Iridium as a High Temperature Material

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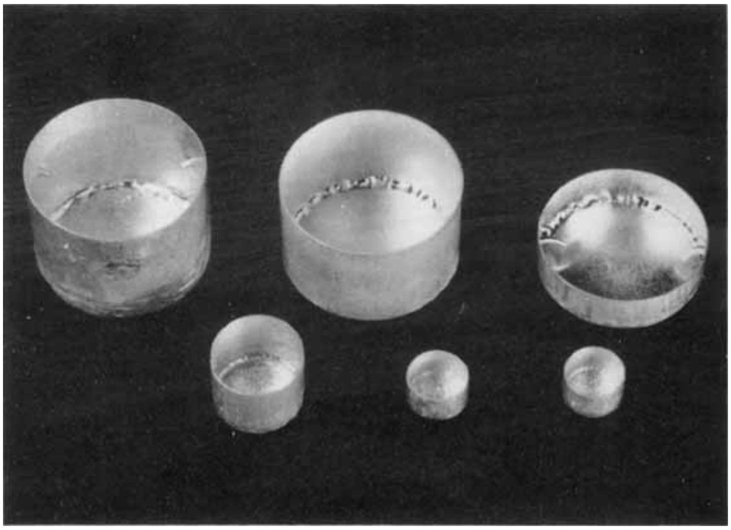
Researches at high temperature are often severely restricted by the inadequate properties of available refractory materials. The problem of chemical attack at high temperatures is so formidable that the research worker has to press into service all kinds of metals, oxides, sulphides and carbides as materials for his tubes and crucibles, using each over a limited range of chemical and physical conditions.

During the past few years iridium has proved particularly useful as a material for crucibles in certain high temperature investigations which have been made in the laboratories of the Nuffield Research Group in Extraction Metallurgy. As crucibles are not normally made from this metal, the following notes on their use may be of general interest to those concerned with high temperatures.

In the course of measurements of the thermodynamic properties of silicate melts containing lead oxide (1, 2), it became necessary to find a container which would be immune from attack by both molten lead and lead oxide at temperatures from 1000°C to 1500°C. Although normal refractory oxide crucibles are quite satisfactory for holding lead at these temperatures, they will not resist attack by silicates containing large concentrations of lead oxide over long periods of time, say six to fifty hours. Most refractory metals are either oxidised by lead oxide (e.g. molybdenum) or are too soluble in lead (e.g. platinum).

It was found that Sir William Crookes had made experiments in 1912 with an iridium crucible which had been presented to him by "Messrs. Johnson and Matthey" (3). He claimed that he had boiled lead in this crucible without harm and that he had also been able to melt copper and iron in it without significant attack.



Parts of the assembly of iridium crucibles used in high temperature investigations on silicate melts containing lead oxide. The diameter and depth of the main crucible at top left were 3.6 and 3.1 cm respectively. The weights from left to right and top to bottom were 4.0, 3.5, 1.9, 0.8 and 0.3 gm.

In view of Crookes' report, tests were made with iridium and it was found to be completely resistant to attack by lead at temperatures of concern in these investigations. As had been hoped, the iridium was not oxidised by lead oxide (PbO) at any temperature. Although a black oxide of iridium forms when the metal is heated and then cooled in air, this oxide requires higher oxygen potentials for its formation than are associated with the system Pb + PbO at any temperature. There may, of course, be a volatile oxide of iridium, as there is of platinum (4), but this probably requires oxygen pressures of the order of an atmosphere for its formation at high temperature.

The assembly of iridium crucibles used in the investigations with lead is shown in the figure. It was made by Johnson, Matthey & Co., Limited, from sheet 0.012 inch thick (99.95 per cent purity), each crucible being of welded construction. The three pieces in the upper part of the figure are, from left to right, the main crucible, its main lid which fitted *closely* outside it, and a small lid which fitted *inside* it. Below them from left to right are a crucible for holding PbO melts, and two smaller crucibles for holding lead. These three were enclosed within the main crucible during the course of an experiment. The entire assembly was robust and kept its shape well throughout many experiments; the iridium metal is much harder than platinum and is not easily deformed.

