Platinum Group Organometallics

COATINGS FOR ELECTRONICS AND RELATED USES

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Platinum group organometallics have recently been the subject of intensive investigation designed to establish the basic characteristics of their decomposition, which results in the formation of metallic or metal-containing coatings. This review has been compiled from a literature search and indicates some of the applications that are, or could be, of commercial significance.

This survey is devoted to some aspects of the use of organometallic platinum group compounds for the preparation of materials suitable for industrial applications, mainly in electronics (1, 2). The detailed chemistry of organometallic platinum group compounds is not included, as a number of monographs on this subject are available (3, 4, 5). In some instances, however, information about co-ordination complexes of platinum group metals will be included. The possible practical use of organometallic platinum group compounds for the deposition of coatings and films by various decomposition techniques was suggested in early works on synthesis, see for example (6). To date, however, organic derivatives of platinoids have found little commercial use despite fairly extensive data, especially in the patent literature. The reasons for this include the high cost of the compounds, the lack of suitable coating equipment, and, in some cases, the lack of routine production processes for the synthesis of the required complexes.

A brief outline of general coating and film deposition techniques based on organometallic platinum group compounds is first given.

To date, there are two main decomposition methods for the production of coatings, namely vapour phase decomposition and decomposition in solutions. The decompositions of organometallic compounds in the solid state and as components of various viscous compositions, such as pastes and polymers, can be regarded as separate techniques. These types of organometallic compounds can decompose to a metal, or to an oxide under the influence of: heat, electric discharge, electron beam, and laser radiation, and these techniques are employed for vapour phase decomposition. Decomposition of organometallic compounds in solution is frequently performed thermally, photochemically, electrochemically or via chemical reduction and hydrolysis. Each method will now be considered separately, and a list of the compounds and metals used in each will be given.

The requirements for vapour phase thermal decomposition are as follows (1, 2):

(a) the compound should be transformed into the vapour phase without decomposition
(b) the compound should be highly volatile
(c) organic products resulting from the decomposition of the organometallic compounds should be gaseous, and should not contaminate the coating
(d) the organometallic compounds should be non-toxic and ideally should be stable to air and moisture.

The first two of these are the determining factors. In order to characterise the volatility of organometallic compounds, the vapour pressure-temperature equation should be applied. However, for organometallic platinum group compounds, this is known only for ruthenocene (7), $CpPtMe_3$ (8) and $MeC_5H_4PtMe_3$ (8). For a number of compounds sublimation point (sublm.p.) and boiling point (b.p.) data are available, but in most cases there are no known quantitative values for the volatility of the organometallic platinum group compounds.

Most of the data on the decomposition of organometallic platinum group compounds is concerned with their thermal decomposition. (The formation of iridium oxide films via vapour deposition in an oxygen discharge (9) is not considered in this review.) Information on each metal is considered separately.

Ruthenium

Complexes potentially suitable for the deposition of ruthenium films are ruthenium carbonyls, ruthenium carbonyl halides, ruthenium cyclopentadienyls, ruthenium acetylacetonates, and some of their organic and co-ordination derivatives. Pentacarbonyl ruthenium, $Ru(CO)_5$, with a vapour pressure of 50 mm Hg at 18°C (10), starts to decompose at -18°C to form $Ru_2(CO)_9$, and at a temperature of 220°C decomposition to the metal occurs. The thermal decomposition of trinuclear $Ru_3(CO)_{12}$ to the metal has been studied by infrared spectroscopy and thermogravimetric analysis (11). A bright metallic film is formed on decomposition of $Ru(CO)_2Cl_2$ or of RuCOBr at 200°C, in the absence of air (10, 12). Annealing $Ru(CO)_2Br$ (b.p. 118°C, sublm.p. 140°C) or $Ru(CO)_3I$ (b.p. 114°C, sublm.p. 120°C) in a stream of oxygen and phosgene leads to the formation of ruthenium films (10).

However, the thermal decomposition of ruthenium carbonyls and ruthenium carbonyl chlorides, like analogous platinum metals derivatives, is accompanied by severe corrosion of the equipment and the support materials, also, the majority of these ruthenium compounds are moisture- and oxygen-sensitive. Thermodynamic functions have been determined for ruthenium and osmium carbonyls, $M(CO)_5$, in the gaseous state (13).

