

# Iridium Platinum Alloys

## A CRITICAL REVIEW OF THEIR CONSTITUTION AND PROPERTIES

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Native crystals of iridium-platinum are frequently found in association with platinum ores. These natural alloys, of rather variable composition, occur as grains, and sometimes as small cubes with rounded edges. Although the geographical distribution is fairly wide the major deposits appear to be in the Urals. One such crystal, described in 1940 by Masing, Eckhardt and Kloiber (1) had a well-defined two-phase micro-structure.

Synthetic alloys were produced at an early date. Gaudin (2), who fused spheres of a 10 per cent iridium-platinum alloy on hearths of lime and magnesia, commented in 1838 upon the lustre, malleability and extreme corrosion resistance of the resultant product. Twenty years later, however, iridium was still regarded as a troublesome impurity in platinum, but the researches of Sainte-Claire Deville and Debray (3) did much to dispel this illusion. On behalf of the Russian Government they carried out extensive trials at the French Mint to determine the suitability of iridium-platinum alloys for coinage. The crude platinum for these experiments came from the mines of Prince Demidoff at Nijne Tagilsk and contained 92.55 per cent of platinum, 7 per cent of iridium and 0.45 per cent of rhodium. Alloys prepared from this material were greatly superior to pure platinum in both strength and corrosion resistance. The alloy obtained by directly fusing the crude platinum was found to be well suited for coinage, as were the synthetic alloys containing up to 20 per cent of iridium. The 15 per cent alloy was extensively employed for the construction of chemical plant. Nicklés (4), in a letter to the American

*Journal of Science*, in 1860, remarked somewhat incredulously: "The platinum makers of Paris are manufacturing these alloys and contrary to the wishes of the discoverers are extracting higher prices for them than for pure platinum".

Prominent physicists were, at this period of the nineteenth century, devoting considerable effort to the problems involved in representing their fundamental and derived units in concrete form. Iridium-platinum alloys came to fill a unique position in the scale of substances capable of retaining indefinitely their mass, form, and linear dimensions. In addition to their corrosion resistance and good mechanical properties they were readily workable and of fairly high electrical resistance. No internal transformations were recognised in those days and the alloys were established as materials *par excellence* for instrument technology.

Iridium-platinum was selected, therefore, as the logical material for the construction of the International Metre (5). A 250 kilogramme ingot for this purpose was cast on May 13th, 1874, at the Conservatoire des Arts et Métiers in Paris. The platinum, weighing 225 kilogrammes, came from Johnson and Matthey, the iridium being supplied by the Director of Mines, St. Petersburg. Henry Tresco and George Matthey made the melt in a lime block under the general supervision of Sainte-Claire Deville and Debray and the ingot, which contained 10 per cent of iridium, was practically perfect and very uniform in composition.

Prototype metres and geodesique rules

were in subsequent years manufactured by George Matthey in accordance with the requirements of the Comité Internationale des Poids et Mesures and the Association Geodesique Internationale. Details of the melting, forging and rolling processes adopted during this work were published in 1879 (6).

The unique combination of strength and high density made the alloys very suitable for the production of standard weights. The 10 per cent iridium alloy was used for the National Kilogramme of France described by Violle in 1889 (7). Prototype kilogrammes were rigorously tested before acceptance by the International Commission of the Metre. Very high pressures were applied to ascertain whether such treatment had any effect upon the apparent density. Material submitted by Johnson and Matthey successfully withstood this proving treatment, the apparent specific gravity of eleven standard kilogrammes submitted falling within the range 21.548 to 21.552 g/cm<sup>3</sup>.

Iridium-platinum was sometimes used for electrical standards. Klamenčič (9) concluded in 1885 that of all the materials available at the time platinum-silver and platinum-iridium best fulfilled the service requirements of standard resistors. Two iridium-platinum coils were included in the group of British Association resistance standards constructed by Matthiesen in 1865 (10). The iridium alloy had a higher temperature coefficient than platinum-silver but its resistance variations, revealed by careful testing over a total period of 67 years, were considerably less capricious (11).

