

Fused Salt Platinum Plating for Industrial Applications

A USEFUL PRODUCTION PROCESS

By J. H. F. Notton

Group Research Centre, Johnson Matthey and Co Limited

Fused salt platinum electroplating has been successfully applied to the continuous cladding of molybdenum wire. The deposit obtained is ductile and has many other attractive features when compared to aqueous platinum plating, such as good adhesion and high purity. The process is equally suitable for thin coatings of a few microns or for electroforming components more than a millimetre thick.

Fused salt processes are finding increasing application in many diverse fields ranging from atomic energy production to domestic waste disposal. The largest everyday use, apart from metal heat treatment baths, is probably in the electrowinning and electroplating of metals. Fused salt electrodeposits frequently have desirable properties, such as increased ductility and a lack of porosity, which cannot be obtained if the same metals are applied by the more conventional aqueous plating methods. This is particularly true for platinum where aqueous plating baths can only produce relatively thin deposits, of the order of a few tens of microns thick, and even these may be hard and highly stressed. Considerable thicknesses of platinum can however be deposited from a fused salt bath and thus the process is eminently suitable for use for electroforming and for the production of composite materials—such as bi-metal sheet or clad rod and wire—suitable for subsequent fabrication. Typical properties of materials produced by the different processes are given in Table I.

The early work of Rhoda (1), and that of Schlain et al, more recently reported in this Journal (2), shows that all the platinum group metals can be electroplated from fused

cyanide baths. In addition certain alloy compositions may be deposited by analogous methods.

The high ductility of a fused salt plated platinum deposit is a direct result of both its high purity and the high temperature at which the salt bath operates, but the latter may appear to limit the use to which the process might be put, by restricting the substrate materials which can be clad. However, in nearly all industrial applications where the platinum metals are used in bulk form, their excellent high temperature and corrosion resistant properties are being utilised. This means that a platinum metal cladding will normally be used to enhance these properties on other refractory metals required for use in hostile environments, so in most instances the processing limitation does not apply.

Platinum Clad Molybdenum Wire

Recently considerable interest has been shown in the production of clad wire by a continuous process using a fused salt electroplating bath, instead of by the more usual mechanical coating method. Provided that the quality of the plated surface is acceptable, such a bath may be fed with wire which can

be plated to the required size. Alternatively oversized wire may be used which, after plating, is given a final draw to produce the required size and surface finish. Both techniques have been developed in the Johnson Matthey Research Centre for platinum clad molybdenum wire. Wires of this material in sizes ranging from 0.12 to 1.5 mm diameter and with cladding weights of from 3 to 40 per cent platinum are required for many uses in the electric lamp and electronic valve industries.

In such applications the resistance to oxidation of platinum clad molybdenum at a fixed temperature has been shown to be proportional to the cladding thickness and to the quality of the bond between the two metals (3). The freedom from porosity and good bonding inherent in the platinum coating produced by the fused salt process allows the minimum coating thickness to be used for a particular requirement.

An example of this occurs with platinum clad molybdenum used to produce lead-in wires for quartz-halogen lamps. In normal service the lead-in wires are exposed to temperatures up to 600°C in an oxidising environment in which unclad molybdenum is attacked and the volatile oxide formed. The traditional solution to this problem was to protect the molybdenum with a 17 weight per cent coating of platinum, giving a nominal

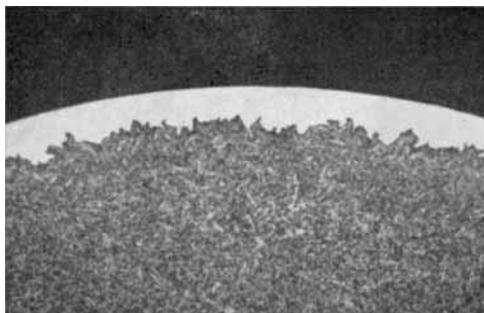


Fig. 1 A cross-section through 17 weight per cent platinum clad molybdenum wire produced by the conventional mechanical bonding process shows the uneven thickness of the coating ×400

coating thickness of 12 μm on 0.7 mm wire. Such a product prepared by the conventional route of hot bonding and cold drawing will have an excellent bond between the coating and the molybdenum. However, this method of production tends to produce a platinum coating of uneven thickness, believed to arise from the fibrous structure of the molybdenum. This is apparent from Figure 1, which shows a normal 17 weight per cent platinum cladding on 0.5 mm molybdenum wire. Since the protection afforded is only as good as the thinnest part of the coating, it is obvious that the thicker parts of the deposit contribute little to the overall performance of the wire. Clearly