Some volatile ruthenium compounds, namely mixed dienecarbonyls (14) and diene-β-diketonate ruthenium complexes (15) and individual ruthenium tris-β-diketonates are mentioned in the literature. The latter compounds are patented for use in the formation of ruthenium films on various substrates via the deposition of $(acac)_3Ru$ or $(F_3acac)_3Ru$ vapour onto a suitable support, heated to the decomposition point of the compound (16–18).

Ruthenocene, $(C_5H_5)_2Ru$, is the most promising compound for the formation of ruthenium films. First, it is a commercially available product, and it is suitably volatile (sublm.p. 100°C/10^{-1} mm), air-stable, non-toxic and may be prepared in a highly pure state. Attention was first drawn to the possibility of preparing high purity ruthenium via ruthenocene decomposition in 1964 (19). A pure ruthenium film was generated at 595°C in a hydrogen atmosphere; iron ($\sim$ 0.01 per cent) and palladium ($\sim$ 0.005 per cent) were present as admixtures, and silicon and boron as trace elements. Patented applications for ruthenocene include: the preparation of layer resistors (20), additives to liquid crystals (21) and for plating multilayer electrodes with oxides and metals (22). The plasma-induced vapour phase decomposition of ruthenocene enables thin metallic films to be produced at a sufficiently high rate (23, 24).

Osmium

According to data in the literature (10), on decomposition, osmium carbonyl halides are capable of forming bright osmium films. Thin films of osmium metal were prepared via the decomposition of OsO_4 complexes with terpenes in a hydrogen stream at 300°C (25, 26). It should be noted that osmium tetroxide exhibits high volatility, but its high toxicity, equal to that of hydrogen cyanide, precludes its use for film preparation. The application of a solid complex of OsO_4 with dioxane has been patented. It is less volatile than osmium tetroxide and also less toxic (27). Among other osmium derivatives, it should be noted that cyclooctatetraene(tricarbonyl)osmium has been patented for the deposition of coatings from the gas phase (14), while osmocene, bis(cyclopentadienyl)osmium, has been recommended as an additive to liquid crystals (21) and also for the preparation of high purity osmium (28). The thermal decomposition of $Os_3(CO)_{12}$ to metallic osmium has been reported in the literature (11).

Rhodium

The ability of rhodium carbonyls and rhodium carbonyl halides to form bright rhodium films on decomposition has been known for some time (10). For example, $[Rh(CO)_3]_n$ on heating without solvent, and $Rh_4(CO)_{12}$ on heating in air, deposit a rhodium film (11). A dimeric carbonylrhodium chloride $[Rh(CO)_2Cl]_2$ melts at 123°C, readily sublimes above 100°C, and decomposes at around 300°C in a stream of carbon dioxide to deposit a bright metallic film. In the presence of oxygen or $COCl_2$, $[Rh(CO)_2Cl]_2$ "flares up" and "burns out", thus depositing bright rhodium films (10).

Among other volatile rhodium compounds, tris(allyl)rhodium and liquid π-allyl-π-allyl(cyclopentadienyl)rhodium (29) as well as rhodium complexes with β-diketones should be mentioned. For example, the reduction of tris(trifluoroacetylacetonato)rhodium with hydrogen in the vapour phase has been proposed for the preparation of thin rhodium films (30). At a vaporisation temperature of 130°C, a reduction temperature of 250°C and a hydrogen flow-rate of 16 ml/min, thick uniform films with good adhesion and good electroconductivity were deposited. X-ray phase analysis revealed no admixtures in the films. The use of acetylacetonates of rhodium and other metals for the production of fuel elements has been patented (31), and data on the vapour pressures and heats of sublimation of rhodium and iridium tris(trifluoroacetonate) complexes have been published (32).

