Vapour Phase Deposition of Iridium

NEW TECHNIQUES FOR APPLYING COATINGS ON GRAPHITE

A reliable, easily worked process for depositing coherent, compact and pore-free layers of iridium could, when fully developed, be the means of making use as never before of the outstanding and indeed unique characteristics of iridium.

Iridium has a very high melting point—2443°C—and as a platinum group metal it does not scale or tarnish when heated in air even to incandescence. It is true that it loses weight through formation of a volatile oxide when it is heated to above about 1000°C in air, but it is not difficult to contain the loss within reasonable limits in most circumstances by controlling free circulation.

Like the other platinum metals it does not when solid react with carbon or graphite, but unlike platinum, palladium or rhodium it is unaffected by molten tin, lead, copper or most base metals and can be heated unchanged in contact with such refractory metals as tungsten, molybdenum, tantalum, and zirconium.

In the past, however, although small iridium crucibles are standard equipment, the difficulties of fabricating iridium have often restricted its wider use. Moreover, iridium cannot be electroplated from aqueous solutions, and only limited experimental success has been achieved with the very difficult process of electrodeposition from molten salts.

More recently, the high melting point of iridium and its compatibility with graphite at high temperatures have made it of special interest to designers of nuclear reactors and missile shields. It has become apparent that iridium coatings would be of particular value in protecting graphite from oxidation at around 2000°C. For this application, iridium has the unexpected additional advantage that its thermal expansion is a good match with that of graphite at temperatures up to 1100°C, over the range in which the metal is relatively unyielding.

It is with this background that the results of experiments recently reported in applying methods of chemical vapour deposition to the formation of iridium coatings on graphite may be viewed.

The process of chemical vapour deposition is probably best known by such examples as the Mond process for making nickel shot or powder by the decomposition of nickel carbonyl and by the Van Arkel process for purifying such metals as titanium. In none of these applications, however, has much control been possible of the density and uniformity of the deposit.

The last decade has seen a considerable interest in expanding and controlling methods of vapour deposition. In particular, the Battelle Memorial Institute and some large American industrial research laboratories have been active in the field and have claimed success in such divergent fields as the production of tungsten tubes and sheets from tungsten fluoride and of titanium oxide pigments from titanium tetrachloride.

Nucleation and Growth

The present state of CVD technology, as it has been termed, was reviewed at a Conference on Chemical Vapour Deposition of Refractory Metals, Alloys and Compounds held at Gatlinburg, Tennessee, in September last. In general, it would appear that the greatest progress has been on the theoretical side, establishing the magnitude and direction of the factors controlling nucleation and growth of the deposits. More specifically, two papers at the conference were concerned with the choice of the iridium compounds most suitable for the production of iridium coatings. In the first (1), B. A. Macklin and J. C. Withers, of General Technologies Corporation, Reston, Virginia, investigated the use of iridium trichloride, iridium tetrachloride, iridium tribromide, and the expensive iridium hexafluoride, to produce iridium coatings on graphite.

Iridium trichloride or tetrachloride can both be decomposed thermally at 800°C or reduced with hydrogen or carbon monoxide at a slightly lower temperature, 700°C. The presence of traces of water also appears to lower the decomposition temperature. It is suggested that an intermediate species of the form $IrCl_x(OH)_yCO_z$ may be produced. The best results were obtained when the graphite substrate was heated to 825° to 975°C using a stream of hydrogen mixed with twice to four times its volume of carbon monoxide to carry iridium trichloride vaporised at 150° to 300°C. No advantages were observed through the use of the tetrachloride or bromide, but by using iridium hexachloride carried in a mixture of argon, hydrogen, and carbon monoxide at a low pressure, very fast rates of deposition of the order of 0.5 mil/hour were achieved on graphite rods heated to 775°C. Two other compounds, iridium acetylacetonate and bis-cyclopentadienyl iridium hydride, have also been considered, and may have advantages through their freedom from halides.

Organometallic Compounds

In the second paper (2), J. A. Papke and R. D. Stevenson, of Ethyl Corporation Research Laboratories, Ferndale, Michigan, describe experiments with two organometallic compounds, acetylacetonato (1,5-cyclooctadiene) iridium (I) and di-μ-methoxybis (1,5-cyclooctadiene) diiridium (I). With both compounds, amorphous and presumably powdery deposits were formed unless the deposition conditions were carefully controlled, but good deposits of 90 to 95 per cent purity were obtainable on copper discs heated to 600 to 750°C at pressures of about 0.2 torr.

Generally speaking, chemical vapour deposition appears capable of deposition rates three to six times as fast as those common in electrodeposition practice and has exceptional throwing power. Provided that conditions can be established which will ensure removal of the gaseous products of the reaction it seems to offer promise of being able to produce sounder and more uniform deposits on hot substrates than can be obtained by any other plating process.

J. C. C.

References

1 B. A. Macklin and J. C. Withers, "The Chemical Vapour Deposition of Iridium", Proceedings of the Conference on Chemical Vapour Deposition of Refractory Metals, Alloys and Compounds, 1967, 161–173

2 J. A. Papke and R. D. Stevenson, "Evaluation of Metal-Organic Compounds as Materials for Chemical Vapour Deposition", *ibid.* 193–204

Palladium and Rhodium: Russian Reviews

A valuable summary of knowledge concerning palladium has been published recently by the "Nauka" publishing house in Moscow. This is "Splavy Palladiya" (Palladium Alloys), 1967, 214 pp, by E. M. Savitskii, V. P. Polyakova and M. A. Tylkina of the Institute of Metallurgy named for A. A. Baikov. Part of the information is from original work by these scientists but the majority of it is a thorough review of international effort, fully referenced.

The book is divided into three main sections: the first deals with the occurence, extraction and fabrication of palladium, with the physical and mechanical properties of the metal, and with its chemical reactions and salts; the second part deals with the properties of the alloys; the third part describes the uses of the metal and its alloys.

This comprehensive study is not the first of its type. In 1966 "Nauka" published I. A. Fedorov's "Rhodium", which has a similar type of coverage but, since Fedorov works at the Institute of General and Inorganic Chemistry named for N. S. Kurnakov, puts greater emphasis on the chemical compounds of the metal.

If such reviews are to be extended to the remaining platinum metals then a very valuable record of Russian interest in this field will be available.

F. J. S.