Deposit	Maximum useful deposit thickness in microns	Hardness, Hv		Deposition rate, microns per hour
		As deposited	Annealed at 800°C	
Fused salt	1500	70	48	20-25
Aqueous, Sodium hexahydroxy platinate	12.5	120	70	5
Aqueous, D.N.S. platinum	25	400-450	70	1.5

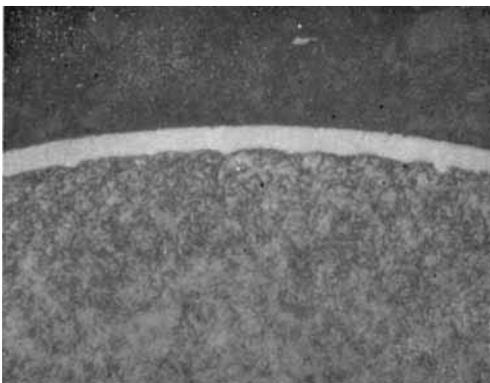


Fig. 2 A sensibly uniform coating is shown on this cross-section of 12 weight per cent platinum clad molybdenum produced by fused salt electroplating at 1 mm diameter, followed by fabrication to 0.7 mm × 350

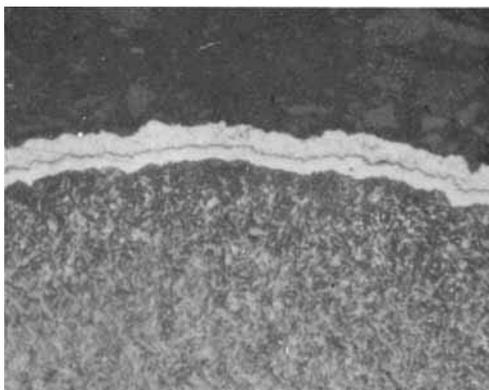


Fig. 3 A particularly uniform deposit, and its ability to cover surface irregularities on the molybdenum, are shown on this section of 6 weight per cent platinum clad molybdenum wire which has been fused salt plated at 0.7 mm. The surface of this specimen is covered by a layer of copper plating, which was applied to assist in the metallographic preparation × 350

then, a technique which produces a coating of greater uniformity can be used either to provide a more effective cladding, or to obtain a saving in platinum metal for the same cladding efficiency.

The continuous fused salt plating process has been found to produce such a coating, two examples being shown as Figures 2 and 3. Figure 2 is a 12 weight per cent platinum clad molybdenum wire plated at 1 mm and

subsequently drawn down to 0.7 mm while Figure 3 shows a 6 weight per cent platinum clad wire as plated; the coating being $5\mu\text{m}$ thick. In both cases the exceptional uniformity of the platinum layer is apparent.

Pilot production trials have shown that this 6 weight per cent platinum plated wire performs as effectively as the much heavier cladding weights produced by the conventional mechanical cladding route when used for lead-in wire applications. The fused salt plated wire is now finding a steadily increasing use for making these lead-in wires and a large production capacity is now available for the 6 weight per cent platinum clad material.