Iridium

Iridium occupies a special place among the refractory metals because of its hardness, high resistance to oxidation and ability to form carbides. The temperature dependence of the coefficient of thermal expansion for iridium is close to that of carbon (6). The known volatile iridium compounds include carbonyl hydrides and chlorides, which are readily decomposed and sublimed to form bright metallic films (10), tris(π-allyl)-iridium (29), π-cyclopentadiene-π-cyclopentadienyliridium (29) and iridium β-diketonates (31–33). The decomposition of tris(acetylacetonato)iridium in a stream of hydrogen at 115 to 132°C, with deposition onto a support heated to between 400 and 750°C, yields an iridium film. The use of tris(acetylacetonato)iridium for the preparation of fuel elements, has been claimed (31). Other volatile organometallic iridium compounds, namely π-cyclooctadiene-π-cyclopentadienyl-iridium (34) and π-cyclooctadieneiridium acetylacetonate (34) should be mentioned. A four nuclear carbonyl, $Ir_4(CO)_{12}$, is readily sublimed in a stream of carbon monoxide under atmospheric pressure (29).

Palladium

Palladium is one of the less expensive platinum group metals, and the chemistry of its organometallic compounds is well developed (4, 5). In decreasing order of volatility, the volatile compounds are: π-allyl-π-cyclopentadienylpalladium $\pi\text{-}C_5H_5Pd\text{-}\pi\text{-}C_3H_5$ (sublm.p. 30–40°C/1–2 mm) (35), bis(π-allyl)palladium $(\pi\text{-}C_3H_5)_2Pd$ (sublm.p. 35–40°C/10^{-2} mm) (36), and bis(trifluoroethyldithiocarbonato) palladium compound $(CF_3CH_2OCS_2)_2Pd$ (sublm.p. 130–150°C/10^{-1}–10^{-2} mm) (5). The volatile co-ordination compounds of the metal with sulphur- and nitrogen-containing ligands have been the subject of a review (37) and reported elsewhere (38–42). π-Allyl-π-cyclopentadienylpalladium (43–45), bis-π-allylpalladium chloride (44, 46), and bis(acetylacetonato)palladium (47, 48) have been used for the preparation of films. The characteristics of the thermal decomposition of bis-π-allylpalladium chloride in the solid state (49–52) and the thermal stability of a series of π-allylpalladium complexes (53) have been studied by differential thermal analysis and thermogravimetric analysis. The thermal decomposition of bis(hexafluoroacetonato) palladium follows a radical mechanism (54), bis-π-allylpalladium chloride decomposes to precipitate metallic palladium which catalyses a further decay of the complex. The initial decomposition temperature is 137°C, and palladium is precipitated at 160–225°C. On precipitation of the palladium, secondary reactions of the allylchloride moieties occur, resulting in the contamination of the metallic palladium by carbon. The catalytic activity of the metal, which precipitates on decomposition of $(C_3H_5PdX)_2$, is considered elsewhere (55). At 130–135°C/10^{-2} mm and at a pumping rate of not less than 1–1.5 μm/s, a palladium film was deposited onto a support heated at 200 to 350°C. The maximum film thickness was 8 μm, and no chlorine was present. The resulting films exhibited good adhesion to ceramics, fluoroplast-4, sodium chloride and potassium chloride crystals.

Bis(acetylacetonato)palladium is vaporised at 150°C/10^{-4} mm and is decomposed to the metal at 350–400°C. The addition of an oxidiser, such as carbon dioxide, suppresses the codeposition of carbon. Good results were obtained for a palladium film deposited from $C_5H_5PdC_3H_5$. The compound vapours entered the reactor either at 40–50°C/1 mm or at 70–80°C/760 mm; and rapid film formation occurred on a suitable support heated to 300°C. The thickness of the palladium film depended on the time that the support was located in the $C_5H_5PdC_3H_5$ vapour stream. The films obtained exhibited good adhesion.

Platinum

Historically, chlorocarbonyl complexes were the first platinum compounds to be employed for film formation. Precipitation of platinum occurs during thermal decomposition of platinum carbonylchloride compounds at 100–120°C/0.01–0.02 mm, the temperature of the metallised support being 600°C. Thus thin uniform films were produced on platinum, molybdenum and nickel wires (56). The use of carbon dioxide as a carrier gas prevents the decomposition of the compound in the evaporator and reduces the possibility of preliminary decomposition taking place on the way to the support. Reduction of the carbonylchloride vapours with hydrogen prevents the formation of coarse grained films, and promotes the formation of smooth, uniform platinum films.