### The Constitutional Diagram

It was generally believed until comparatively recently that platinum and iridium when alloyed synthetically were completely miscible in all proportions. Nearly all the experimental evidence appeared to confirm this view. Feussner and Müller's melting point determinations (12), obtained by optical

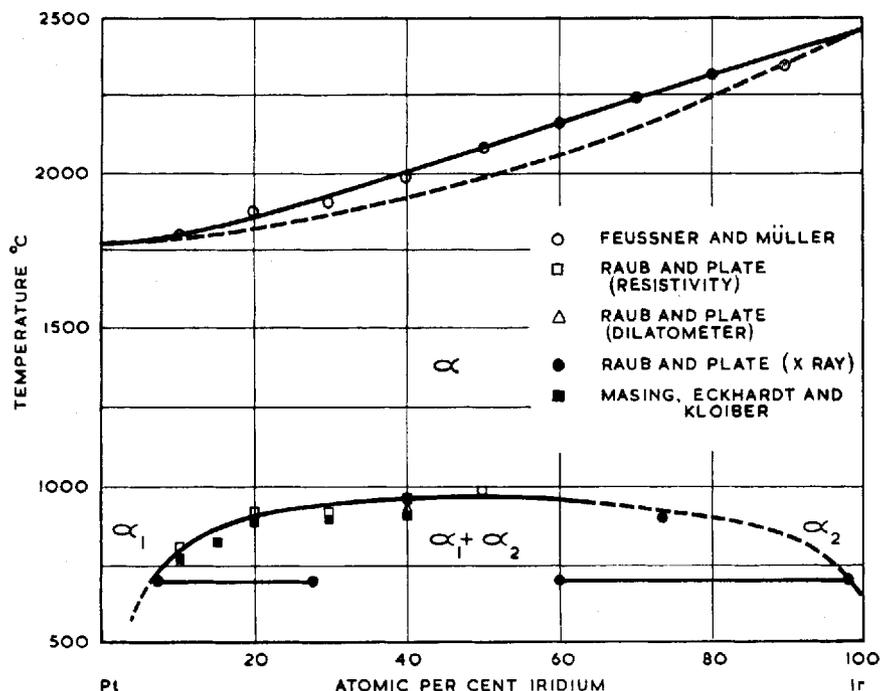


Fig. 1 Equilibrium diagram of the iridium-platinum system

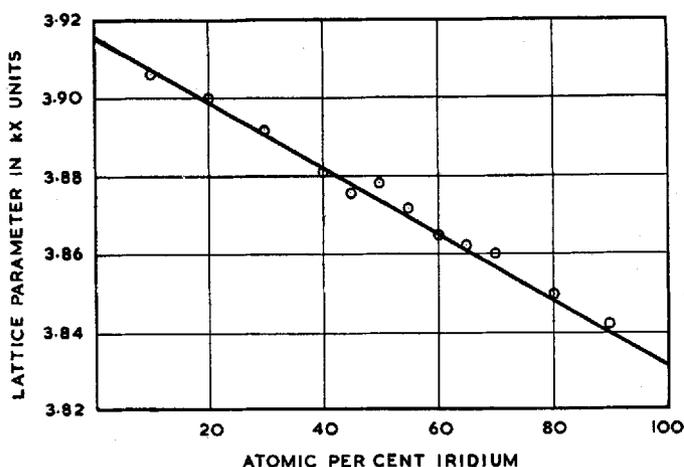


Fig. 2 Variation of lattice parameter with iridium concentration for alloys quenched from 1700°C (Raub and Plate)

methods, lay on a smooth curve which suggested the existence of a continuous range of solubility below the solidus. Nemilow (13), who studied the whole system metallographically had previously arrived at the same conclusion. He prepared alloys by oxy-hydrogen melting and drew those containing up to 20 per cent by weight of iridium into wire. Electrical resistivity measurements were made upon these wire samples, and temperature coefficient determinations on cast and homogenised specimens covering the entire composition range. Time and temperature, it was concluded, had little effect upon the electrical properties, which were typical of those expected from simple solid solution alloys. Heavy coring was observed in alloys containing more than 20 per cent by weight of iridium. None of the heat treatments adopted completely eliminated this coarse dendritic structure.

Weerts (14), in confirmation of previous evidence, showed that the lattice parameter of quenched alloys varied with concentration in a perfectly linear manner.