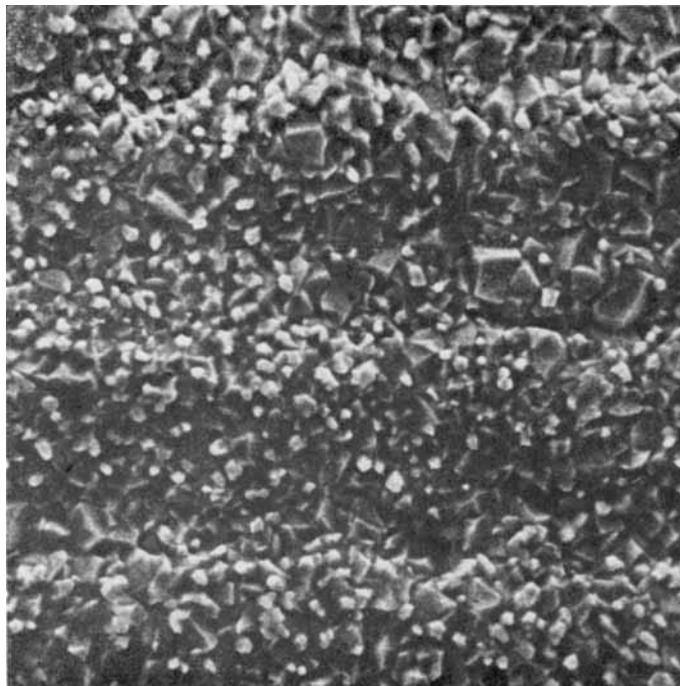
Production Process

The prototype continuous plating unit uses a eutectic salt mixture, 53 per cent sodium cyanide and 47 per cent potassium cyanide, which has a melting temperature of about 520°C . Earlier workers have reported operating temperatures of 600°C and higher, but the lower temperature leads to the production of smoother deposits. Fused salt deposits are not normally as bright as the best aqueous deposits, but often have a pleasing matt finish. A scanning electron micrograph of a typical surface is seen in Figure 4, which shows clearly the microcrystalline nature of the deposit produced in the low temperature bath. In such deposits the individual grains are in the range 1 to $2\mu\text{m}$ diameter.

The wire to be plated is passed through the molten salt by means of a system of insulating pulleys. After plating, a wash with circulating water completely removes the small amount of salt remaining on the wire and it has been found that the aeration of the water is sufficient to oxidise all the cyanide to carbonate or cyanate without further treatment.

Normal control of plating thickness can be achieved by varying either the plating current or the speed of the wire through the bath while major adjustments can be obtained by altering the length of wire immersed. The size of the bath is such that by simple engineering several strands of wire can be

Fig. 4 Scanning electron micrograph showing the surface of a typical fused salt plated platinum clad molybdenum wire. The lower temperature bath produces the fine crystallites seen on the surface ×2500



accommodated in the same electrolyte thus achieving very economical production.

Two different methods have been used for maintaining the platinum content of the melt at a suitable value. Platinum may be introduced using consumable sheet anodes as described by other authors, or alternatively it has proved possible to use a salt of platinum which can be added to the melt periodically, and which permits the use of insoluble anodes.

Laboratory Testing of Platinum Clad Wire

The laboratory assessment of this product has included oxidation resistance tests, plate adhesion measurements and tensile tests; the last to ensure that the properties of the molybdenum substrate are unaffected by the temperature of the salt bath.

In oxidation tests lengths of wire were heated at 600°C in air. With thin coatings this is a good, rapid test for indicating the presence of occasional pinholes in the plating, which can be readily detected with a lens after the first signs of formation of

volatile molybdenum oxide have been observed. It has, however, proved more difficult to quantify life testing on sound coatings. Measurement of the adhesion of the deposit on wire specimens has also proved difficult although qualitative tests using adhesive tape or deformation of the wire by bending or twisting to remove the deposit have been used effectively for process control. Quantitative pull-off tests on specially prepared specimens of larger size material have been made using epoxy resin adhesive to attach lugs to the specimen. In these tests the material has shown good bond strengths, failure always occurring in the adhesive. It is concluded that the bond strength is at least 6 to 8 kilograms per square mm, the tensile strength of the epoxy resin. Corresponding tests on small diameter wires are not possible for quantitative measurement of this type.

The results of tensile tests are included in Table II. From these it is apparent that the mechanical properties of the molybdenum are virtually unaffected by the high temperature of the plating process, the elongation and

Sample	Elongation per cent (10 cm gauge length)	Tensile strength kg/mm ²
Unplated 0.7 mm diameter	15	110
Plated with 5 microns platinum, which is equivalent to 6 weight per cent platinum	13.5	107
	13.0	105
	14.0	102

Specimen	Shear strength kg/mm ²
Molybdenum	61.4
Platinum	12.3
Platinum/Molybdenum Hot bonded	17.3
Platinum/Molybdenum As fused salt plated	20.0

tensile strength values remaining substantially unchanged.