The preparation of thin platinum films via the thermal decomposition of bis (acetylacetonato)platinum has been described (57, 58). The $(acac)_2Pt$ compound vaporises at 180°C/10^{-4} mm, and the deposition of 10–100Å thick films onto a silicon support heated to 500–600°C is carried out at a vapour pressure of 20–200 mm. Hydrogen is not suitable as a carrier gas, because it results in the formation of a black non-volatile compound. The films are contaminated by carbon.

The thermal decomposition of trimethyl(acetylacetonato)platinum at 165°C was investigated in a flow type system, with pumping of the decomposition products at 250–300°C (59–61). Platinum was deposited as a bright metallic film, and acetylacetone and methane were identified in the decomposition products.

The other most suitable platinum derivatives for film formation via deposition from the vapour phase, are tetrakis(trifluorophosphine)platinum $Pt(PF_3)_4$ (b.p. 70°C) (62), bis-π-allylplatinum $(C_3H_5)_2Pt$ (sublm.p. 40°C/10^{-2} mm (63), π-allyl-π-cyclopentadienylplatinum $C_3H_5PtC_5H_5$ (sublm.p. 40°C/10^{-2} mm) (63), trimethyl-π-cyclopentadienylplatinum Me_3Pt-π-C_5H_5 (sublm.p. 100°C/10^{-2} mm) (8, 65) and its monomethyl derivative (8). The production of platinum-gallium films has been reported (66).

Decomposition in Solution

Having reviewed the literature on the application of organometallic platinum group compounds for the preparation of coatings and films via vapour phase deposition, the decomposition of organometallic compounds in solutions is now considered. In this case the majority of the data is concerned with thermal decompositions which is due to the fact that electrochemical and chemical deposition of

Organometallic Platinum Group Compounds for Film Deposition

Organometallic compound	Support	Temperature	Reference
$C_5H_5Pt\ Me_2$	Synthetic fibres		67
$(C_5H_5)_2Os$	,,		67
$C_5H_5Ru(CO)_2Me$	,,		67
(Diene)$PdCl_2$	Polymer	50–150°C	68
OsO_4terpene	Glass	300°C H_2 stream	69
(Diene)$PdCl_2$	,,		70
LML′ (M = Pd, Pt, Rh, Ir, Ru, Os; L,L′ = cyclic hydrocarbon ligands)	Electrodes		71
Pd_2DBA_3 (DBA = dibenzylideneacetone)	Plastics		72
$Rh_2(CO)_4Cl_2$	Glass*		73
$[C_2H_4PtCl_3]H$	Zeolites, metal oxides		74
$CODPtCl_2$	,,		74
$CpRh(CO)_nH$	Divinylbenzene, polystyrene		75

For data on application of the compounds: $C_5H_5M(X)C_5H_5$ (M = Rh, Ir; X = SR, SeR, TeR, AsR_2, PR_2); $(LMX)_2$ (L = cyclic π-enyl; M = Pd, Pt; X = halogen); $[QM(CO)_nE]^+A^-$ (M = Ru, Os; Q = C_5H_5, C_6H_6; E = olefin; A = AlX_4, PF_6, BPh_4, halogenide); $M(Cs)_n(PR_3)X$ (M = Ru, Rh, Pd, Pt; R = Ph; X = Cl, Br); $L_2Rh(CO)Cl$, see Refs. 76–80

*Preliminary treatment with $Cl_3S(CH_2)_2CN$

metals from solutions are being seldom used.

Films of metals and metal oxides may be produced on a variety of supports from organometallic compounds and their mixtures via thermal decomposition. The method is technologically facile, and as a rule the following procedures are carried out (1):

(i) The solution is applied to a sample, the solvent is evaporated, the organometallic compound is decomposed at ambient temperature and the film formed is then annealed into the sample at elevated temperatures.

(ii) The heated sample is placed in the solution, held there until it becomes coated, and the film is then annealed into the sample.

(iii) A stream of the solution is directed under pressure onto the sample being plated, which is heated to the specified temperature.