Nemilow experienced great difficulty in etching his alloys, and for those containing more than 40 per cent of iridium resorted to immersion in a fused bath of manganese dioxide and sodium chloride. Raub and Buss

(15), who published their results in 1940, used an alternating current electrolytic etching technique which revealed with great facility the structure of alloys containing up to 40 per cent of iridium. Hot forging and heat treatment for long periods at temperatures up to 1725°C were required to eliminate the heavily cored structure previously reported by Nemilow. All the micro-structures shown in this paper were of typical solid solutions.

Zvyagintsev, Raikhstadt and Vladimirova (16) studied the mutual diffusion of platinum and iridium in the solid state and concluded that platinum diffused into iridium faster than iridium diffused into platinum. Electrical resistivity measurements showed that fairly homogeneous solid solutions could be produced by normal powder metallurgical processes.

### The Miscibility Gap

The behaviour of iridium-platinum alloys was, however, incompatible with the view that no transformations occurred. As early as 1886, for example, Le Chatelier (17) observed transformations in a 20 per cent iridium-platinum alloy which were accompanied by an absorption of heat at 700°C and at a second temperature midway between the melting points of gold and silver. Thermo-electric studies by Barus in 1892 (29) did not, however, reveal any e.m.f. discontinuities at these points. Geibel (18) reported in 1911 that the tensile strength of wires containing more than 10 per cent of iridium could be considerably increased by heat treatment at 750°C and suggested that the effect was caused by an allotropic modification in the iridium. Nowack (19), commenting on these findings in 1930, attributed the phenomenon to

precipitation hardening although he had no evidence to support his hypothesis.

Ten years later Masing, Eckhardt and Kloiber (1) were still unable to demonstrate the existence of a second phase. These investigators carried out resistance measurements at temperatures up to 1150°C. The resistance-temperature curves had sharp discontinuities providing evidence of transformations at temperatures in good agreement with those obtained from the results of tensile testing. X-ray examination provided no evidence of precipitation, however. It was concluded that the changes in physical properties were caused by an order-disorder reaction which was not revealed because of the similar scattering power to X-rays of platinum and iridium atoms.

The true nature of the platinum-iridium diagram was finally elucidated by Raub and Plate (20), who published their results in 1956. These investigators provided definite metallographic evidence of a miscibility gap which had its highest point at 975°C and 50 atomic per cent of iridium. At 700°C the gap extended from 7 to 99 atomic per cent of iridium. Microscopic evidence of a duplex structure over this composition range was confirmed by the results of electrical resistivity, X-ray diffraction, and dilatometric measurements.

Previous workers had not arrived at these conclusions for the simple reason that they had not annealed their specimens for long enough periods. Raub and Plate showed that heat treatment periods of the order of one year were required to establish some semblance of equilibrium in the two-phase region. In order to avoid loss of iridium due to oxidation, heating was carried out in argon

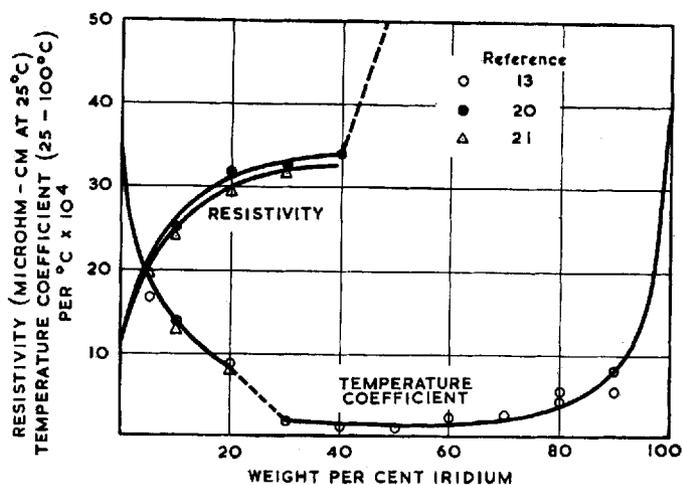


Fig. 3 Electrical resistivity and temperature coefficient of resistance of iridium-platinum alloys

or in vacuum. The slow rate of establishment of equilibrium made the decomposition process difficult to follow by X-ray methods, and because of the small differences in lattice constants between platinum and iridium X-ray determinations of the true solubility limits were not particularly accurate. Electrical resistance measurements provided the most accurate phase boundary determinations.

