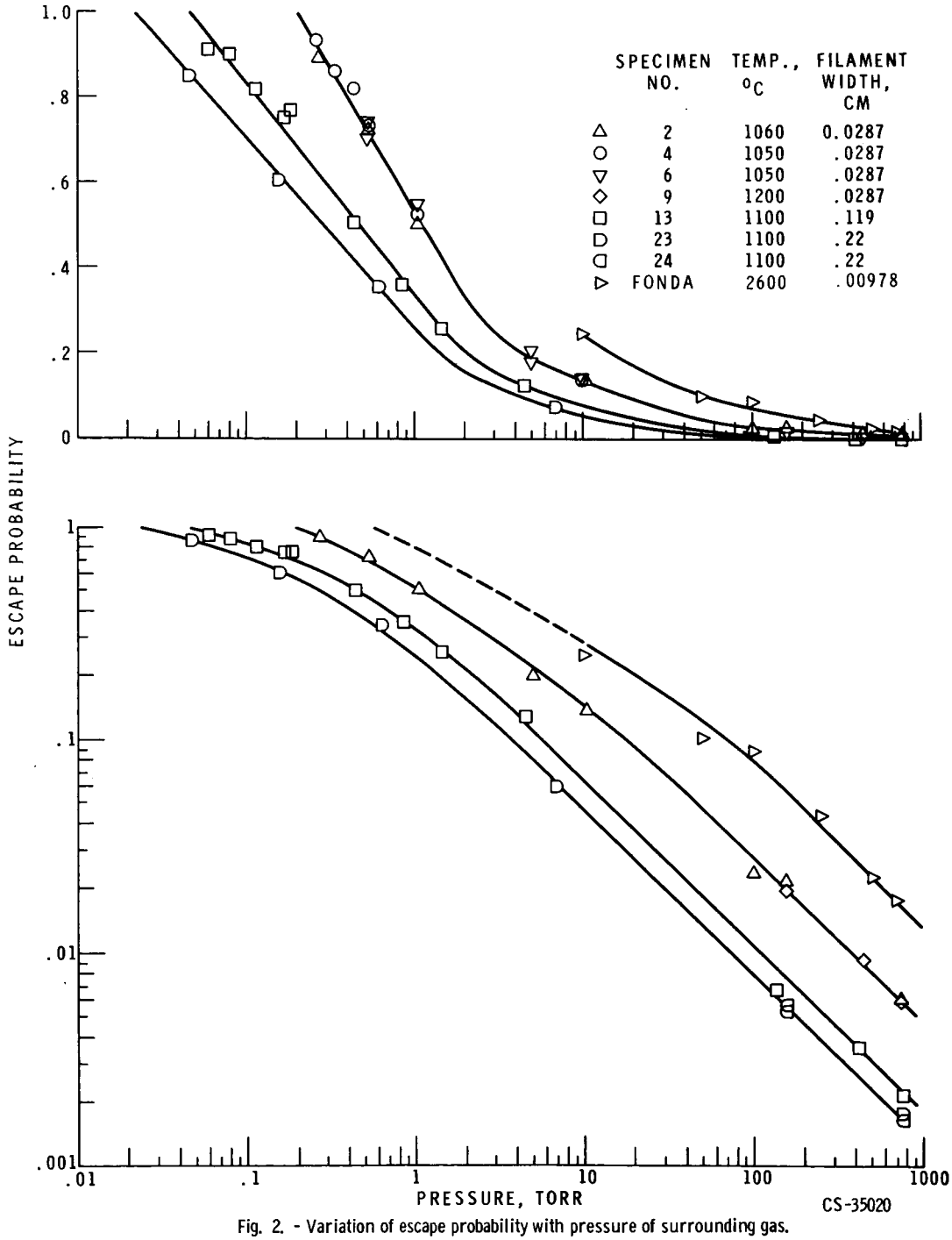

Fig. 2. - Variation of escape probability with pressure of surrounding gas.

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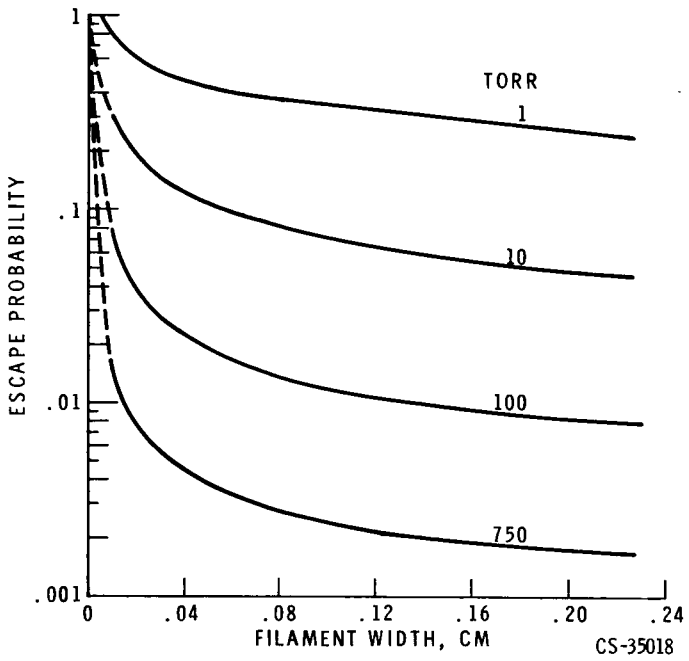

Fig. 3. - Variation of escape probability with filament diameter at several pressures.