

Coating Methods for Use with the Platinum Metals

A REVIEW OF THE AVAILABLE TECHNIQUES

By Christopher Hood

Group Research Centre, Johnson Matthey & Co Limited

The economic use of platinum group metal coatings requires that the most appropriate coating method should be used for any particular application. This article reviews the techniques available for various substrate materials and outlines some of the more important properties obtained with different types of deposit.

There is now a wide variety of methods that can be employed to form coatings of the platinum group metals. The choice of materials and methods to be used can best be made after the manufacturer and the user of the product have considered the required properties and related factors such as the thickness and physical properties of the coating, the properties of suitable substrates, and the cost of alternative processes. This review describes processes which can be used to deposit a coating of a platinum group metal on to a substrate. The properties of the coating and the type of substrate to which the various methods are applicable, and the thickness normally to be obtained, are also discussed. For the purpose of this article the main methods of coating are considered to be as follows:

- Vacuum deposition
- Thermal decomposition and chemical vapour plating
- Electroless plating
- Aqueous electroplating
- Fused salt electroplating
- Metallic bonding
- Metallising

Vacuum Deposition

The most versatile method of depositing very thin coatings is vacuum deposition

which can be carried out by two techniques: vacuum evaporation and sputtering. These methods are used for the large-scale production of micro-electronic components where platinum provides the required properties of good electrical conductivity and complete freedom from atmospheric corrosion (1, 2).

Vacuum evaporation is carried out at a pressure of 10^{-5} Torr or below. The metal from which the coating is to be formed is heated to a sufficiently high temperature to cause it to volatilise at the extremely low pressure of the chamber, the substrate being arranged to condense this vaporised metal. Excellent films can be formed by this method although there are a number of difficulties, the main one encountered with the platinum group metals being the high temperatures required for evaporation. The most effective heating method is by an electron beam using a water-cooled copper crucible to contain the platinum group metal and as only the central part of the exposed surface of this metal is heated, contamination is avoided. The high temperatures involved may, however, cause additional problems because, as both radiant heat and the evaporated atoms are propagated rectilinearly from the source, it is not possible to shield the substrate from the radiant heat during deposition. The resulting temperature

rise could not only damage a sensitive substrate such as plastic, but may also change the structure and properties of the deposited film. In addition, the pressure in the vacuum chamber must be sufficiently low for the mean free path of the evaporated atoms to exceed the source to substrate distance, otherwise the metal will tend to nucleate before reaching the substrate and produce a soot-like deposit instead of a continuous film of metal.

Many substrates have substantial amounts of adsorbed gas on their surfaces, and this can take a long time to remove by pumping, water being particularly troublesome in this respect. Poor adhesion is often a problem with evaporated films of the platinum group metals especially on oxide surfaces such as ceramic and glass. This results from their low chemical reactivity so can generally be overcome by coating the substrate with a more reactive metal such as chromium before the platinum metal is deposited. Adhesion to plastic substrates, however, is usually very good.

Many of the problems associated with thermal evaporation can be avoided by sputtering techniques. Instead of vaporising the coating material by thermal energy, the surface of the target—the source of the platinum group metal—is bombarded with positive ions from a low pressure plasma of an inert gas, usually argon. The ions are accelerated towards this target by a potential of several kilovolts and as they collide with it their kinetic energy is transferred to the platinum group atoms so giving them sufficient energy to leave the surface and travel to the substrate. These sputtered platinum metal atoms have much greater kinetic energy than thermally volatilised atoms and can undergo collisions en route to the substrate without nucleation occurring. This means that higher pressures in the 10^{-3} to 10^{-2} Torr range can be used, thus easing the pumping requirements. As the sputtered atoms arrive at the substrate with much higher energies than evaporated atoms the adhesion between this coating and

the substrate is improved because gas adsorbed on the substrate surface is displaced and the sputtered atoms embed themselves in the surface layers. Although ion bombardment does raise the temperature of the target the radiant heat emission is small compared with that from a thermal source, and in most commercial plants is completely suppressed by cooling the target. One disadvantage of sputtering in comparison with thermal evaporation is that the deposition rate is much lower, unless powerful radio frequency plasma is employed.

With both types of vacuum deposition, a vast range of materials can be coated, almost the only condition being that the substrate can be safely subjected to vacuum conditions. Unless the substrate being coated is very small in relation to the source, it is necessary to move it around during deposition in order to obtain an even coating. The size of the substrate being coated is obviously limited by the capacity of the vacuum chamber, and the shape by the rectilinear form of the emission from the source; it is not possible to coat surfaces which cannot be placed approximately perpendicular to the line of emission.

The thickness of deposit which can usefully be formed is limited by the amount of strain which can be accommodated in the coating. This strain may be caused by structural imperfections at the atomic level or by incorporated impurities, and leads to crazing, cracking and peeling of the coating. Although the strain can be reduced to some extent by heating the substrate during deposition, so annealing the deposit, the process is best suited to the production of thin coatings in the range from a few atomic layers up to 1 micrometre.