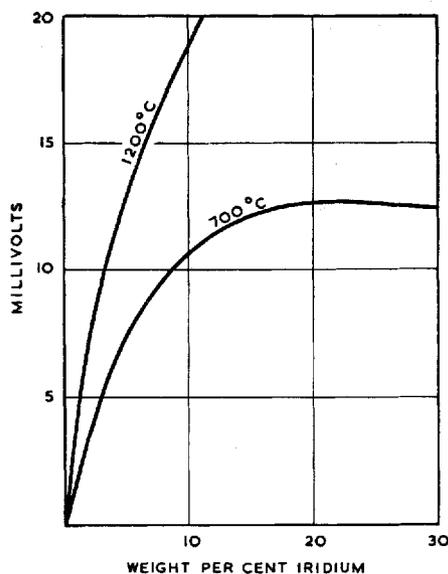


Fig. 4 Thermal e.m.f. between iridium-platinum alloys and pure platinum

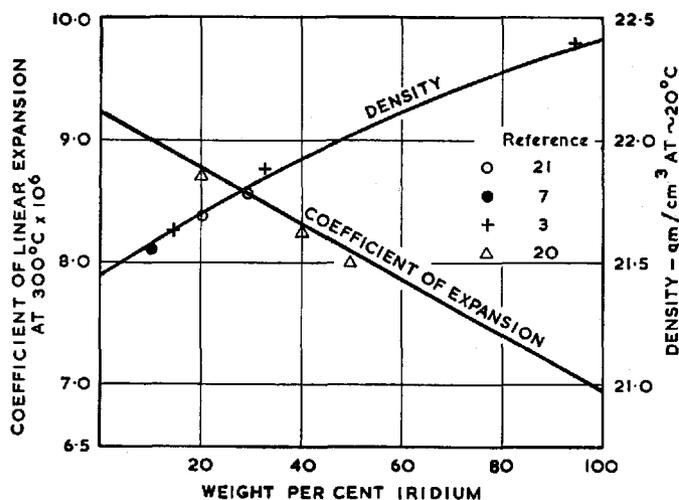


Fig. 5 Density and instantaneous linear expansion coefficients of iridium-platinum alloys

Hardness and electrical conductivity changes occurred after heat treatment periods of several hours. The development of a reasonably well-defined duplex microstructure in the 50 atomic per cent iridium alloy required 360 hours of heat treatment at 800°C. X-ray diffraction examination first detected the second phase after 1440 hours at 800°C, but the lattice parameters of the two phases approached constancy only after 3600 hours of heat treatment. After 9000 hours at 600°C no sign of decomposition was evident in the

50 per cent alloy. The table below, taken from Raub and Plate, gives the concentration limits of the duplex region for various temperatures between 700 and 976°C.

The equilibrium diagram shown in Fig. 1 is based upon the findings of Feussner and Müller (12), Masing, Eckhardt and Kloiber (1), and Raub and Plate (20).

Fig. 2 illustrates the linear variation of lattice parameter with iridium concentration for alloys

quenched from 1700°C (20).

### Electrical Properties

Fig. 3 shows that the electrical resistivity, after a rather rapid initial rise, reaches a fairly flat maximum of 32 to 34 microhm-cm at an iridium concentration of approximately 40 per cent. Differences in purity probably explain the slight differences between the two sets of values quoted. Although Raub and Plate illustrate the resistivity of the 50 atomic per cent alloy as approximately 62 microhm-cm at 20°C, this value requires verification.

Nemilow's temperature coefficient data agree closely with recent determinations made in the Johnson Matthey Research Laboratories.

The alloys have a positive thermal e.m.f. with respect to pure platinum. Fig. 4 illustrates the effect of composition upon the e.m.f.s generated at 700°C and 1200°C (21). Above 1000°C volatilisation and oxidation losses render iridium-platinum alloys less stable than rhodium-platinum alloys for high temperature measurement.