Organometallic platinum group compounds for use with this technology require the following (1):

(a) high solubility of the organometallic compound in organic solvents

(b) the organometallic compounds should not undergo sublimation, even at elevated temperatures

(c) the organic solvent and organic decomposition products should be completely vaporised at the decomposition temperature of the organometallic compounds.

In view of these requirements, the literature is now considered. It should be noted that the majority of organometallic platinum group compounds exhibit higher solubility than inorganic compounds. The first requirement, therefore, is easy to meet. Any organometallic platinum group compound is potentially suitable for the formation of films from solution, via thermal decomposition. The determining factor is the availability of the compound and its possible commercial production. Information on the use of organometallic platinum group compounds for film deposition via thermal decomposition is given in the Table. This shows that a wide range of compounds, covering practically all types of platinum group organometallic compounds, have been patented. These compounds can be readily prepared under both laboratory and industrial conditions.

The literature contains no data on the photochemical and electrochemical decomposition of organometallic platinum group compound solutions.

There is however information on the chemical deposition of platinum metals from solutions of the corresponding organometallic compounds. The deposition is carried out in the presence of a suitable reducing agent, frequently hydrogen. Thus platinum films can be deposited on aluminium oxide and other non-conducting supports by the reaction of hydrogen with solutions of the diene platinum complexes (81–84).

Therefore, by this method, platinum metals alloyed with silver and gold (85) or nickel (86) may be deposited from mixed π-complex solutions. One-electron reagents of the sodium naphthalenide type have been patented as reducing agents (87).

Coatings may be prepared by thermal decomposition of organometallic compounds which are generally applied to the support as a paste, or in a pure form. (The preparation of metallic ruthenium and platinum by thermolysis of $Ru_2(OOCPh)_4(PhCOOH)_2$ and $(DMSO)_2PtCl_2$, respectively, has been reported (88, 89)). Osmium films were also produced on glass by heating osmium tetroxide complexes with terpenes (90, 91). Ruthenium films were prepared by the pyrolysis of $Ru_3(CO)_{12}$ (92), and platinum films by the decomposition of $Me_3PtC_5H_5$ (66, 92). Ruthenium plated electrodes were made by annealing pastes containing tris(acetylacetonato)ruthenium and trichlorosilane (93), and thick palladium and platinum films were produced by thermolysis of the corresponding resinates (94, 95).

Another application of organometallic platinum group compounds in electronics relates to the production of multilayer circuits for computers. Usually circuit boards or substrates prepared from a polymeric material, such as polyamides or polyphenolformaldehyde, are subjected to chemical and electrochemical metallisation, frequently with copper or nickel. The metallic films thus formed become metallic patterns and the prepared circuits are layered and perforated. It is desirable that the holes are metallised. In order to produce well metallised circuits, chemical metallisation catalysts are employed, these being incorporated into the polymer. The composition is then heated to the decomposition temperature of the organometallic compound to form the metal. Copper and nickel are deposited on the materials thus formed. Palladium compounds are mainly used for these applications and there are a number of patents relating to complexes with phosphines (96), with phosphites (97, 98), tris(dibenzylideneacetone)dipalladium and olefinic and acetylacetonate derivatives of palladium (98–103). For the metallising of polymers, see also (104–108).

Summary

It is apparent, therefore, that organic platinum metals compounds have some specific applications in electronics, but to date these have been limited due to difficulties in producing the compounds on an industrial scale.

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Osmium-Ruthenium Coatings

To accommodate new uses, the cathodes in travelling wave tubes need to operate at higher frequencies and output powers; thus they have to function at higher temperatures and current densities. The life of coated tungsten cathodes is limited by tungsten diffusion; to prevent this the cathodes operate at 950°C_B (brightness temperature).

Therefore the degradation of a porous tungsten cathode impregnated with barium calcium aluminate and coated with an osmium-ruthenium film has been studied (N. Mita, *IEEE Trans. Electron Devices*, 1991, **38**, (11), 2554). During tests tungsten diffused into the surface, converting it to osmium-ruthenium-tungsten. The activation energy for the tungsten diffusion coefficient was 8.4 eV, giving a stable period for the coating of over 100,000 hours at a cathode temperature of 1050°C_B, and the coating could be operated at a current density of 30 A/cm^2.