The throwing power of the electrolyte is so good that even without special anode design no variation of the coating thickness around the wire circumference can be detected by metallographic measurement.

Additional Applications

Thicker coatings of platinum have been prepared for a variety of applications where resistance to aqueous chemical corrosion is of paramount importance. Typical uses include electrodes for chemical processing or anti-corrosion devices, and components in chemical plant.

A titanium thermometer pocket plated

with a 25 μm coating of platinum is illustrated in Figure 5. The integrity of the coating was checked by boiling in 50 per cent hydrochloric acid for 24 hours and no titanium could be detected in the acid after this test.

The corrosion resistance of fused salt platinum coatings on niobium electrodes used in water, and with high alternating currents applied, has also been measured and has been shown to be equal to that of pure platinum. A typical value of the weight loss in both cases is 5×10^{-6} g/amp-h/cm² for a current density of 0.3 amp/cm².

The fused salt process has also been used to produce very thick, 0.2 to 1.5 mm, coatings on various metals and alloys for subsequent fabrication to clad wire or sheet. Such thick deposits on rod samples can be tested for good adhesion using a ring shear test, and bond shear strengths are given in Table III, together with the shear strengths of the two component metals. It is seen that the electroplated deposit has a bond strength which compares very favourably with the conventional high temperature mechanically bonded product. The excellent ductility of the coating is well illustrated by the fact that clad niobium sheet can be given a 98 per cent reduction in thickness without intermediate annealing. The microstructure of a clad niobium electrode, for use in impressed current corrosion protection systems, produced in this manner is shown in Figure 6.

An electroformed platinum crucible 0.75

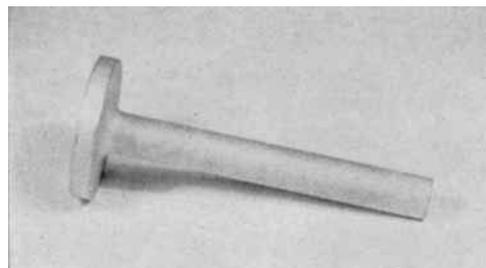


Fig. 5 The coating of this titanium thermometer pocket, which is clad with 25 μm of fused salt plated platinum, showed no defects when boiled in 50 per cent hydrochloric acid for 24 hours

mm thick produced by the fused salt process, is shown in Figure 7. With such components the purity of the electroformed platinum is of crucial importance, both to maintain the high temperature properties of the platinum and to prevent contamination of any materials processed in them. Some analysis values for a platinum sheet anode compared with fused salt deposited platinum are presented in Table IV and these show a general reduction in the levels of base metal impurities. However, owing to the highly corrosive nature of the molten cyanide great care is necessary to prevent contamination of the fused salt.

In addition, the fused salt process has been used to provide a jobbing plating service for a wide variety of components and considerably greater use is expected for this in the near future. Components plated



Fig. 7 This platinum crucible, shown here approximately twice full size, was produced by an electro-forming process

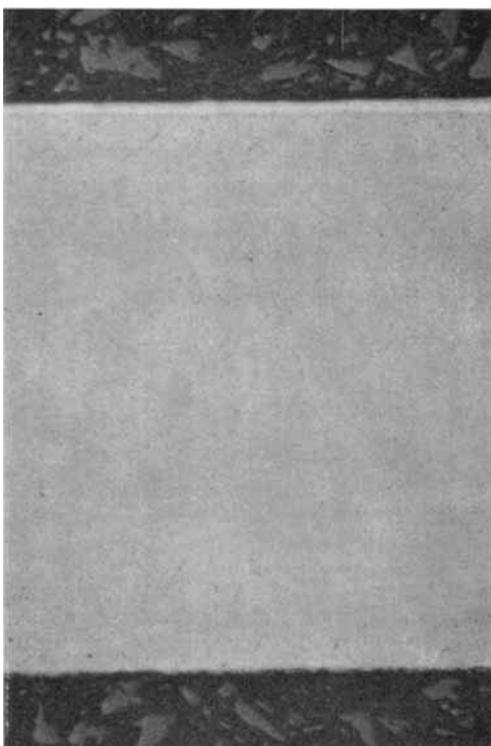


Fig. 6 The excellent ductility of fused salt plated platinum is shown by this section of platinum clad niobium sheet which has been reduced in thickness by 98 per cent after plating and without intermediate annealing $\times 150$

