

# Electrodeposited Ruthenium as an Electrical Contact Material

## A REVIEW OF ITS PROPERTIES AND ECONOMIC ADVANTAGES

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*The potential advantages of ruthenium plating are becoming increasingly appreciated in the electrical contact field. By comparison with rhodium, electrodeposited ruthenium is much less costly and possesses very similar properties of extremely high hardness and resistance to corrosion but with superior resistance to wear; while the dramatic increase in the price of gold has further emphasised the importance of evaluating its merits of low contact resistance and much lower density, offering great economy for a given thickness of deposit.*

Ruthenium, a member of the light triad of the platinum metals group together with rhodium and palladium, has been electrodeposited for many years, initially as a corrosion resistant finish for silver. As might be expected, its properties show a close resemblance to those of rhodium, with extremely high hardness and good resistance to corrosion, but somewhat superior in terms of resistance to wear. Unlike other noble metals it develops a thin adherent surface film of ruthenium oxide that is highly protective and prevents further oxidation, but has the curious and useful property of a conductivity equal to that of the metal. Both the metal and its oxide film are resistant to sulphide attack in high humidity environments.

Electrodeposited ruthenium thus offers an attractive alternative to both rhodium and gold, with considerable economy, in the plating of electrical contacts, reed switches and slip rings. Low contact resistance is assured, while the much lower density of ruthenium, 12.45 as against 19.3 for gold, achieves a still further saving for a given thickness of deposit.

This review covers the development of ruthenium electrolytes with particular

reference to the properties of the deposits in electrical contact applications.

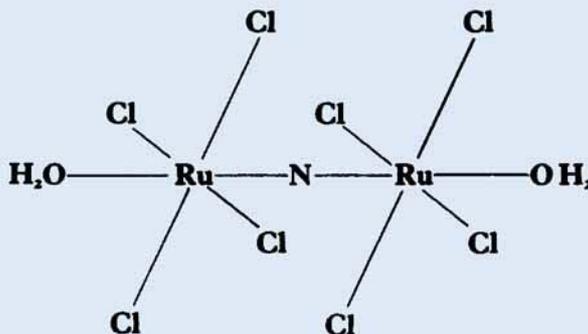
### Development of Electrolytes

An early patent by Zimmermann and Zschiegner in 1936 (1) disclosed the use of electrolytes based on a variety of nitrosyl ruthenium complexes, but while adequate deposits were obtained, cathode efficiencies were generally in the range of 10 to 20 per cent.

The first report on ruthenium electrodeposits on silver for electrical contact applications was by Volterra of Metals and Controls in 1952 (2). This worker used an electrolyte prepared by dissolving ruthenium hydroxide in sulphamic acid and deposits up to 5  $\mu\text{m}$  in thickness were obtained, operating at 50 to 70°C and 2 to 8 A/dm<sup>2</sup> with cathode efficiencies up to 20 per cent, but evolution of RuO<sub>4</sub> occurred at the anode. These deposits were stated to withstand high-intensity arcing and to be free from sticking or pitting.

A later survey by Reid and Blake (3) screened ruthenium sulphate and phosphate preparations but concentrated on variants of the original nitrosyl systems. The preferred electrolyte was prepared by the dissolution of

**Fig. 1** The structure of the  $[Ru_2NCl_8(H_2O)_2]^{3-}$  ion first reported by Cleare and Griffith in 1968 showing the linear nitrido bridge. This species now forms the basis of all successful modern commercial electrolytes



$[Ru(NO)(OH)_3]$  in sulphamic acid and deposits were obtained in operating conditions similar to those for the sulphamate electrolyte, with very low evolution of  $RuO_4$ . However, problems were encountered with the reproducibility of the electrolyte and deposit performance for larger scale preparations, and there was no large scale ruthenium plating until the late 1960's.

A marked advance in the electrodeposition of ruthenium particularly in respect of current efficiency, occurred in 1969. Prior to this Cleare of Johnson Matthey together with W. P. Griffith of Imperial College (4) had been studying the chemistry of ruthenium nitrosyl compounds and discovered the potassium salt of the binuclear nitrido-bridged species  $[Ru_2NCl_8(H_2O)_2]^{3-}$ . This compound, shown as Figure 1, was then investigated in the Johnson Matthey Research Laboratories as a likely electrolyte by Bradford, Cleare and Middleton (5), who found that it gave excellent results with the addition of ammonium formate to suppress anodic oxidation. Operated at 0.8 A/dm<sup>2</sup>, 70°C and a pH of 1.3, cathode efficiencies of 90 per cent were obtained for bright, pore-free deposits up to 2.5 μm in thickness.

Independently, at the same time Reddy and Taimsalu (6) obtained similar results with the ammonium salt of the same complex with ammonium sulphamate as addition agent.