### Physical and Mechanical Properties

The specific gravity curve, shown in Fig. 5, displays a slight positive displacement from

Limiting solubility concentrations of iridium-platinum alloys (Atomic percentage of iridium)			
Temperature °C	Method of Determination		
	Resistance	Dilatometric	X-Ray Diffraction
976		50	
974	50		
958	40		
946		40	
922	30		
910	20		
900			40 and 74
800	10		26-40 and 72-86
700			7-28 and 60-99

linearity although the effect is not pronounced. The second curve in this illustration shows an approximately uniform decrease of linear expansion coefficient with iridium concentration (20).

The mechanical properties of the alloys increase rapidly with iridium content as shown by Fig. 6 (21). With 30 per cent of iridium the ultimate tensile strength of quenched test pieces rises to 56 tons per square inch. The hardness data show that the maximum mechanical properties of the series are obtained with iridium contents of approximately 60 per cent. The hardness and tensile strength of all the alloys increases very rapidly with the degree of cold working; the tensile strength of hard drawn 20 per cent iridium-platinum wire, for example, frequently exceeds 100 tons per square inch. Fig. 7 illustrates the effect of cold rolling upon the hardness of the 20 and 25 per cent iridium alloys. A reduction in thickness of 70 per cent increases the hardness of the 25 per cent alloy from 246 to 370 V.P.N. (21).

Very high hardness values can be developed by quenching and subsequently ageing alloys containing more than 10 per cent by weight of iridium. Fig. 8 illustrates the hardness changes which result when alloys quenched from 1400°C are subsequently aged at 700°C. The steady rate of hardness increase after

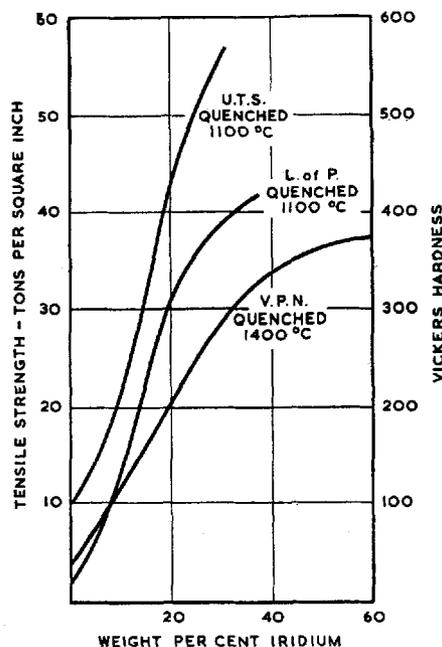


Fig. 6 Ultimate tensile strength, limit of proportionality and hardness of quenched iridium-platinum alloys

heat treatment for 16 hours illustrates the low rate of precipitation in this alloy system (21).

## Workability

Alloys containing up to 40 per cent of iridium have been hot forged for many years, although the ease of working decreases rapidly when the iridium content exceeds 20 per cent. In 1879 for example George Matthey (6) reported that although the 25 per cent iridium alloy could be worked into sheet and wire great difficulty was experienced at higher percentages, the 50 per cent alloy being unworkable. W. C. Heraeus (22) was able, in 1891, to produce cold drawn 40 per cent iridium-platinum wire but regarded this composition as a practical working limit.

The ease of working increases with the purity of the materials employed, and argon arc melted material appears to be more malleable than that melted in the open. Small samples of sheet capable of being subsequently rolled have been produced by carefully hot forging at temperatures just below the melting point of the alloy, argon arc melted ingots