Thermal Decomposition and Chemical Vapour Plating

Thin coatings of platinum and of gold-palladium alloys can be applied to heat resistant substrates by the thermal decomposition of organometallic compounds of

these metals to which resins and solvents have been added to give the required properties for application by such methods as brushing, spraying or screen printing. After drying, the substrate is fired in air in the temperature range 500 to 900°C to decompose the organo-metallic compound and to oxidise all carbonaceous residue, leaving the required metal film. Obviously, this process can only be carried out with a metal which does not oxidise at the required temperature.

An alternative method of utilising thermal decomposition is known as chemical vapour plating (3). The substrate is heated in an atmosphere containing the vapour of a metal compound which decomposes to the metal at the temperature of the substrate. The process is usually carried out under reduced pressure in order to obtain the necessary volatility without decomposing the metal-bearing compound prematurely. Furthermore, the process can be, and normally is, conducted in an inert atmosphere, so coatings of materials sensitive to oxidation at elevated temperature, such as palladium, can be applied by this method. The coating is deposited over the entire surface of the substrate, application to selected areas can therefore be achieved only by masking or by subsequent etching of unwanted areas. This ability to coat the entire surface of the substrate extends to the interior of fine pores and crevices so the method is well suited to the impregnation of porous materials. For this purpose, the process can be modified with advantage. The material to be treated is first impregnated with a solution of the volatile organometallic compound, dried, and then heated to volatilise the compound and decompose it throughout the pore structure. A remarkably even distribution of metal is obtained throughout the porous substrate by this technique (4).

Electroless Plating

Thermal decomposition methods cannot be used with heat sensitive substrates such as plastics, but coatings can be formed on such materials, as well as on many others, by

chemical reduction methods, often called electroless plating. The substrate is usually first treated chemically or mechanically to roughen the surface, thus providing a mechanical key which improves the adhesion of the coating, before being treated with palladium chloride followed by stannous chloride. The resulting layer of colloidal palladium then acts as a catalyst for the formation of the coating proper, which is formed by immersion in a bath containing a salt of the coating metal together with a reducing agent such as sodium hypophosphite. This method can be used to produce coatings of base metals such as copper or nickel which can subsequently be electroplated with one of the platinum group metals.

Because of the position of the platinum group metals at the bottom of the electrochemical series, coatings can often be obtained on the base metals simply by immersing the substrate in an aqueous solution of a platinum group metal salt. The quality of coating obtained is not usually good, but the method is a simple way of producing composite metal powders containing small proportions of platinum group metals.

Aqueous Electroplating

Aqueous electroplating is a well-established and widely practised method of applying many metals to metallic substrates, and good results can be obtained with most of the platinum metals (5, 6). The nature and thickness of the deposits obtainable with the various members of the group vary considerably. Platinum deposited from baths containing dinitro sulphato platinous acid is highly stressed and the resulting hard, bright plate cracks at thicknesses greater than 4 micrometres. If thicker deposits are required, intermediate stress relieving anneals must be carried out when thicknesses up to 40 micrometres may be obtained. The thickness obtainable with ruthenium is limited to 4 micrometres.

Rhodium, however, can be plated from acidic rhodium sulphate solution in thick-

nesses up to 40 micrometres without cracking problems, but heavy deposits are dull in appearance. Palladium is the most amenable of the platinum group metals to electroplating and bright, heavy deposits are obtained from electrolytes based on tetrammino palladous nitrite.

Fused Salt Electroplating

In addition to electrodeposition from aqueous solution, electroplating of platinum from a fused salt electrolyte is also an established process (7). The advantage of this process is that stress-free and ductile deposits up to 200 micrometres thick can be readily produced, but the process is limited to substrates which can withstand the high temperature of the fused salt. Titanium, tantalum, niobium, molybdenum, tungsten and even graphite have been coated by this technique. Other members of the platinum group metals have also been successfully plated by this method.

Metallic Bonding

When substantial coatings of platinum group metals are required on metallic substrates recourse has to be made to metallurgical bonding techniques to produce the required composite. The process of joining two pieces of metal by diffusion bonding is carried out by bringing them into close contact under pressure and raising the temperature until the rate of interdiffusion is appreciable.

The simplest application of this technique is hot pressing, when the composite is bonded by heating while under a hydraulic press. This process can only be used for bonding flat plates, although these can subsequently be rolled into sheet and fabricated by normal workshop practice. However, not all metal combinations can be bonded in this way. In some cases the base metal substrate may form a very thin tenacious film of oxide on its surface which prevents the formation of the diffusion bond, or oxygen may cause embrittlement in the vicinity of the bond which

results in failure of the bond when rolling operations are carried out or when the composite is subjected to other stresses. Similar embrittlement and subsequent failure may also be caused by the formation of brittle inter-metallic compounds at the substrate-coating interface.