Table IV
Analysis of Platinum Anode and Fused Salt Plated Deposit

Impurities	Anode, parts per million	Plated deposit, parts per million
Gold	50	7
Boron	5	n.d.
Calcium	<1	<1
Copper	20	5
Iron	70	9
Lead	2	n.d.
Magnesium	<1	<1
Manganese	<1	n.d.
Nickel	7	9
Silicon	10	<1
Silver	30	1
Zinc	10	n.d.
Total	204	31

n.d. - not detected

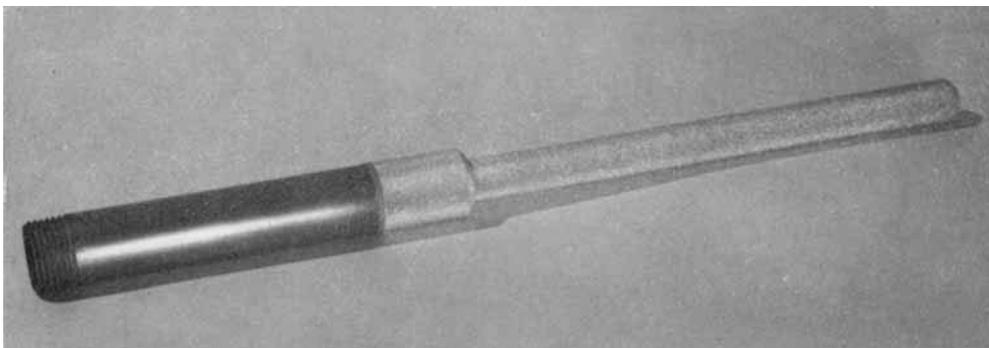


Fig. 8 The 18 inch long stainless steel thermocouple probe illustrated here is just one of many components which have been successfully platinum plated by the fused salt plating process. The technique is no longer confined to laboratory conditions but is now established as a viable commercial process

include experimental spark ignition electrodes, which were found to have a considerably improved service life when platinum plated, and the plated thermocouple sheath shown in Figure 8, which has been successfully employed in a corrosive environment.

Conclusions

It can now be stated with confidence that fused salt plating has emerged from being a critical laboratory technique to a useful and

economical method of applying platinum coatings with unique properties to a variety of substrates. Research is in progress at the Johnson Matthey Research Centre aimed at developing similar commercial fused salt plating processes for other platinum metals.

References

- 1 R. N. Rhoda, *Plating*, 1962, **49**, (1), 69
- 2 D. Schlain, F. X. McCawley and G. R. Smith, *Platinum Metals Rev.*, 1977, **21**, (2), 38
- 3 A. S. Darling and G. L. Selman, *Platinum Metals Rev.*, 1968, **12**, (3), 92

Russian Research on the Platinum Metals

Alloys of the Precious Metals, Nauka, Moscow, 1977, 292 pages (in Russian)

The great importance which the Soviet Union attaches to the platinum metals is once again in evidence with the publication of this collection of papers. There are no less than ninety-five contributions by a number of authors headed by Professor E. M. Savitskii and his colleague Madame V. P. Polyakova of the A. A. Baikov Metallurgical Institute of the Academy of Sciences, and originally given at a conference in 1974. All but four or five of the papers, despite the general title, are concerned with the properties and applications of the platinum group metals.

The subjects covered range from the mineralogy of the platinum group to the technique of welding platinum and its alloys, taking in on the way such varied subjects as gas analysis, the solubility and diffusion of impurities in platinum at high temperatures, the phase diagrams of platinum

with some of the rare earth elements, the interaction of platinum with molybdenum and rhenium, and studies of the interaction of molten platinum and palladium with various refractory materials.

Some of the more interesting applications discussed include the study of platinum alloys containing both palladium and rhodium for handling molten glass, the properties of cobalt-platinum permanent magnets, potentiometer wire and sliding contact materials, alloys for thermocouples, palladium alloys for the diffusion of hydrogen and ruthenium based catalysts.

As we have come to accept, all but very few of the numerous references are to Russian work, but clearly this fairly short book is a valuable source of information on current work in this field in the Soviet Union.

L. B. H.