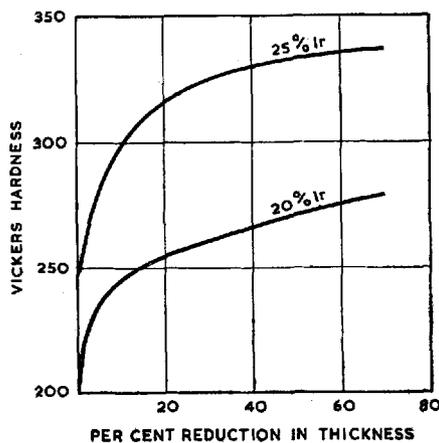


Fig. 7 Work-hardening curves of iridium-platinum alloys

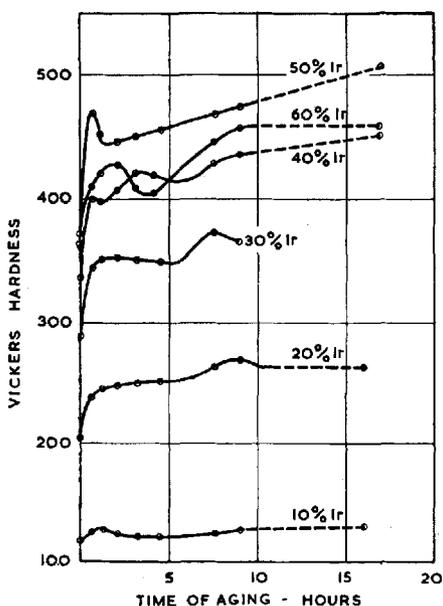


Fig. 8 Age-hardening curves of iridium-platinum alloys quenched from 1400°C and subsequently heat treated at 700°C

containing up to 60 per cent of iridium (21). Raub and Plate in their recent work employed drawn 50 per cent iridium-platinum wire (20). Such alloys are, however, even more difficult to work than pure iridium, and fabrication has so far been restricted to purposes of research.

### Corrosion and Oxidation Resistance

Iridium additions increase considerably the corrosion resistance of platinum. At a very early date it was appreciated that iridium-platinum boilers used for sulphuric acid concentration resisted the attack initiated by nitrous compounds better than those of pure platinum. Heraeus (23) stated for example that the rate of corrosion of the 10 per cent iridium-platinum alloy in sulphuric acid was only 58 per cent that of the pure metal. The resistance to halogen attack increases with iridium content in a similar fashion. The 40 per cent iridium alloy is virtually unattacked by boiling aqua regia but can be slowly etched by nascent chlorine at elevated temperatures. An alternating current process utilising a saturated electrolyte of sodium

chloride in hydrochloric acid facilitates the solution of this material (15).

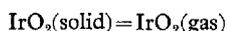
Alloys containing more than about 5 per cent of iridium oxide when heated in air. The bluish film which develops above 700°C disappears at temperatures above 1200°C leaving a clean matt surface upon the alloy. Iridium-platinum thermocouples were shown by Burgess in 1908 (24) to be less stable than those of rhodium-platinum. Crookes in 1912 (25) emphasised that the volatility of iridium in air was many times higher than that of platinum, and Wise, at a later date, quoted an evaporation ratio, at 1227°C of one hundred to one. The high evaporation losses from heated iridium-platinum alloys can, in fact, be attributed to the volatility of iridium oxide. The table below, taken from Raub and Plate (26) summarises the results of some tests made upon sheets of iridium-platinum alloys, 0.5 mm thick, heated for 23 hours at 1100°C in a current of oxygen. The weight loss of the alloy with 10 per cent of iridium amounts to 2.8 per cent of the iridium content, while the corresponding value for the 40 per cent iridium alloy is 46.6 per cent.

Fig. 9 illustrates some results obtained at 900°C. Small sheet samples were suspended for various periods in a furnace through which an oxygen current of 0.4 litre per minute was passed. The weight losses at 900°C are less than a tenth of those at 1100°C. The sudden increase in volatility when the iridium content exceeds 20 per cent is

Evaporation losses from iridium-platinum alloys heated in a current of oxygen at 1100°C for 23 hours (After Raub and Plate)			
Iridium (Wt.%)	Decrease in wt. (mg/cm <sup>2</sup> )	Evaporation loss related to iridium content	
		mg/g of alloy	% of iridium content
10	1.35	2.8	2.8
20	13.99	29.2	14.6
30	58.10	123.6	41.2
40	89.29	186.4	46.6

associated with the fact that the 30 and 40 per cent alloys are, at 900°C, well within the duplex region. Raub and Plate postulated that under such conditions most of the evaporation occurred from the iridium-rich phase. The evaporation mechanism suggested was simple volatilisation of the oxide formed when metal atoms diffused to the surface of an oxygen layer adsorbed on the solid metal.