Further studies were carried out by Lerwill and Mason of Engelhard (7), Branik and

Kummer of W. C. Heraeus (8) and by Conn of Westinghouse Research Laboratories (9) who showed that operating under similar conditions bright, smooth and crack-free deposits could be obtained up to 2.5 μm in thickness, although with somewhat lower cathode efficiencies.

Most commercially available electrolytes are based on these binuclear ruthenium complexes.

More recently an investigation on ruthenium electrolytes has been reported from the Bell Laboratories. These have demonstrated that by minimising the amount of sulphamic acid used in the preparation of the  $[Ru_2NCl_8(H_2O)_2]^{3-}$  complex and by operating in a divided cell a substantial improvement in performance can be obtained (10). The reduction of the sulphamic acid concentration from earlier formulations is claimed to decrease the level of impurities in the electrolyte by reducing the formation of trinuclear ruthenium species without adversely affecting the rate of formation of  $[Ru_2NCl_8(H_2O)_2]^{3-}$ , while the use of appropriate buffering agents and of a cation transport membrane between anode and cathode compartments further improved deposition.

The results of an evaluation of this process for production plating, in an application where it appears attractive as a replacement for gold, have recently been given by T. A. Palumbo, also of Bell Laboratories (11). A pilot plating line was set up to plate the contact surfaces of reeds for sealed contacts, normally plated with 2 μm of cobalt-gold. For this evaluation the reeds were plated with 1 μm of ruthenium over 1 μm

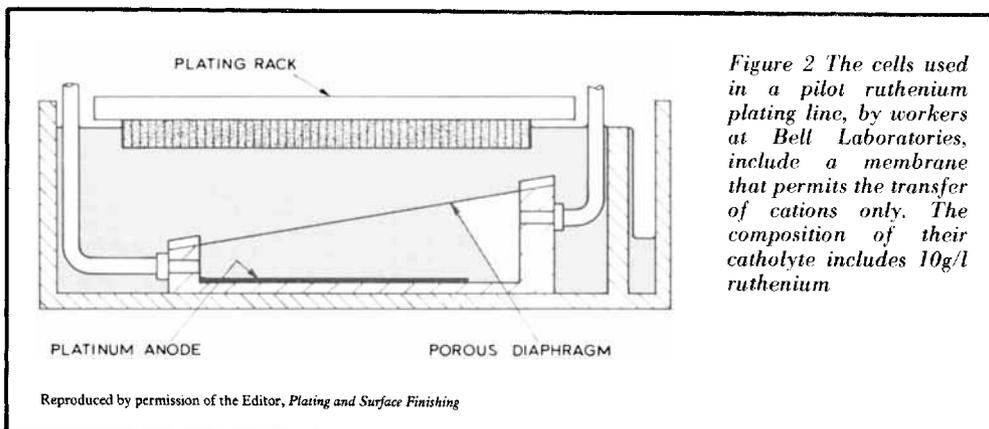


Figure 2 The cells used in a pilot ruthenium plating line, by workers at Bell Laboratories, include a membrane that permits the transfer of cations only. The composition of their catholyte includes 10g/l ruthenium

of pure gold. Altogether some 50,000 reeds were plated in this investigation over a period of several months without any visible deterioration in the solution.

The divided cell configuration, shown in Figure 2, prevents the formation of  $\text{RuO}_4$  and contains an acid phosphate buffer in both sections, which are separated by a cation transport membrane. The potassium salt of the ruthenium complex was used in the catholyte and when operated at  $70^\circ\text{C}$ , pH 1.7 and  $1 \text{ A/dm}^2$  the cathode efficiency remained stable at 60 per cent. The  $1 \mu\text{m}$  deposit of ruthenium remained free from cracking after a simulated thermal shock test—inserting the reeds into a furnace at  $500^\circ\text{C}$  for 30 seconds and then cooling rapidly to room temperature.

In acid electrolytes a flash gold deposit is necessary to prevent attack on the substrate during ruthenium plating. Provided comparable performance could be secured, a high pH electrolyte should offer a significant improvement with only one plating operation and little risk of contamination of the electrolyte. A recently devised electrolyte by J. N. Crosby of International Nickel (12) consists of the nitrido-bridged complex  $[\text{Ru}_2\text{N}(\text{NH}_3)_8\text{Cl}_2]^{3+}$  with a phosphoric acid/phosphate mixture as a buffer. Operated at  $70^\circ\text{C}$ , pH 13 and a current density of 2 to  $3 \text{ A/dm}^2$  in a single compartment cell, bright adherent deposits were obtained up to  $1 \mu\text{m}$  in thickness. Monitoring of the anode potential was necessary, however, to prevent

the formation of an insoluble ruthenium species. Cathode efficiencies varied from 10 to 58 per cent.