Successful bonding even in the presence of oxide films can sometimes be achieved by hot rolling, instead of hot pressing, if the metallurgical properties of the materials permit this. The metals to be joined are heated to a suitable temperature and then reduced in thickness by 20 to 50 per cent in a single pass through a rolling mill. The gross deformation produced by this treatment breaks up the oxide film and enables bonding to take place. Similar results can be obtained by hot swaging a tube of a platinum group metals on to a rod of substrate material. Unfortunately, failures resulting from embrittlement may still occur.

The problems of surface oxide scale and brittle intermetallic compound formation, both of which may impede diffusion bonding, can be circumvented by the use of an explosion bonding technique. Flat plates of the two materials are laid together with a small gap between them and a charge of low detonation velocity explosive on top. The detonator is fixed to one edge so that the explosion progresses across the sheet. The first effect of the explosion is to peel off a layer from the upper sheet which then scours across the face of the substrate. The clean surfaces so produced are then bonded by the pressure of the explosion. As the oxide scale is actually blown out of the interface, no oxygen embrittlement can occur, and the heating effects are too low in temperature and too short in duration to allow intermetallic compounds to form by diffusion.

Metallising

Where the purpose of a coating is to provide an electrically conductive area, resistant to atmospheric corrosion, on a glass or ceramic substrate, metallising pastes can be used.

These consist of powdered noble metal mixed with ground glass and suspended in an organic vehicle suited to the chosen method of application; usually dipping for complete coating, or silk-screen printing for selected areas. After drying, the films are fired in air, to remove the organic vehicle and sinter the glass-metal mixture into a coherent and adherent coating. When correctly formulated using a suitable metal or alloy, the coating formed is highly conductive and solderable, and this type of metallising finds wide use in the electronics industry.

The application of substantial coatings of some platinum group metals to non-metallic and metallic substrates can be achieved by a second metallising technique which utilises flame spraying methods. The coating metal is fed to a high temperature flame where it is melted, and the molten metal is then atomised and sprayed on to the substrate by a jet of high-pressure gas, usually air. The coating obtained is porous and as the adhesion is by mechanical keying it may be rather weak. With metallic substrates the composite can be heated and rolled so compacting the coating and improving the adhesion. On non-metallic substances such as refractory bricks where the surfaces are of a very rough and porous nature the adhesion can be very good, but the difficulty of obtaining pore-free coatings remains. Clearly if the purpose of the coating is to prevent corrosion of the substrate, for example by molten glass, then a continuous layer is essential.

Conclusion

The methods of coating available fall into two main groups: those suitable for the production of thin films below 1 micrometre in thickness, and those suitable for thicker deposits in the range above 20 micrometres. Vacuum deposition and thermal decomposition methods belong to the first group, metallic bonding and metallising belong to the second, while chemical vapour plating and electro-plating can bridge the gap.

Of the 'thin' coating group, vacuum coating

methods are the most versatile, being applicable to all the metals and most substrates. They do, however, require expensive plant, and there are limitations on the size and shape of substrates that can be coated. Although thermal decomposition methods are limited to heat resistant substrates, they are much cheaper to operate and set little limitation on size or shape. This coating procedure is particularly adaptable; size is limited only by the size of furnace available to carry out the firing, application to selected areas is easy, and complex shapes as well as sheet and rod can be coated.

Except for the metallising paste process the "thick" coating group is most applicable to metallic substrates. Metallurgical bonding processes are limited in practice to the production of clad sheet and rod, more complex shapes having to be produced by subsequent fabrication. For example, to produce a thick layer of platinum on a refractory brick for use in the glass industry, recourse has to be made to the fabrication of a thin metal shell which is then fitted round the refractory core and mechanically attached to it.

Thus the widest choice of methods is available for metallic substrates, other substrate materials limiting the choice by their various electrical, mechanical and thermal properties. The practicability of employing a particular process may, of course, also be affected by economic factors, limitations on the size or shape of the substrate, or particular properties required of the coating.

References

- 1 L. Holland, *Electron. Components*, 1970, **11**, (2), 181; (3), 285; (4), 429; (5), 533
- 2 "Handbook of Thin Film Technology," ed. L. I. Maissel and R. Glang, McGraw-Hill, New York, 1970
- 3 "Vapour Deposition," ed. C. F. Powell, J. H. Oxley and J. M. Blocher, Wiley, New York, 1966
- 4 J. P. Heffer, British Patent 1,399,237
- 5 "Precious Metal Plating," ed. J. Fischer and D. E. Weimer, Robert Draper, Teddington, 1964
- 6 F. H. Reid, *Trans. Inst. Metal Finish.*, 1970, **48**, 115
- 7 *Platinum Metals Rev.*, 1975, **19**, (1), 15