The rather limited thermodynamic data support this hypothesis. Holborn and Austen (27) reported that the volatility of iridium at 1670°C increased less rapidly than the first power of the oxygen pressure. Raub and Plate demonstrated that the rate of volatilisation of iridium-platinum alloys was practically independent of oxygen pressure except when this was very low indeed. This behaviour suggests the volatilisation of an oxide rather than the dissociation of an unstable oxide. Brewer (28) assumed the oxide to be  $\text{IrO}_2$  and estimated  $\Delta H_{298}$  for the expression



to be  $85 \pm 7$  Kcals. For the reaction

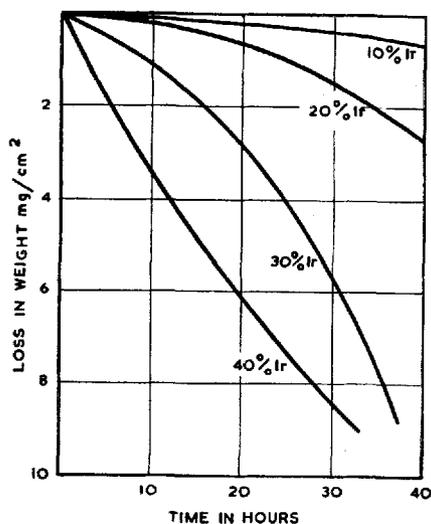
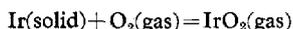


Fig. 9 Evaporation losses from iridium-platinum alloys heated in a current of oxygen at 900°C (Raub and Plate)

a value of  $\Delta H_{298} = 41 \pm 10$  Kcals was arrived at. At very high temperatures it was suggested that evaporation occurred via an  $\text{Ir}_2\text{O}$  molecule, since this was the only one having a positive entropy of formation from atomic oxygen. Iridium-platinum alloys melt before such conditions arise.

## Applications

Electrical contact applications account for a fair proportion of the iridium-platinum alloys supplied to industry. The high hardness and low contact resistance of the 10 and 20 per cent iridium alloys make them particularly suitable for low current, low pressure applications where dust contamination prejudices the performance of softer materials. In medium current applications when resistance to hammering becomes important alloys containing up to 20 per cent of iridium are sometimes employed. A recent study showed that material transfer from the cathode was proportional to the number of coulombs passed through the arc and decreased steadily with iridium contents up to 35 per cent (30). Pfann (31) has shown that interesting results can be achieved by pairing a negative 20 per cent iridium-platinum contact with a positive contact of pure gold. With medium currents the material transfer caused by an asymmetrical molten bridge was found to balance the other transfer processes, thus minimising contact wear.

Precision resistors and slide wire potentiometers utilise considerable quantities of 10 and 20 per cent iridium-platinum wire. The combination of moderate resistivity, low temperature coefficient and high corrosion resistance exhibited by these alloys is of great value in the construction of high quality transducers. In the temperature measurement field we find the 10 per cent iridium-platinum alloy used in combination with a 40 per cent palladium-gold wire. This thermocouple, capable of generating 34 millivolts at 600°C, has wide applications at moderately high temperatures.

The bridge wires used in electric detonators

fuses, and cartridge igniters must be very strong and resistant to corrosion, and iridium-platinum alloys have long been preferred for such applications. Needles used for the initial perforation of diamond dies by electro-sparking are sometimes made from the 20 per cent iridium alloy.

The elasticity and high mechanical properties of alloys containing up to 30 per cent of iridium can be successfully employed in instrument suspensions. Over the range 0–100°C the modulus of rigidity of the 10 per cent iridium-platinum alloy decreases by only 0.8 per cent (21). Where complete

freedom from corrosion is essential the age hardening properties of the 20 per cent iridium alloy render it very suitable for the production of high quality hairsprings.

Little is known about the creep properties of iridium-platinum at high temperatures. Some tests by Stauss (32) suggested that the 10 per cent iridium alloy was slightly inferior to the 10 per cent rhodium alloy, but the results were not conclusive. To avoid fracture at 1100°C, the applied stress, it was concluded, should not exceed 1.5 per cent of the normal room temperature tensile strength or 6 per cent of the short term strength at 1100°C.

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