The co-deposition of another metal to produce ruthenium alloy deposits has also been considered. The incorporation of small concentrations of gallium, indium or thallium as stress relieving agents in  $(\text{NH}_4)_3\text{[Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]$  electrolytes was investigated by Sel Rex Corporation (13). This group also developed alloys containing 1 to 1.5 per cent indium, which give crack-free deposits up to  $10 \mu\text{m}$  thick; Russian workers have published data on electrolytes based on  $[\text{Ru}(\text{NO})\text{Cl}_3]$  using palladium and iridium (14) as additives.

## Deposit Performance and Applications

The major ruthenium plating application is for electrical contacts and several authors have compared the performance of gold, rhodium and ruthenium deposits for insertion contacts, slip rings and reed switches.

Ruthenium is substantially harder than cobalt-hardened gold and could be expected to be more resistant to abrasion in insertion contacts where the contact surfaces mate with a reciprocal action. Tests on deposits formed on a  $5 \mu\text{m}$  nickel pre-plate, carried out by Horn and Merl of Doduco and reproduced in the Table, indicate that wear on the components is much lower for ruthenium, but wear through to the pre-plate occurs more rapidly (15). This is due

Evaluation of Ruthenium* and Cobalt-Gold Deposits as Insertion Contacts		
	Ruthenium	Cobalt hardened gold
Density, g/cm <sup>3</sup>	11.8	18.4
Hardness, daN/mm <sup>2</sup>	500	160-180
Deposit thickness, μm	2	3
Weight loss, mg – Plug	0.24	0.56
– Socket	0.45	0.78
Wear through operation number	4,000	7,500

\*Unspecified acid electrolyte

in part to the lower deposit thickness compared with cobalt-gold, but also to the greater abrasion by the harder ruthenium particles once the surface layers have been disrupted (16). A recent report, again from Bell Laboratories, indicates that ruthenium and ruthenium oxide coated titanium separable connectors show high resistance to sulphidation, but no details were given of the wear resistance parameters for these contact surfaces (17).

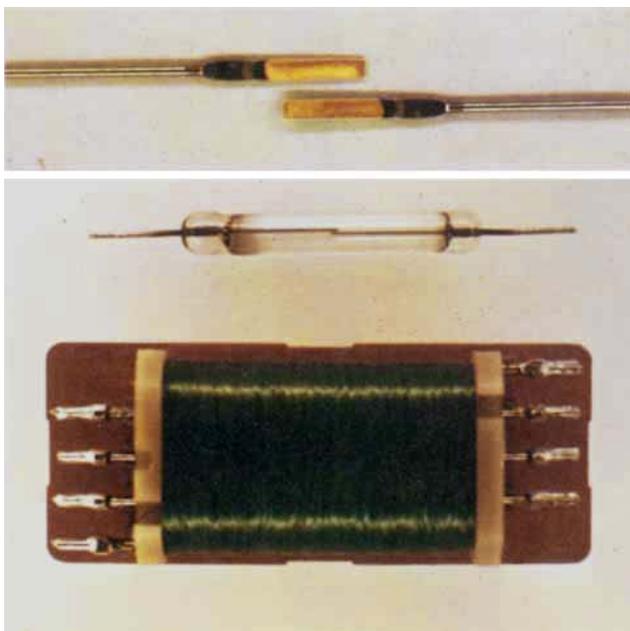
In slip ring applications, a contact brush, in this case made from a 60 per cent palladium-40 per cent silver alloy, sweeps around a ring shaped contact and some years ago Angus (18) compared the wear resistance of rhodium deposits with those from two ruthenium electrolytes. The latter were prepared from nitrosylruthenium(II) complexes in sulphamic acid and sulphuric acid, respectively, and gave deposits ranging in thickness from 0.6 to 2.5 μm. Brush wear increased with deposit thickness for all of the electrolytes but polished 2.5 μm deposits from the sulphamate electrolyte gave marginally less wear than equivalent rhodium deposits during a 100 to 400 hour test period. However, in the absence of polishing, brush wear was more extensive by a factor of ten because of the presence of nodules on the deposit surface and the nitrosyl sulphamate electrolyte was not exploited commercially due to problems of reproducibility during scale-up of the preparation.

There are no available data on the performance of deposits from the  $[\text{Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]^{3-}$

electrolytes in slip ring or insertion contact applications, although the physical properties are similar to those from the nitrosyl sulphamate electrolyte. Edge cracking has been observed after several days for these deposits, presumably due to occluded impurities, but this effect can be minimised by a post-treatment with warm 50 per cent aqueous ammonia (19).

Reed switches are high volume electrical components, with a predicted level of 300 million in operation in U.K. telephone exchanges by 1981. Utilisation varies with the type of exchange, but they are primarily used in circuits requiring less than 100,000 operations per year. The contact blades are prepared from magnetically soft 51 per cent nickel-49 per cent iron wire, hermetically encapsulated in glass with an inert atmosphere, as shown in Figure 3. Wires used for coining the blades range in diameter from 0.056 to 0.071 cm, and they are traditionally coated with cobalt- or nickel-hardened gold (2 μm) or, alternatively, a thin gold deposit which is subsequently heat treated to diffuse into the substrate.

