Oxidation and Volatilisation of Platinum at High Temperature

It is generally accepted that platinum (as well as the other platinum metals) can form at least one unstable volatile oxide when heated in air or oxygen. The evidence for this belief, however, is mainly circumstantial, and surprisingly little is known about the resulting oxide or oxides or about the precise conditions necessary for their formation, volatilisation or decomposition.

As a step towards gaining a better appreciation of the reaction, R. Lacroix has recently presented in *Revue de Metallurgie*, 1956, **53**, (11), 809-818, the results of an interesting study of the changes observed in the appearance of the polished surfaces of platinum specimens after heating to temperatures of the order of 1000°C and over. The work was done in the laboratories of Comptoir Lyon Alemand, Paris, and the results are discussed with special reference to their relation to heat etching effects which have been recorded in the past on other metals.

In the introduction to this paper, M. Lacroix provides a useful survey of the literature on the oxidation of platinum. The earliest reference is to measurements made in 1903 by Wöhler, who records that platinum leaf turned to various shades of red or blue after heating at 425-450°C for 16 days in pure dry oxygen, and gained in weight by 1.9 per cent after 37 days. M. Lacroix quotes this without comment, but it may perhaps be permissible to question whether the platinum was as pure as Wöhler thought, and particularly whether it was entirely free from contamination by iron from the forging hammer and rolls. The first direct evidence of the effects of oxygen on heated platinum was provided by the work of Jones, Langmuir

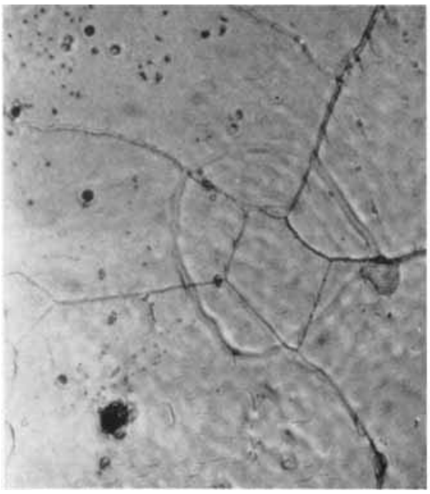

Fig. 1—Traces of grooves at former grain boundaries on a sample which has undergone grain growth ×520

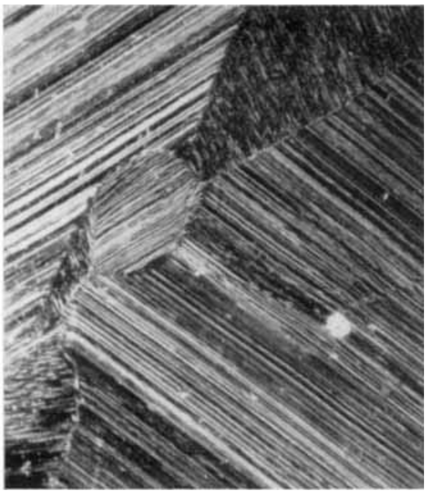

Fig. 2—Striations following crystallographic directions ×260

Fig. 3—Curved striations, possibly due to imperfections in the crystals ×780

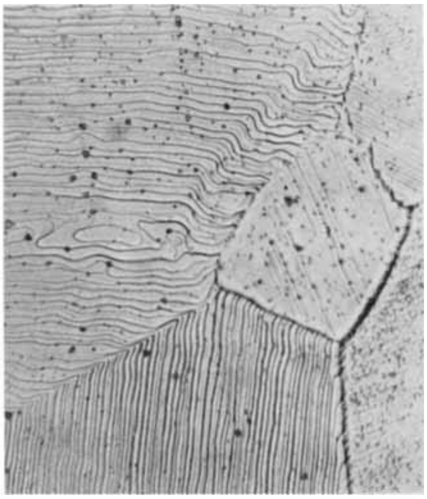

Fig. 4—Striation pattern unchanged by migration of grain boundary ×780

and Mackay, carried out in the early days of development of the incandescent electric lamp, in which the loss of weight of platinum filaments heated in vacuum was measured and shown to be very much less than that of filaments heated in air. A striking demonstration of the volatility of platinum from a wire heated in air is provided by the appearance of any platinum resistance furnace which is dismantled after operating for some time at a high temperature. Small brilliant crystals of metallic platinum are always seen as a coating on the refractory for some distance on each side of the windings, and have obviously been either deposited from platinum vapour or have grown by decomposition of an oxide at their surfaces.