The crucibles lost weight slightly during use and became etched in appearance, whether they held slags or metal. The metal grains so revealed ranged in size up to 1 mm across. The following losses of iridium were typical: 0.0002 g. into 18 g. lead in 444 hours at 1000°C; 0.0014 g. into 20 g. slag and 20 g. lead in 144 hours at 1000°C.

After continuous daily use for about a year the crucibles became slightly porous and brittle, and although they were patched from time to time by welding, they ultimately had to be scrapped. The cost of the sheet is about three times that of platinum and the working cost rather more than for platinum. If allowance is made for the scrap value of the crucibles, the refractory bill for the research was relatively small. It was much less than it would have been if alumina crucibles had been suitable, for at least two would have been expended in each experiment.

Some Properties of Iridium and Platinum

	Iridium	Platinum
Atomic number	**77**	**78**
Atomic weight	**193.1**	**195.23**
Density, at *20°C, gm per cc*	**22.4**	**21.4**
Melting point, *°C*	**2442**	**1769**
Hardness *(annealed), VPN*	**220**	**40**
Tensile strength *(annealed), tons/in²*	**16**	**10**
Modulus of elasticity, *lb/in²*	**74×10^6**	**22×10^6**

Attempts were made to confirm Crookes' claim that iridium can resist molten copper and iron. Experiments at 1500°C to 1600°C showed that both these metals attack iridium too quickly for them to be held for any useful time in contact with it.

Tests with iridium as a container for slags at 1500°C to 1650°C show that it can hold calcium phosphates (23 to 45 mole per cent P_2O_5) at oxygen pressures of 10^{-6} to 10^{-7} atm. These are conditions under which platinum crucibles melt, on account of the reduction of phosphorus into the metal. In this connection it is interesting to note that the eutectics of iridium with boron, phosphorus and silicon lie well above those of platinum with this same series of elements (5).

Iridium is clearly less reactive than platinum towards a variety of elements, so it has potentialities as a special refractory for both research and restricted industrial purposes. Its principal physical properties, compared in the table above with those of platinum, are attractive from the standpoints of stiffness (as shown by its extremely high modulus of elasticity) and creep. Allen and Carrington (6) carried out a series of compression creep tests on metals of high melting point. The strength at 1000°C was assessed by measuring the stress needed to give 1 per cent deformation in 24 hours. The value obtained for iridium was 6 tons per square inch compared with approximately 0.1 ton for platinum, 0.3 tons for palladium and 3 tons for rhodium. Of the base metals examined only tungsten, which has the disadvantage of being easily oxidised at these temperatures, had a strength comparable with that of iridium.

References

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The Catalytic Oxidation of Ammonia

A STUDY OF THE REACTION KINETICS

Among the papers presented to the first European Symposium on Chemical Engineering, held last year in Amsterdam, was a contribution on the catalytic oxidation of ammonia by means of a rhodium-platinum alloy gauze by Dr. A. P. Oele, of the Dutch State Mines (*Chemical Reaction Engineering*, Pergamon Press, London, 1958, pp. 146–157).

The process was studied as a typical fast heterogeneous reaction conducted in an adiabatic reactor. The main oxidation reaction is accompanied by side reactions leading to the decomposition of ammonia and nitric oxide, but these can be suppressed by employing suitable working conditions. The feed gas normally contains between 8 and 11 per cent of ammonia, and it flows through the flat circular platinum or rhodium-platinum gauzes which have a large area per unit of weight and which are set as close together as possible.

Within the usual range of ammonia concentration, the physical transport of ammonia molecules to the gauze surface is the principal rate-determining factor. The transport distance is very short, and the ammonia transport may be considered as a stationary diffusion process in a laminar flow. A calculation of the mass transfer may be made by using an empirical formula for flow perpendicular to the wires. The resulting data agree fairly well with the practical results, and it is possible to determine by relatively simple calculation most of the design data for a burner using a given type of gauze at a chosen gas loading.

The remaining factors may be determined by making a rough examination of the temperature distribution. When there is thermal equilibrium the heat evolved, which is determined by the heat of combustion and the local ammonia concentration for each unit area of gauze, is equal to the heat released by radiation and convection.

The optimum operating conditions in relation to platinum loss are also considered. These losses constitute a significant element in the costs of the process and may range from 200 to 2000 mgm. per ton of nitrogen throughput. Observation and calculation indicate that minimum losses may be realised by limiting the gas load and temperature and by using a pad of not more than five gauzes.