Contact performance problems are generally associated with high contact resistance or contact adhesion due to microwelding. Incidence was more frequent with the cobalt-gold electrolyte due to problems of electrolyte control and the use of 0.056 cm diameter wires for the reeds and hence a smaller contact surface area (20). This electrolyte has now been discontinued in the U.K., although it is still used in the U.S.A. Glow diffused contacts are



*Fig. 3 The reeds in a relay are formed by flattening part of a magnetic alloy wire, which is then plated on the contact area with noble metal before being sealed into a glass tube filled with an inert atmosphere. During use, an electrical coil surrounds such switches and activates them when a current is applied. These switches are widely used for fast switching at low currents and have a useful life of several million operations*

Photograph by courtesy of Bell Laboratories

also susceptible to microwelding which increases with the extent of deposit diffusion due to enhanced thermal conductivity of the reed. However, both the nickel-gold and diffused gold reed switches were used in the first TXE4 exchange (300,000 reeds) and the annual failure rate was less than 1 per 10,000 reeds.

The first reference to the use of ruthenium as a contact material, as already mentioned, was in 1952 when Volterra (2) produced a 2.5  $\mu\text{m}$  deposit on silver contacts that reduced contact welding caused by high intensity arcing. It has recently been demonstrated by Augis and Hines (21) that reduced arcing and low erosion per arcing operation are characteristic for ruthenium contact surfaces, although in this work they were prepared by d.c. sputtering. An additional contributory factor in the incidence of microwelding for contacts is the plastic deformation of asperities, the submicron sized protrusions on the deposit surface. In order to assess this effect, Sharma determined at Bell Laboratories the adhesion coefficient for ruthenium, cobalt-gold and diffused gold plated contacts, although the electrolytes and

ruthenium deposit thickness were not specified (22). The adhesion coefficient, the ratio of the force required to separate the contacts to the force used to compress them prior to separation, was determined on contact surfaces cleaned by argon ion bombardment. Ruthenium had a similar coefficient to diffused gold, but only half that for the cobalt-gold contact, an effect attributed to the hexagonal structure of ruthenium which limits crystal deformation.

Ruthenium plated reeds have also been shown by workers at Nippon Electric (23) to have a 0.5 nm surface layer of ruthenium oxide which has little effect on contact resistance, but prevents formation on the contact surface of organic polymers from atmospheric contaminants. The surface film also helps to prevent contact adhesion and is absent from standard rhodium plated reeds. The ruthenium electrolyte used in this work was not specified, but has been used to produce several million reed switches since 1969. Annealing the plated reeds at 400 to 600°C resulted in migration of iron and nickel from the substrate on to the contact surface, but it was shown that this did not occur during encapsulation owing to the

transient heating period involved in this process. However, the thermal shock experienced by the reeds during encapsulation has been shown by Palumbo to result in cracking of the deposits from standard commercial ruthenium electrolytes (11).

The use of a 1  $\mu\text{m}$  soft gold pre-plate and a 1  $\mu\text{m}$  ruthenium deposit reduced this effect as differential expansion of the ruthenium and the 49 per cent cobalt-49 per cent iron-2 per cent vanadium reed blade is compensated by the gold pre-plate, whereas conventional deposition methods rely on only a flash deposit of gold. However, the authors found that the ruthenium deposits still cracked due to their inherent

stress unless a pure  $\text{K}_3[\text{Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]$  electrolyte and divided cell assembly were employed. Over 50,000 reed blades have been plated by this technique, but no details of long-term contact performance have so far been published.

Clearly considerable interest has been taken in ruthenium plating for electrical applications over the last decade by a number of industrial establishments. Stimulated by the greatly increased price differential between ruthenium and gold, development work is continuing and will no doubt include rigorous studies of long-term electrolyte and deposit performance for electrical contact purposes.

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## Ullmann's Encyklopädie on Platinum

Since 1914 Ullmann's Encyklopädie der technischen Chemie has been a valuable work of reference to German-speaking chemists and has passed through several editions. The fourth edition, much enlarged and revised, is now in course of publication and Volume 18 has now appeared, including a section on the platinum metals.

This has been prepared by Dr. Hermann Renner of Degussa, who has succeeded in com-

pressing a great deal of information on their refining, properties, chemical compounds and applications into some 32 pages. This replaces the former chapter in the third edition of 1963, written by the late Dr. Ruthardt of Heraeus. Many developments have taken place in the meantime, and the references—totalling 177—include a mention of everything of importance to an industrial chemist, or metallurgist, that has been reported up to the end of 1979.