In the present paper M. Lacroix has recorded that the following changes can take place on the surface of platinum after heating in air:

(1) Grooves may develop at the crystal boundaries, as shown in Fig. 1 (and diagrammatically in Fig. 5) and when, on prolonged heating, the boundaries move as a result of crystal growth, the abandoned grooves fill in gradually.

(2) Striations may occur in certain crystals, as shown in Figs. 2, 3 and 4. These only appear distinctly on surfaces which have been alternately polished and etched or have been electrolytically polished so that they are entirely free from any mechanically altered layers.

(3) In some instances a portion of the surface of the platinum may appear coated by small needle-shaped or more regular thin crystals which often exhibit interference colours. These crystals have not been very fully studied and no really complete explanation is offered of their composition or mode of formation. The number and size of the crystals is not greatly affected by the temperature or time of heating, or whether heating takes place in oxygen or in air.

M. Lacroix is concerned in his paper to discuss more particularly the striations

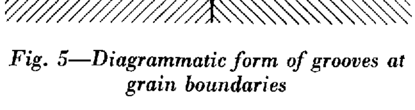

Fig. 5—Diagrammatic form of grooves at grain boundaries

observed on the platinum after heating, and an attempt is made to show that some of these phenomena are characteristic of the effects produced on heating metals which display limited oxidation at high temperature. The intergranular grooves do not seem of particular significance to the present discussion and are considered to represent the typical form of heat etching which results from the heating of a metal in vacuo or in a neutral atmosphere. In their production there is no evidence that any reaction of the surface with oxygen is involved.

On the other hand, the striations appear to be a consequence of an exchange between the metal surface and either a metal vapour or an adsorbed compound. Striations have been previously observed in the heat etching of iron, silver, copper, nickel-chromium alloys and nickel, and it is possible that they are the result of such an exchange on these metals, as well as on platinum. It is noted that in general, striations can only clearly be seen on surfaces which have not been disturbed by mechanical polishing. The conception as presented by M. Lacroix is by no means fully worked out, but the underlying thought is that in the presence of oxygen the mobility of the surface atoms is increased. As a result, surface markings such as the striations observed, as well, perhaps, as the small isolated crystals, are encouraged to form.

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Arc Erosion of Electrical Contacts

Erosion under the action of the arc is one of the determining factors in the operating life of electrical contacts which are required to interrupt currents of the order of several amperes. The loss or transfer of material from the contact surfaces which takes place during arcing may occur by a number of processes, but that most frequently encountered involves a loss of material from the negative contact under the action of the so-called " normal arc ".

Relatively little experimental data are available on the magnitude of arc transfer, but a study now published by Dr. W. B. Ittner and H. B. Ulsh of the International Business Machines Corporation, New York, (*Proc. Inst. Elec. Eng.*, Part B, 1957, **104**, Jan., 63-68), provides a valuable contribution to this subject, more particularly as the materials investigated include a number normally used in industrial practice.

The paper describes measurements of the " normal arc " transfer in resistive and inductive 50 volt circuits interrupting currents of 1.5 to 5 amp. Within the experimental errors the material transfer from the cathode was found to be directly proportional to the total charge passed in the arc, confirming a relationship first proposed by R. Holm. A summary of the results is shown in the table, which gives the average measured values of the cathode loss in microgrammes per coulomb, and—by dividing by the density of the material—in cubic centimetres per coulomb.

Material	Cathode loss	
	$g \times 10^{-6}/C$	$cm^3 \times 10^{-6}/C$
Palladium	**19.4**	**1.59**
Platinum	**8.7**	**0.41**
Silver	**3.6**	**0.34**
Tungsten	**1.1**	**0.06**
50% Copper-palladium ..	**20.5**	**1.94**
10% Iridium-platinum ..	**17.6**	**0.82**
15% Iridium-platinum ..	**16.5**	**0.77**
20% Iridium-platinum ..	**14.5**	**0.67**
35% Iridium-platinum ..	**11.6**	**0.54**
5% Ruthenium-palladium	**14.1**	**1.15**
11% Ruthenium-platinum	**13.2**	**0.65**

Agreement between the experimental data and those computed from a modified Llewellyn Jones formula was found to be good, from which it follows that the desirable properties for minimum arc erosion are a high boiling temperature, a high thermal conductivity and a high density.